Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic supplementary information

A Substrate-controlled Ru(II)-catalyzed C-H Activation/[5+2] Annulation Cascade and Unusual Acyl Migration to Diversified Indoline Scaffolds

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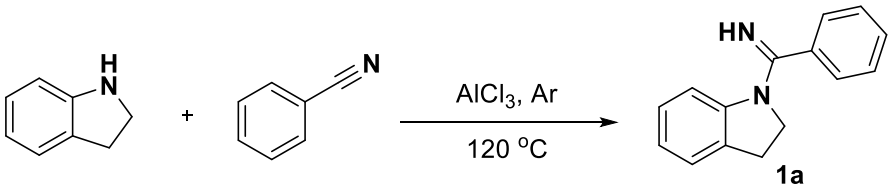
I. General Information

Unless otherwise specified, commercially available reagents were purchased from commercial sources and used without further purification. Analytical thin layer chromatography (TLC) was performed on HSGF 254 (0.15-0.2 mm thickness), visualized by irradiation with UV light (254 nm). Column chromatography was performed on silica gel FCP 200-400 or 300-400 using ethyl acetate (EA)/petroleum ether (PE). All products were characterized by their NMR and HRMS spectra. ^{1}H and ^{13}C NMR spectra were recorded on a 500, or 600 MHz instrument. The chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane (TMS). Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), and broad (br). High-resolution mass spectra (HRMS) were measured on a Micromass Ultra Q-TOF spectrometer.

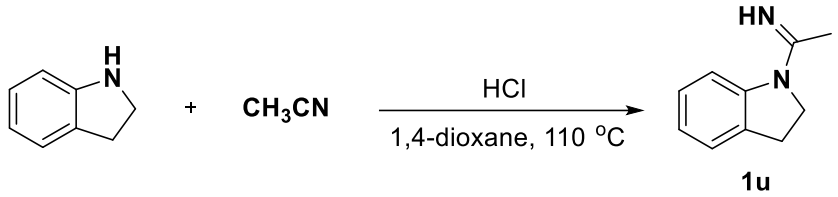
II. Synthesis of Substrates

(a) The known substrates **1w**[1] was not characterized. The substrates **1a-1t** and **1w** were synthesized according to the reported procedure[2].



Anhydrous $AlCl_3$ (3.88 g, 29.09 mmol) was added slowly to a mixture of indoline (4.16 g, 34.91 mmol) and benzonitrile (3 g, 29.09 mmol) at room temperature in a 25 mL round-bottomed flask, under an argon atmosphere. The resulting mixture was heated to 120 °C (oil bath temperature) for 12 h. The mixture was treated with NaOH aqueous solution, filtered with diatomite, and extracted with ethyl acetate for 3 times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to remove the solvent. The residue was purified by flash column chromatography on silica gel (PE/EA = 4:1) to afford the desired product.

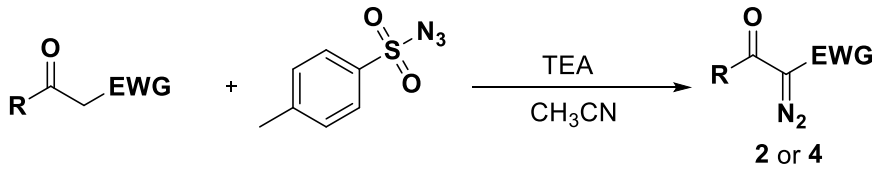
The substrates **1u** and **1v** were synthesized according to the following procedure.



A pressure tube was charged with indoline (1.0 g, 8.39 mmol) and acetonitrile (689 mg, 16.78 mmol) and hydrochloric acid 1,4-dioxane (20 mL). The reaction mixture was stirred at 110 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by reslurry using EA to afford the desired product.

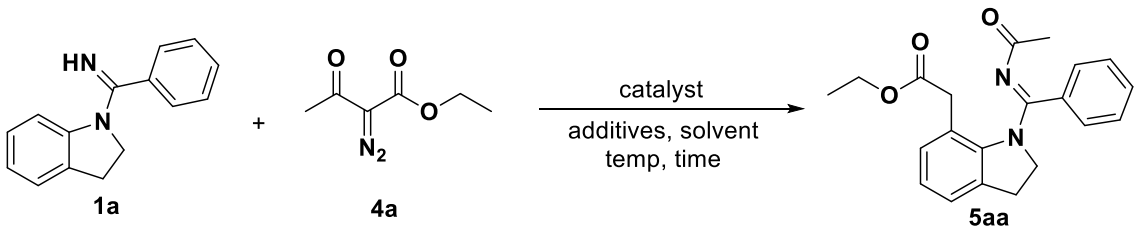
(b) General procedure for the preparation of diazo compounds.

The known substrates **2a-2d**[3], **2e**[4] and **2f**[3] were not characterized. The substrate **4a** was purchased from commercial sources, and used without further purification. The known substrates **4b**[5], **4c**[3], **4d**[6], **4e**[7], and **4f**[4] were not characterized.



To a solution of β-ketoester (5 mmol, 1.0 equiv.) and 4-methylbenzenesulfonyl azide (6 mmol, 1.2 equiv.) in 20 mL CH_3CN at 0 °C was added triethylamine (6 mmol, 1.2 equiv.). The resulting solution was stirred at 0 °C for 3 h and slowly brought to r.t. Upon completion as indicated by thin layer chromatography (TLC), the reaction was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography.

III. Optimization of Reaction Conditions[a]



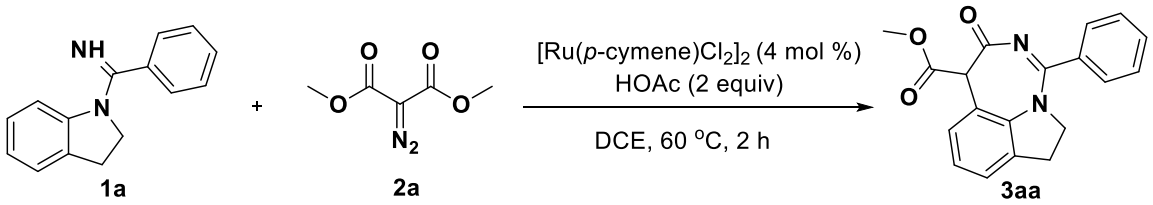
entry	Ag salt	additive	solvent	yield (%)[b]
1	-	HOAc	DCE	32
2	-	CsOAc	DCE	38

3	AgOTf	CsOAc	DCE	40
4	$AgNTf_2$	CsOAc	DCE	38
5	$AgCO_2CF_3$	CsOAc	DCE	42
6	$AgSbF_6$	$Zn(OAc)_2$	DCE	trace
7	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	DCE	trace
8[c]	$AgSbF_6$	CsOAc	DCE	46
9[d]	$AgSbF_6$	CsOAc	DCE	40
10[e]	$AgSbF_6$	CsOAc+ HOAc	DCE	58
11	$AgSbF_6$	NaOAc	DCE	57
12	$AgSbF_6$	KOAc	DCE	61
13	AgOTf	KOAc	DCE	55
14	$AgCO_3CF_3$	KOAc	DCE	55
15	$AgBF_4$	KOAc	DCE	60
16	AgOAc	KOAc	DCE	40
17	$AgSbF_6$	KOAc	Acetone	57
18	$AgSbF_6$	KOAc	Toluene	20
19	$AgSbF_6$	KOAc	DMF	trace
20	$AgSbF_6$	KOAc	CH_3CN	42
21	$AgSbF_6$	KOAc	MeOH	0
22	$AgSbF_6$	KOAc	1,4-Dioxane	10
23[f]	$AgSbF_6$	KOAc	DCE	30
24[g]	$AgSbF_6$	KOAc	DCE	63
25[h]	**$AgSbF_6$**	**KOAc**	**DCE**	**66**
26[i]	$AgSbF_6$	KOAc+HOAc	DCE	64
27	$AgSbF_6$	KOPiv	DCE	45
28	$AgSbF_6$	NaOPiv	DCE	50
29	$AgSbF_6$	CsOPiv	DCE	25

[a]General reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (4 mol %), Ag salt (20 mol %), additive (0.2 mmol), in solvent (2 mL) at 80 °C in oil bath, under air, for 12 h. [b]Determined by crude ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. [c][Cp*$RhCl_2$]$_2$ (4 mol %). [d][Cp*$IrCl_2$]$_2$ (4 mol %). [e]Additive (CsOAc 0.2 mmol+HOAc 0.05 mmol). [f]Additive (0.05 mmol). [g]Additive (0.1 mmol). [h]Additive (0.3 mmol). [i]Additive (KOAc 0.2 mmol+HOAc 0.05 mmol). DCE: 1,2-dichloroethane. THF: tetrahydrofuran.

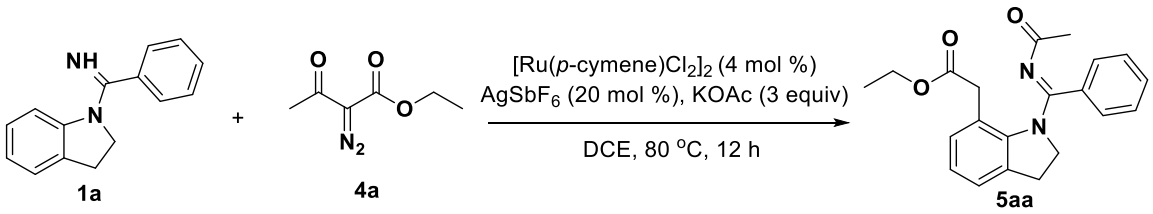
IV. General procedures for the reaction

(a) General procedure for the synthesis of **3aa**



A pressure tube was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (9.8 mg, 4 mol %), HOAc (48 mg, 0.8 mmol), indolin-1-yl(phenyl)methanimine **1a** (88.9 mg, 0.4 mmol), dimethyl diazomalonate **2a** (94.9 mg, 0.6 mmol) and DCE (4 mL). The reaction mixture was stirred at 60 °C for 2 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA = 2:1 to afford the product **3aa**.

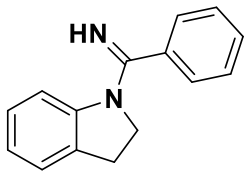
(b) General procedure for the synthesis of **5aa**



A pressure tube was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (9.8 mg, 4 mol %), $AgSbF_6$ (27.5 mg, 20 mol %), KOAc (117.8 mg, 1.2 mmol), indolin-1-yl(phenyl)methanimine **1a** (88.9 mg, 0.4 mmol), ethyl diazoacetate **4a** (93.7 mg, 0.6 mmol) and DCE (4 mL). The reaction mixture was stirred at 80 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA = 3:1 to afford the product **5aa**.

V. Characterization Data for Substrates

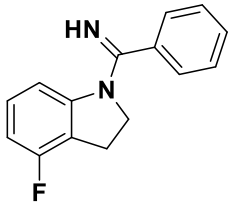
indolin-1-yl(phenyl)methanimine (1a)



^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (s, 1H), 7.52 – 7.44 (m, 3H), 7.44 – 7.39 (m, 2H), 7.16 (d, J = 7.3 Hz, 1H), 6.85 (t, J = 7.7 Hz, 1H), 6.76 (t, J = 7.3 Hz, 1H), 6.54 (s, 1H), 3.89 (t, J = 8.4 Hz, 2H), 3.04 (t, J = 8.4 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d_6)** δ 164.4, 145.0, 138.6, 132.8, 129.9, 129.2, 127.3, 126.8, 125.3, 121.2, 114.1,

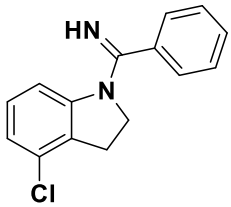
50.9, 27.5; **HRMS (ESI) m/z:** calculated for $C_{15}H_{15}N_2$ $(M+H)^+$: 223.123, found: 223.1234.

(4-fluoroindolin-1-yl)(phenyl)methanimine (1b)



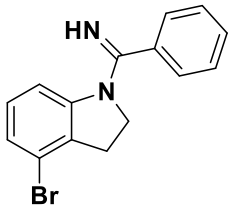
^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.33 (s, 1H), 7.79 – 7.73 (m, 1H), 7.71 – 7.62 (m, 4H), 7.00 – 6.91 (m, 2H), 5.53 (d, *J* = 7.4 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 161.5, 158.6 (d, *J* = 244.5 Hz), 142.9 (d, *J* = 8.7 Hz), 132.9, 129.4, 129.0 (d, *J* = 7.9 Hz), 128.7, 128.6, 121.5 (d, *J* = 23.5 Hz), 112.2 (d, *J* = 19.9 Hz), 112.0 (d, *J* = 3.3 Hz), 53.2, 23.5; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}FN_2$ $(M+H)^+$: 241.1136, found: 241.1133.

(4-chloroindolin-1-yl)(phenyl)methanimine (1c)



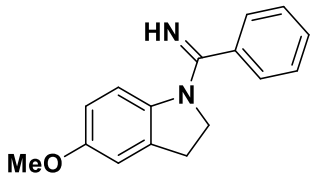
^{1}H NMR (600 MHz, Methanol-*d*$_4$) δ 7.82 – 7.75 (m, 1H), 7.75 – 7.60 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 8.2 Hz, 1H), 5.87 (d, *J* = 8.4 Hz, 1H), 4.43 – 4.35 (m, 2H), 3.41 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR (150 MHz, Methanol-*d*$_4$)** δ 162.8, 141.5, 133.4, 133.2, 131.4, 129.5, 128.7, 128.4, 128.3, 125.8, 114.6, 52.0, 26.7; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}ClN_2$ $(M+H)^+$: 257.084, found: 257.0837.

(4-bromoindolin-1-yl)(phenyl)methanimine (1d)



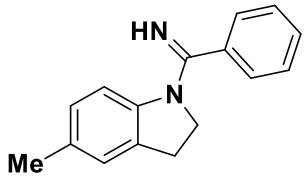
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.29 (s, 1H), 7.78 – 7.73 (m, 1H), 7.72 – 7.60 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 8.2 Hz, 1H), 5.68 (s, 1H), 4.34 (t, *J* = 7.9 Hz, 2H), 3.27 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 162.1, 142.0, 135.9, 133.5, 129.9, 129.3, 129.2, 129.0, 128.7, 120.2, 115.4, 52.7, 29.4; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}BrN_2$ $(M+H)^+$: 301.0335, found: 301.0332.

(5-methoxyindolin-1-yl)(phenyl)methanimine (1e)



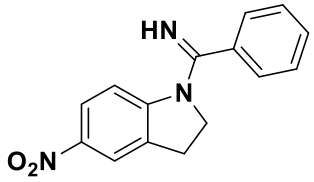
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.39 (m, 5H), 6.79 – 6.71 (m, 1H), 6.40 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.22 (s, 1H), 4.07 (t, *J* = 8.3 Hz, 2H), 3.71 (s, 3H), 3.09 (t, *J* = 8.3 Hz, 2H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 165.3, 154.8, 138.2, 138.1, 134.1, 129.7, 128.9, 127.0, 114.5, 111.4, 111.4, 55.7, 50.8, 27.9; **HRMS (ESI) m/z:** calculated for $C_{16}H_{17}N_2O$ $(M+H)^+$: 253.1335, found: 253.1328.

(5-methylindolin-1-yl)(phenyl)methanimine (1f)



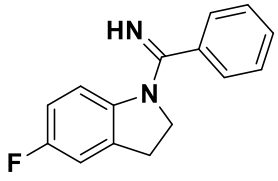
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 5H), 6.98 (s, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.04 (d, *J* = 8.3 Hz, 1H), 4.09 (t, *J* = 8.4 Hz, 2H), 3.08 (t, *J* = 8.3 Hz, 2H), 2.22 (s, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 165.5, 142.0, 138.3, 132.8, 130.8, 129.7, 128.9, 127.1, 127.0, 125.7, 113.6, 50.7, 27.6, 20.7; **HRMS (ESI) m/z:** calculated for $C_{16}H_{17}N_2$ $(M+H)^+$: 237.1386, found: 237.1389.

(5-nitroindolin-1-yl)(phenyl)methanimine (1g)



^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.61 (s, 1H), 8.05 – 8.01 (m, 1H), 7.89 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.54 – 7.43 (m, 5H), 6.96 (s, 1H), 3.99 (t, *J* = 8.6 Hz, 2H), 3.15 (t, *J* = 8.6 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 164.4, 151.2, 140.9, 137.4, 134.6, 130.4, 129.4, 127.3, 124.6, 120.8, 113.3, 52.1, 26.8; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}N_3O_2$ $(M+H)^+$: 268.1081, found: 268.1079.

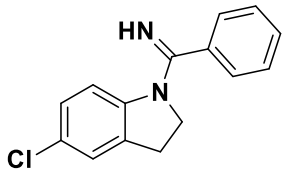
(5-fluoroindolin-1-yl)(phenyl)methanimine (1h)



^{1}H NMR (500 MHz, Methanol-*d*$_4$) δ 7.81 – 7.76 (m, 1H), 7.72 – 7.63 (m, 4H), 7.21 – 7.12 (m, 1H), 6.68 (s, 1H), 5.88 (s, 1H), 4.36 (t, *J* = 7.8 Hz, 2H), 3.40

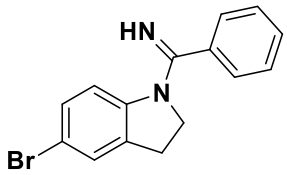
(t, *J* = 7.8 Hz, 2H); **^{13}C NMR (125 MHz, Methanol-*d*$_4$)** δ 161.4, 160.4 (d, *J* = 241.6 Hz), 137.2 (d, *J* = 8.5 Hz), 135.7, 132.6, 129.1, 128.1, 127.9, 116.9 (d, *J* = 8.9 Hz), 112.9 (d, *J* = 24.4 Hz), 112.4 (d, *J* = 24.4 Hz), 52.2, 26.8; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}FN_2$ $(M+H)^+$: 241.1136, found: 241.1133.

(5-chloroindolin-1-yl)(phenyl)methanimine (1i)



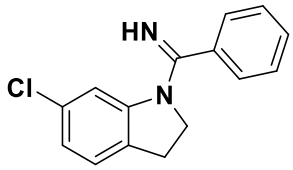
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.89 (s, 1H), 7.50 – 7.45 (m, 3H), 7.44 – 7.37 (m, 2H), 7.25 – 7.18 (m, 1H), 6.95 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.82 (s, 1H), 3.87 (t, *J* = 8.5 Hz, 2H), 3.04 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 164.4, 144.1, 138.3, 135.3, 130.0, 129.3, 127.2, 126.6, 125.2, 124.7, 115.4, 51.3, 27.4; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}ClN_2$ $(M+H)^+$: 257.084, found: 257.0839.

(5-bromoindolin-1-yl)(phenyl)methanimine (1j)



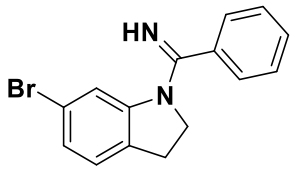
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.34 (m, 5H), 7.24 (d, *J* = 2.1 Hz, 1H), 6.94 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.18 (d, *J* = 8.6 Hz, 1H), 4.07 (t, *J* = 8.5 Hz, 2H), 3.09 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 165.5, 143.6, 137.8, 134.9, 129.9, 129.5, 129.0, 127.9, 126.9, 115.3, 113.5, 50.8, 27.4; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}BrN_2$ $(M+H)^+$: 301.0335, found: 301.033.

(6-chloroindolin-1-yl)(phenyl)methanimine (1k)



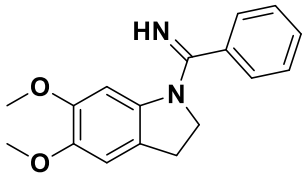
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.52 – 7.47 (m, 3H), 7.44 – 7.40 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 6.83 (dd, *J* = 7.8, 2.0 Hz, 1H), 3.87 (t, *J* = 8.5 Hz, 2H), 3.02 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 164.4, 146.3, 138.0, 131.9, 131.2, 130.1, 129.3, 127.2, 126.2, 120.9, 114.6, 51.6, 27.1; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}ClN_2$ $(M+H)^+$: 257.084, found: 257.0843.

(6-bromoindolin-1-yl)(phenyl)methanimine (1l)



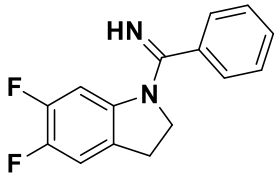
^{1}H NMR (500 MHz, DMSO-d_6) δ 10.29 (s, 1H), 7.82 – 7.76 (m, 1H), 7.70 – 7.65 (m, 4H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.25 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.73 (s, 1H), 4.31 (t, *J* = 8.0 Hz, 2H), 3.25 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d_6)** δ 162.0, 142.4, 135.0, 133.4, 130.0, 129.2, 129.1, 128.6, 128.1, 119.3, 119.2, 53.6, 27.4; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}BrN_2$ $(M+H)^+$: 301.0335, found: 301.0338.

(5,6-dimethoxyindolin-1-yl)(phenyl)methanimine (1m)



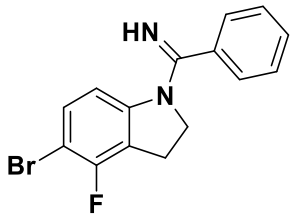
^{1}H NMR (600 MHz, Methanol-d_4) δ 7.83 – 7.77 (m, 1H), 7.77 – 7.66 (m, 4H), 6.99 (s, 1H), 5.44 (s, 1H), 4.35 (t, *J* = 7.7 Hz, 2H), 3.80 (s, 3H), 3.34 (d, *J* = 7.8 Hz, 2H), 3.26 (s, 3H); **^{13}C NMR (150 MHz, Methanol-d_4)** δ 160.3, 148.4, 147.9, 132.8, 132.6, 129.5, 129.0, 128.6, 126.9, 108.6, 100.9, 55.4, 54.6, 52.6, 27.1; **HRMS (ESI) m/z:** calculated for $C_{17}H_{19}N_2O_2$ $(M+H)^+$: 283.1441, found: 283.144.

(5,6-difluoroindolin-1-yl)(phenyl)methanimine (1n)



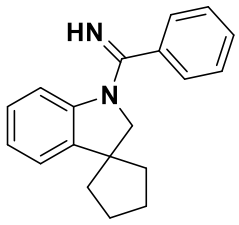
^{1}H NMR (500 MHz, Methanol-d_4) δ 7.85 – 7.80 (m, 1H), 7.73 – 7.68 (m, 4H), 7.37 – 7.30 (m, 1H), 5.70 (s, 1H), 4.38 (t, *J* = 7.9 Hz, 2H), 3.39 – 3.35 (m, 2H); **^{13}C NMR (125 MHz, Methanol-d_4)** δ 161.8, 148.1 (d, *J* = 245.2, 14.1 Hz), 147.9 (d, *J* = 247.7, 13.7 Hz), 135.6 (d, *J* = 9.8, 3.1 Hz), 132.9, 131.2 (dd, *J* = 6.9, 3.0 Hz), 129.2, 127.9, 127.7, 113.9 (d, *J* = 20.0 Hz), 105.3 (d, *J* = 24.7 Hz), 52.6, 26.4; **HRMS (ESI) m/z:** calculated for $C_{15}H_{13}F_2N_2$ $(M+H)^+$: 259.1041, found: 259.1049.

(5-bromo-4-fluoroindolin-1-yl)(phenyl)methanimine (1o)



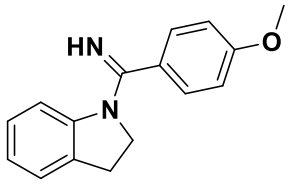
^{1}H NMR (500 MHz, Methanol-*d*$_4$) δ 7.82 – 7.76 (m, 1H), 7.71 – 7.64 (m, 4H), 7.18 (dd, *J* = 8.8, 6.9 Hz, 1H), 5.66 (d, *J* = 8.4 Hz, 1H), 4.41 (td, *J* = 8.0, 2.7 Hz, 2H), 3.43 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR (125 MHz, Methanol-*d*$_4$)** δ 162.5, 155.0 (d, *J* = 246.9 Hz), 141.6 (d, *J* = 7.5 Hz), 132.8, 131.5, 129.1, 128.0, 127.8, 122.7 (d, *J* = 26.9 Hz), 112.6 (d, *J* = 3.4 Hz), 104.5 (d, *J* = 19.8 Hz), 52.4, 23.2; **HRMS (ESI) m/z:** calculated for $C_{15}H_{13}BrFN_2$ $(M+H)^+$: 319.0241, found: 319.0238.

phenyl(spiro[cyclopentane-1,3'-indolin]-1'-yl)methanimine (1p)



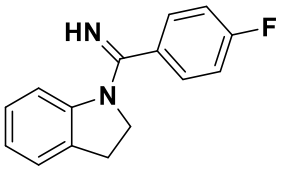
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.19 (s, 1H), 7.79 – 7.74 (m, 1H), 7.71 – 7.63 (m, 4H), 7.41 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.9 Hz, 1H), 5.67 (s, 1H), 4.15 (s, 2H), 2.03 – 1.94 (m, 2H), 1.95 – 1.85 (m, 4H), 1.82 – 1.72 (m, 2H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.6, 142.2, 140.2, 133.5, 130.0, 129.2, 129.2, 127.6, 126.7, 124.2, 115.9, 65.6, 51.4, 39.9, 24.7; **HRMS (ESI) m/z:** calculated for $C_{19}H_{21}N_2$ $(M+H)^+$: 277.1699, found: 277.1702.

indolin-1-yl(4-methoxyphenyl)methanimine (1q)



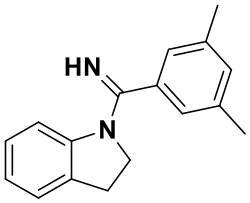
^{1}H NMR (500 MHz, Methanol-*d*$_4$) δ 7.67 – 7.61 (m, 2H), 7.38 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.12 (td, *J* = 7.5, 0.9 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.15 (d, *J* = 8.3 Hz, 1H), 4.32 (t, *J* = 7.9 Hz, 2H), 3.93 (s, 3H), 3.37 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR (125 MHz, Methanol-*d*$_4$)** δ 163.9, 162.1, 140.4, 134.9, 130.7, 126.7, 126.0, 125.8, 120.3, 116.2, 114.7, 54.9, 52.8, 27.4; **HRMS (ESI) m/z:** calculated for $C_{16}H_{17}N_2O$ $(M+H)^+$: 253.1335, found: 253.1335.

(4-fluorophenyl)(indolin-1-yl)methanimine (1r)



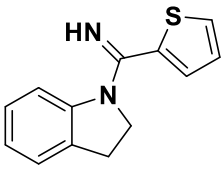
^{1}H NMR (600 MHz, Methanol-*d*$_4$) δ 7.82 – 7.73 (m, 2H), 7.44 – 7.37 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 9.6 Hz, 1H), 6.00 (s, 1H), 4.34 (t, *J* = 7.8 Hz, 2H), 3.39 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR (150 MHz, Methanol-*d*$_4$)** δ 165.1 (d, *J* = 253.8 Hz), 160.6, 139.4, 134.6, 131.0 (d, *J* = 9.2 Hz), 126.3, 125.9, 125.5, 124.5, 116.2 (d, *J* = 22.8 Hz), 115.7, 52.2, 26.8; **HRMS (ESI) m/z:** calculated for $C_{15}H_{14}FN_2$ $(M+H)^+$: 241.1136, found: 241.1136.

(3,5-dimethylphenyl)(indolin-1-yl)methanimine (1s)



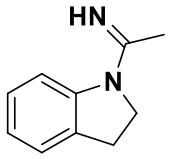
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.05 (s, 1H), 7.42 – 7.35 (m, 2H), 7.29 (s, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 1H), 5.79 (s, 1H), 4.29 (t, *J* = 7.9 Hz, 2H), 3.30 (t, *J* = 7.9 Hz, 2H), 2.34 (s, 6H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 161.5, 140.7, 139.4, 135.4, 134.6, 129.3, 127.2, 126.6, 126.3, 126.2, 116.1, 53.1, 27.6, 21.2; **HRMS (ESI) m/z:** calculated for $C_{17}H_{19}N_2$ $(M+H)^+$: 251.1543, found: 251.155.

indolin-1-yl(thiophen-2-yl)methanimine (1t)



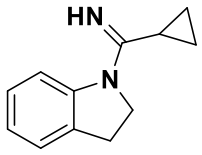
^{1}H NMR (600 MHz, Methanol-*d*$_4$) δ 8.04 (d, *J* = 5.0 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 4.4 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.31 (s, 1H), 4.36 (t, *J* = 7.7 Hz, 2H), 3.38 – 3.34 (m, 2H); **^{13}C NMR (150 MHz, Methanol-*d*$_4$)** δ 156.1, 140.0, 135.1, 133.9, 133.3, 128.3, 127.6, 126.8, 126.5, 125.9, 116.2, 53.6, 27.5; **HRMS (ESI) m/z:** calculated for $C_{13}H_{13}N_2S$ $(M+H)^+$: 229.0794, found: 229.0796.

1-(indolin-1-yl)ethan-1-imine (1u)



^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 9.64 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.31 (td, *J* = 7.8, 1.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 4.11 (t, *J* = 8.1 Hz, 2H), 3.23 (t, *J* = 8.0 Hz, 2H), 2.66 (s, 3H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 162.1, 140.1, 134.7, 127.5, 126.1, 125.9, 116.4, 51.1, 26.9, 19.9; **HRMS (ESI) m/z:** calculated for $C_{10}H_{13}N_2$ $(M+H)^+$: 161.1073, found: 161.1072.

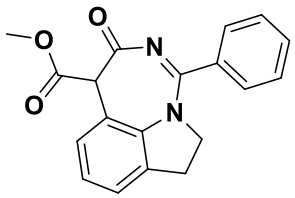
cyclopropyl(indolin-1-yl)methanimine (1v)



^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 9.34 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.30 (td, *J* = 7.8, 1.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 2H), 3.23 (t, *J* = 7.9 Hz, 2H), 2.34 – 2.23 (m, 1H), 1.43 – 1.34 (m, 2H), 1.30 – 1.23 (m, 2H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 164.9, 140.1, 135.0, 127.4, 126.0, 125.9, 116.7, 52.4, 27.1, 13.9, 8.9; **HRMS (ESI) m/z:** calculated for $C_{12}H_{15}N_2$ $(M+H)^+$: 187.123, found: 187.1227.

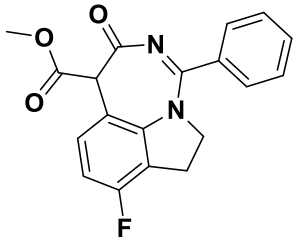
VI. Characterization Data for Products

methyl 6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carbox ylate (3aa)



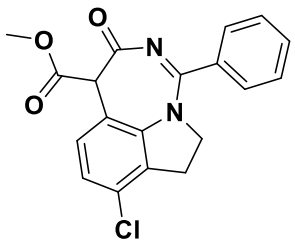
Following by general procedure for the synthesis of **3aa**. White solid, 120.5 mg, yield: 94% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.66 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.52 – 7.42 (m, 3H), 7.32 – 7.26 (m, 2H), 7.20 – 7.13 (m, 1H), 5.04 (s, 1H), 4.34 (q, *J* = 10.0 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.59 (s, 3H), 3.30 – 3.20 (m, 1H), 3.15 – 3.06 (m, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.7, 163.1, 153.5, 139.9, 136.3, 134.5, 130.7, 128.7, 128.4, 128.2, 127.5, 124.8, 118.8, 63.0, 55.0, 52.7, 28.1; **HRMS (ESI) m/z:** calculated for $C_{19}H_{17}N_2O_3$ $(M+H)^+$: 321.1234, found: 321.1232.

methyl 10-fluoro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ba)



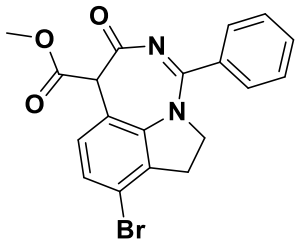
Following by general procedure for the synthesis of **3aa**. White solid, 109.6 mg, yield: 81% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.68 – 7.61 (m, 2H), 7.53 – 7.43 (m, 3H), 7.14 (dd, *J* = 8.7, 4.9 Hz, 1H), 7.01 (t, *J* = 8.3 Hz, 1H), 5.01 (s, 1H), 4.38 (q, *J* = 10.2 Hz, 1H), 3.99 (ddd, *J* = 10.8, 9.2, 3.3 Hz, 1H), 3.60 (s, 3H), 3.25 – 3.14 (m, 2H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 167.2, 162.6, 158.2 (d, *J* = 247.7 Hz), 152.9, 141.7 (d, *J* = 8.7 Hz), 135.5, 130.5, 130.0 (d, *J* = 8.2 Hz), 128.3, 127.7, 119.7 (d, *J* = 22.7 Hz), 114.2 (d, *J* = 21.3 Hz), 114.1 (d, *J* = 3.2 Hz), 61.8, 54.8, 52.4, 24.1; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}FN_2O_3$ $(M+H)^+$: 339.1139, found: 339.1142.

methyl 10-chloro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ca)



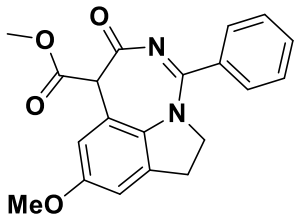
Following by general procedure for the synthesis of **3aa**. White solid, 110.7 mg, yield: 78% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.64 (m, 2H), 7.55 – 7.46 (m, 3H), 7.30 – 7.28 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 5.03 (s, 1H), 4.44 – 4.36 (m, 1H), 4.00 (ddd, *J* = 11.0, 9.5, 3.3 Hz, 1H), 3.63 (s, 3H), 3.29 – 3.15 (m, 2H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.4, 162.8, 153.4, 141.1, 135.9, 132.7, 130.9, 130.8, 129.9, 128.7, 128.2, 127.2, 116.9, 62.5, 54.5, 52.8, 27.6; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}ClN_2O_3$ $(M+H)^+$: 355.0844, found: 355.0853.

methyl 10-bromo-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3da)



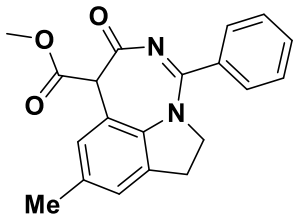
Following by general procedure for the synthesis of **3aa**. White solid, 121.4 mg, yield: 76% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.68 – 7.61 (m, 2H), 7.53 – 7.49 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 5.00 (s, 1H), 4.41 – 4.32 (m, 1H), 3.97 (ddd, *J* = 11.0, 9.7, 3.0 Hz, 1H), 3.60 (s, 3H), 3.24 – 3.17 (m, 1H), 3.12 (ddd, *J* = 16.6, 9.9, 3.0 Hz, 1H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 166.9, 162.2, 153.1, 140.4, 135.4, 134.6, 130.5, 129.7, 128.3, 127.7, 119.0, 116.9, 62.1, 53.8, 52.4, 29.2; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}BrN_2O_3$ $(M+H)^+$: 399.0339, found: 399.0351.

methyl 9-methoxy-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ea)



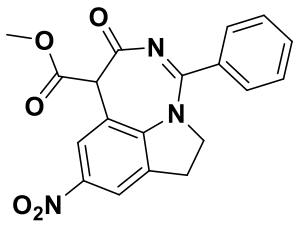
Following by general procedure for the synthesis of **3aa**. White solid, 67.3 mg, yield: 48% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 7.58 – 7.49 (m, 5H), 7.06 – 6.99 (m, 1H), 6.94 (d, *J* = 2.6 Hz, 1H), 5.06 (s, 1H), 4.31 (q, *J* = 9.7 Hz, 1H), 3.96 – 3.89 (m, 1H), 3.79 (s, 3H), 3.52 (s, 3H), 3.27 – 3.18 (m, 1H), 3.07 (ddd, *J* = 16.3, 9.5, 2.5 Hz, 1H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 167.1, 161.7, 159.1, 151.7, 137.1, 136.1, 132.9, 130.5, 128.5, 128.0, 119.5, 111.7, 111.6, 62.1, 55.7, 55.1, 52.4, 28.0; **HRMS (ESI) m/z:** calculated for $C_{20}H_{19}N_2O_4$ $(M+H)^+$: 351.1339, found: 351.1336.

methyl 9-methyl-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3fa)



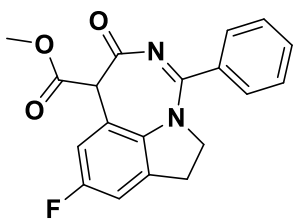
Following by general procedure for the synthesis of **3aa**. White solid, 104.3 mg, yield: 78% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.66 (dt, *J* = 6.6, 1.5 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.11 (s, 1H), 6.97 (s, 1H), 4.99 (s, 1H), 4.33 (q, *J* = 10.0 Hz, 1H), 3.95 (ddd, *J* = 10.8, 9.5, 2.5 Hz, 1H), 3.59 (s, 3H), 3.26 – 3.15 (m, 1H), 3.05 (ddd, *J* = 16.1, 9.5, 2.5 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.8, 163.2, 153.2, 137.9, 137.6, 136.3, 134.6, 130.7, 128.6, 128.6, 128.2, 125.7, 118.5, 62.9, 55.1, 52.7, 28.1, 21.1; **HRMS (ESI) m/z:** calculated for $C_{20}H_{19}N_2O_3$ $(M+H)^+$: 335.139, found: 335.1384.

methyl 9-nitro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ga)



Following by general procedure for the synthesis of **3aa**. Light yellow solid, 106.7 mg, yield: 73% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.17 – 8.07 (m, 2H), 7.67 – 7.62 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 5.10 (s, 1H), 4.44 (q, *J* = 10.2 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.62 (s, 3H), 3.34 (dt, *J* = 16.4, 9.9 Hz, 1H), 3.23 (ddd, *J* = 16.5, 9.9, 3.2 Hz, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.0, 162.3, 153.5, 145.8, 145.4, 136.1, 135.3, 131.3, 128.9, 128.2, 125.4, 120.1, 118.1, 62.7, 55.5, 53.1, 27.6; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}N_3O_5$ $(M+H)^+$: 366.1084, found: 366.1075.

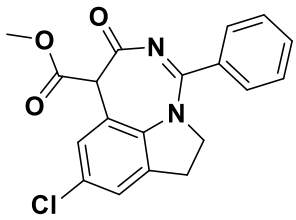
methyl 9-fluoro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ha)



Following by general procedure for the synthesis of **3aa**. White

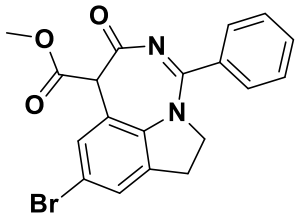
solid, 123.2 mg, yield: 91% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 7.59 – 7.50 (m, 5H), 7.37 – 7.26 (m, 2H), 5.14 (s, 1H), 4.35 (q, *J* = 9.9 Hz, 1H), 3.96 (td, *J* = 10.1, 2.7 Hz, 1H), 3.53 (s, 3H), 3.30 – 3.23 (m, 1H), 3.12 (ddd, *J* = 16.6, 9.5, 2.7 Hz, 1H); **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 166.8, 161.5, 161.0 (d, *J* = 243.3 Hz), 152.3, 138.1 (d, *J* = 9.7 Hz), 136.0, 135.9, 130.7, 128.6, 128.0, 119.7 (d, *J* = 9.6 Hz), 113.8 (d, *J* = 24.4 Hz), 112.6 (d, *J* = 24.7 Hz), 61.6, 55.3, 52.6, 27.9; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}FN_2O_3$ $(M+H)^+$: 339.1139, found: 339.114.

methyl 9-chloro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ia)



Following by general procedure for the synthesis of **3aa**. White solid,113.5 mg, yield: 80% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.67 – 7.59 (m, 2H), 7.52 – 7.42 (m, 3H), 7.26 (d, *J* = 2.1 Hz, 1H), 7.19 – 7.14 (m, 1H), 4.96 (s, 1H), 4.35 (q, *J* = 10.2 Hz, 1H), 4.01 – 3.92 (m, 1H), 3.59 (s, 3H), 3.23 (dt, *J* = 16.2, 9.9 Hz, 1H), 3.09 (ddd, *J* = 16.3, 9.6, 2.6 Hz, 1H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 166.7, 162.1, 152.9, 138.2, 136.0, 135.4, 132.1, 130.5, 128.3, 127.7, 127.6, 124.7, 119.1, 62.1, 54.7, 52.4, 27.6; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}ClN_2O_3$ $(M+H)^+$: 355.0844, found: 355.0848.

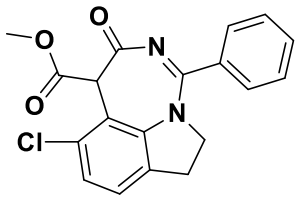
methyl 9-bromo-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ja)



Following by general procedure for the synthesis of **3aa**. White solid, 140.5 mg, yield: 88% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.64 (d, *J* = 7.0 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.32 (s, 1H), 4.96 (s, 1H), 4.36 (q, *J* = 10.2 Hz, 1H), 3.96 (td, *J* = 11.3, 10.6, 2.6 Hz, 1H), 3.60 (s, 3H), 3.25 (dt, *J* = 16.3, 9.9 Hz, 1H), 3.10 (ddd, *J* = 16.2, 9.6, 2.6 Hz, 1H); **^{13}C NMR**

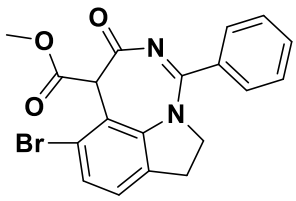
(150 MHz, Chloroform-*d*) δ 166.8, 162.1, 152.9, 138.7, 136.2, 135.4, 130.5, 130.5, 128.3, 127.7, 127.5, 119.6, 119.5, 62.0, 54.7, 52.4, 27.6; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}BrN_2O_3$ $(M+H)^+$: 399.0339, found: 399.0339.

methyl 8-chloro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ka)



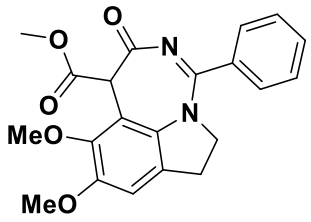
Following by general procedure for the synthesis of **3aa**. White solid, 78.1 mg, yield: 55% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 7.61 – 7.49 (m, 6H), 7.42 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 1H), 4.36 (q, *J* = 10.1 Hz, 1H), 3.95 (td, *J* = 10.1, 2.3 Hz, 1H), 3.55 (s, 3H), 3.28 – 3.16 (m, 1H), 3.13 – 3.03 (m, 1H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 166.8, 161.9, 153.4, 141.6, 136.2, 135.5, 131.3, 131.0, 129.1, 128.4, 127.6, 126.3, 116.5, 59.5, 56.2, 53.3, 27.7; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}ClN_2O_3$ $(M+H)^+$: 355.0844, found: 355.0845.

methyl 8-bromo-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3la)



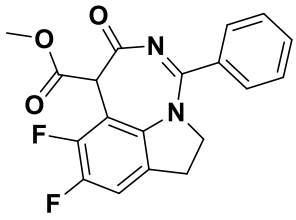
Following by general procedure for the synthesis of **3aa**. White solid, 47.9 mg, yield: 30% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.67 – 7.59 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.13 (d, *J* = 7.9 Hz, 1H), 5.79 (s, 1H), 4.32 (q, *J* = 10.4 Hz, 1H), 3.95 (ddd, *J* = 11.1, 9.7, 2.3 Hz, 1H), 3.61 (s, 3H), 3.24 – 3.14 (m, 1H), 3.02 (ddd, *J* = 16.1, 9.5, 2.3 Hz, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.2, 162.9, 153.7, 141.5, 136.2, 134.3, 131.1, 131.0, 128.8, 128.2, 125.7, 123.0, 118.9, 62.2, 55.7, 53.0, 27.9; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}BrN_2O_3$ $(M+H)^+$: 399.0339, found: 399.0345.

methyl 8,9-dimethoxy-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*] indole-7-carboxylate (3ma)



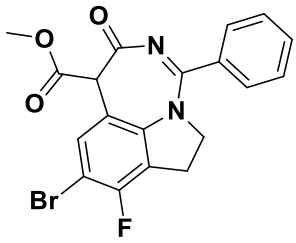
Following by general procedure (last for 12 h) for the synthesis of **3aa**. White solid, 41.1 mg, yield: 27% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.66 – 7.59 (m, 2H), 7.49 – 7.40 (m, 3H), 6.91 (s, 1H), 5.56 (s, 1H), 4.39 – 4.25 (m, 1H), 3.95 – 3.90 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.58 (s, 3H), 3.27 – 3.14 (m, 1H), 3.01 (ddd, *J* = 15.7, 9.4, 2.1 Hz, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.2, 163.1, 152.3, 151.7, 144.9, 135.8, 133.3, 130.1, 129.0, 128.1, 127.7, 114.1, 109.2, 61.5, 56.0, 55.2, 55.0, 52.2, 28.0; **HRMS (ESI) m/z:** calculated for $C_{21}H_{21}N_2O_5$ $(M+H)^+$: 381.1445, found: 381.1437.

methyl 8,9-difluoro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*] indole -7-carboxylate (3na)



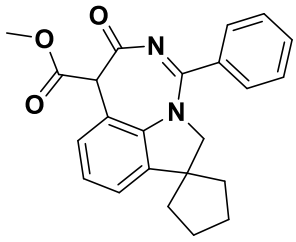
Following by general procedure for the synthesis of **3aa**. White solid, 125.4 mg, yield: 88% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.62 – 7.55 (m, 4H), 7.55 – 7.50 (m, 2H), 5.25 (s, 1H), 4.40 (q, *J* = 10.0 Hz, 1H), 3.96 (td, *J* = 10.1, 2.5 Hz, 1H), 3.56 (s, 3H), 3.30 – 3.21 (m, 1H), 3.13 – 3.05 (m, 1H); **^{13}C NMR (125 MHz, DMSO-d_6)** δ 166.4, 161.4, 152.8, 148.4 (dd, *J* = 245.1, 13.8 Hz), 145.9 (dd, *J* = 243.7, 14.7 Hz), 136.8, 136.0, 132.1 (dd, *J* = 7.6, 3.8 Hz), 131.3, 129.1, 128.5, 114.5 (d, *J* = 20.0 Hz), 108.7 (d, *J* = 17.6 Hz), 56.1, 55.1, 53.4, 28.0; **HRMS (ESI) m/z:** calculated for $C_{19}H_{15}F_2N_2O_3$ $(M+H)^+$: 357.1045, found: 357.1046.

methyl 9-bromo-10-fluoro-6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*] indole-7-carboxylate (3oa)



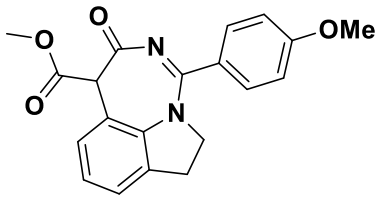
Following by general procedure for the synthesis of **3aa**. White solid, 103.5 mg, yield: 62% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.68 – 7.61 (m, 2H), 7.53 – 7.49 (m, 1H), 7.49 – 7.44 (m, 2H), 7.38 (d, *J* = 6.2 Hz, 1H), 4.95 (s, 1H), 4.41 (q, *J* = 10.2 Hz, 1H), 4.00 (ddd, *J* = 11.0, 9.1, 3.6 Hz, 1H), 3.61 (s, 3H), 3.31 – 3.15 (m, 2H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.2, 162.7, 154.9 (d, *J* = 248.1 Hz), 153.2, 141.5 (d, *J* = 7.8 Hz), 135.7, 133.3, 131.1, 128.8, 128.2, 121.6 (d, *J* = 23.6 Hz), 115.4 (d, *J* = 3.8 Hz), 107.0 (d, *J* = 21.2 Hz), 61.9, 55.4, 52.9, 24.9; **HRMS (ESI) m/z:** calculated for $C_{19}H_{15}BrFN_2O_3$ $(M+H)^+$: 417.0245, found: 417.0241.

methyl 6'-oxo-4'-phenyl-6',7'-dihydro-2'H-spiro[cyclopentane-1,1'-[1,3]diazepino [6,7,1-*hi*]indole] -7'-carboxylate (3pa)



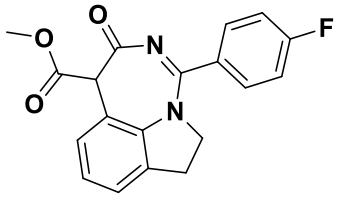
Following by general procedure for the synthesis of **3aa**. White solid, 112.3 mg, yield: 75% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.62 (m, 2H), 7.52 – 7.43 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.05 (s, 1H), 4.13 (d, *J* = 10.7 Hz, 1H), 3.69 (d, *J* = 10.7 Hz, 1H), 3.59 (s, 3H), 2.23 – 2.15 (m, 1H), 1.90 – 1.74 (m, 4H), 1.73 – 1.66 (m, 1H), 1.62 – 1.52 (m, 2H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.7, 163.1, 153.3, 143.0, 139.0, 136.2, 130.7, 128.7, 128.4, 128.2, 127.9, 122.2, 118.8, 68.8, 63.0, 52.7, 51.6, 41.7, 38.3, 25.3, 25.0; **HRMS (ESI) m/z:** calculated for $C_{23}H_{23}N_2O_3$ $(M+H)^+$: 375.1703, found: 375.1705.

methyl 4-(4-methoxyphenyl)-6-oxo-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole -7-carboxylate (3qa)



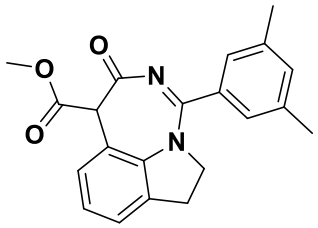
Following by general procedure for the synthesis of **3aa**. White solid, 134.5 mg, yield: 96% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.59 (m, 2H), 7.33 – 7.23 (m, 2H), 7.19 – 7.11 (m, 1H), 7.01 – 6.90 (m, 2H), 5.02 (s, 1H), 4.39 (q, *J* = 10.1 Hz, 1H), 4.02 (ddd, *J* = 10.9, 9.6, 2.6 Hz, 1H), 3.85 (s, 3H), 3.58 (s, 3H), 3.24 (dt, *J* = 15.7, 9.8 Hz, 1H), 3.10 (ddd, *J* = 16.0, 9.6, 2.6 Hz, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.7, 162.8, 161.7, 153.3, 140.0, 134.4, 130.2, 128.5, 128.4, 127.3, 124.7, 118.8, 113.9, 63.0, 55.5, 55.1, 52.6, 28.2; **HRMS (ESI) m/z:** calculated for $C_{20}H_{19}N_2O_4$ $(M+H)^+$: 351.1339, found: 351.1346.

methyl 4-(4-fluorophenyl)-6-oxo-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ra)



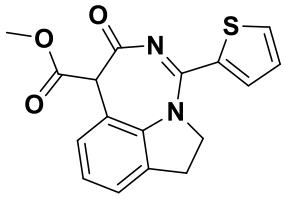
Following by general procedure for the synthesis of **3aa**. White solid, 115.0 mg, yield: 85% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 – 7.64 (m, 2H), 7.33 – 7.27 (m, 2H), 7.20 – 7.11 (m, 3H), 5.03 (s, 1H), 4.34 (q, *J* = 10.1 Hz, 1H), 3.97 (ddd, *J* = 10.8, 9.6, 2.5 Hz, 1H), 3.59 (s, 3H), 3.27 (dt, *J* = 15.7, 9.8 Hz, 1H), 3.12 (ddd, *J* = 15.9, 9.6, 2.5 Hz, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.7, 164.1 (d, *J* = 251.5 Hz), 162.9, 152.5, 139.8, 134.4, 132.4 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 8.7 Hz), 128.5, 127.6, 124.9, 118.8, 115.8 (d, *J* = 21.9 Hz), 62.9, 55.0, 52.7, 28.2; **HRMS (ESI) m/z:** calculated for $C_{19}H_{16}FN_2O_3$ $(M+H)^+$: 339.1139, found: 339.1138.

methyl 4-(3,5-dimethylphenyl)-6-oxo-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*] indole-7-carboxylate (3sa)



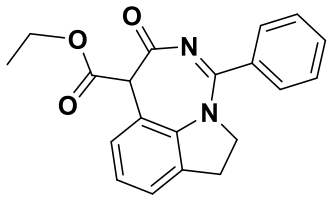
Following by general procedure for the synthesis of **3aa**. White solid, 111.5 mg, yield: 80% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.32 – 7.28 (m, 4H), 7.20 – 7.16 (m, 1H), 7.14 (s, 1H), 5.06 (s, 1H), 4.37 (q, *J* = 10.2 Hz, 1H), 4.00 (ddd, *J* = 11.0, 9.6, 2.6 Hz, 1H), 3.63 (s, 3H), 3.26 (dt, *J* = 15.7, 9.8 Hz, 1H), 3.12 (ddd, *J* = 16.0, 9.6, 2.6 Hz, 1H), 2.38 (s, 6H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.7, 163.1, 153.9, 139.9, 138.4, 136.2, 134.4, 132.4, 128.4, 127.4, 125.9, 124.8, 118.8, 63.0, 55.0, 52.7, 28.1, 21.2; **HRMS (ESI) m/z:** calculated for $C_{21}H_{21}N_2O_3$ $(M+H)^+$: 349.1547, found: 349.1553.

methyl 6-oxo-4-(thiophen-2-yl)-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ta)



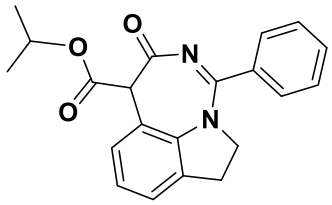
Following by general procedure for the synthesis of **3aa**. White solid, 104.4 mg, yield: 80% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (ddd, *J* = 14.8, 4.4, 1.1 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.14 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.97 (s, 1H), 4.63 – 4.55 (m, 1H), 4.44 (ddd, *J* = 10.6, 9.5, 2.5 Hz, 1H), 3.55 (s, 3H), 3.29 (dt, *J* = 15.8, 9.8 Hz, 1H), 3.15 (ddd, *J* = 16.0, 9.5, 2.4 Hz, 1H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.5, 162.6, 147.2, 139.8, 138.5, 134.3, 130.7, 130.3, 128.4, 127.6, 127.6, 124.8, 119.0, 62.9, 55.4, 52.6, 28.4; **HRMS (ESI) m/z:** calculated for $C_{17}H_{15}N_2O_3S$ $(M+H)^+$: 327.0798, found: 327.0802.

ethyl 6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ab)



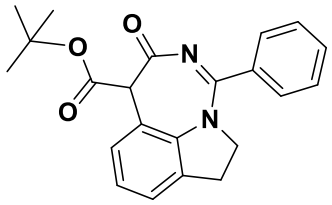
Following by general procedure for the synthesis of **3aa**. White solid, 121.7 mg, yield: 91% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.66 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.31 – 7.27 (m, 2H), 7.19 – 7.14 (m, 1H), 5.02 (s, 1H), 4.33 (q, *J* = 10.2 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.95 (ddd, *J* = 10.9, 9.6, 2.5 Hz, 1H), 3.24 (dt, *J* = 15.8, 9.8 Hz, 1H), 3.09 (ddd, *J* = 15.9, 9.6, 2.5 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 167.1, 163.2, 153.4, 139.9, 136.3, 134.4, 130.7, 128.6, 128.4, 128.2, 127.5, 124.8, 118.9, 63.2, 61.7, 55.0, 28.2, 13.9; **HRMS (ESI) m/z:** calculated for $C_{20}H_{19}N_2O_3$ $(M+H)^+$: 335.139, found: 335.1395.

isopropyl 6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate(3ac)



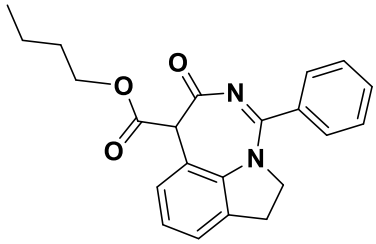
Following by general procedure for the synthesis of **3aa**. White solid, 103.1 mg, yield: 74% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.63 (m, 2H), 7.50 – 7.41 (m, 3H), 7.29 (d, *J* = 4.7 Hz, 2H), 7.20 – 7.13 (m, 1H), 5.00 (s, 1H), 4.90 – 4.77 (m, 1H), 4.34 (q, *J* = 10.2 Hz, 1H), 4.03 – 3.89 (m, 1H), 3.25 (dt, *J* = 15.7, 9.9 Hz, 1H), 3.10 (ddd, *J* = 15.8, 9.5, 2.5 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H), 0.97 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 166.6, 163.4, 153.2, 139.9, 136.2, 134.3, 130.7, 128.5, 128.5, 128.3, 127.4, 124.7, 119.0, 69.4, 63.5, 55.0, 28.2, 21.6, 21.1; **HRMS (ESI) m/z:** calculated for $C_{21}H_{21}N_2O_3$ $(M+H)^+$: 349.1547, found: 349.1551.

tert-butyl 6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ad)



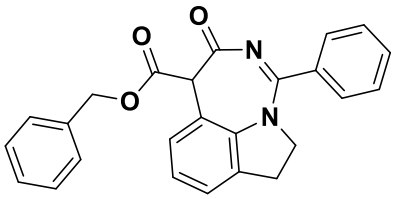
Following by general procedure for the synthesis of **3aa**. White solid, 53.6 mg, yield: 37% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 – 7.63 (m, 2H), 7.49 – 7.41 (m, 3H), 7.30 – 7.27 (m, 2H), 7.18 – 7.13 (m, 1H), 4.97 (s, 1H), 4.36 (q, *J* = 10.2 Hz, 1H), 4.03 – 3.89 (m, 1H), 3.24 (dt, *J* = 15.8, 9.8 Hz, 1H), 3.09 (ddd, *J* = 15.9, 9.5, 2.3 Hz, 1H), 1.28 (s, 9H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 166.0, 163.8, 153.1, 140.0, 136.2, 134.2, 130.6, 128.6, 128.4, 128.4, 127.4, 124.6, 119.1, 82.1, 64.3, 54.9, 28.2, 27.7; **HRMS (ESI) m/z:** calculated for $C_{22}H_{23}N_2O_3$ $(M+H)^+$: 363.1703, found: 363.1715.

butyl 6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3ae)



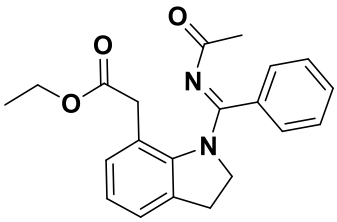
Following by general procedure for the synthesis of **3aa**. White solid, 101.5 mg, yield: 70% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.71 – 7.62 (m, 2H), 7.52 – 7.40 (m, 3H), 7.35 – 7.26 (m, 2H), 7.16 (t, *J* = 4.5 Hz, 1H), 5.03 (s, 1H), 4.35 (q, *J* = 10.2 Hz, 1H), 4.03 (dt, *J* = 10.6, 6.5 Hz, 1H), 3.99 – 3.90 (m, 2H), 3.25 (dt, *J* = 15.8, 9.9 Hz, 1H), 3.10 (ddd, *J* = 15.9, 9.6, 2.4 Hz, 1H), 1.48 – 1.39 (m, 2H), 1.23 – 1.15 (m, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 167.2, 163.2, 153.4, 139.9, 136.2, 134.4, 130.7, 128.6, 128.4, 128.3, 127.5, 124.7, 118.9, 65.5, 63.2, 55.0, 30.4, 28.2, 18.8, 13.5; **HRMS (ESI) m/z:** calculated for $C_{22}H_{23}N_2O_3$ $(M+H)^+$: 363.1703, found: 363.1698.

benzyl 6-oxo-4-phenyl-1,2,6,7-tetrahydro-[1,3]diazepino[6,7,1-*hi*]indole-7-carboxylate (3af)



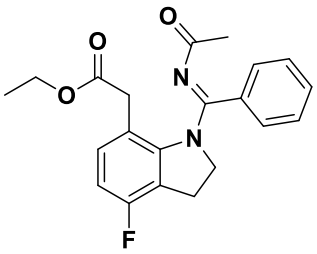
Following by general procedure for the synthesis of **3aa**. White solid, 145.9 mg, yield: 92% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 4.7 Hz, 2H), 7.25 – 7.05 (m, 6H), 5.10 (s, 1H), 5.03 (s, 2H), 4.30 (q, *J* = 10.2 Hz, 1H), 3.94 (td, *J* = 10.2, 2.4 Hz, 1H), 3.24 (dt, *J* = 15.9, 9.8 Hz, 1H), 3.09 (ddd, *J* = 15.9, 9.6, 2.4 Hz, 1H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 166.9, 162.9, 153.4, 139.9, 136.1, 135.2, 134.4, 130.6, 128.6, 128.5, 128.3, 128.3, 128.2, 127.9, 127.5, 124.8, 118.8, 67.2, 63.2, 55.0, 28.2; **HRMS (ESI) m/z:** calculated for $C_{25}H_{21}N_2O_3$ $(M+H)^+$: 397.1547, found: 397.1545.

ethyl 2-(1-((acetylimino)(phenyl)methyl)indolin-7-yl)acetate (5aa)



Following by general procedure for the synthesis of **5aa**. White solid, 89.7 mg, yield: 64% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.49 – 7.41 (m, 5H), 7.18 – 7.14 (m, 1H), 7.12 – 7.08 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.79 (t, *J* = 7.5 Hz, 2H), 3.74 (s, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.99 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.8, 171.3, 158.5, 142.0, 135.5, 135.0, 130.9, 129.8, 129.0, 128.2, 125.8, 125.4, 123.7, 60.8, 54.5, 39.7, 29.9, 27.0, 14.2; **HRMS (ESI) m/z:** calculated for $C_{21}H_{23}N_2O_3$ $(M+H)^+$: 351.1703, found: 351.1696.

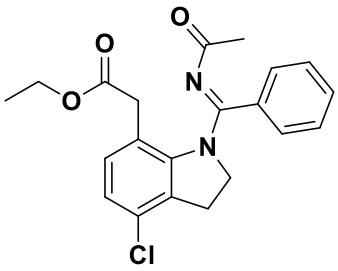
ethyl 2-(1-((acetylimino)(phenyl)methyl)-4-fluoroindolin-7-yl)acetate (5ba)



Following by general procedure for the synthesis of **5aa**. Yellow

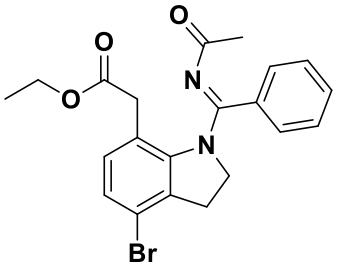
solid, 88.4 mg, yield: 60% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.52 – 7.41 (m, 5H), 7.08 (dd, *J* = 8.6, 5.4 Hz, 1H), 6.82 (t, *J* = 8.3 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.81 (t, *J* = 7.6 Hz, 2H), 3.70 (s, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 1.98 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.2, 170.7, 157.6, 157.6 (d, *J* = 245.4 Hz), 143.8 (d, *J* = 7.5 Hz), 134.2, 131.0 (d, *J* = 7.8 Hz), 130.6, 128.6, 127.7, 121.0 (d, *J* = 21.5 Hz), 120.7 (d, *J* = 3.5 Hz), 112.1 (d, *J* = 20.5 Hz), 60.4, 54.2, 38.7, 26.4, 25.5, 13.7; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}FN_2O_3$ $(M+H)^+$: 369.1609, found: 369.1604.

ethyl 2-(1-((acetylimino)(phenyl)methyl)-4-chloroindolin-7-yl)acetate (5ca)



Following by general procedure for the synthesis of **5aa**. Yellow solid, 98.5 mg, yield: 64% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.54 – 7.39 (m, 5H), 7.15 – 7.02 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.81 (t, *J* = 7.6 Hz, 2H), 3.70 (s, 2H), 3.02 (t, *J* = 7.6 Hz, 2H), 1.99 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.2, 170.5, 157.7, 142.8, 134.1, 133.4, 130.8, 130.7, 128.8, 128.6, 127.7, 125.1, 123.3, 60.4, 53.5, 38.8, 28.7, 26.4, 13.7; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}ClN_2O_3$ $(M+H)^+$: 385.1313, found: 385.1305.

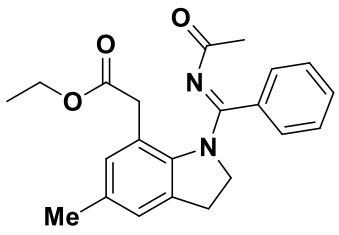
ethyl 2-(1-((acetylimino)(phenyl)methyl)-4-bromoindolin-7-yl)acetate (5da)



Following by general procedure for the synthesis of **5aa**. White solid, 125.4 mg, yield: 73% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 – 7.43 (m, 5H), 7.24 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.81 (t, *J* = 7.5 Hz, 2H), 3.68 (s, 2H), 3.01 (t, *J* = 7.6 Hz,

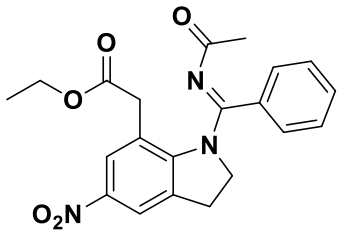
2H), 2.00 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.6, 170.8, 158.3, 143.1, 136.0, 134.5, 131.5, 131.2, 129.1, 128.5, 128.2, 124.4, 118.1, 60.9, 53.7, 39.3, 31.3, 26.9, 14.2; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}BrN_2O_3$ $(M+H)^+$: 429.0808, found: 429.0804.

ethyl 2-(1-((acetylimino)(phenyl)methyl)-5-methylindolin-7-yl)acetate (5fa)



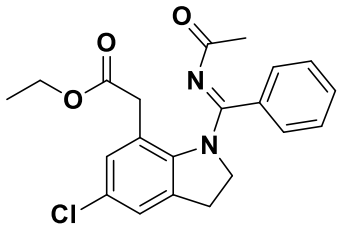
Following by general procedure for the synthesis of **5aa**. Yellow oil, 83.1 mg, yield: 57% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.44 (dt, *J* = 14.2, 7.4 Hz, 5H), 6.98 (s, 1H), 6.92 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.77 (t, *J* = 7.5 Hz, 2H), 3.70 (s, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.99 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.8, 171.4, 158.7, 139.7, 135.7, 135.6, 135.1, 130.9, 130.4, 129.0, 128.2, 125.0, 124.5, 60.8, 54.7, 39.6, 29.9, 27.0, 21.1, 14.2; **HRMS (ESI) m/z:** calculated for $C_{22}H_{25}N_2O_3$ $(M+H)^+$: 365.186, found: 365.1866.

ethyl 2-(1-((acetylimino)(phenyl)methyl)-5-nitroindolin-7-yl)acetate (5ga)



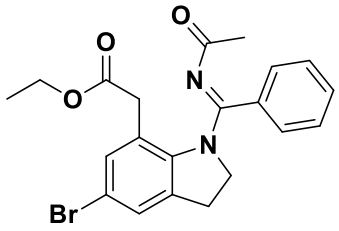
Following by general procedure for the synthesis of **5aa**. Yellow solid, 98.1mg, yield: 62% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.06 (d, *J* = 2.3 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.53 – 7.49 (m, 1H), 7.46 (d, *J* = 4.0 Hz, 4H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.87 (t, *J* = 7.8 Hz, 2H), 3.82 (s, 2H), 3.10 (t, *J* = 7.8 Hz, 2H), 2.00 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.4, 170.1, 157.2, 148.0, 145.0, 137.0, 133.9, 131.5, 129.3, 128.1, 126.6, 125.4, 119.1, 61.2, 54.7, 39.8, 29.3, 26.8, 14.1; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}N_3O_5$ $(M+H)^+$: 396.1554, found: 396.155.

ethyl 2-(1-((acetylimino)(phenyl)methyl)-5-chloroindolin-7-yl)acetate (5ia)



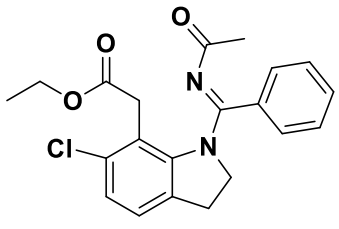
Following by general procedure for the synthesis of **5aa**. Yellow solid, 120.1 mg, yield: 78% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.49 – 7.40 (m, 5H), 7.11 (dd, *J* = 13.2, 2.3 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.77 (t, *J* = 7.5 Hz, 2H), 3.69 (s, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.96 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.7, 170.7, 158.3, 140.9, 137.4, 134.6, 131.1, 130.7, 129.7, 129.1, 128.1, 126.6, 123.8, 61.0, 54.6, 39.4, 29.8, 27.0, 14.2; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}ClN_2O_3$ $(M+H)^+$: 385.1313, found: 385.1314.

ethyl 2-(1-((acetylimino)(phenyl)methyl)-5-bromoindolin-7-yl)acetate (5ja)



Following by general procedure for the synthesis of **5aa**. White solid, 116.8 mg, yield: 68% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.53 – 7.44 (m, 5H), 7.31 (d, *J* = 1.9 Hz, 1H), 7.29 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.81 (t, *J* = 7.6 Hz, 2H), 3.72 (s, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.01 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.7, 170.6, 158.2, 141.5, 137.7, 134.6, 132.6, 131.1, 129.1, 128.2, 127.1, 126.8, 118.4, 61.0, 54.5, 39.4, 29.7, 26.9, 14.2; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}BrN_2O_3$ $(M+H)^+$: 429.0808, found: 429.0796.

