Easy Synthesis of Imidazo[1,5-*a*]indol-3-ones through Rh(III)-Catalyzed C−H Allenylation/Annulation

Bin Zhu, Zhenyu Yao, Lang Huang, and Xiuling Cui*

Engineering Research Centre of Molecular Medicine of Ministry of Education, Key Laboratory of Fujian Molecular Medicine, Key Laboratory of Precision Medicine and Molecular Diagnosis of Fujian Universities, Key Laboratory of Xiamen Marine and Gene Drugs, School of Biomedical Sciences, Huaqiao University, Xiamen 361021, P. R. China

Corresponding Author: Xiuling Cui
Email: cuixl@hqu.edu.cn
Tel & Fax: +86-592-6162996

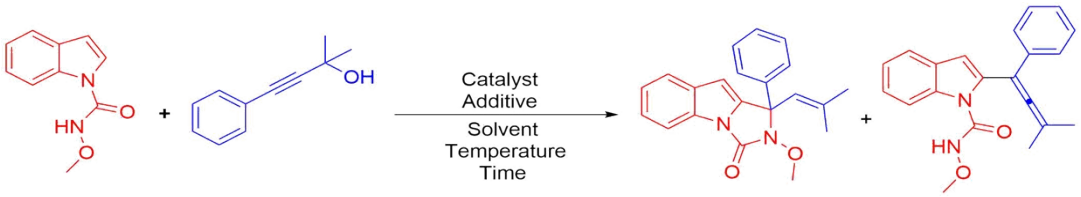
1. General information……S1
2. Optimization of the Reaction Conditions……S1
3. General procedure for the synthesis of **3**……S2
4. The scale-up reaction procedure……S2
5. General procedure for the synthesis of compounds **5** and **6**……S2
6. Mechanism Experiments……S3
7. References……S6
8. X-ray Crystallographic data of **3ka**……S7
9. Characterization of compounds **3** and **4**……S13
10. Copies of the ^{1}H, ^{13}C and ^{19}F NMR Spectra……S27

1. General information

Unless otherwise stated, all commercial materials and solvents were used directly without further purification. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400MHz, ^{13}C 100MHz, ^{19}F NMR 376 MHz), using $CDCl_3$ (spectra were referenced to the solvent peaks ^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.0 ppm) or DMSO-d_6 (spectra were referenced to the solvent peaks ^{1}H: residual DMSO-d_6 = 2.50 ppm, ^{13}C: DMSO-d_6 = 39.5 ppm) as the solvent. High-resolution mass spectra (HRMS) were measured on ESI-TOF. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluent. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Starting materials *N*-methoxycarbamoyl indoles **1**[1] and propargylic alcohols **2**[2] were prepared according to the literatures.

2. Optimization of the Reaction Conditions

Table S1 Optimization of the Reaction Conditions [a]



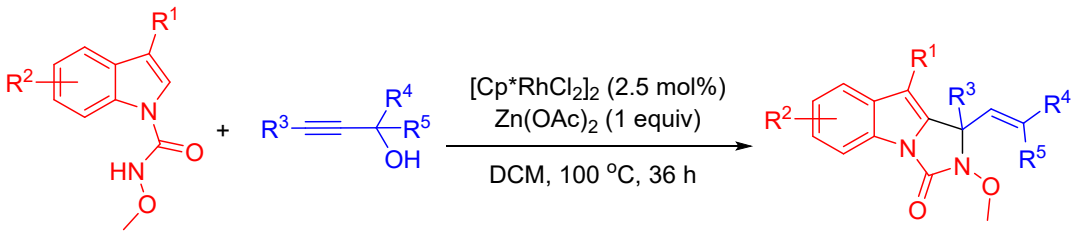
1a **2a** **3aa** **4aa**

Entry	Additive	Solvent	T (°C)	Yield [b]	
				3aa (%)	4aa (%)
1	NaOAc	DCM	100	47	
2	KOAc	DCM	100	22	
3	$Mn(OAc)_2$	DCM	100	12	
4	LiOAc	DCM	100	N.D.	N.D.
5	$Zn(OAc)_2$	DCM	100	55	9
6 [c]	$Zn(OAc)_2$	DCM	100	38	30
7 [d]	$Zn(OAc)_2$	DCM	100	30	34
8 [e]	$Zn(OAc)_2$	DCM	100	45	32
9	$Zn(OAc)_2$	DCE	100	47	
10	$Zn(OAc)_2$	Acetone	100	28	
11	$Zn(OAc)_2$	CH_3OH	100	N.D.	N.D.
12	$Zn(OAc)_2$	MeCN	100	27	
13	$Zn(OAc)_2$	Toluene	100	25	
14 [f]	$Zn(OAc)_2$	DCM	100	59	24
15 [g]	$Zn(OAc)_2$	DCM	100	71	trace
16 [h]	$Zn(OAc)_2$	DCM	100	71	trace
17 [g]	$Zn(OAc)_2$	DCM	120	72	trace
18 [g]	$Zn(OAc)_2$	DCM	80	53	21
19 [g]	$Zn(OAc)_2$	DCM	60	34	46
20 [g, i]		DCM	100	60	24
21 [j]	$Zn(OAc)_2$	DCM	100	N.D.	N.D.

22 [k]	$Zn(OAc)_2$	DCM	100	N.D.	N.D.
23 [l]	$Zn(OAc)_2$	DCM	100	N.D.	N.D.

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), additives (0.2 mmol, 1 equiv), solvent (2.0 mL), 100 °C, 12 h, sealed tube. [b] Isolated yields. [c] $Zn(OAc)_2$ (0.5 equiv). [d] $Zn(OAc)_2$ (0.2 equiv). [e] $Zn(OAc)_2$ (2 equiv). [f] 24 h. [g] 36 h. [h] 48 h. [i] $Cp^*Rh(OAc)_2$ (5 mol%). [j] $[Cp^*IrCl_2]_2$ (2.5 mol%). [k] $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%). [l] without $[Cp^*RhCl_2]_2$. N.D. = not detected.

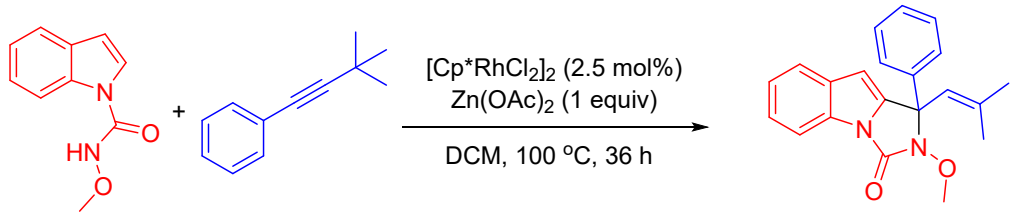
3. General procedure for the synthesis of 3



1 **2** **3**

To a tube equipped with magnetic stir bar, *N*-methoxycarbamoyl indoles (**1,** 0.2 mmol), propargyl alcohols (**2**, 0.2 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mmol%), and $Zn(OAc)_2$ (0.2 mmol, 1 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100 °C in a heating mantle for 36 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 40:1 to 30:1) as eluent to give the corresponding compounds **3**.

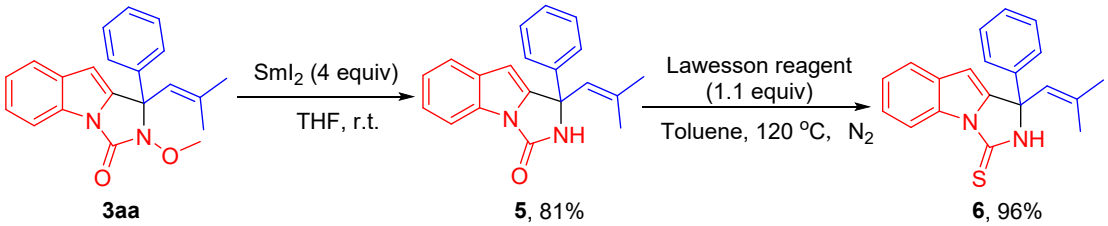
4. The scale-up reaction procedure



1a **2a** **3aa**

To a round bottle charged with magnetic stir bar, *N*-methoxycarbamoyl indoles (**1a,** 5.5 mmol), propargyl alcohols (**2a**, 5.5 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mmol%), and $Zn(OAc)_2$ (0.2 mmol, 1 equiv) were added in DCM (55.0 mL). The system was refluxed at 100 °C for 36 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 40:1 to 30:1) as eluent to give the corresponding compounds **3aa (**60%, 1.09 g).

5. General procedure for the synthesis of compounds 5 and 6



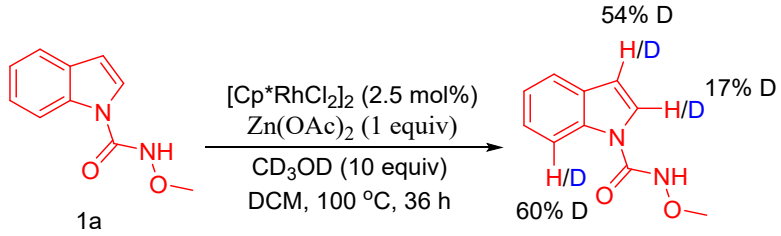
3aa **5**, 81% **6**, 96%

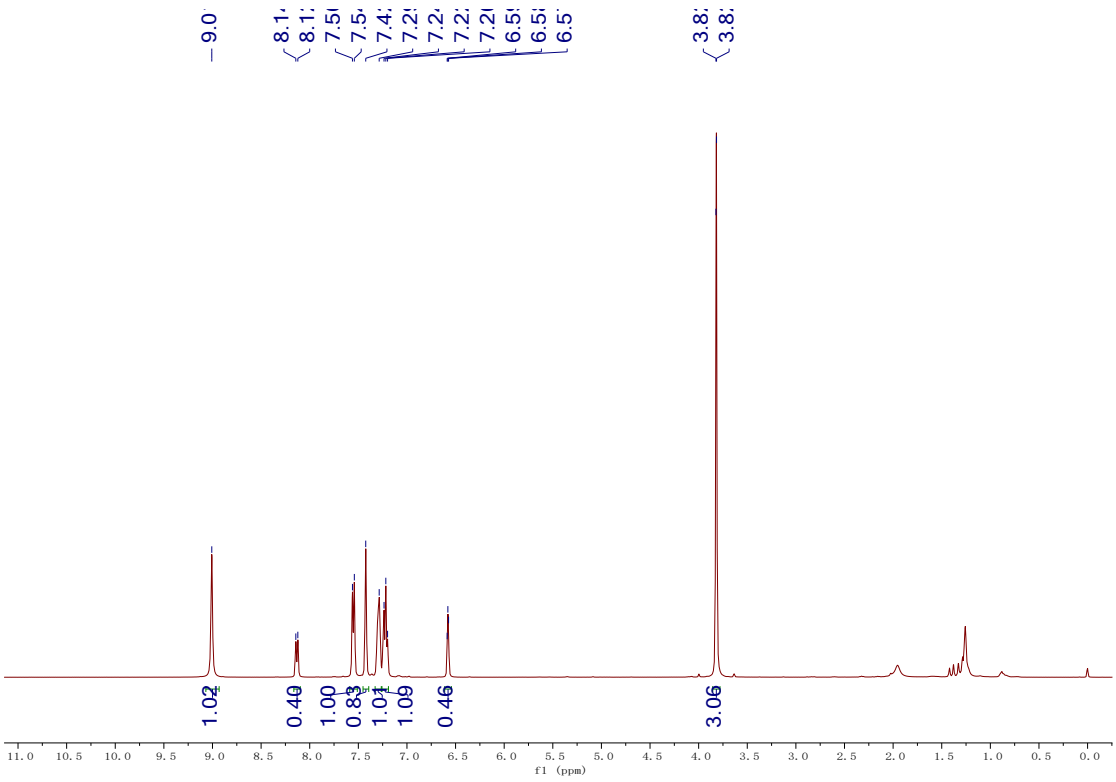
In a flame-dried round-bottom flask, 3aa (67.0 mg, 0.2 mmol, 1.0 equiv) was dissolved in dry THF (5.0 mL). SmI2-solution (0.1 M in THF, 8.0 mL, 4.0 equiv) was added dropwise at room temperature. The reaction was stirred at room temperature for 5 h under the protection of nitrogen. The solvent was removed under reduced pressure and the compound 5 was obtained as white solid (49.0 mg, 81% yield) after purification by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 30:1 to 5:1).

A mixture of 5 (30.2 mg, 0.1 mmol, 1.0 equiv), Lawesson reagent (44.5 mg, 0.11 mmol, 1.1 equiv) dissolved in 2.0 mL toluene in sealed tube was stirred vigorously at 120 ℃ in a heating mantle for 12 h under a N2 atmosphere. The solvent was removed under reduced pressure and compound 6 was obtained as white solid (30.6 mg, 96% yield) after purification by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 20:1 to 10:1).

6. Mechanism Exploration

Deuterium-Labeling Experiment: To a tube equipped with magnetic stir bar, *N*-methoxy -1*H*-indole-1-carboxamide **1a** (38.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Zn(OAc)_2$ (36.7 mg, 0.2 mmol), methanol-d_4 (10 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100 °C in a heating mantle for 36 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel to give the corresponding product **[D]-1a**. Approximately 17% deuteration at the C2 position of **1a**, 54% deuteration at the C3 position and 60% deuteration at the C7 position.



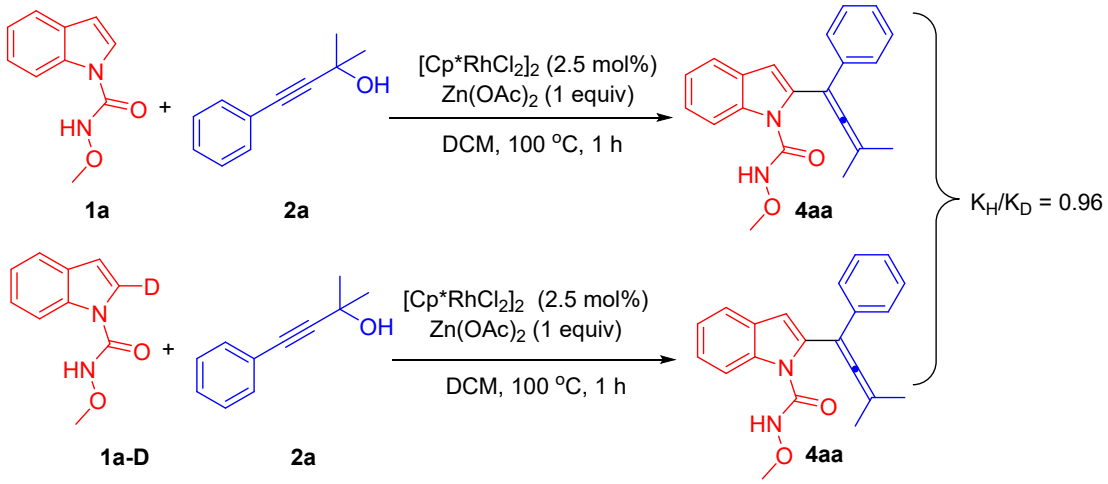


To a tube equipped with magnetic stir bar, *N*-methoxy-1*H*-indole-1-carboxamide **1a** (38.0 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), methanol-d_4 (10 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100 °C in a heating mantle for 36 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, purification was performed by flash column chromatography on silica gel to give the corresponding product **[D]-1a**. No deuteration of **1a** was observed without the $Zn(OAc)_2$.

Kinetic Isotope Effect (KIE) Study: 2-Deuterium indole was prepared according to literature,[3] and **[D]-1a** was synthesized according to the following procedure.

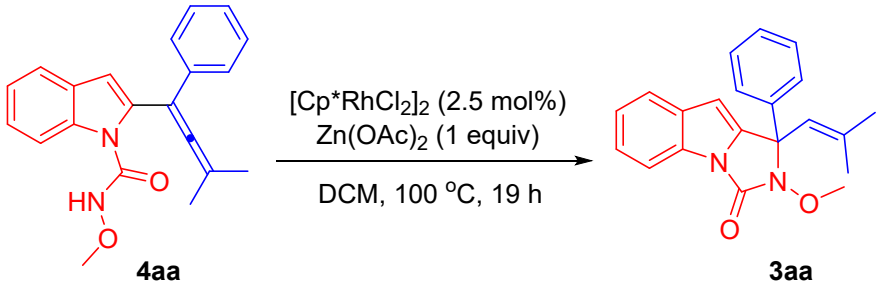
To a tube equipped with magnetic stir bar, **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mmol%), and $Zn(OAc)_2$ (0.2 mmol, 1 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100 °C in a heating mantle for 1 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the compound **4aa** was obtained as colorless oil (33.9 mg, 51% yield) after purification by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 30:1 to 5:1).

To a tube equipped with magnetic stir bar, **[D]-1a** (0.2 mmol), propargyl alcohol (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mmol%), and $Zn(OAc)_2$ (0.2 mmol, 1 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100°C in a heating mantle for 1 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the compound **4aa** was obtained as colorless oil (35.2 mg, 53% yield) after purification by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 30:1 to 5:1). An kinetic isotopic effect of this reaction was thus determined to be $k_H/k_D = 0.96$.



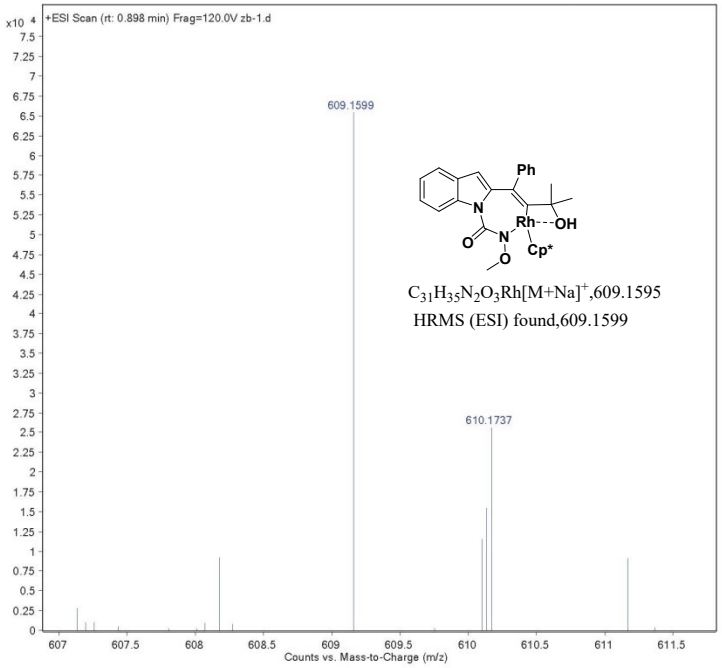
Reaction of the Intermediate

To a tube equipped with magnetic stir bar, **4aa** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mmol%), and $Zn(OAc)_2$ (0.2 mmol, 1 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100 °C in a heating mantle for 19 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the compound **3aa** was obtained as colorless oil (43.2 mg, 65% yield) after purification by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 40:1 to 30:1).



To a tube equipped with magnetic stir bar, **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mmol%), and $Zn(OAc)_2$ (0.2 mmol, 1 equiv) were added in DCM (2.0 mL). The mixture was sealed and stirred at 100 °C in a heating mantle for 0.5 h. Then, the reaction was cooled to room temperature. The reaction mixture was detected by HRMS-ESI.

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable
User Name	Unavailable	**Inj Vol**	Unavailable	**InjPosition**	Unavailable
Sample Type	Unavailable	**IRM Calibration Status**	Success	**Data Filename**	zb-1.d
ACQ Method		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



$C_{31}H_{35}N_2O_3Rh[M+Na]^+$,609.1595

HRMS (ESI) found,609.1599

7.References

(1) W. J. Kong, X. Chen, M. Wang, H. X. Dai, J. Q. Yu, *Org. Lett*. 2018, **20**, 284-287.

(2) Z. Jiao, Q. Shi, Steve Zhou, J. *Angew. Chem., Int. Ed*. 2017, **56**, 14567-14571.

(3) C. S. Sevov, J. F. *J.* Hartwig, *Am. Chem. Soc*. 2013, **135**, 2116-2119.

8.X-ray data of compound 3ka:

Single crystal suitable for X-ray diffraction experiment were obtained by slow evaporation of DCM/*n*-hexane (1:10, V/V) solution containing the compound **3aa.**

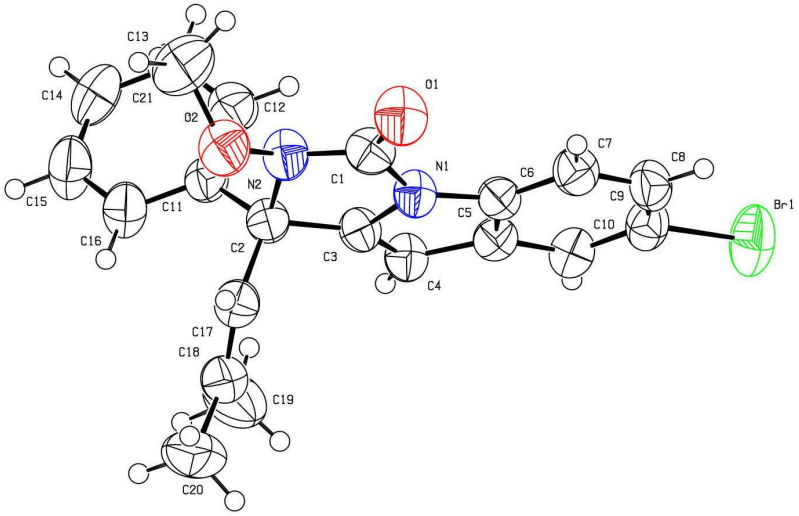


Figure S1. X-ray molecular structure of 3aa with the probability at 50% level.

Table S2 Crystal data and structure refinement for **3ka**.