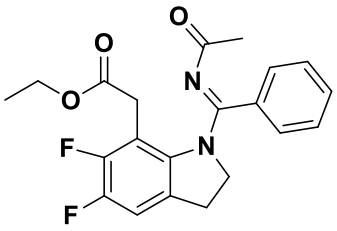
ethyl 2-(1-((acetylimino)(phenyl)methyl)-6-chloroindolin-7-yl)acetate (5ka)



Following by general procedure for the synthesis of **5aa**. Yellow solid, 55.4 mg, yield: 36% (purified by silica gel chromatography using PE/EA 5:1-

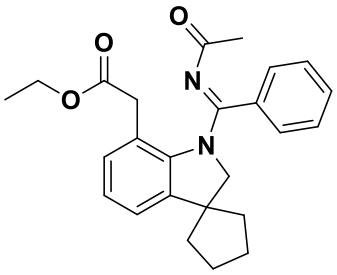
1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.51 – 7.42 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 2H), 3.80 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.98 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.7, 170.2, 158.4, 144.1, 134.6, 134.5, 134.3, 131.1, 129.1, 128.1, 126.7, 124.5, 124.2, 60.9, 55.0, 36.9, 29.7, 26.8, 14.1; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}ClN_2O_3$ $(M+H)^+$: 385.1313, found: 385.1310.

ethyl 2-(1-((acetylimino)(phenyl)methyl)-5,6-difluoroindolin-7-yl)acetate (5na)



Following by general procedure for the synthesis of **5aa**. White solid, 111.3 mg, yield: 72% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.49 – 7.41 (m, 5H), 6.98 (dd, *J* = 9.0, 7.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.83 – 3.73 (m, 4H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.96 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.7, 169.7, 158.3, 148.7 (dd, *J* = 244.1, 13.4 Hz), 148.4 (dd, *J* = 245.1, 13.4 Hz), 138.5 (d, *J* = 5.3 Hz), 134.5, 131.2, 130.5 (dd, *J* = 6.9, 3.4 Hz), 129.1, 128.0, 116.2 (d, *J* = 16.2 Hz), 112.0 (d, *J* = 19.3 Hz), 61.1, 54.9, 33.0, 29.6, 26.8, 14.1; **HRMS (ESI) m/z:** calculated for $C_{21}H_{21}F_2N_2O_3$ $(M+H)^+$: 387.1515, found: 387.1519.

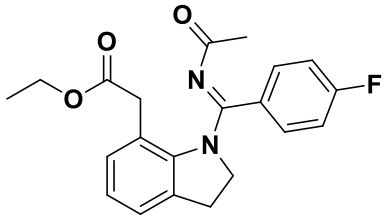
ethyl 2-(1'-((acetylimino)(phenyl)methyl)spiro[cyclopentane-1,3'-indolin]-7'-yl)acetate (5pa)



Following by general procedure for the synthesis of **5aa**. Yellow solid, 113.3 mg, yield: 70% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.50 – 7.42 (m, 5H), 7.17 – 7.08 (m, 3H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 2H), 3.54 (s, 2H), 1.98 (s, 3H), 1.87 – 1.77 (m, 4H), 1.73 – 1.66 (m, 2H), 1.60 – 1.51 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz,**

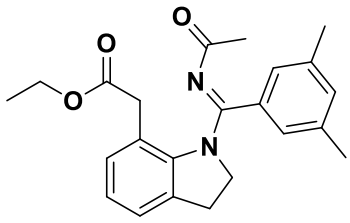
Chloroform-*d*) δ 183.7, 171.3, 158.7, 143.8, 141.6, 135.2, 130.8, 129.6, 129.1, 128.1, 126.2, 125.4, 120.9, 67.2, 60.7, 53.0, 39.4, 38.1, 27.0, 25.1, 14.2; **HRMS (ESI) m/z:** calculated for $C_{25}H_{29}N_2O_3$ $(M+H)^+$: 405.2173, found: 405.2179.

ethyl 2-(1-((acetylimino)(4-fluorophenyl)methyl)indolin-7-yl)acetate (5ra)



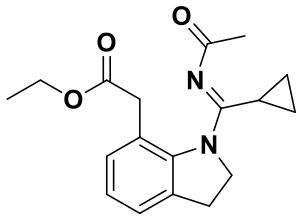
Following by general procedure for the synthesis of **5aa**. Yellow oil, 84.0 mg, yield: 57% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.48 (dd, *J* = 8.1, 5.2 Hz, 2H), 7.19 – 7.09 (m, 5H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.79 (t, *J* = 7.5 Hz, 2H), 3.72 (s, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.01 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.6, 171.2, 164.1 (d, *J* = 251.8 Hz), 157.5, 141.9, 135.5, 131.1, 130.4 (d, *J* = 8.7 Hz), 129.9, 125.9, 125.3, 123.7, 116.3 (d, *J* = 22.0 Hz), 60.8, 54.5, 39.7, 29.9, 27.0, 14.2; **HRMS (ESI) m/z:** calculated for $C_{21}H_{22}FN_2O_3$ $(M+H)^+$: 369.1609, found: 369.1604.

ethyl 2-(1-((acetylimino)(3,5-dimethylphenyl)methyl)indolin-7-yl)acetate (5sa)



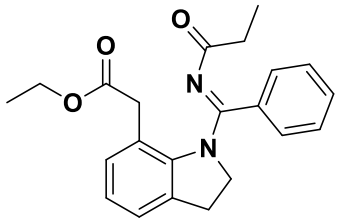
Following by general procedure for the synthesis of **5aa**. Yellow solid, 98.4 mg, yield: 65% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.15 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.13 – 7.07 (m, 3H), 7.05 (d, *J* = 1.8 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.78 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 6H), 1.98 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.9, 171.4, 159.0, 142.1, 138.7, 135.5, 135.1, 132.6, 129.6, 125.8, 125.7, 125.4, 123.6, 60.7, 54.6, 39.6, 29.9, 27.0, 21.3, 14.2; **HRMS (ESI) m/z:** calculated for $C_{23}H_{27}N_2O_3$ $(M+H)^+$: 379.2016, found: 379.2017.

ethyl-2-(1-((acetylimino)(cyclopropyl)methyl)indolin-7-yl)acetate (5va)



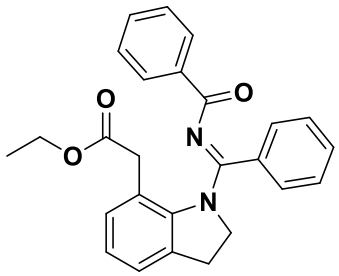
Following by general procedure for the synthesis of **5aa**. White solid, 20.1 mg, yield: 16% (purified by silica gel chromatography using PE/EA 2:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.15 – 7.11 (m, 1H), 7.04 – 6.98 (m, 2H), 4.48 – 4.41 (m, 1H), 4.16 – 4.09 (m, 1H), 4.05 – 3.98 (m, 1H), 3.90 – 3.81 (m, 1H), 3.69 (s, 1H), 3.14 – 3.04 (m, 1H), 2.89 – 2.81 (m, 1H), 1.83 – 1.77 (m, 1H), 1.68 (s, 3H), 1.30 – 1.20 (m, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.05 – 1.00 (m, 1H), 0.89 – 0.84 (m, 1H), 0.77 – 0.71 (m, 1H), 0.61 – 0.55 (m, 1H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 173.4, 169.0, 157.7, 141.9, 135.3, 132.6, 127.1, 123.5, 122.7, 66.6, 58.5, 50.6, 29.0, 20.3, 14.1, 13.3, 8.4, 8.2. **HRMS (ESI) m/z:** calculated for $C_{18}H_{23}N_2O_3$ $(M+H)^+$: 315.1703, found: 315.1701.

ethyl 2-(1-(phenyl(propionylimino)methyl)indolin-7-yl)acetate (5ab)



Following by general procedure for the synthesis of **5aa**. White solid, 103.5 mg, yield: 71% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.55 – 7.35 (m, 5H), 7.20 – 7.01 (m, 3H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.83 – 3.69 (m, 4H), 2.98 (q, *J* = 10.8, 9.0 Hz, 2H), 2.23 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 186.8, 170.9, 157.6, 141.7, 135.1, 134.8, 130.4, 129.2, 128.5, 127.7, 125.2, 124.9, 123.2, 60.3, 54.0, 39.3, 32.4, 29.4, 13.8, 8.7; **HRMS (ESI) m/z:** calculated for $C_{22}H_{25}N_2O_3$ $(M+H)^+$: 365.186, found: 365.1859.

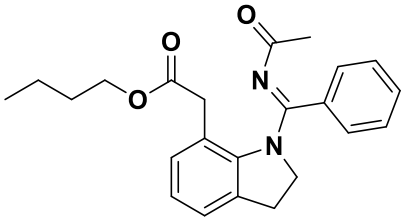
ethyl 2-(1-((benzoylimino)(phenyl)methyl)indolin-7-yl)acetate (5ac)



Following by general procedure for the synthesis of **5aa**. White

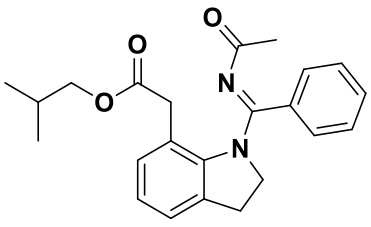
solid, 82.5 mg, yield: 50% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.34 (m, 8H), 7.23 (dd, *J* = 6.5, 2.1 Hz, 1H), 7.18 – 7.13 (m, 2H), 3.98 – 3.89 (m, 4H), 3.72 (s, 2H), 3.06 (t, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 177.0, 171.3, 161.8, 142.0, 136.1, 135.4, 134.6, 131.9, 130.8, 130.0, 129.6, 128.8, 128.3, 128.0, 125.9, 125.8, 123.6, 60.7, 54.7, 39.4, 29.9, 14.1; **HRMS (ESI) m/z:** calculated for $C_{26}H_{25}N_2O_3$ $(M+H)^+$: 413.186, found: 413.1856.

butyl 2-(1-((acetylimino)(phenyl)methyl)indolin-7-yl)acetate (5ad)



Following by general procedure for the synthesis of **5aa**. Yellow oil, 112.0 mg, yield: 74% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.50 – 7.40 (m, 5H), 7.15 (dd, *J* = 5.9, 2.8 Hz, 1H), 7.11 – 7.06 (m, 2H), 4.07 (t, *J* = 6.8 Hz, 2H), 3.82 – 3.70 (m, 4H), 2.97 (t, *J* = 7.5 Hz, 2H), 1.97 (s, 3H), 1.60 – 1.54 (m, 2H), 1.36 – 1.28 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 183.7, 171.3, 158.4, 142.1, 135.5, 135.1, 130.9, 129.8, 129.0, 128.2, 125.7, 125.5, 123.6, 64.7, 54.5, 39.7, 30.6, 29.9, 27.0, 19.1, 13.7; **HRMS (ESI) m/z:** calculated for $C_{23}H_{27}N_2O_3$ $(M+H)^+$: 379.2016, found: 379.2016.

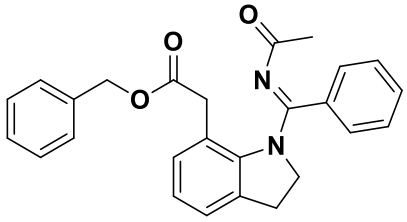
isobutyl 2-(1-((acetylimino)(phenyl)methyl)indolin-7-yl)acetate (5ae)



Following by general procedure for the synthesis of **5aa**. Yellow oil, 93.9 mg, yield: 62% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.49 – 7.40 (m, 5H), 7.15 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.12 – 7.06 (m, 2H), 3.85 (d, *J* = 6.7 Hz, 2H), 3.81 – 3.71 (m, 4H), 2.97 (t, *J* = 7.5 Hz, 2H), 1.97 (s, 3H), 1.92 – 1.85 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.9, 171.4, 158.5, 142.0, 135.6, 135.0, 131.0, 129.8, 129.1, 128.2, 125.8, 125.5, 123.7, 70.9, 54.6, 39.6, 29.9, 27.7, 27.0, 19.1; **HRMS (ESI) m/z:** calculated

for $C_{23}H_{27}N_2O_3$ $(M+H)^+$: 379.2016, found: 379.2012.

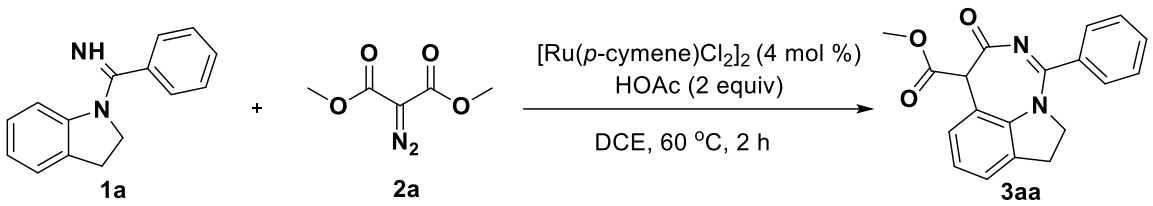
benzyl 2-(1-((acetylimino)(phenyl)methyl)indolin-7-yl)acetate (5af)



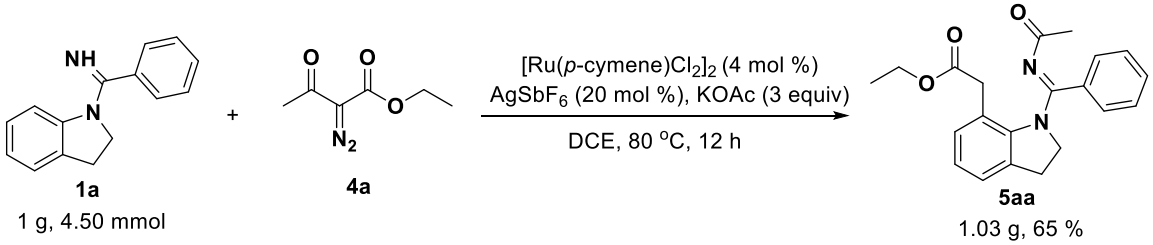
Following by general procedure for the synthesis of **5aa**. Yellow solid, 107.2 mg, yield: 65% (purified by silica gel chromatography using PE/EA 5:1-1:1). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.49 – 7.38 (m, 5H), 7.35 – 7.28 (m, 5H), 7.18 (t, *J* = 4.4 Hz, 1H), 7.11 (d, *J* = 3.7 Hz, 2H), 5.12 (s, 2H), 3.83 (s, 2H), 3.73 (t, *J* = 7.5 Hz, 2H), 2.98 (t, *J* = 7.5 Hz, 2H), 1.96 (s, 3H); **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 183.9, 171.1, 158.4, 142.0, 136.0, 135.6, 135.0, 130.9, 129.9, 129.0, 128.5, 128.4, 128.2, 125.8, 125.2, 123.8, 66.6, 54.5, 39.8, 29.9, 27.0; **HRMS (ESI) m/z:** calculated for $C_{26}H_{25}N_2O_3$ $(M+H)^+$: 413.186, found: 413.1858.

VII. Gram-scale Preparation and Conversion of the Product

(a) Gram-scale preparation of product



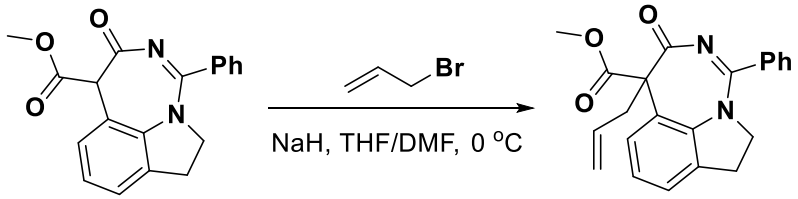
A pressure tube was charged with [Ru(*p*-cymene)Cl_2]$_2$ (110.2 mg, 4 mol %), HOAc (540.5 mg, 9 mmol), **1a** (1 g, 4.5 mmol), **2a** (1.07 g, 6.75 mmol) and DCE (50 mL). The reaction mixture was stirred at 60 °C for 2 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA = 2:1 to afford the product **3aa** (1.23 g, yield: 85%).



A pressure tube was charged with [Ru(*p*-cymene)Cl_2]$_2$ (110.2 mg, 4 mol %), $AgSbF_6$ (309.3 mg, 20 mol %), KOAc (1.32 g, 13.5 mmol), **1a** (1 g, 4.5 mmol), **4a** (1.05 g, 6.75 mmol) and DCE (50 mL). The reaction mixture was stirred at 80 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA = 3:1 to afford the product **5aa** (1.03 g, yield: 65%).

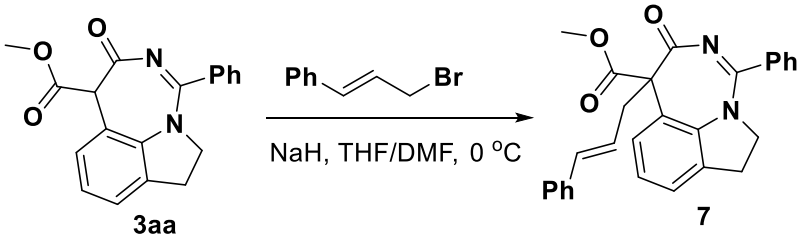
(b) Transformations of product

(1) Transformations of **3aa** to **6**[8]



Dissolved **3aa** (50 mg, 0.16 mmol) with THF (10 mL) and DMF (2 ml) in a three-necked flask, added NaH (37.5 mg, 0.94 mmol) under argon protection, and stirred for 10 minutes at 0°C. Then, allyl bromide (56.7 mg, 0.47 mmol) was added and stirred for 4 h at room temperature. After the reaction was completed, added methanol to the system for quenching, and the solvent was removed under reduced pressure, then extracted with DCM (30 mL×3). The organic layer was then dried with Na_2SO_4 and concentrated by rotary evaporation to give the crude product. The crude product was purified by silica gel column chromatography to give **6** (20 mg, yield: 36%). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 7.59 – 7.51 (m, 5H), 7.44 – 7.38 (m, 3H), 5.92 – 5.81 (m, 1H), 5.25 (dd, *J* = 17.1, 1.9 Hz, 1H), 5.12 (dd, *J* = 10.3, 2.0 Hz, 1H), 4.31 (q, *J* = 10.1 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.41 (s, 3H), 3.31 – 3.21 (m, 2H), 3.21 – 3.13 (m, 1H), 3.09 (ddd, *J* = 16.1, 9.5, 2.2 Hz, 1H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 169.2, 162.9, 151.8, 139.7, 135.8, 135.1, 133.5, 130.6, 128.5, 127.9, 127.5, 124.5, 124.1, 121.6, 118.6, 64.7, 54.9, 52.2, 36.3, 27.9; **HRMS (ESI) m/z:** calculated for $C_{22}H_{21}N_2O_3$ $(M+H)^+$: 361.1547, found: 361.1543.

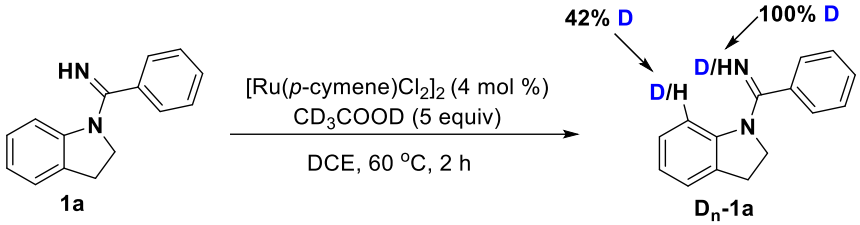
(2) Transformations of **3aa** to **7**[8]



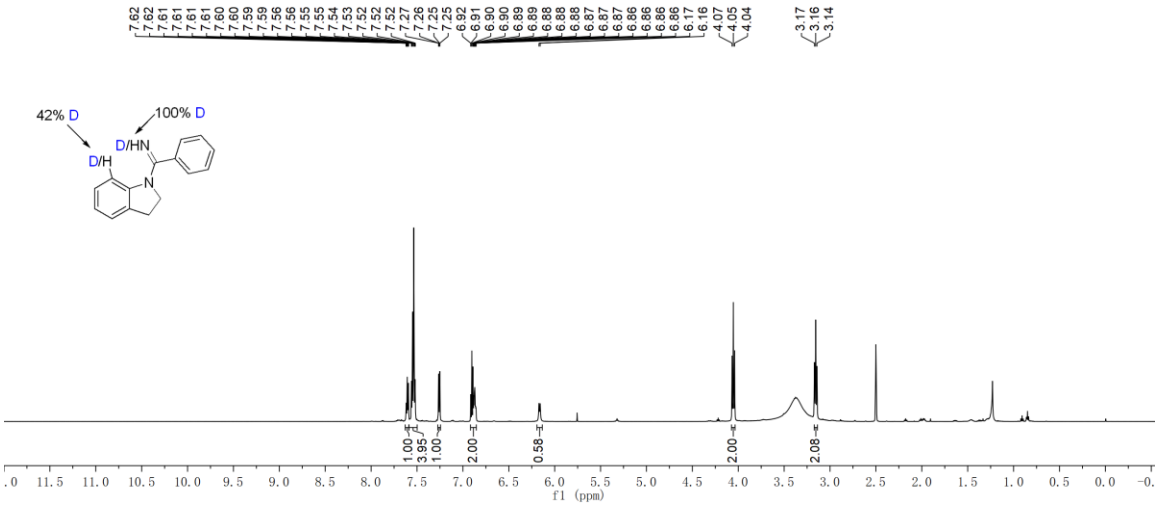
Dissolved **3aa** (80 mg, 0.25 mmol) with THF (15 mL) and DMF (3 ml) in a three-necked flask, added NaH (60 mg, 1.5 mmol) under argon protection, and stirred for 10 minutes at 0°C. Then, (*E*)-3-bromo-1-phenyl-1-propene (147.8 mg, 0.75 mmol) was added and stirred for 4 h at room temperature. After the reaction was completed, added methanol to the system for quenching, and the solvent was removed under reduced pressure, then extracted with DCM (40 mL×3). The organic layer was then dried with Na_2SO_4 and concentrated by rotary evaporation to give the crude product. The crude product was purified by silica gel column chromatography to give **7** (35 mg, yield: 32%). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 7.59 – 7.49 (m, 6H), 7.47 – 7.42 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.29 (dt, *J* = 15.6, 7.2 Hz, 1H), 4.31 (q, *J* = 10.1 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.40 (s, 3H), 3.39 – 3.33 (m, 2H), 3.31 – 3.25 (m, 1H), 3.10 (ddd, *J* = 16.2, 9.5, 2.2 Hz, 1H); **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 169.3, 163.0, 152.0, 139.6, 136.8, 135.8, 135.1, 133.0, 130.6, 128.6, 128.5, 127.9, 127.7, 127.4, 125.9, 125.0, 124.5, 124.2, 121.8, 65.1, 54.9, 52.3, 35.5, 27.9; **HRMS (ESI) m/z:** calculated for $C_{28}H_{25}N_2O_3$ $(M+H)^+$: 437.186, found: 437.1859.

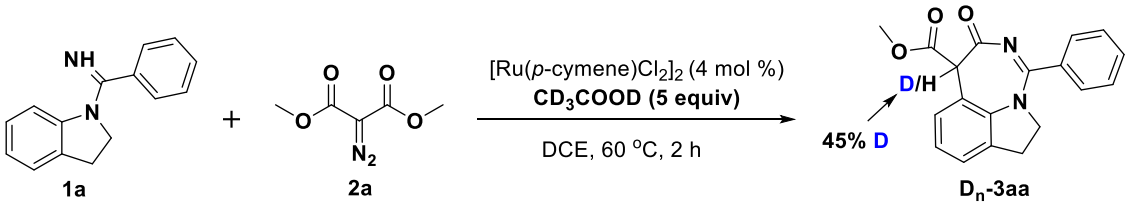
VIII. Mechanistic Studies

(a) H/D exchange

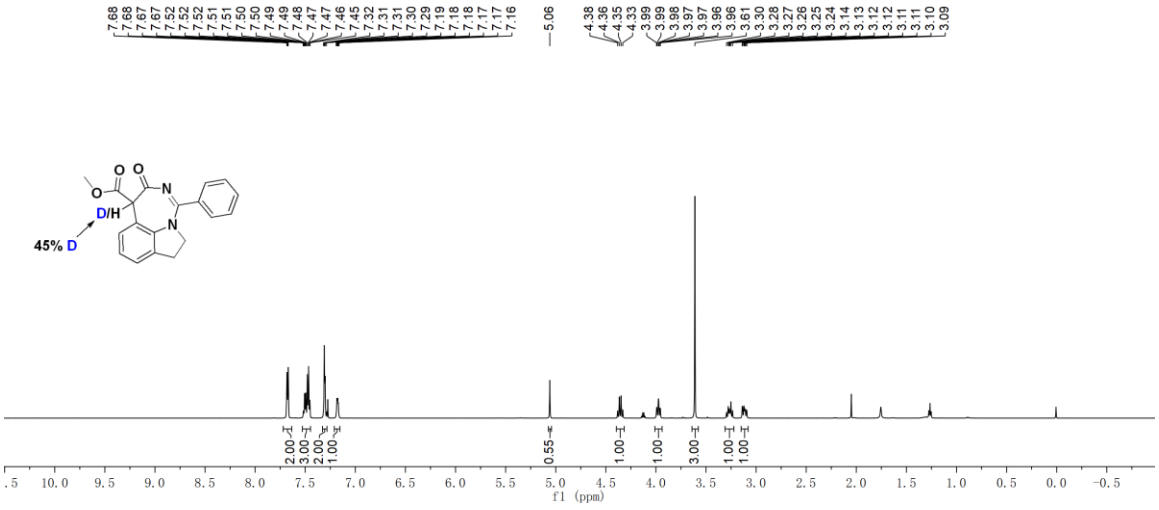


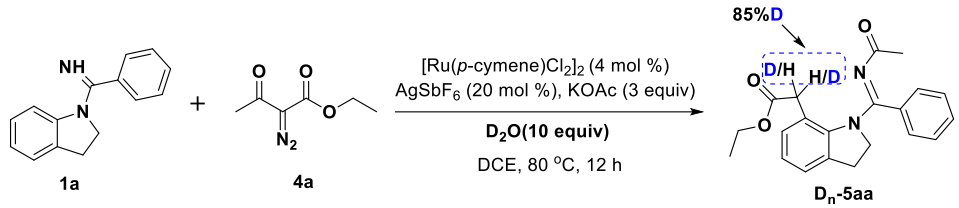
A pressure tube was charged with [Ru(*p*-cymene)Cl_2]$_2$ (9.8 mg, 4 mol %), CD_3COOD (128.2 mg, 2 mmol), **1a** (88.9 mg, 0.4 mmol) and DCE (4 mL). The reaction mixture was stirred at 60 ºC for 2 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to afford the product **D$_n$-1a**.



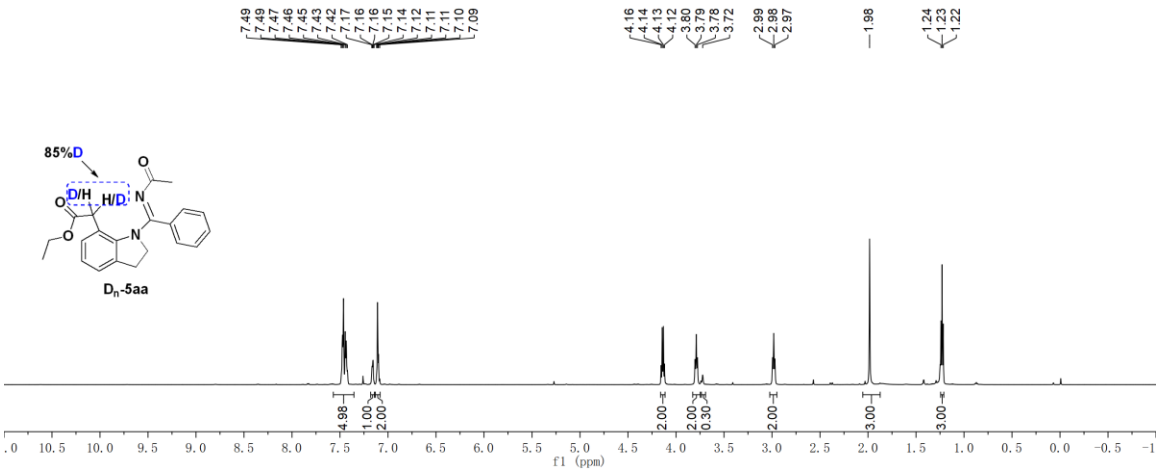


A pressure tube was charged with [Ru(*p*-cymene)Cl_2]$_2$ (9.8 mg, 4 mol %), CD_3COOD (128.2 mg, 2 mmol), **1a** (88.9 mg, 0.4 mmol), **2a** (94.9 mg, 0.6 mmol) and DCE (4 mL). The reaction mixture was stirred at 60 °C for 2 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to afford the product **D_n-3aa**.

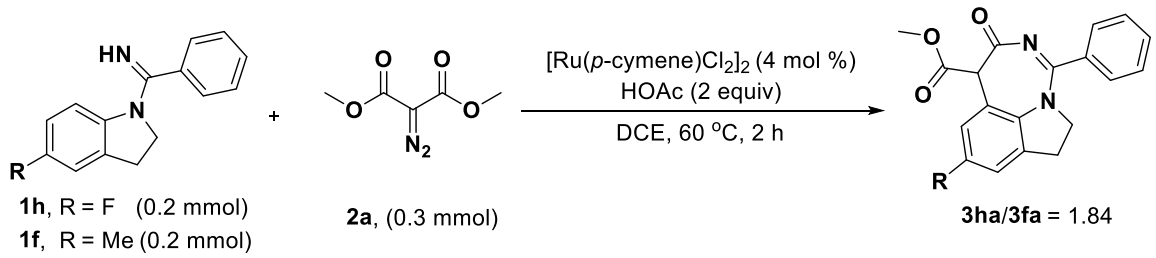




A pressure tube was charged with [Ru(*p*-cymene)Cl_2]$_2$ (9.8 mg, 4 mol %), $AgSbF_6$ (27.5 mg, 20 mol %), KOAc (117.8 mg, 1.2 mmol), **1a** (88.9 mg, 0.4 mmol), **4a** (93.7 mg, 0.6 mmol), D_2O (80.1 mg, 4 mmol) and DCE (4 mL). The reaction mixture was stirred at 80 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to afford the product **D_n-5aa**.

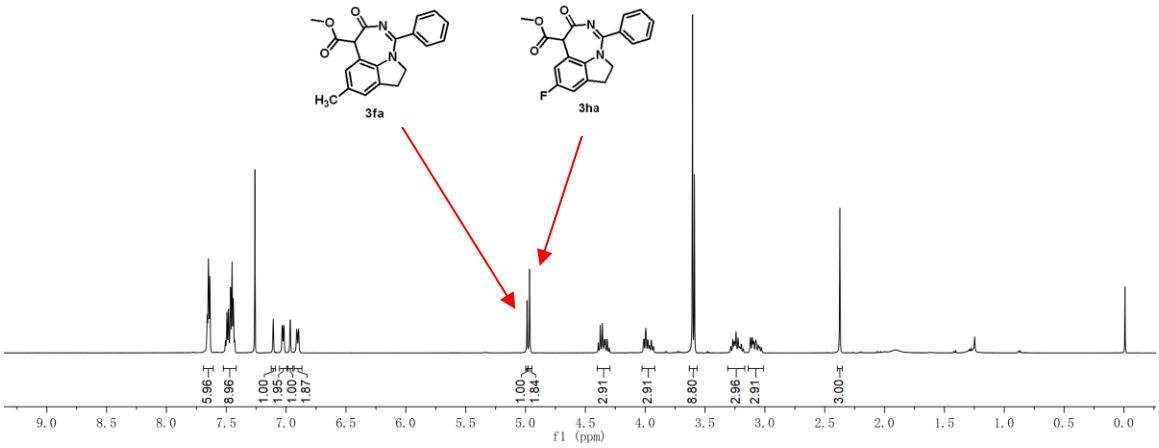


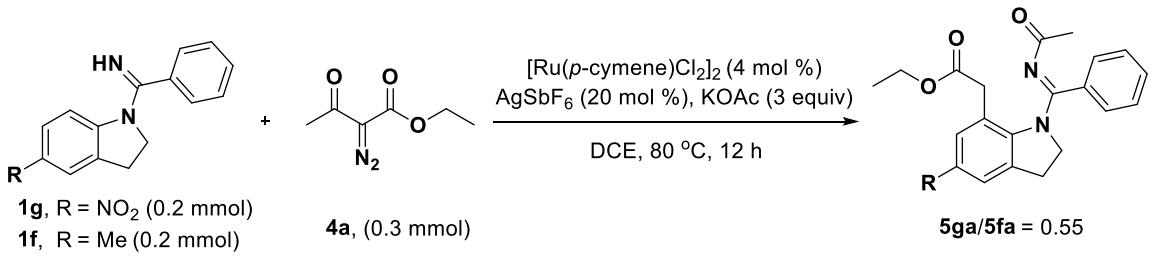
(b) Competition experiment



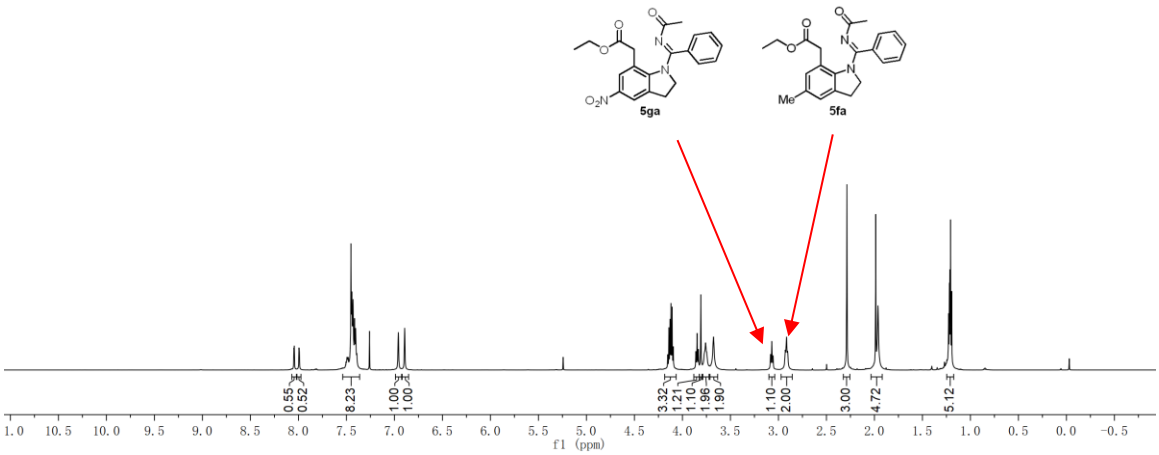
A pressure tube was charged with an equimolar mixture of **1h** (48.1 mg, 0.2 mmol) and **1f** (47.3 mg, 0.2 mmol) were allowed to react with **2a** (47.4 mg, 0.3 mmol) in DCE (4 mL) in the presence of [Ru(*p*-cymene)Cl_2]$_2$ (4.9 mg, 4 mol %), HOAc (24 mg, 0.4 mmol). The reaction mixture was stirred at 60 °C for 2 h. After that, the solvent was removed under

reduced pressure and the residue was purified by silica gel chromatography using PE/EA = 2:1 to afford the crude mixed products. The mixture of products **3ha** and **3fa** was determined to be 1.84/1 by ^{1}H NMR spectra (see as below).





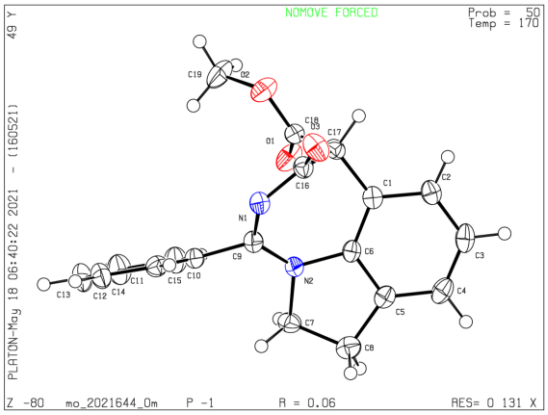
A pressure tube was charged with an equimolar mixture of **1g** (53.5 mg, 0.2 mmol) and **1f** (47.3 mg, 0.2 mmol) were allowed to react with **4a** (46.8 mg, 0.3 mmol) in DCE (4 mL) in the presence of [Ru(*p*-cymene)Cl_2]$_2$ (4.9 mg, 4 mol %), $AgSbF_6$ (13.7 mg, 20 mol %), KOAc (58.9 mg, 0.6 mmol). The reaction mixture was stirred at 80 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA = 3:1 to afford the crude mixed products. The mixture of products **5ga** and **5fa** was determined to be 0.55/1 by ^{1}H NMR spectra (see as below).



IX. X-ray Crystallographic Data

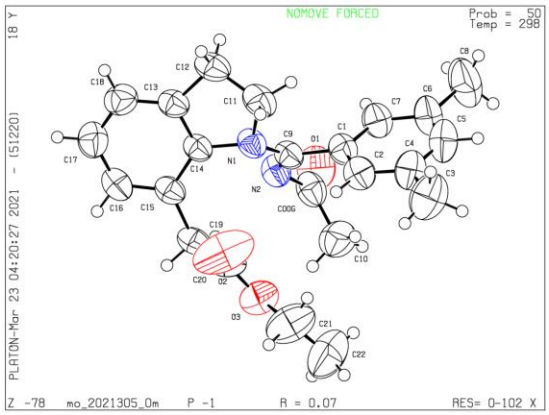
(a) The Single Crystal Structure of **3aa**

X-ray Single Crystal Structure Analysis of 3aa: X-ray crystallographic data of **3aa** were solutions at T = 170.0 K, $C_{19}H_{16}N_2O_3$, Mr = 320.34, triclinic, space group: P-1, a = 8.9991(5) Å, b = 9.6163(5) Å, c = 10.1420(6) Å, α = 75.919(2)°, β = 78.998(2)°, γ = 69.344(2)°, V = 791.22(8) $Å^3$, Z = 2. Displacement ellipsoids are drawn at the 50% probability level.



(b) The Single Crystal Structure of **5sa**

X-ray Single Crystal Structure Analysis of 5sa: X-ray crystallographic data of **5sa** were solutions at T = 298 K, $C_{23}H_{26}N_2O_3$, Mr = 378.46, triclinic, space group: P-1, a = 8.6896(13) Å, b = 8.6893(12) Å, c = 14.548(2) Å, α = 94.344(5)°, β = 100.076(4)°, γ = 96.441(4)°, V = 1069.6(3) $Å^3$, Z = 2. Displacement ellipsoids are drawn at the 50% probability level.



X. References

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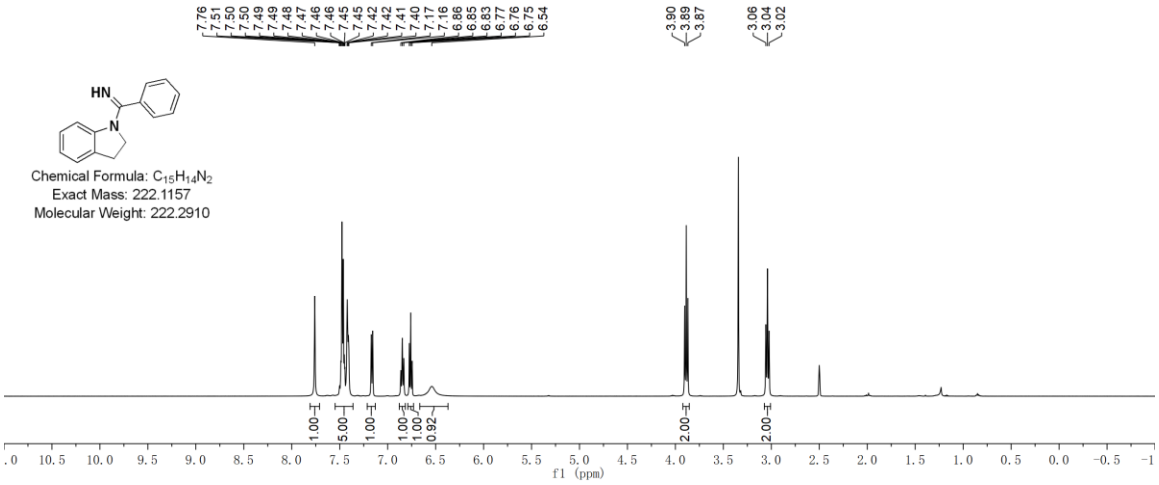
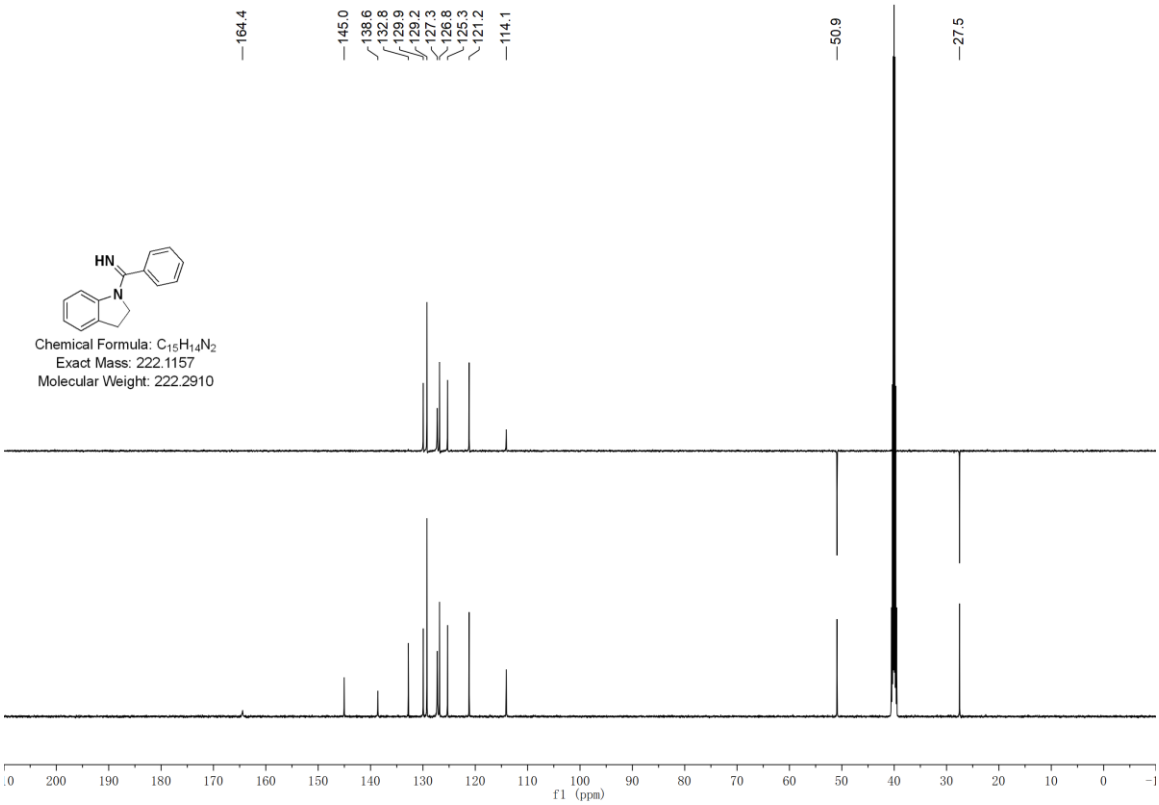
XI. NMR Spectra and HR-MS Spectra of Substrates and Products

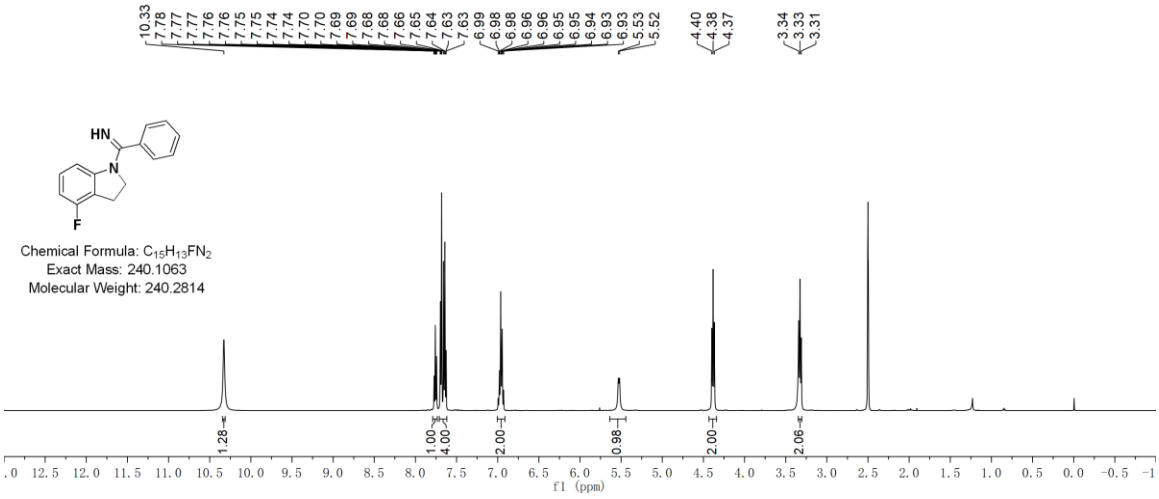
(a) ^{1}H NMR and ^{13}C NMR Spectra



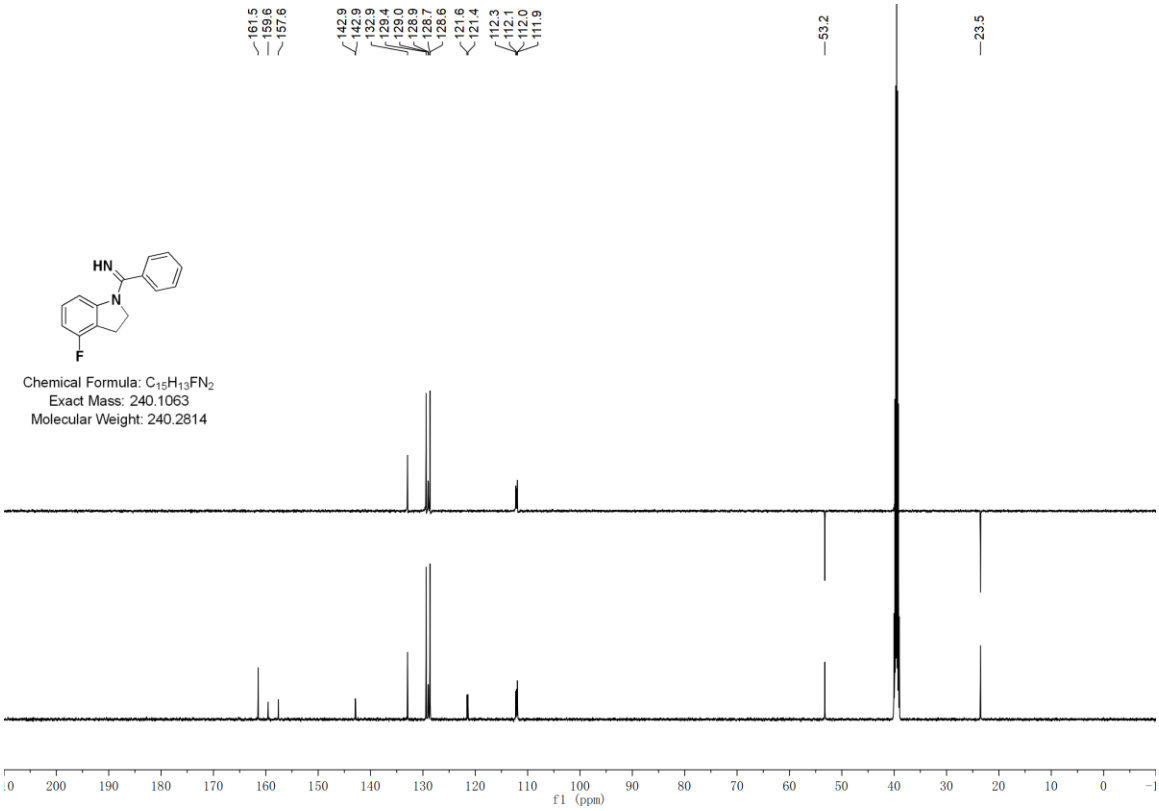
^{1}H NMR spectrum of **1a** (500 MHz, DMSO-d_6)



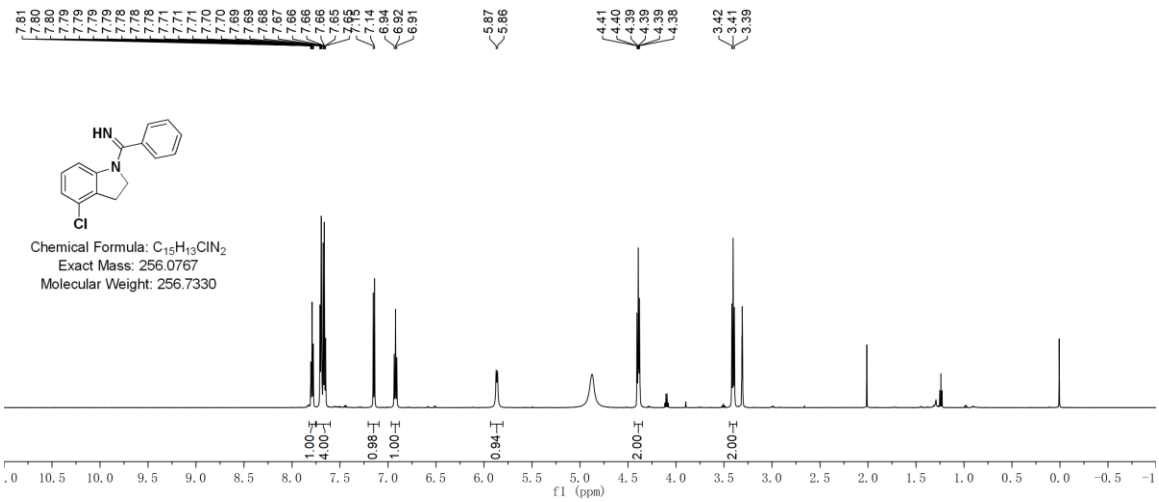
^{13}C NMR spectrum of **1a** (125 MHz, DMSO-d_6)



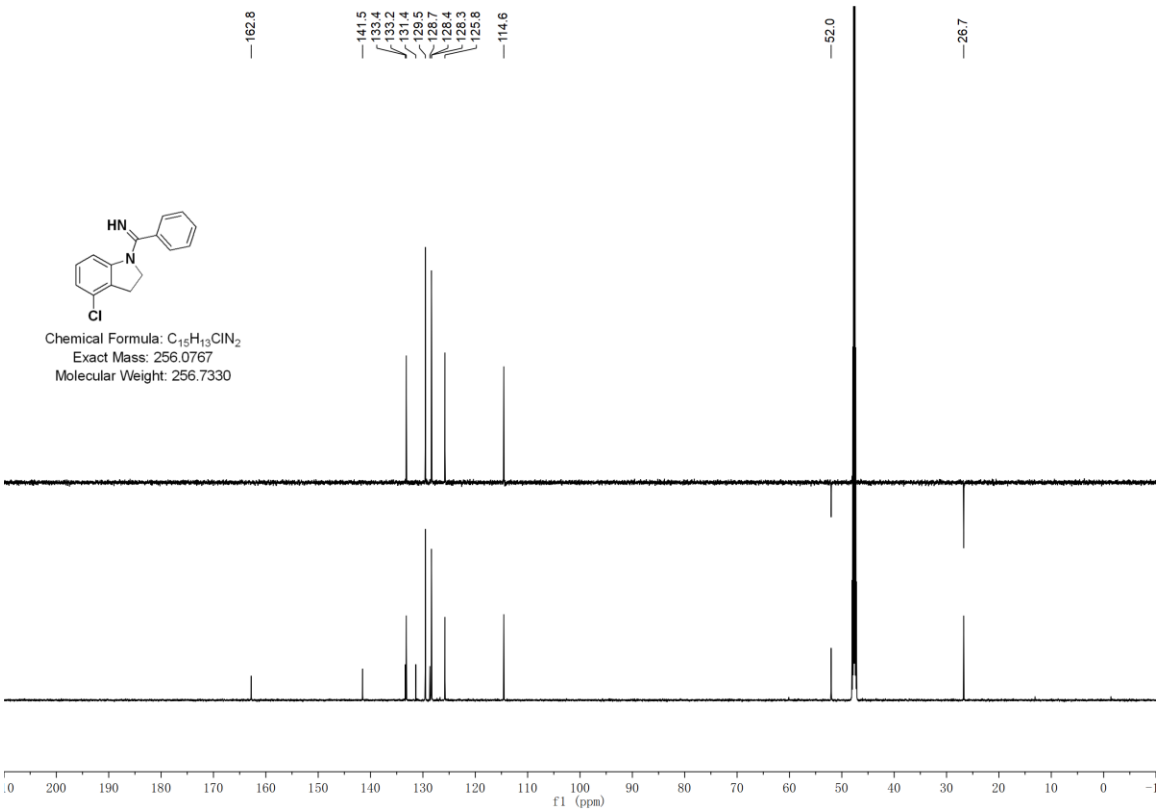
^{1}H NMR spectrum of **1b** (500 MHz, DMSO-d_6)



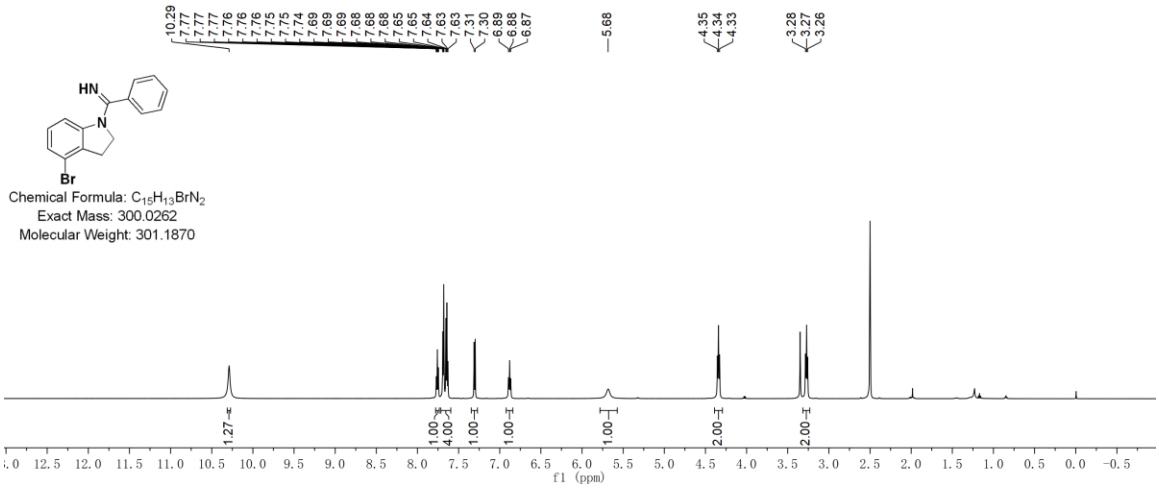
^{13}C NMR spectrum of **1b** (125 MHz, DMSO-d_6)



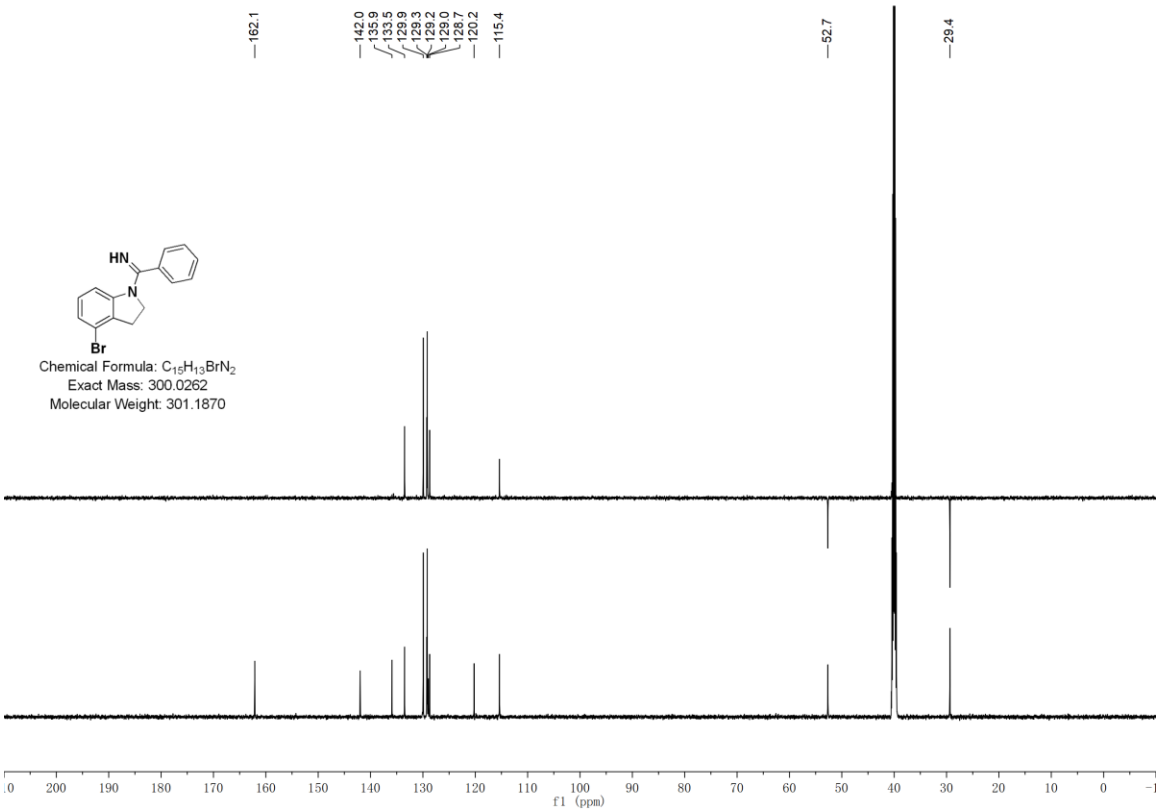
^{1}H NMR spectrum of **1c** (600 MHz, Methanol-d_4)



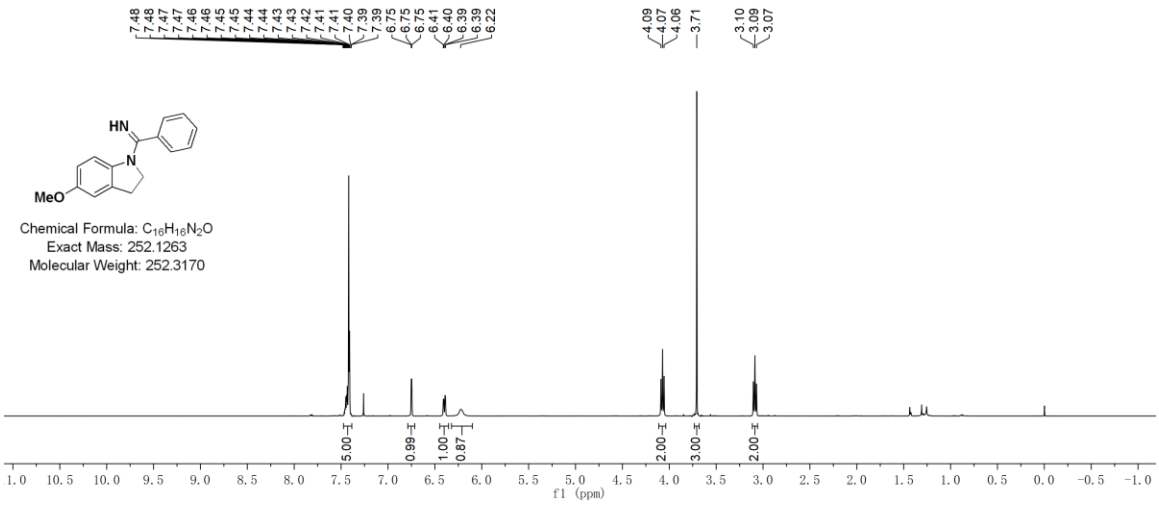
^{13}C NMR spectrum of **1c** (150 MHz, Methanol-d_4)



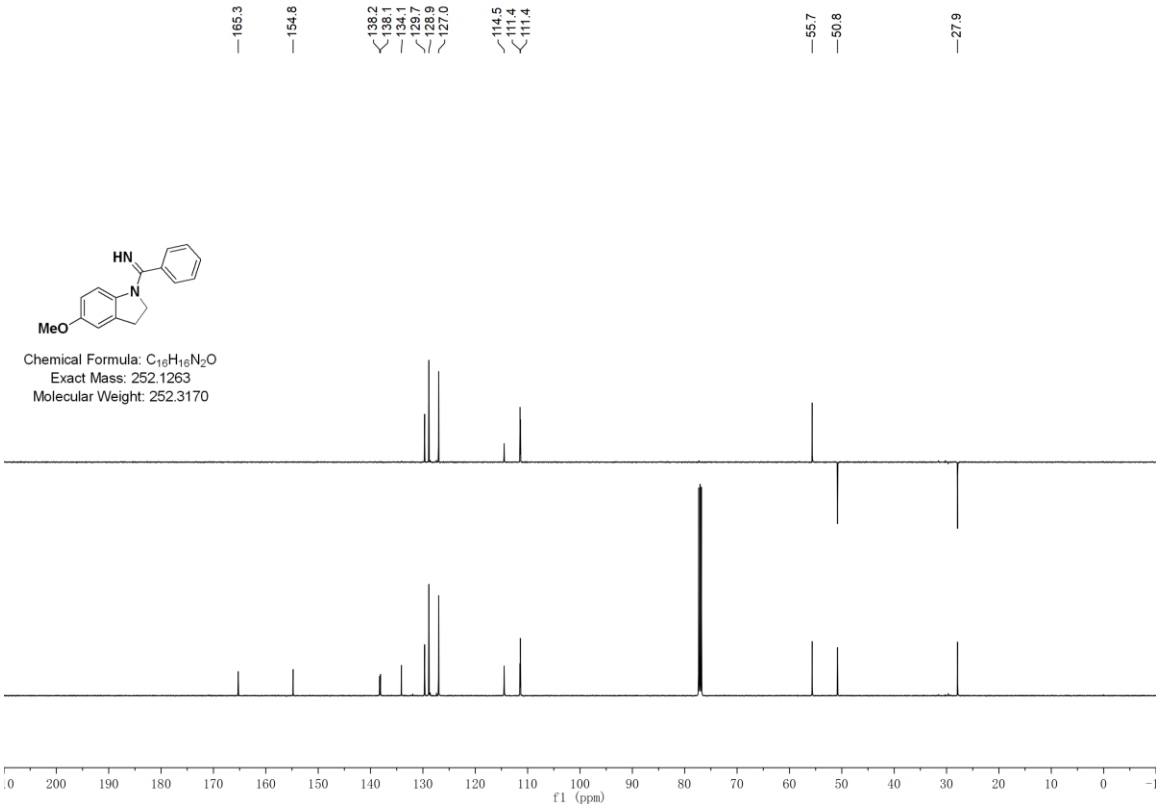
^{1}H NMR spectrum of **1d** (600 MHz, DMSO-d_6)



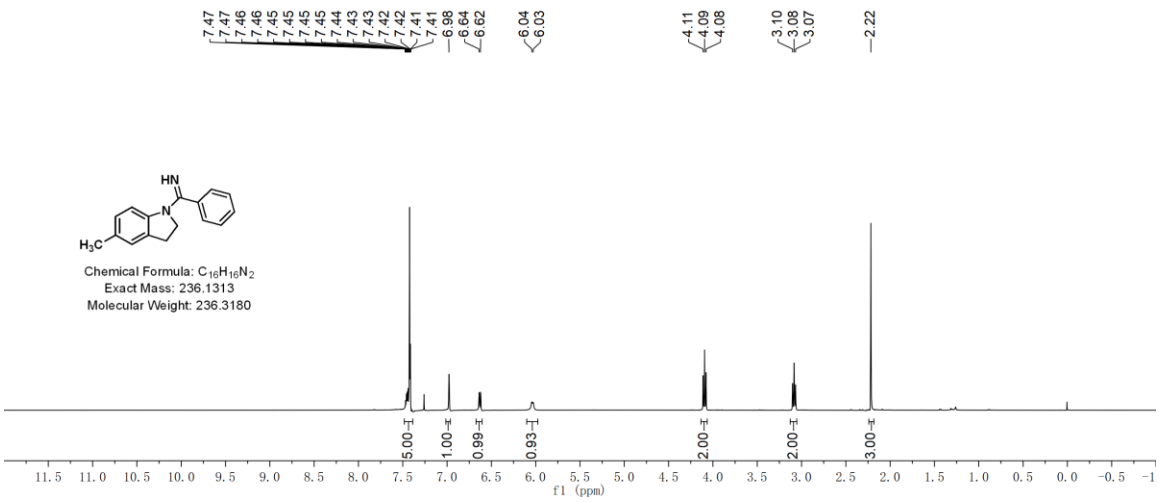
^{13}C NMR spectrum of **1d** (150 MHz, DMSO-d_6)



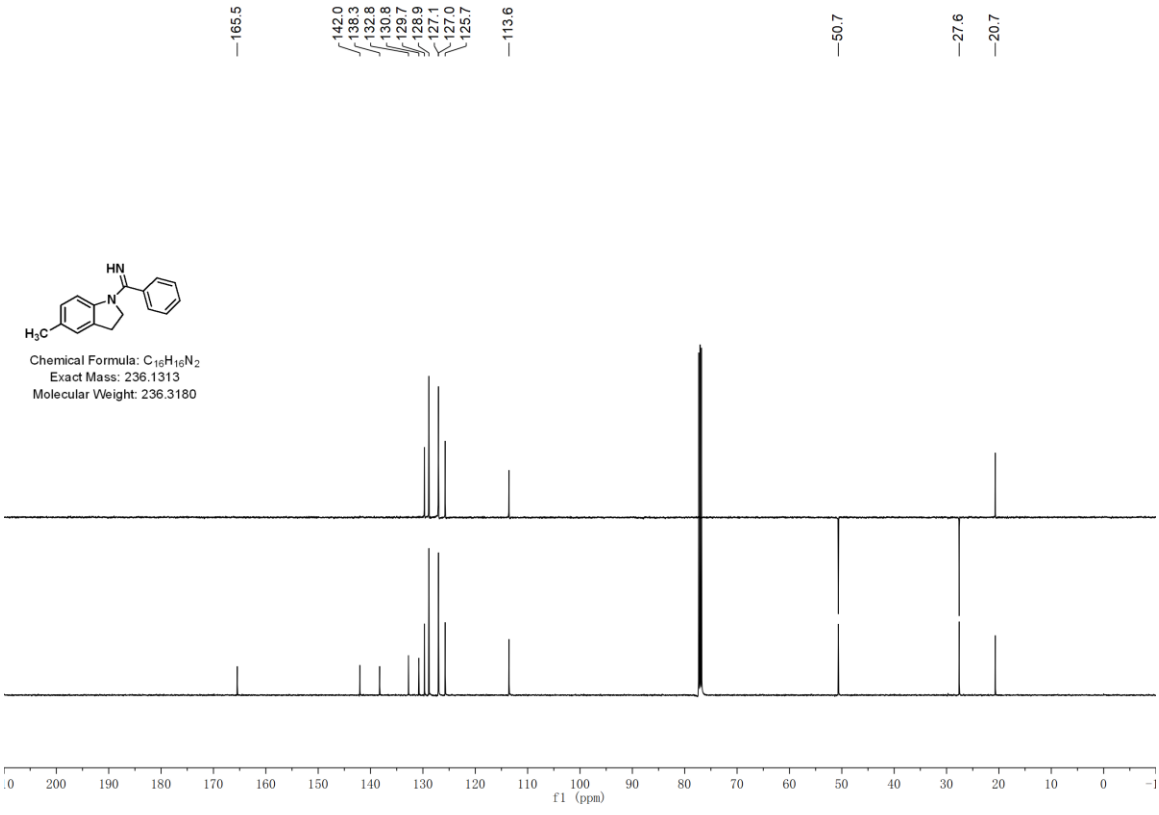
^{1}H NMR spectrum of **1e** (500 MHz, Chloroform-*d*)



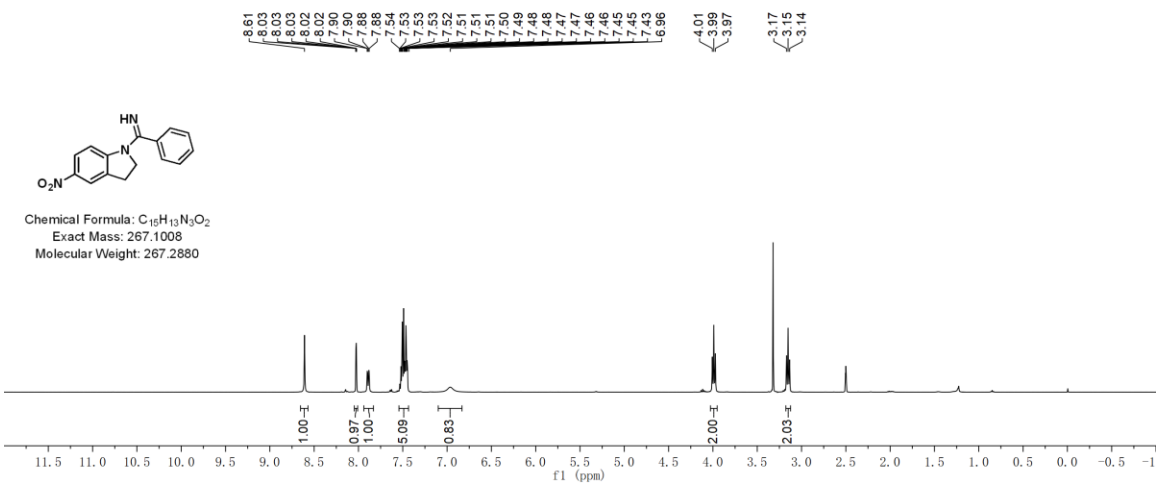
^{13}C NMR spectrum of **1e** (125 MHz, Chloroform-*d*)



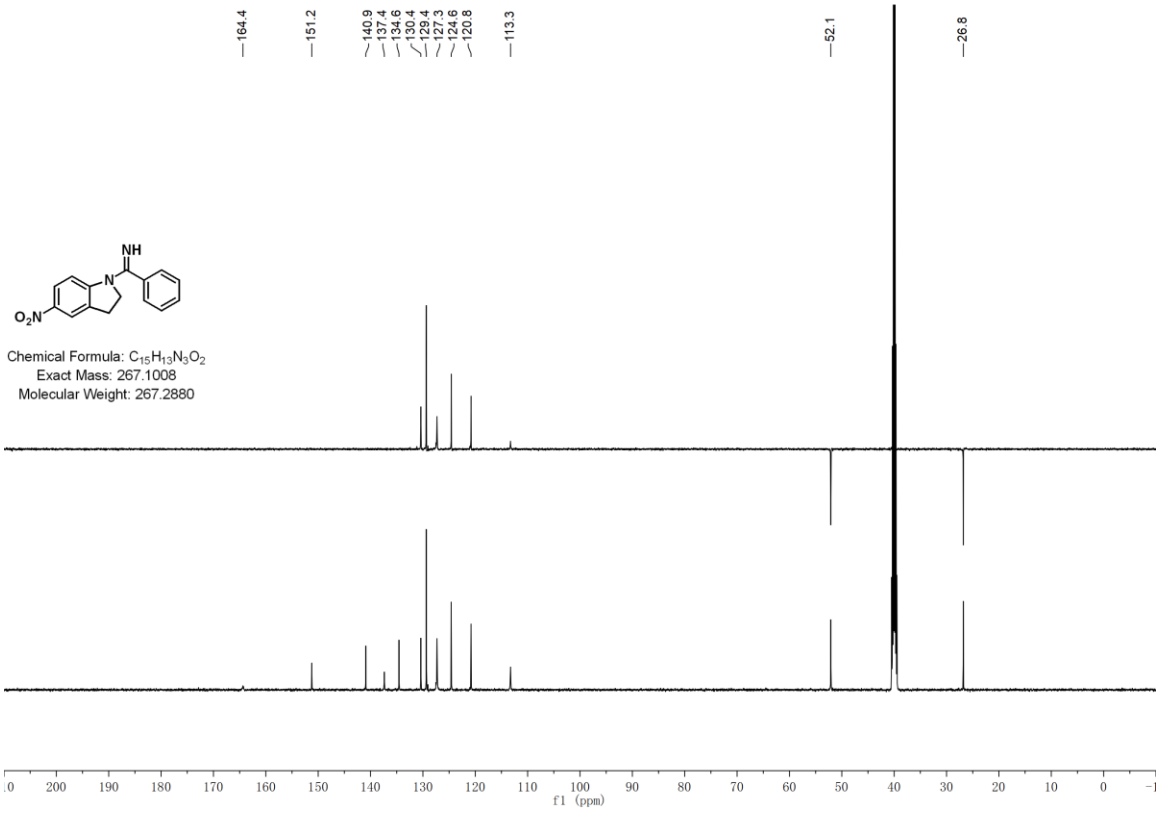
^{1}H NMR spectrum of **1f** (500 MHz, Chloroform-*d*)



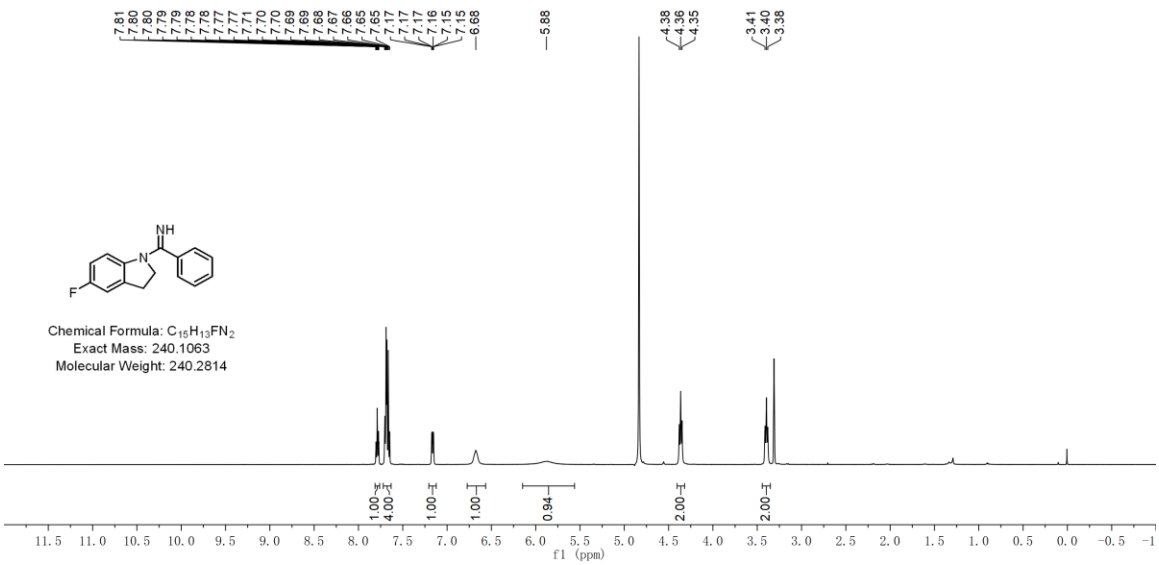
^{13}C NMR spectrum of **1f** (125 MHz, Chloroform-*d*)



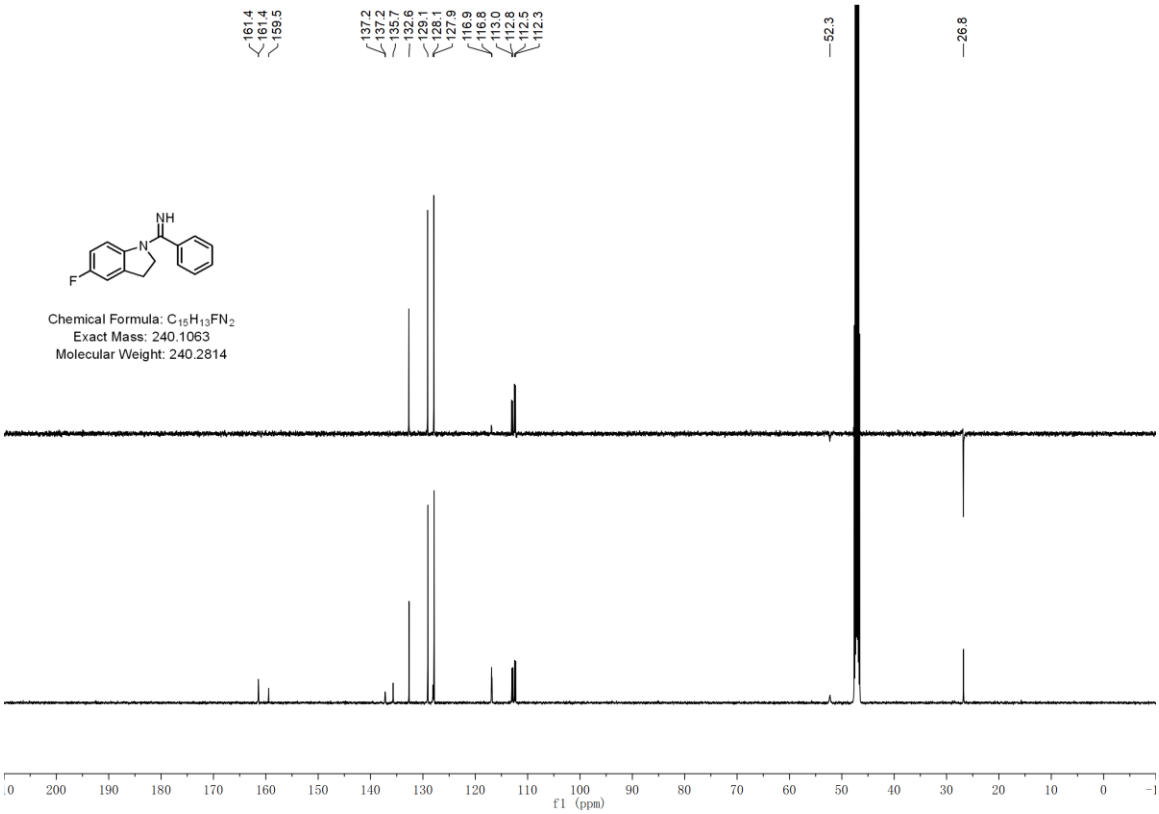
^{1}H NMR spectrum of **1g** (500 MHz, DMSO-d_6)



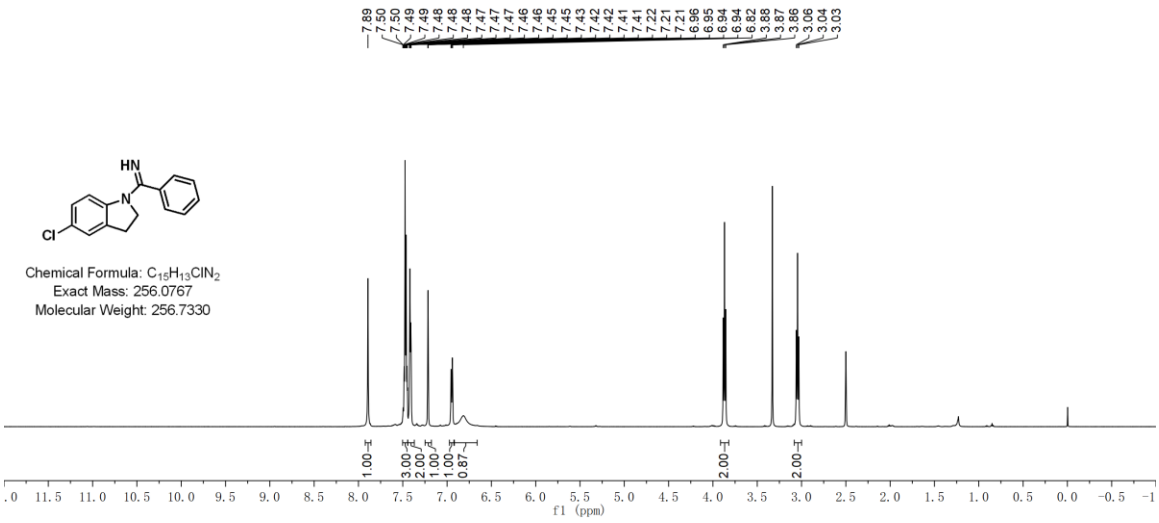
^{13}C NMR spectrum of **1g** (125 MHz, DMSO-d_6)



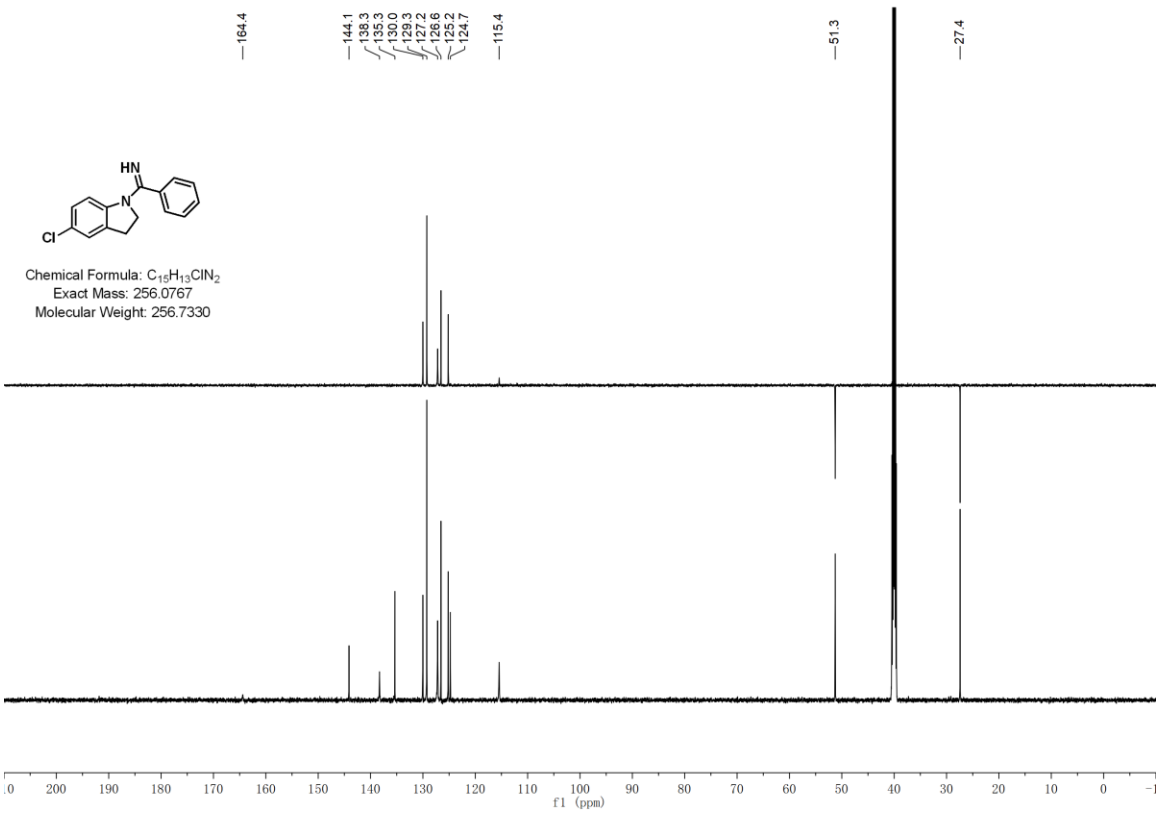
^{1}H NMR spectrum of **1h** (500 MHz, Methanol-d_4)



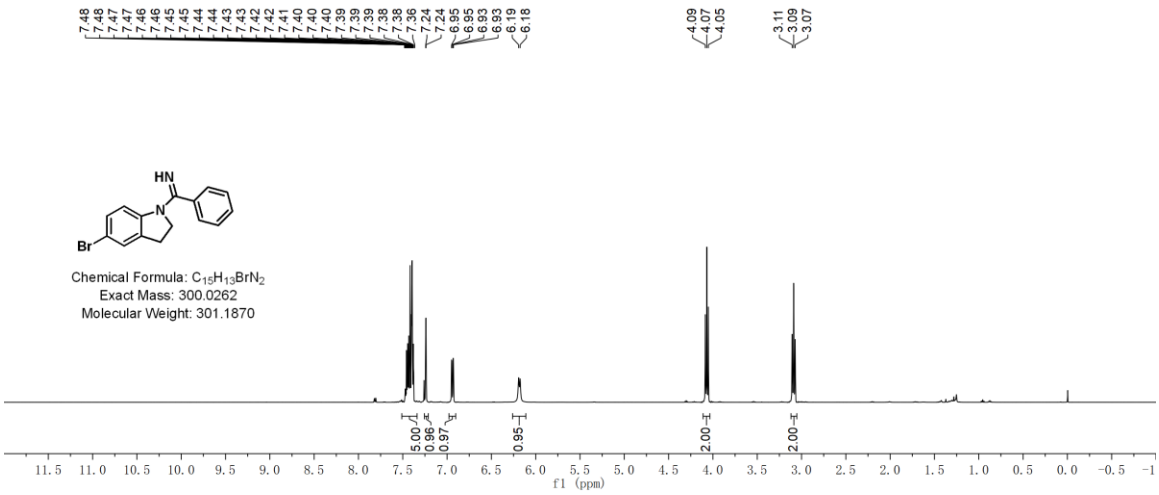
^{13}C NMR spectrum of **1h** (125 MHz, Methanol-d_4)



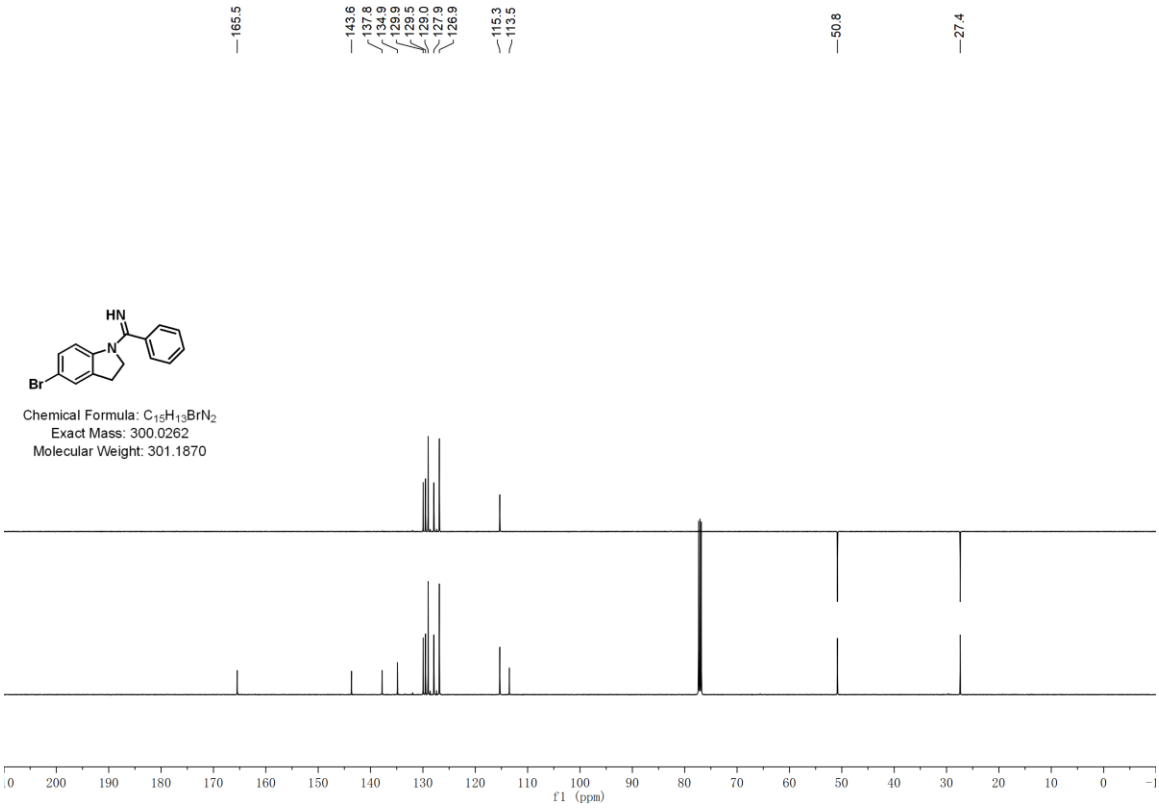
^{1}H NMR spectrum of **1i** (600 MHz, DMSO-d_6)



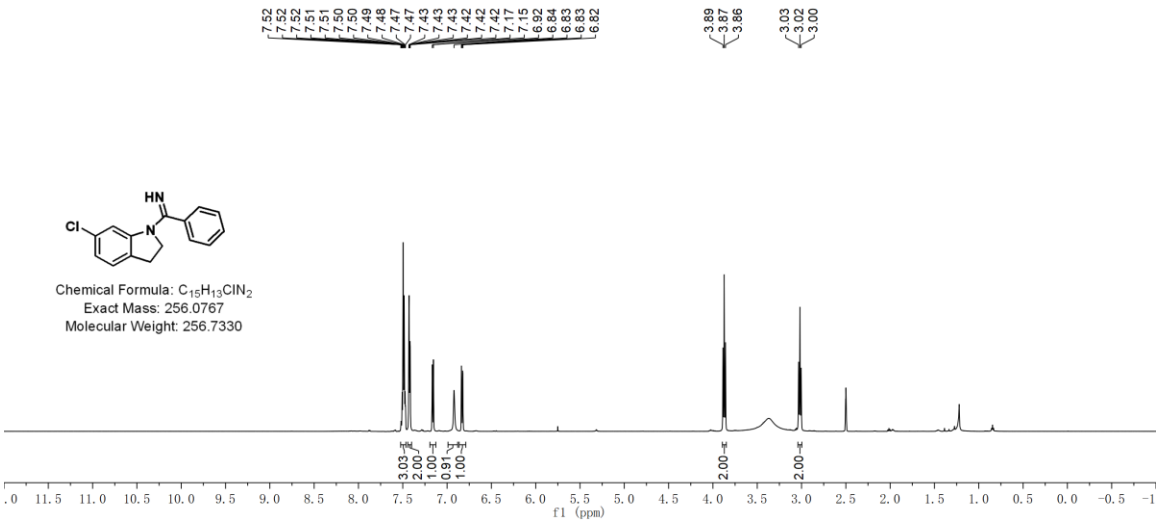
^{13}C NMR spectrum of **1i** (150 MHz, DMSO-d_6)



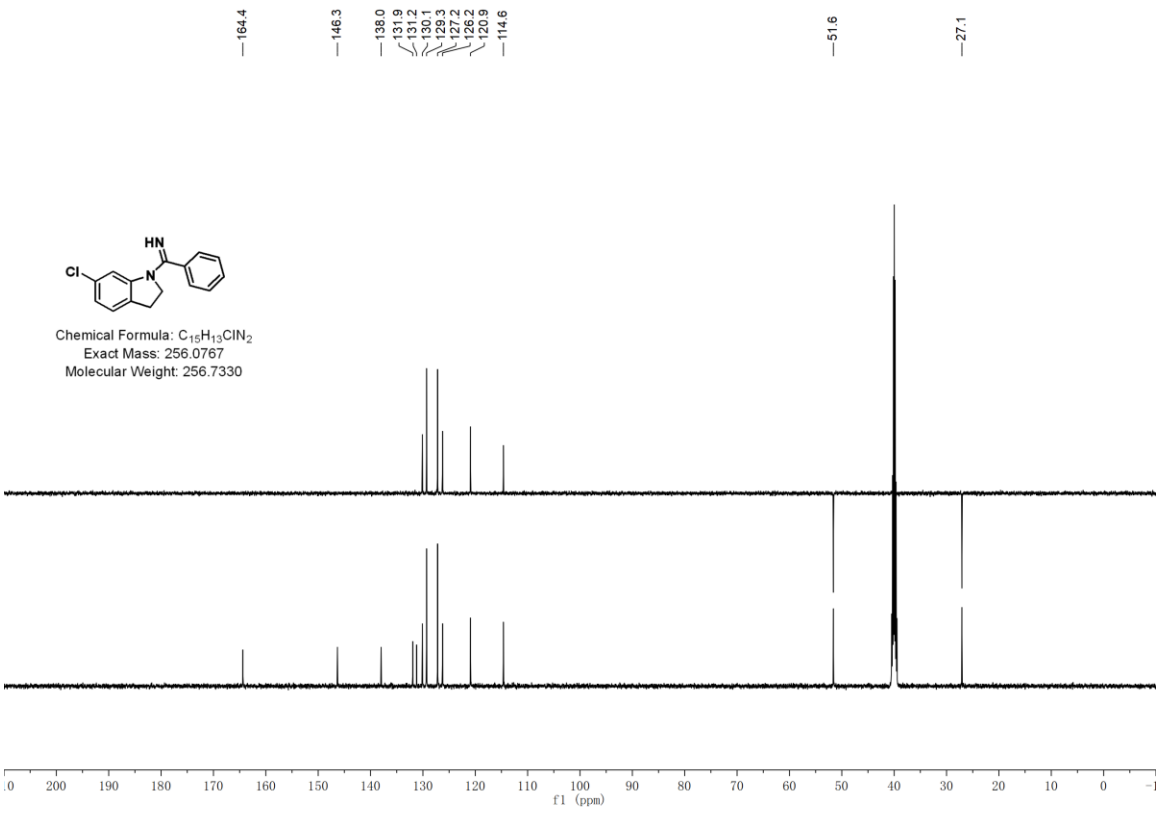
^{1}H NMR spectrum of **1j** (500 MHz, Chloroform-*d*)



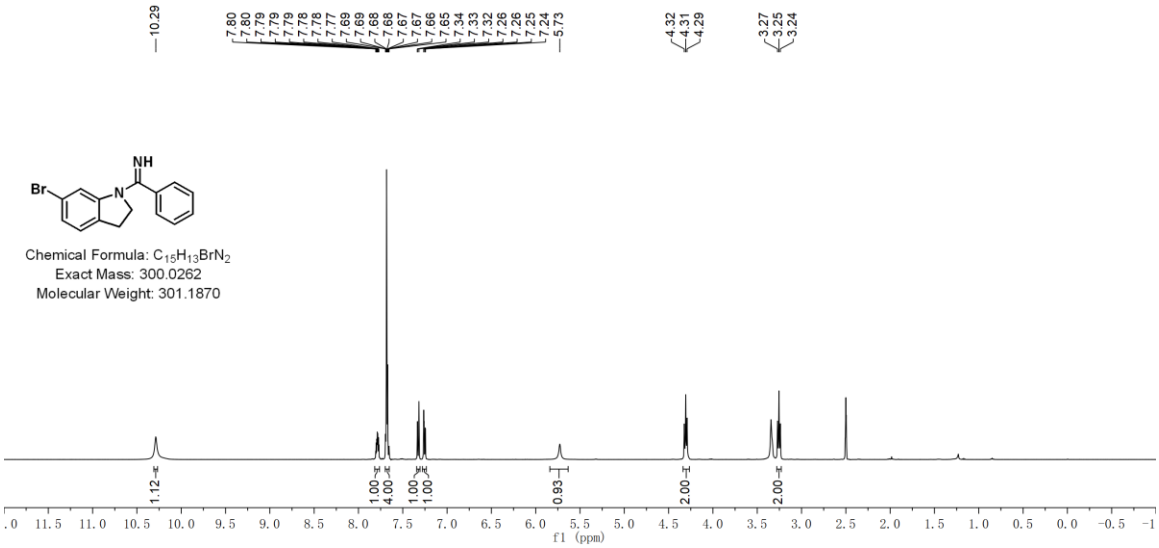
^{13}C NMR spectrum of **1j** (125 MHz, Chloroform-*d*)



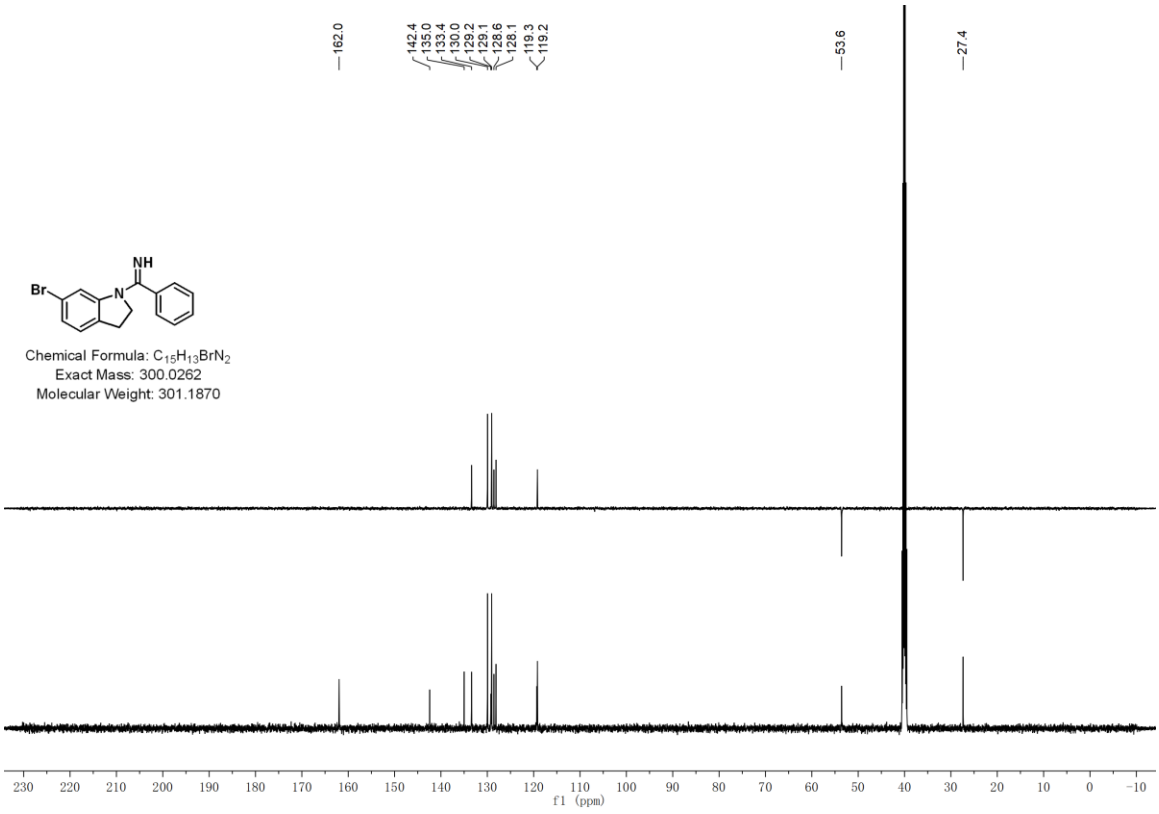
^{1}H NMR spectrum of **1k** (600 MHz, DMSO-d_6)



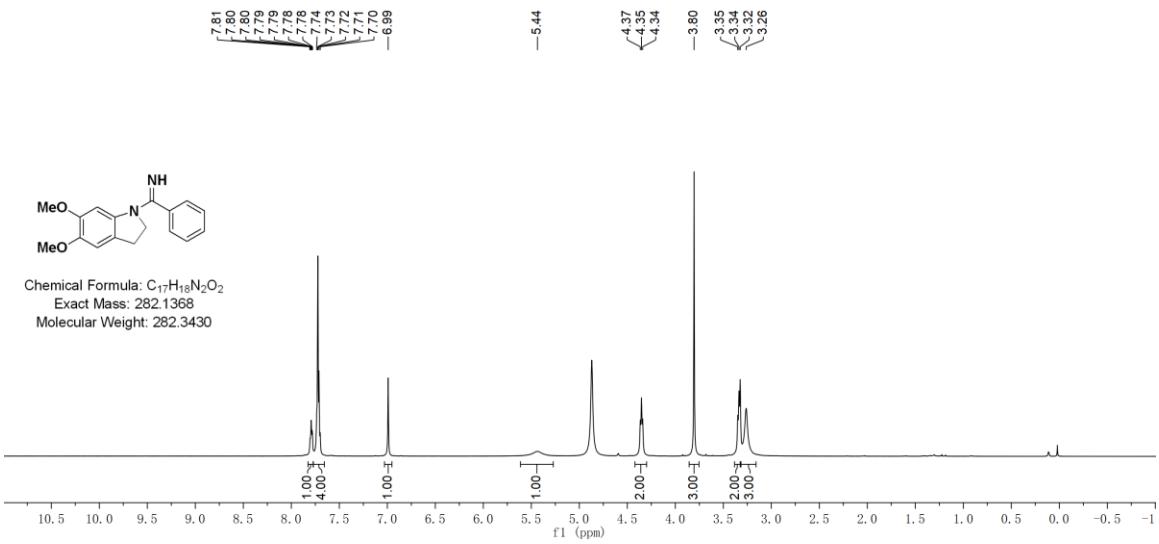
^{13}C NMR spectrum of **1k** (125 MHz, DMSO-d_6)



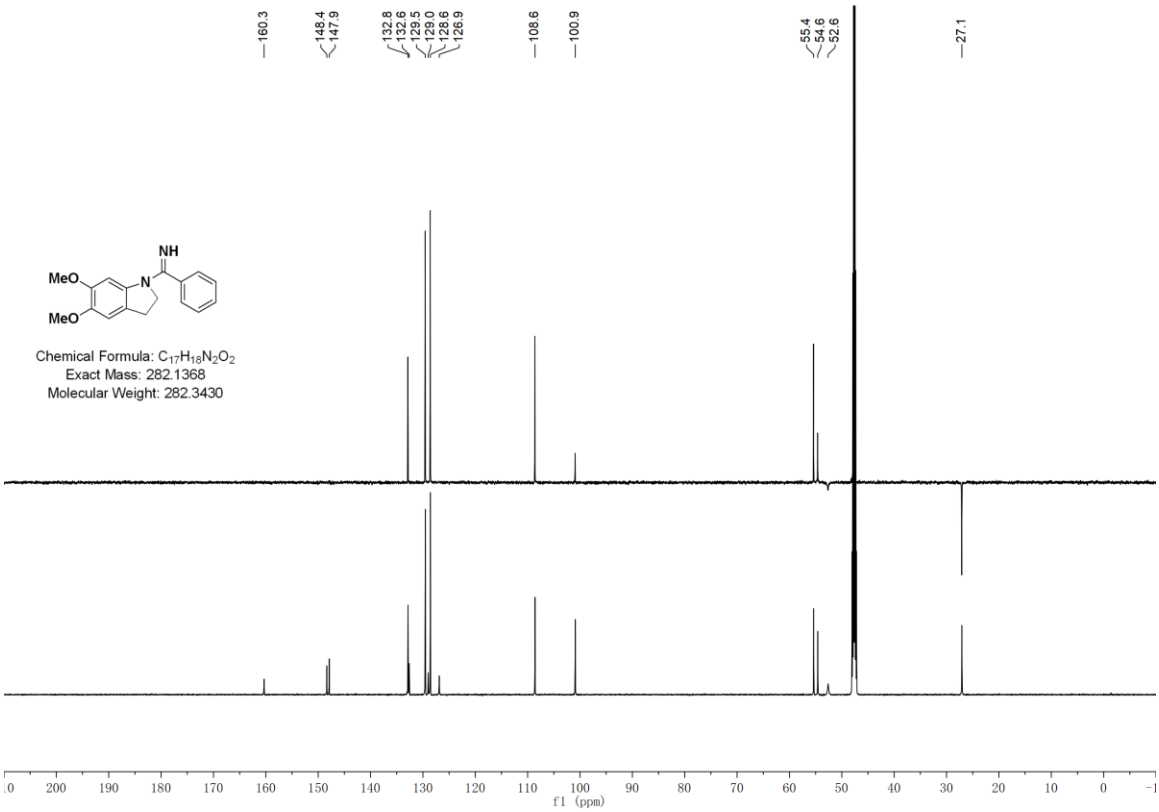
^{1}H NMR spectrum of **1l** (500 MHz, DMSO-d_6)



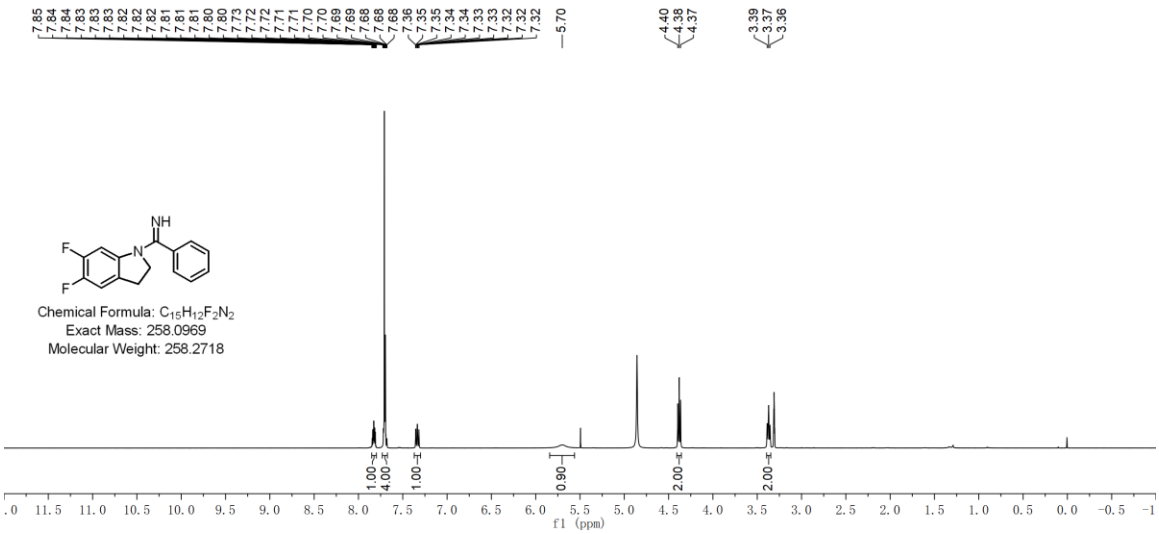
^{13}C NMR spectrum of **1l** (125 MHz, DMSO-d_6)



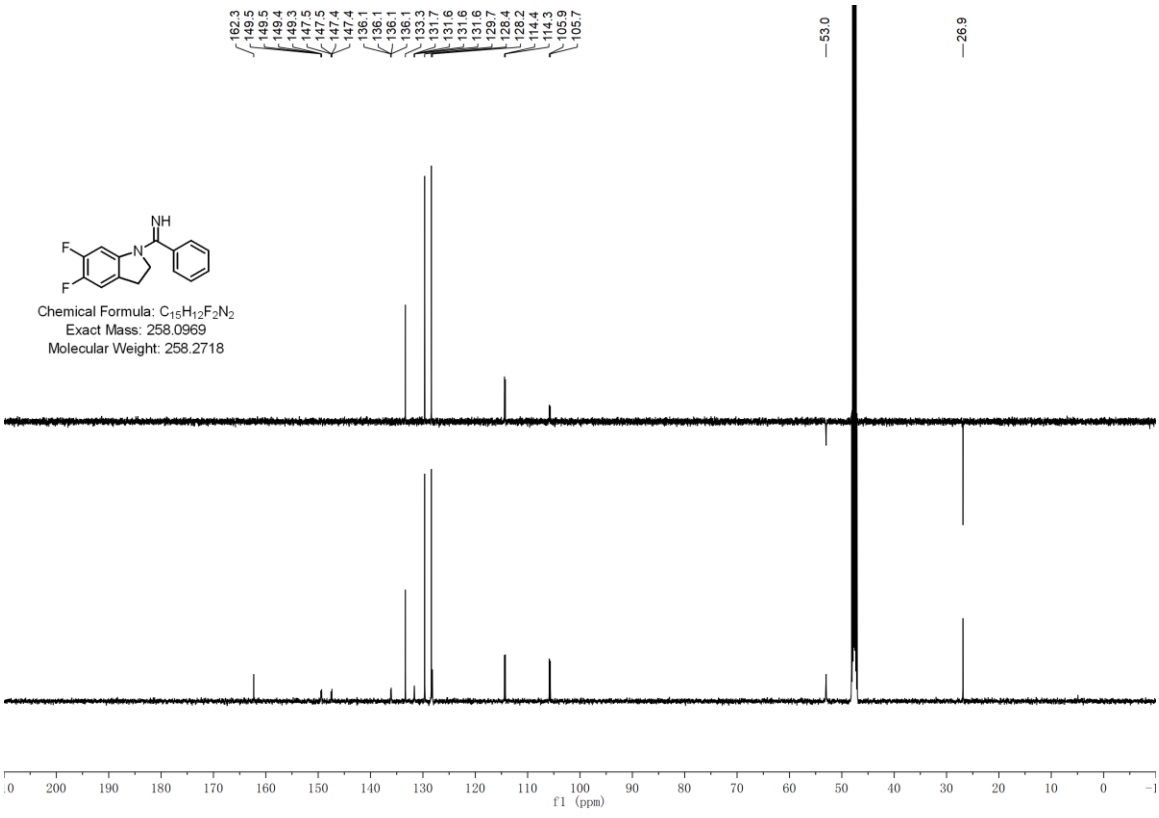
^{1}H NMR spectrum of **1m** (600 MHz, Methanol-d_4)



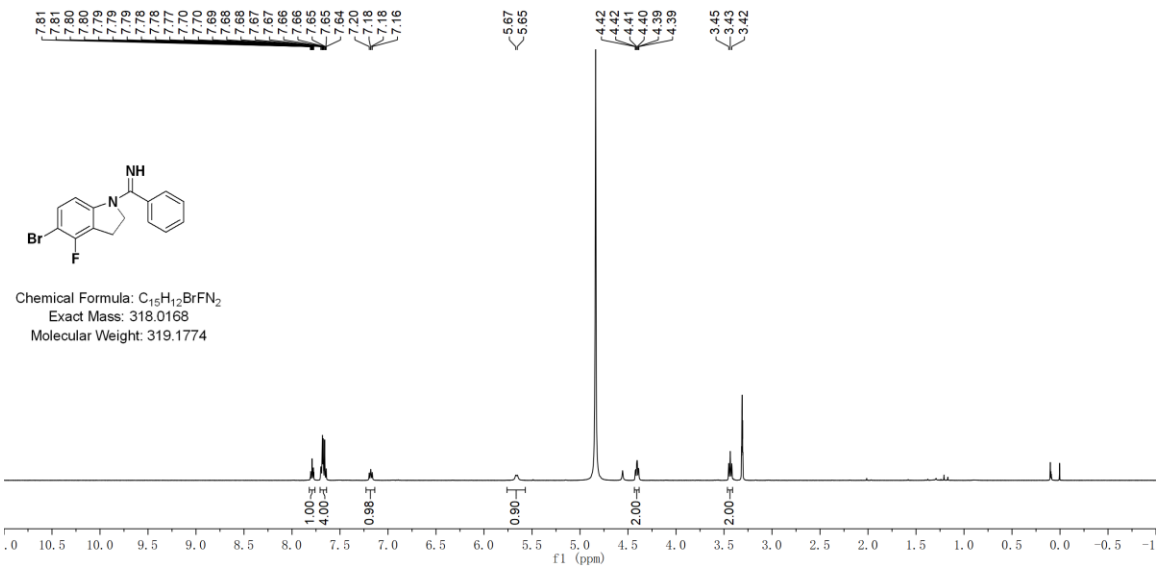
^{13}C NMR spectrum of **1m** (150 MHz, Methanol-d_4)



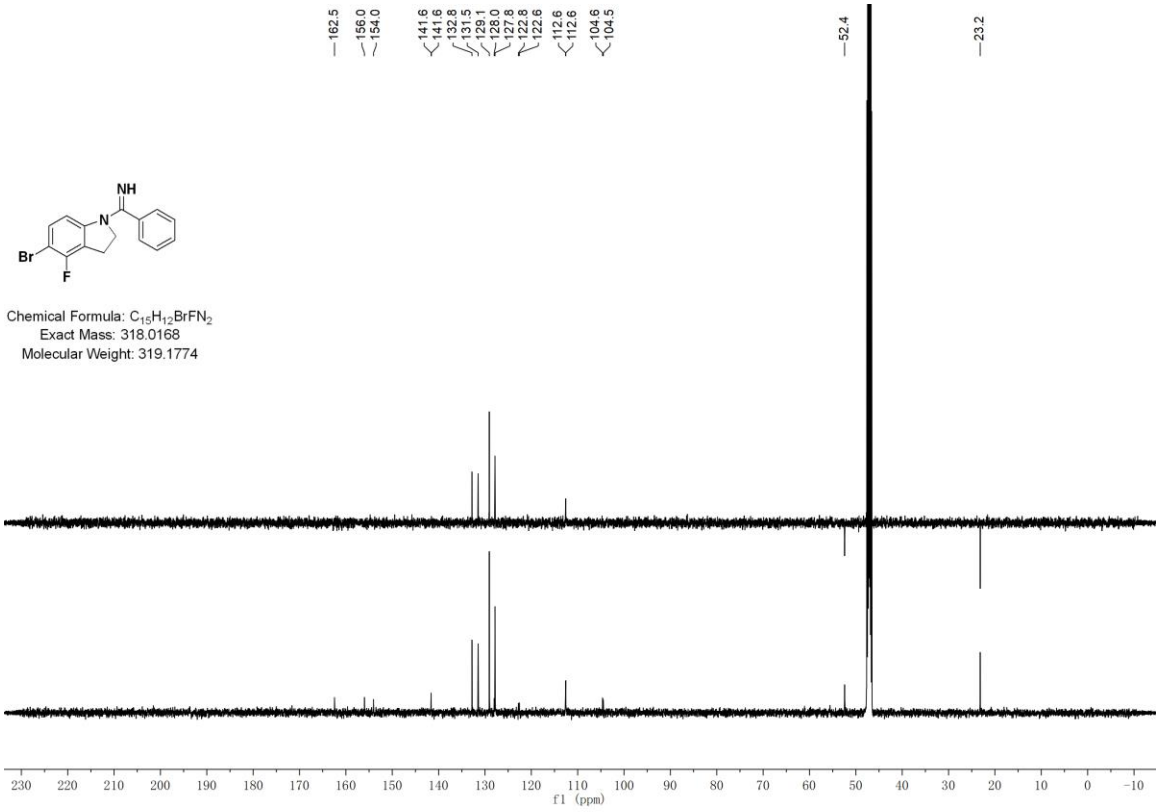
^{1}H NMR spectrum of **1n** (500 MHz, Methanol-d_4)



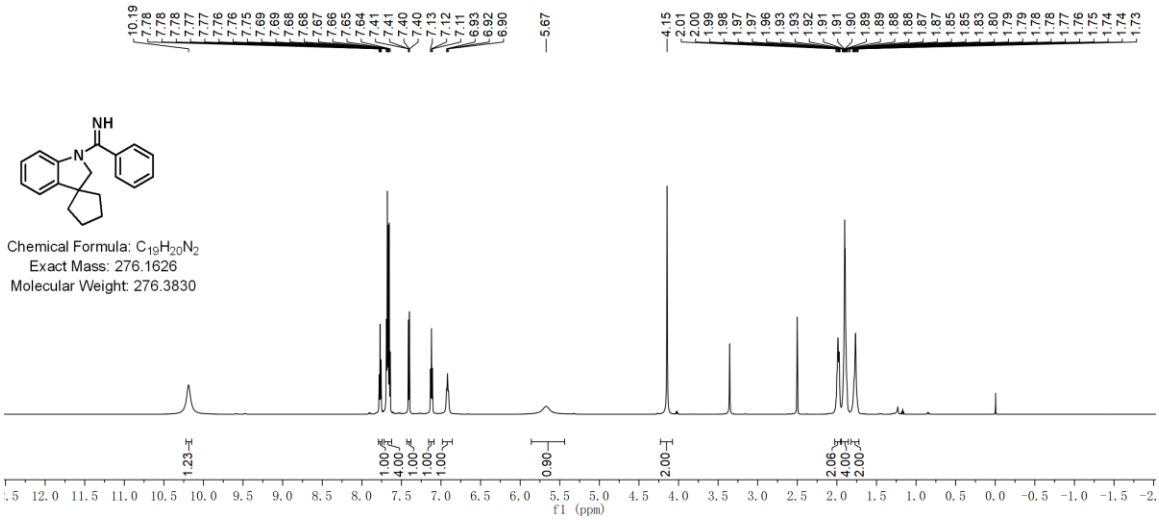
^{13}C NMR spectrum of **1n** (125 MHz, Methanol-d_4)



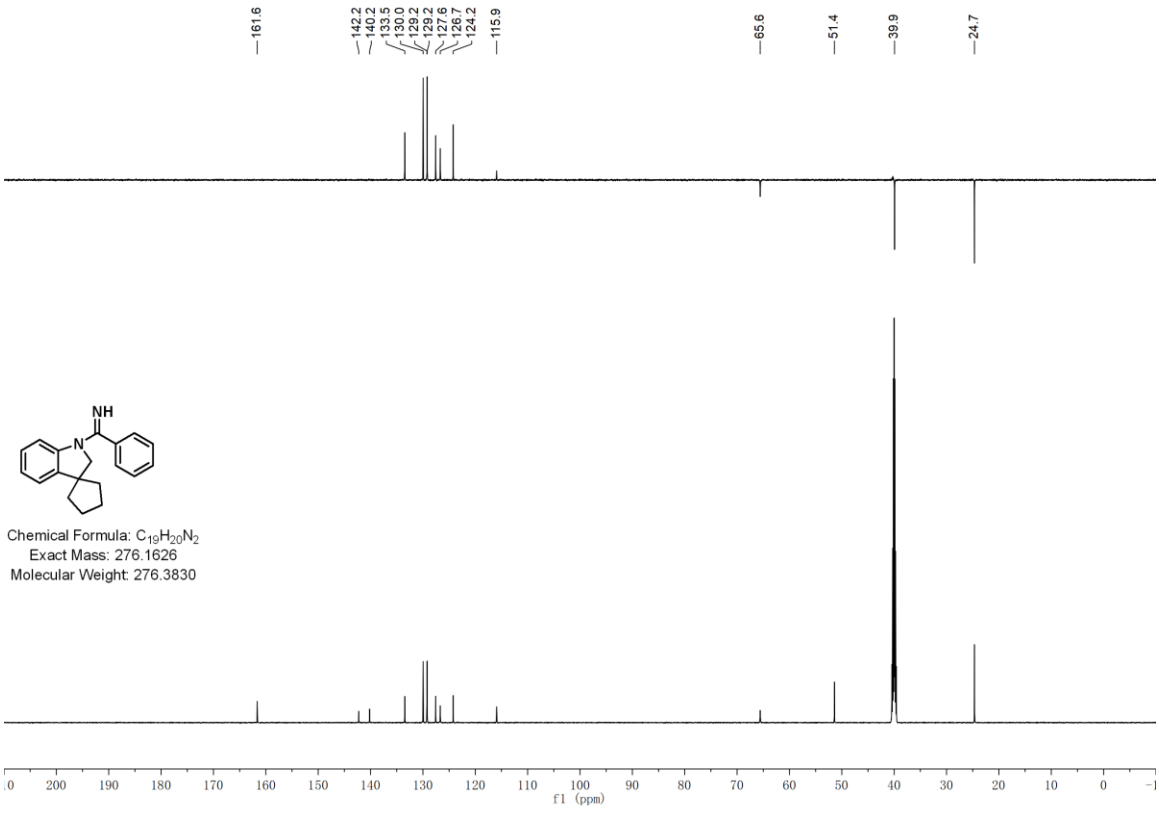
^{1}H NMR spectrum of **1o** (500 MHz, Methanol-d_4)



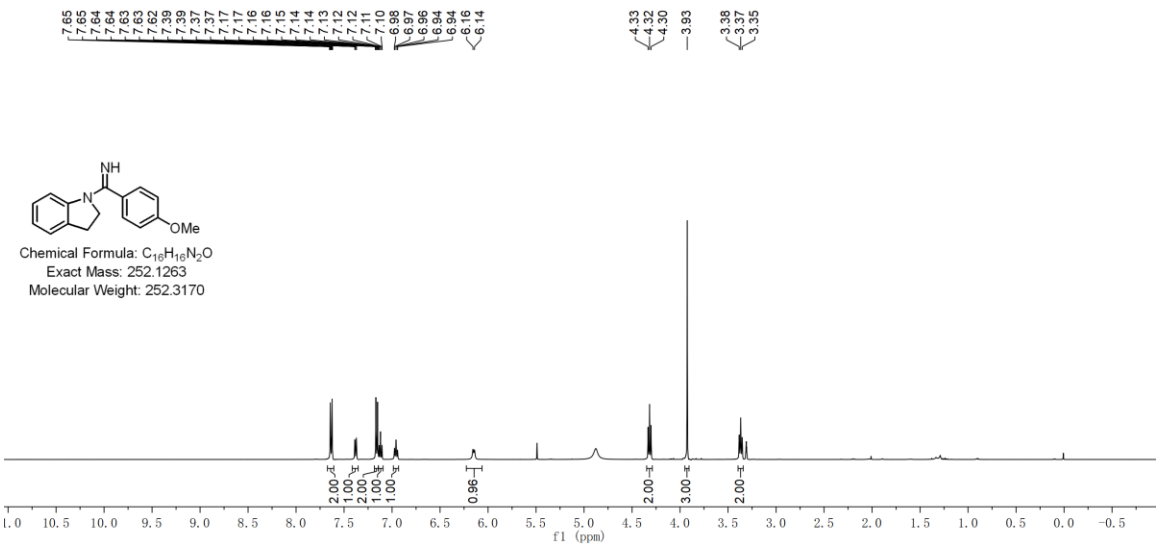
^{13}C NMR spectrum of **1o** (125 MHz, Methanol-d_4)



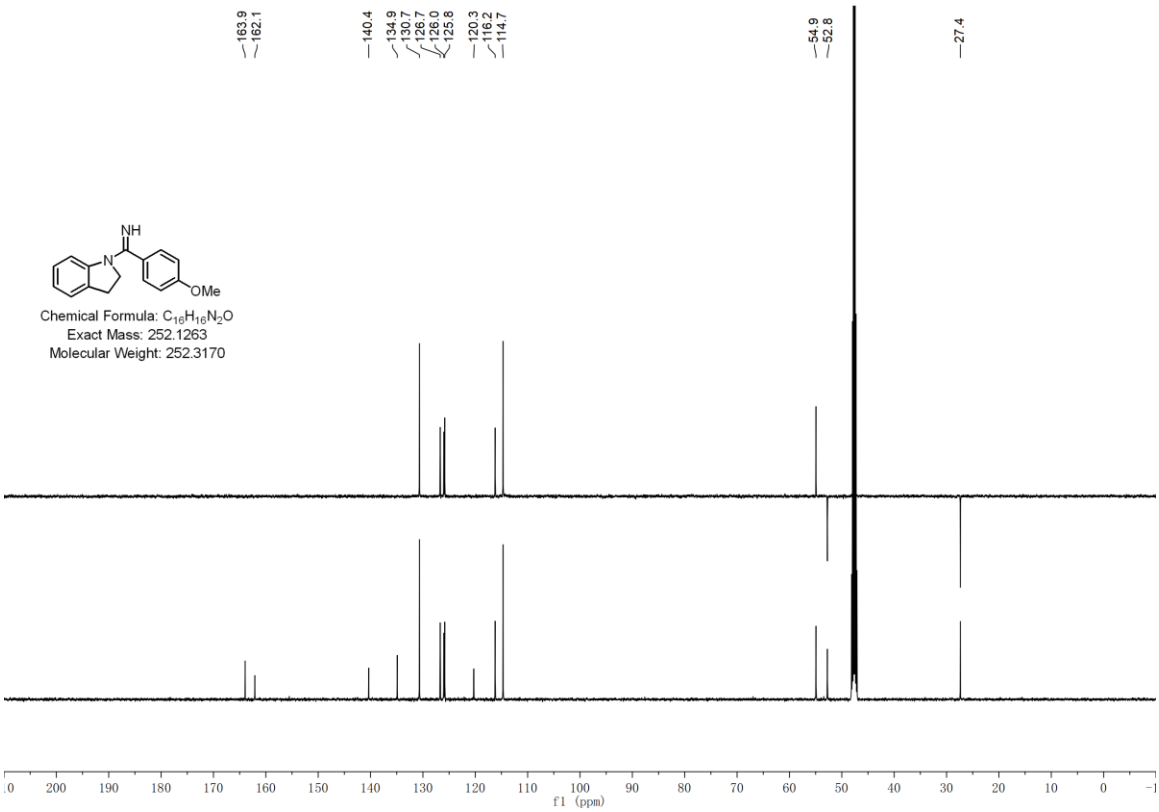
^{1}H NMR spectrum of **1p** (600 MHz, DMSO-d_6)



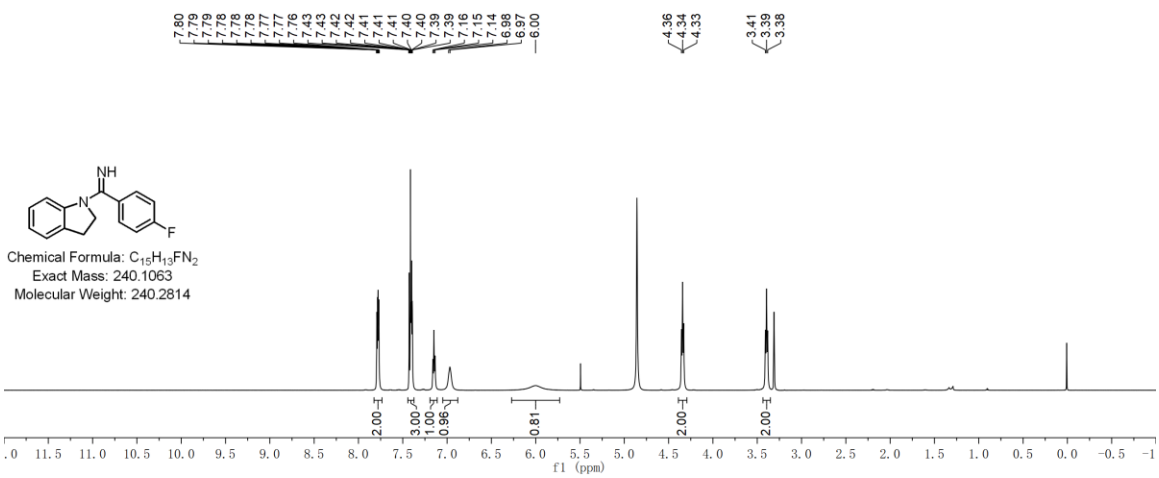
^{13}C NMR spectrum of **1p** (150 MHz, DMSO-d_6)



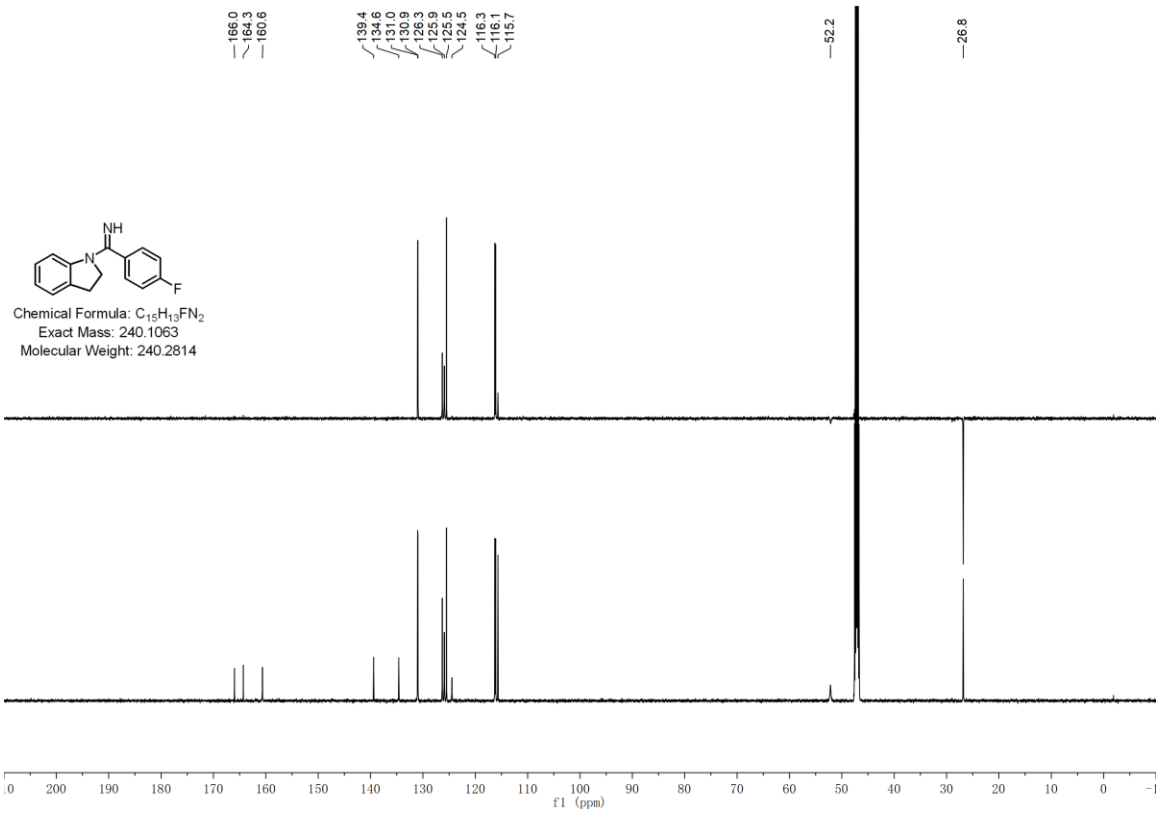
^{1}H NMR spectrum of **1q** (500 MHz, Methanol-d_4)



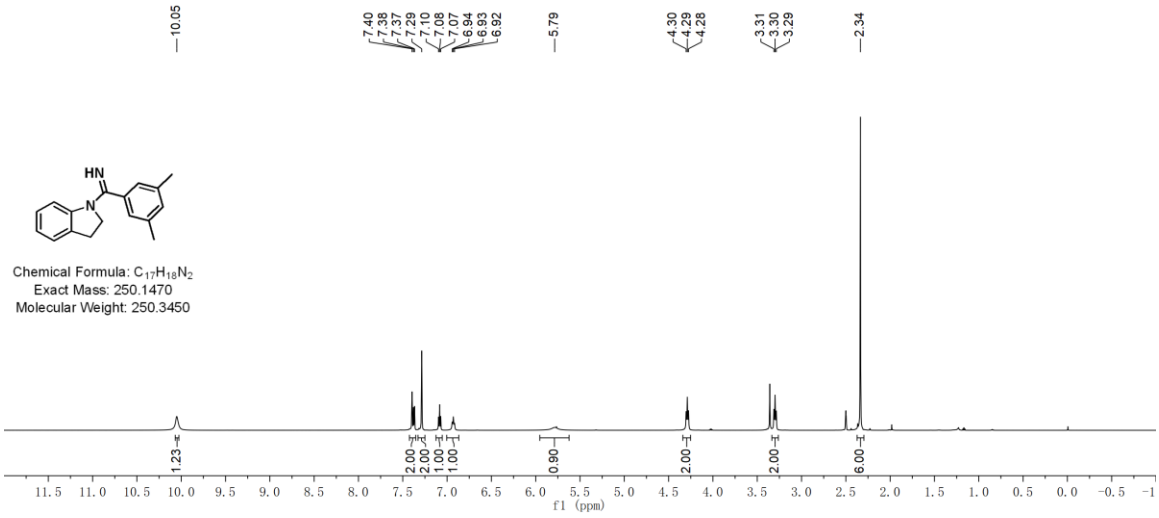
^{13}C NMR spectrum of **1q** (125 MHz, Methanol-d_4)