Identification code	3ka
Empirical formula	$C_{21}H_{19}BrN_2O_2$
Formula weight	411.29
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.6120(5)
b/Å	10.8082(10)
c/Å	12.5550(7)
α/°	85.011(6)
β/°	73.475(6)
γ/°	79.776(7)
Volume/Å^3	973.80(13)
Z	2
ρ_{calc}g/cm^3	1.403
μ/mm^{-1}	3.010
F(000)	420.0
Crystal size/mm^3	0.16 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.35 to 134.158
Index ranges	-9 ≤ h ≤ 7, -12 ≤ k ≤ 12, -14 ≤ l ≤ 9
Reflections collected	6968
Independent reflections	3451 [R_{int} = 0.0277, R_{sigma} = 0.0402]

Data/restraints/parameters	3451/0/238
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1018
Final R indexes [all data]	R_1 = 0.0661, wR_2 = 0.1155
Largest diff. peak/hole / e $Å^{-3}$	0.65/-0.56

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ka. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	5421.7(7)	7966.6(5)	4593.1(4)	87.4(2)
C1	11224(4)	4135(3)	7624(3)	53.3(8)
C2	9310(4)	2513(3)	8298(3)	47.4(8)
C3	8485(4)	3511(3)	7562(3)	45.7(7)
C4	6965(4)	3885(3)	7206(3)	49.2(8)
C5	7269(4)	5012(3)	6520(3)	47.3(7)
C6	9007(4)	5291(3)	6503(3)	46.9(7)
C7	9726(5)	6328(3)	5921(3)	55.9(9)
C8	8625(5)	7103(3)	5348(3)	60.4(9)
C9	6908(5)	6839(3)	5369(3)	56.8(9)
C10	6193(5)	5809(3)	5932(3)	53.0(8)
C11	7991(4)	2331(3)	9453(3)	49.0(8)
C12	7032(6)	3379(4)	10035(3)	66.8(10)
C13	5910(6)	3260(4)	11117(3)	77.6(12)
C14	5727(6)	2093(5)	11600(3)	80.0(13)
C15	6651(6)	1053(4)	11022(3)	80.0(13)
C16	7790(5)	1166(4)	9951(3)	64.3(10)
C17	10231(5)	1327(3)	7672(3)	53.8(8)
C18	9479(6)	542(4)	7271(3)	64.0(10)
C19	7450(7)	635(4)	7397(5)	96.6(16)
C20	10685(7)	-586(4)	6653(4)	98.8(16)
C21	12257(7)	2794(5)	9826(4)	104.4(17)
N1	9747(3)	4346(3)	7145(2)	48.1(6)
N2	10783(4)	3204(3)	8428(2)	54.9(7)
O1	12518(3)	4692(3)	7409(2)	70.1(7)
O2	12273(3)	2473(2)	8742(2)	69.5(7)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3ka**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	78.6(3)	89.3(4)	79.4(3)	26.2(3)	-19.8(2)	8.6(2)

C1	42.5(18)	58(2)	64(2)	-3.7(17)	-17.1(16)	-13.0(16)
C2	45.2(18)	47.5(19)	54.2(19)	2.0(15)	-20.1(15)	-11.0(14)
C3	42.0(17)	45.1(18)	49.5(18)	1.6(14)	-9.9(14)	-11.9(14)
C4	40.7(17)	53(2)	55.8(19)	5.6(15)	-14.3(15)	-13.7(15)
C5	42.4(17)	52.0(19)	44.6(17)	-3.7(15)	-8.2(14)	-5.3(14)
C6	47.4(18)	44.7(18)	47.6(18)	-2.1(14)	-11.1(14)	-7.8(14)
C7	54(2)	58(2)	55(2)	2.7(17)	-10.8(16)	-16.3(17)
C8	71(2)	51(2)	53(2)	7.0(16)	-7.7(18)	-12.8(18)
C9	55(2)	57(2)	50.2(19)	3.0(16)	-10.8(16)	3.9(17)
C10	43.0(18)	62(2)	51.6(19)	2.3(17)	-11.7(15)	-5.9(16)
C11	46.7(18)	52(2)	52.2(19)	1.3(16)	-19.4(15)	-9.1(15)
C12	78(3)	58(2)	63(2)	-2.1(19)	-13(2)	-18(2)
C13	86(3)	84(3)	58(2)	-20(2)	-7(2)	-14(2)
C14	81(3)	105(4)	48(2)	14(2)	-12(2)	-19(3)
C15	90(3)	73(3)	67(3)	22(2)	-16(2)	-8(2)
C16	66(2)	61(2)	59(2)	9.6(18)	-13.6(18)	-2.8(18)
C17	50.6(19)	55(2)	51.8(19)	-1.2(16)	-11.5(16)	-2.6(16)
C18	79(3)	54(2)	64(2)	-2.1(18)	-29(2)	-6.4(19)
C19	101(4)	74(3)	141(4)	-7(3)	-67(3)	-25(3)
C20	129(4)	74(3)	97(4)	-33(3)	-40(3)	3(3)
C21	120(4)	119(4)	104(4)	3(3)	-78(3)	-22(3)
N1	40.0(14)	52.2(16)	54.0(16)	6.0(13)	-13.7(12)	-14.5(12)
N2	44.5(15)	59.8(18)	67.7(18)	8.3(14)	-26.7(14)	-14.2(13)
O1	50.3(14)	80.4(18)	88.4(19)	12.6(15)	-26.3(13)	-29.3(14)
O2	59.4(15)	71.1(17)	89.1(19)	5.7(14)	-42.0(14)	-8.2(13)

Table S5 Bond Lengths for **3ka**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	C9	1.909(3)	C7	C8	1.382(5)
C1	N1	1.396(4)	C8	C9	1.380(5)
C1	N2	1.376(4)	C9	C10	1.376(5)
C1	O1	1.199(4)	C11	C12	1.377(5)
C2	C3	1.526(4)	C11	C16	1.370(5)
C2	C11	1.530(4)	C12	C13	1.393(5)
C2	C17	1.515(5)	C13	C14	1.363(6)
C2	N2	1.505(4)	C14	C15	1.363(6)

C3	C4	1.341(4)	C15	C16	1.386(5)
C3	N1	1.397(4)	C17	C18	1.309(5)
C4	C5	1.443(4)	C18	C19	1.492(6)
C5	C6	1.402(4)	C18	C20	1.514(5)
C5	C10	1.393(4)	C21	O2	1.430(5)
C6	C7	1.391(4)	N2	O2	1.396(3)
C6	N1	1.386(4)			

Table S6 Bond Angles for **3ka**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N2	C1	N1	104.0(3)	C10	C9	Br1	117.9(3)
O1	C1	N1	127.0(3)	C10	C9	C8	123.5(3)
O1	C1	N2	128.9(3)	C9	C10	C5	117.4(3)
C3	C2	C11	113.6(3)	C12	C11	C2	118.8(3)
C17	C2	C3	111.1(3)	C16	C11	C2	122.5(3)
C17	C2	C11	116.1(3)	C16	C11	C12	118.6(3)
N2	C2	C3	97.2(2)	C11	C12	C13	120.8(4)
N2	C2	C11	107.8(3)	C14	C13	C12	119.7(4)
N2	C2	C17	109.1(3)	C15	C14	C13	119.7(4)
C4	C3	C2	142.3(3)	C14	C15	C16	120.7(4)
C4	C3	N1	109.7(3)	C11	C16	C15	120.3(4)
N1	C3	C2	107.9(3)	C18	C17	C2	129.0(3)
C3	C4	C5	106.6(3)	C17	C18	C19	125.0(4)
C6	C5	C4	108.4(3)	C17	C18	C20	120.0(4)
C10	C5	C4	132.7(3)	C19	C18	C20	115.0(4)
C10	C5	C6	118.9(3)	C1	N1	C3	112.8(3)
C7	C6	C5	123.3(3)	C6	N1	C1	136.8(3)
N1	C6	C5	105.9(3)	C6	N1	C3	109.3(3)
N1	C6	C7	130.8(3)	C1	N2	C2	114.3(3)
C8	C7	C6	116.5(3)	C1	N2	O2	116.0(3)
C9	C8	C7	120.4(3)	O2	N2	C2	116.4(3)
C8	C9	Br1	118.6(3)	N2	O2	C21	109.8(3)

Table S7 Torsion Angles for **3ka**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Br1	C9	C10	C5	-178.3(2)	C10	C5	C6	N1	-179.7(3)

C1	N2	O2	C21	107.3(4)	C11	C2	C3	C4	-48.5(6)
C2	C3	C4	C5	177.5(4)	C11	C2	C3	N1	128.7(3)
C2	C3	N1	C1	-8.0(4)	C11	C2	C17	C18	66.9(5)
C2	C3	N1	C6	-177.9(3)	C11	C2	N2	C1	-137.8(3)
C2	C11	C12	C13	-175.8(3)	C11	C2	N2	O2	82.8(3)
C2	C11	C16	C15	176.6(3)	C11	C12	C13	C14	-1.3(6)
C2	C17	C18	C19	-2.8(6)	C12	C11	C16	C15	-0.4(6)
C2	C17	C18	C20	179.2(4)	C12	C13	C14	C15	0.3(7)
C2	N2	O2	C21	-114.0(4)	C13	C14	C15	C16	0.6(7)
C3	C2	C11	C12	-45.6(4)	C14	C15	C16	C11	-0.5(7)
C3	C2	C11	C16	137.5(3)	C16	C11	C12	C13	1.3(6)
C3	C2	C17	C18	-65.0(5)	C17	C2	C3	C4	84.7(6)
C3	C2	N2	C1	-20.1(4)	C17	C2	C3	N1	-98.1(3)
C3	C2	N2	O2	-159.5(3)	C17	C2	C11	C12	-176.3(3)
C3	C4	C5	C6	-0.9(4)	C17	C2	C11	C16	6.7(5)
C3	C4	C5	C10	180.0(4)	C17	C2	N2	C1	95.3(3)
C4	C3	N1	C1	170.2(3)	C17	C2	N2	O2	-44.2(4)
C4	C3	N1	C6	0.3(4)	N1	C1	N2	C2	16.5(4)
C4	C5	C6	C7	-179.6(3)	N1	C1	N2	O2	156.1(3)
C4	C5	C6	N1	1.0(4)	N1	C3	C4	C5	0.4(4)
C4	C5	C10	C9	178.7(3)	N1	C6	C7	C8	179.7(3)
C5	C6	C7	C8	0.4(5)	N2	C1	N1	C3	-4.8(4)
C5	C6	N1	C1	-167.2(4)	N2	C1	N1	C6	161.3(4)
C5	C6	N1	C3	-0.8(4)	N2	C2	C3	C4	-161.5(5)
C6	C5	C10	C9	-0.4(5)	N2	C2	C3	N1	15.6(3)
C6	C7	C8	C9	0.1(5)	N2	C2	C11	C12	60.9(4)
C7	C6	N1	C1	13.5(6)	N2	C2	C11	C16	-116.1(4)
C7	C6	N1	C3	179.9(3)	N2	C2	C17	C18	-171.1(3)
C7	C8	C9	Br1	178.4(3)	O1	C1	N1	C3	178.5(4)
C7	C8	C9	C10	-0.8(6)	O1	C1	N1	C6	-15.5(7)
C8	C9	C10	C5	0.9(5)	O1	C1	N2	C2	-166.8(4)
C10	C5	C6	C7	-0.3(5)	O1	C1	N2	O2	-27.2(6)

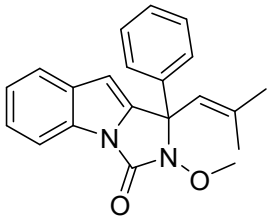
Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3ka**.

Atom	***x***	***y***	***z***	**U(eq)**
H4	5920	3495	7369	59
H7	10886	6490	5919	67
H8	9045	7808	4946	72
H10	5036	5651	5921	64

H12	7136	4175	9702	80
H13	5287	3974	11508	93
H14	4974	2008	12321	96
H15	6516	257	11351	96
H16	8421	448	9569	77
H17	11509	1129	7557	65
H19A	7038	-128	7747	145
H19B	7225	760	6678	145
H19C	6783	1332	7848	145
H20A	11962	-567	6604	148
H20B	10530	-560	5919	148
H20C	10327	-1344	7046	148
H21A	12438	3654	9807	157
H21B	13237	2254	10058	157
H21C	11085	2692	10342	157

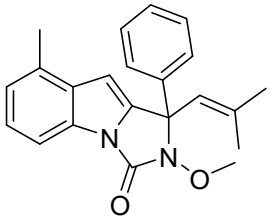
9.Characterization data for products (3aa-3ta, 3ab-3aq, 4aa-4ba, 5, 6)

2-Methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3aa)



Yellow oil. 47.2 mg, Yield: 71%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.37 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 6.33 (s, 1H), 5.92 (s, 1H), 3.70 (s, 3H), 1.83 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 140.6, 140.4, 139.7, 132.5, 130.8, 128.6, 128.4, 127.5, 123.7, 123.2, 123.1, 121.2, 113.0, 99.3, 69.6, 65.5, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}N_2O_2$ $[M + H]^+$ 333.1598, found 333.1598.

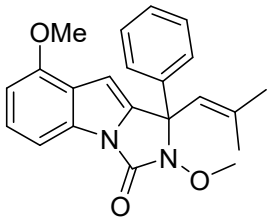
2-Methoxy-8-methyl-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ba)



White solid. 40.9 mg, Yield: 59%, mp 141-142 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.40 – 7.29 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.34 (s, 1H), 5.92 (s, 1H), 3.70 (s, 3H), 2.51 (s, 3H), 1.83 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 140.6, 139.8, 139.8, 132.2, 130.7, 130.5, 128.6, 128.4, 127.5, 123.8, 123.5, 123.2, 110.4, 97.7, 69.6, 65.4, 26.6, 20.4, 18.7. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + H]^+$ 347.1754, found 347.1752.

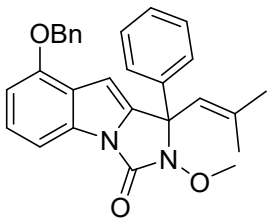
2,8-Dimethoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ca)



Yellow solid. 46.4 mg, Yield: 64%, mp 163-164 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.36 – 7.31 (m, 3H), 7.25 (t, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 5.92 (s, 1H), 3.92 (s, 3H), 3.69 (s, 3H), 1.81 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 151.1, 140.5, 139.7, 138.7, 131.9, 128.6, 128.4, 127.6, 124.9, 123.4, 122.7, 106.1, 103.4, 96.6, 69.7, 65.5, 55.4, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_3$ $[M + H]^+$ 363.1703, found 363.1704.

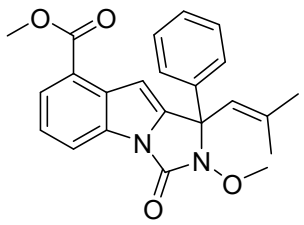
8-(Benzyloxy)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3da)



Yellow solid. 61.5 mg, Yield: 70%, mp 187-188 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:20;

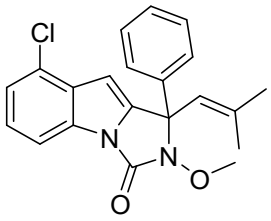
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.2, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.40-7.29 (m, 6H), 7.26 – 7.21 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.49 (s, 1H), 5.91 (s, 1H), 5.17 (s, 2H), 3.70 (s, 3H), 1.81 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 151.1, 140.5, 139.7, 138.7, 136.9, 132.0, 128.5, 128.5, 128.3, 127.9, 127.4, 124.7, 123.2, 123.0, 106.3, 104.7, 96.7, 70.1, 69.6, 65.4, 26.5, 20.4. HRMS (ESI) *m/z* calcd for $C_{28}H_{26}N_2O_3$ $[M + Na]^+$ 461.1836, found 461.1833.

Methyl-2-methoxy-1-(2-methylprop-1-en-1-yl)-3-oxo-1-phenyl-2,3-dihydro-1*H*-imidazo[1,5-*a*]indole-8-carboxylate (3ea)



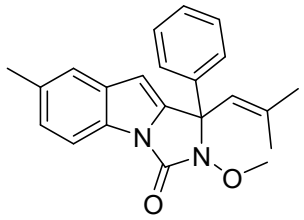
Yellow oil. 34.4 mg, Yield: 44%, column chromatography eluent, EtOAc/PE = 1:40 → 1:20;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.40-7.34 (m, 4H), 7.08 (s, 1H), 5.92 (s, 1H), 3.95 (s, 3H), 3.72 (s, 3H), 1.84 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 150.6, 142.3, 141.2, 139.2, 132.5, 131.4, 128.7, 128.5, 127.4, 125.8, 123.0, 122.8, 122.2, 117.4, 100.2, 69.8, 65.5, 51.9, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}N_2O_4$ $[M + H]^+$ 391.1652, found 391.1649.

8-Chloro-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3fa)



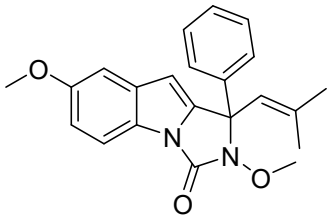
Yellow solid. 34.4 mg, Yield: 47%, mp 148-150 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:20;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.40 – 7.33 (m, 3H), 7.25 – 7.22 (m, 2H), 6.46 (s, 1H), 5.91 (s, 1H), 3.71 (s, 3H), 1.84 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 141.1, 140.9, 139.2, 131.3, 131.2, 128.7, 128.5, 127.4, 126.2, 124.5, 122.9, 122.8, 111.4, 97.5, 69.7, 65.5, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN_2O_2$ $[M + H]^+$ 367.1208, found 367.1206.

2-Methoxy-7-methyl-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ga)



Yellow oil. 43.6 mg, Yield: 63%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.36 – 7.30 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.24 (s, 1H), 5.92 (s, 1H), 3.69 (s, 3H), 2.43 (s, 3H), 1.81 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 140.4, 140.4, 139.7, 132.8, 132.6, 128.9, 128.5, 128.3, 127.4, 125.0, 123.2, 121.0, 112.4, 98.9, 69.5, 65.3, 26.5, 21.4, 20.2. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + H]^+$ 347.1754, found 347.1754.

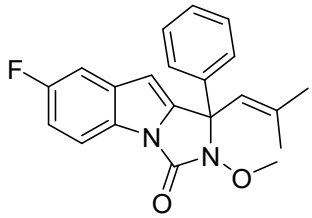
2,7-Dimethoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ha)



Yellow solid. 45.6 mg, Yield: 63%, mp 122-123 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:20;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.38 – 7.30 (m, 3H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.26 (s, 1H), 5.92 (s, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 1.82 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 151.2, 141.2, 140.6, 139.7, 133.6, 128.7, 128.4, 127.5, 125.6, 123.3, 113.6, 112.8, 104.0, 99.3, 69.7, 65.5, 55.8, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_3$ $[M + H]^+$ 363.1703, found 363.1702.

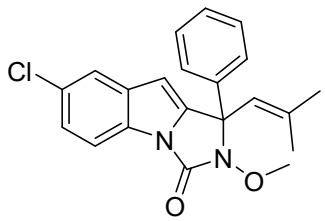
7-Fluoro-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ia)



White solid. 37.1 mg, Yield: 53%, mp 149-150 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 1H), 7.52 – 7.46 (m, 2H), 7.39 – 7.33 (m, 3H), 7.25 – 7.19 (m, 1H), 7.06 (t, *J* = 9.2 Hz, 1H), 6.30 (s, 1H), 5.91 (s, 1H), 3.70 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.48 (d, $J_{C\text{-}F}$ = 237.8 Hz), 150.8, 142.1, 140.9, 139.4, 133.4 (d, $J_{C\text{-}F}$ = 10.2 Hz), 128.7, 128.5, 127.4, 127.2, 122.9, 113.6 (d, $J_{C\text{-}F}$ = 9.7 Hz), 111.8 (d, $J_{C\text{-}F}$ = 25.7Hz), 106.7 (d, $J_{C\text{-}F}$ = 24.1 Hz), 99.1 (d, $J_{C\text{-}F}$ = 4.2 Hz), 69.6, 65.5, 26.6, 20.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ-119.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}FN_2O_2$ $[M + H]^+$ 351.1503, found 351.1503.

7-Chloro-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3*j*a)

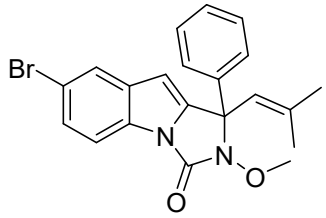


Yellow solid. 33.7 mg, Yield: 46%, mp 160-161 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.53 (s, 1H), 7.51 – 7.46 (m, 2H), 7.39 – 7.33 (m, 3H), 7.27 (d, *J* = 8.7, 1H), 6.28 (s, 1H), 5.91 (s, 1H), 3.70 (s, 3H), 1.83 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 141.7, 141.0, 139.2, 133.6, 129.0, 128.7, 128.5, 127.3, 123.9, 122.8,

120.8, 113.7, 98.6, 69.6, 65.4, 26.5, 20.3. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN_2O_2$ $[M + H]^+$ 367.1208, found 367.1208.

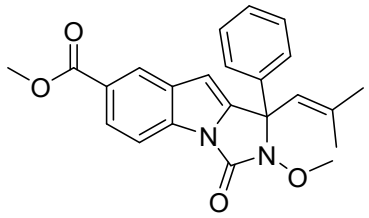
7-Bromo-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ka)



White solid. 46.0 mg, Yield: 56%, mp 166-167 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.38 – 7.33 (m, 3H), 6.28 (s, 1H), 5.90 (s, 1H), 3.69 (s, 3H), 1.83 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 141.6, 141.0, 139.3, 134.2, 129.4, 128.7, 128.6, 127.4, 126.6, 123.9, 122.8, 116.3, 114.2, 98.5, 69.6, 65.5, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}BrN_2O_2$ $[M + H]^+$ 411.0703, found 411.0702.

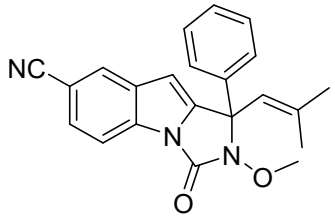
Methyl-2-methoxy-1-(2-methylprop-1-en-1-yl)-3-oxo-1-phenyl-2,3-dihydro-1*H*-imidazo[1,5-*a*]indole-7-carboxylate (3la)



White solid. 37.5 mg, Yield: 48%, mp 184-185 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:20;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.04 (s, 2H), 7.53 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 6.42 (s, 1H), 5.92 (s, 1H), 3.94 (s, 3H), 3.70 (s, 3H), 1.84 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 150.4, 141.5, 141.1, 139.3, 133.3, 132.3, 128.8, 128.6, 127.4, 125.1, 125.1, 123.7, 122.9, 112.6, 99.8, 69.7, 65.5, 52.1, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}N_2O_4$ $[M + H]^+$ 391.1652, found 391.1651.