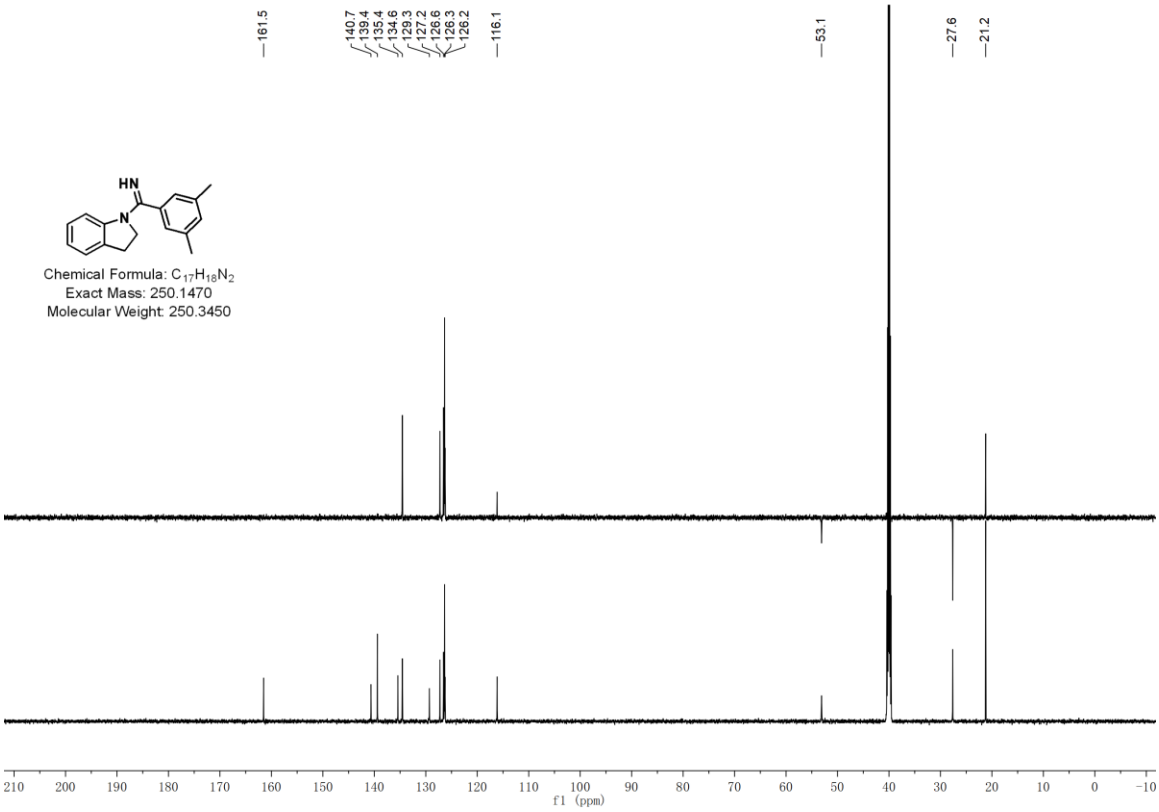
^{1}H NMR spectrum of **1r** (600 MHz, Methanol-d_4)



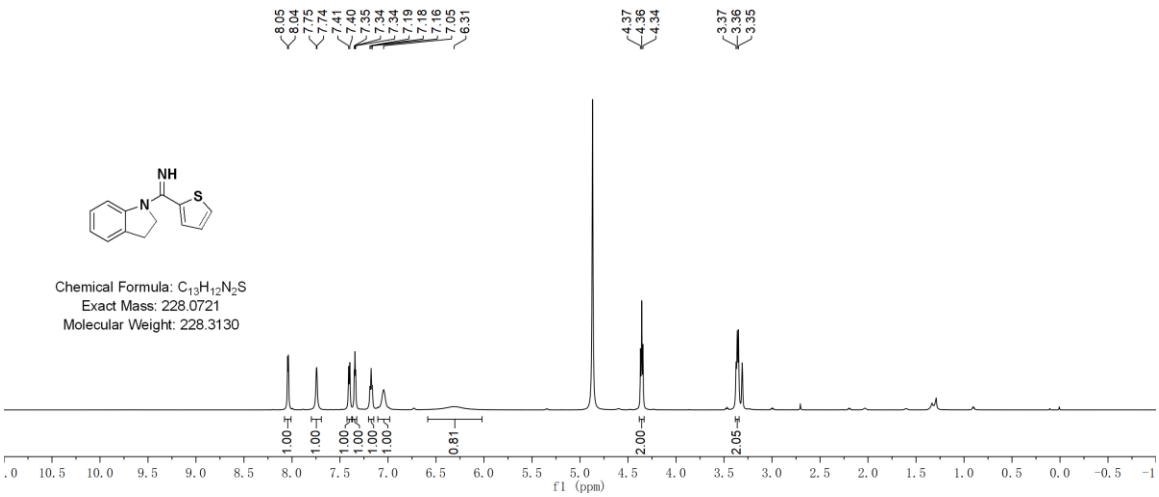
^{13}C NMR spectrum of **1r** (150 MHz, Methanol-d_4)



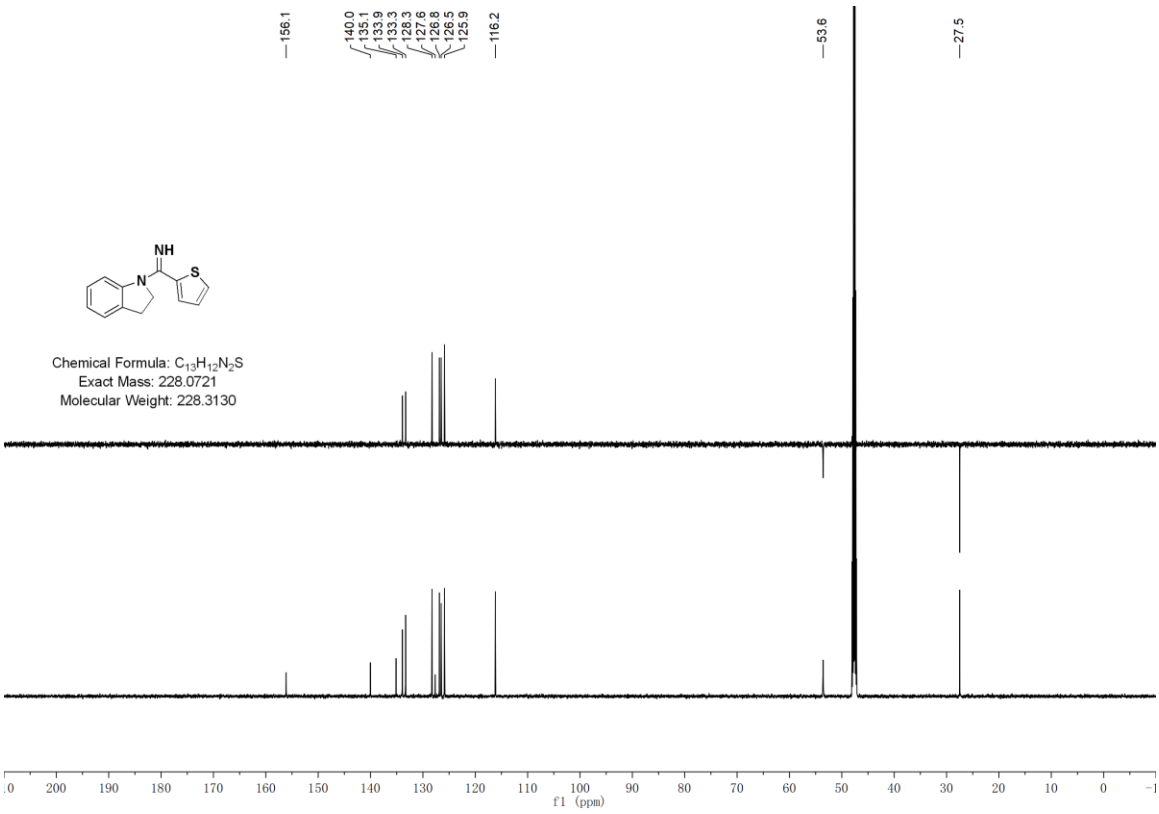
^{1}H NMR spectrum of **1s** (600 MHz, DMSO-d_6)



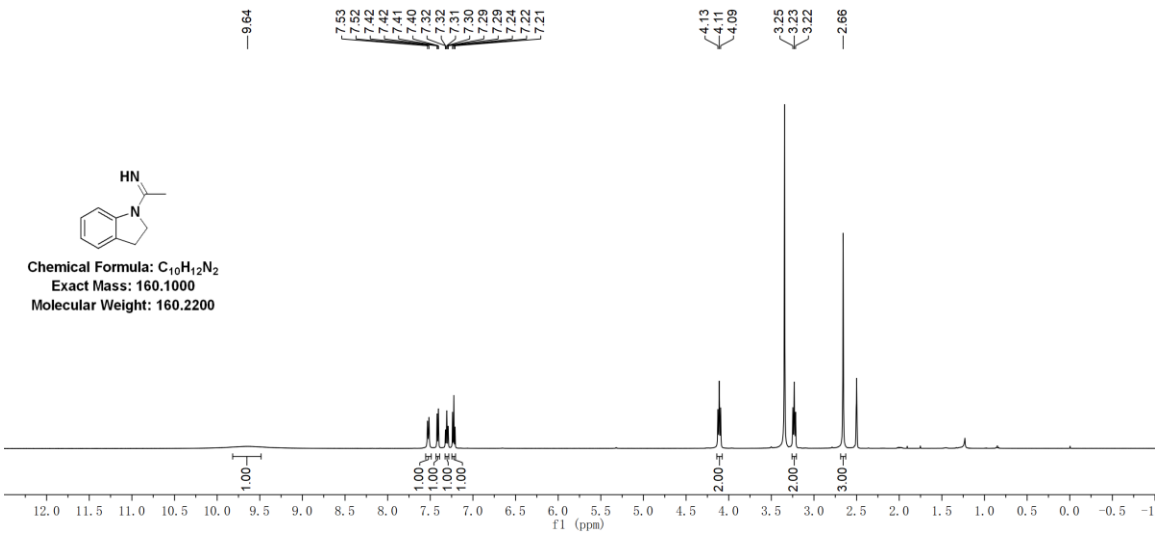
^{13}C NMR spectrum of **1s** (150 MHz, DMSO-d_6)



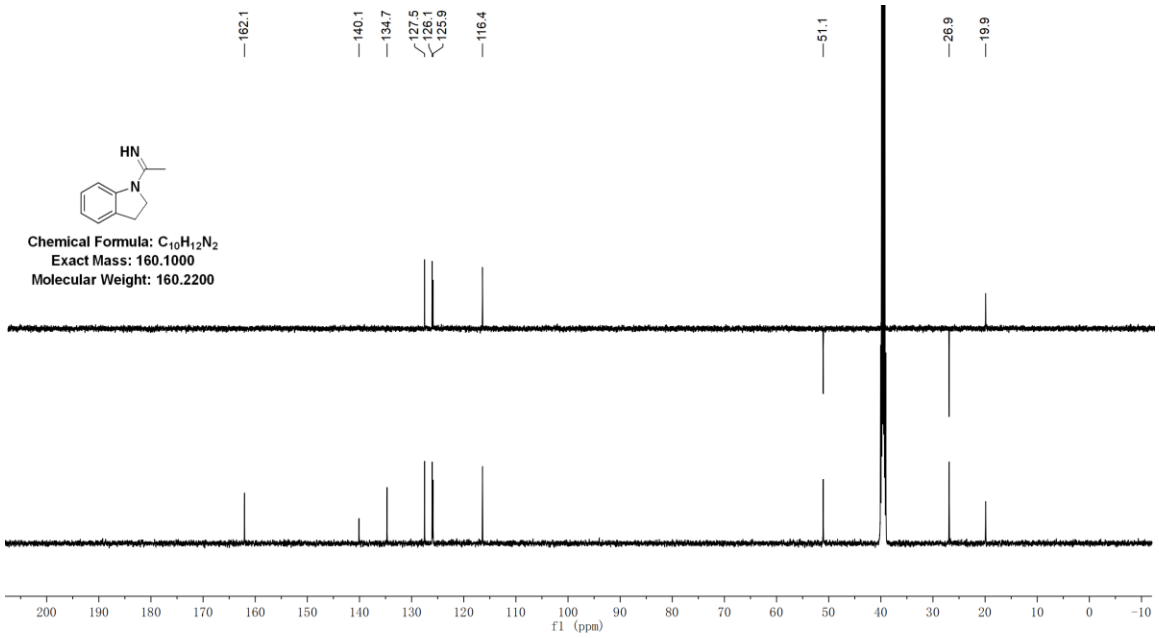
^{1}H NMR spectrum of **1t** (600 MHz, Methanol-d_4)



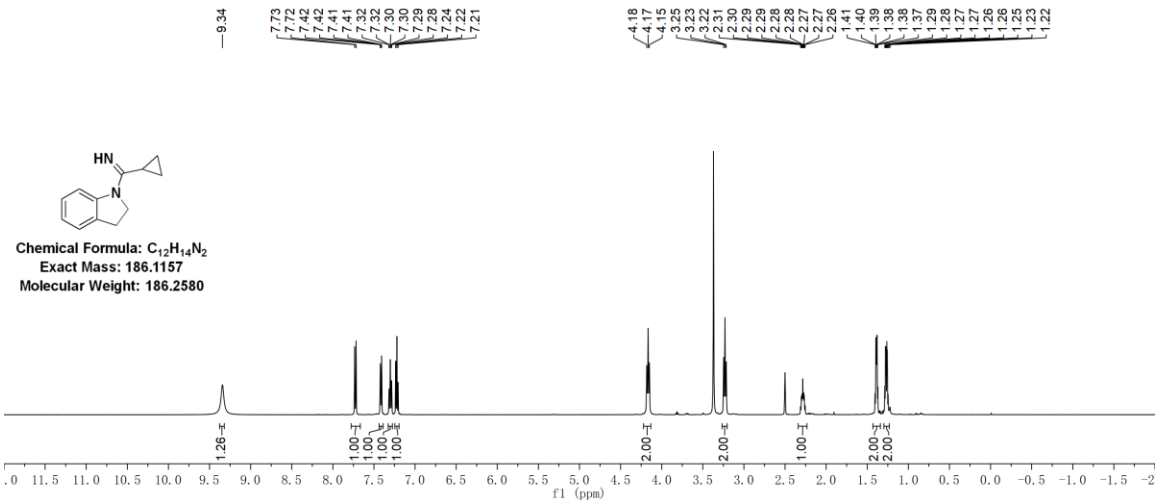
^{13}C NMR spectrum of **1t** (150 MHz, Methanol-d_4)



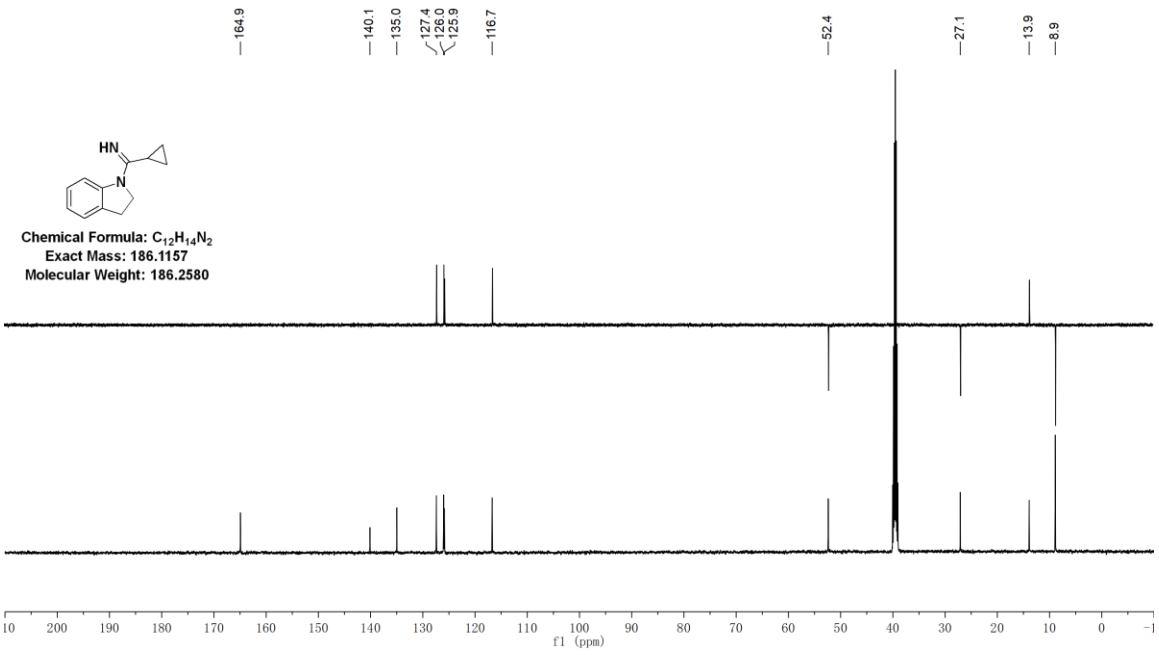
^{1}H NMR spectrum of **1u** (500 MHz, DMSO-d_6)



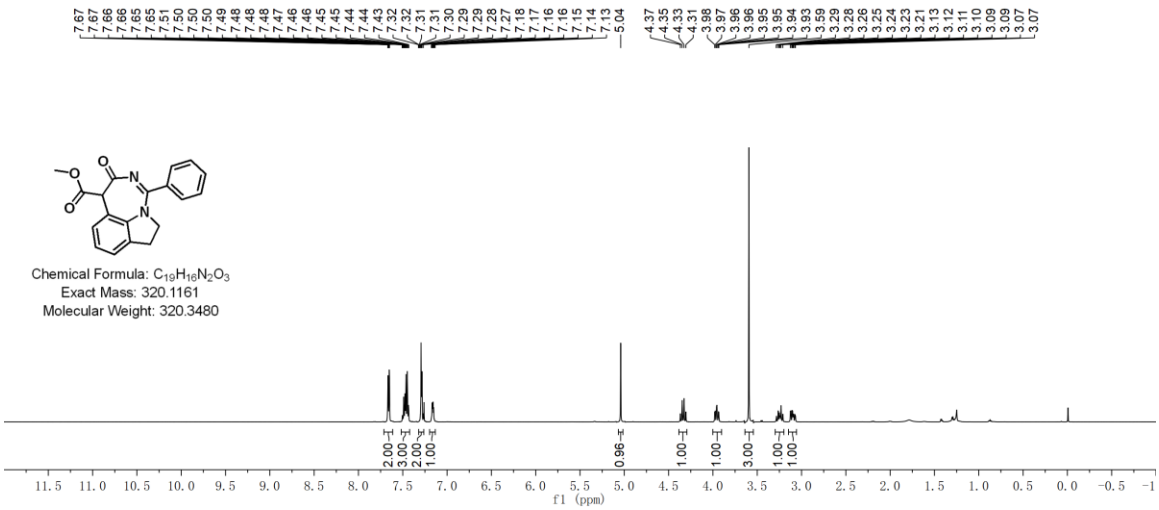
^{13}C NMR spectrum of **1u** (125 MHz, DMSO-d_6)



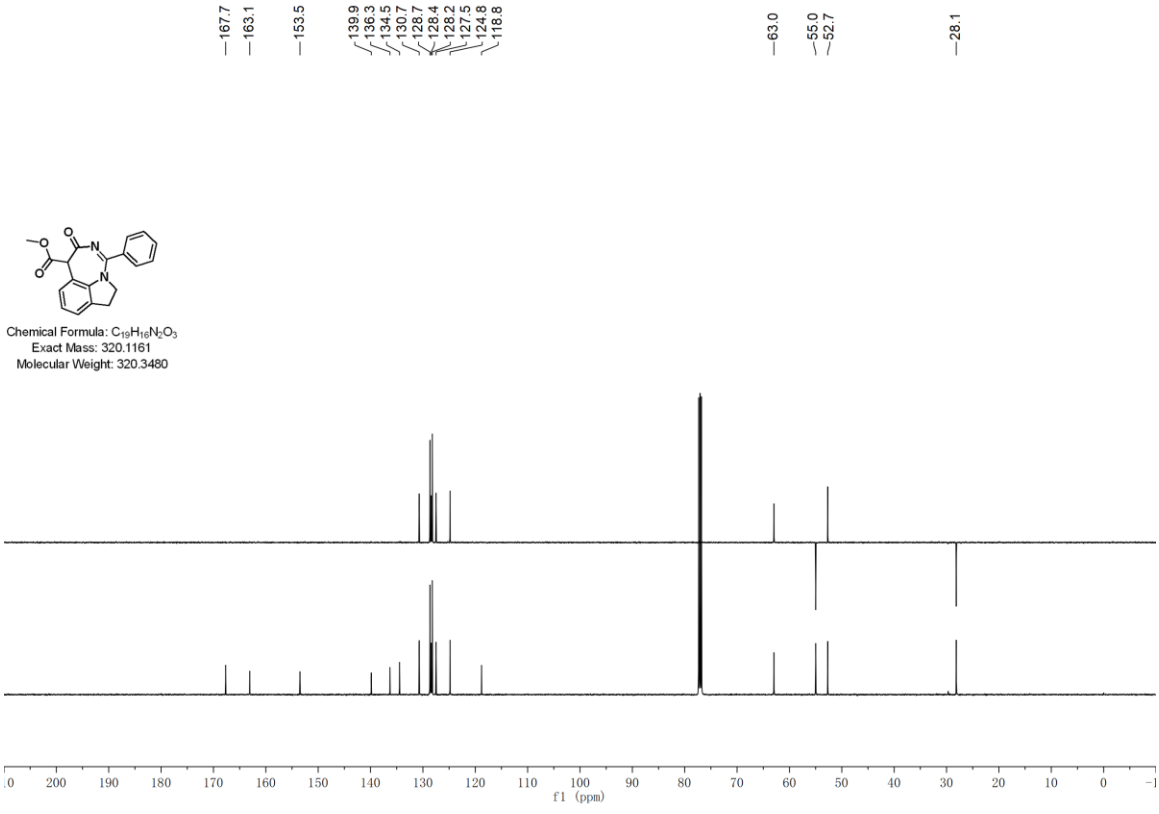
^{1}H NMR spectrum of **1v** (500 MHz, DMSO-d_6)



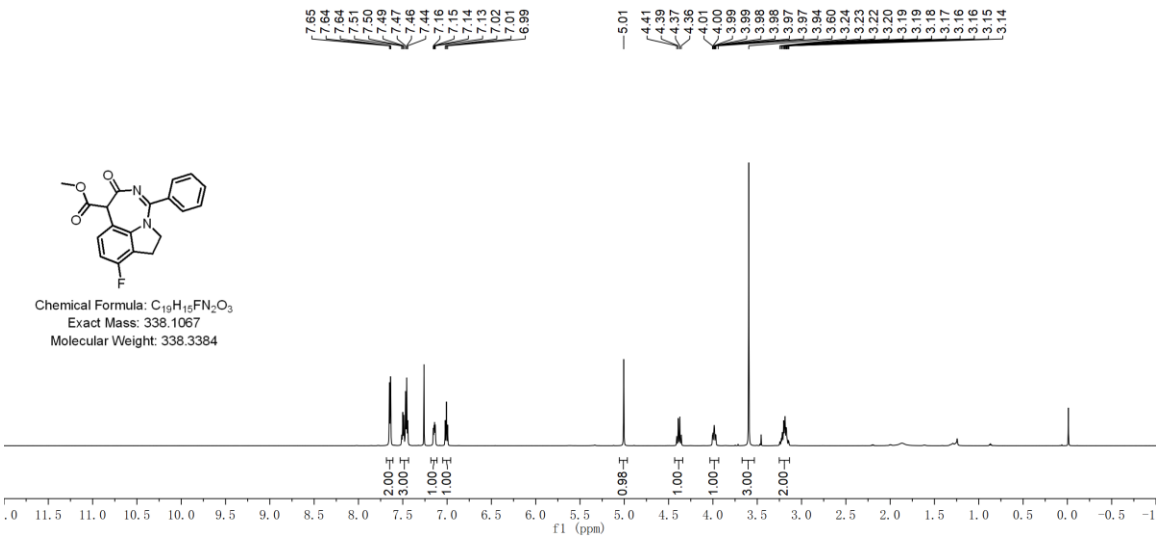
^{13}C NMR spectrum of **1v** (125 MHz, DMSO-d_6)



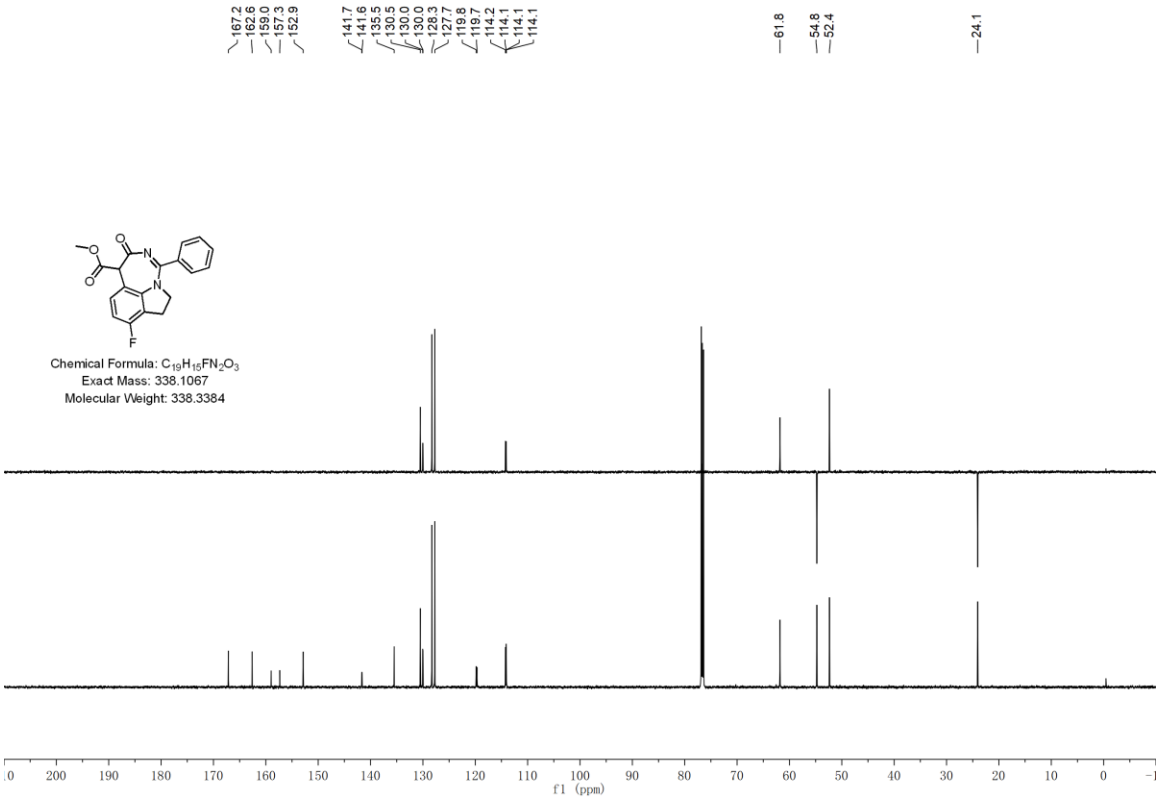
^{1}H NMR spectrum of **3aa** (500 MHz, Chloroform-*d*)



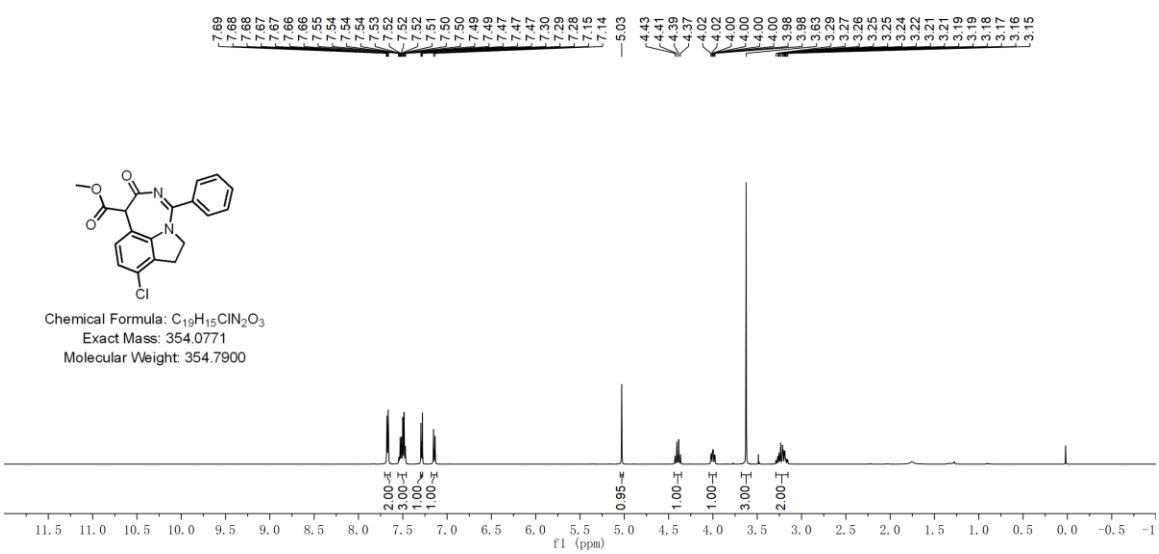
^{13}C NMR spectrum of **3aa** (125 MHz, Chloroform-*d*)



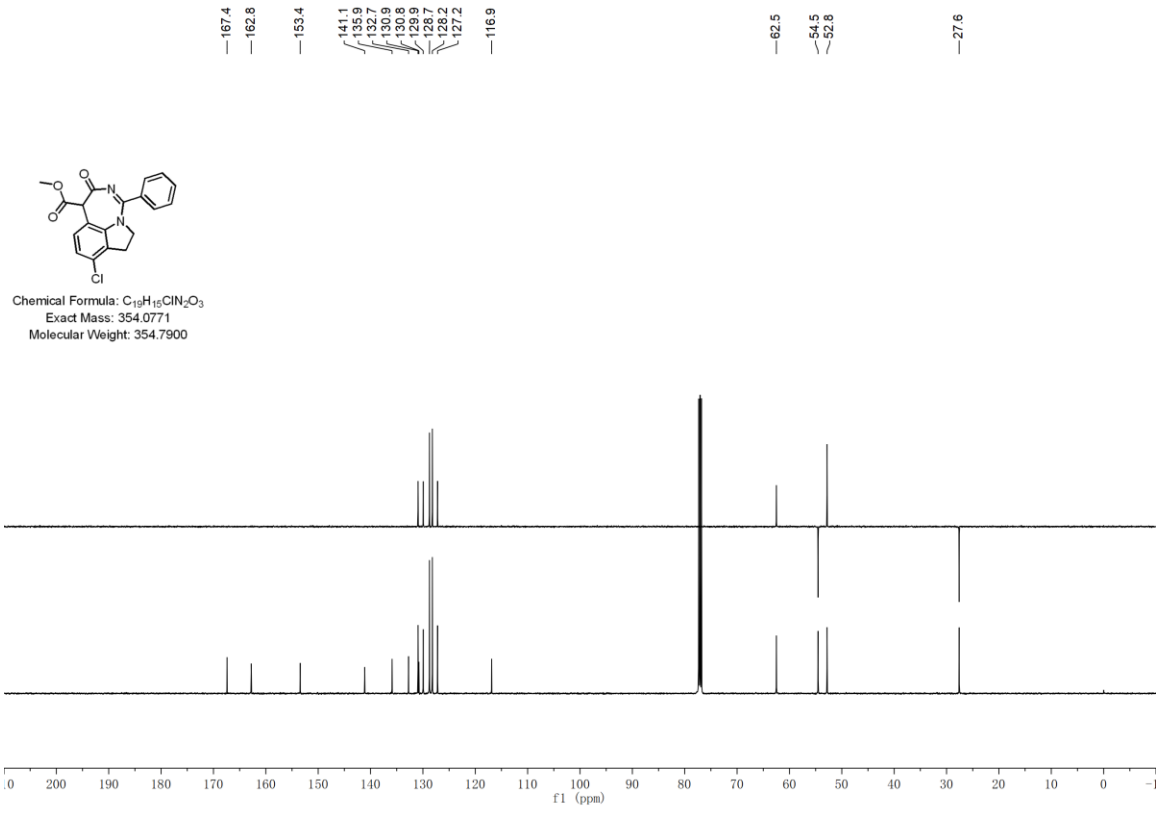
^{1}H NMR spectrum of **3ba** (600 MHz, Chloroform-*d*)



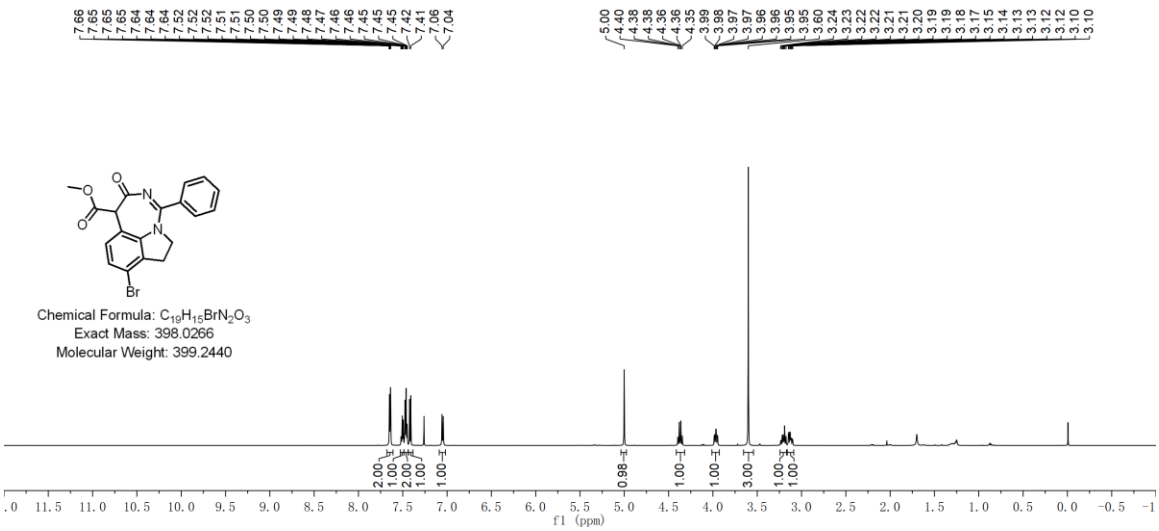
^{13}C NMR spectrum of **3ba** (150 MHz, Chloroform-*d*)



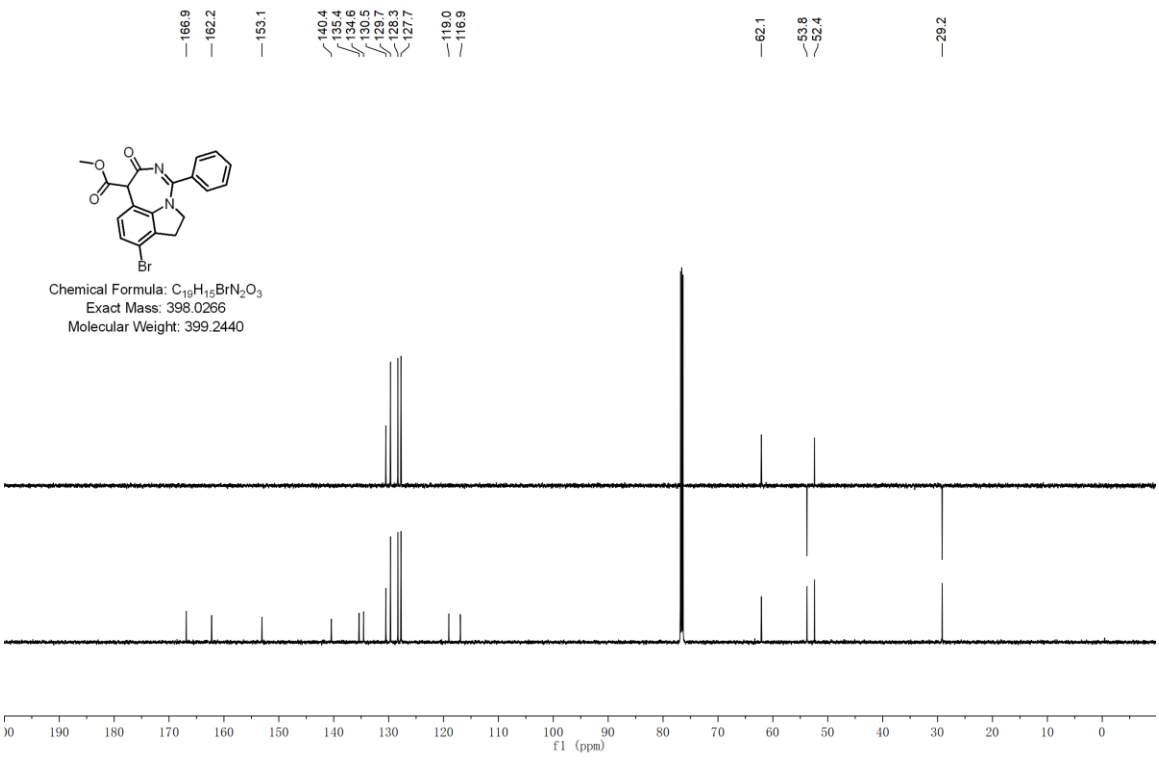
^{1}H NMR spectrum of **3ca** (500 MHz, Chloroform-*d*)



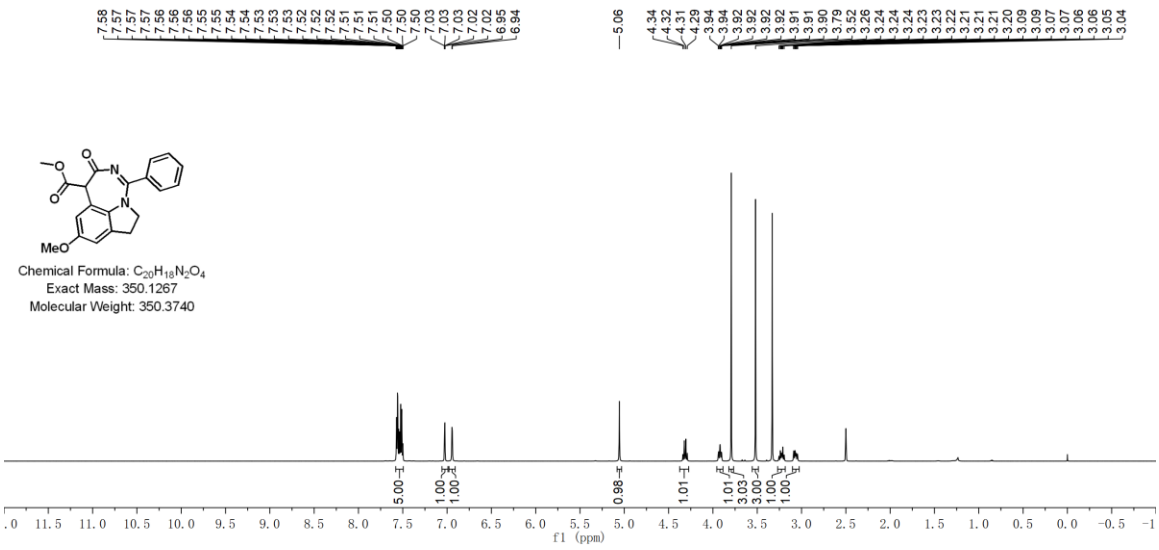
^{13}C NMR spectrum of **3ca** (125 MHz, Chloroform-*d*)



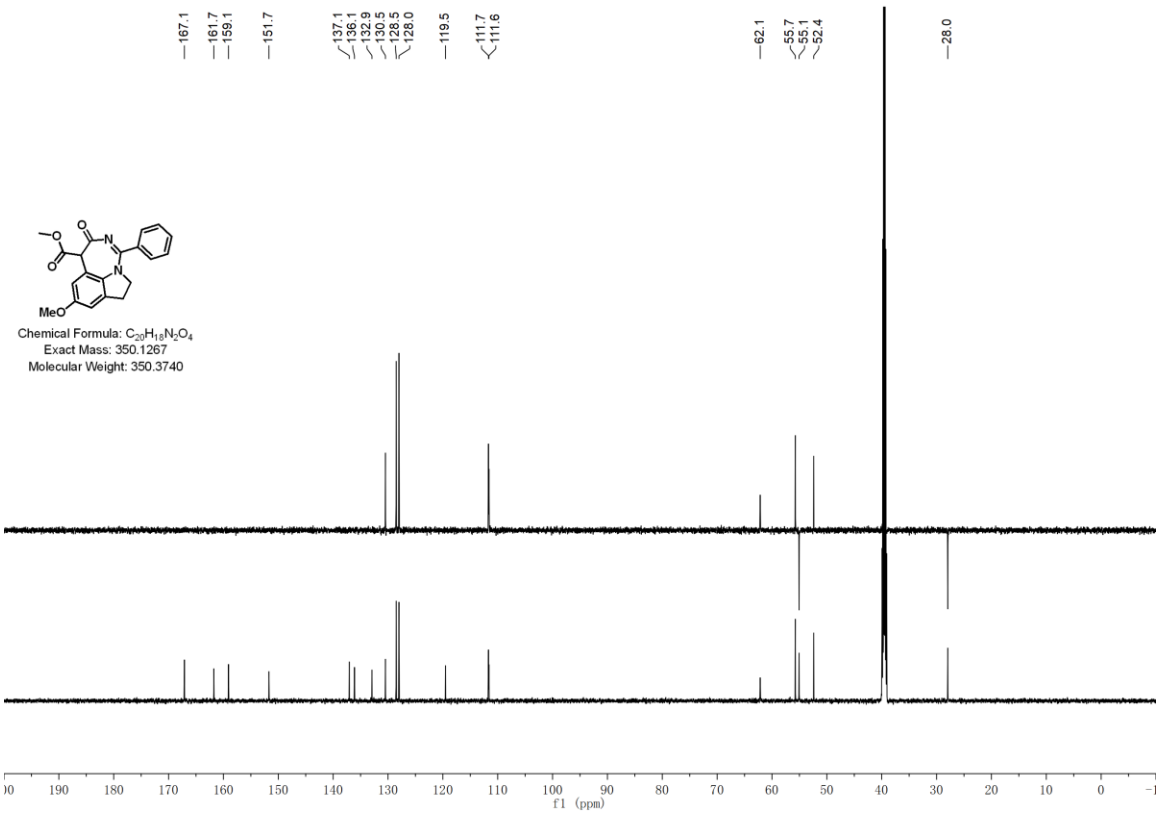
^{1}H NMR spectrum of **3da** (600 MHz, Chloroform-*d*)



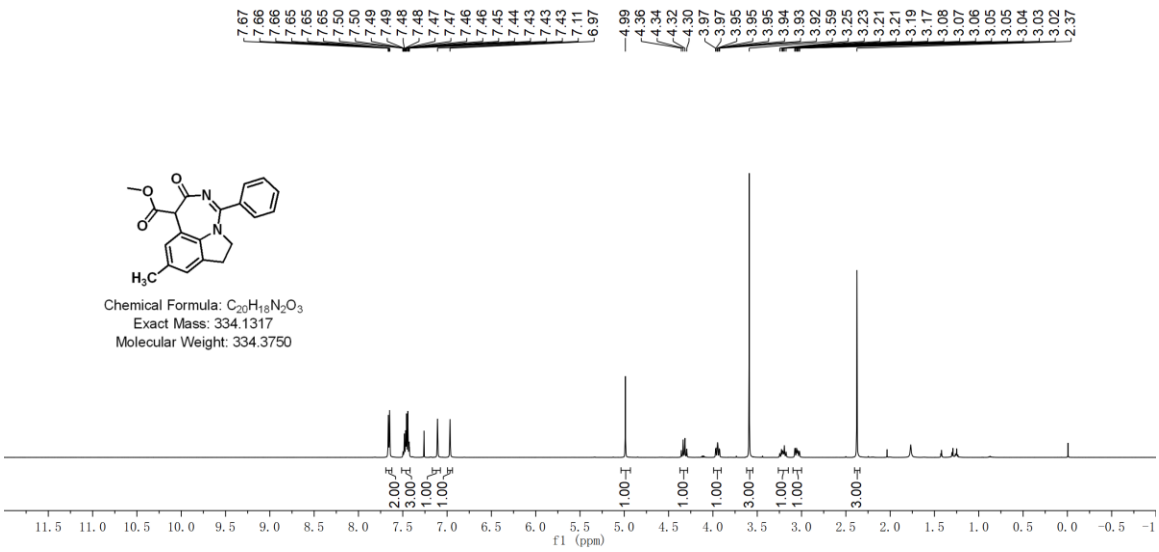
^{13}C NMR spectrum of **3da** (150 MHz, Chloroform-*d*)



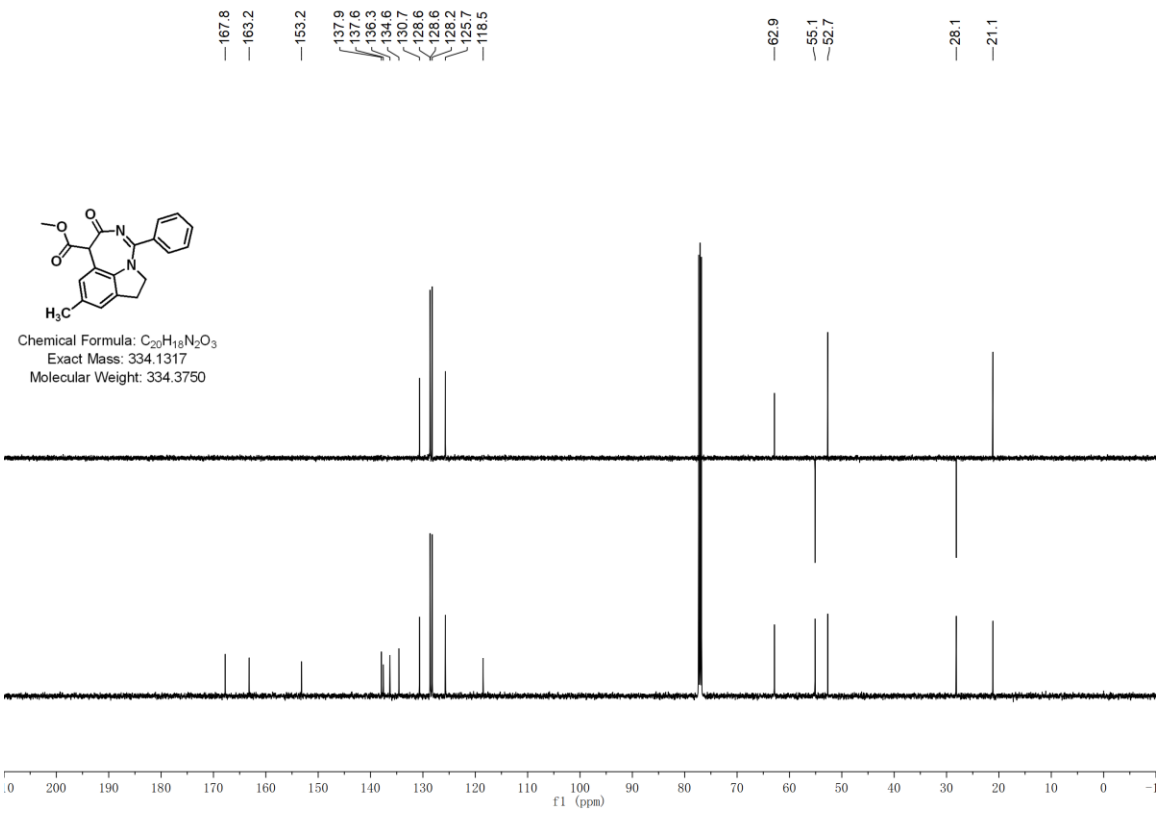
^{1}H NMR spectrum of **3ea** (600 MHz, DMSO-d_6)



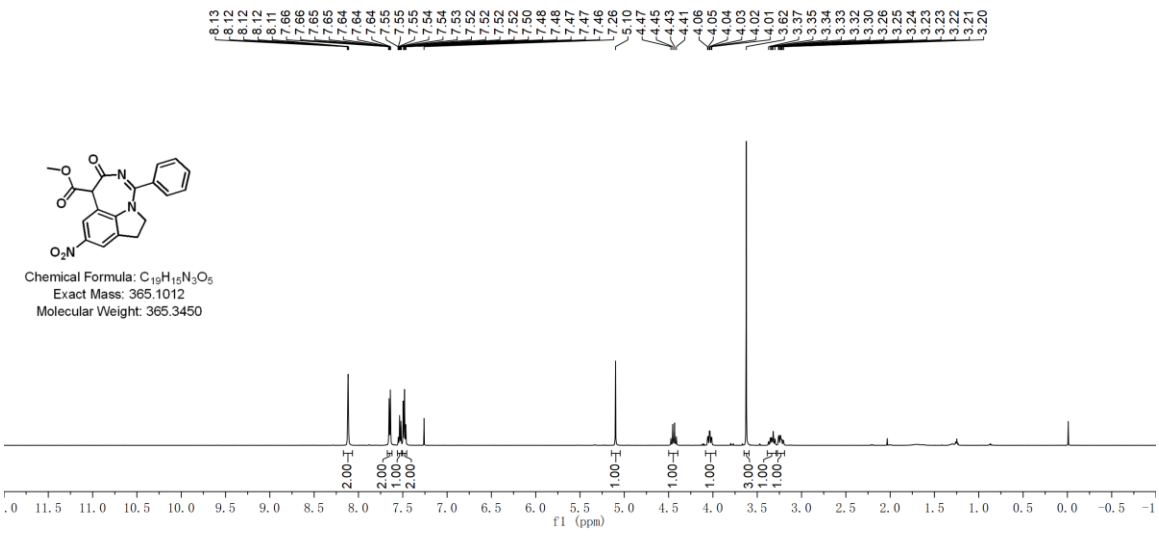
^{13}C NMR spectrum of **3ea** (150 MHz, DMSO-d_6)



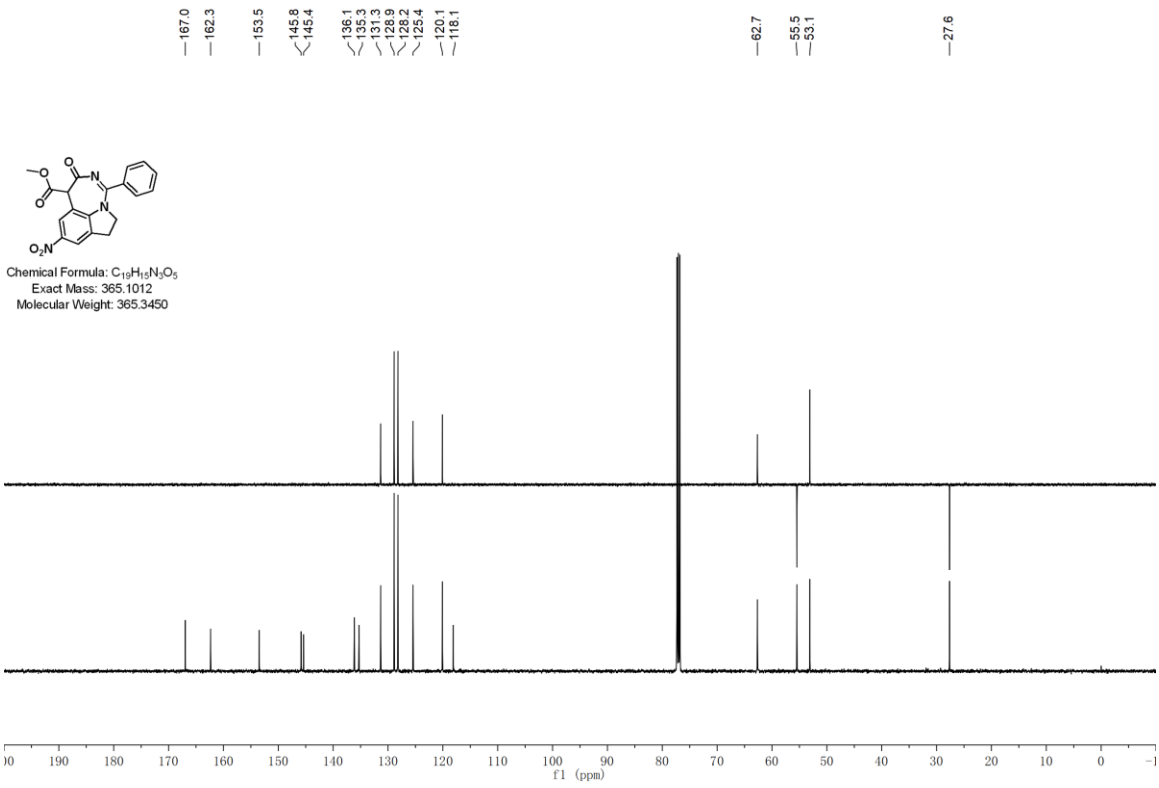
^{1}H NMR spectrum of **3fa** (500 MHz, Chloroform-*d*)



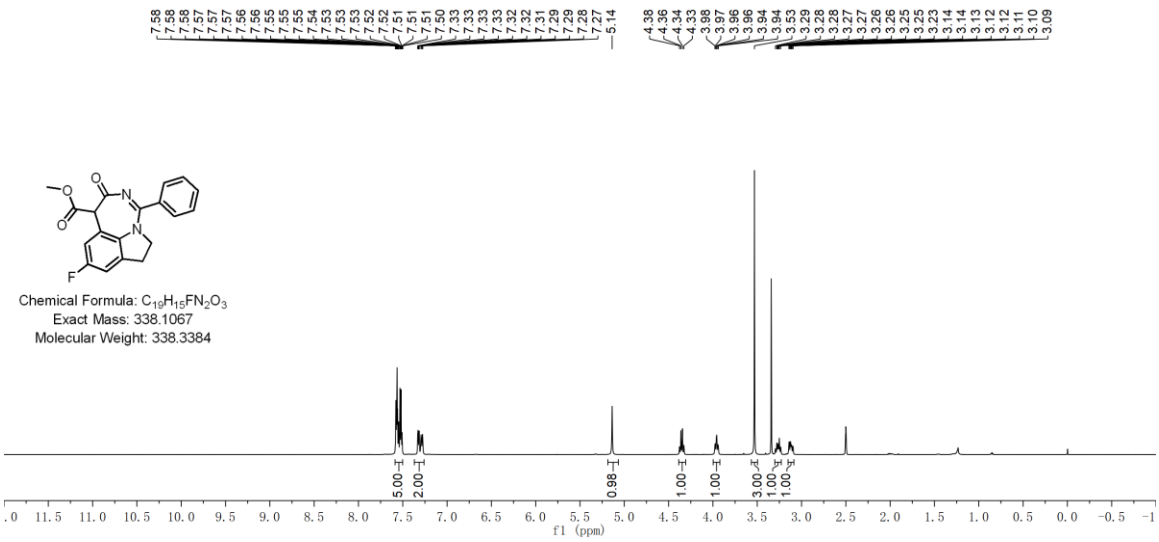
^{13}C NMR spectrum of **3fa** (125 MHz, Chloroform-*d*)



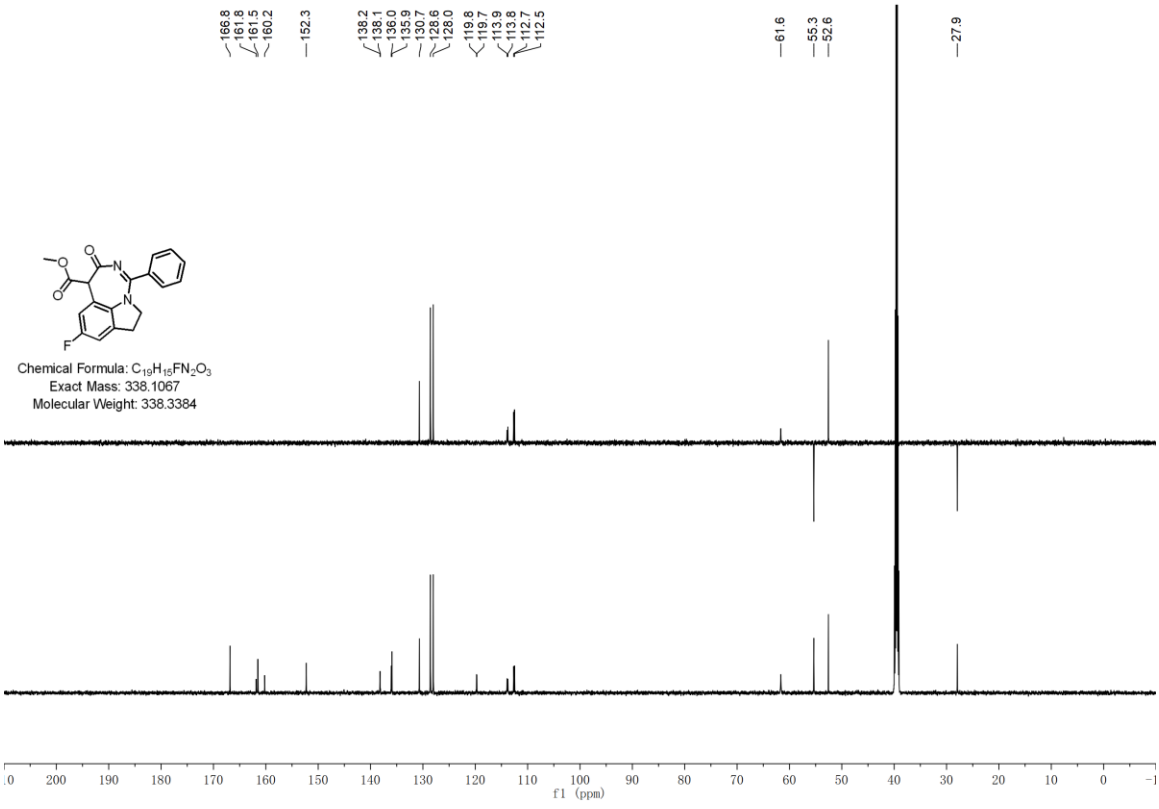
^{1}H NMR spectrum of **3ga** (500 MHz, Chloroform-*d*)



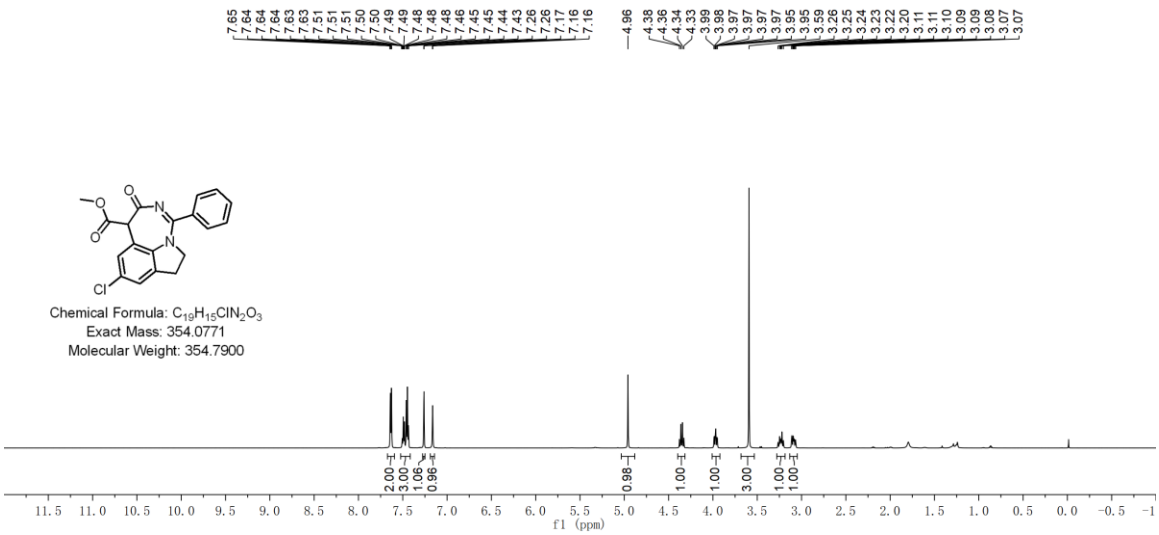
^{13}C NMR spectrum of **3ga** (125 MHz, Chloroform-*d*)



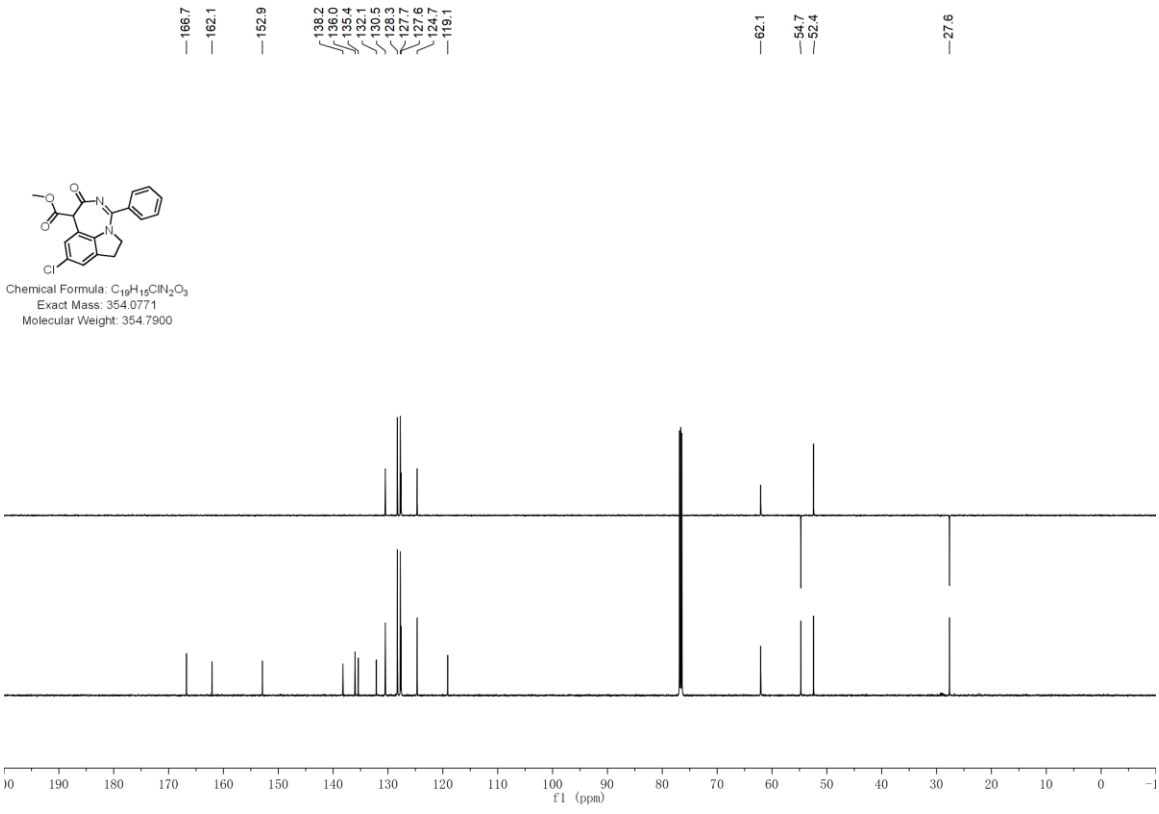
^{1}H NMR spectrum of **3ha** (600 MHz, DMSO-d_6)



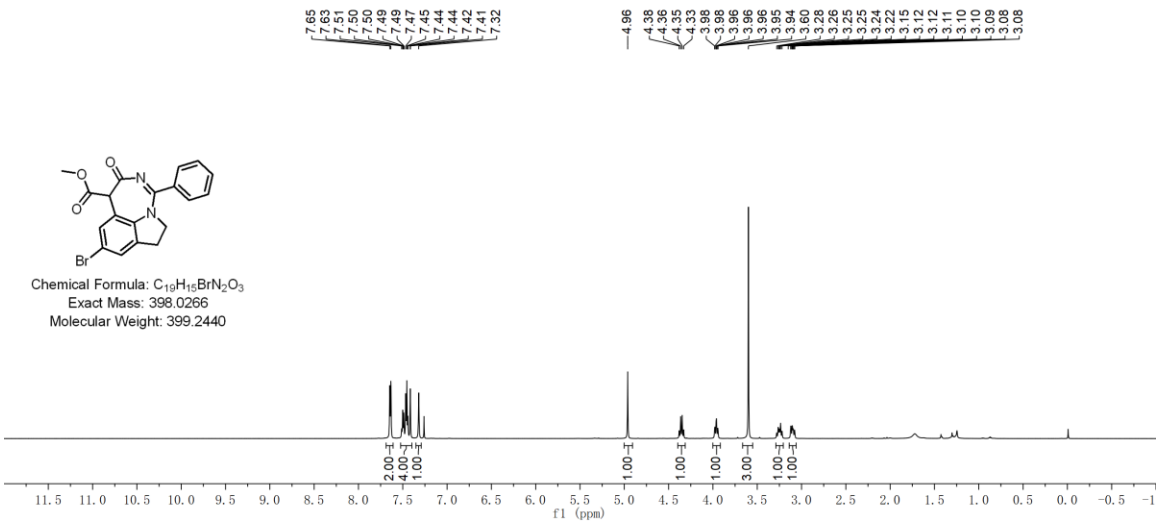
^{13}C NMR spectrum of **3ha** (150 MHz, DMSO-d_6)



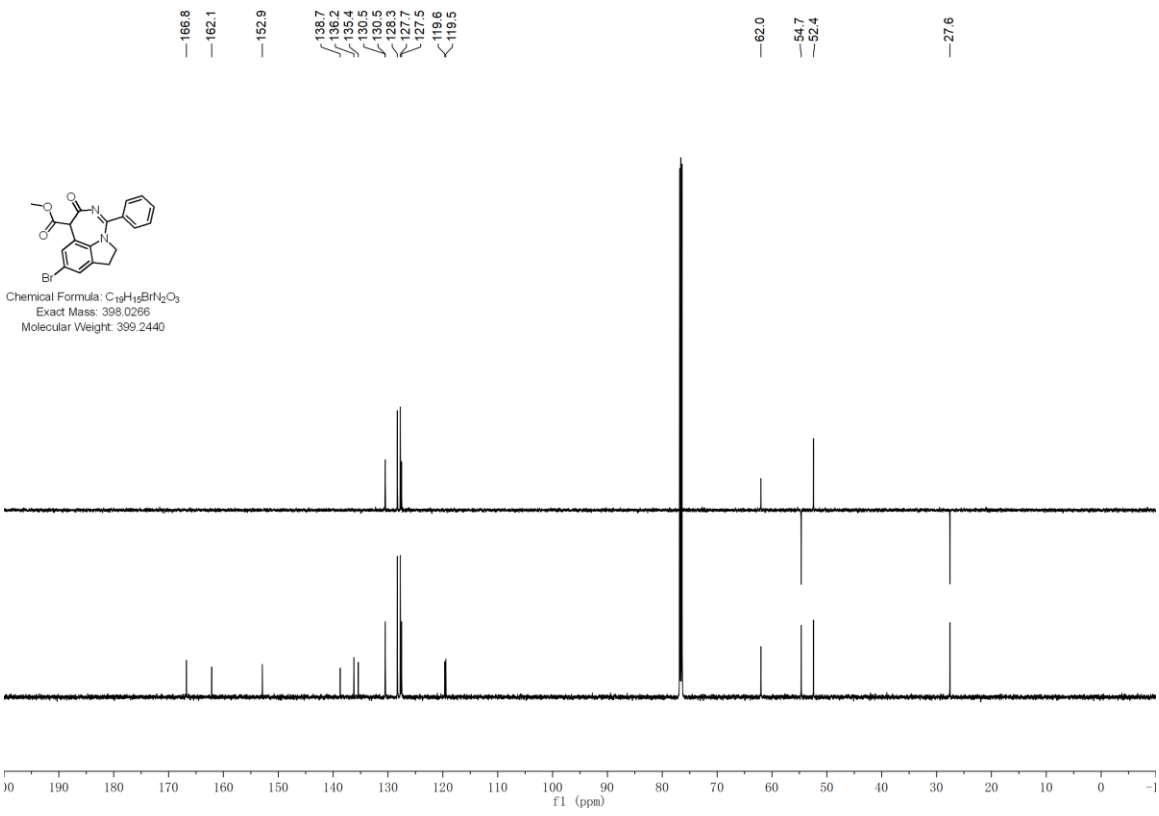
^{1}H NMR spectrum of **3ia** (600 MHz, Chloroform-*d*)



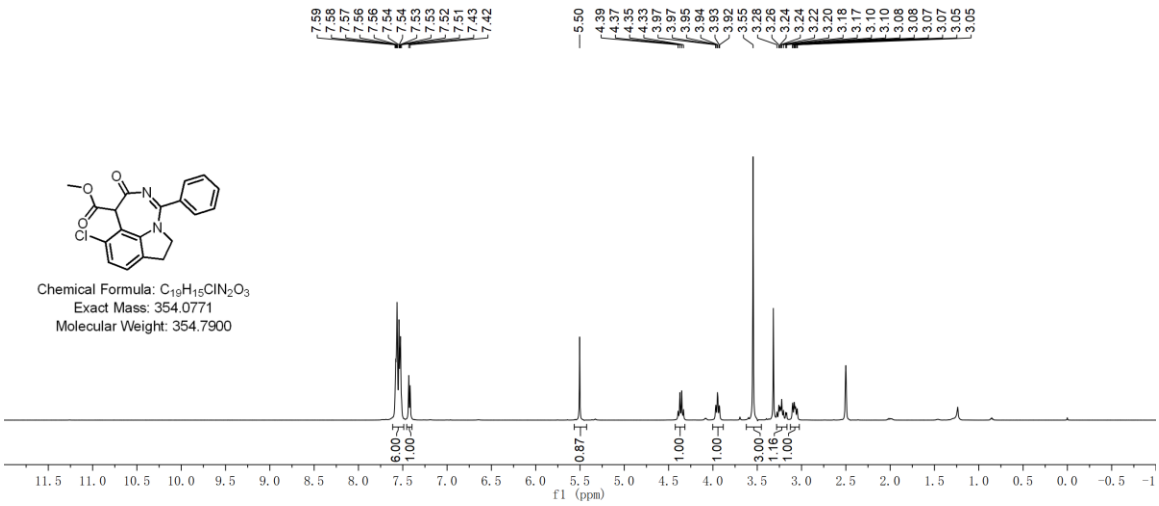
^{13}C NMR spectrum of **3ia** (150 MHz, Chloroform-*d*)



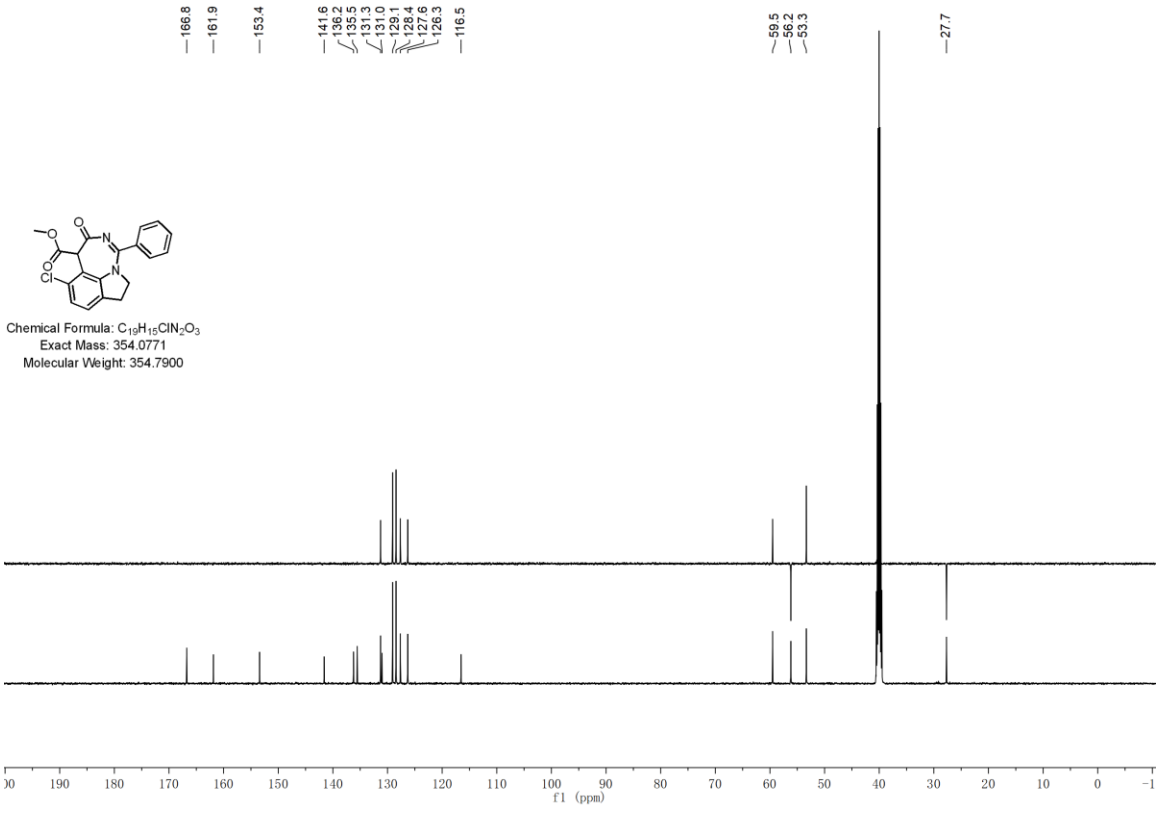
^{1}H NMR spectrum of **3ja** (600 MHz, Chloroform-*d*)



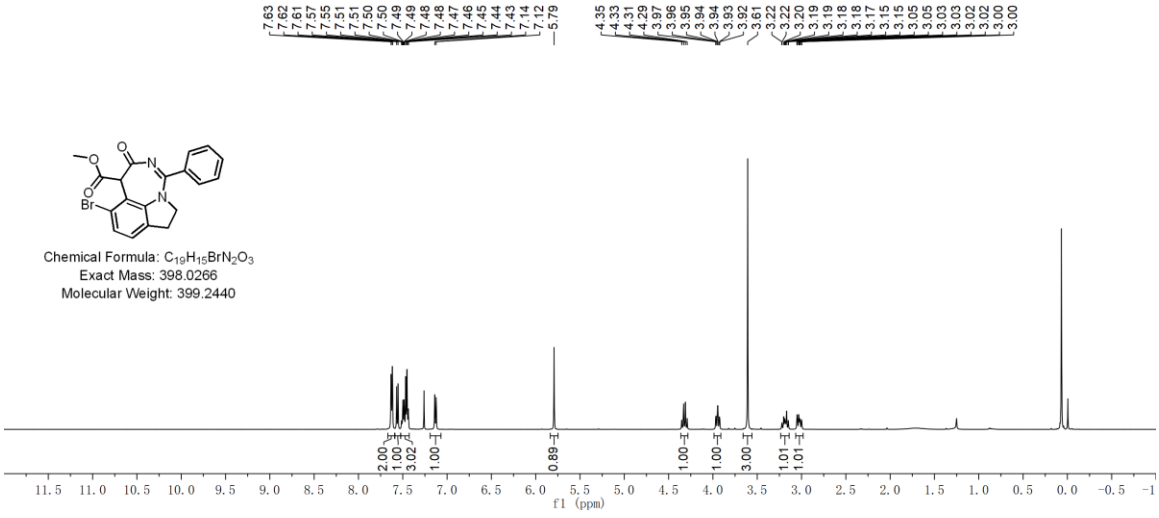
^{13}C NMR spectrum of **3ja** (150 MHz, Chloroform-*d*)



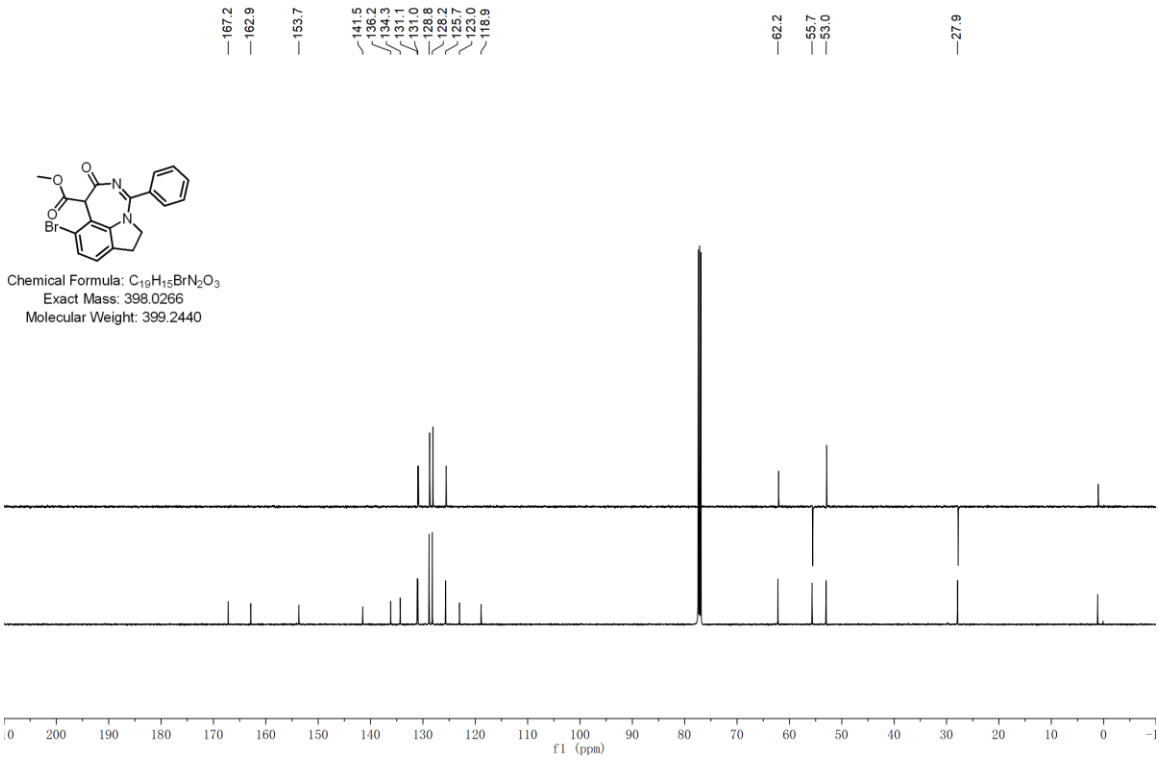
^{1}H NMR spectrum of **3ka** (500 MHz, DMSO-d_6)



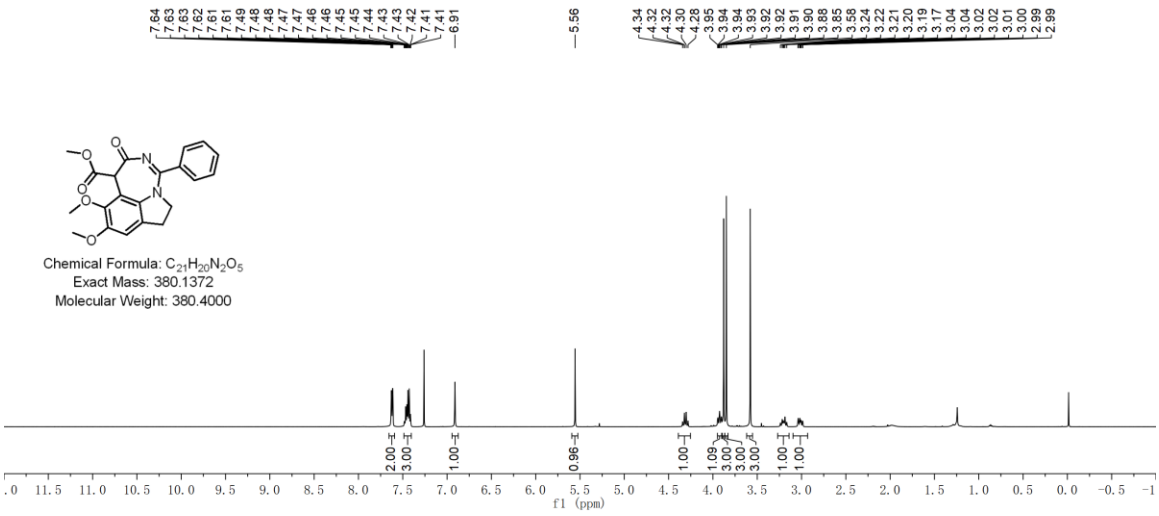
^{13}C NMR spectrum of **3ka** (125 MHz, DMSO-d_6)



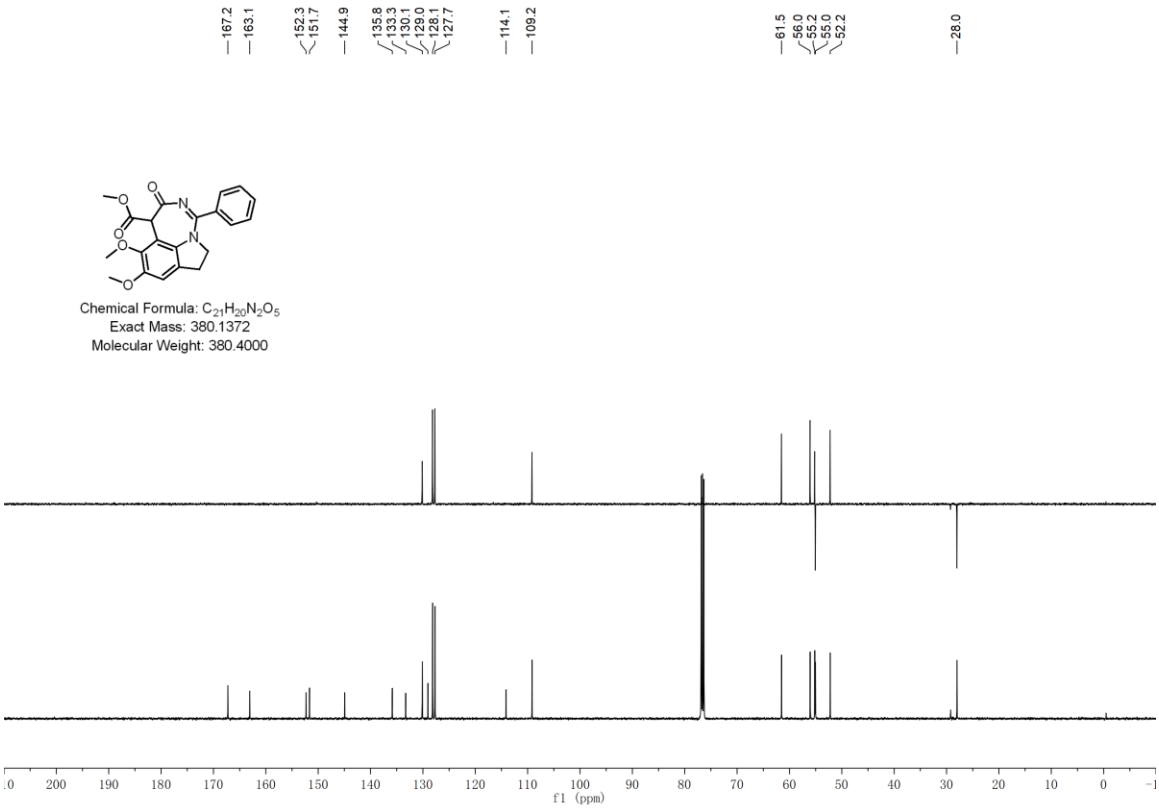
^{1}H NMR spectrum of **3la** (500 MHz, Chloroform-*d*)



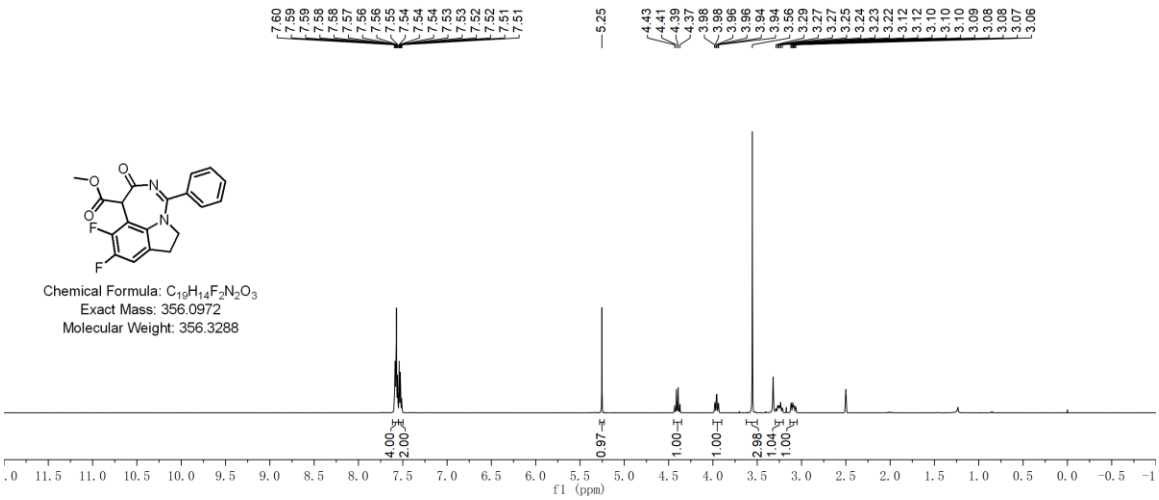
^{13}C NMR spectrum of **3la** (125 MHz, Chloroform-*d*)



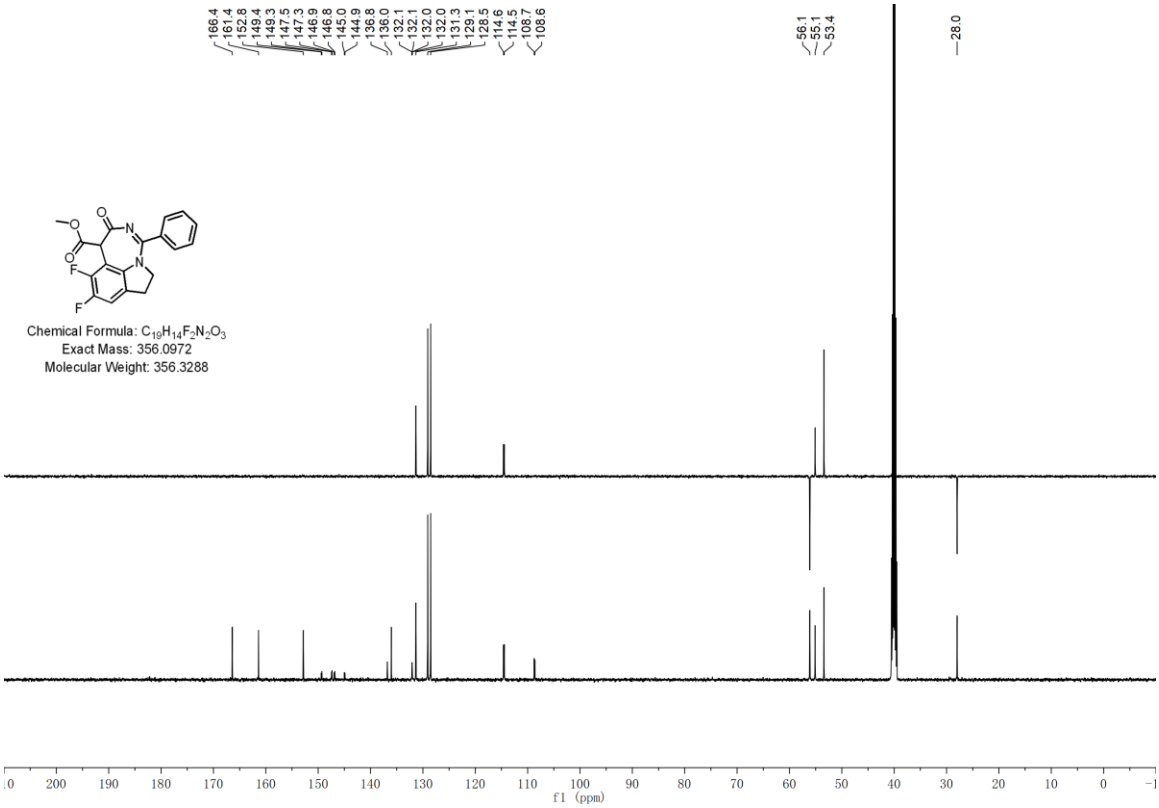
^{1}H NMR spectrum of **3ma** (500 MHz, Chloroform-*d*)



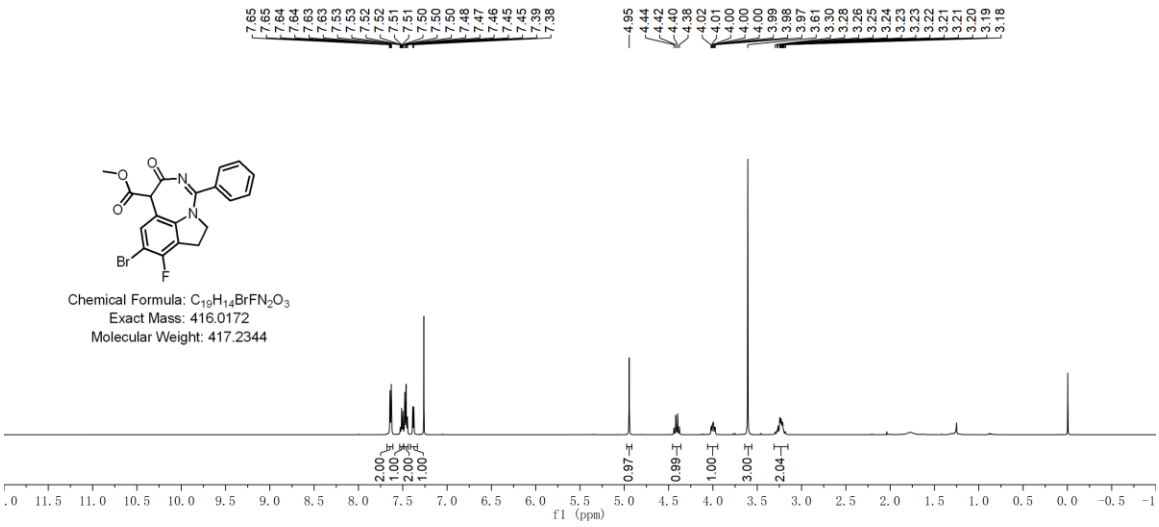
^{13}C NMR spectrum of **3ma** (125 MHz, Chloroform-*d*)



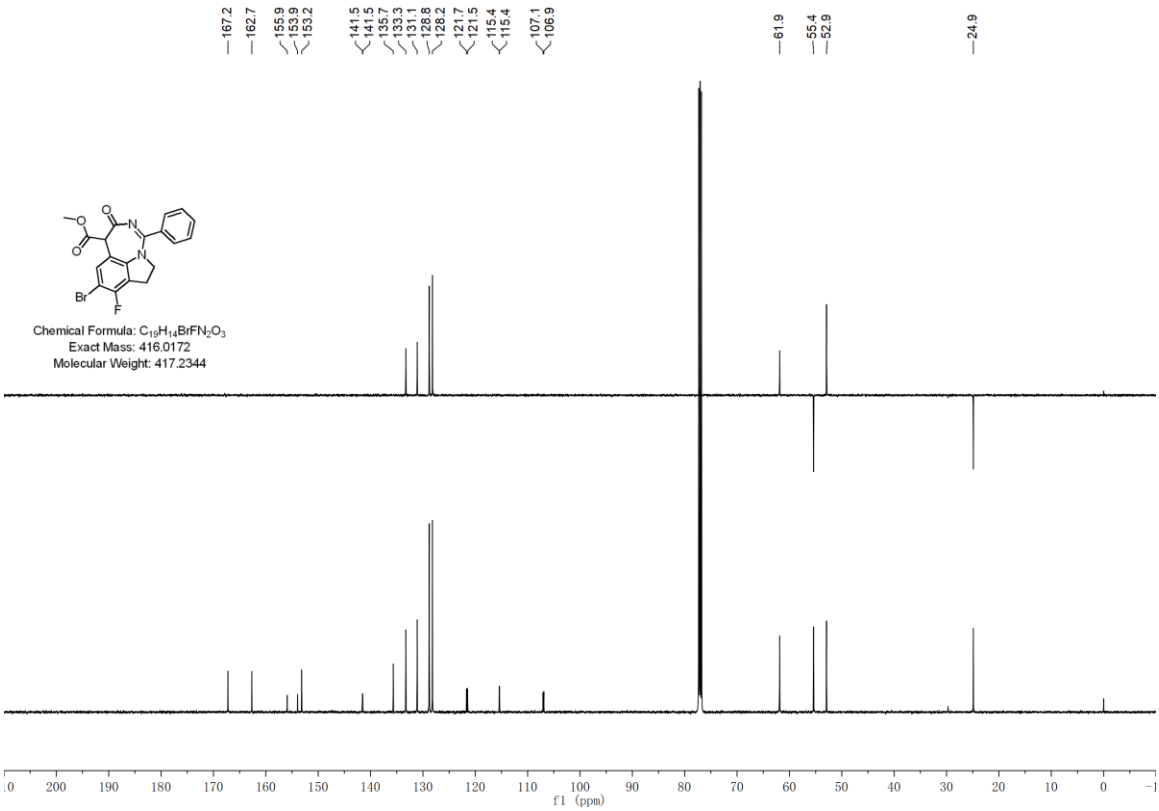
^{1}H NMR spectrum of **3na** (500 MHz, DMSO-d_6)



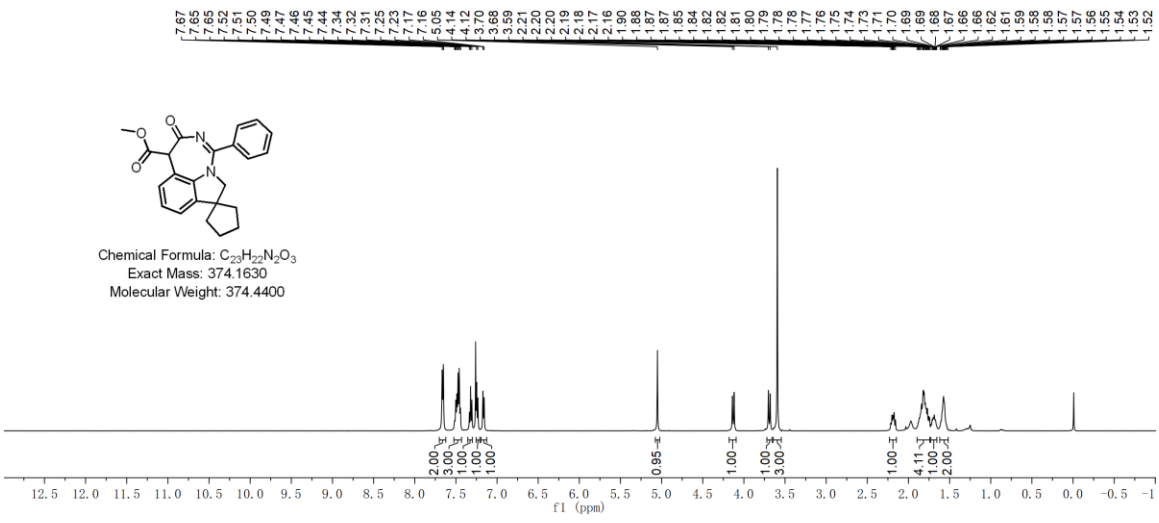
^{13}C NMR spectrum of **3na** (125 MHz, DMSO-d_6)



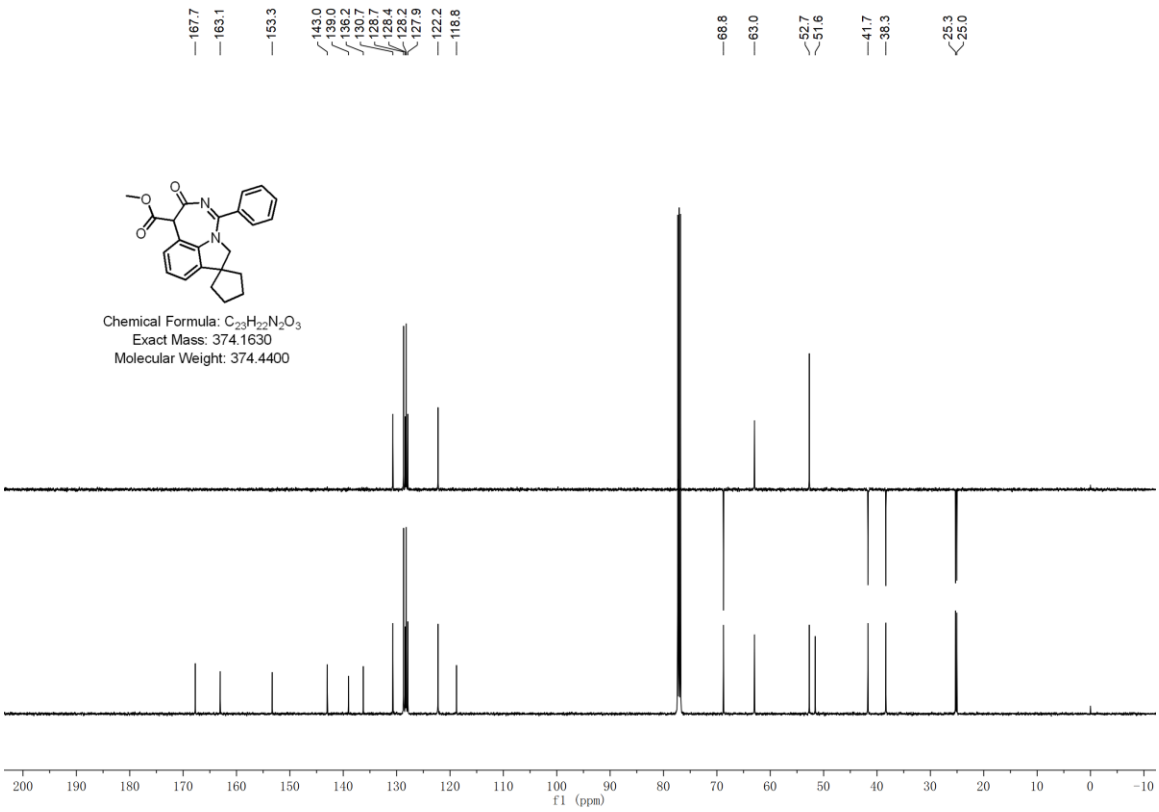
^{1}H NMR spectrum of **3oa** (500 MHz, Chloroform-*d*)



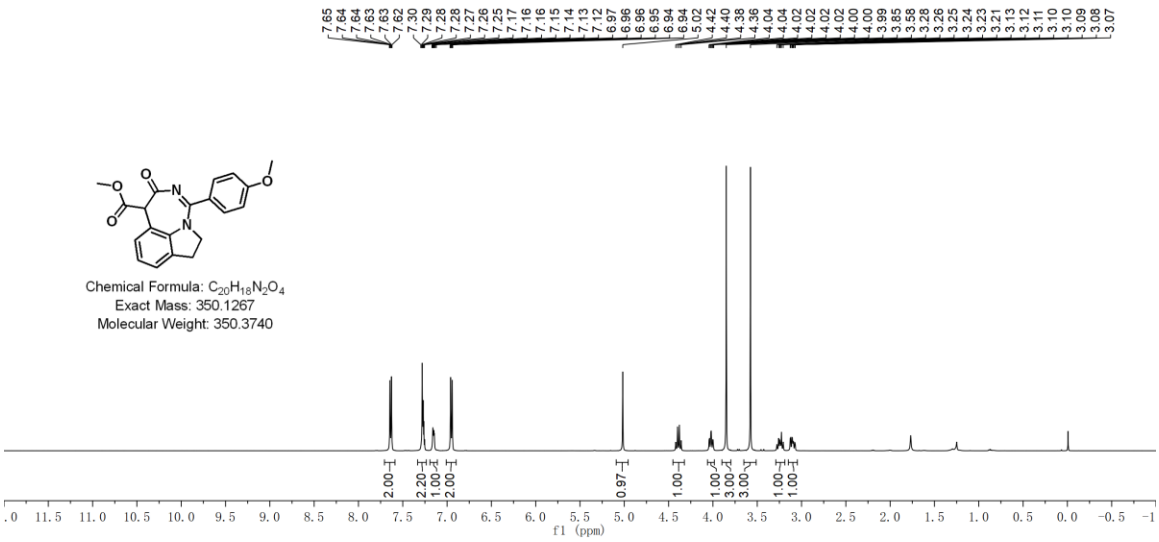
^{13}C NMR spectrum of **3oa** (125 MHz, Chloroform-*d*)



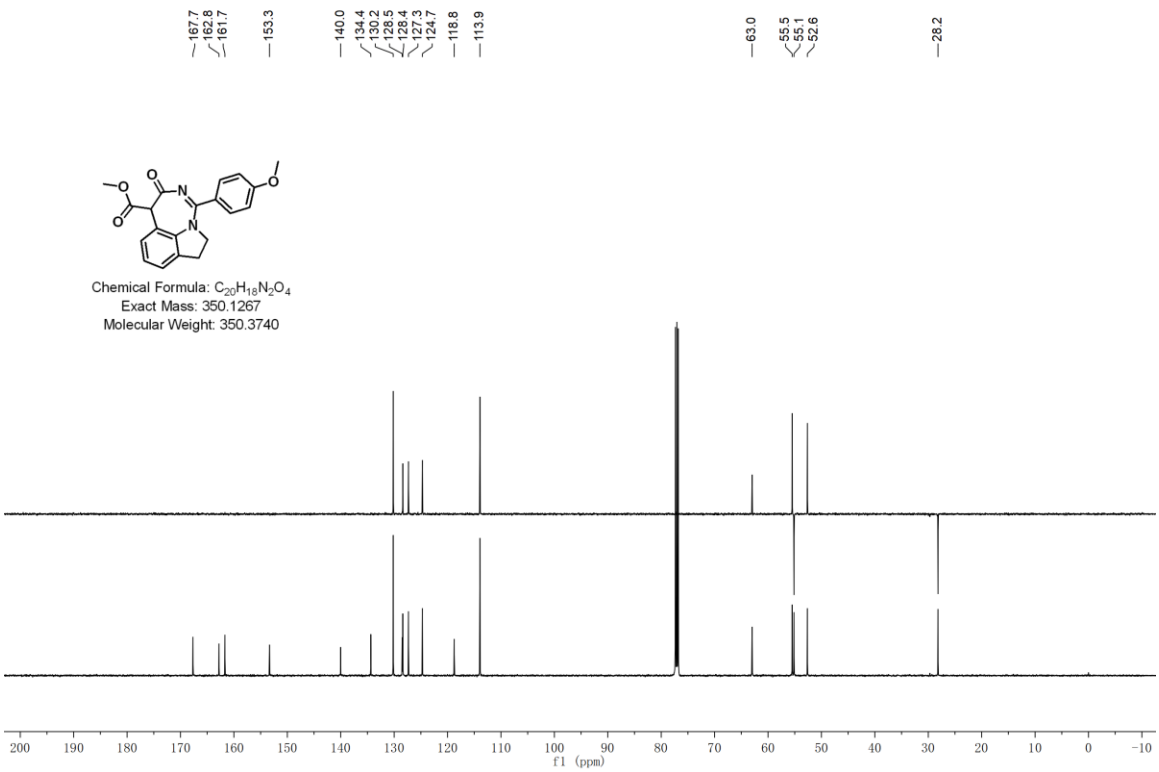
^{1}H NMR spectrum of **3pa** (500 MHz, Chloroform-*d*)



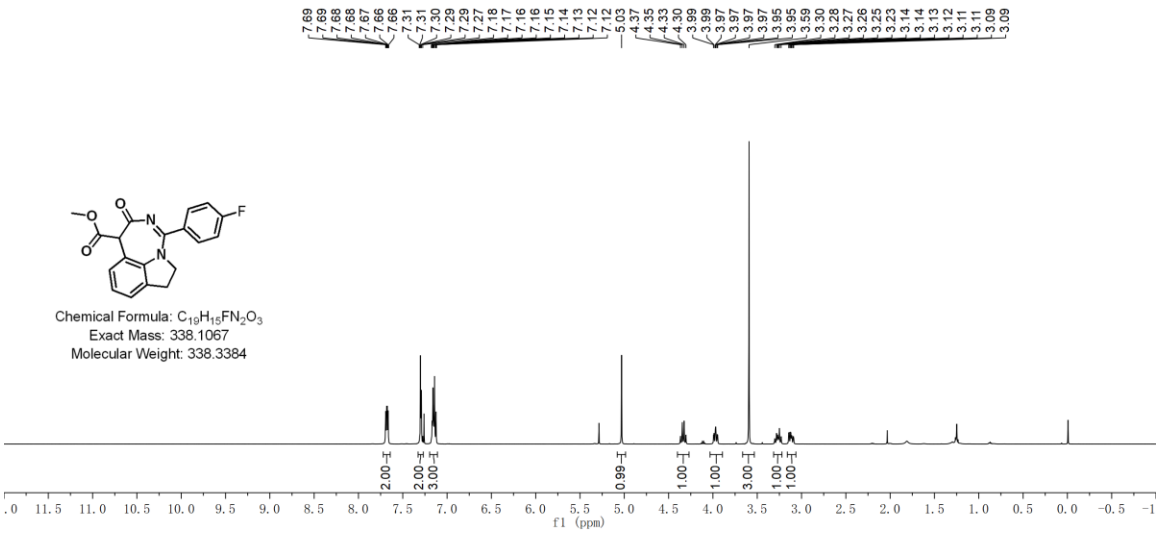
^{13}C NMR spectrum of **3pa** (125 MHz, Chloroform-*d*)



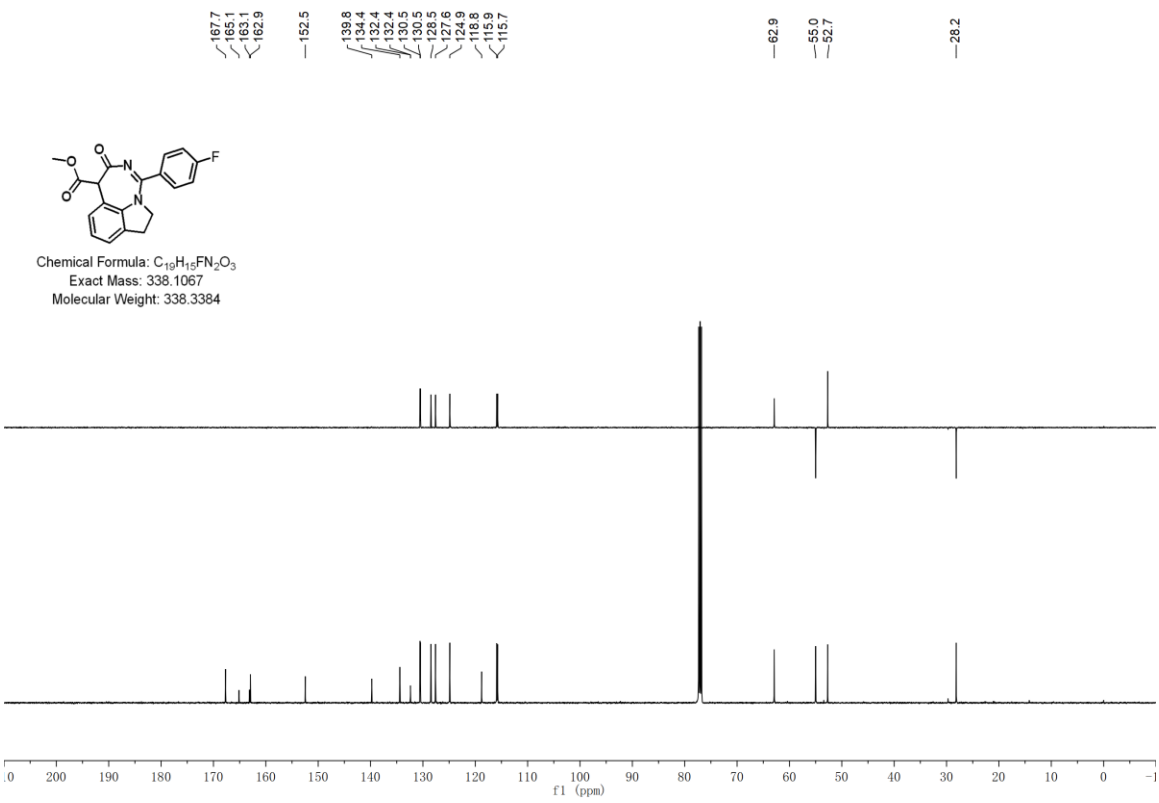
^{1}H NMR spectrum of **3qa** (500 MHz, Chloroform-*d*)



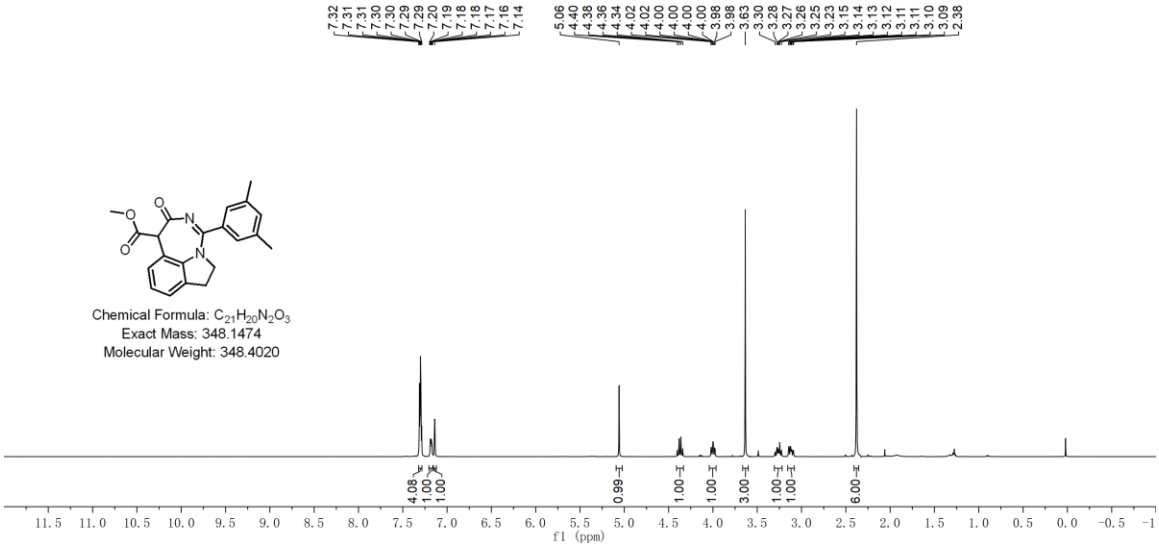
^{13}C NMR spectrum of **3qa** (125 MHz, Chloroform-*d*)



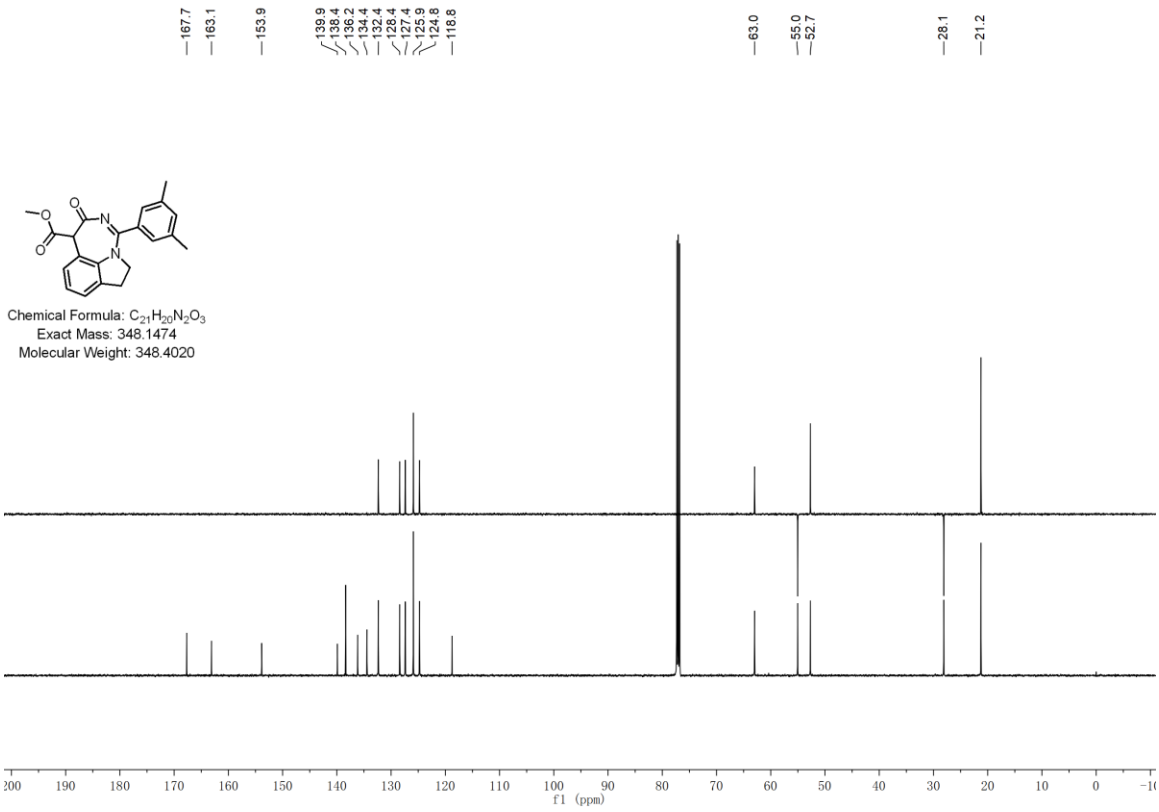
^{1}H NMR spectrum of **3ra** (500 MHz, Chloroform-*d*)



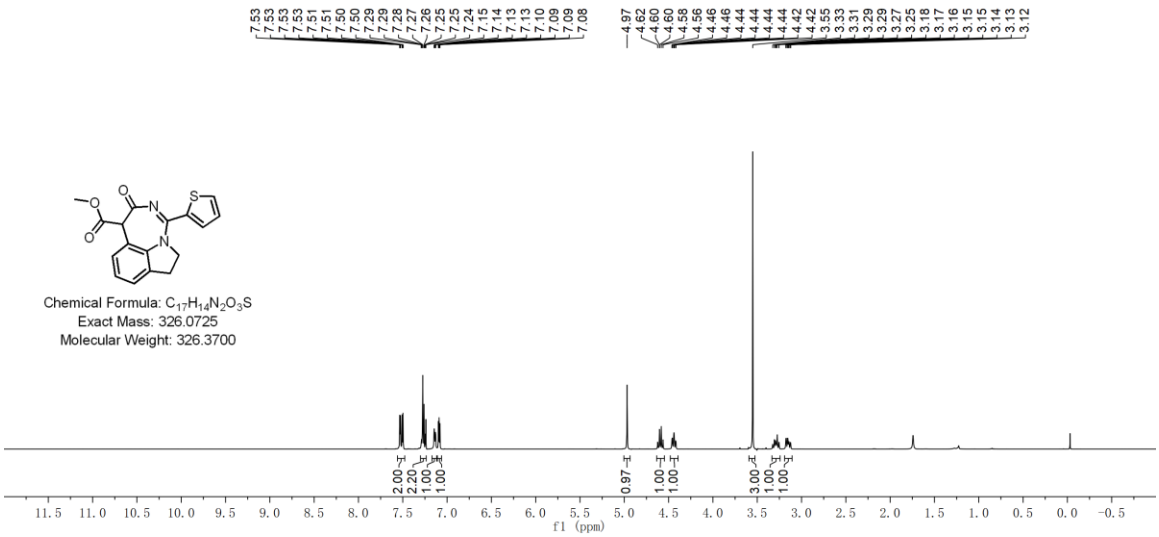
^{13}C NMR spectrum of **3ra** (125 MHz, Chloroform-*d*)



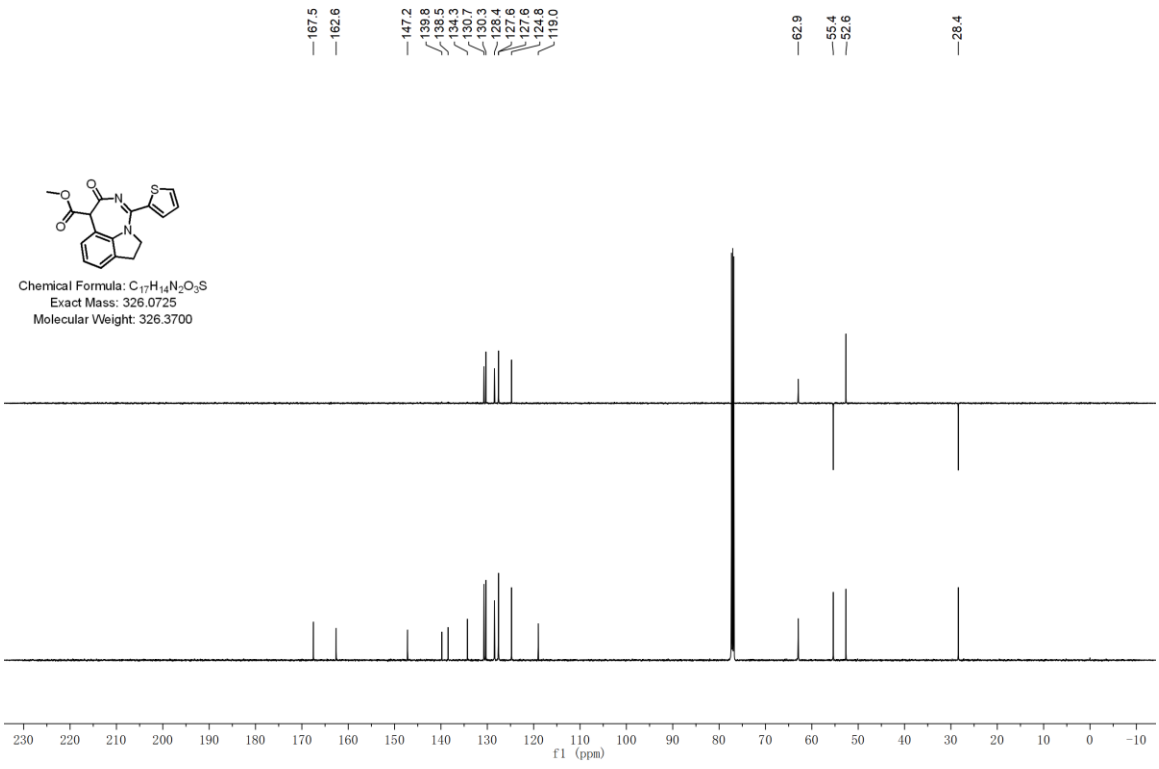
^{1}H NMR spectrum of **3sa** (500 MHz, Chloroform-*d*)



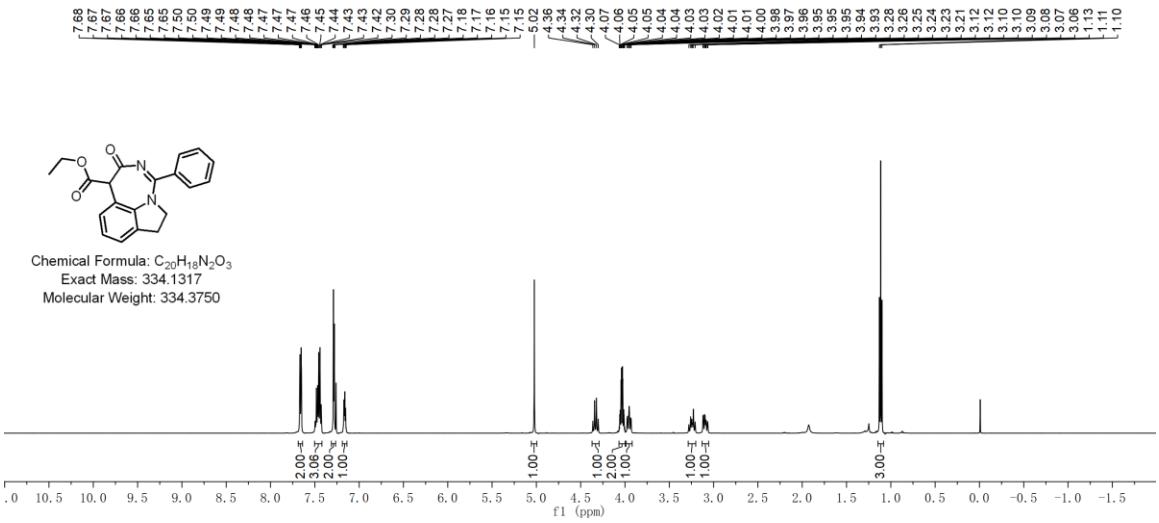
^{13}C NMR spectrum of **3sa** (125 MHz, Chloroform-*d*)



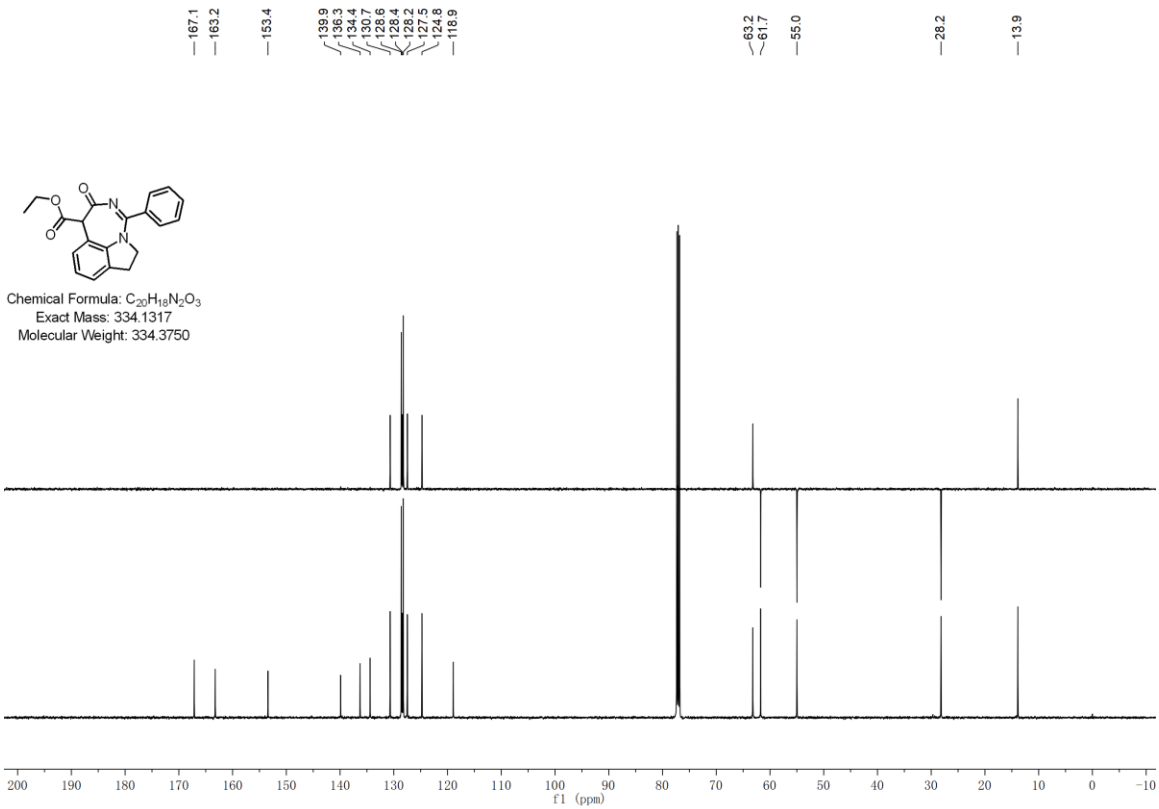
^{1}H NMR spectrum of **3ta** (500 MHz, Chloroform-*d*)



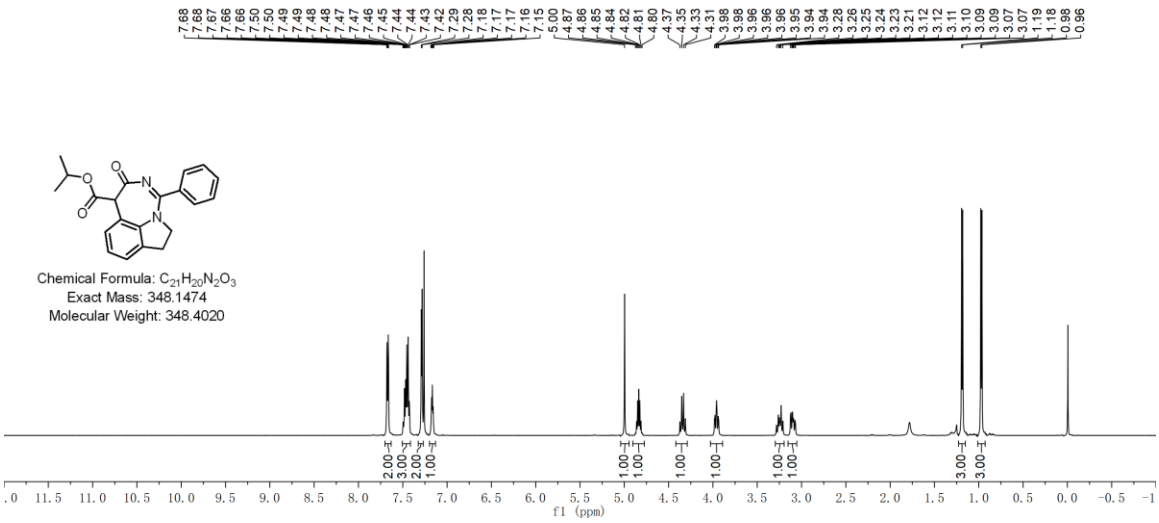
^{13}C NMR spectrum of **3ta** (125 MHz, Chloroform-*d*)



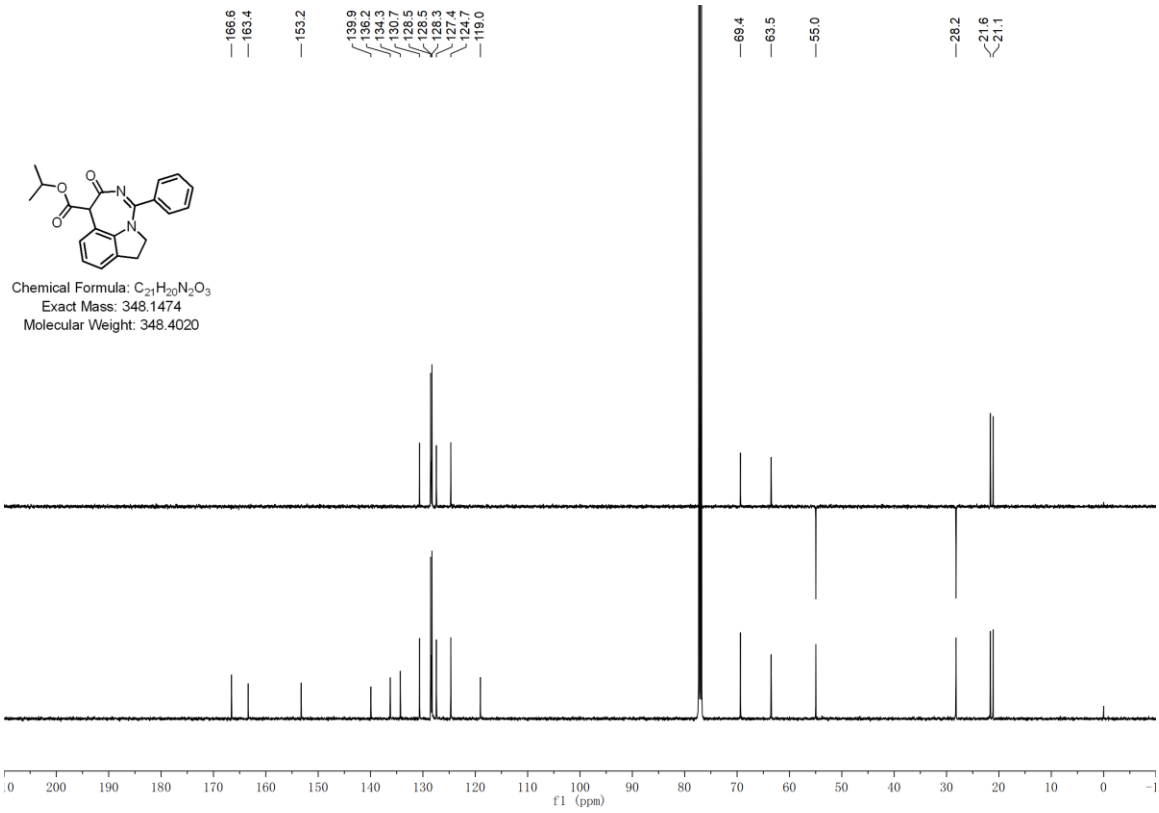
^{1}H NMR spectrum of **3ab** (500 MHz, Chloroform-*d*)



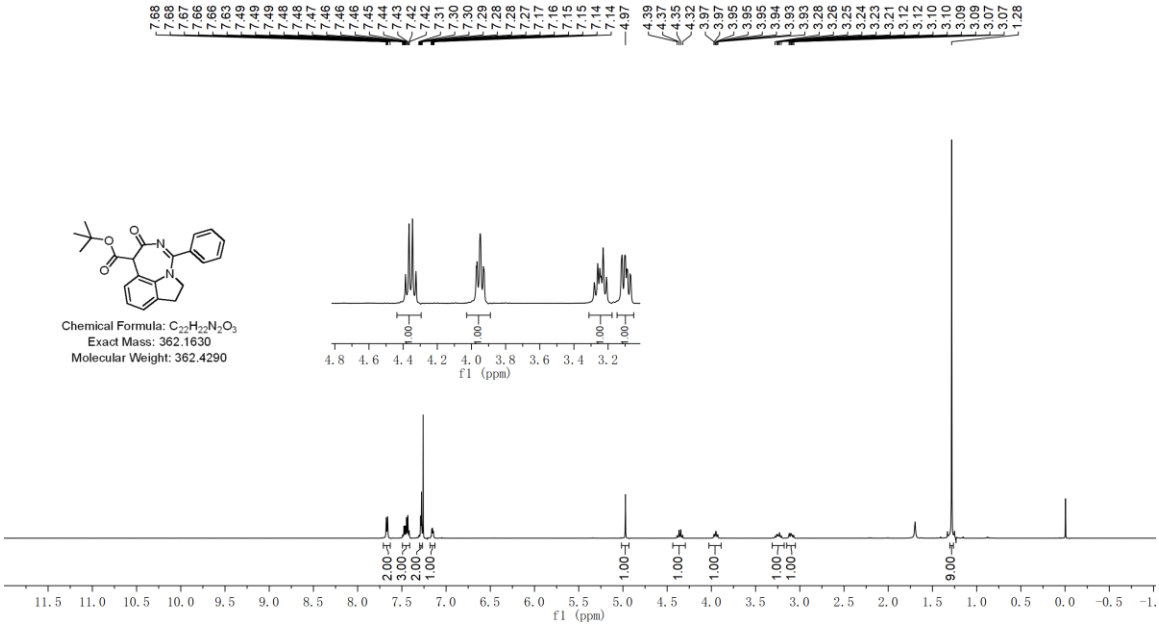
^{13}C NMR spectrum of **3ab** (125 MHz, Chloroform-*d*)



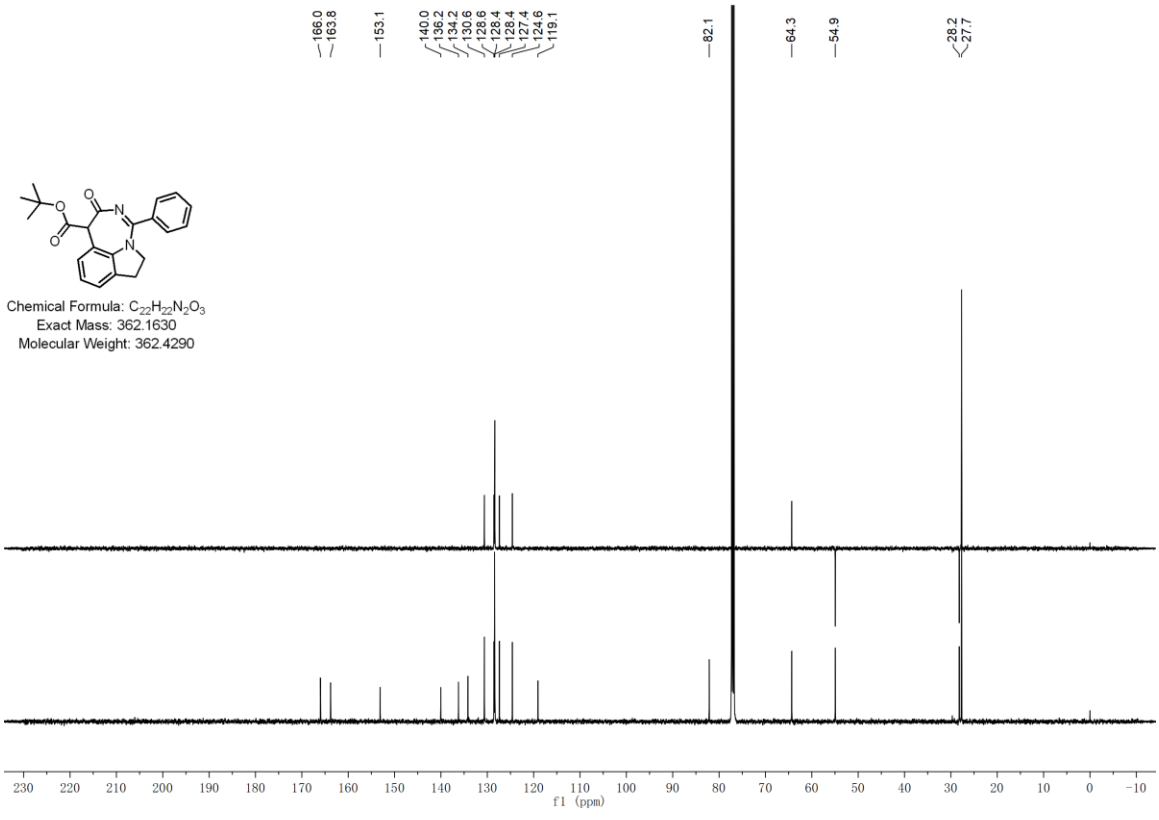
^{1}H NMR spectrum of **3ac** (500 MHz, Chloroform-*d*)



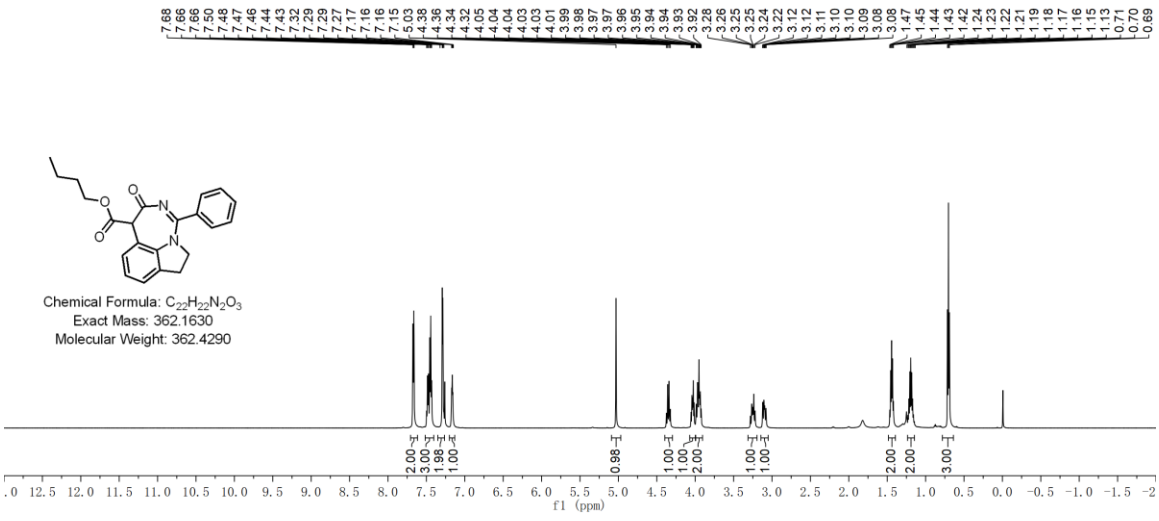
^{13}C NMR spectrum of **3ac** (125 MHz, Chloroform-*d*)