2-Methoxy-1-(2-methylprop-1-en-1-yl)-3-oxo-1-phenyl-2,3-dihydro-1*H*-imidazo[1,5-*a*]indole-7-carbonitrile (3ma)

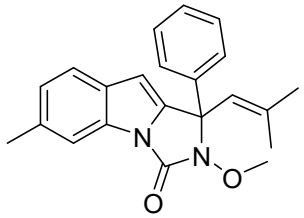


White solid. 22.2 mg, Yield: 31%, mp 203-204 ℃. column chromatography eluent, EtOAc/PE = 1:30 → 1:10;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.40 – 7.34 (m, 3H), 6.41 (s, 1H), 5.90 (s, 1H), 3.70 (s, 3H), 1.84 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 142.6, 141.7, 139.0, 132.6, 132.5, 129.0, 128.9, 127.4, 127.0, 126.4, 122.7, 119.8, 113.9, 106.6, 99.1, 69.8, 65.7, 26.7, 20.6. HRMS (ESI) *m/z* calcd for $C_{22}H_{19}N_3O_2$ $[M + Na]^+$ 380.1369, found 380.1372.

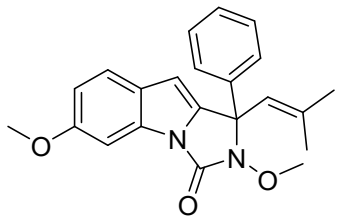
2-Methoxy-6-methyl-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3na)



White solid. 42.3 mg, Yield: 61%, mp 132-133 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.53 – 7.47 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.27 (s, 1H), 5.92 (s, 1H), 3.69 (s, 3H), 2.48 (s, 3H), 1.82 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 140.5, 139.9, 139.7, 134.0, 131.2, 130.3, 128.6, 128.4, 127.5, 124.7, 123.4, 120.8, 113.1, 99.3, 69.7, 65.5, 26.6, 21.7, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + H]^+$ 347.1754, found 347.1753.

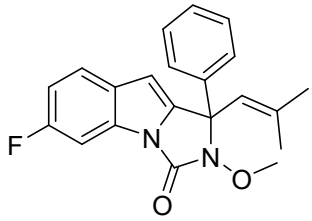
2,6-Dimethoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3oa)



Yellow oil. 42.0 mg, Yield: 58%, column chromatography eluent, EtOAc/PE = 1:40 → 1:20;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 3H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.37 – 7.31 (m, 3H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.25 (s, 1H), 5.92 (s, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 1.82 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 151.2, 140.4, 139.9, 138.9, 131.7, 128.6, 128.4, 127.5, 126.2, 123.5, 121.8, 113.1, 99.3, 96.5, 69.7, 65.5, 55.8, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_3$ $[M + H]^+$ 363.1703, found 363.1703.

6-Fluoro-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3pa)

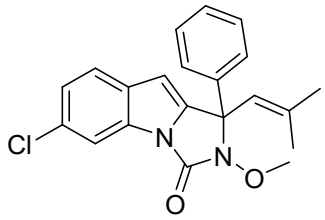


Yellow solid. 51.8 mg, Yield: 74%, mp 125-126 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.40 – 7.31 (m, 3H), 7.00 (t, *J* = 9.0 Hz, 1H), 6.31 (s, 1H), 5.92 (s, 1H), 3.69 (s, 3H), 1.83 (s, 3H), 1.46(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 159.1 (d, J_{C-F} = 239.9 Hz), 150.6, 140.7, 140.6 (d, J_{C-F} = 3.9 Hz), 139.4, 130.6 (d, J_{C-F} = 13.0 Hz), 128.7, 128.7, 128.6, 128.5, 127.4, 123.0, 121.8 (d, J_{C-F} = 9.8 Hz), 111.5 (d, J_{C-F} = 24.1 Hz),100.0 (d, J_{C-F} = 27.2 Hz), 99.0, 69.6, 65.5, 26.5, 20.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}FN_2O_2$ $[M + H]^+$ 351.1503, found 351.1503.

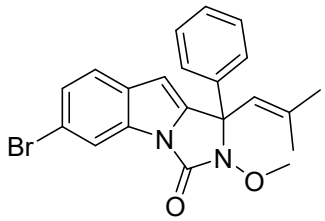
6-Chloro-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3qa)



Yellow solid. 44.7 mg, Yield: 61%, mp 135-136 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.51 – 7.44 (m, 3H), 7.39 – 7.33 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.31 (s, 1H), 5.91 (s, 1H), 3.69 (s, 3H), 1.83 (s, 3H), 1.45(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 141.0, 140.9, 139.4, 131.0, 131.0, 129.7, 128.7, 128.6, 127.4, 123.8, 123.0, 122.0, 113.1, 99.1, 69.7, 65.6, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN_2O_2$ $[M + H]^+$ 367.1208, found 367.1207.

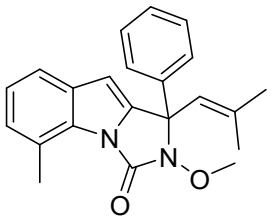
6-Bromo-2-methoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ra)



White solid. 47.6 mg, Yield: 58%, mp 156-157 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.51 – 7.46 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.33 (m, 4H), 6.30 (s, 1H), 5.91 (s, 1H), 3.69 (s, 3H), 1.83(s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 150.5, 141.0, 140.9, 139.4, 131.4, 131.4, 128.7, 128.6, 127.4, 126.4, 122.9, 122.4, 117.2, 116.1, 99.1, 69.7, 65.6, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}BrN_2O_2$ $[M + Na]^+$ 433.0522, found 433.0520.

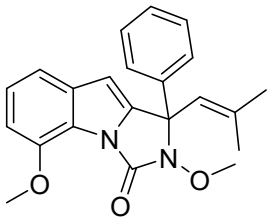
2-Methoxy-5-methyl-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3sa)



White solid. 38.8 mg, Yield: 56%, mp 147-148 ℃. column chromatography eluent, EtOAc/PE = 1:50 → 1:40;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.39 – 7.31 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.33 (s, 1H), 5.91 (s, 1H), 3.72 (s, 3H), 2.93 (s, 3H), 1.83 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 141.5, 140.5, 140.0, 133.3, 131.4, 128.6, 128.3, 127.5, 126.3, 125.0, 123.5, 118.5, 100.0, 68.8, 65.3, 26.7, 21.0, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + H]^+$ 347.1754, found 347.1752.

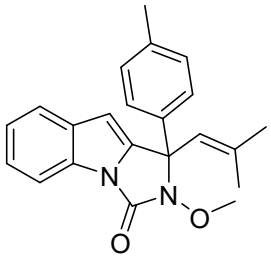
2,5-Dimethoxy-1-(2-methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ta)



White solid. 21.8 mg, Yield: 30%, mp 160-161 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:10;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.38 – 7.29 (m, 3H), 7.21 – 7.11 (m, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.32 (s, 1H), 5.90 (s, 1H), 4.03 (s, 3H), 3.73 (s, 3H), 1.82 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 140.5, 140.3, 138.2, 136.5, 132.5, 130.7, 129.3, 127.4, 123.6, 123.3, 123.0, 121.2, 112.9, 99.1, 69.5, 65.5, 26.5, 21.1, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_3$ $[M + H]^+$ 363.1703, found 363.1701.

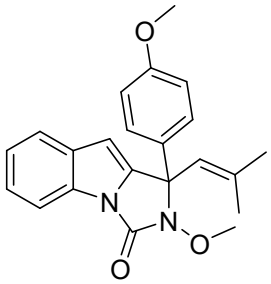
2-Methoxy-1-(2-methylprop-1-en-1-yl)-1-(p-tolyl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ab)



Yellow oil. 48.5 mg, Yield: 70%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.3Hz, 1H), 7.57 (d, *J* = 6.84 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 7.26 – 7.23 (m, 1H), 7.18 – 7.12 (m, 2H), 6.32 (s, 1H), 5.91 (s, 1H), 3.69 (s, 3H), 2.35 (s, 3H), 1.82 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 140.6, 140.4, 138.3, 136.6, 132.6, 130.8, 129.4, 127.5, 123.7, 123.4, 123.1, 121.2, 113.0, 99.2, 69.6, 65.6, 26.6, 21.2, 20.5. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + H]^+$ 347.1754, found 347.1754.

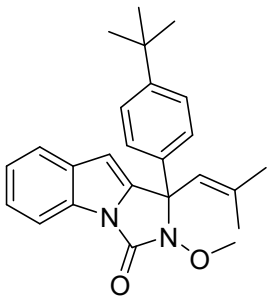
2-Methoxy-1-(4-methoxyphenyl)-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ac)



White solid. 51.5 mg, Yield: 71%, mp 103-104 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:20;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.35 – 7.22 (m, 2H), 6.91 – 6.83 (m, 2H), 6.33 (s, 1H), 5.91 (s, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 1.81 (s, 3H), 1.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 151.1, 140.6, 140.2, 132.6, 131.4, 130.8, 129.0, 123.7, 123.5, 123.1, 121.2, 113.9, 113.0, 99.3, 69.4, 65.6, 55.3, 26.6, 20.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_3$ $[M + H]^+$ 363.1703, found 363.1705.

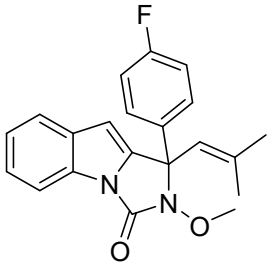
1-(4-(Tert-butyl)phenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ad)



Yellow oil. 48.9 mg, Yield: 63%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.29 (m, 5H), 7.27 – 7.22 (m, 1H), 6.32 (s, 1H), 5.92 (s, 1H), 3.72 (s, 3H), 1.82 (s, 3H), 1.46 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 151.1, 140.6, 136.6, 132.5, 130.8, 127.0, 125.4, 123.6, 123.3, 123.0, 121.1, 112.9, 99.1, 69.4, 65.4, 34.5, 31.3, 26.6, 20.2. HRMS (ESI) *m/z* calcd for $C_{25}H_{28}N_2O_2$ $[M + H]^+$ 389.2224, found 389.2223.

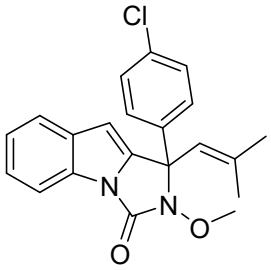
1-(4-Fluorophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ae)



Yellow oil. 42.7 mg, Yield: 61%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.34 (s, 1H), 5.91 (s, 1H), 3.71 (s, 3H), 1.82 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6 (d, J_{C-F} = 246.6Hz), 151.0, 140.6, 140.0, 135.4 (d, J_{C-F} = 3.2Hz), 132.4, 130.7, 129.4 (d, J_{C-F} = 8.1 Hz), 123.8, 123.2, 123.2, 121.2, 115.4 (d, J_{C-F} = 21.5 Hz), 112.9, 99.4, 69.1, 65.5, 26.5, 20.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.3. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}FN_2O_2$ $[M + H]^+$ 351.1503, found 351.1502.

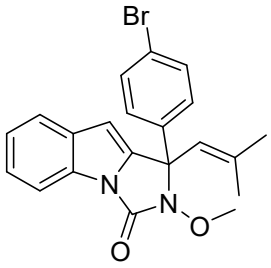
1-(4-Chlorophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3af)



Yellow solid. 35.2 mg, Yield: 48%, mp 122-123 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.29 – 7.36 (m, 3H), 7.25 (t, *J* = 6.8 Hz, 1H), 6.33 (s, 1H), 5.90 (s, 1H), 3.72 (s, 3H), 1.82 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 140.9, 139.8, 138.2, 134.4, 132.4, 130.7, 129.0, 128.8, 123.9, 123.2, 122.9, 121.2, 112.9, 99.4, 69.1, 65.5, 26.5, 20.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN_2O_2$ $[M + H]^+$ 367.1208, found 367.1208.

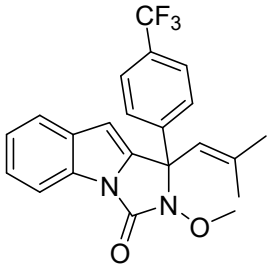
1-(4-Bromophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ag)



White solid. 41.9 mg, Yield: 51%, mp 130-131 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.41 – 7.31 (m, 3H), 7.29 – 7.23 (m, 1H), 6.33 (s, 1H), 5.89 (s, 1H), 3.72 (s, 3H), 1.82 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 140.9, 139.7, 138.8, 132.4, 131.8, 130.8, 129.3, 123.9, 123.2, 122.8, 122.7, 121.3, 113.0, 99.5, 69.2, 65.6, 26.5, 20.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}BrN_2O_2$ $[M + H]^+$ 411.0703, found 411.0701.

2-methoxy-1-(2-methylprop-1-en-1-yl)-1-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ah)

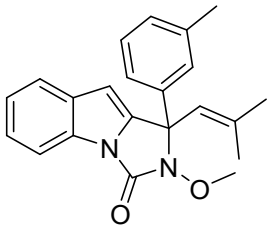


Yellow oil. 20.0 mg, Yield: 25%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.56(m, 5H), 7.39 – 7.32 (m, 1H), 7.31 – 7.25(m, 1H), 6.35 (s, 1H), 5.92 (s, 1H), 3.75 (s, 3H), 1.85 (s, 3H), 1.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 143.9, 141.5, 139.6, 132.4, 130.8, 130.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 127.9, 125.6 (q, $J_{C\text{-}F}$ = 3.5 Hz), 124.1, 123.3, 123.8(q, $J_{C\text{-}F}$ = 270.5 Hz), 122.6, 121.3, 113.0, 99.6, 69.2, 65.6, 26.6, 20.5. **^{19}F NMR**

(376 MHz, $CDCl_3$) δ -62.59. HRMS (ESI) *m/z* calcd for $C_{22}H_{19}F_3N_2O_2$ $[M + Na]^+$ 423.1291, found 423.1292.

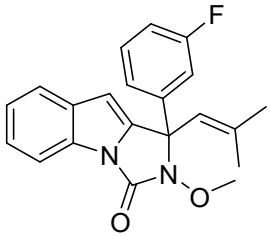
2-Methoxy-1-(2-methylprop-1-en-1-yl)-1-(m-tolyl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one（3ai）



Yellow oil. 44.3 mg, Yield: 64%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.27-7.22 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.33 (s, 1H), 5.91 (s, 1H), 3.71 (s, 3H), 2.33 (s, 3H), 1.82 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 140.5, 140.4, 139.5, 138.3, 132.5, 130.7, 129.1, 128.4, 127.8, 124.6, 123.6, 123.2, 123.0, 121.1, 112.9, 99.1, 69.5, 65.4, 26.5, 21.5, 20.3. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + Na]^+$ 369.1573, found 369.1572.

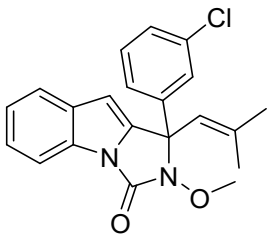
1-(3-Fluorophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3a*j*)



White solid. 34.3 mg, Yield: 49%, mp 131-133 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.16 (m, 5H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.31 (s, 1H), 5.86 (s, 1H), 3.70 (s, 3H), 1.79 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 245.0 Hz), 151.0, 142.3 (d, $J_{C\text{-}F}$ = 27.2 Hz), 141.1, 139.7, 132.4, 130.7, 130.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 123.9, 123.2, 123.0 (d, $J_{C\text{-}F}$ = 2.9Hz), 122.8, 121.3, 115.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.7 (d, $J_{C\text{-}F}$ = 23.0 Hz), 113.0, 99.5, 69.1 , 65.5, 26.5, 20.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.9. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}FN_2O_2$ $[M + H]^+$ 351.1503, found 351.1501.

1-(3-chlorophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ak)

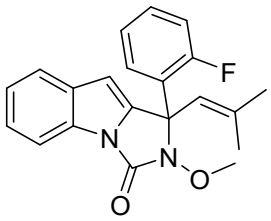


Yellow oil. 27.9 mg, Yield: 38%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.51 (s , 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.24 (m, 4H), 6.35 (s, 1H), 5.89 (s, 1H), 3.74 (s, 3H), 1.83 (s, 3H) , 1.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 142.0, 141.3, 139.6, 134.7, 132.5, 130.8, 130.0, 128.7, 127.7,

125.7, 124.0, 123.3, 122.8, 121.4, 113.1, 99.7, 69.2, 65.6, 26.6, 20.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN_2O_2$ $[M + H]^+$ 367.1208, found 367.1206.

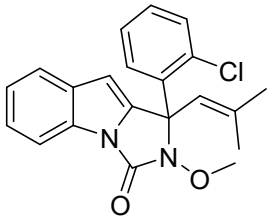
1-(2-Fluorophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3al)



Yellow solid. 30.8 mg, Yield: 44%, mp 147-148 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.12 – 7.03 (m, 2H), 6.43 (s, 1H), 5.86 (s, 1H), 3.89 (s, 3H), 1.83 (s, 3H), 1.47 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8 (d, J_{C-F} = 249.0 Hz), 150.7, 140.3, 139.5, 132.4, 130.7, 130.3 (d, J_{C-F} = 8.4 Hz), 128.4 (d, J_{C-F} = 2.3 Hz), 127.7 (d, J_{C-F} = 10.3 Hz) , 124.1 (d, J_{C-F} = 3.4 Hz), 123.7, 123.0, 122.1, 121.2, 116.5 (d, J_{C-F} = 22.0 Hz), 112.8, 99.2 (d, J_{C-F} = 3.9 Hz), 67.1, 65.4, 26.7, 19.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}FN_2O_2$ $[M + H]^+$ 351.1503, found 351.1505.

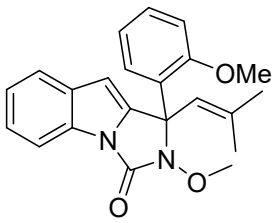
1-(2-Chlorophenyl)-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3am)



Yellow solid. 25.7 mg, Yield: 35%, mp 144-146 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.32 – 7.20 (m,4H), 6.51 (s, 1H), 5.85 (s, 1H), 3.79 (s, 3H), 1.84 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 140.2, 138.9, 136.0, 133.7, 132.2, 131.8, 130.8, 129.6, 129.4, 126.9, 123.7, 123.0, 121.4, 121.3, 112.8, 99.7, 68.9, 65.2, 26.5, 20.1. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN_2O_2$ $[M + H]^+$ 367.1208, found 367.1208.

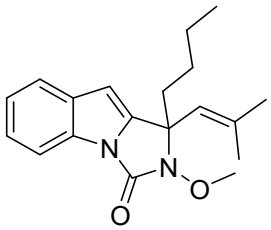
2-Methoxy-1-(2-methoxyphenyl)-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3an)



White solid. 27.6 mg, Yield: 38%, mp 155-156 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:20;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.23(m, 2H), 7.23 – 7.17 (m, 1H), 6.98 – 6.91 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.32 (s, 1H), 5.81 (s, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 1.83 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 150.8, 140.9, 138.9, 132.4, 130.6, 129.7, 128.3, 127.5, 123.1, 122.8, 122.6, 120.9, 120.4, 112.6, 112.1, 98.1, 67.9, 65.1, 55.5, 26.6, 20.1. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_3$ $[M + H]^+$ 363.1703, found 363.1700.

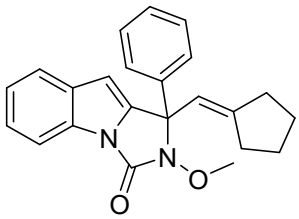
1-Butyl-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ao)



Yellow solid. 40.6 mg, Yield: 65%, mp 101-102 ℃. column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.19 (m, 2H), 6.23 (s, 1H), 5.46 (s, 1H), 3.94 (s, 3H), 2.12 – 1.94 (m, 2H), 1.76 (s, 3H), 1.30 – 1.17 (m, 6H), 0.90 – 0.75 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.9, 141.7, 140.1, 132.7, 130.6, 123.4, 123.3, 122.9, 121.1, 113.0, 97.7, 65.9, 65.4, 39.5, 26.9, 25.1, 22.5, 18.9, 13.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{24}N_2O_2$ $[M + H]^+$ 313.1911, found 313.1911.

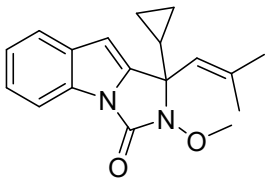
1-(Cyclopentylidenemethyl)-2-methoxy-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3ap)



Yellow oil. 32.3 mg, Yield: 45%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;

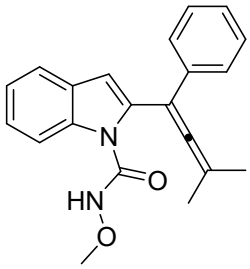
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.44 – 7.34 (m, 4H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.34 (s, 1H), 6.09 (s, 1H), 3.80 (s, 3H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.01 (d, *J* = 16.9, 1H), 1.76 (d, *J* = 17.2 Hz, 1H), 1.60 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 151.3, 140.0, 139.7, 132.6, 130.8, 128.7, 128.4, 127.4, 123.7, 123.1, 121.3, 118.2, 113.1, 99.6, 69.8, 65.4, 35.6, 29.7, 26.9, 25.6. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}N_2O_2$ $[M + H]^+$ 359.1754, found 359.1753.

1-Cyclopropyl-2-methoxy-1-(2-methylprop-1-en-1-yl)-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (3aq)



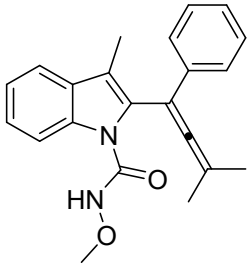
Yellow oil. 36.8 mg, Yield: 62%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.17 (s, 1H), 5.65 (s, 1H), 3.99 (s, 3H), 1.78 (s, 4H), 1.28 (s, 3H), 0.73 – 0.62 (m, 1H), 0.6-0.51 (m, 1H), 0.41 – 0.32 (m, 1H), -0.26 – -0.35 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 141.4, 136.4, 132.1, 130.6, 123.4, 123.1, 122.8, 121.0, 112.8, 99.3, 67.5, 65.3, 26.7, 19.0, 18.1, 1.6, 1.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}N_2O_2$ $[M + H]^+$ 297.1598, found 297.1597.