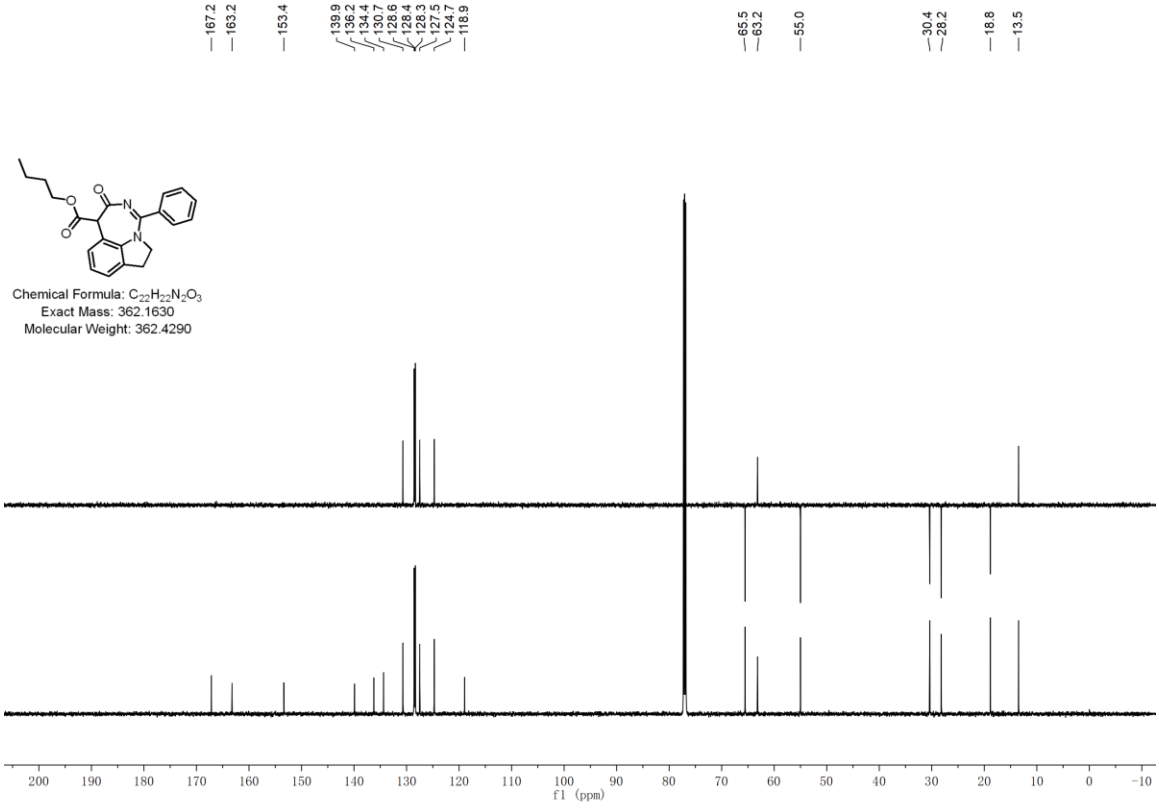
^{1}H NMR spectrum of **3ad** (500 MHz, Chloroform-*d*)



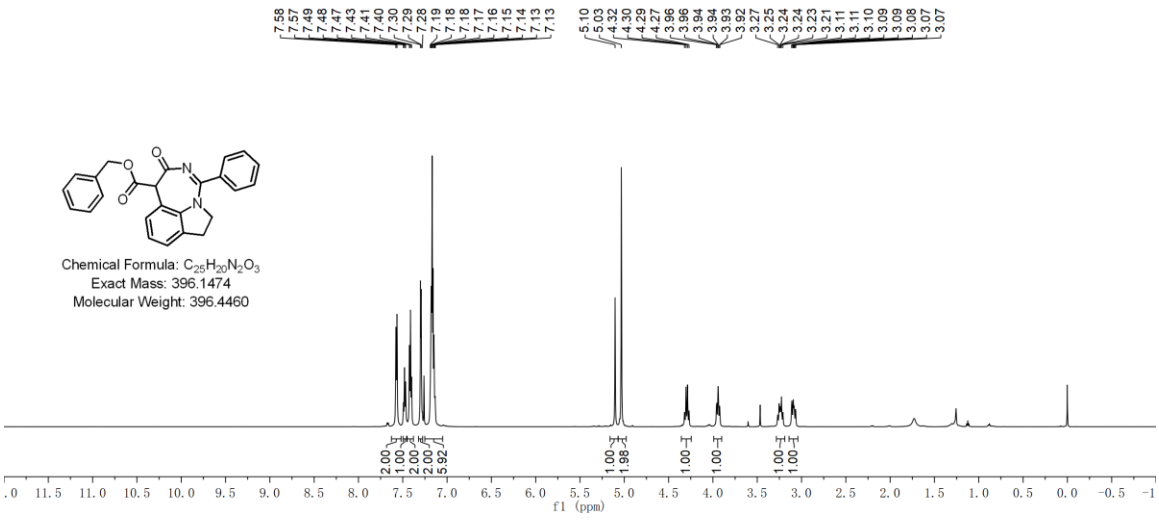
^{13}C NMR spectrum of **3ad** (125 MHz, Chloroform-*d*)



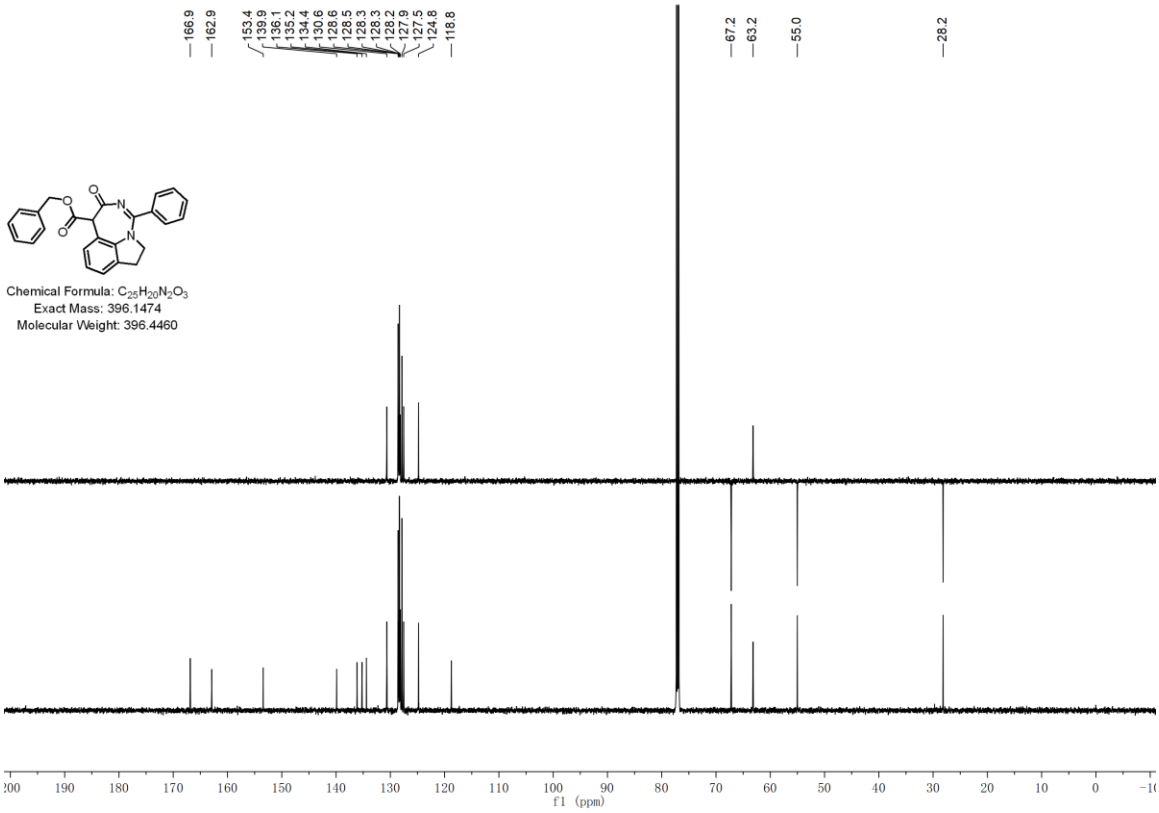
^{1}H NMR spectrum of **3ae** (600 MHz, Chloroform-*d*)



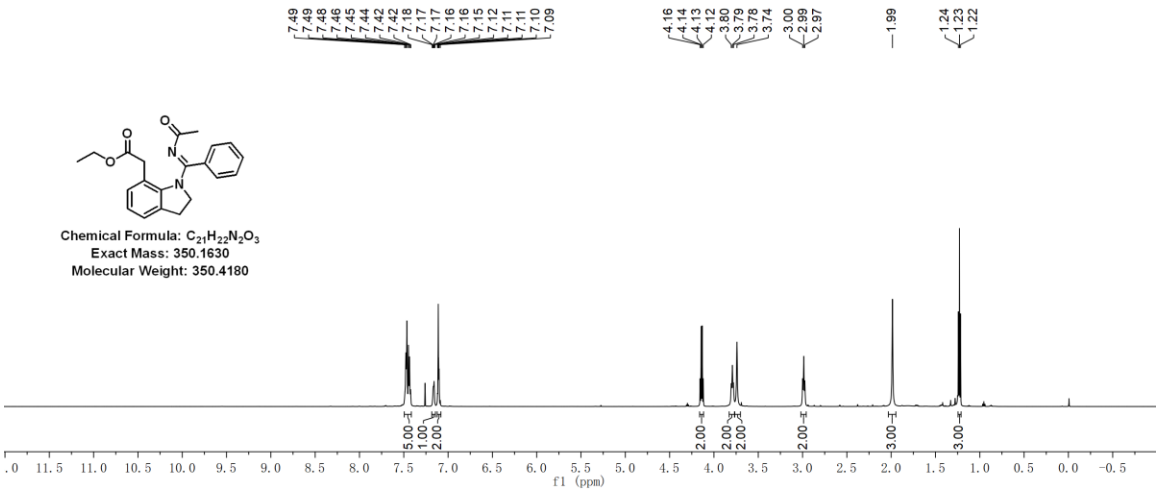
^{13}C NMR spectrum of **3ae** (150 MHz, Chloroform-*d*)



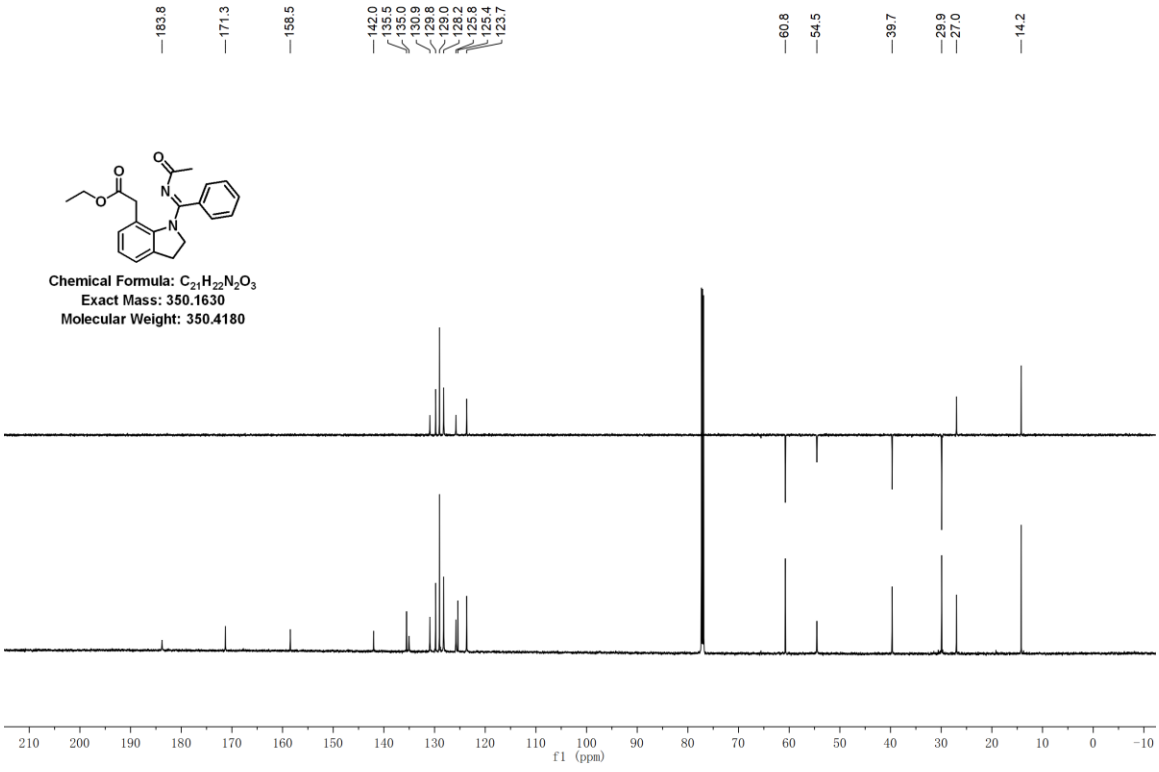
^{1}H NMR spectrum of **3af** (600 MHz, Chloroform-*d*)



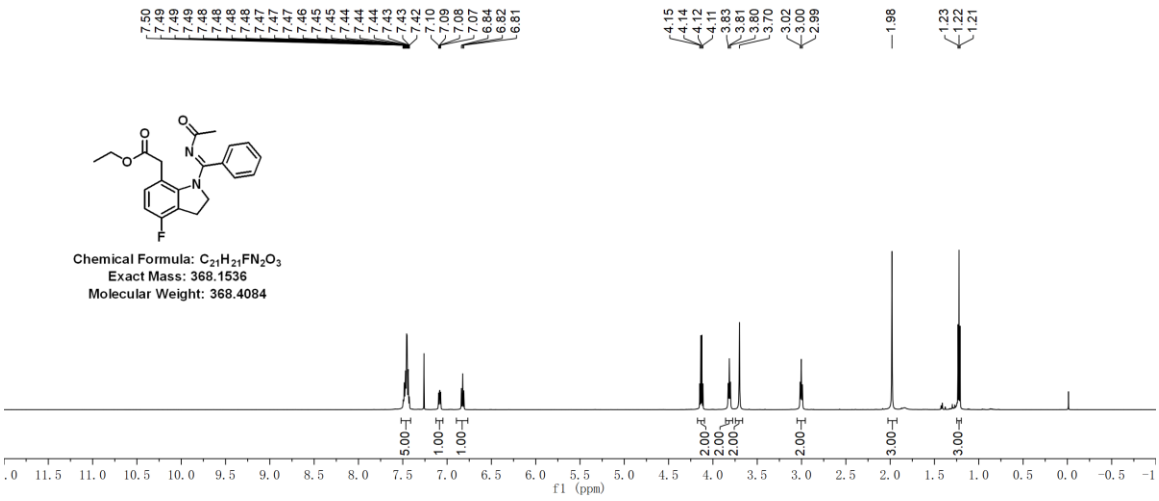
^{13}C NMR spectrum of **3af** (150 MHz, Chloroform-*d*)



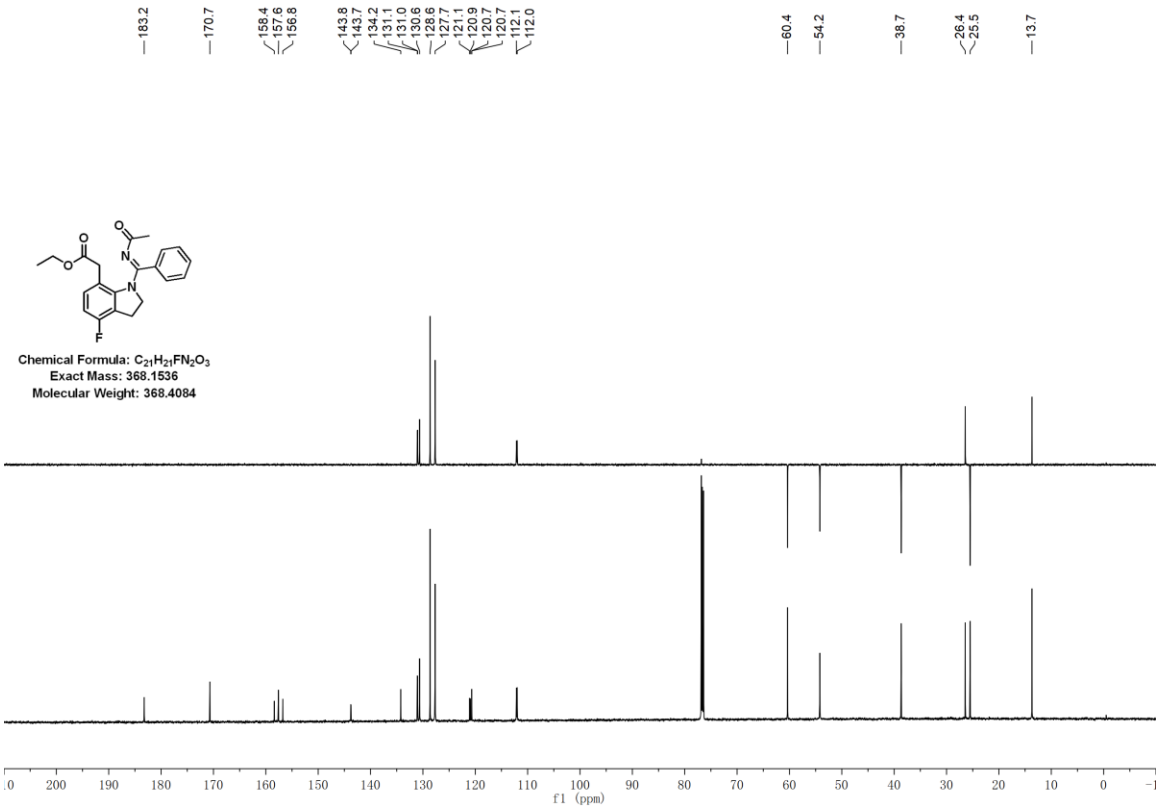
^{1}H NMR spectrum of **5aa** (600 MHz, Chloroform-*d*)



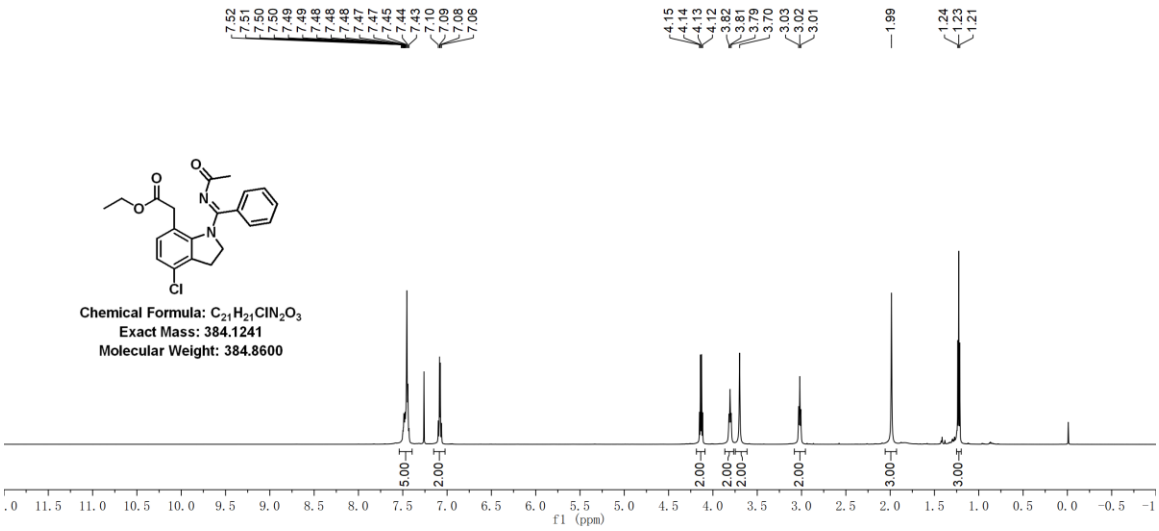
^{13}C NMR spectrum of **5aa** (150 MHz, Chloroform-*d*)



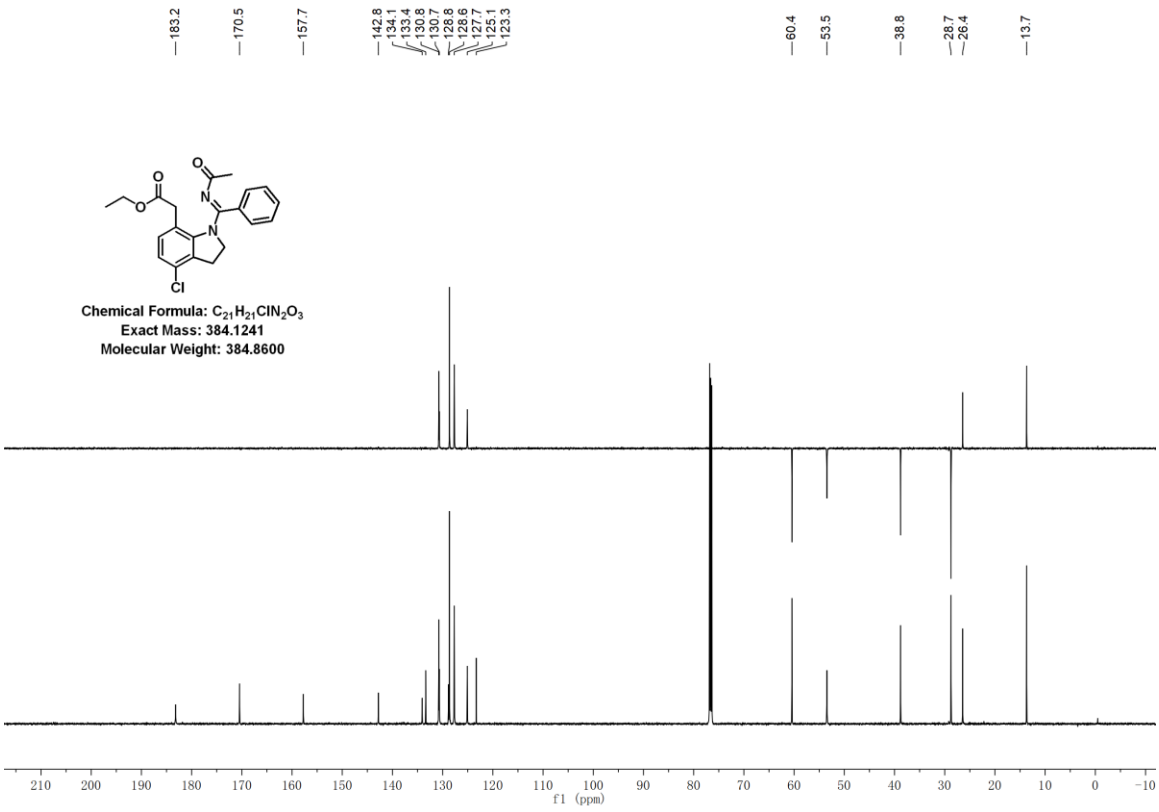
^{1}H NMR spectrum of **5ba** (600 MHz, Chloroform-*d*)



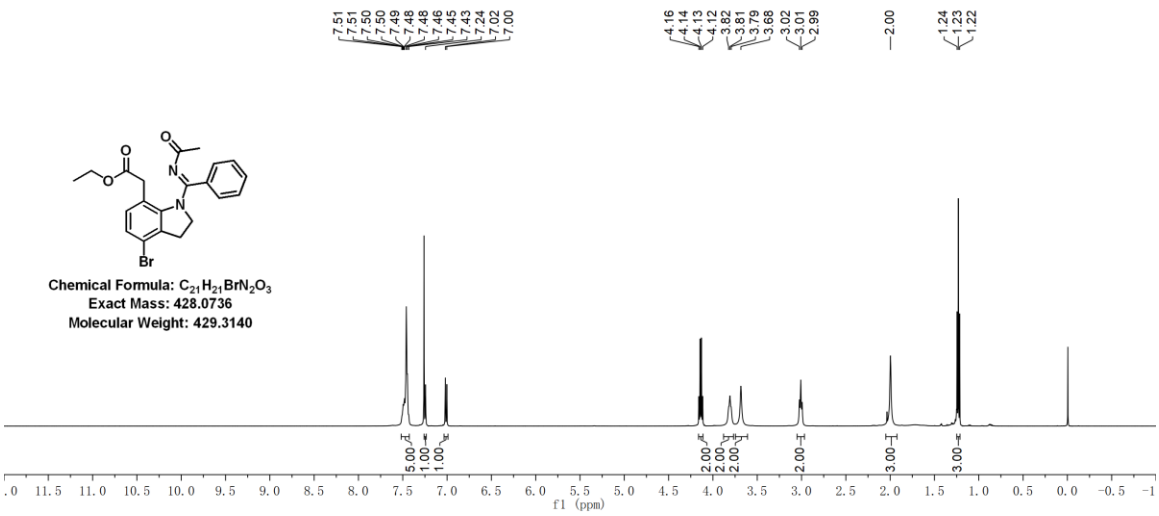
^{13}C NMR spectrum of **5ba** (150 MHz, Chloroform-*d*)



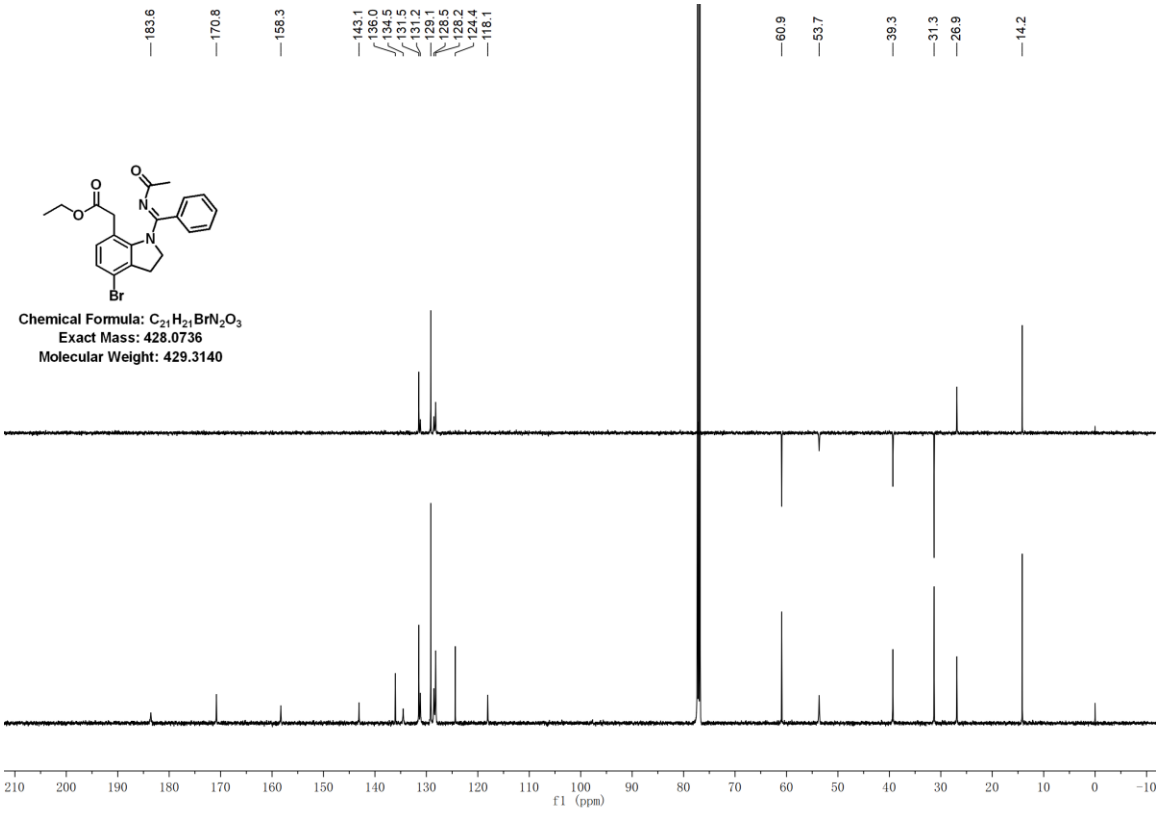
^{1}H NMR spectrum of **5ca** (600 MHz, Chloroform-*d*)



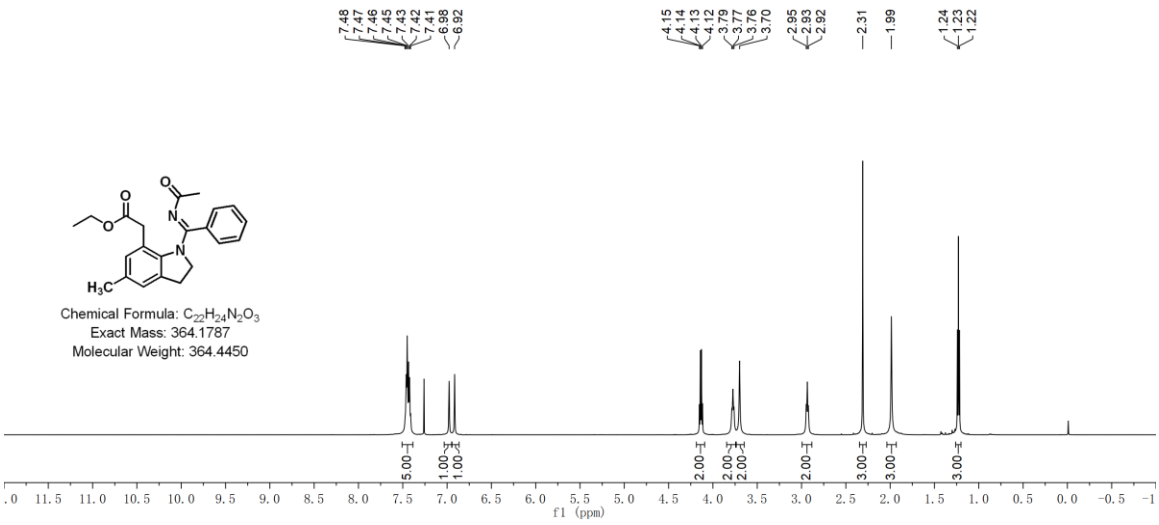
^{13}C NMR spectrum of **5ca** (150 MHz, Chloroform-*d*)



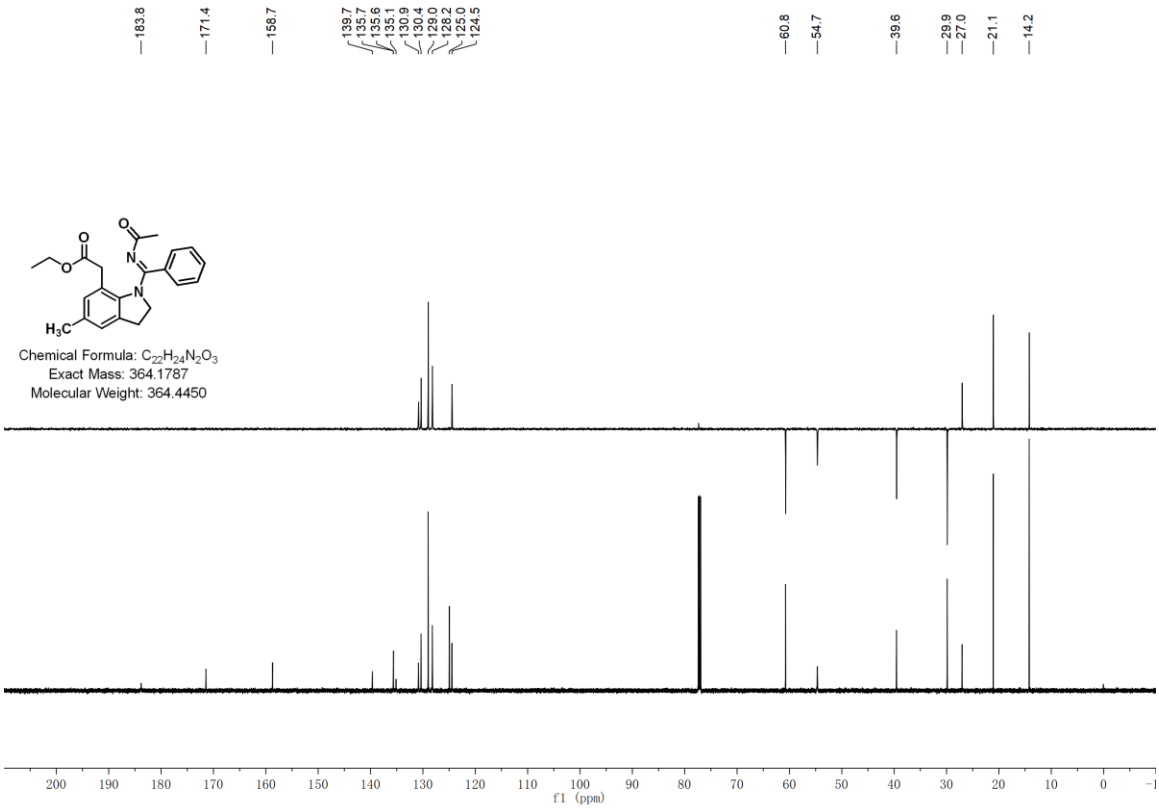
^{1}H NMR spectrum of **5da** (500 MHz, Chloroform-*d*)



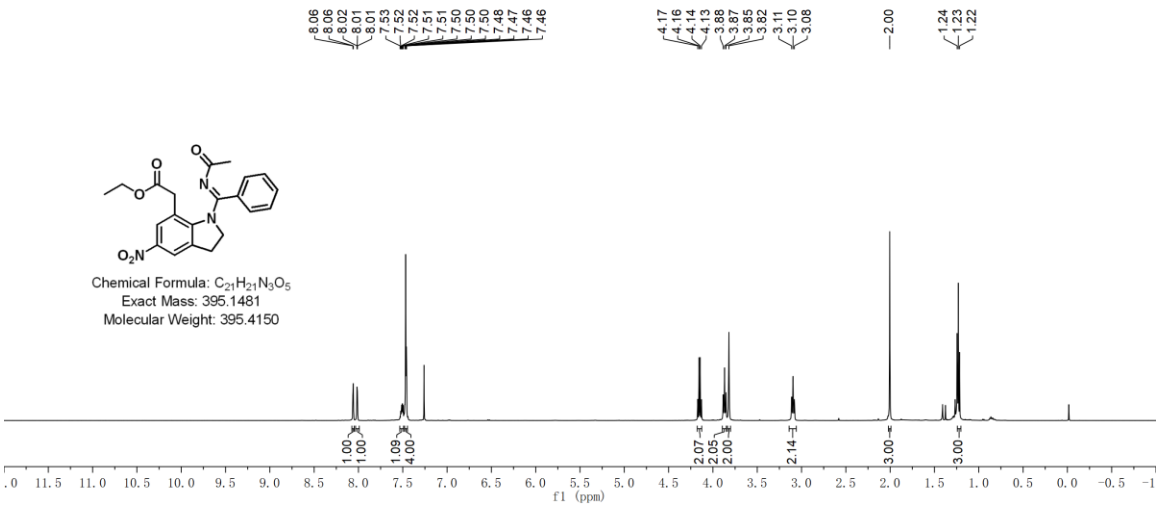
^{13}C NMR spectrum of **5da** (125 MHz, Chloroform-*d*)



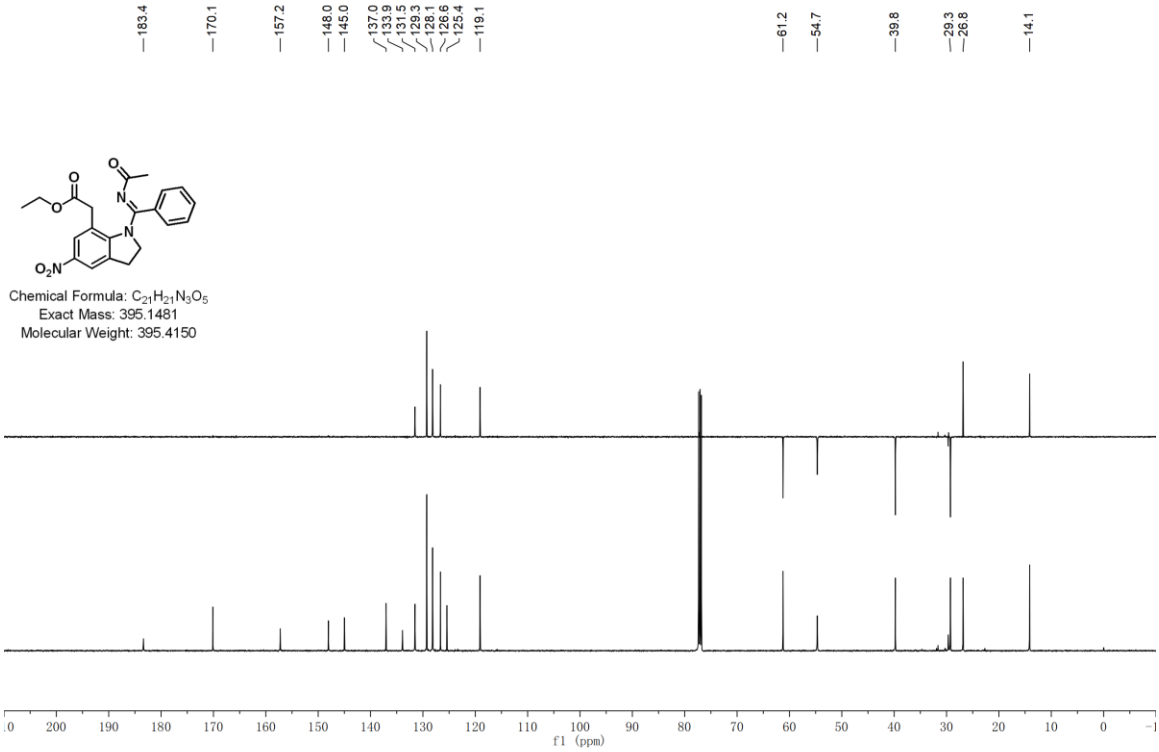
^{1}H NMR spectrum of **5fa** (600 MHz, Chloroform-*d*)



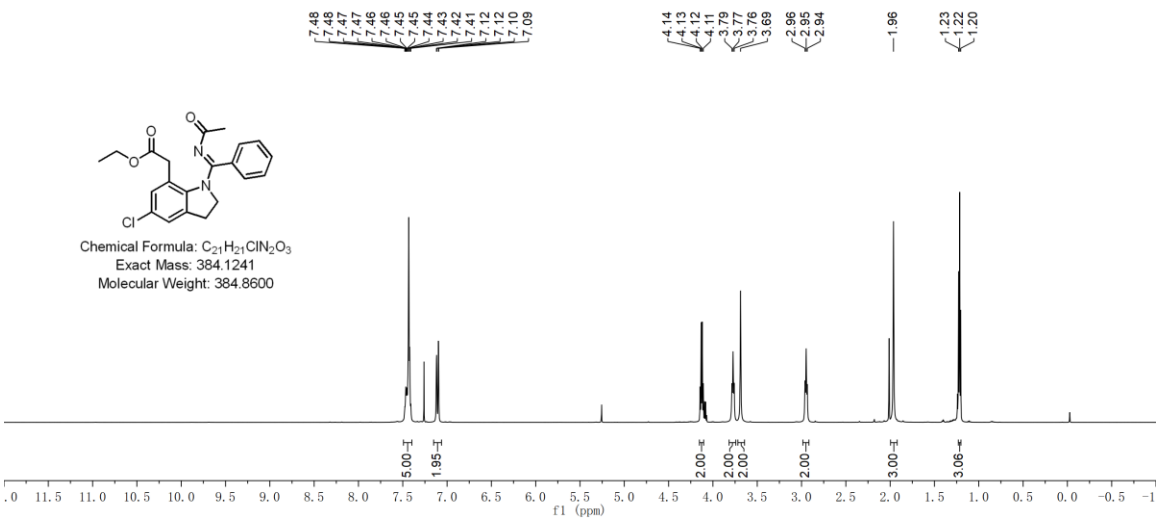
^{13}C NMR spectrum of **5fa** (150 MHz, Chloroform-*d*)



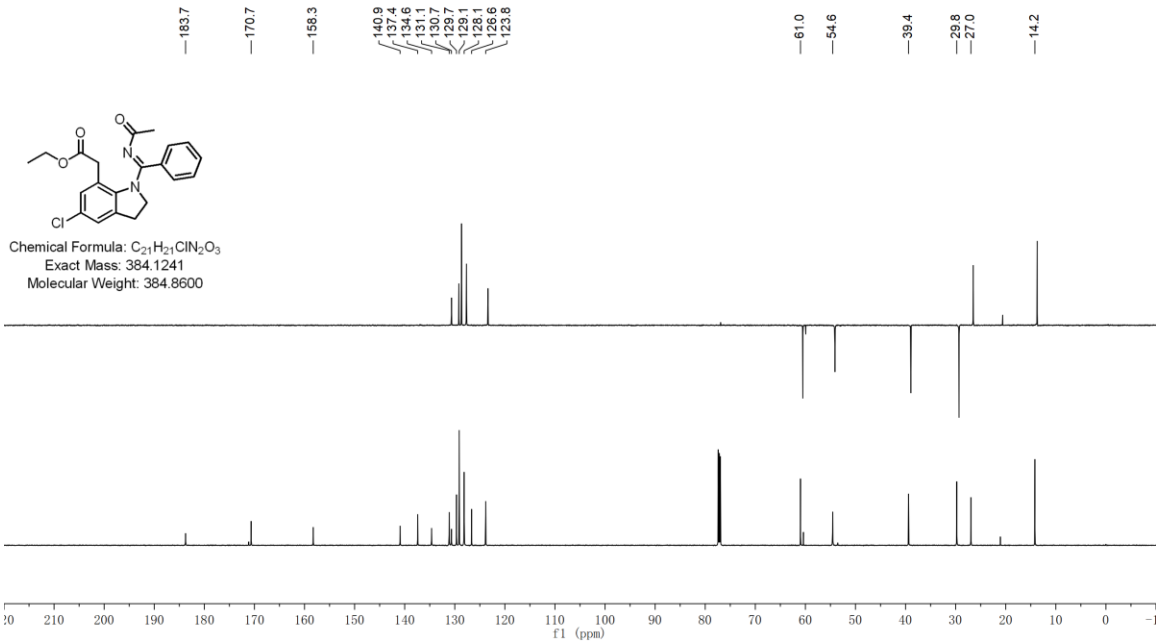
^{1}H NMR spectrum of **5ga** (500 MHz, Chloroform-*d*)



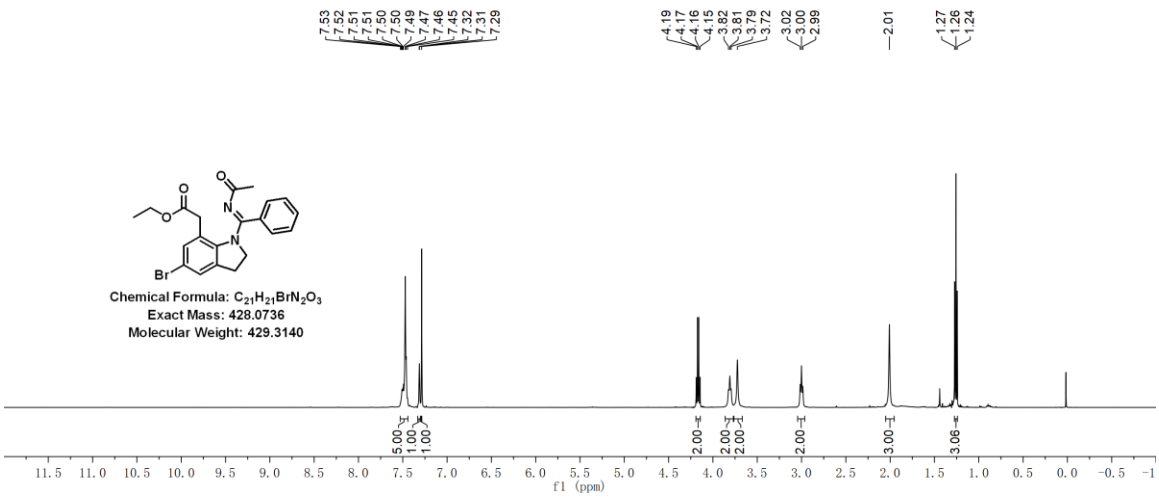
^{13}C NMR spectrum of **5ga** (125 MHz, Chloroform-*d*)



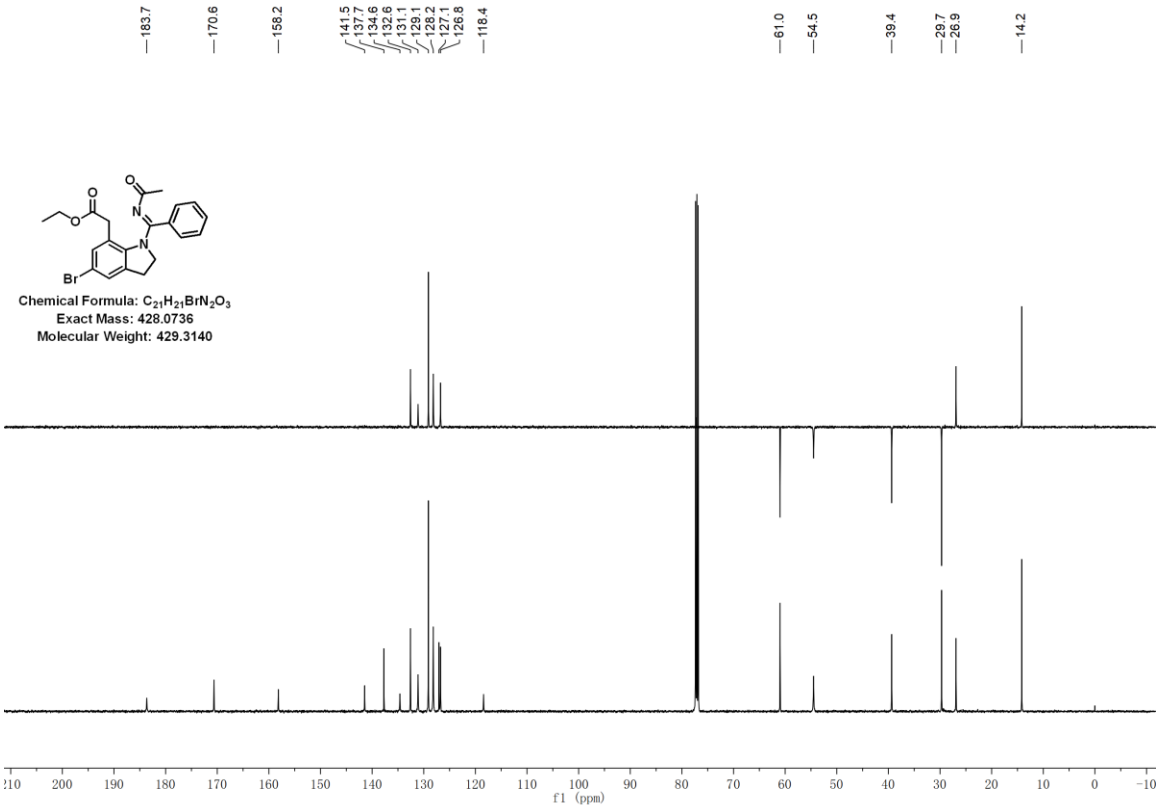
^{1}H NMR spectrum of **5ia** (600 MHz, Chloroform-*d*)



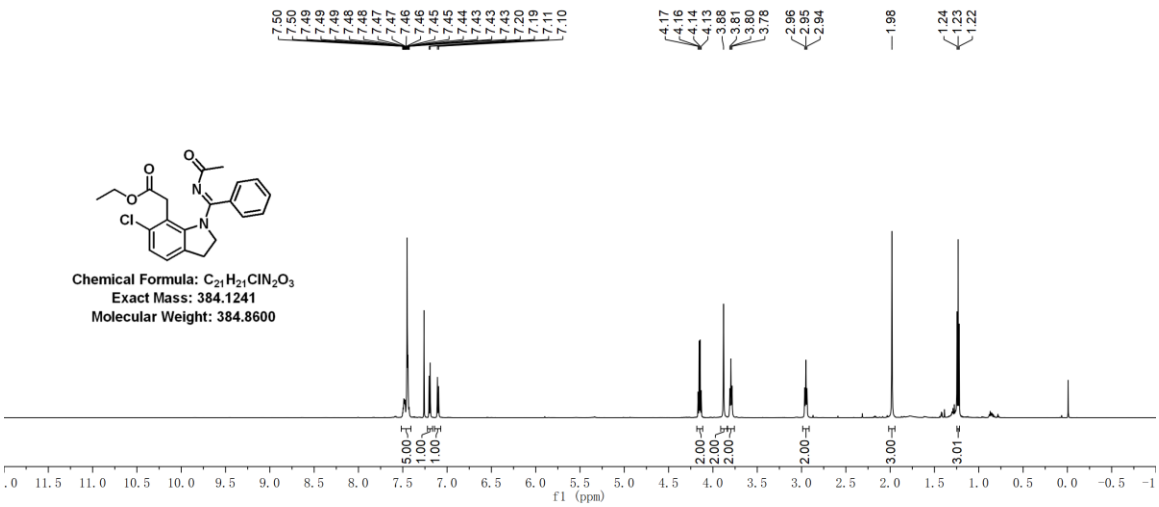
^{13}C NMR spectrum of **5ia** (150 MHz, Chloroform-*d*)



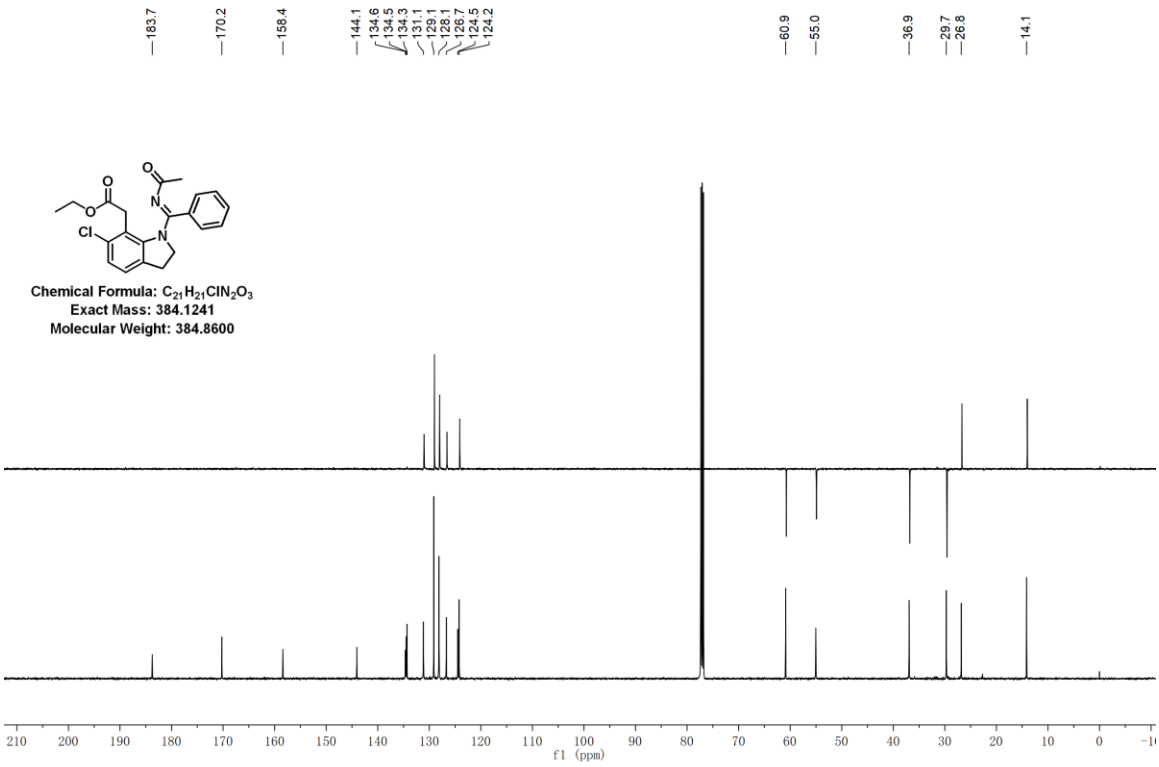
^{1}H NMR spectrum of **5ja** (500 MHz, Chloroform-*d*)



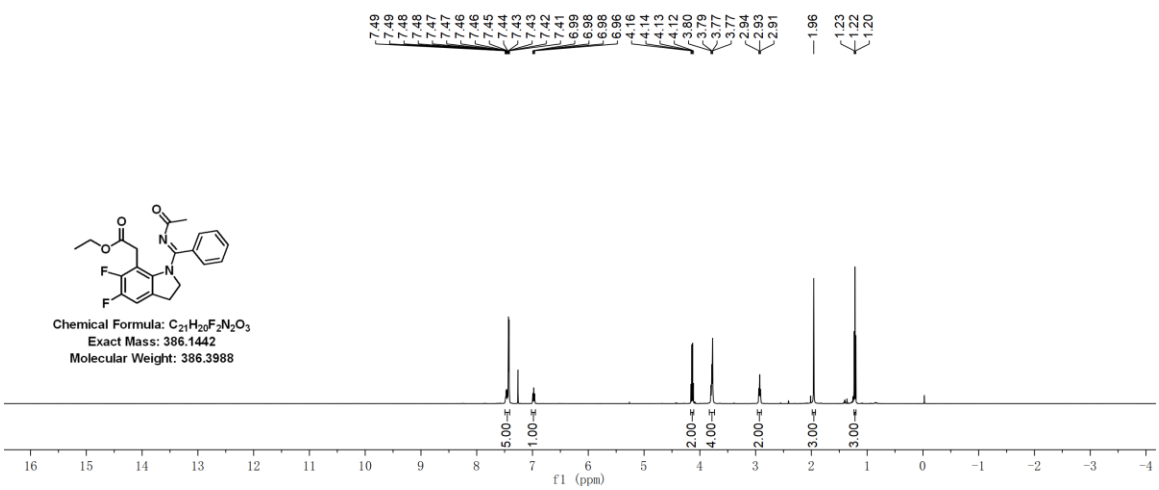
^{13}C NMR spectrum of **5ja** (125 MHz, Chloroform-*d*)



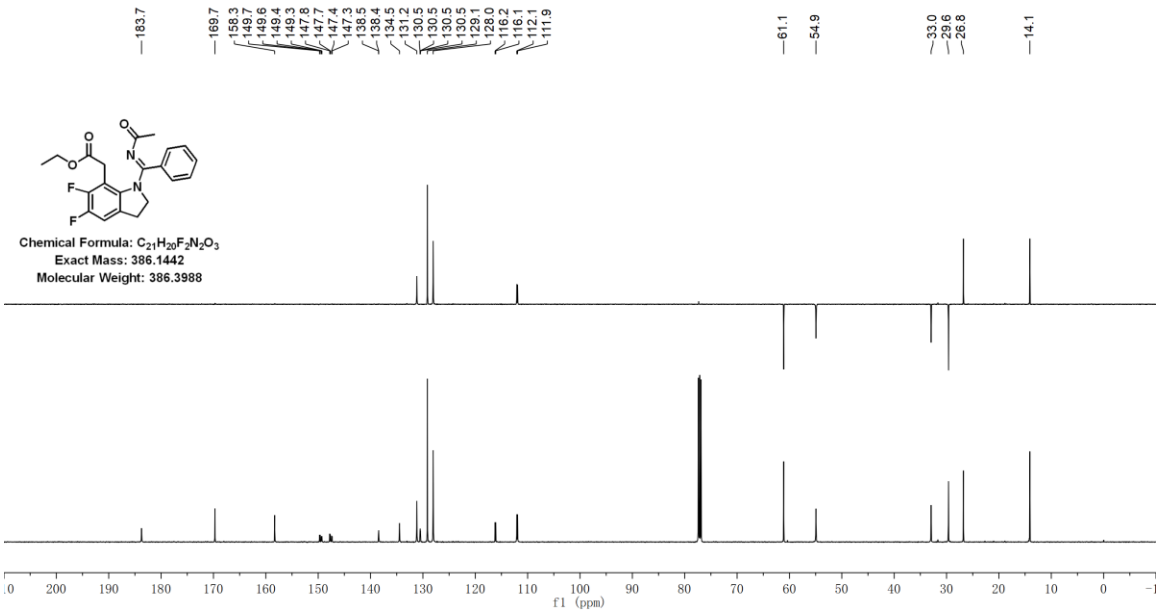
^{1}H NMR spectrum of **5ka** (500 MHz, Chloroform-*d*)



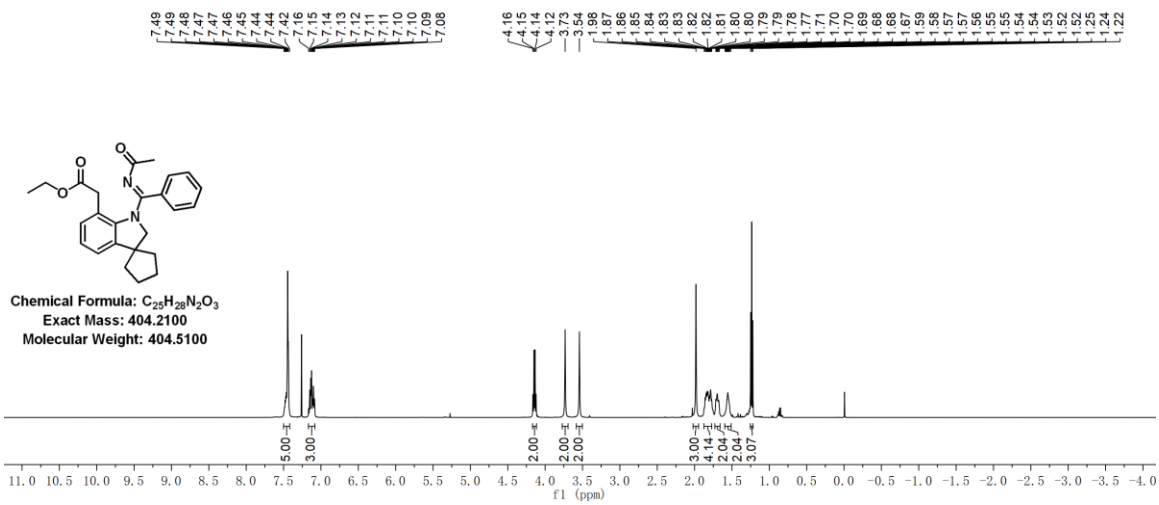
^{13}C NMR spectrum of **5ka** (125 MHz, Chloroform-*d*)



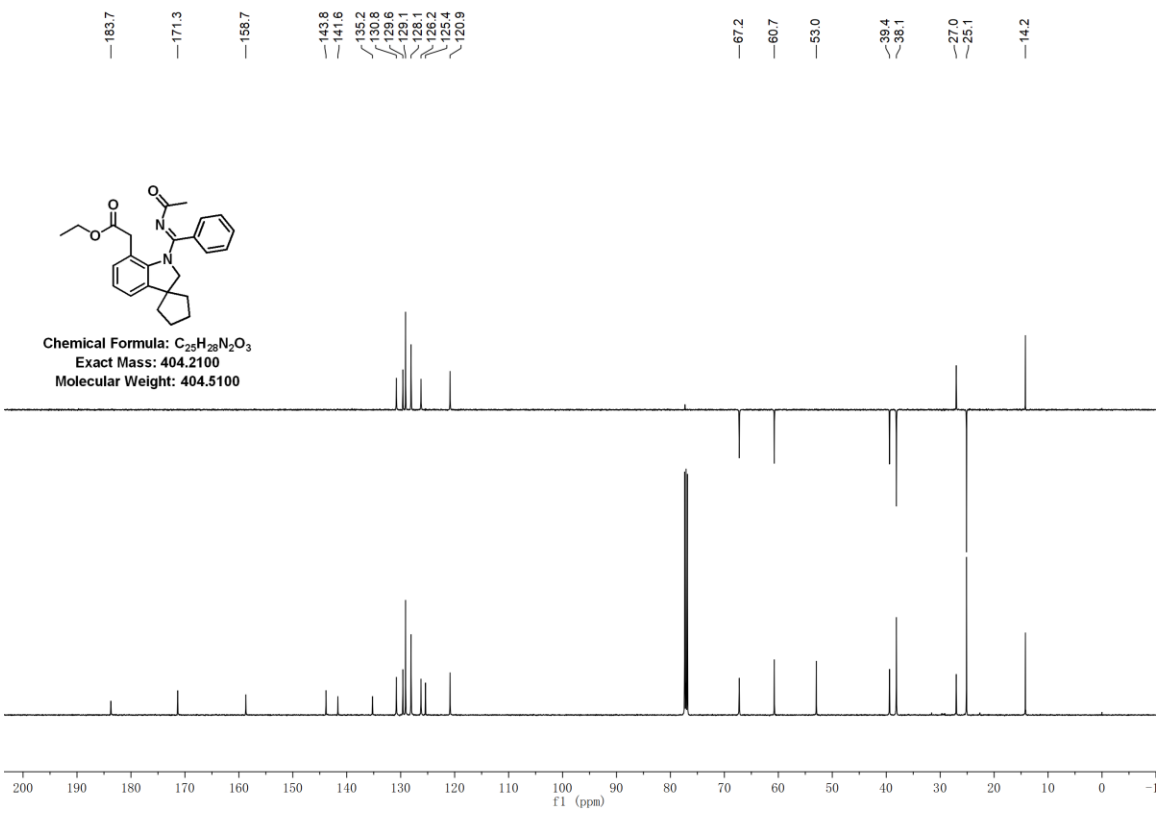
^{1}H NMR spectrum of **5na** (500 MHz, Chloroform-*d*)



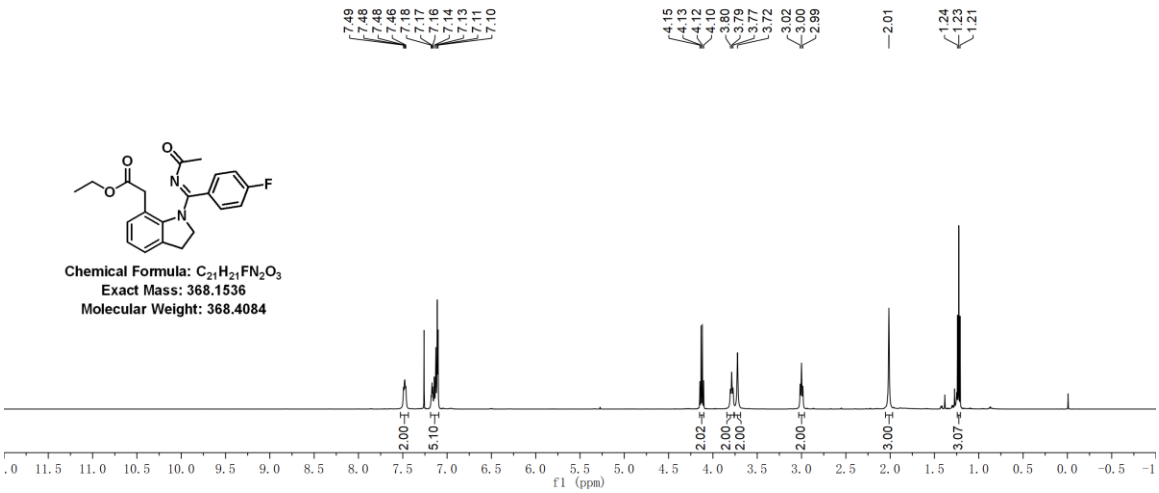
^{13}C NMR spectrum of **5na** (125 MHz, Chloroform-*d*)



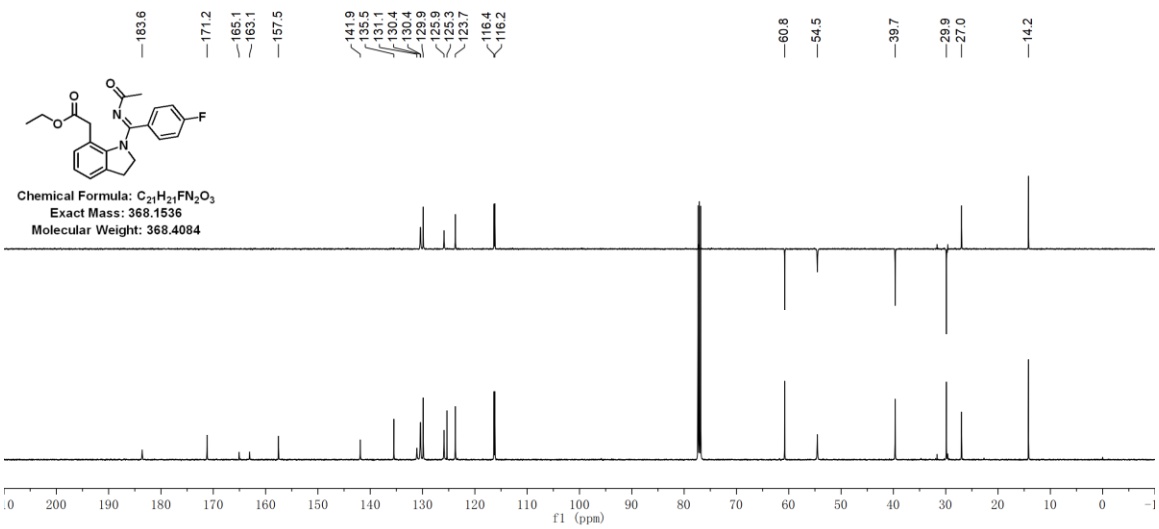
^{1}H NMR spectrum of **5pa** (500 MHz, Chloroform-*d*)



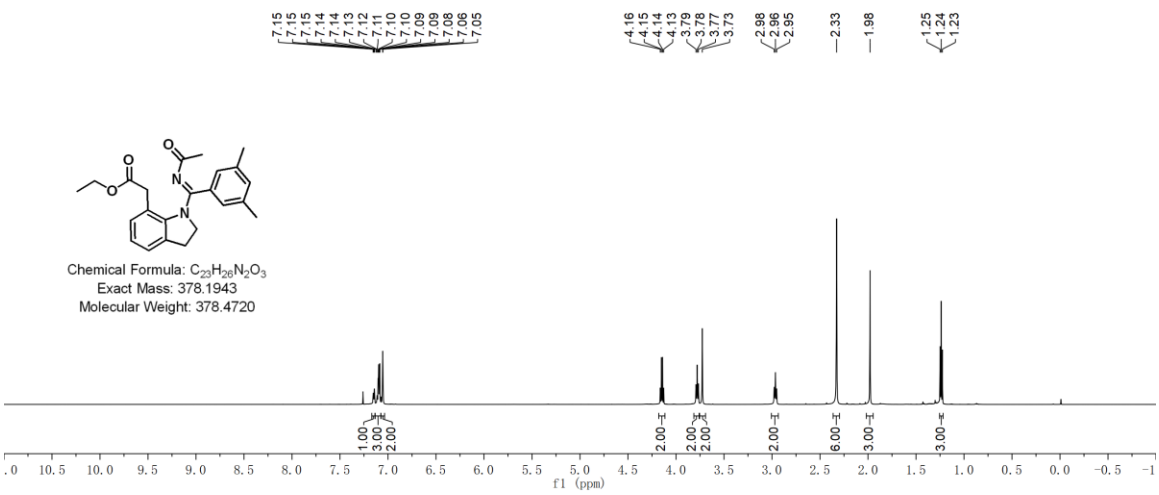
^{13}C NMR spectrum of **5pa** (125 MHz, Chloroform-*d*)



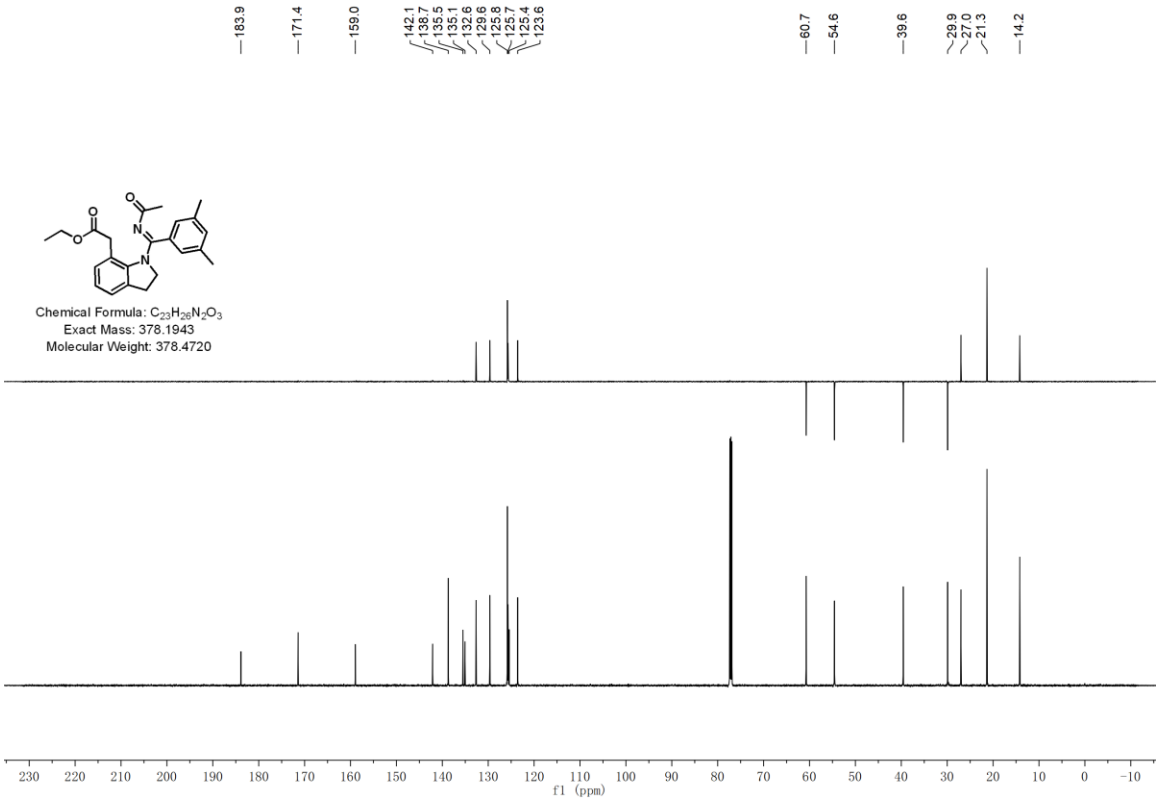
^{1}H NMR spectrum of **5ra** (500 MHz, Chloroform-*d*)



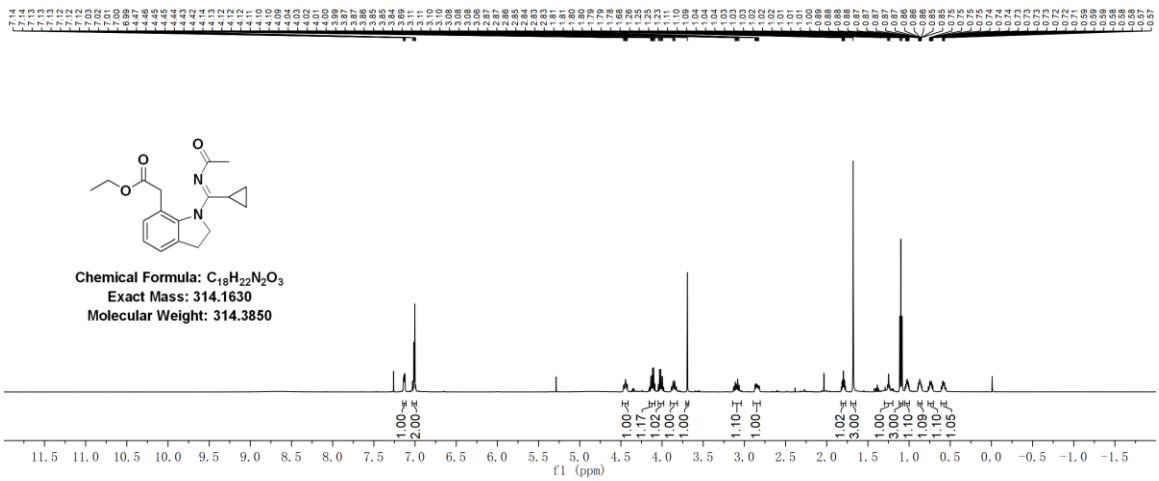
^{13}C NMR spectrum of **5ra** (125 MHz, Chloroform-*d*)



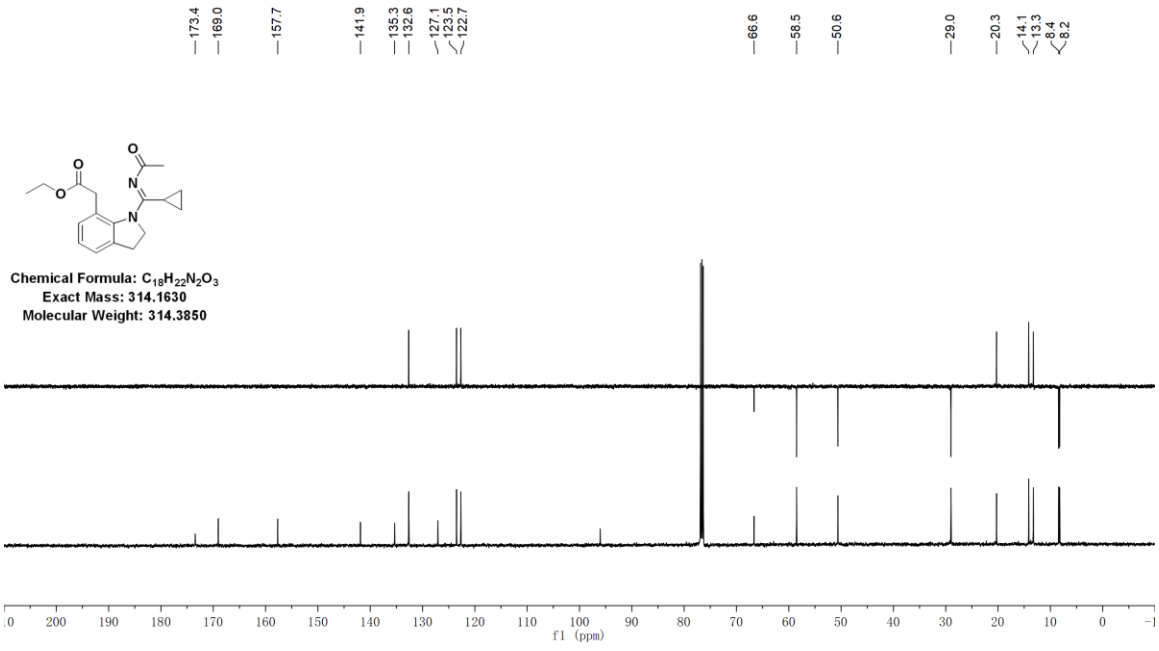
^{1}H NMR spectrum of **5sa** (600 MHz, Chloroform-*d*)



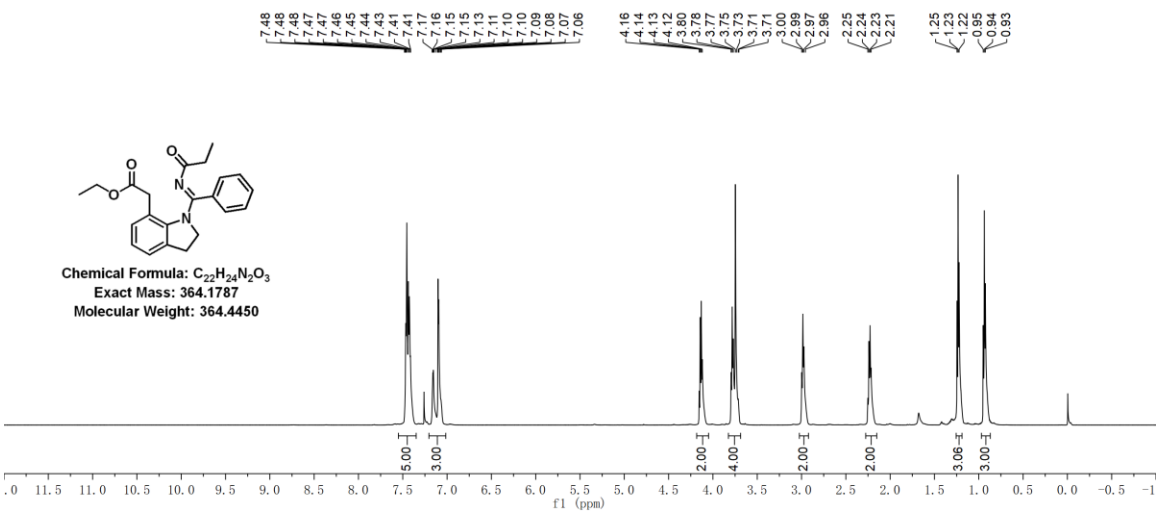
^{13}C NMR spectrum of **5sa** (150 MHz, Chloroform-*d*)



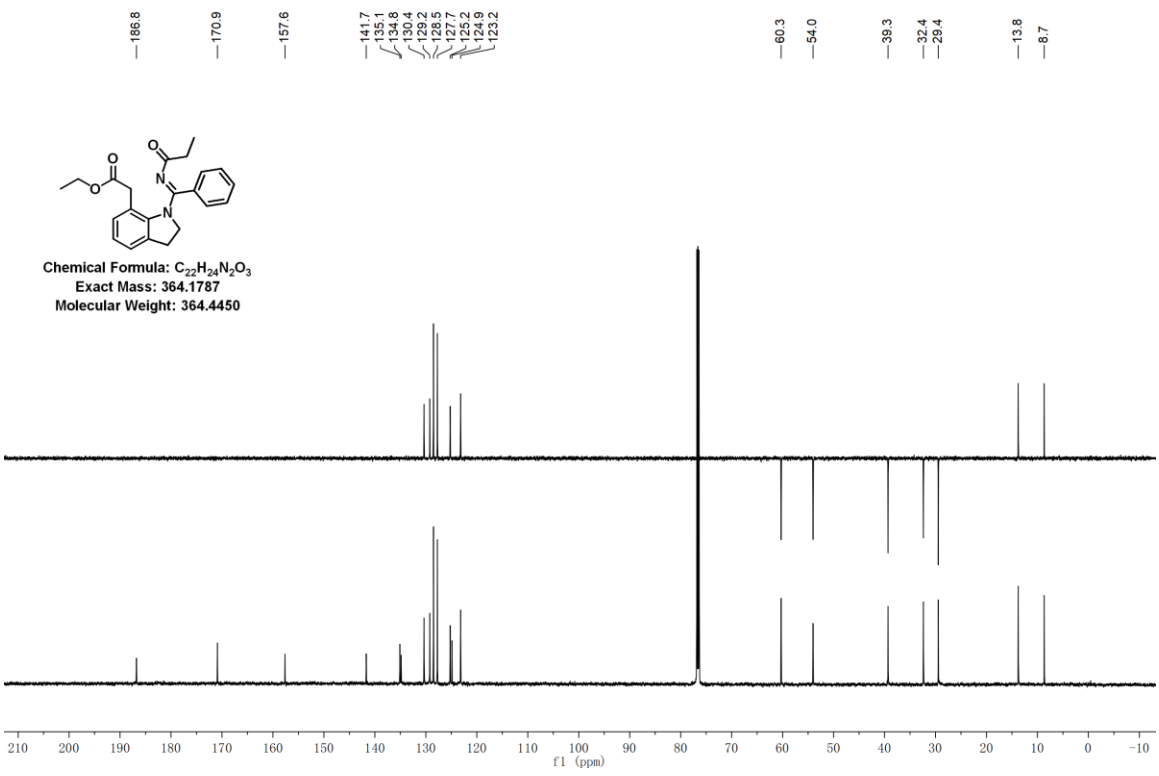
^{1}H NMR spectrum of **5va** (500 MHz, Chloroform-*d*)



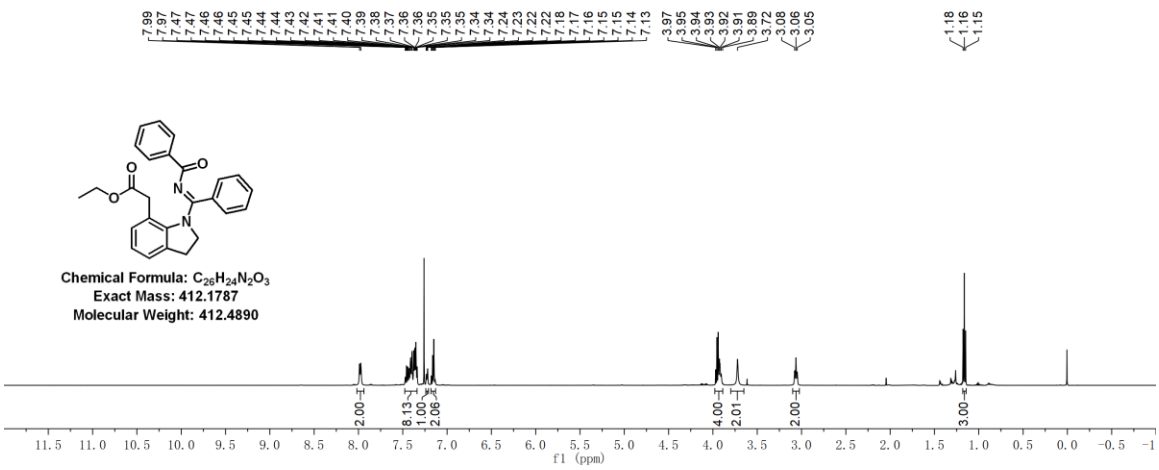
^{13}C NMR spectrum of **5va** (125 MHz, Chloroform-*d*)



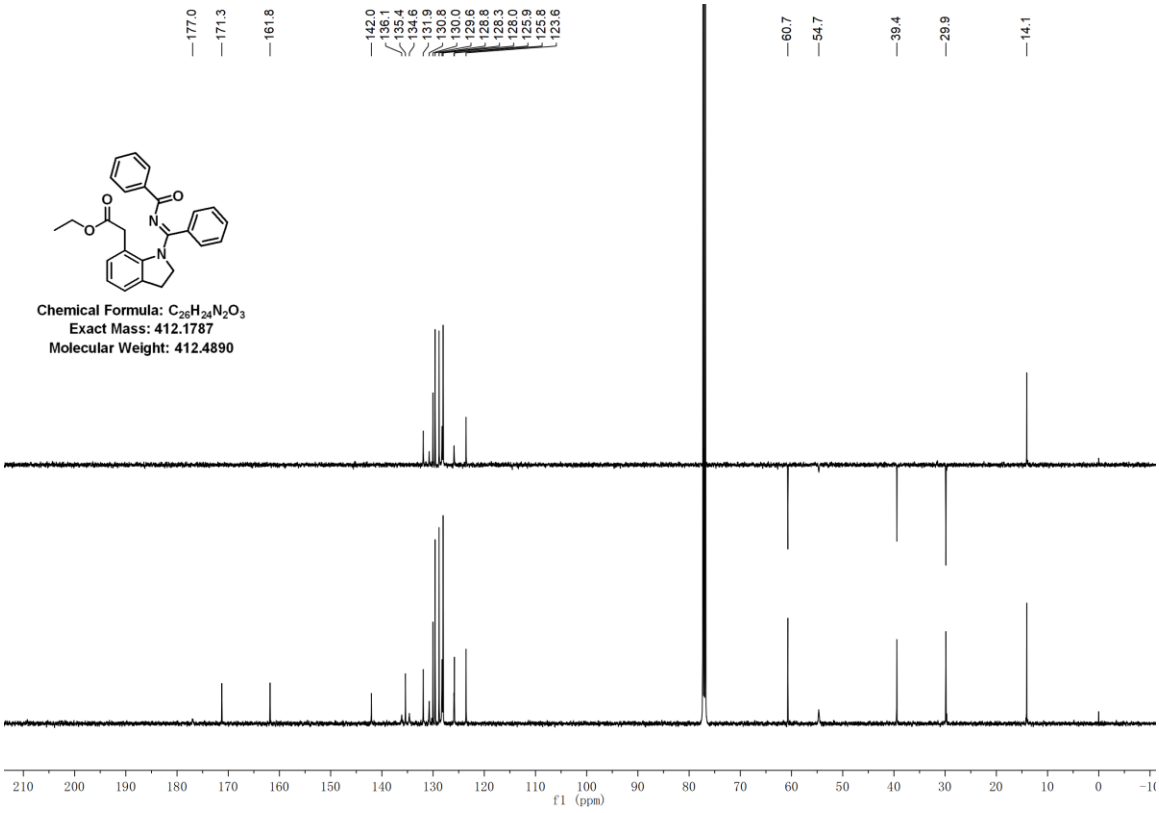
^{1}H NMR spectrum of **5ab** (600 MHz, Chloroform-*d*)



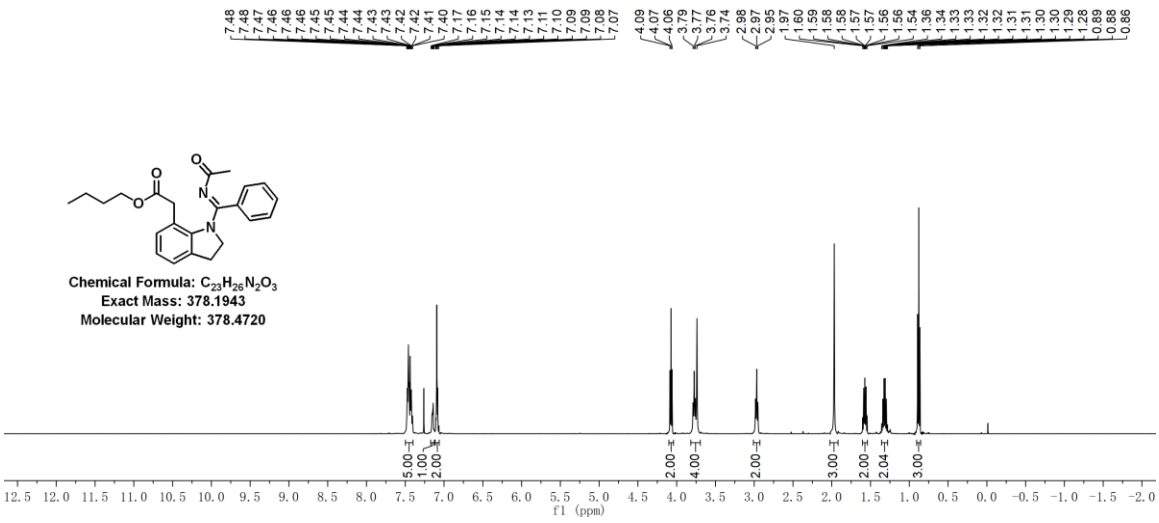
^{13}C NMR spectrum of **5ab** (150 MHz, Chloroform-*d*)



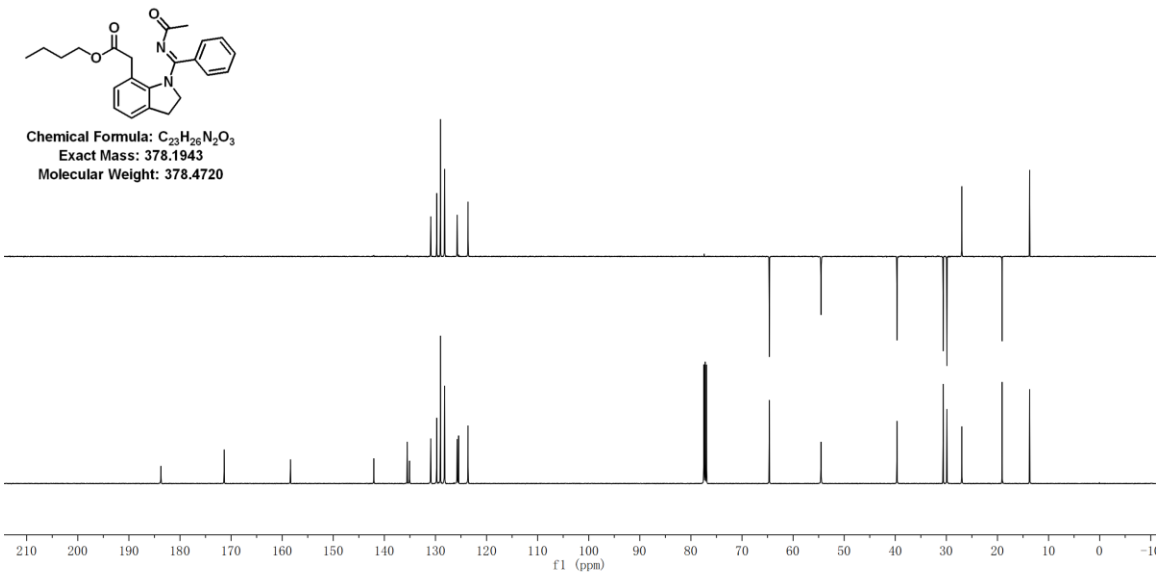
^{1}H NMR spectrum of **5ac** (500 MHz, Chloroform-*d*)



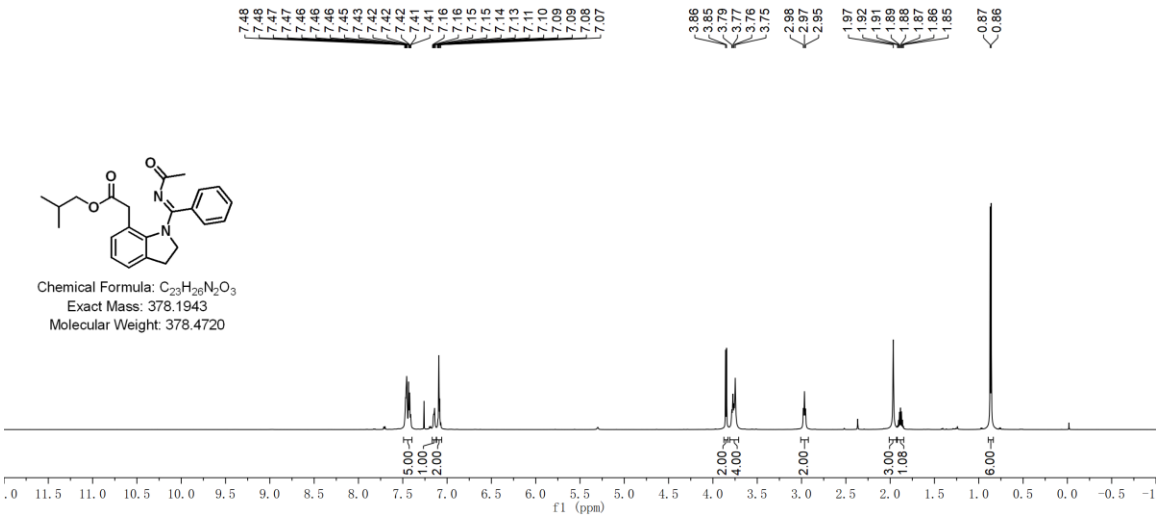
^{13}C NMR spectrum of **5ac** (125 MHz, Chloroform-*d*)



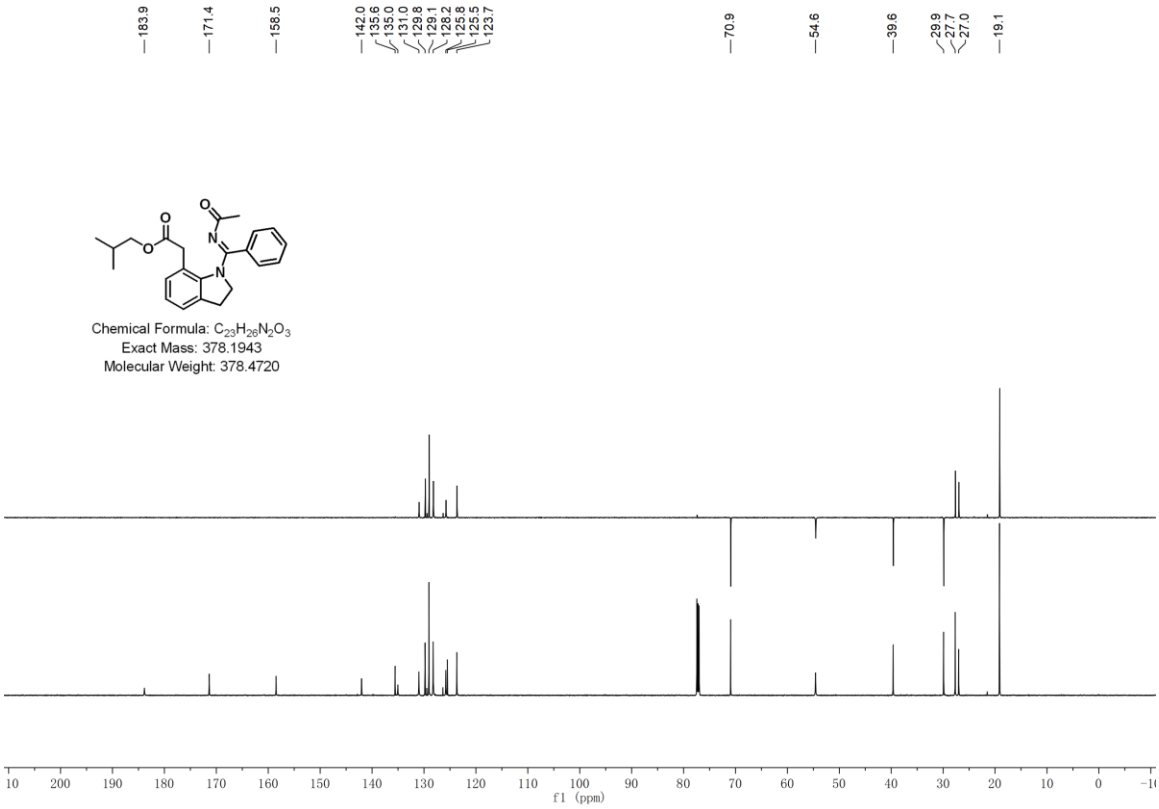
^{1}H NMR spectrum of **5ad** (500 MHz, Chloroform-*d*)



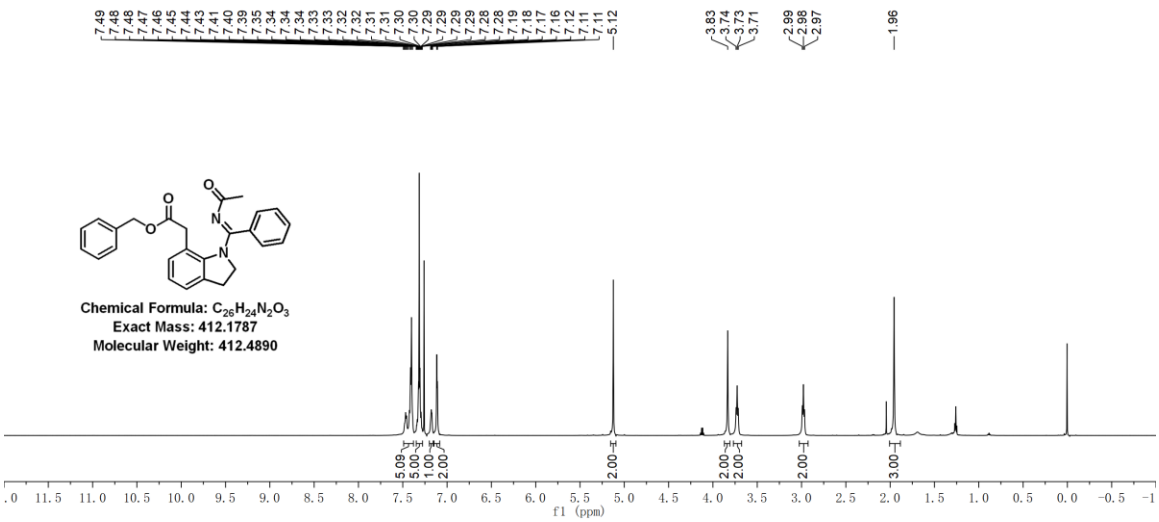
^{13}C NMR spectrum of **5ad** (125 MHz, Chloroform-*d*)



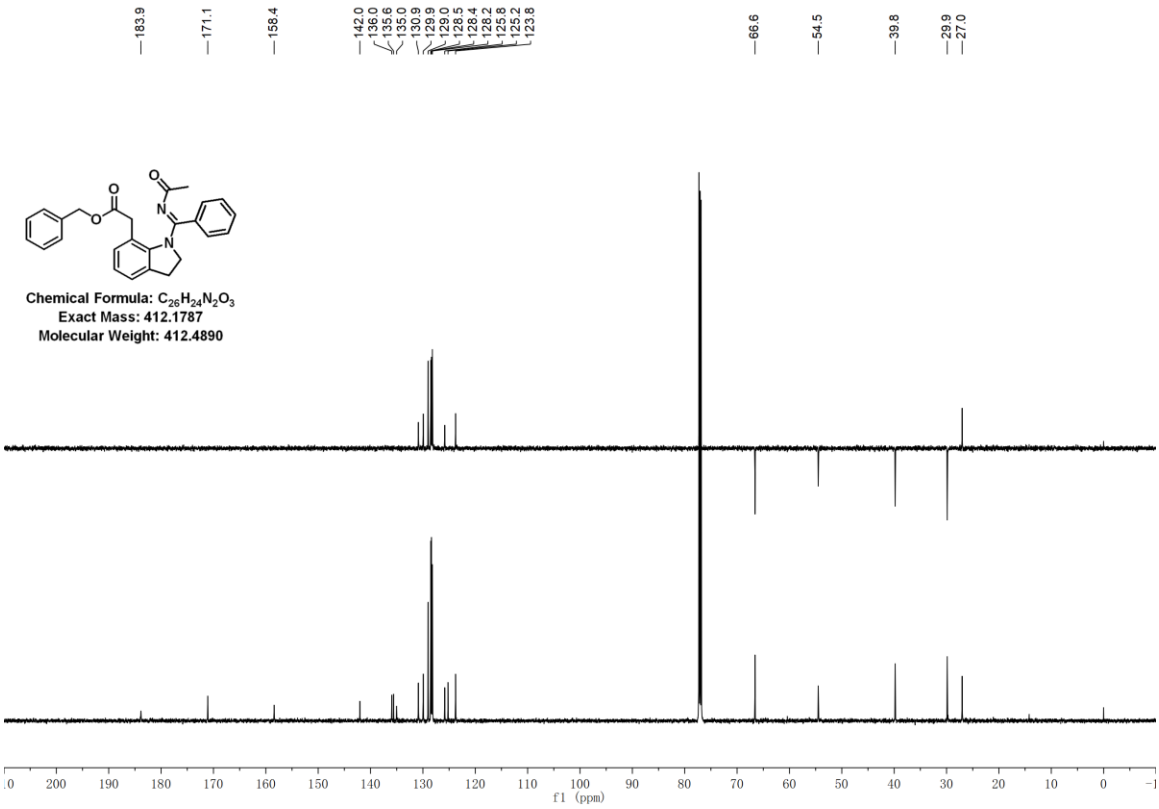
^{1}H NMR spectrum of **5ae** (600 MHz, Chloroform-*d*)



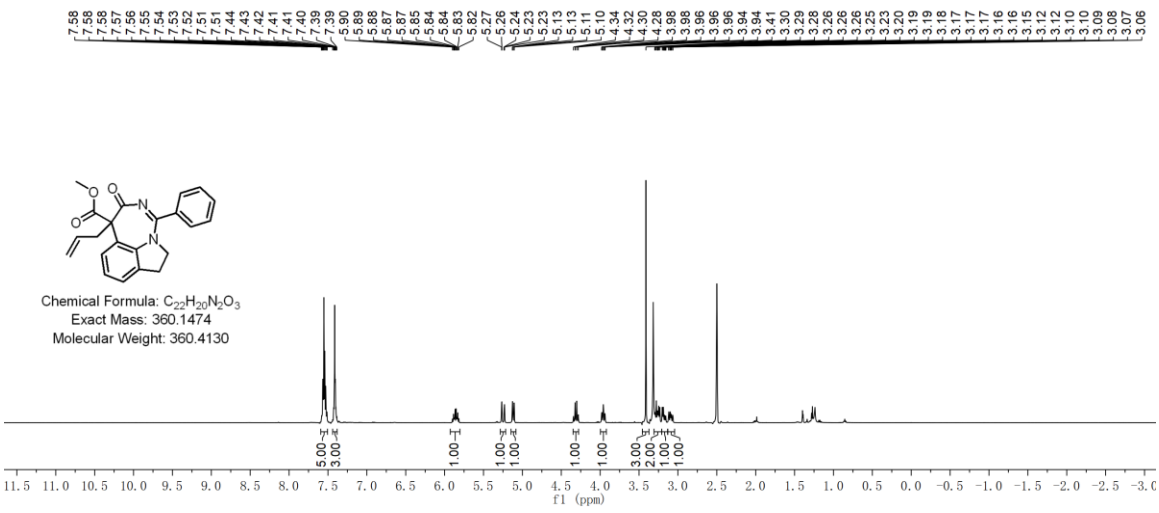
^{13}C NMR spectrum of **5ae** (150 MHz, Chloroform-*d*)



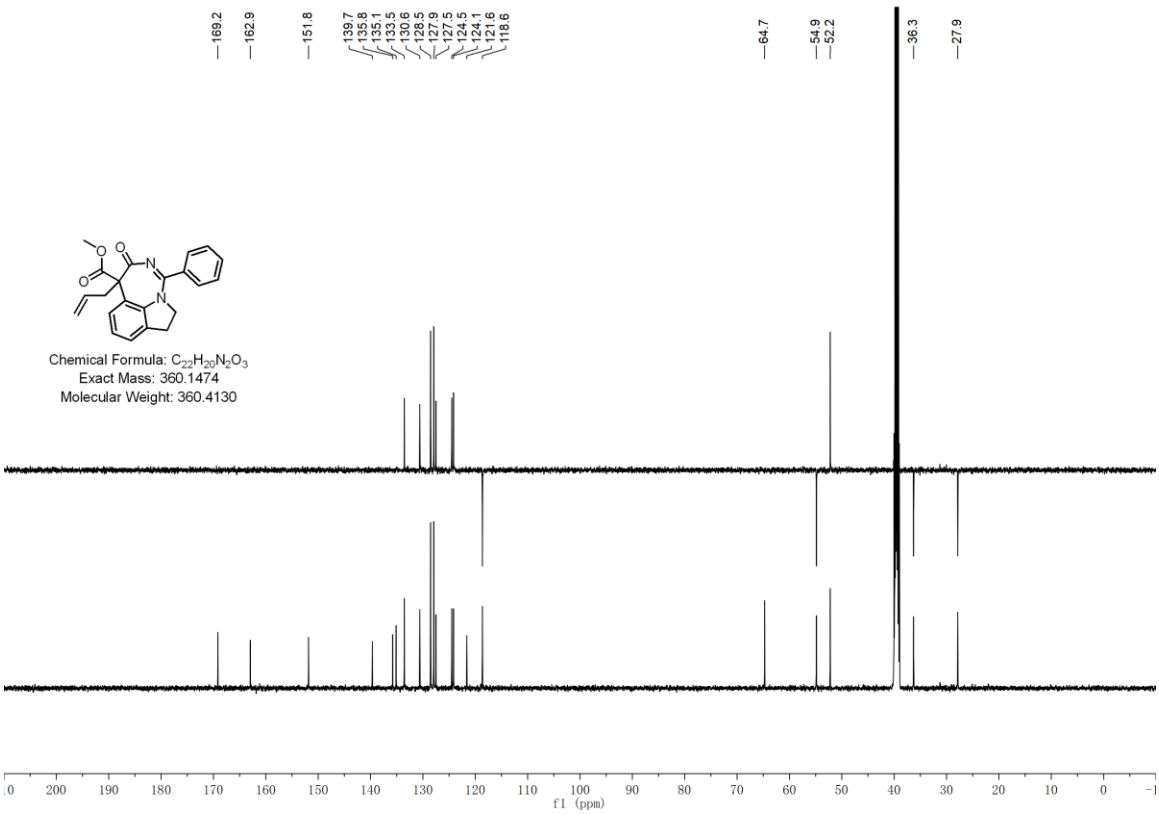
^{1}H NMR spectrum of **5af** (600 MHz, Chloroform-*d*)



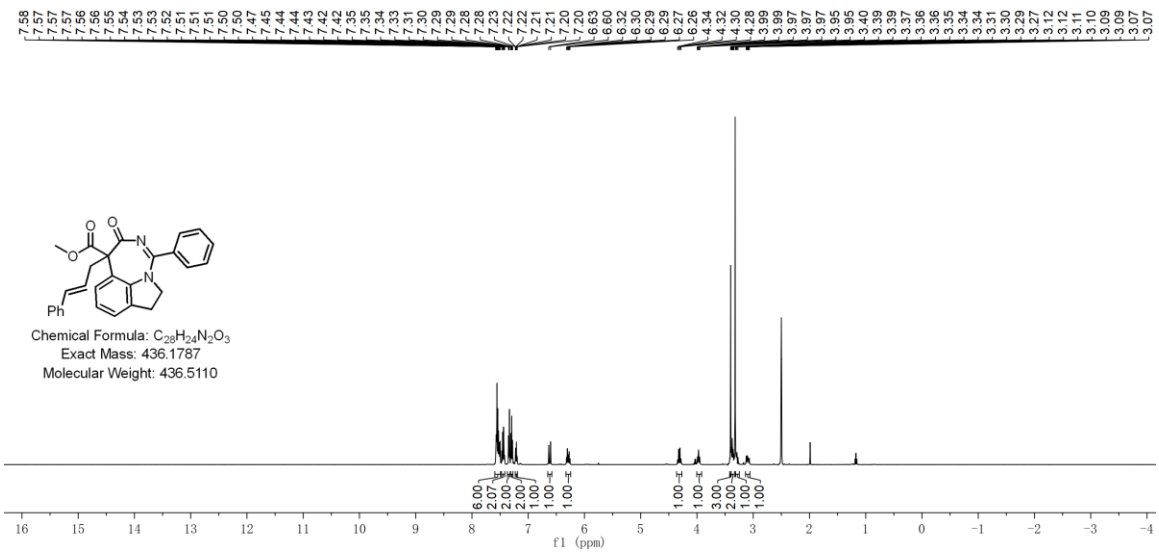
^{13}C NMR spectrum of **5af** (150 MHz, Chloroform-*d*)



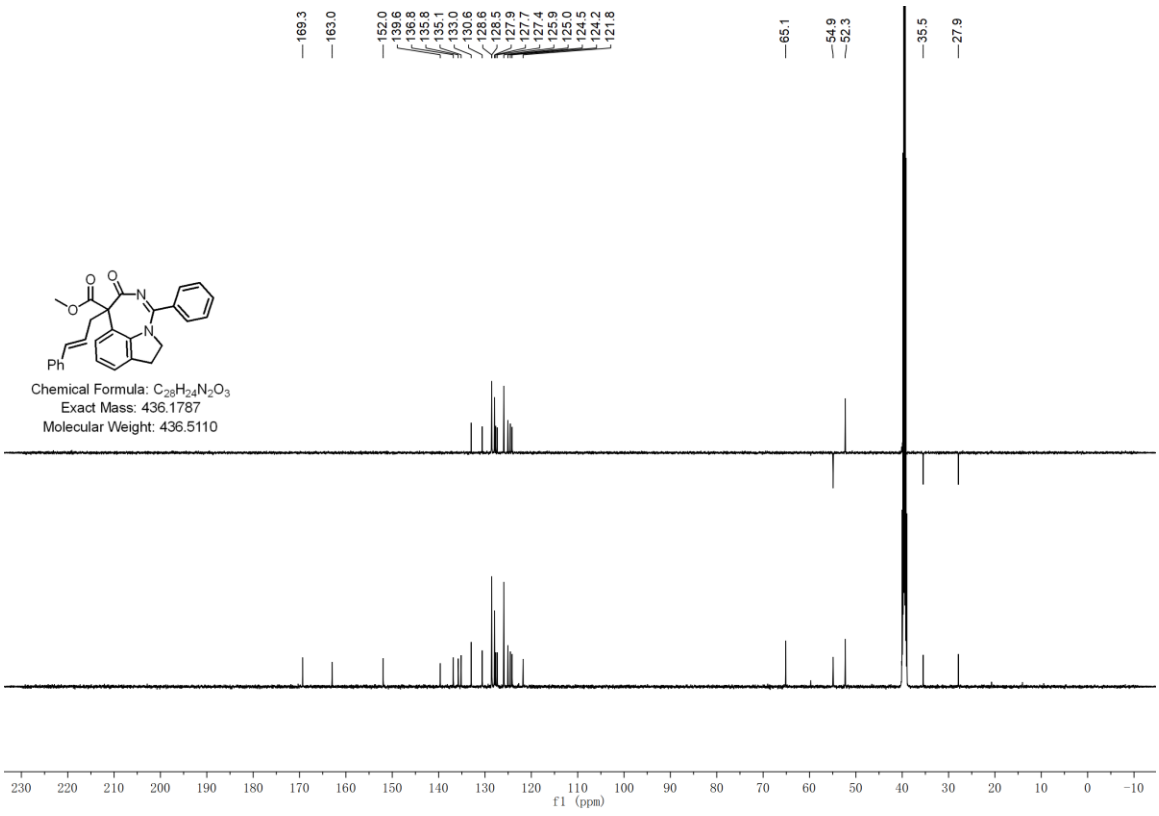
^{1}H NMR spectrum of **6** (500 MHz, DMSO-d_6)



^{13}C NMR spectrum of **6** (125 MHz, DMSO-d_6)

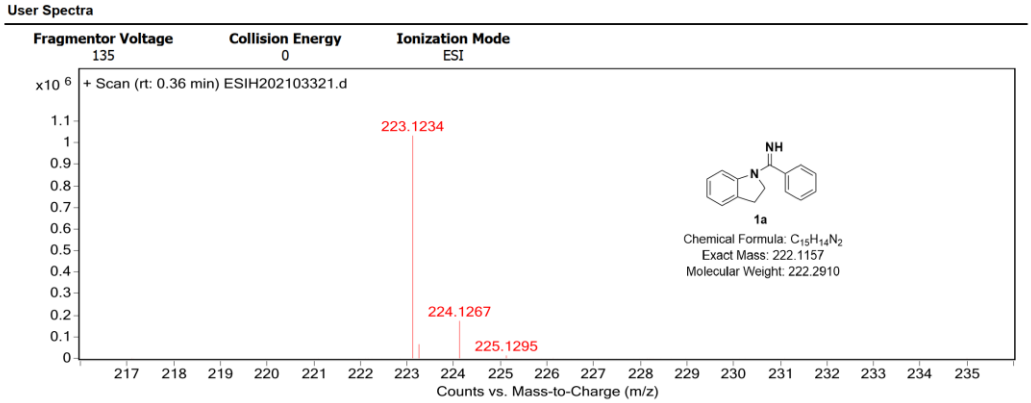


^{1}H NMR spectrum of **7** (500 MHz, DMSO-d_6)



^{13}C NMR spectrum of **7** (125 MHz, DMSO-d_6)

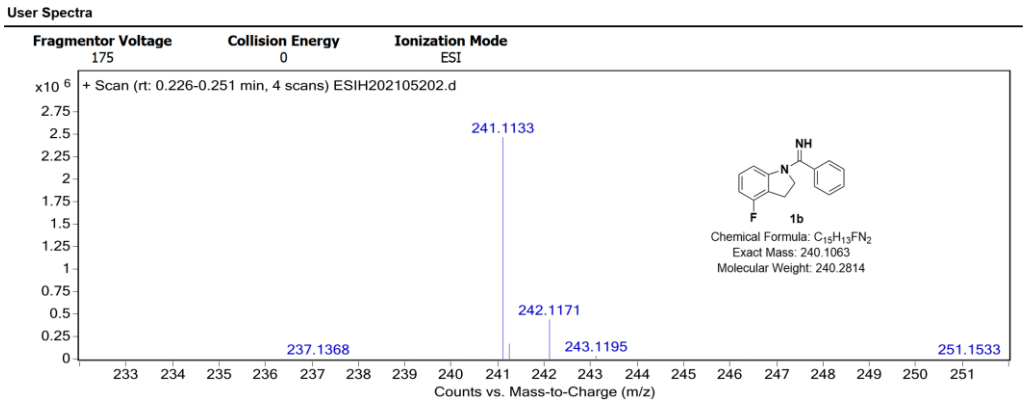
(b) HRMS (ESI) Spectra



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
223.1234	223.123	-0.4	-1.79	C15 H15 N2	(M+H)+

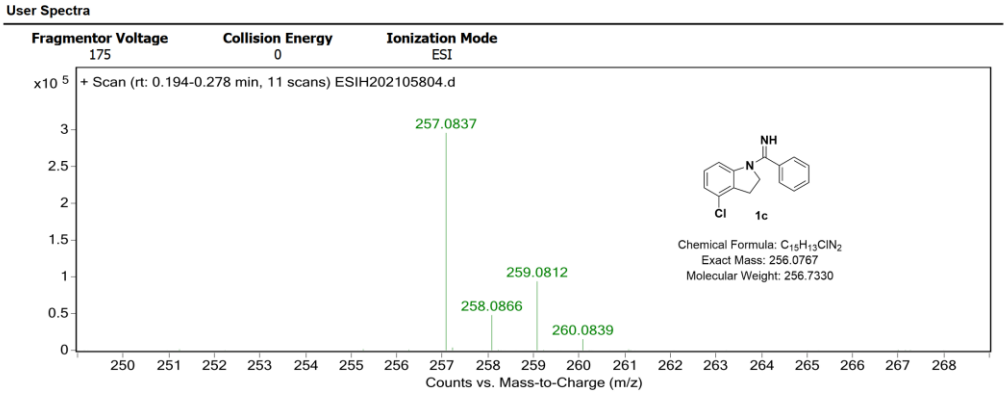
Compound 1a



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
241.1133	241.1136	0.24	0.99	C15 H14 F N2	(M+H)+

Compound 1b



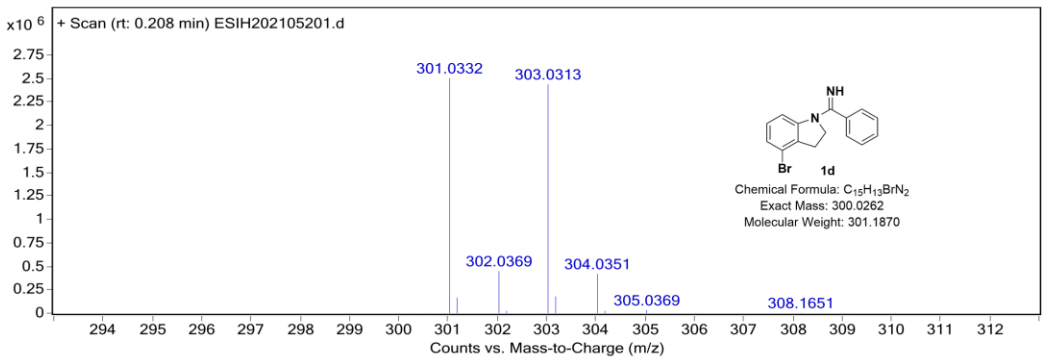
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
257.0837	257.084	0.32	1.25	C15 H14 Cl N2	(M+H)+

Compound 1c

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



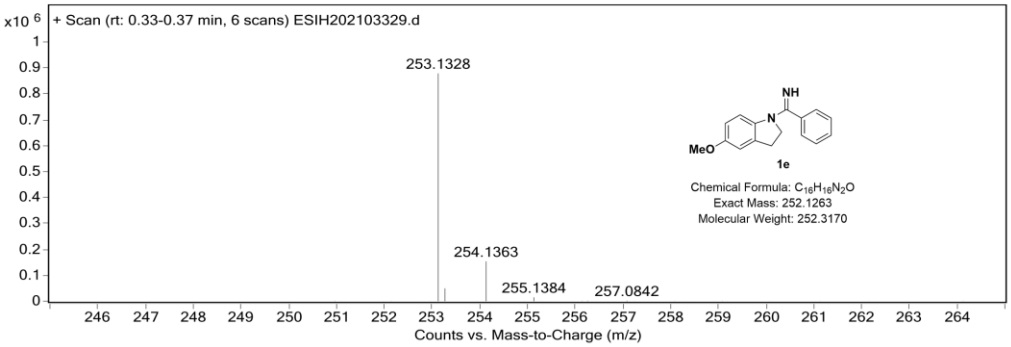
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
301.0332	301.0335	0.26	0.85	C15 H14 Br N2	(M+H)+

Compound 1d

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



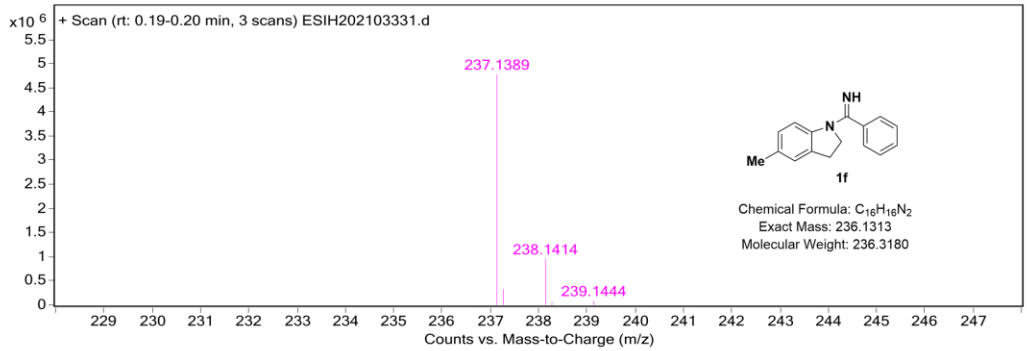
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
253.1328	253.1335	0.72	2.85	C16 H17 N2 O	(M+H)+

Compound 1e

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



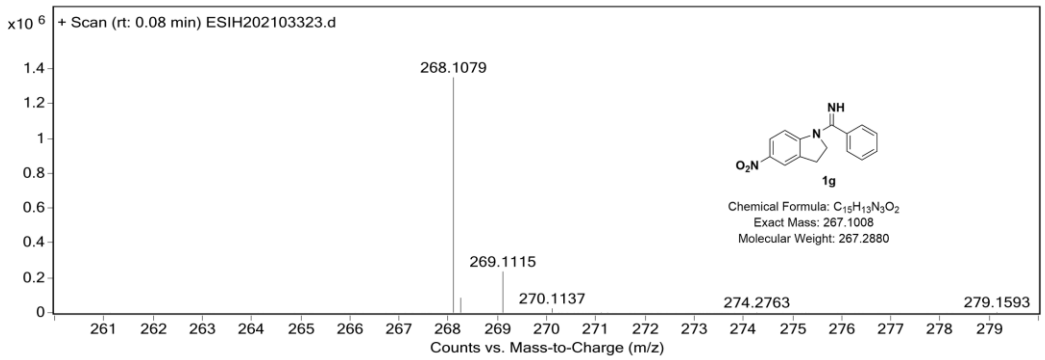
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
237.1389	237.1386	-0.25	-1.07	C16 H17 N2	(M+H)+

Compound 1f

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



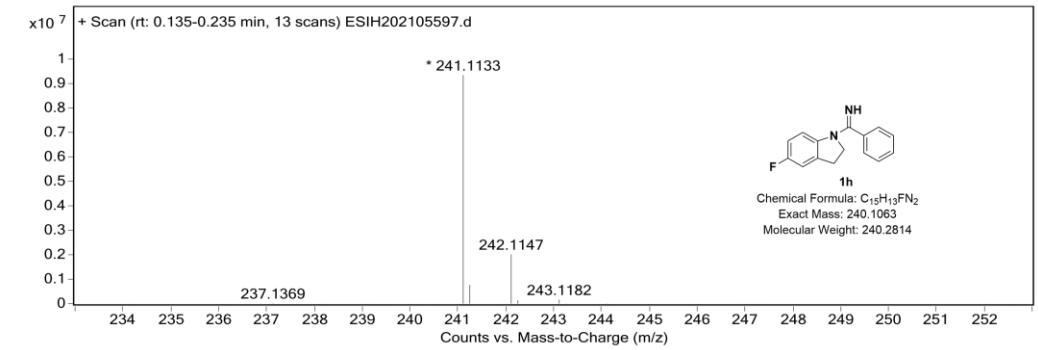
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
268.1079	268.1081	0.12	0.43	C15 H14 N3 O2	(M+H)+

Compound 1g

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



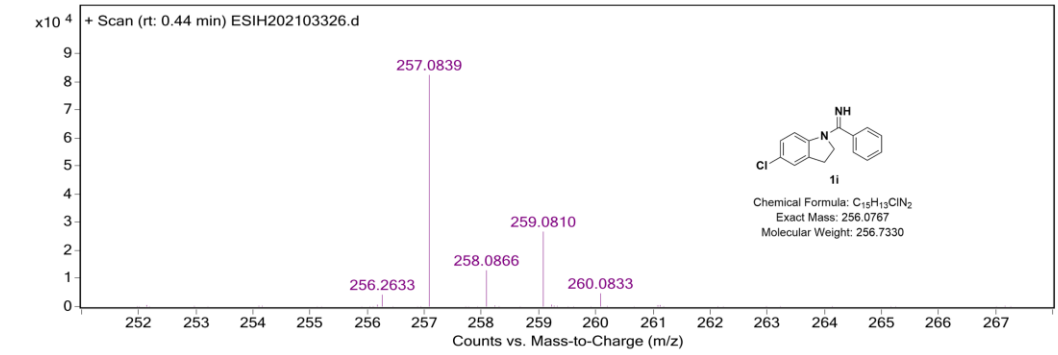
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
241.1133	241.1136	0.29	1.2	C15 H14 F N2	(M+H)+

Compound 1h

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



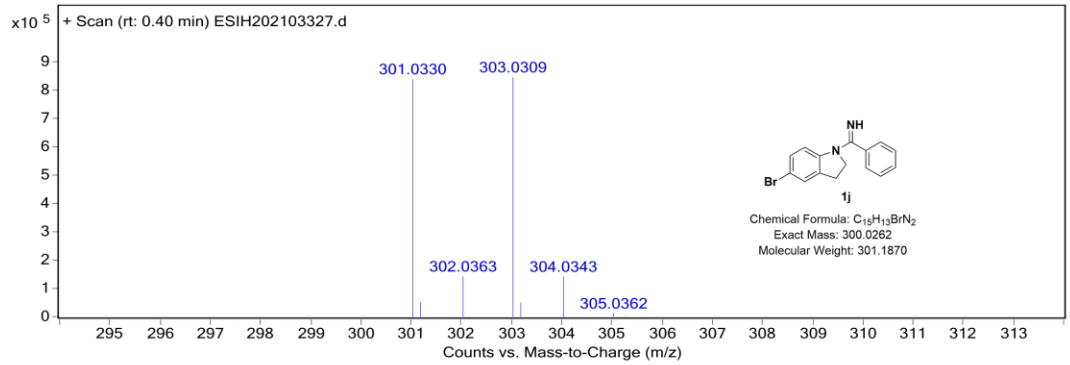
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
257.0839	257.084	0.11	0.44	C15 H14 Cl N2	(M+H)+

Compound 1i

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



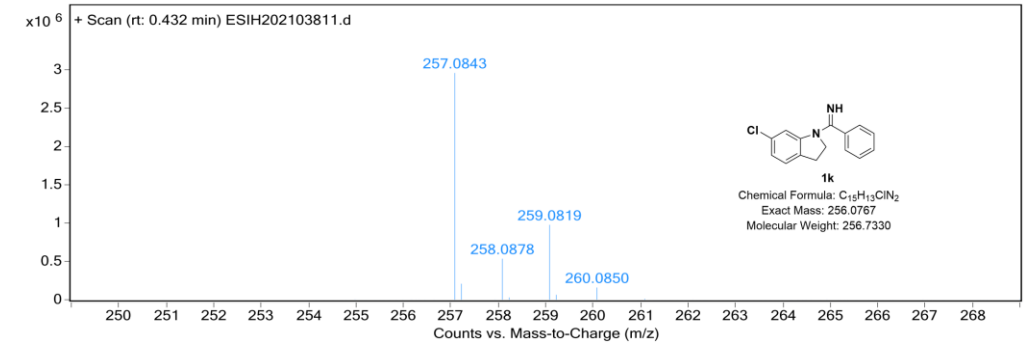
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
301.033	301.0335	0.44	1.46	C15 H14 Br N2	(M+H)+

Compound 1j

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



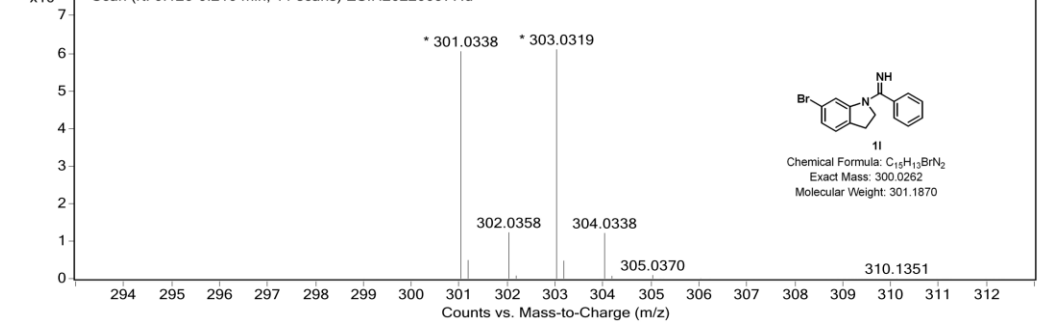
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
257.0843	257.084	-0.28	-1.08	C15 H14 Cl N2	(M+H)+

Compound 1k

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



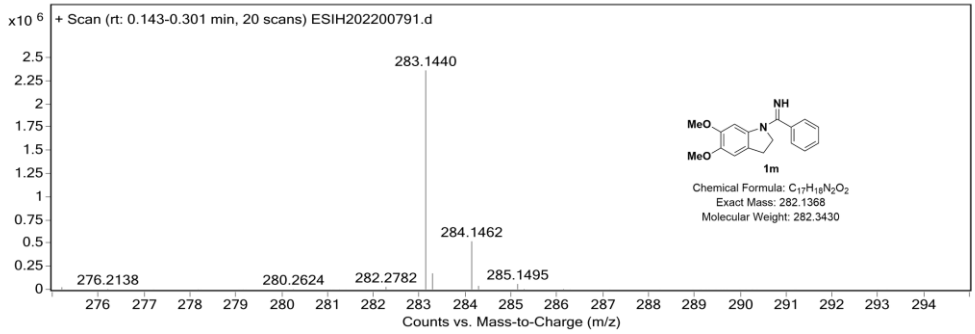
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
301.0338	301.0335	-0.35	-1.15	C15 H14 Br N2	(M+H)+

Compound 1l

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



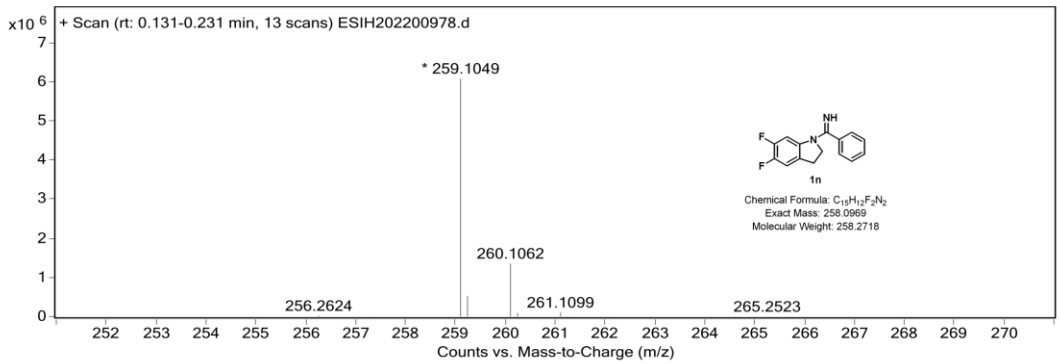
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
283.144	283.1441	0.15	0.53	C17 H19 N2 O2	(M+H)+

Compound 1m

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



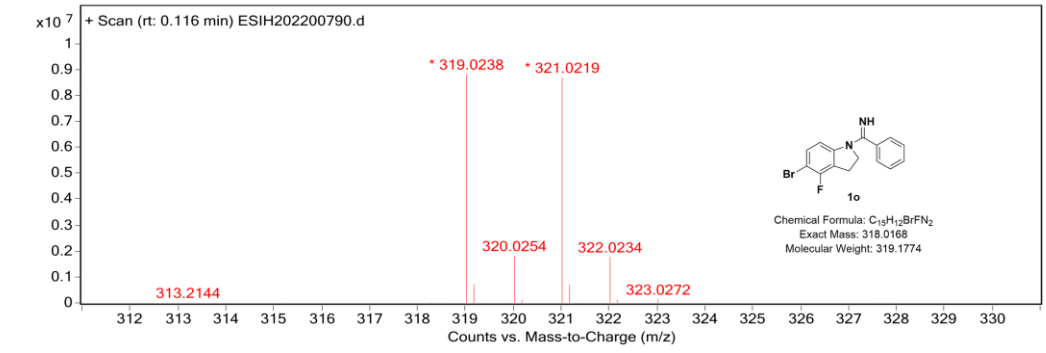
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
259.1049	259.1041	-0.74	-2.87	C15 H13 F2 N2	(M+H)+

Compound 1n

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

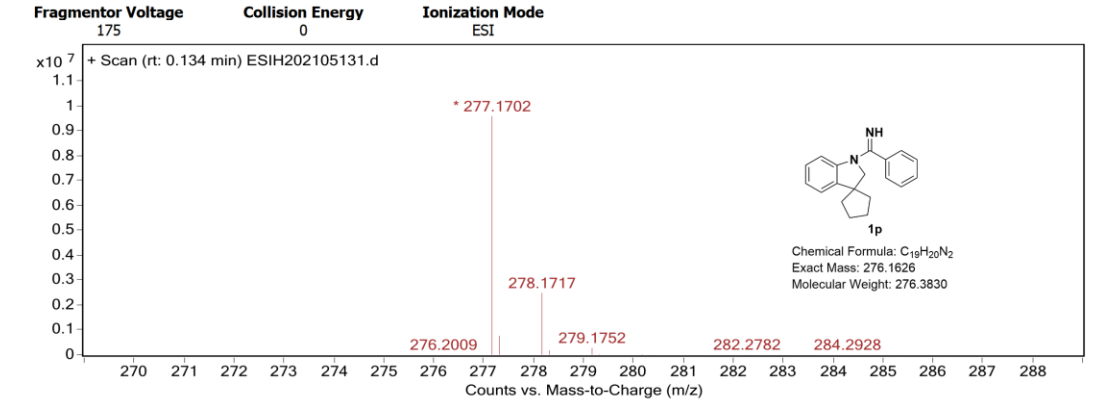


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
319.0238	319.0241	0.25	0.77	C15 H13 Br F N2	(M+H)+

Compound 1o

User Spectra

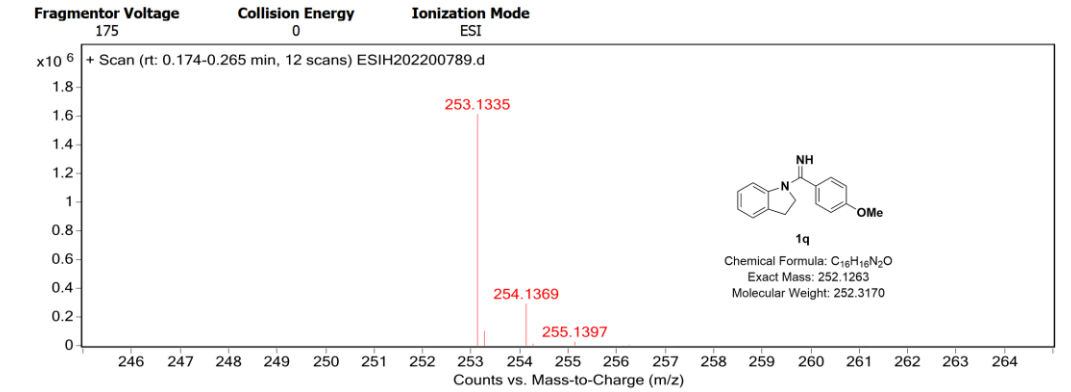


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
277.1702	277.1699	-0.29	-1.03	C19 H21 N2	(M+H)+

Compound 1p

User Spectra

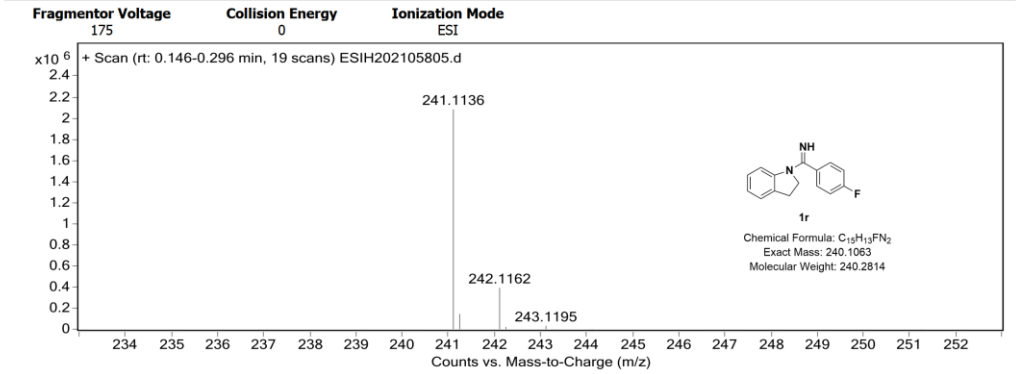


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
253.1335	253.1335	0.06	0.23	C16 H17 N2 O	(M+H)+