N-methoxy-2-(3-methyl-1-phenyl-2λ^5-buta-1,2-dien-1-yl)-1*H*-indole-1-carboxamide (4aa)



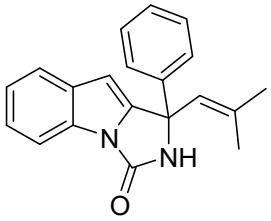
Yellow oil. column chromatography eluent, EtOAc/PE = 1:40 → 1:5;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.22 (m, 7H), 6.60 (s, 1H), 3.48 (s, 3H), 1.92 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.8, 151.9, 137.4, 136.1, 132.8, 128.9, 128.7, 127.7, 126.6, 124.4, 122.8, 120.4, 114.6, 110.4, 100.6, 99.7, 64.2, 20.2. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}N_2O_2$ $[M + H]^+$ 333.1598, found 333.1598.

N-methoxy-3-methyl-2-(3-methyl-1-phenyl-2λ^5-buta-1,2-dien-1-yl)-1*H*-indole-1-carboxamide (4ba)



Yellow oil. 54.7 mg, Yield: 79%, column chromatography eluent, EtOAc/PE = 1:40 → 1:30;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.23 (d, *J* = 7.4, 1H), 7.54 (d, *J* = 6.1, 1H), 7.36 – 7.26 (m, 4H), 7.25 – 7.19 (m, 3H), 3.46 (s, 3H), 2.24 (m, 3H), 1.94 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.3, 152.3, 136.7, 135.9, 129.8, 129.0, 127.9, 127.7, 126.2, 124.8, 122.5, 118.8, 117.6, 115.1, 99.9, 98.4, 64.2, 19.9, 9.4. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_2$ $[M + H]^+$ 347.1754, found 347.1751.

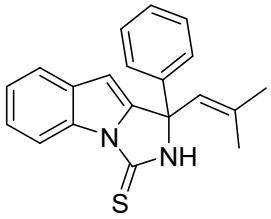
1-(2-Methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indol-3-one (5)



White solid. 49.0 mg, Yield: 81%, mp 226-227 ℃. column chromatography eluent, EtOAc/PE = 1:30 → 1:5;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8, 1H), 7.56 – 7.49 (m, 3H), 7.37 – 7.31 (m, 2H), 7.30 – 7.20 (m, 3H), 6.71 (s, 1H), 6.33 (s, 1H), 5.88 (s, 1H), 1.79 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 152.4, 145.3, 143.2, 140.0, 133.5, 130.0, 128.9, 127.8, 126.8, 125.5, 123.3, 122.7, 121.0, 112.7, 97.7, 63.6, 26.7, 19.4. HRMS (ESI) *m/z* calcd for $C_{20}H_{18}N_2O$ [M + H]$^+$ 303,1492, found 303,1489.

1-(2-Methylprop-1-en-1-yl)-1-phenyl-1,2-dihydro-3*H*-imidazo[1,5-*a*]indole-3-thione (6)

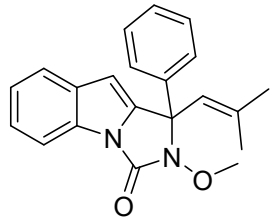


White solid. 30.7 mg, Yield: 96%, mp 230-231 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:10;

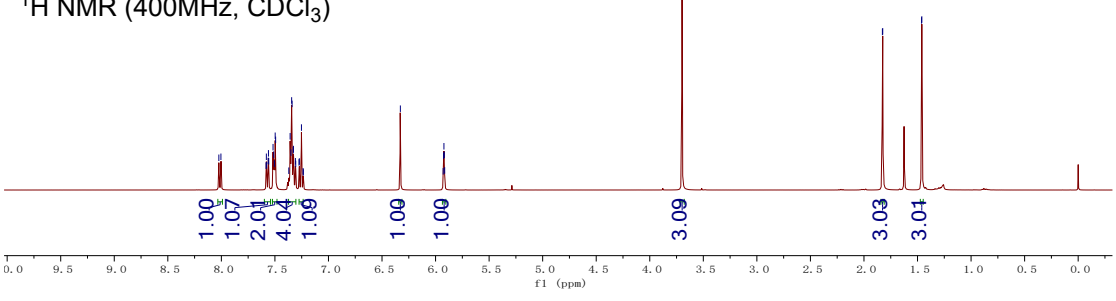
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1H), 8.58 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.36 – 7.25 (m, 3H), 6.67 (s, 1H), 5.75 (s, 1H), 1.76 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 173.5, 145.3, 142.2, 139.6, 133.6, 130.4, 128.9, 127.9, 125.5, 125.3, 123.4, 123.2, 121.4, 112.6, 98.0, 67.0, 26.6, 18.7. HRMS (ESI) *m/z* calcd for $C_{20}H_{18}N_2S$ [M + H]$^+$ 319.1263, found 319.1263.

10.NMR spectra of products

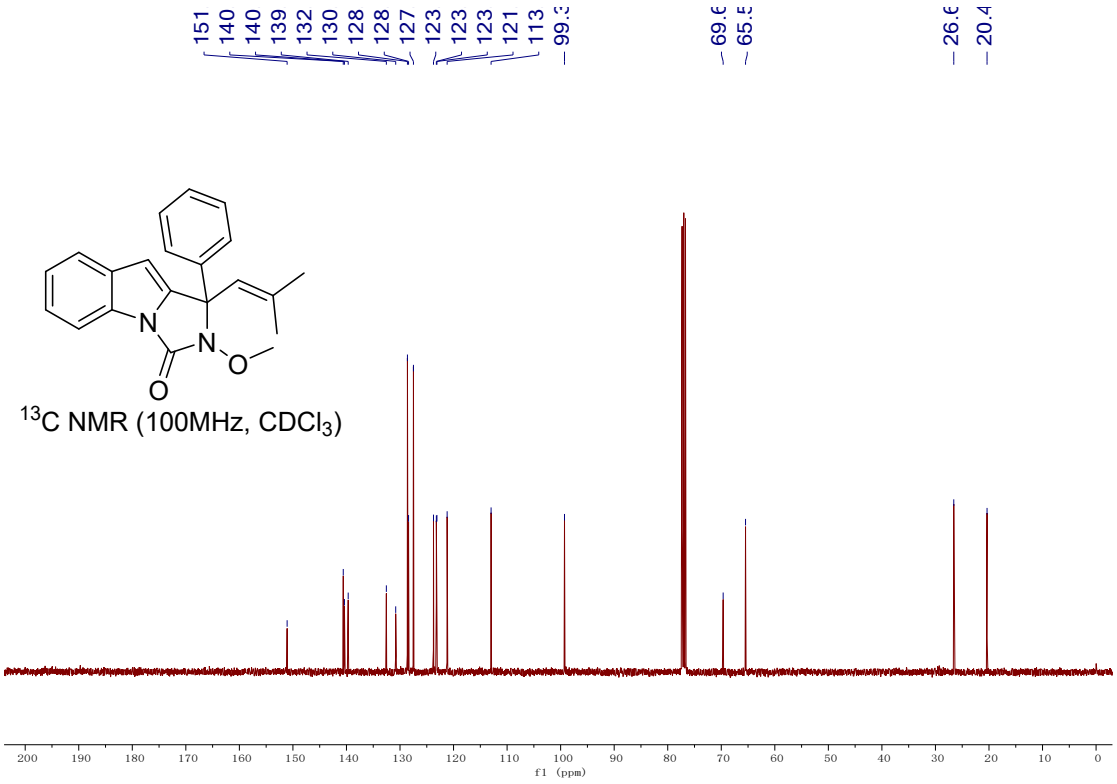
^{1}H NMR spectrum of **3aa**



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

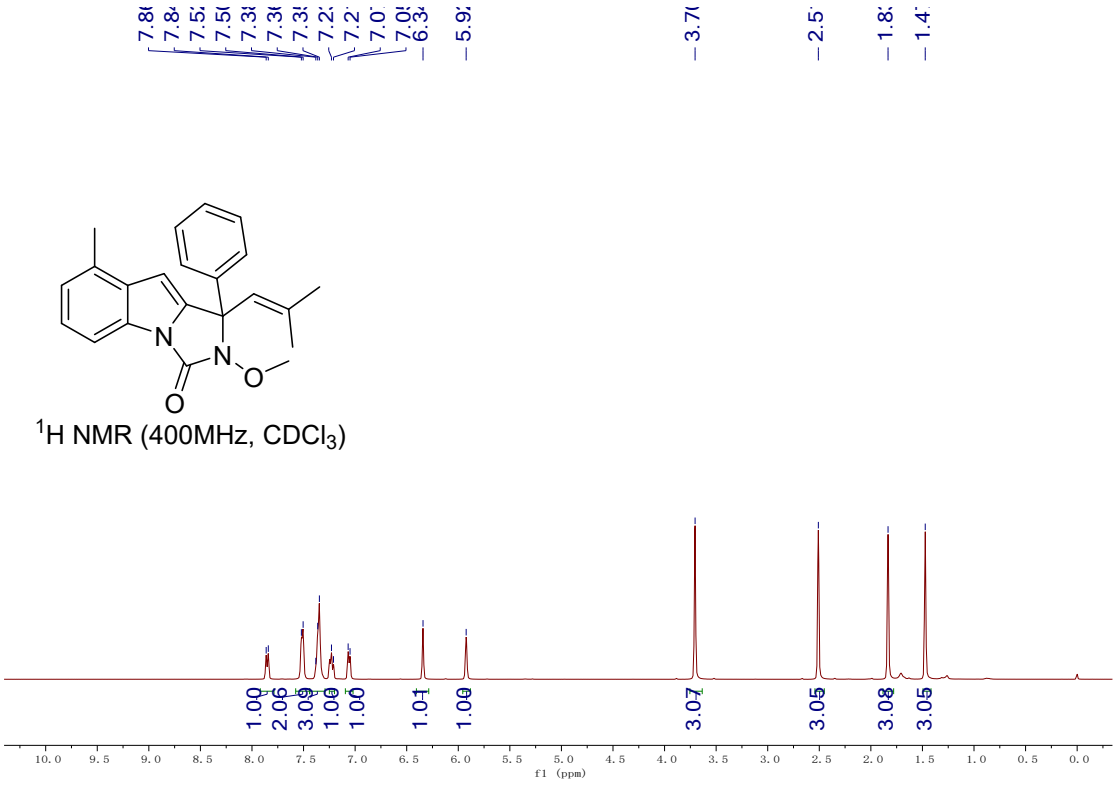


^{13}C NMR spectrum of **3aa**



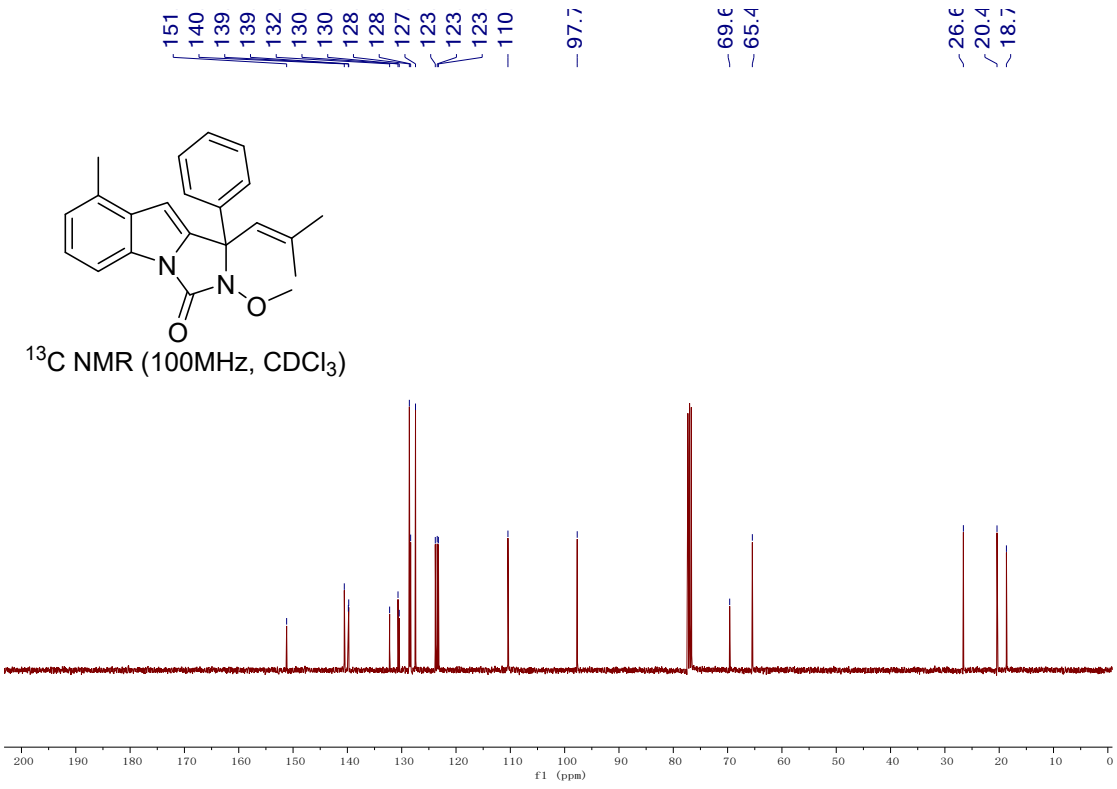
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ba**

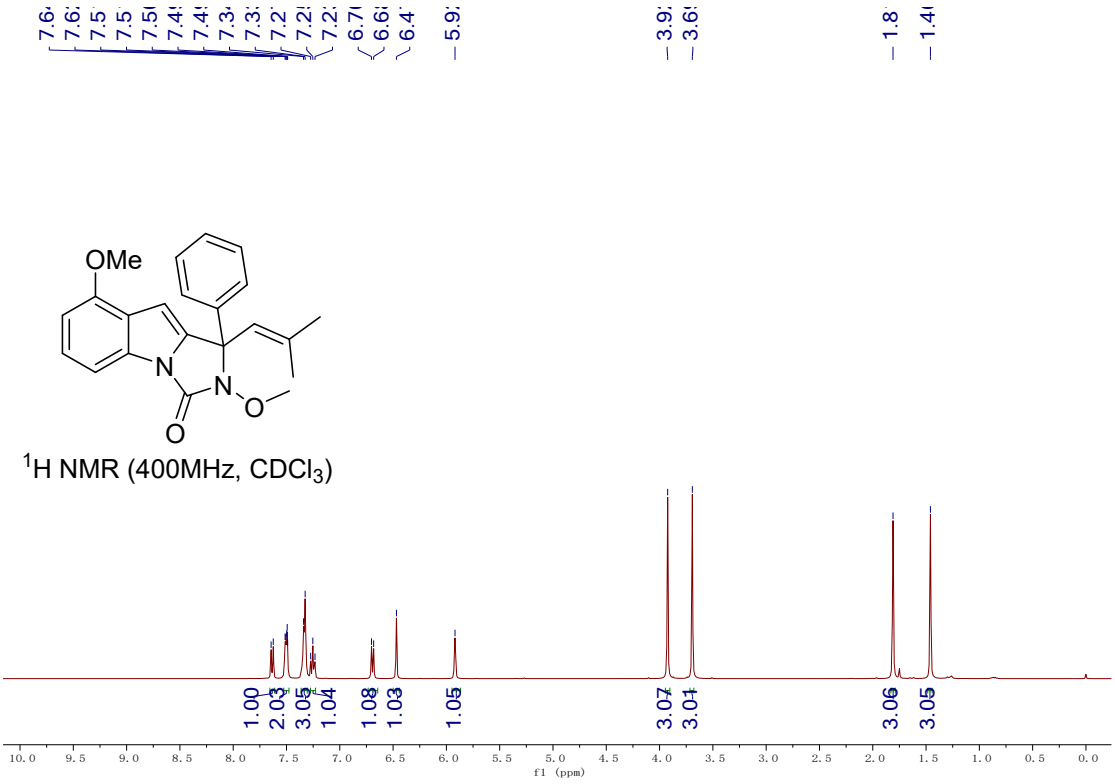


^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ba**

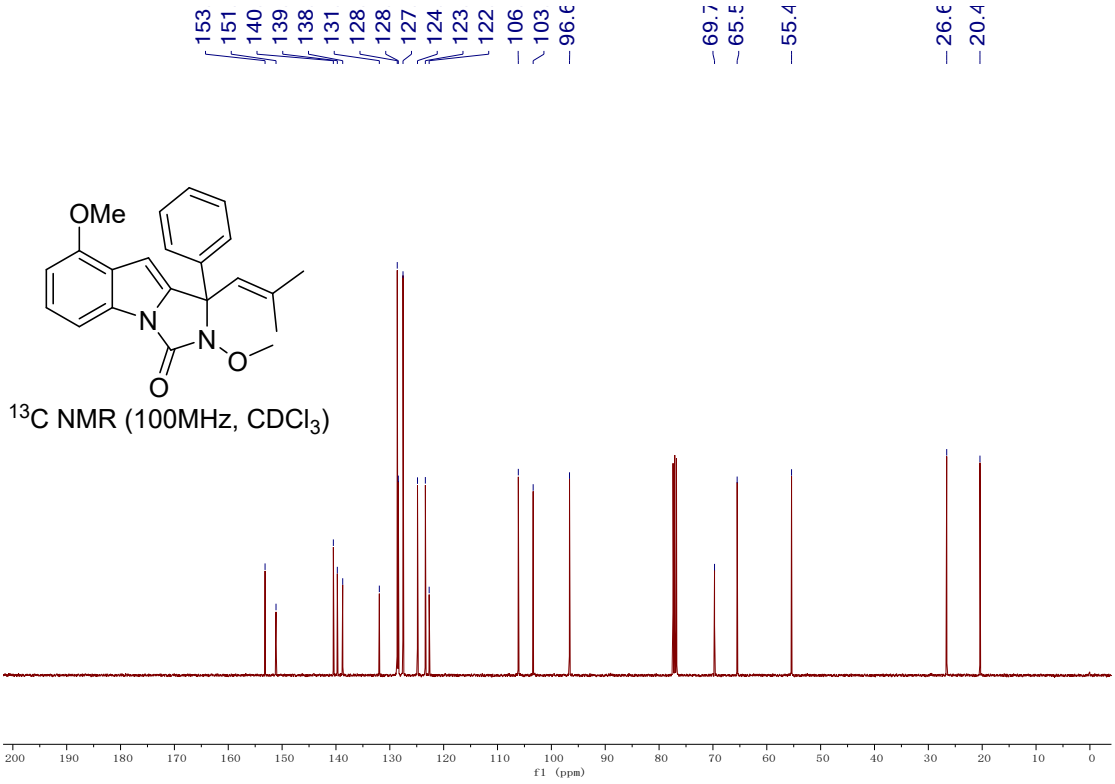


^{1}H NMR spectrum of **3ca**



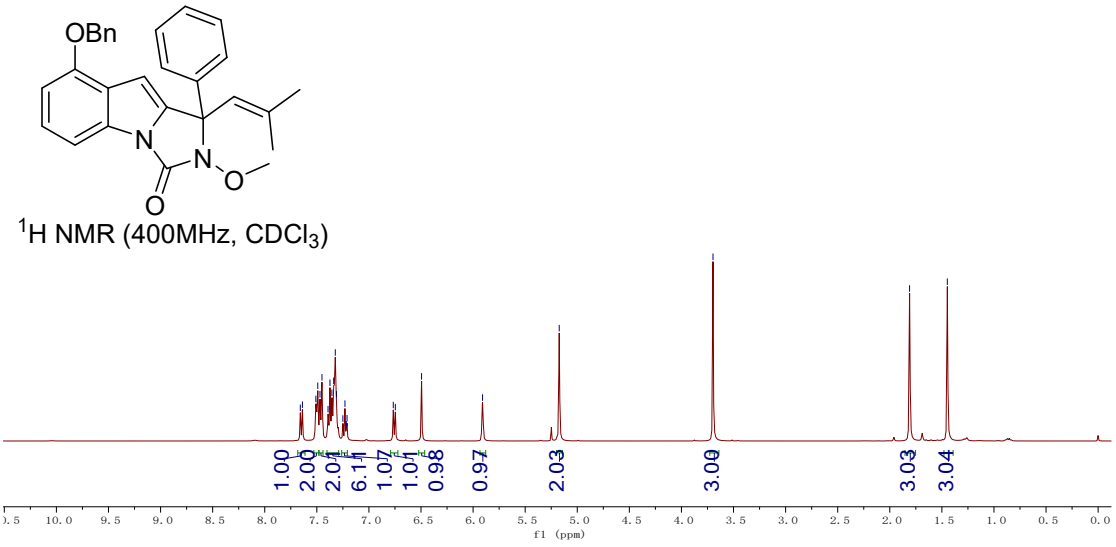
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ca**

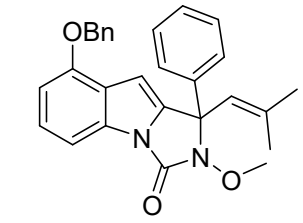


^{13}C NMR (100MHz, $CDCl_3$)