Compound 1q

User Spectra



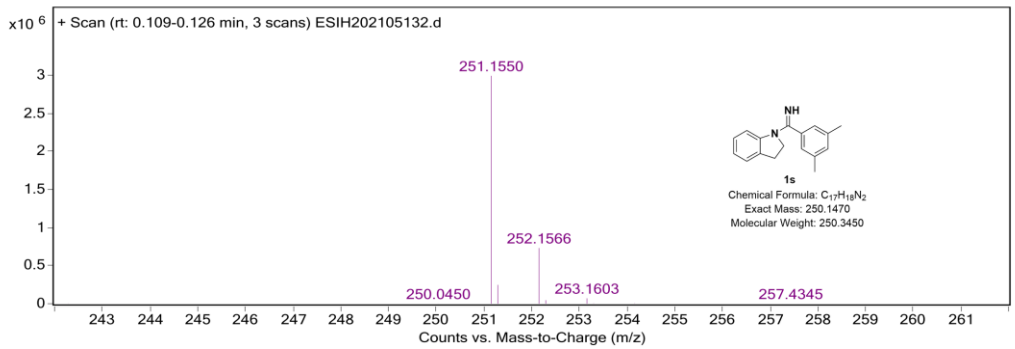
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
241.1136	241.1136	-0.08	-0.35	C15 H14 F N2	(M+H)+

Compound 1r

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



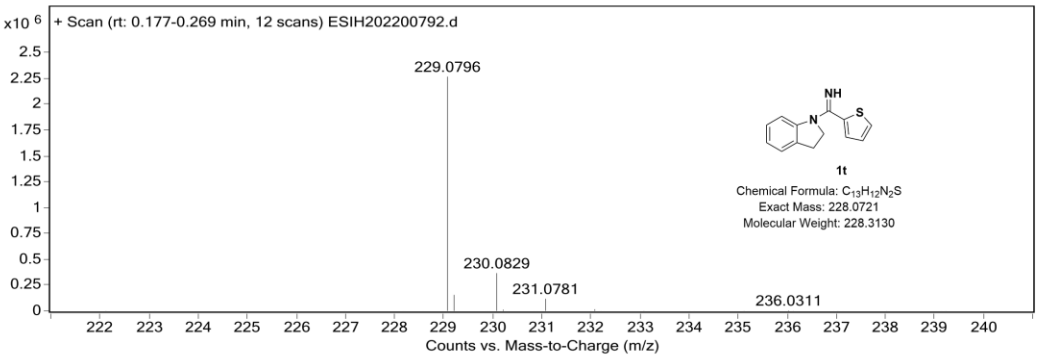
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
251.155	251.1543	-0.68	-2.71	C17 H19 N2	(M+H)+

Compound 1s

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



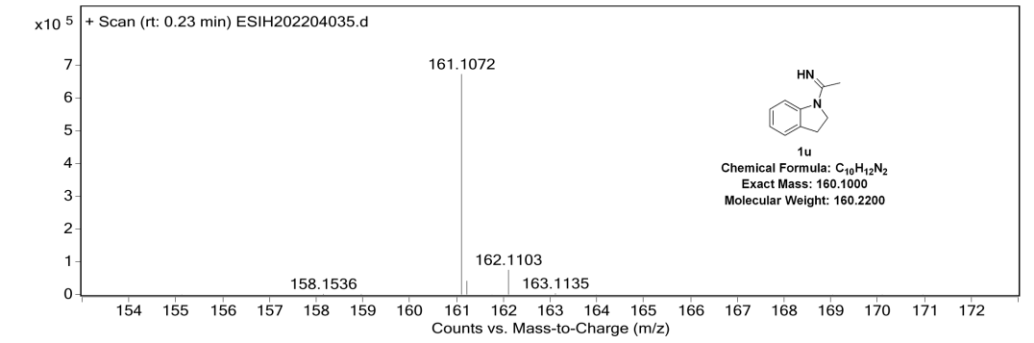
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
229.0796	229.0794	-0.17	-0.74	C13 H13 N2 S	(M+H)+

Compound 1t

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



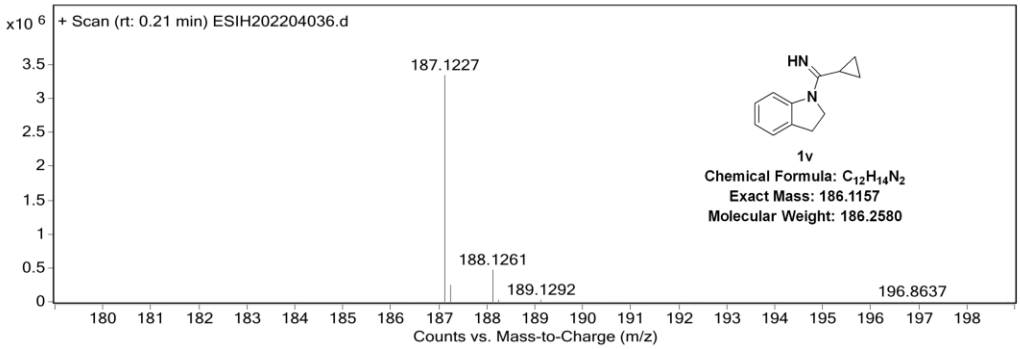
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
161.1072	161.1073	0.14	0.84	C10 H13 N2	(M+H)+

Compound 1u

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



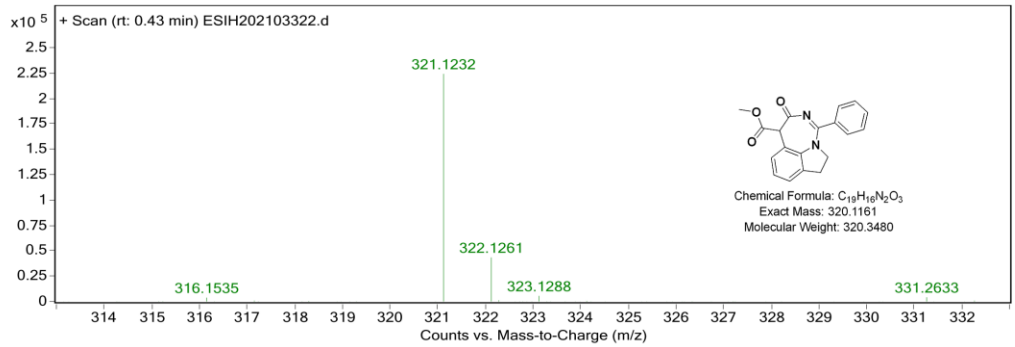
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
187.1227	187.123	0.29	1.53	C12 H15 N2	(M+H)+

Compound 1v

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



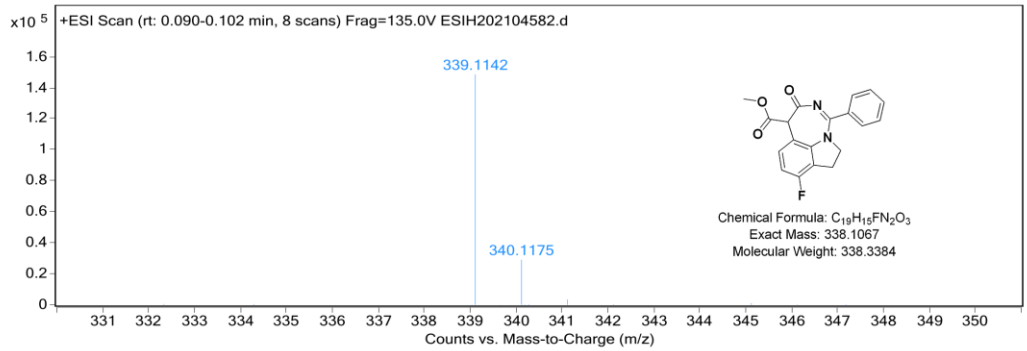
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
321.1232	321.1234	0.13	0.39	C19 H17 N2 O3	(M+H)+

Compound 3aa

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



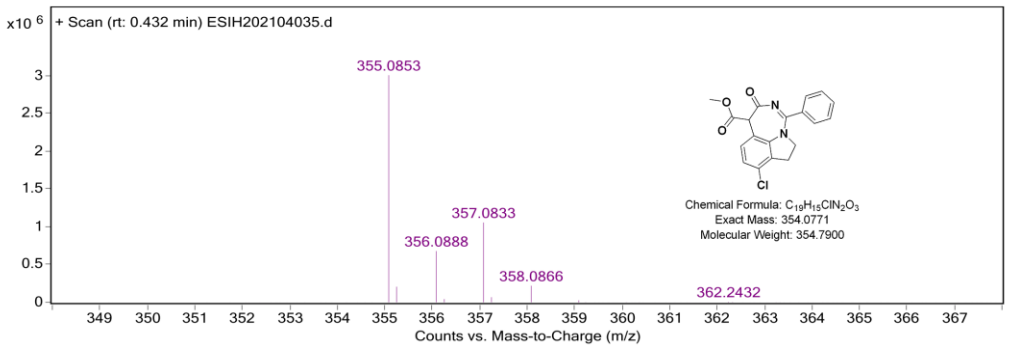
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
339.1142	339.1139	-0.27	-0.78	C19 H16 F N2 O3	(M+H)+

Compound 3ba

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



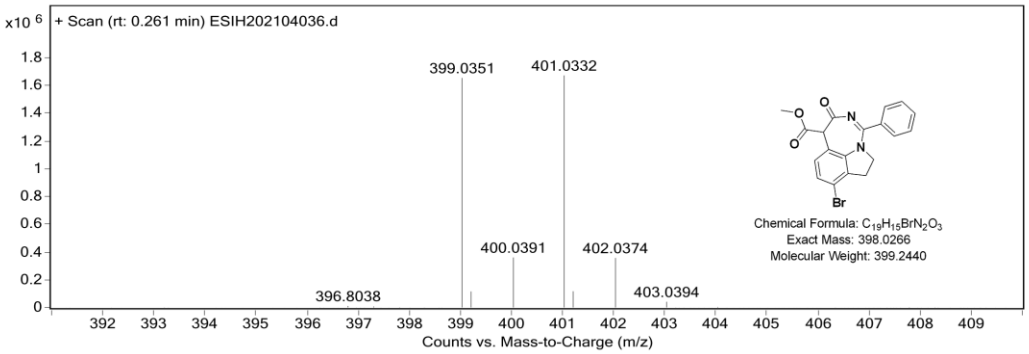
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
355.0853	355.0844	-0.94	-2.65	C19 H16 Cl N2 O3	(M+H)+

Compound 3ca

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



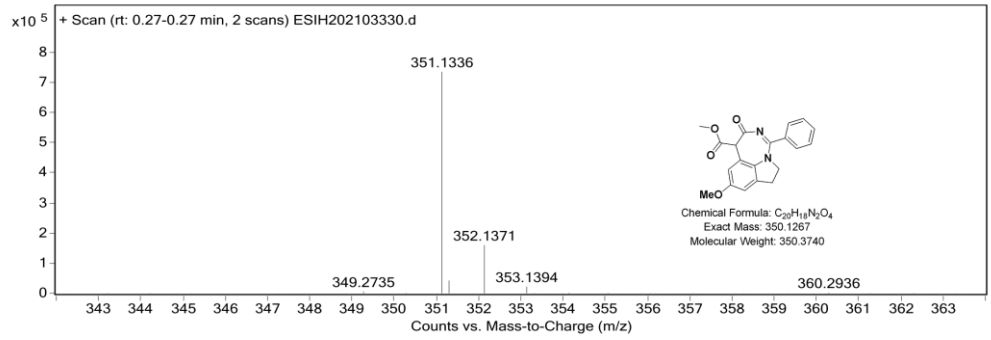
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
399.0351	399.0339	-1.19	-2.97	C19 H16 Br N2 O3	(M+H)+

Compound 3da

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



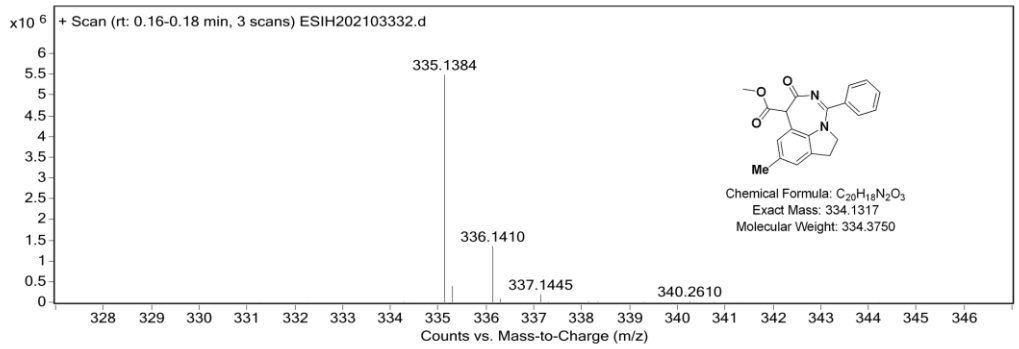
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
351.1336	351.1339	0.31	0.87	C20 H19 N2 O4	(M+H)+

Compound 3ea

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



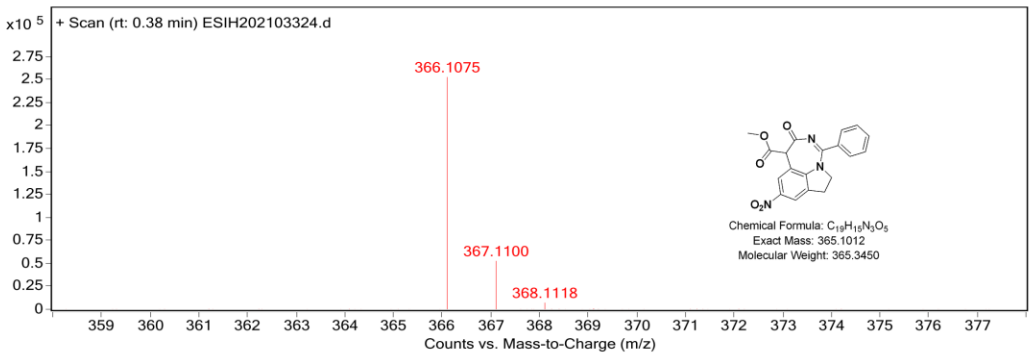
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
335.1384	335.139	0.65	1.94	C20 H19 N2 O3	(M+H)+

Compound 3fa

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



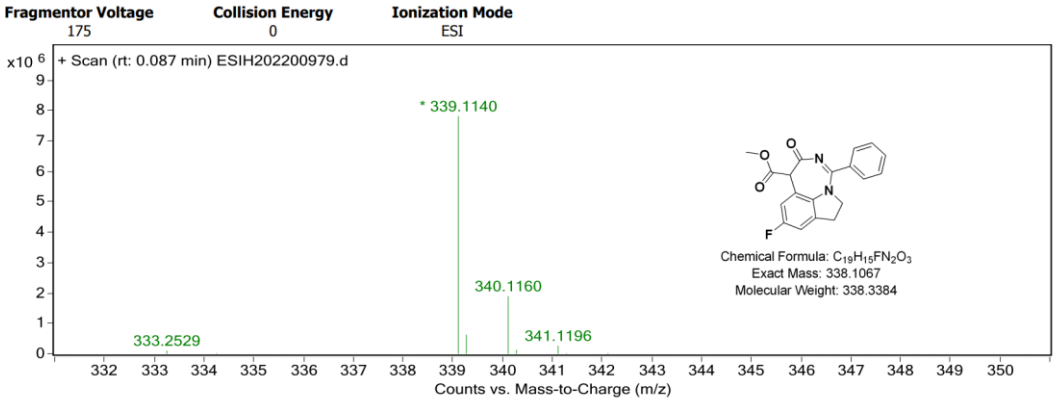
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
366.1075	366.1084	0.94	2.56	C19 H16 N3 O5	(M+H)+

Compound 3ga

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



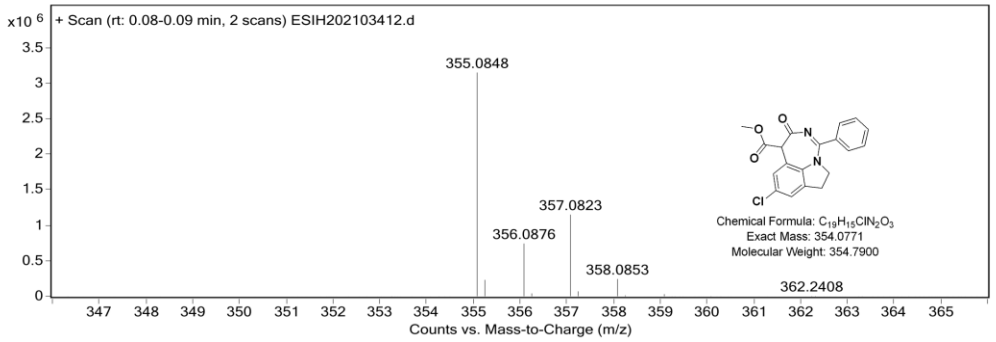
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
339.114	339.1139	-0.06	-0.17	C19 H16 F N2 O3	(M+H)+

Compound 3ha

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



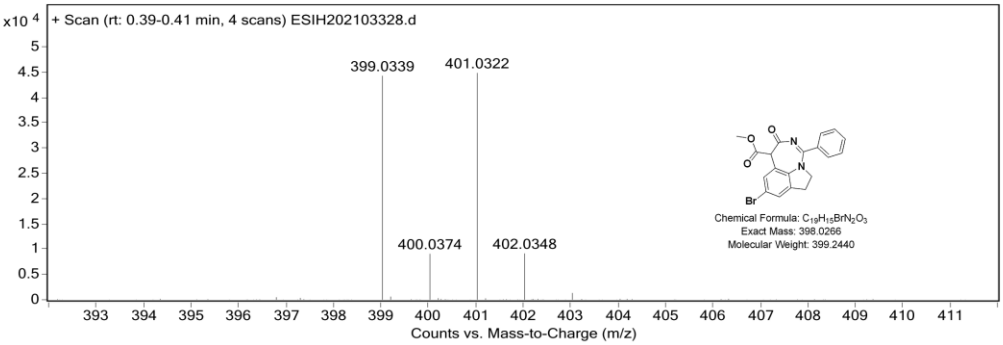
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
355.0848	355.0844	-0.43	-1.21	C19 H16 Cl N2 O3	(M+H)+

Compound 3ia

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



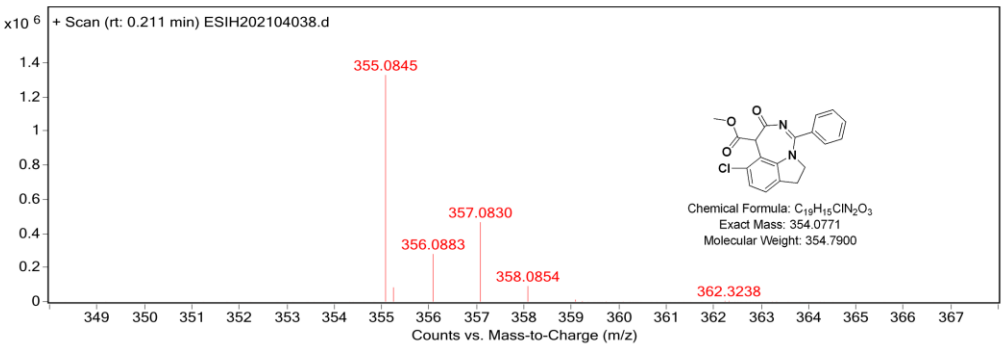
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
399.0339	399.0339	-0.06	-0.14	C19 H16 Br N2 O3	(M+H)+

Compound 3ja

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



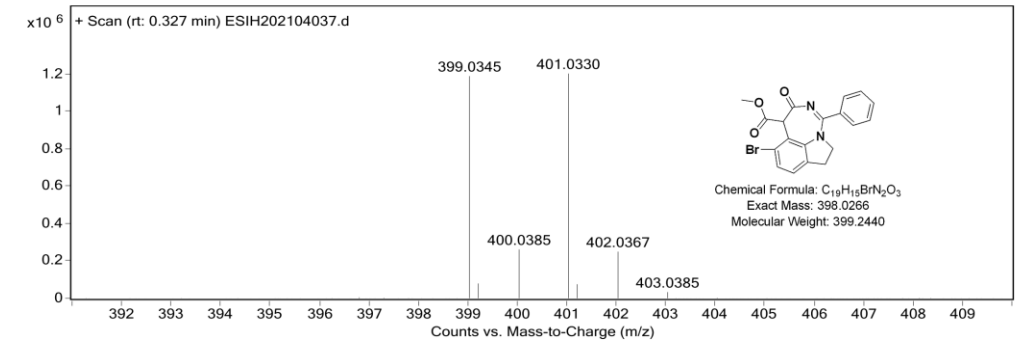
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
355.0845	355.0844	-0.09	-0.27	C19 H16 Cl N2 O3	(M+H)+

Compound 3ka

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



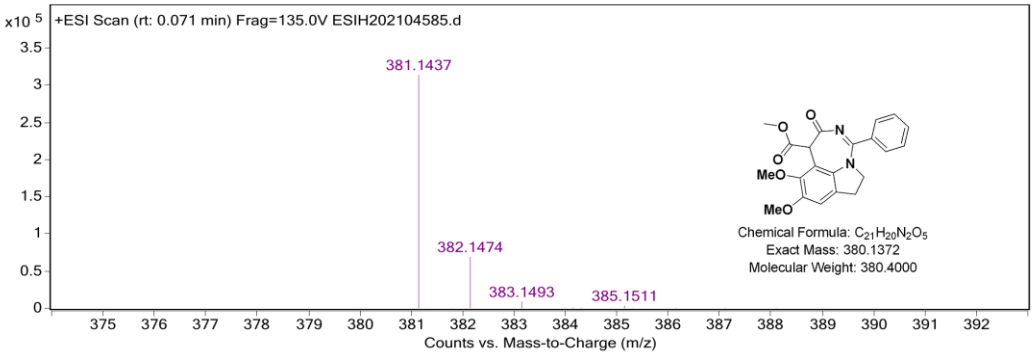
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
399.0345	399.0339	-0.63	-1.57	C19 H16 Br N2 O3	(M+H)+

Compound 3la

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



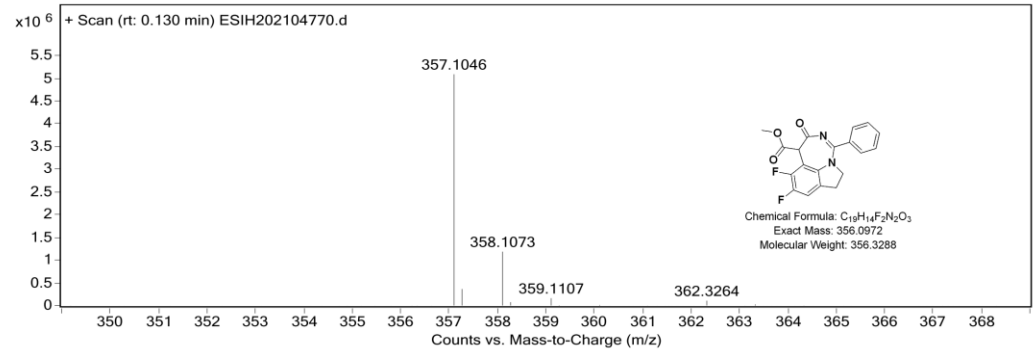
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
381.1437	381.1445	0.76	2	C21 H21 N2 O5	(M+H)+

Compound 3ma

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



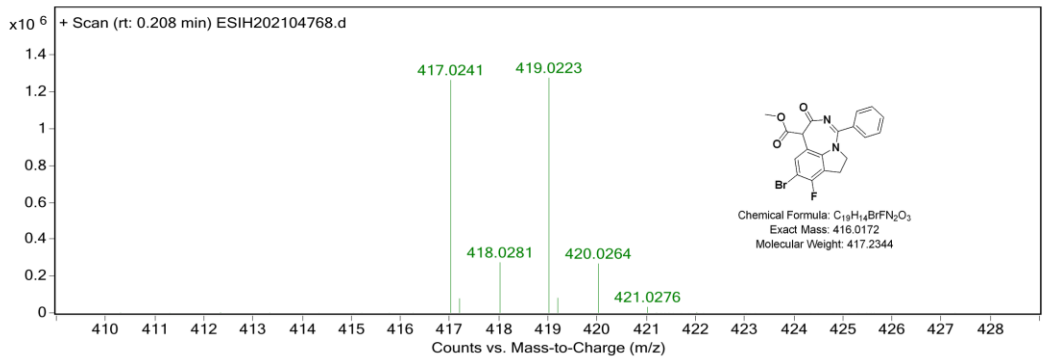
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
357.1046	357.1045	-0.08	-0.21	C19 H15 F2 N2 O3	(M+H)+

Compound 3na

User Spectra

Fragmentor Voltage 175 | Collision Energy 0 | Ionization Mode ESI



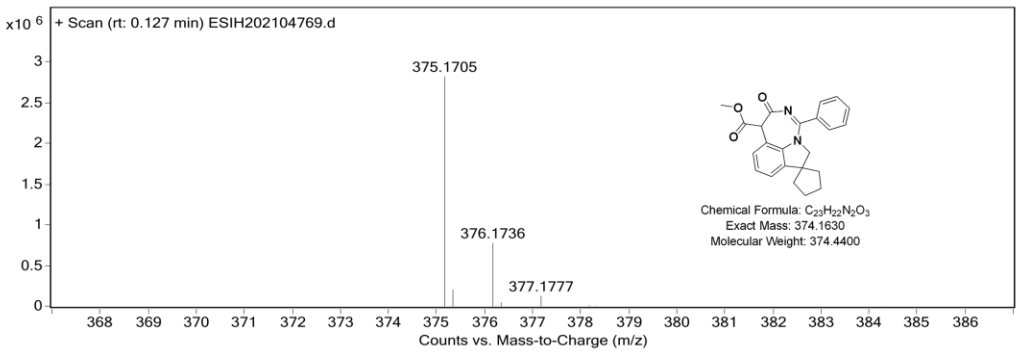
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
417.0241	417.0245	0.32	0.76	C19 H15 Br F N2 O3	(M+H)+

Compound 3oa

User Spectra

Fragmentor Voltage 175 | Collision Energy 0 | Ionization Mode ESI



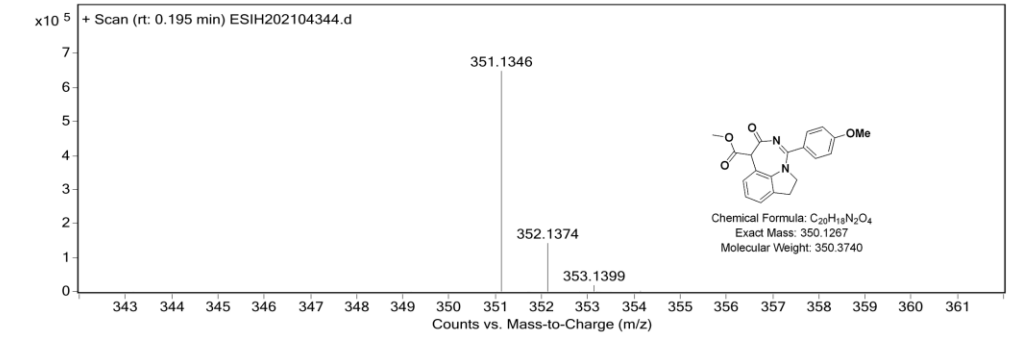
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
375.1705	375.1703	-0.16	-0.42	C23 H23 N2 O3	(M+H)+

Compound 3pa

User Spectra

Fragmentor Voltage 135 | Collision Energy 0 | Ionization Mode ESI



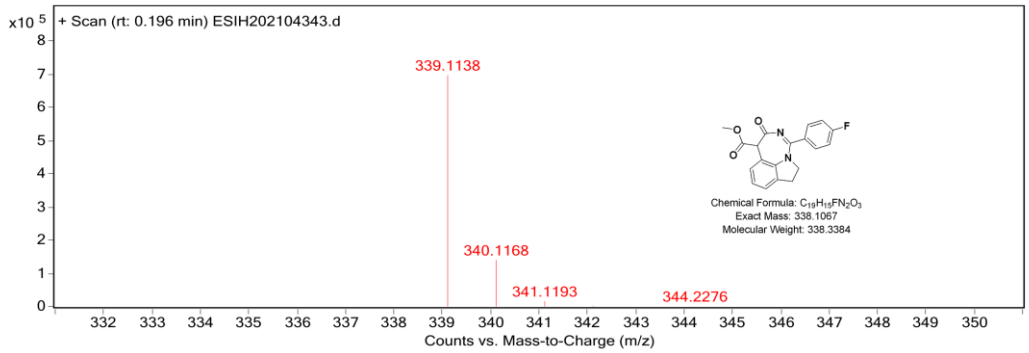
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
351.1346	351.1339	-0.63	-1.8	C20 H19 N2 O4	(M+H)+

Compound 3qa

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



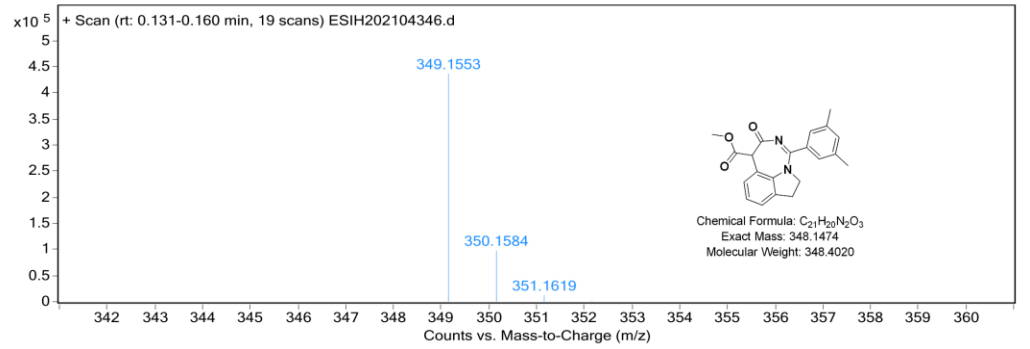
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
339.1138	339.1139	0.11	0.34	C19 H16 F N2 O3	(M+H)+

Compound 3ra

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



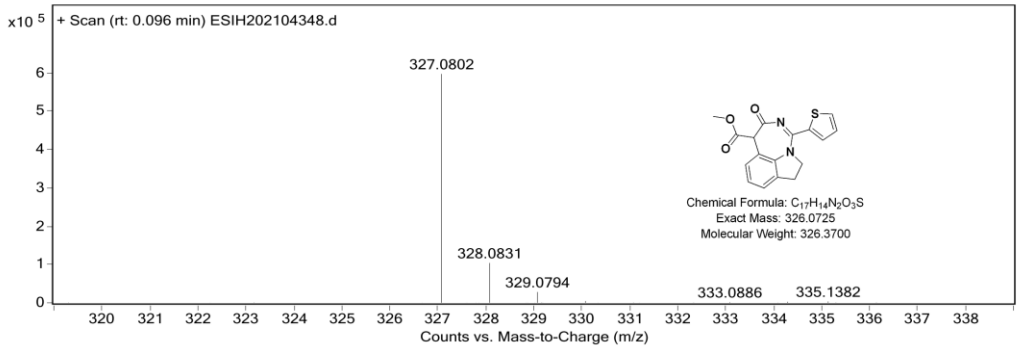
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
349.1553	349.1547	-0.6	-1.72	C21 H21 N2 O3	(M+H)+

Compound 3sa

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI

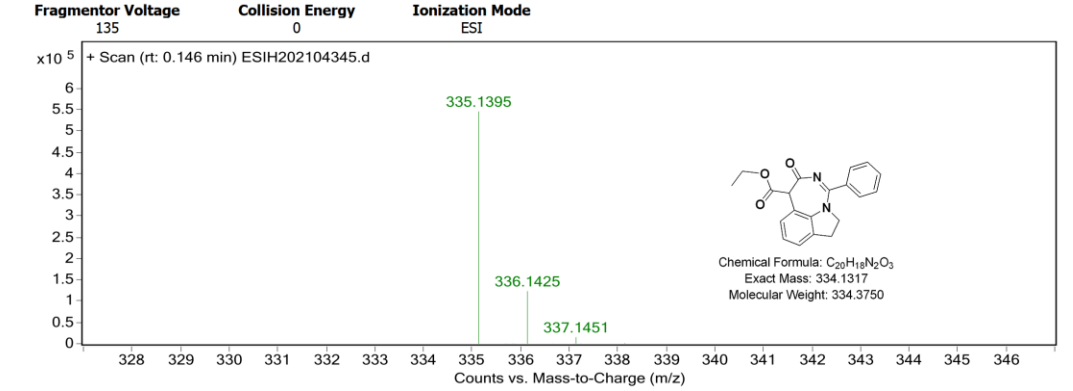


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
327.0802	327.0798	-0.46	-1.4	C17 H15 N2 O3 S	(M+H)+

Compound 3ta

User Spectra

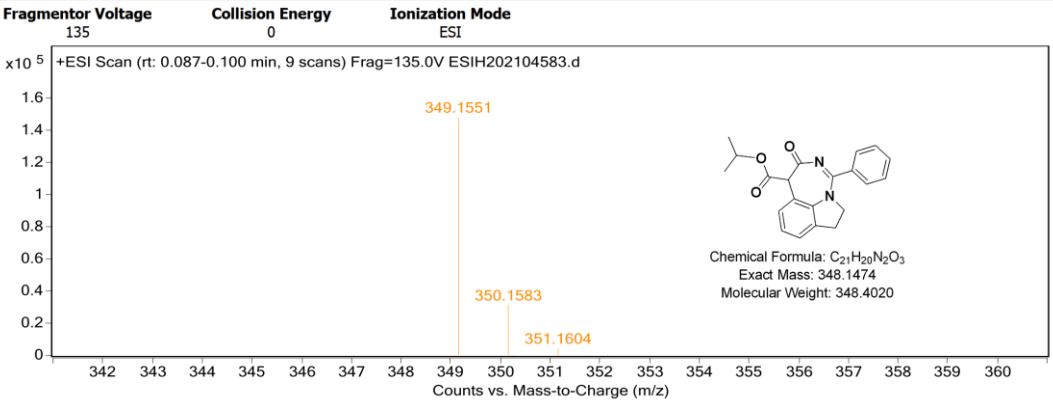


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
335.1395	335.139	-0.47	-1.4	C20 H19 N2 O3	(M+H)+

Compound 3ab

Spectra

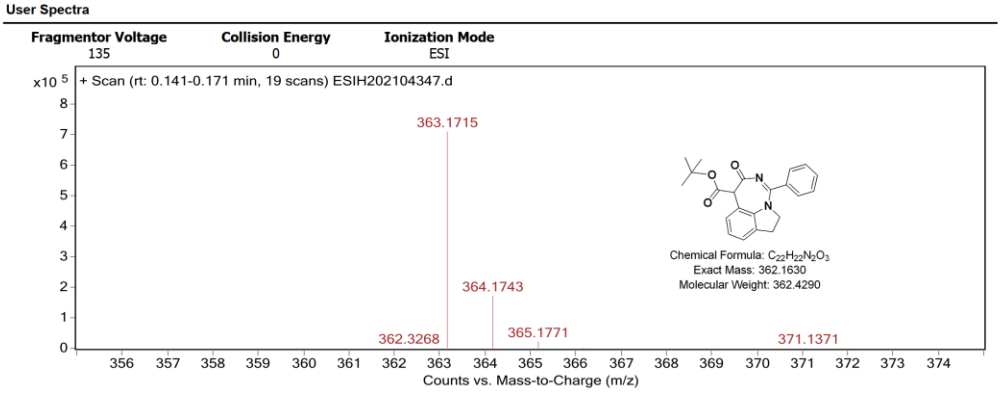


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
349.1551	349.1547	-0.42	-1.21	C21 H21 N2 O3	(M+H)+

Compound 3ac

User Spectra



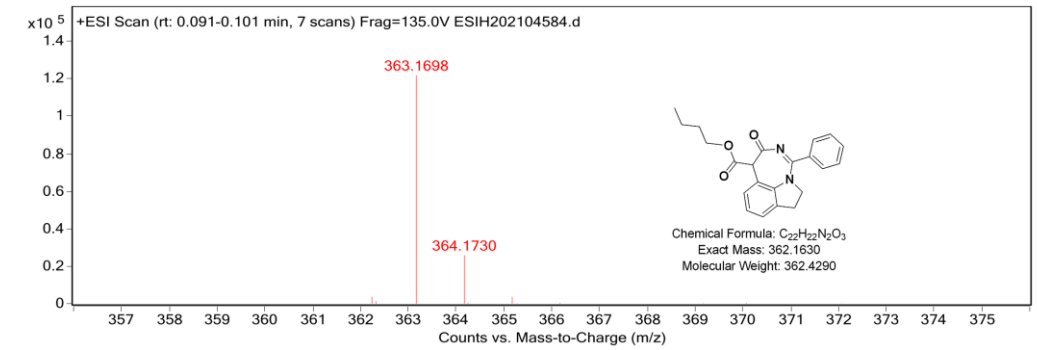
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
363.1715	363.1703	-1.17	-3.21	C22 H23 N2 O3	(M+H)+

Compound 3ad

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



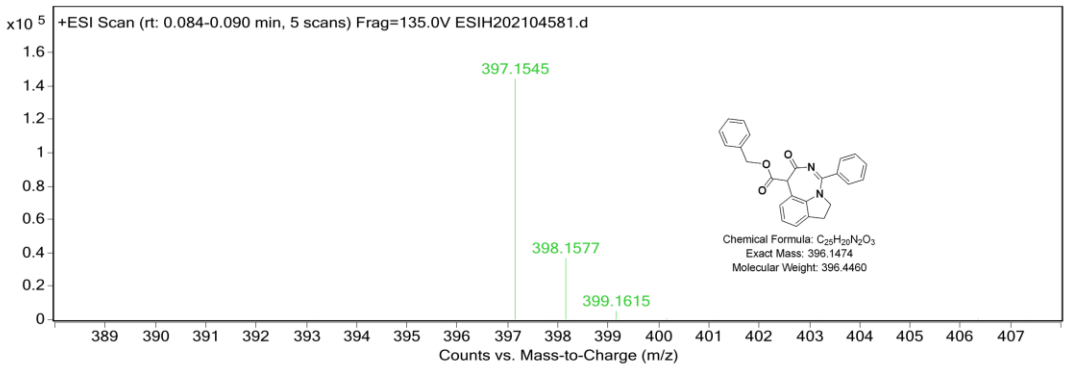
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
363.1698	363.1703	0.53	1.47	C22 H23 N2 O3	(M+H)+

Compound 3ae

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



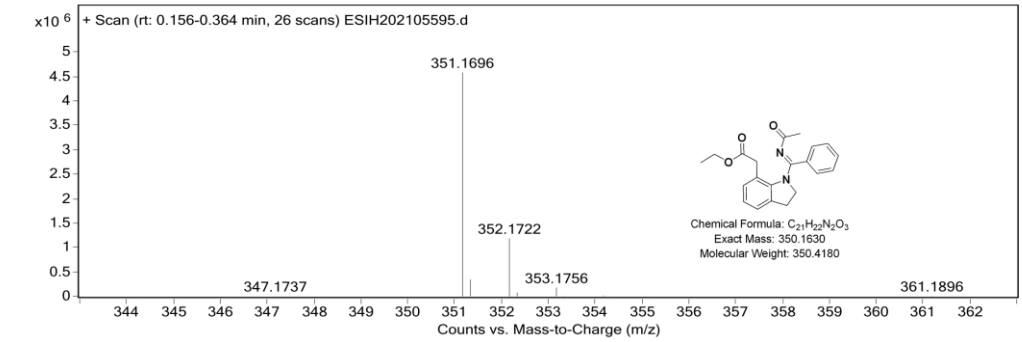
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
397.1545	397.1547	0.19	0.48	C25 H21 N2 O3	(M+H)+

Compound 3af

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



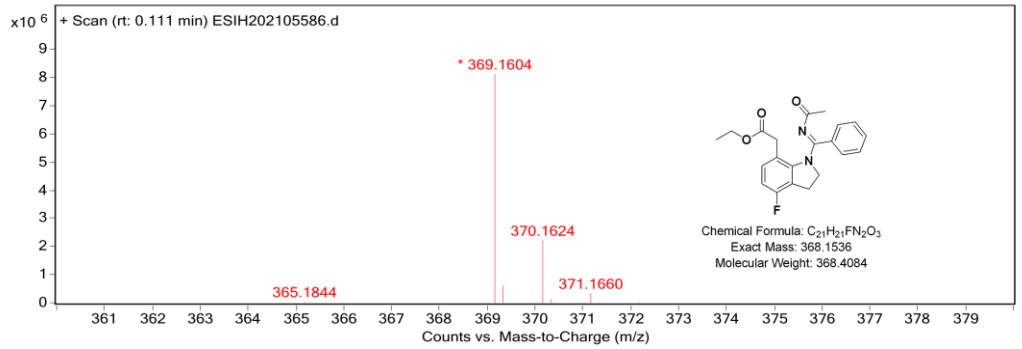
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
351.1696	351.1703	0.72	2.05	C21 H23 N2 O3	(M+H)+

Compound 5aa

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



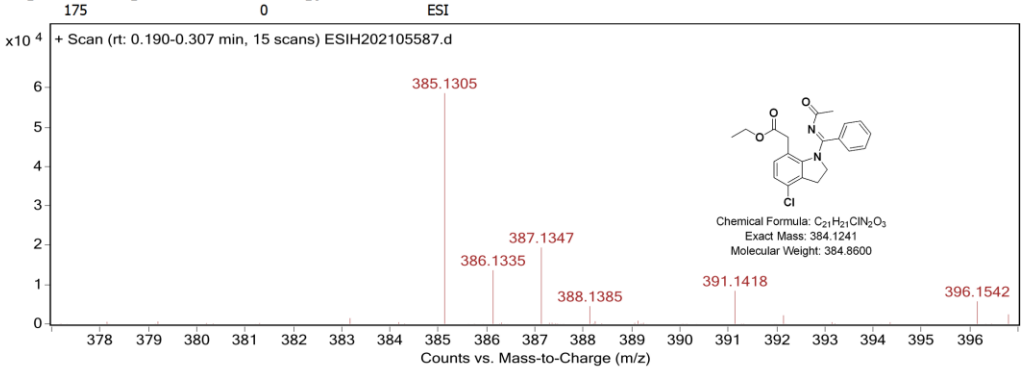
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
369.1604	369.1609	0.47	1.27	C21 H22 F N2 O3	(M+H)+

Compound 5ba

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



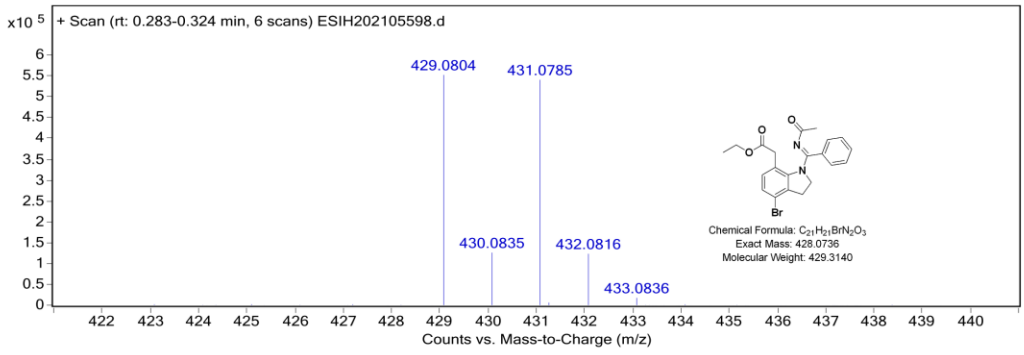
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
385.1305	385.1313	0.82	2.14	C21 H22 Cl N2 O3	(M+H)+

Compound 5ca

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



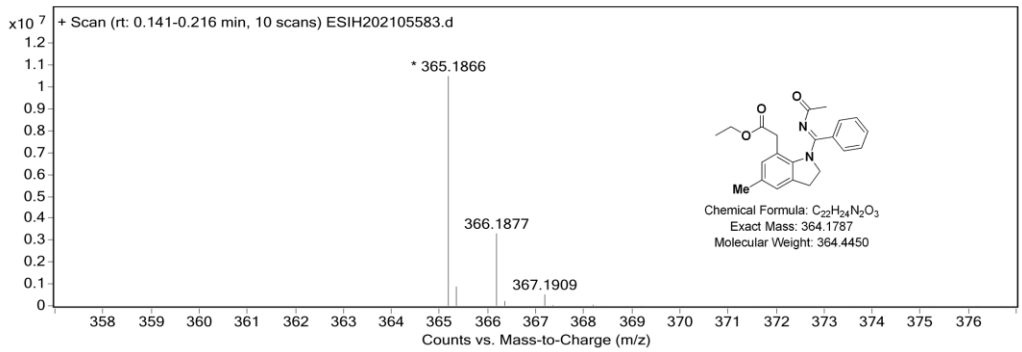
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
429.0804	429.0808	0.44	1.01	C21 H22 Br N2 O3	(M+H)+

Compound 5da

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



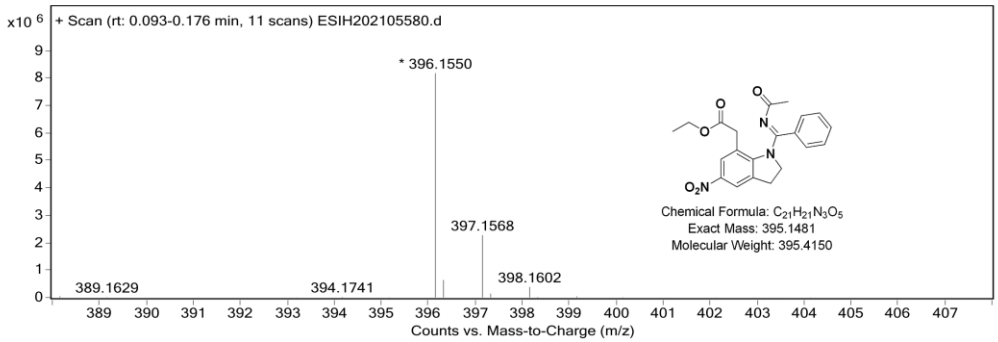
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
365.1866	365.186	-0.64	-1.74	C22 H25 N2 O3	(M+H)+

Compound 5fa

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



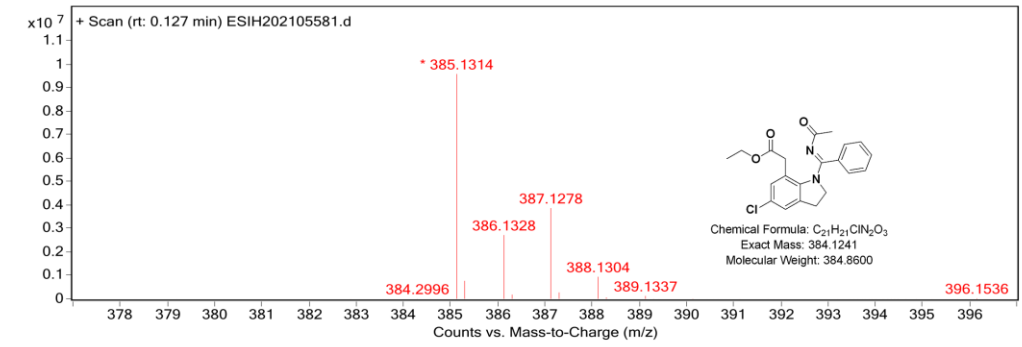
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
396.155	396.1554	0.42	1.07	C21 H22 N3 O5	(M+H)+

Compound 5ga

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



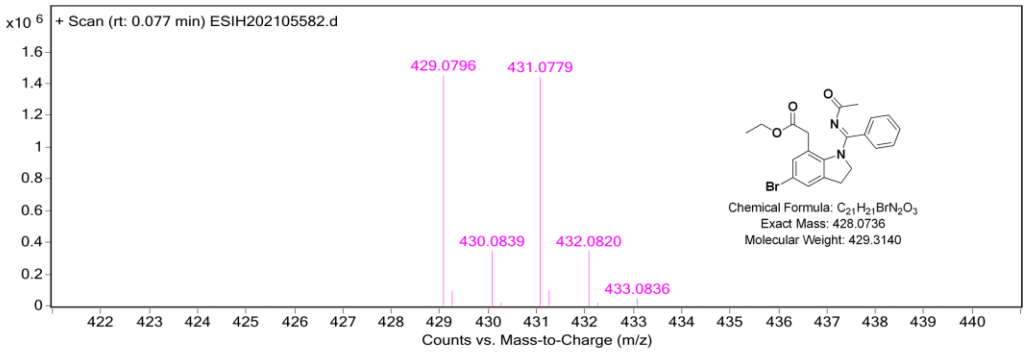
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
385.1314	385.1313	-0.09	-0.24	C21 H22 Cl N2 O3	(M+H)+

Compound 5ia

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



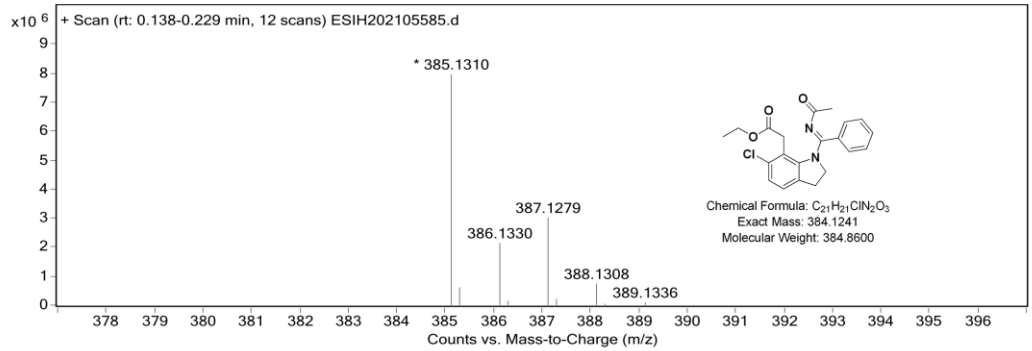
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
429.0796	429.0808	1.22	2.85	C21 H22 Br N2 O3	(M+H)+

Compound 5ja

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



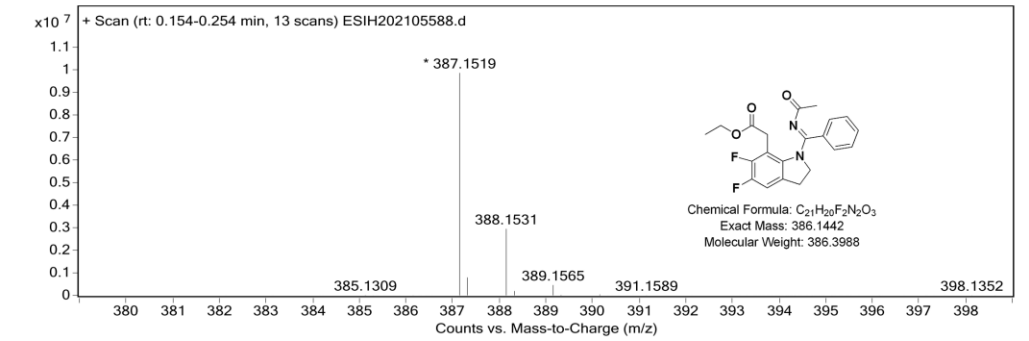
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
385.131	385.1313	0.37	0.95	C21 H22 Cl N2 O3	(M+H)+

Compound 5ka

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

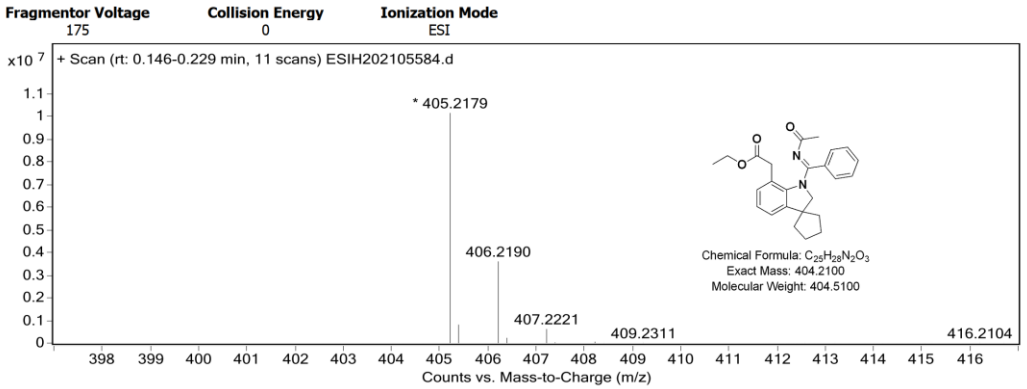


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
387.1519	387.1515	-0.39	-1	C21 H21 F2 N2 O3	(M+H)+

Compound 5na

User Spectra

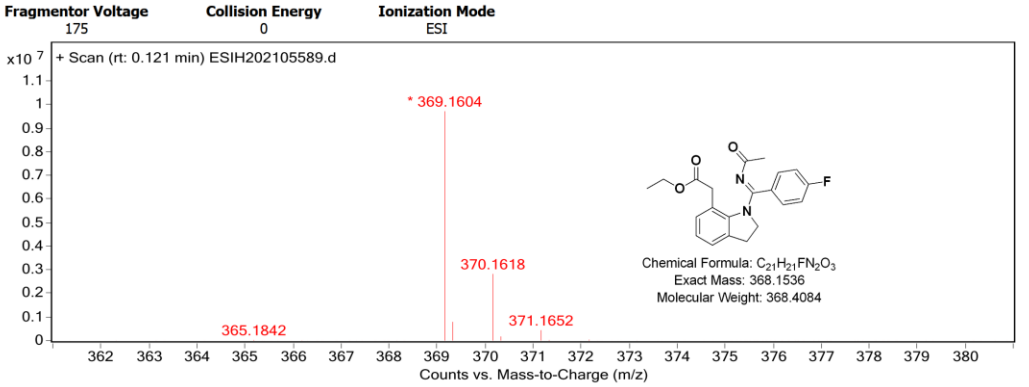


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
405.2179	405.2173	-0.62	-1.54	C25 H29 N2 O3	(M+H)+

Compound 5pa

User Spectra

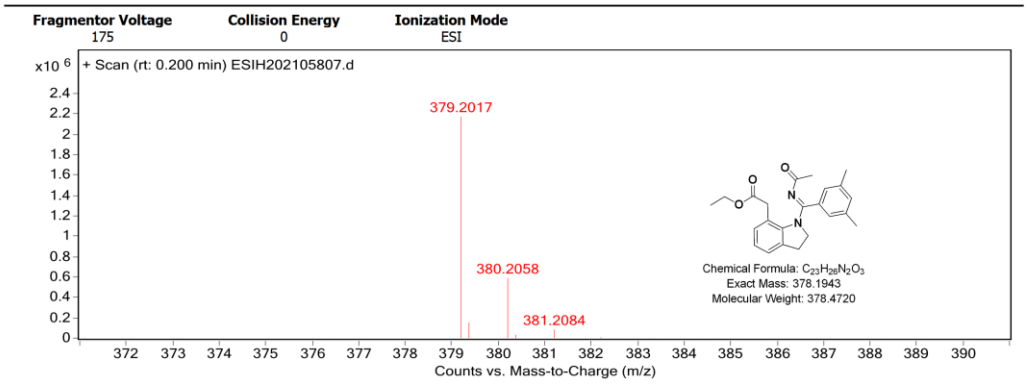


Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
369.1604	369.1609	0.46	1.26	C21 H22 F N2 O3	(M+H)+

Compound 5ra

User Spectra



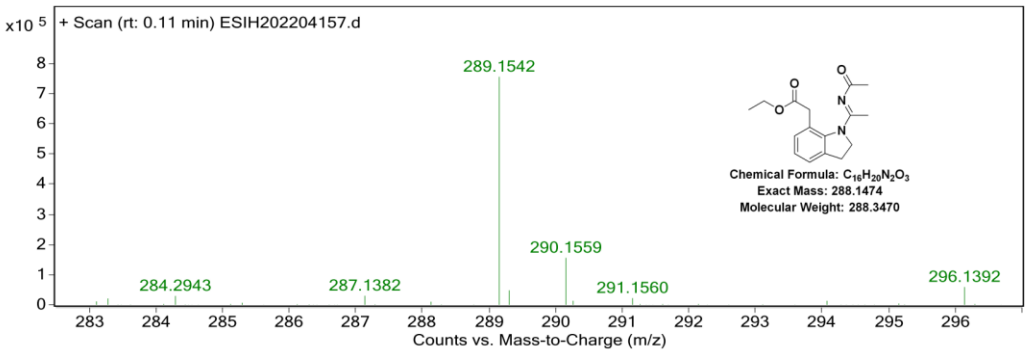
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
379.2017	379.2016	-0.09	-0.25	C23 H27 N2 O3	(M+H)+

Compound 5sa

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



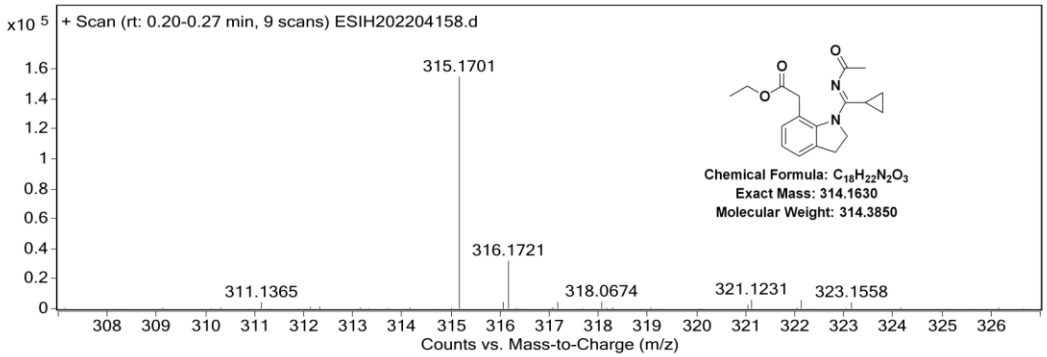
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
289.1542	289.1547	0.47	1.63	C16 H21 N2 O3	(M+H)+

Compound 5ua

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
170	0	ESI



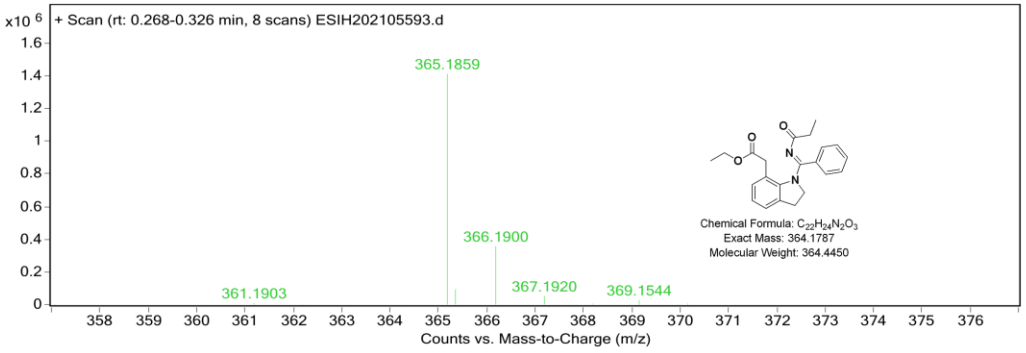
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
315.1701	315.1703	0.23	0.72	C18 H23 N2 O3	(M+H)+

Compound 5va

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



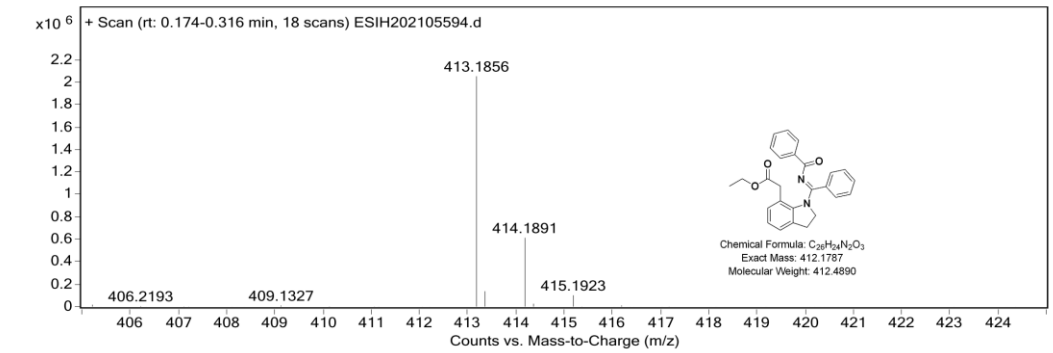
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
365.1859	365.186	0.1	0.28	C22 H25 N2 O3	(M+H)+

Compound 5ab

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



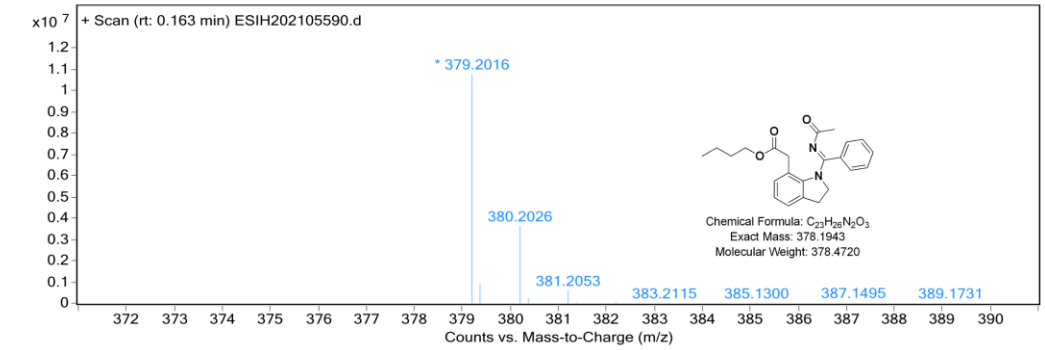
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
413.1856	413.186	0.37	0.88	C26 H25 N2 O3	(M+H)+

Compound 5ac

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



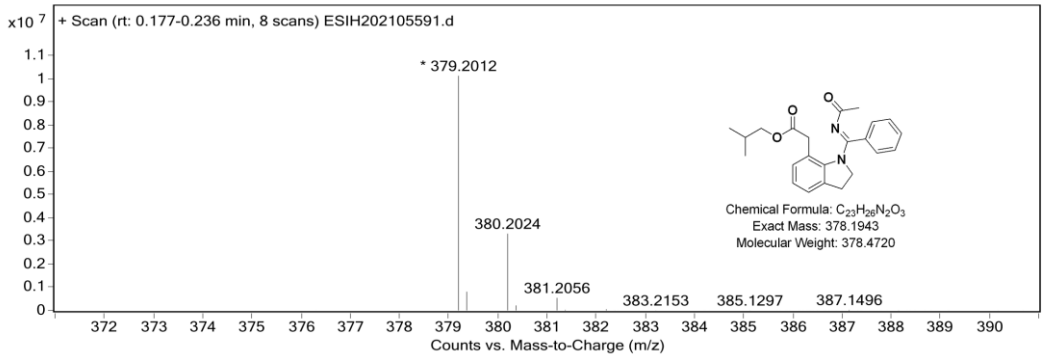
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
379.2016	379.2016	-0.01	-0.02	C23 H27 N2 O3	(M+H)+

Compound 5ad

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



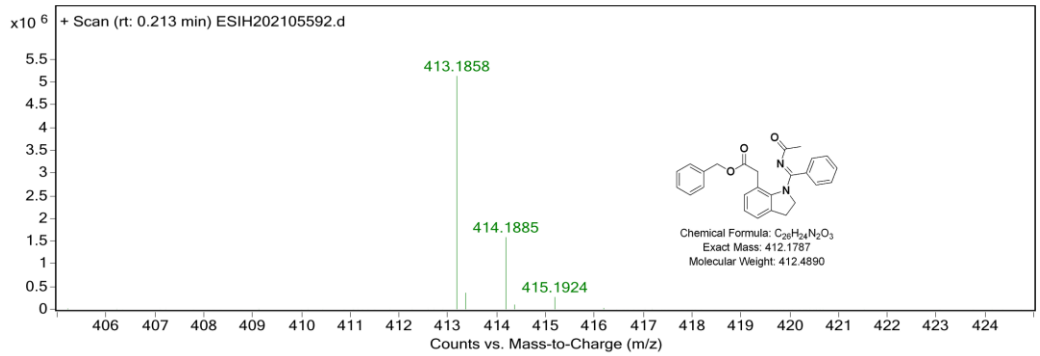
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
379.2012	379.2016	0.39	1.04	C23 H27 N2 O3	(M+H)+

Compound 5ae

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



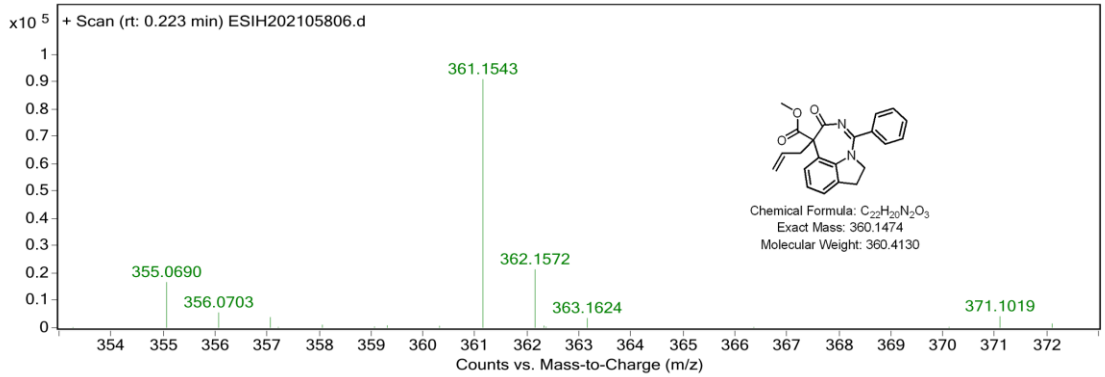
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
413.1858	413.186	0.21	0.52	C26 H25 N2 O3	(M+H)+

Compound 5af

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



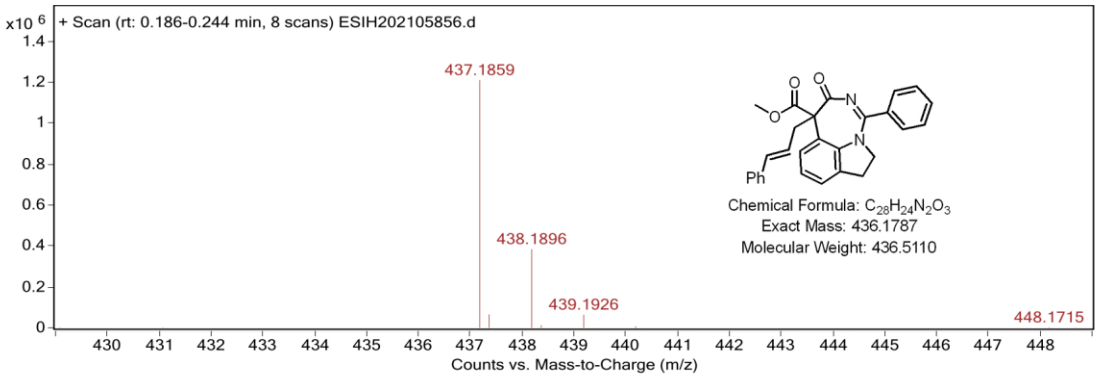
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
361.1543	361.1547	0.37	1.03	C22 H21 N2 O3	(M+H)+

Compound 6

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
437.1859	437.186	0.1	0.24	C28 H25 N2 O3	(M+H)+

Compound 7