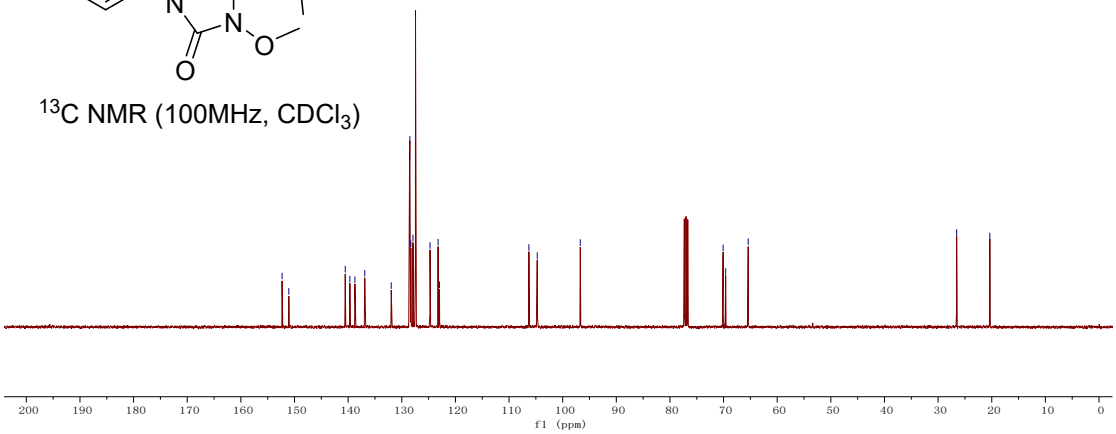
^{1}H NMR spectrum of **3da**



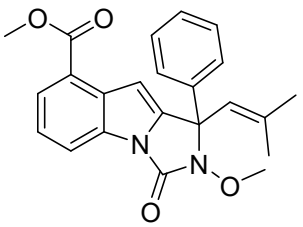
^{13}C NMR spectrum of **3da**



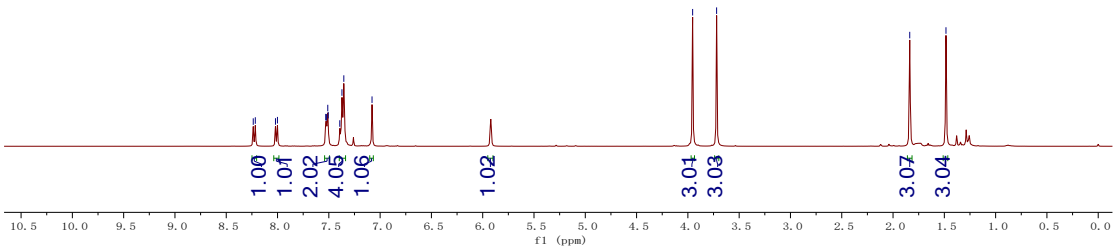
^{13}C NMR (100MHz, $CDCl_3$)



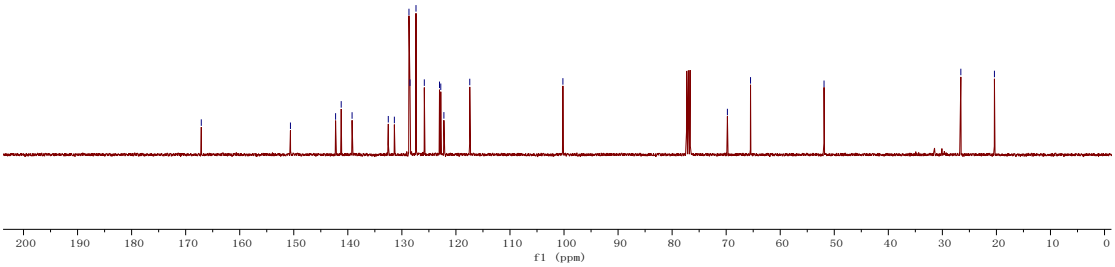
^{1}H NMR spectrum of **3ea**



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

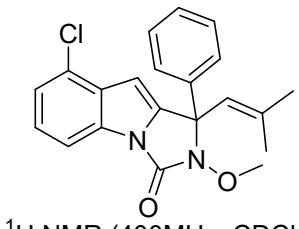


^{13}C NMR spectrum of **3ea**

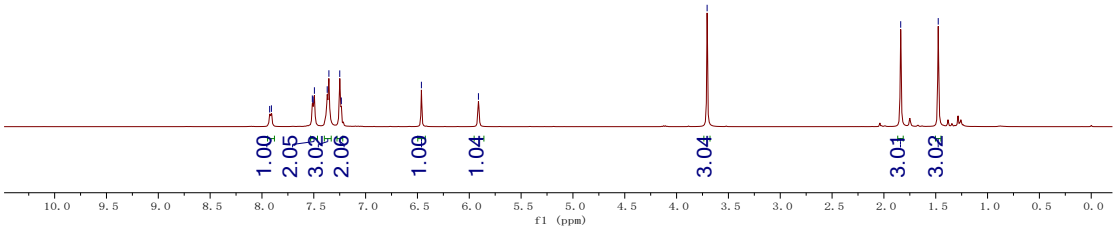


^{13}C NMR (100MHz, $CDCl_3$)

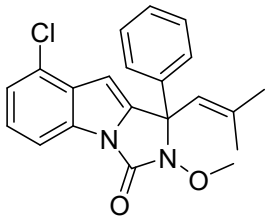
^{1}H NMR spectrum of **3fa**



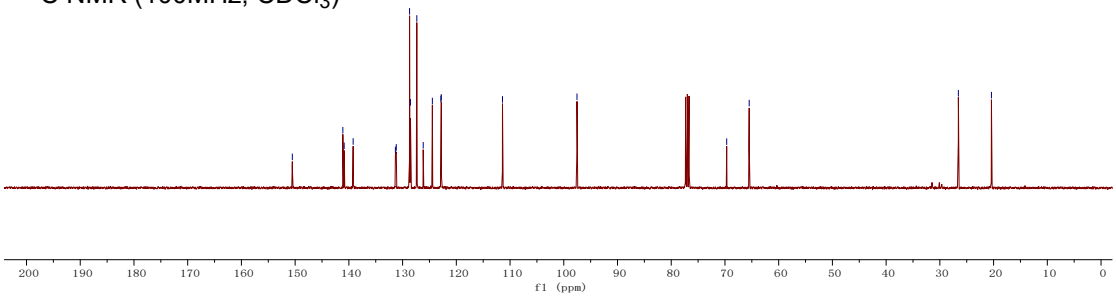
^{1}H NMR (400MHz, $CDCl_3$)



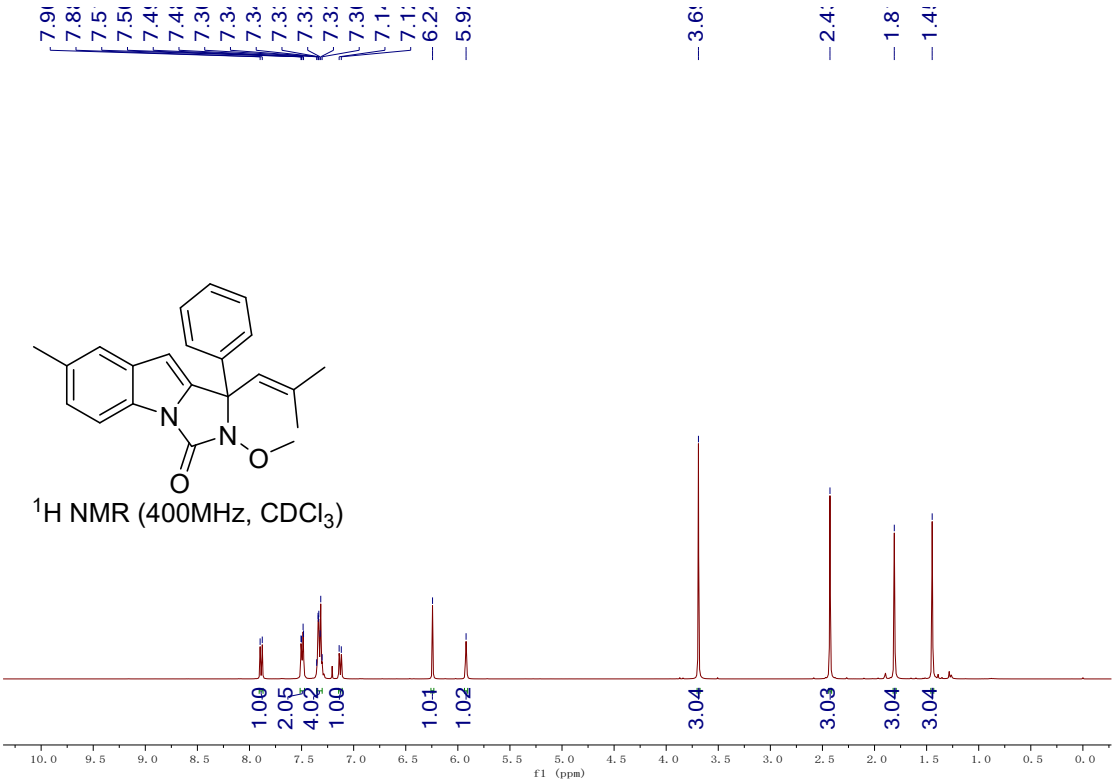
^{13}C NMR spectrum of **3fa**



^{13}C NMR (100MHz, $CDCl_3$)

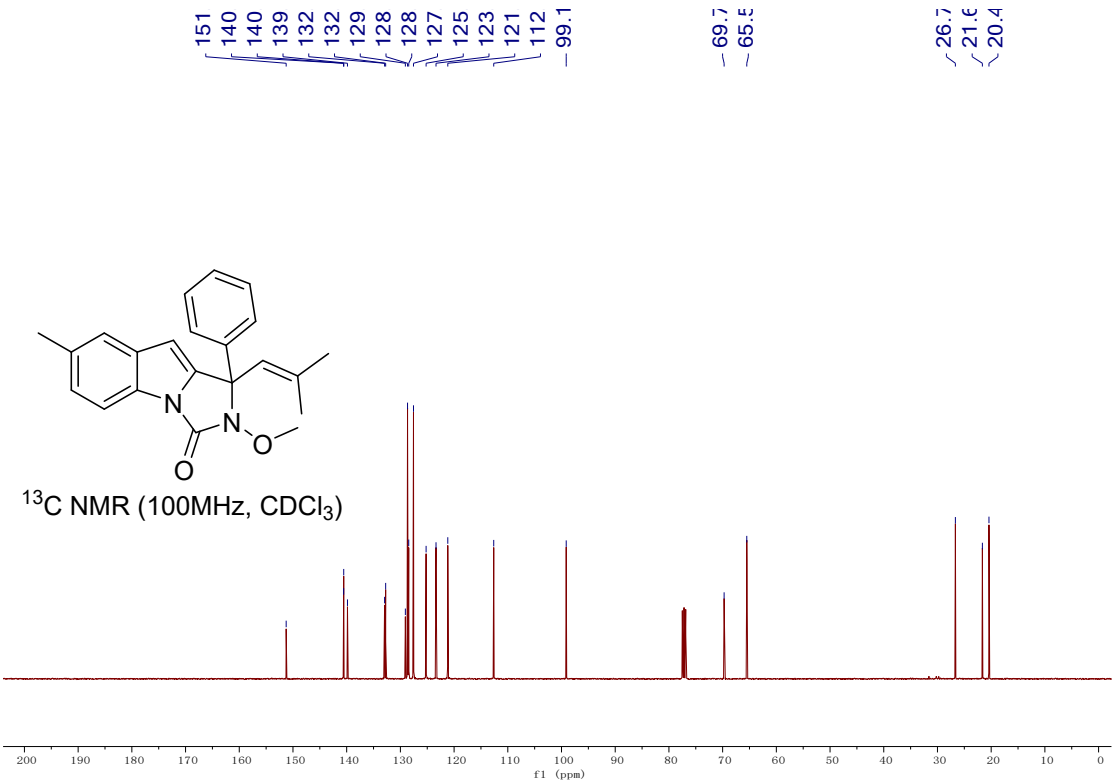


^{1}H NMR spectrum of **3ga**



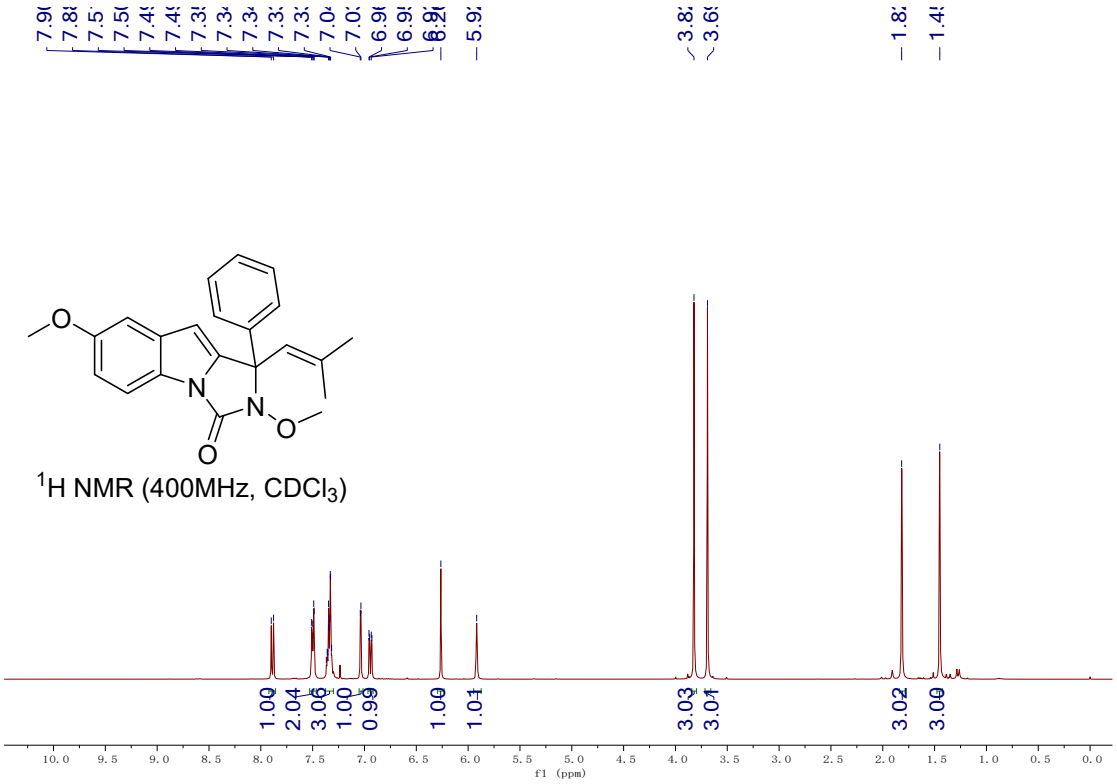
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ga**

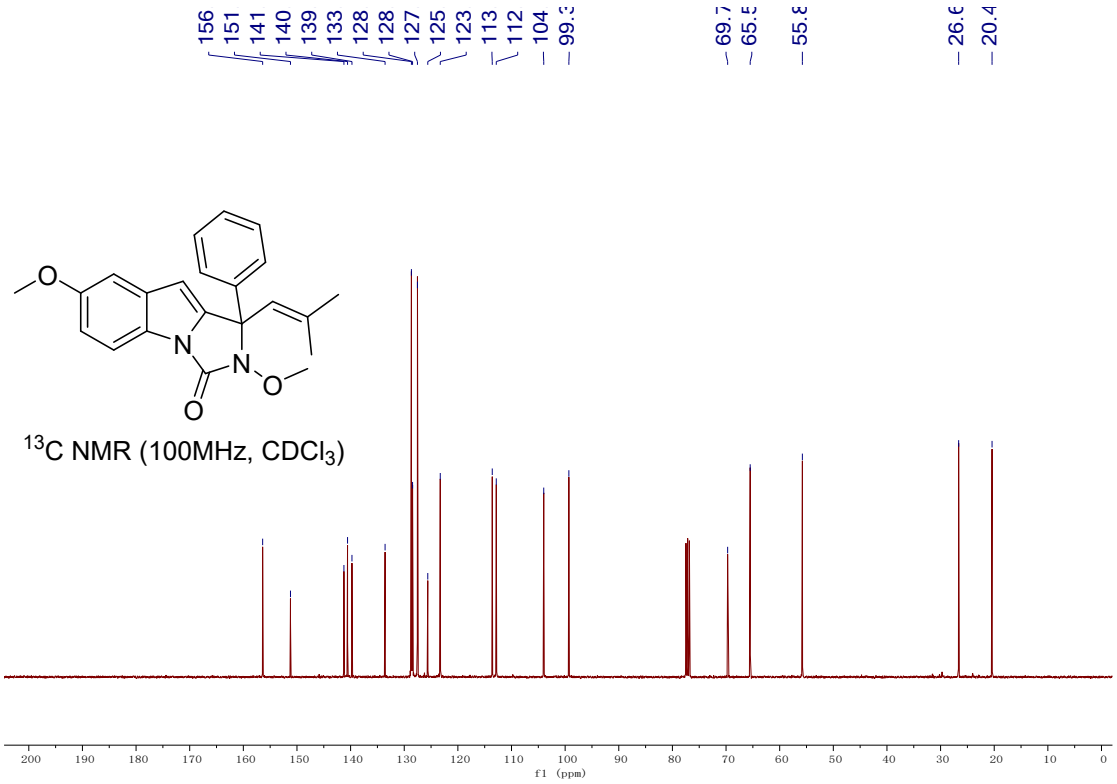


^{13}C NMR (100MHz, $CDCl_3$)

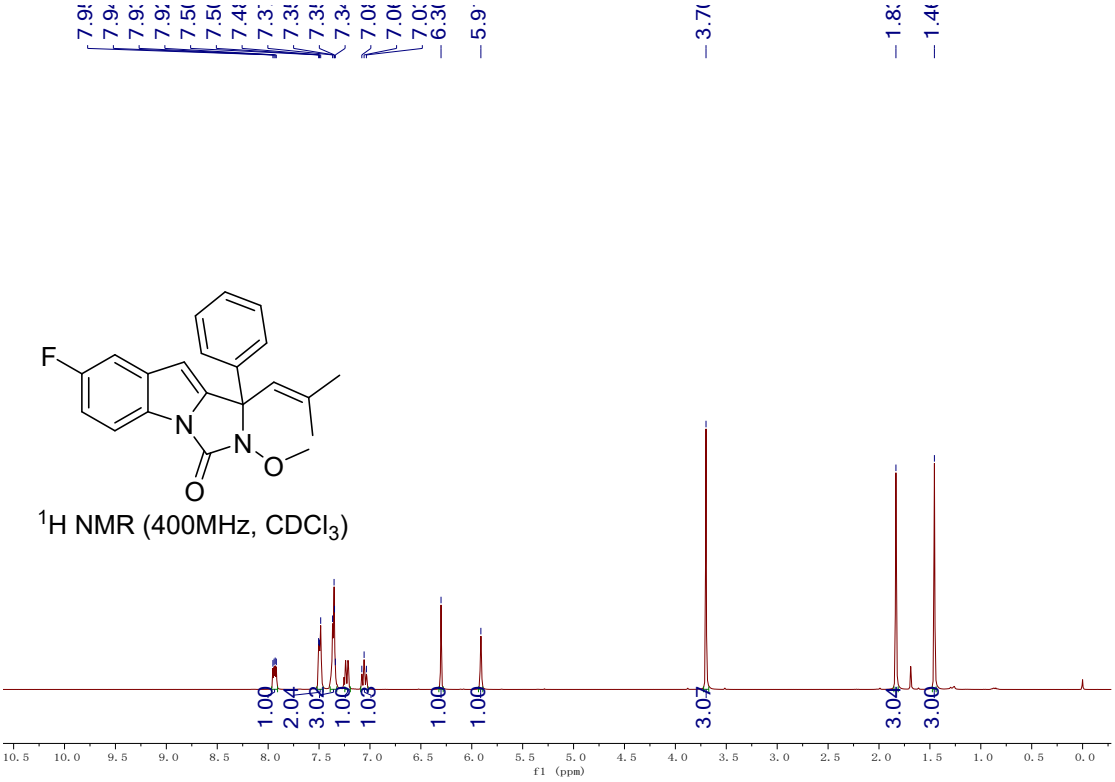
^{1}H NMR spectrum of **3ha**



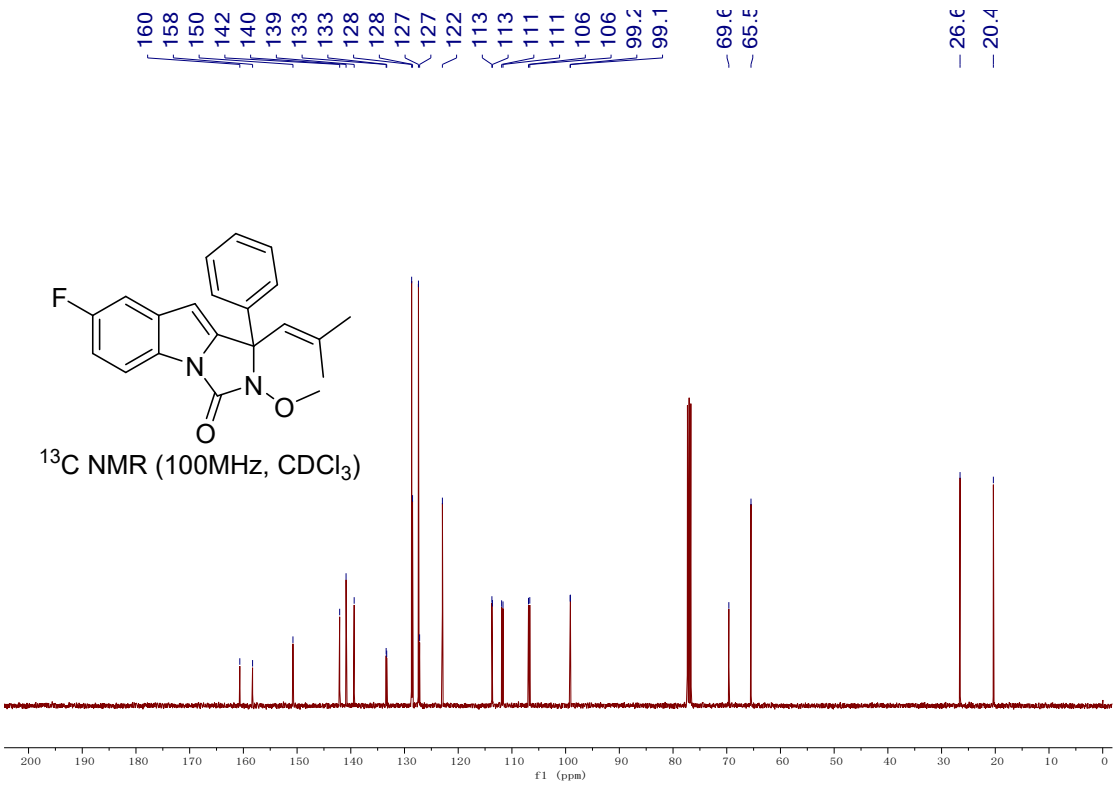
^{13}C NMR spectrum of **3ha**



^{1}H NMR spectrum of **3ia**

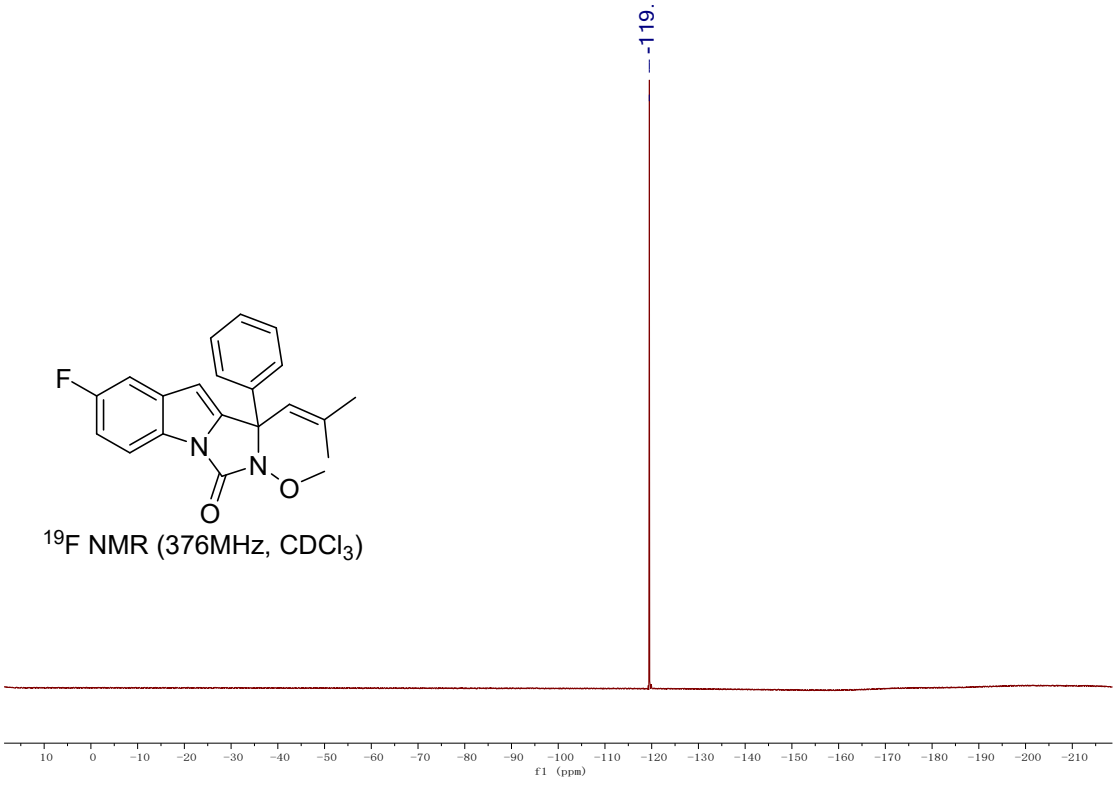


^{13}C NMR spectrum of **3ia**



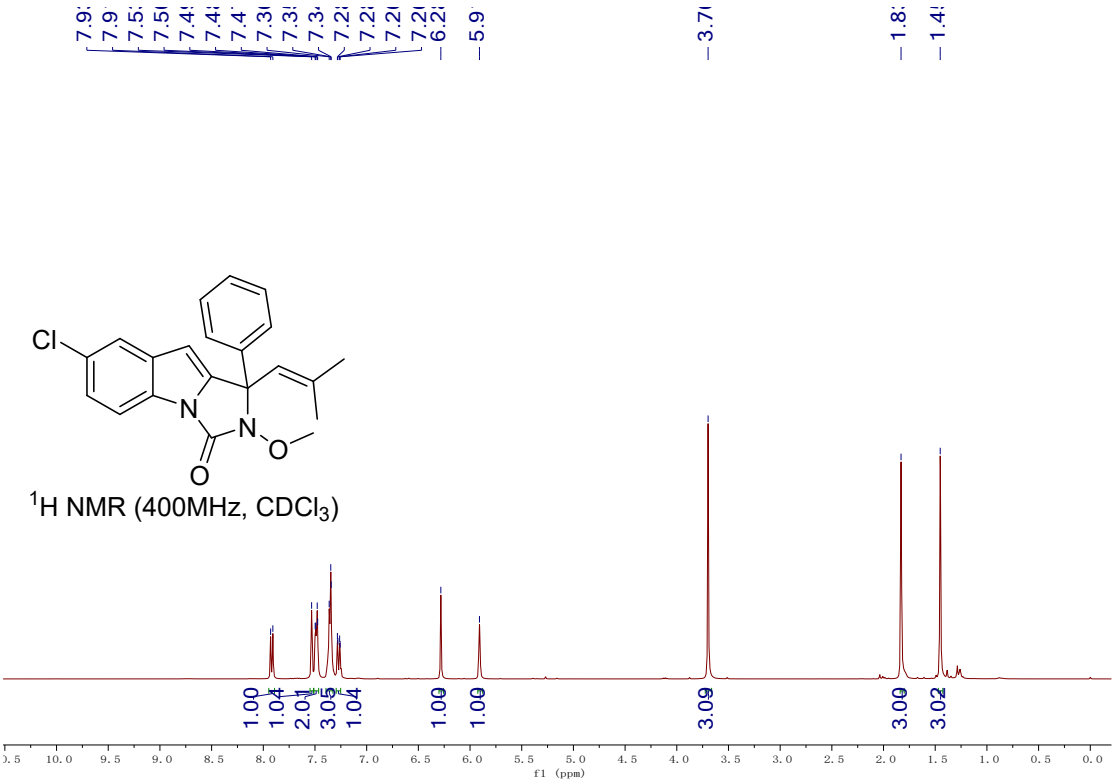
^{13}C NMR (100MHz, $CDCl_3$)

^{19}F NMR spectrum of **3ia**

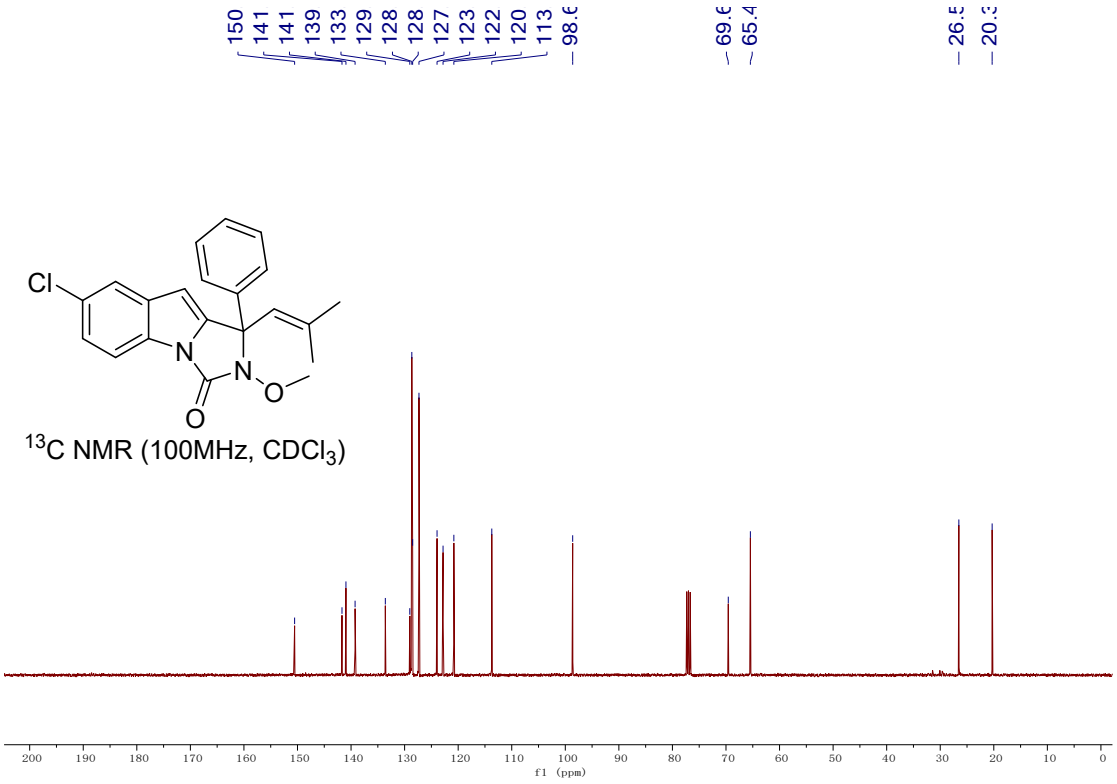


^{19}F NMR (376MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ja**

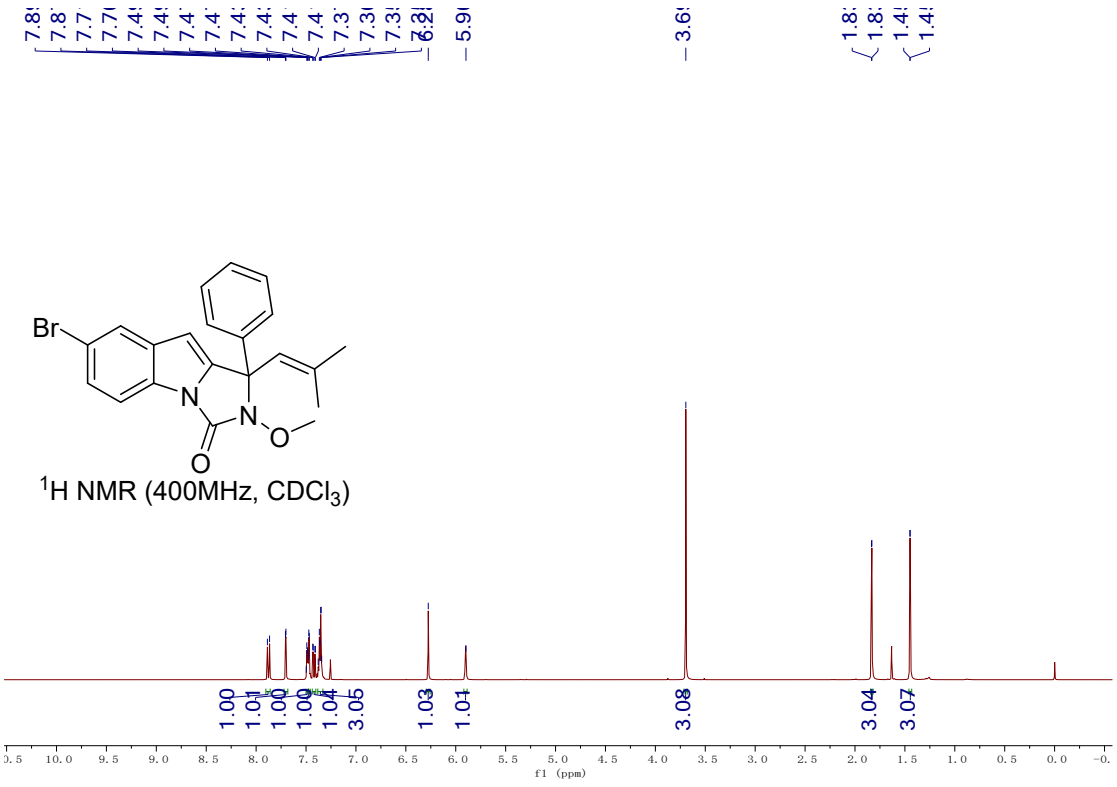


^{13}C NMR spectrum of **3ja**



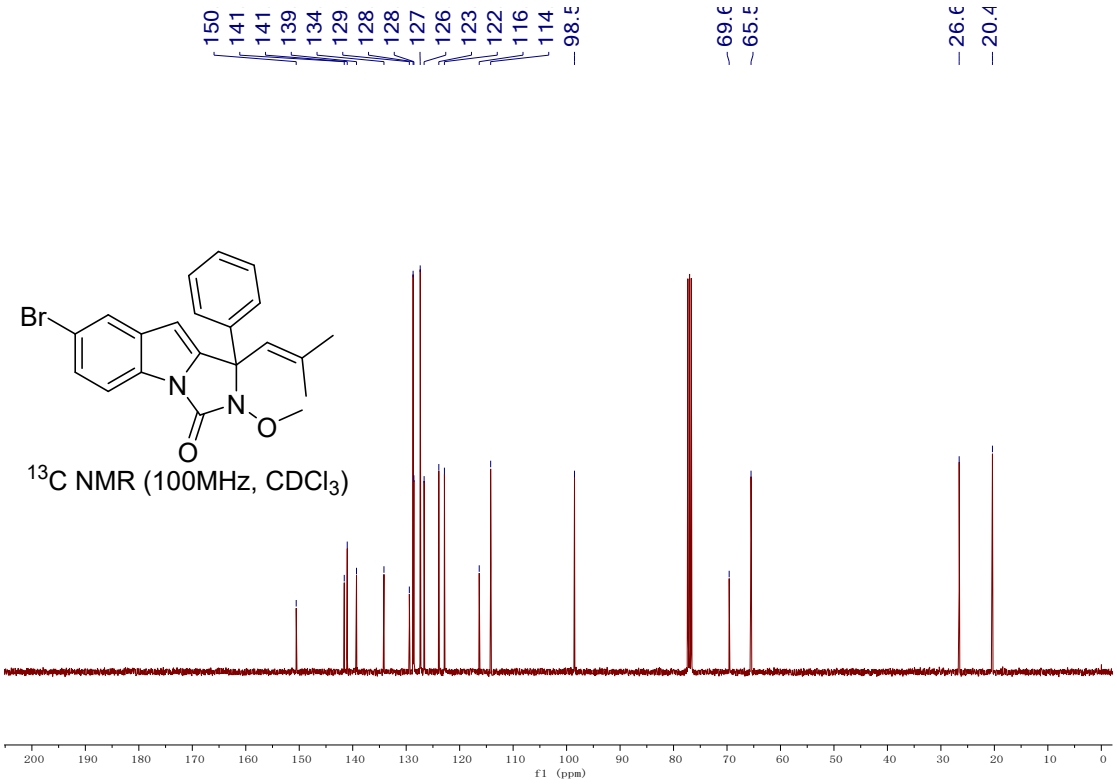
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ka**

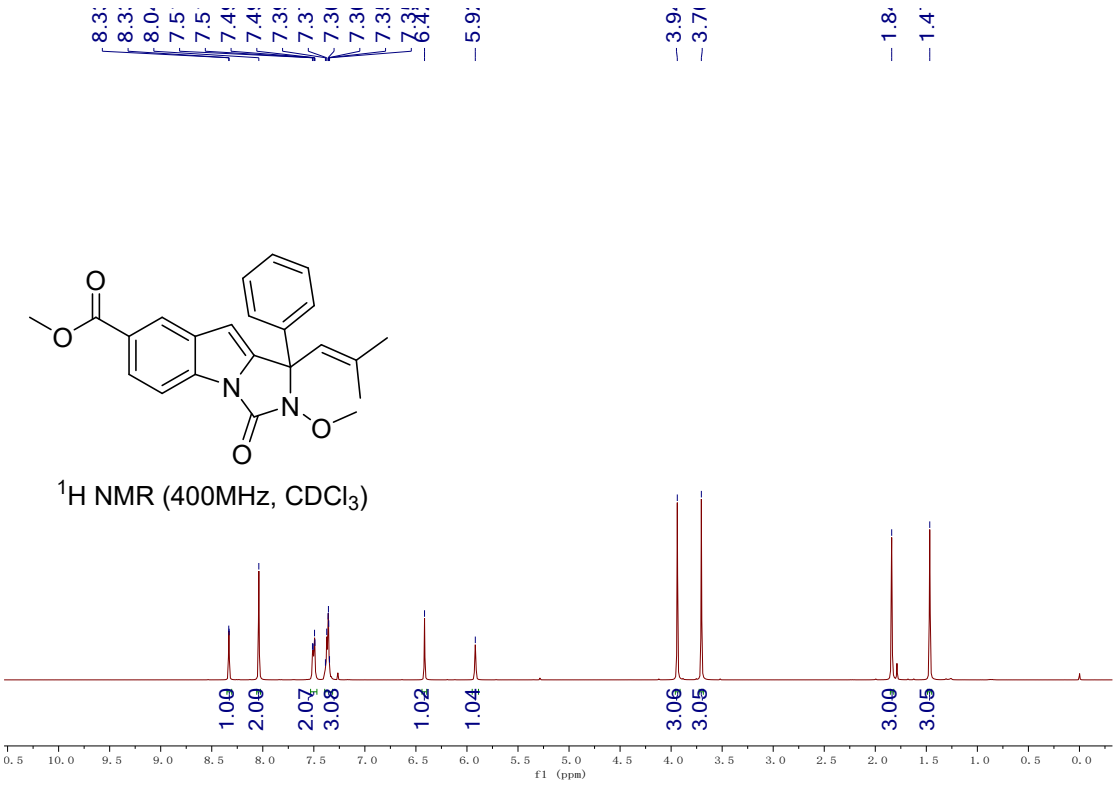


^{1}H NMR (400MHz, $CDCl_3$)

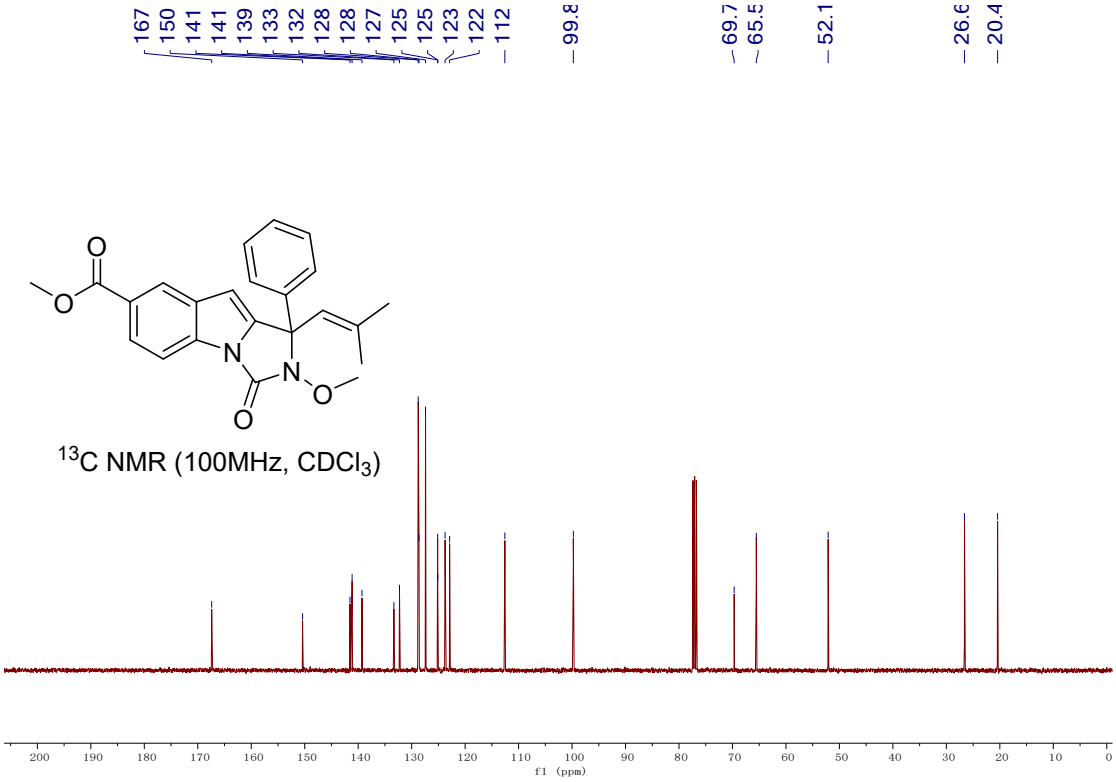
^{13}C NMR spectrum of **3ka**



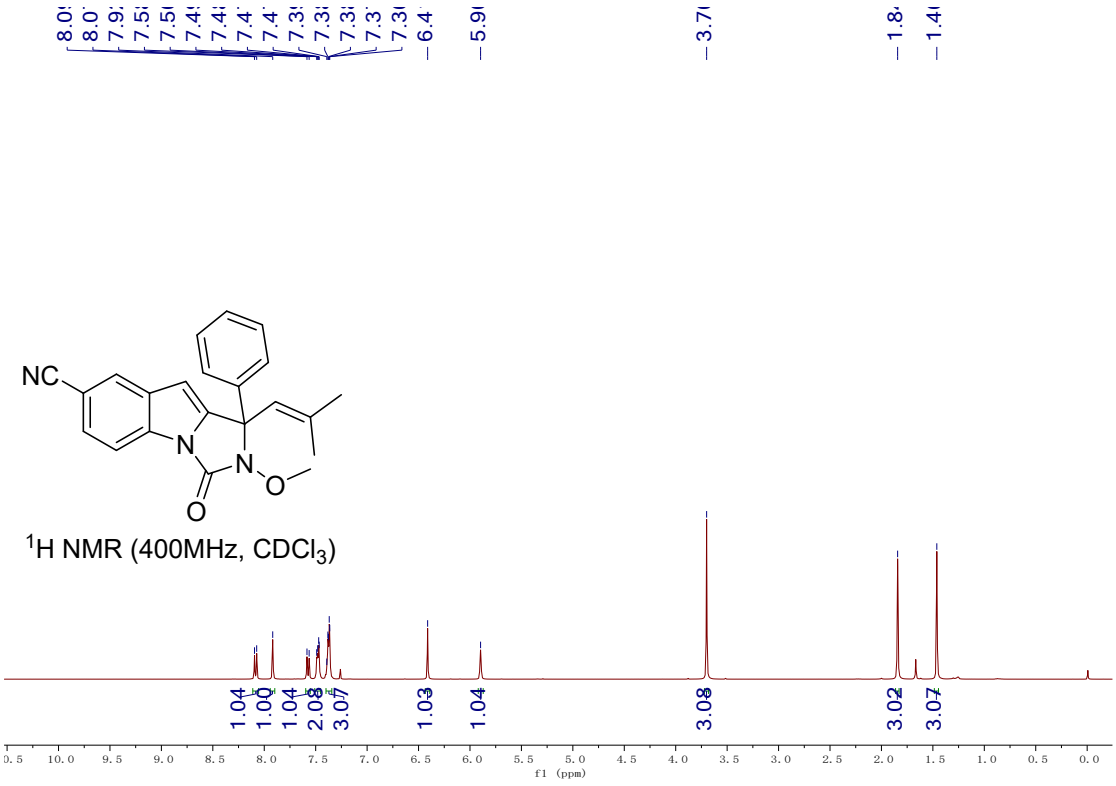
^{1}H NMR spectrum of **3la**



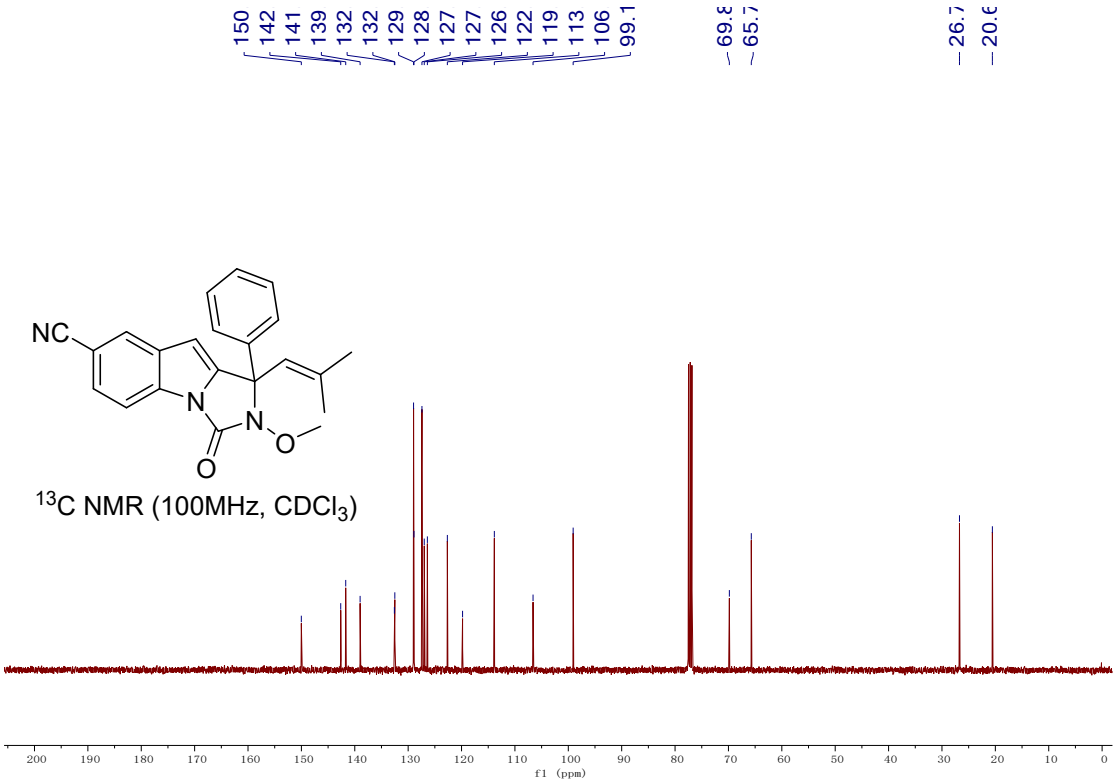
^{13}C NMR spectrum of **3la**



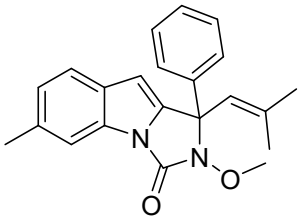
^{1}H NMR spectrum of **3ma**



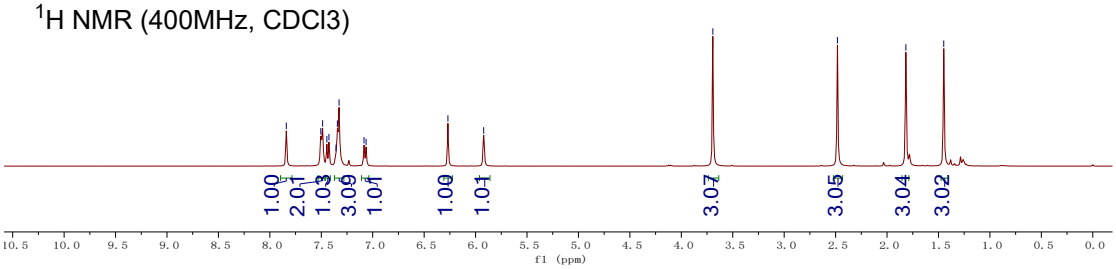
^{13}C NMR spectrum of **3ma**



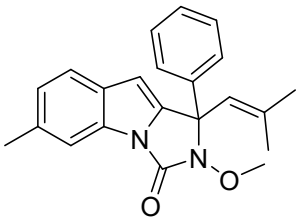
^{1}H NMR spectrum of **3na**



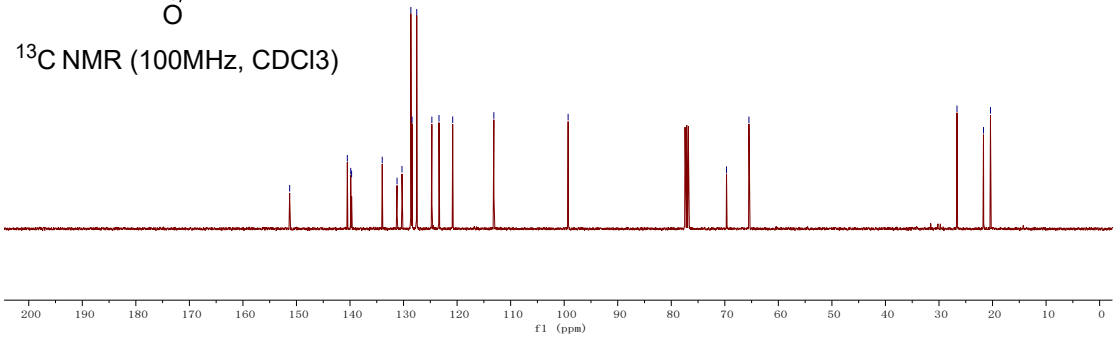
^{1}H NMR (400MHz, CDCl3)



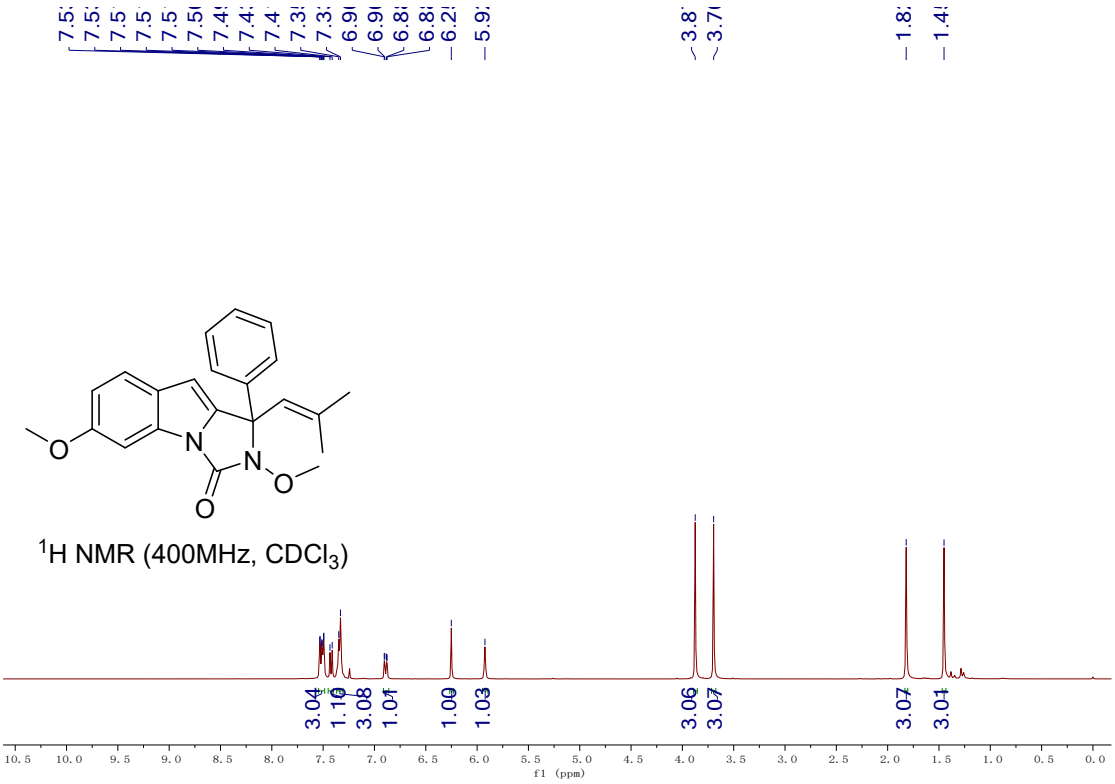
^{13}C NMR spectrum of **3na**



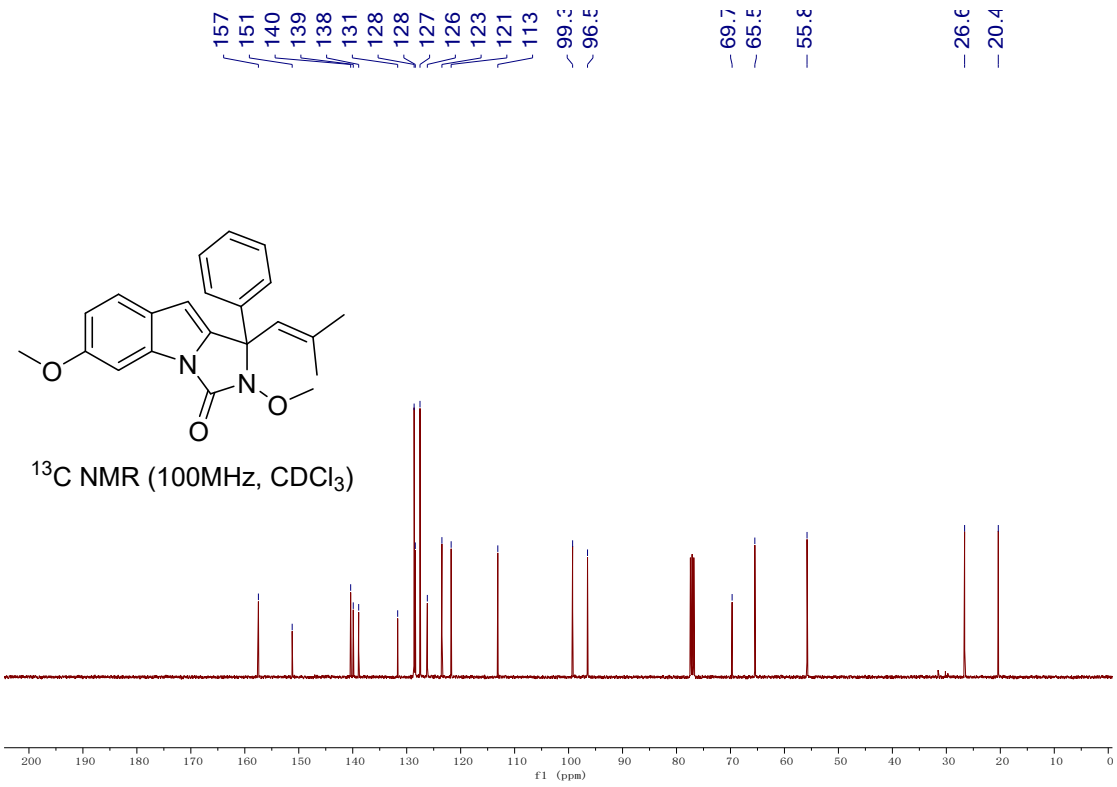
^{13}C NMR (100MHz, CDCl3)



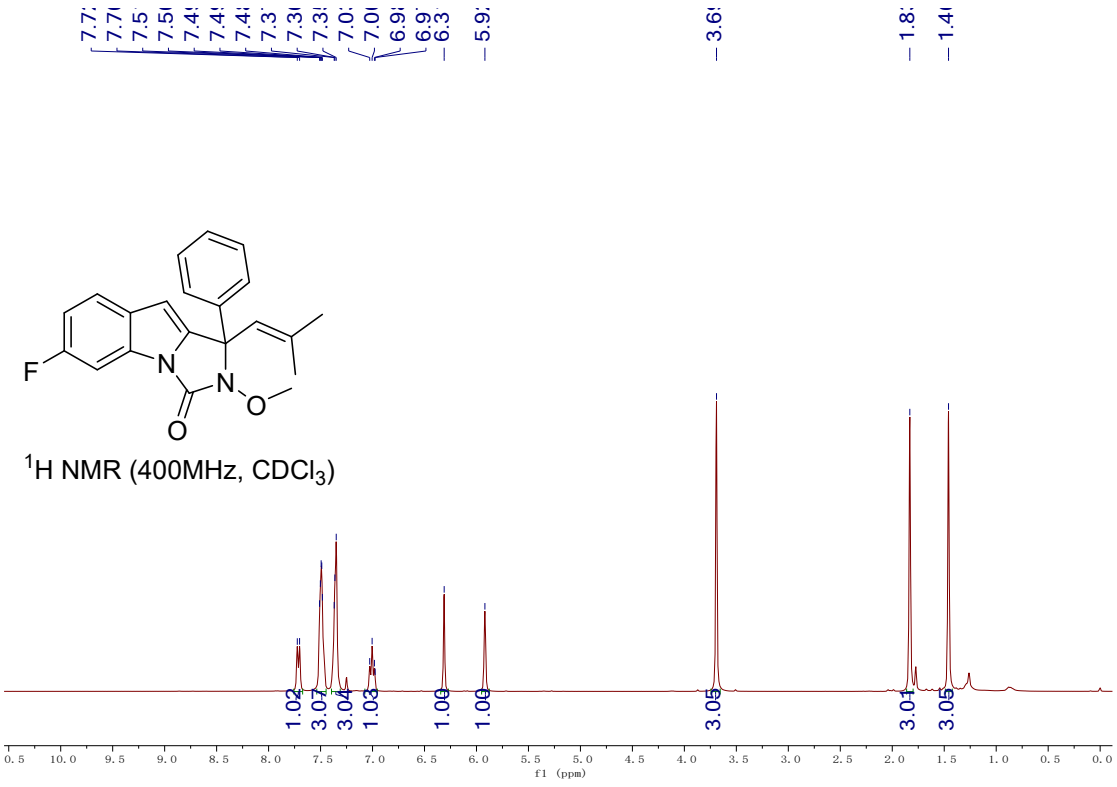
^{1}H NMR spectrum of **3oa**



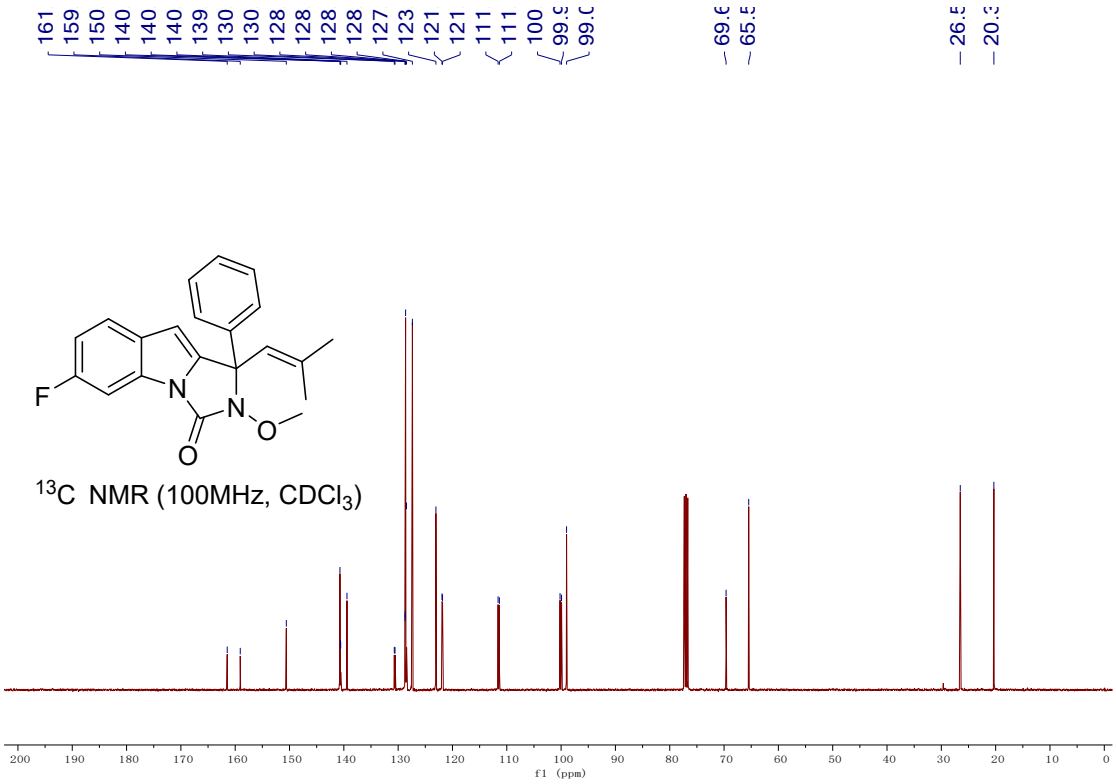
^{13}C NMR spectrum of **3oa**



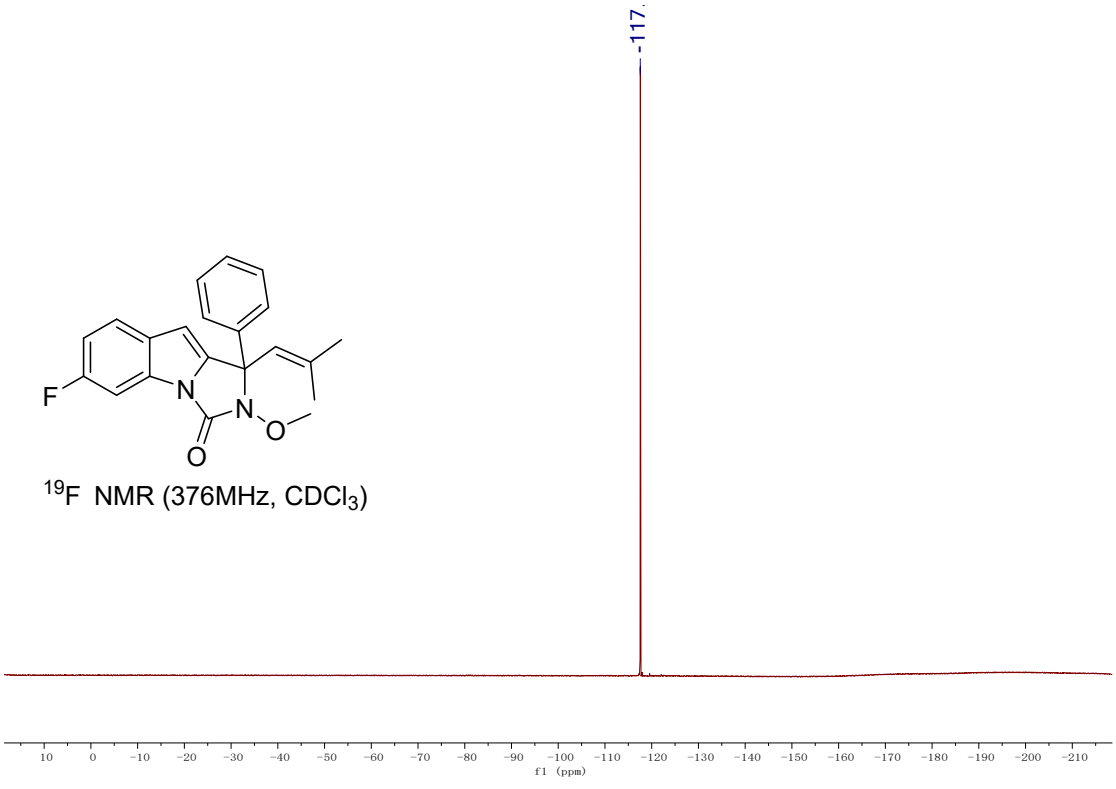
^{1}H NMR spectrum of **3pa**



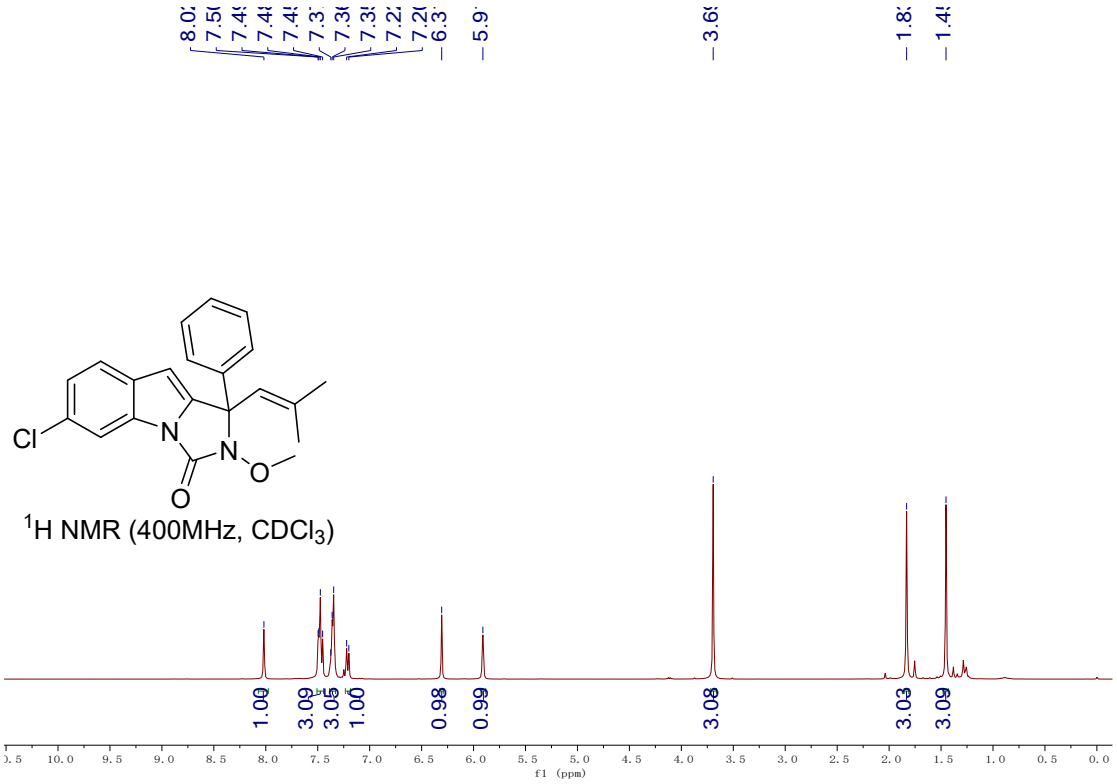
^{13}C NMR spectrum of **3pa**



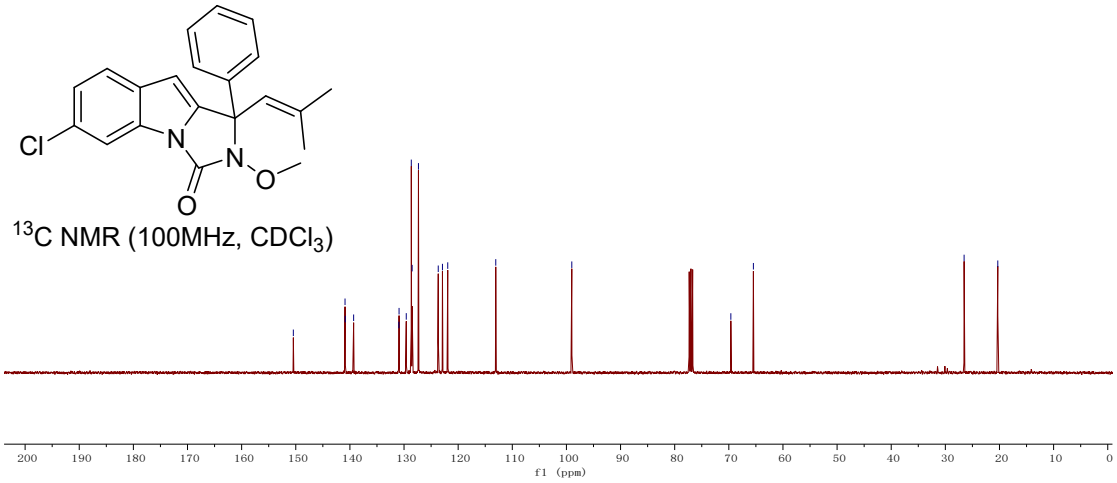
^{19}F NMR spectrum of **3pa**



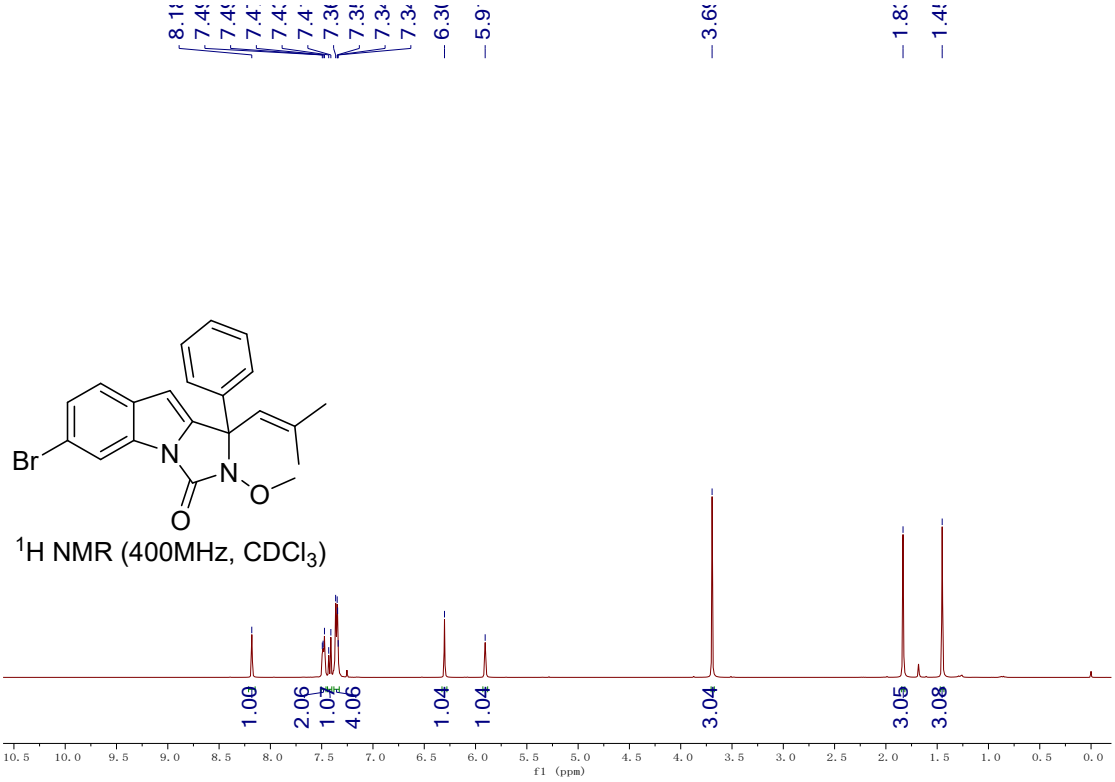
^{1}H NMR spectrum of **3qa**



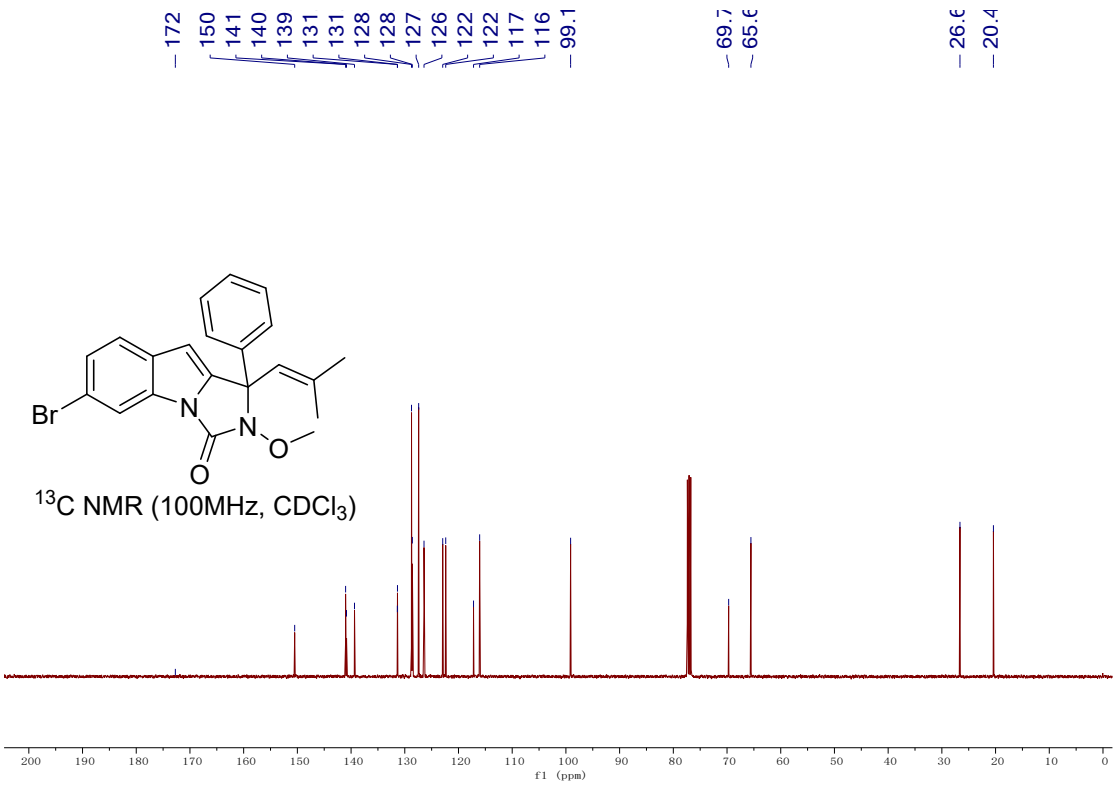
^{13}C NMR spectrum of **3qa**



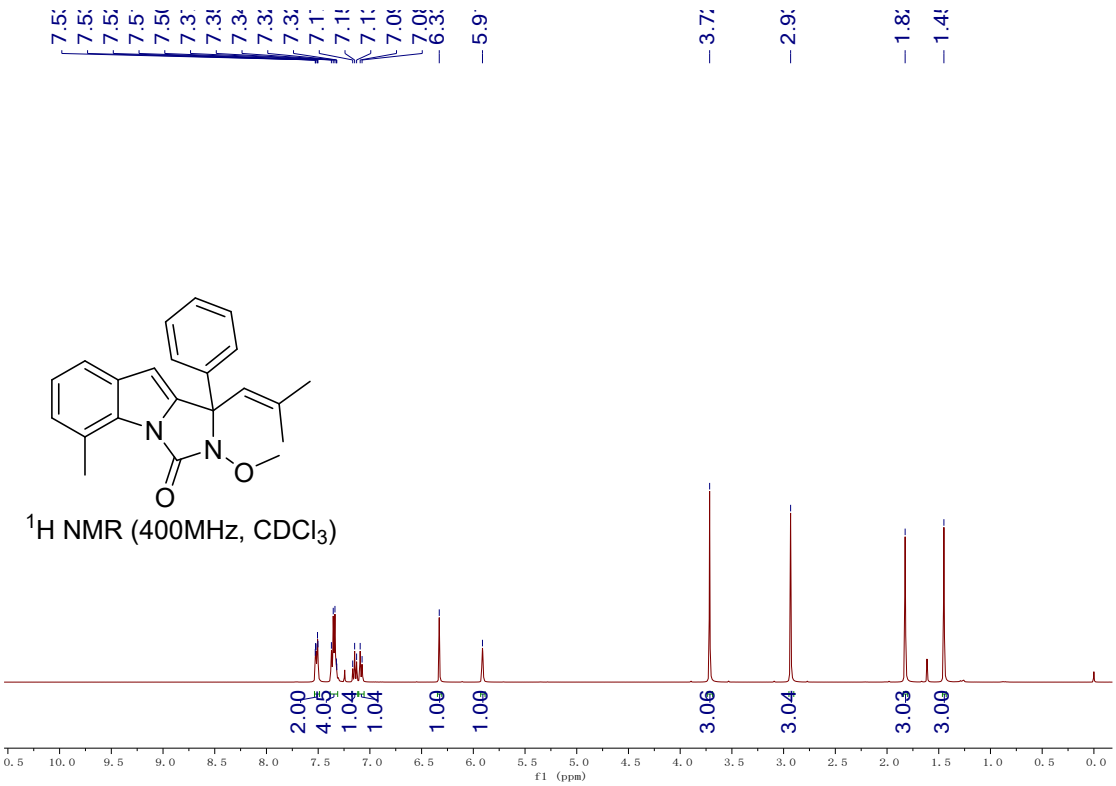
^{1}H NMR spectrum of **3ra**



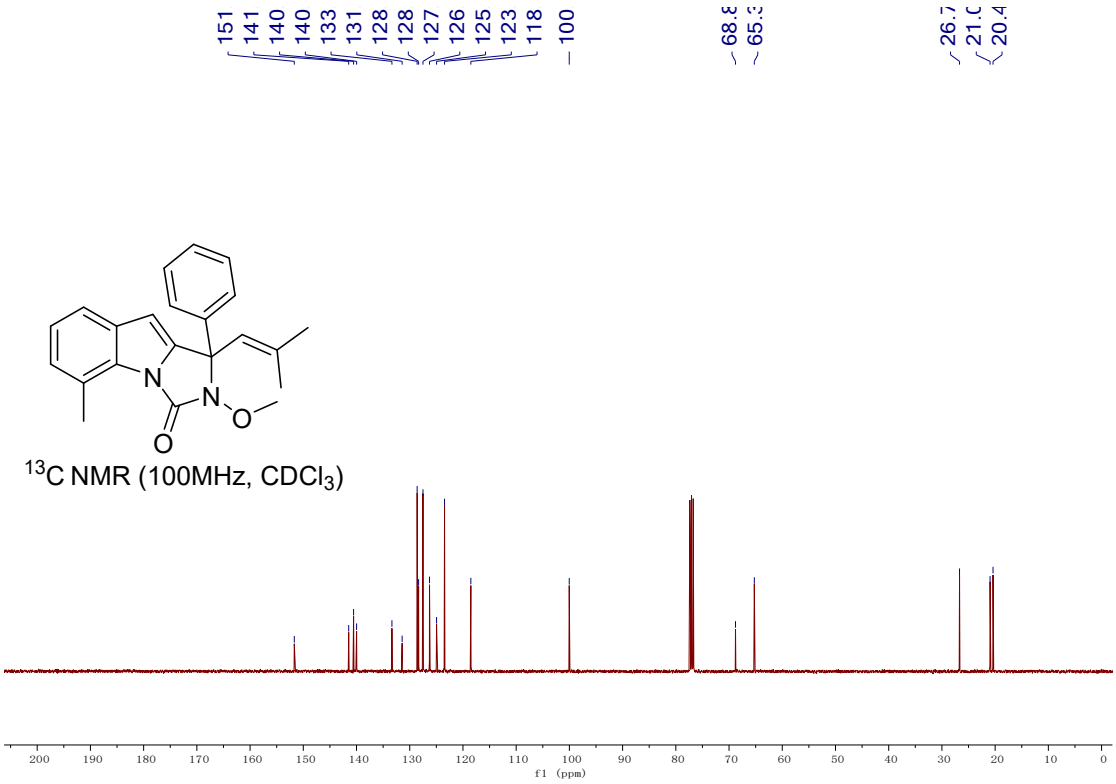
^{13}C NMR spectrum of **3ra**



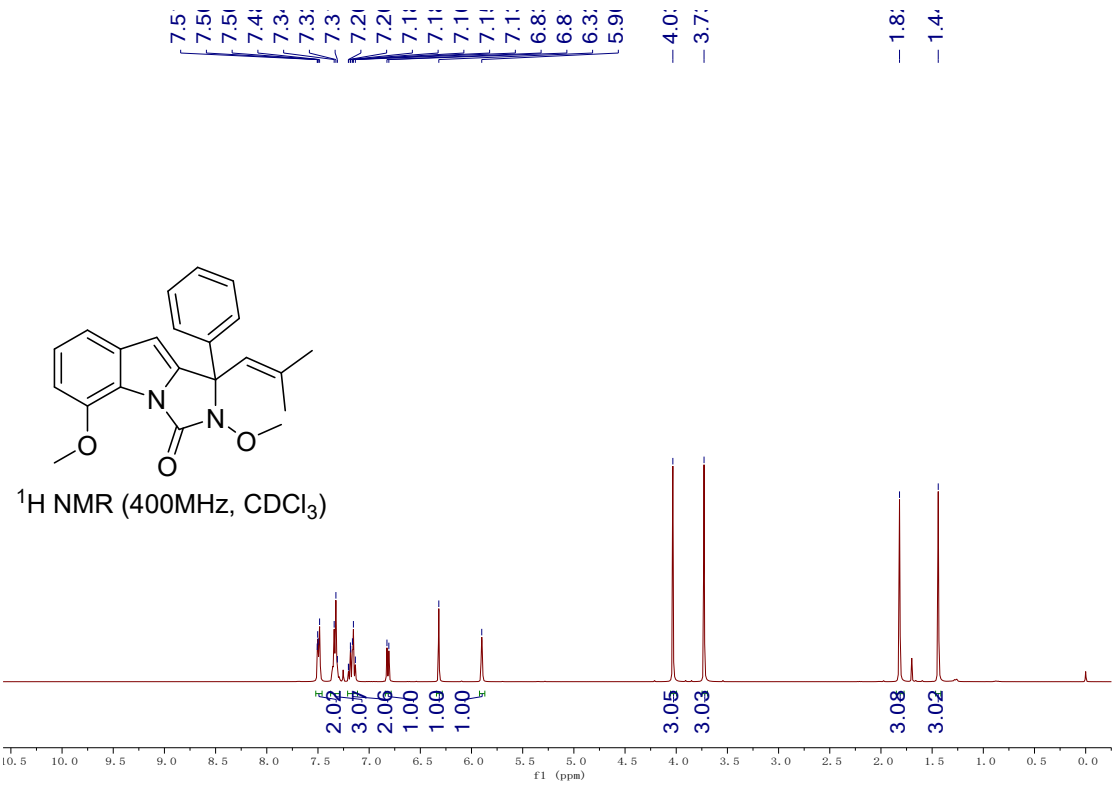
^{1}H NMR spectrum of **3sa**



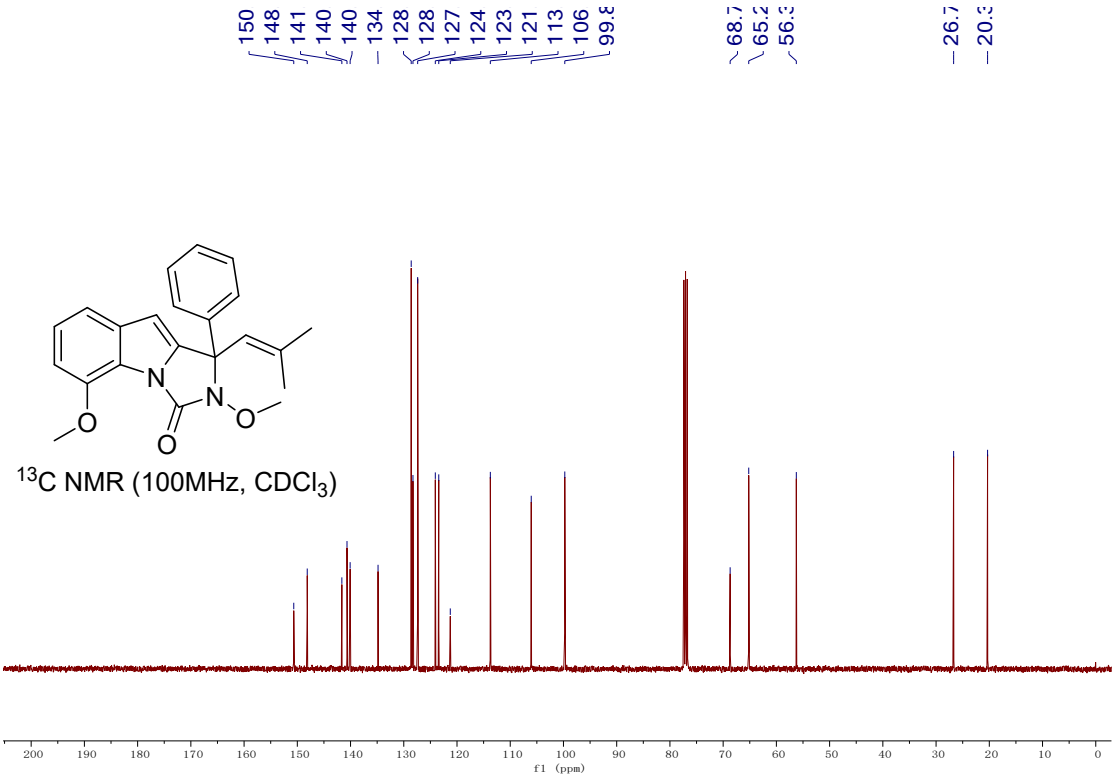
^{13}C NMR spectrum of **3sa**



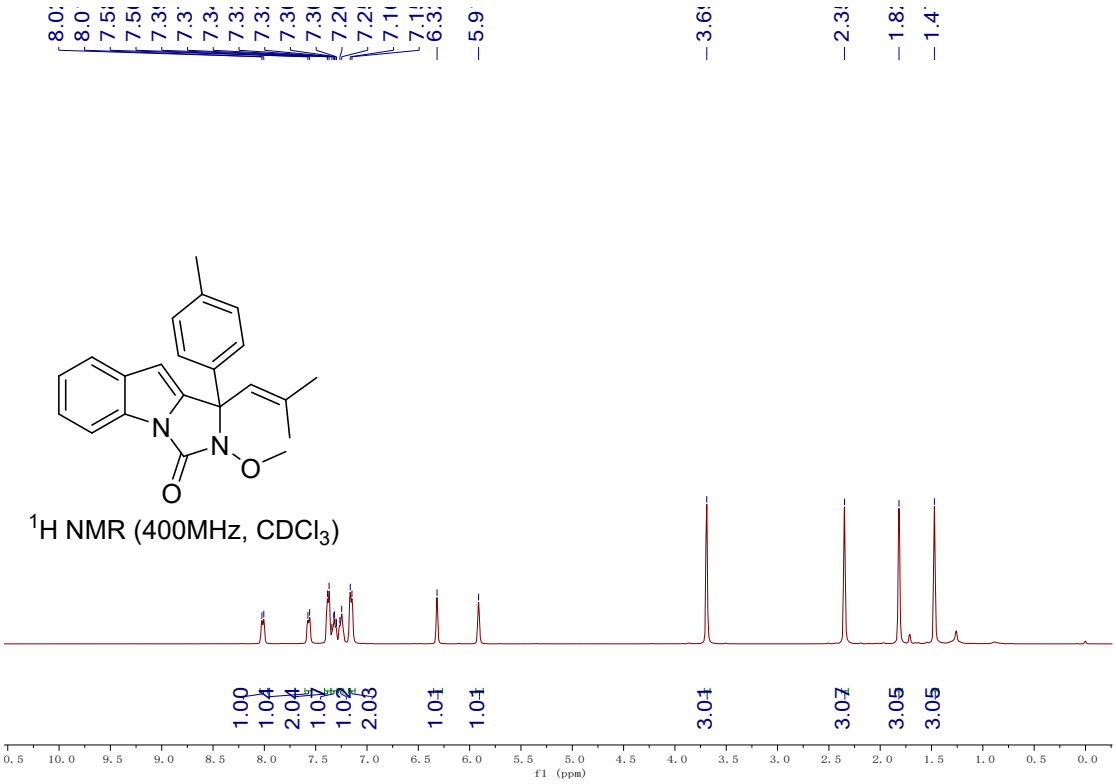
^{1}H NMR spectrum of **3ta**



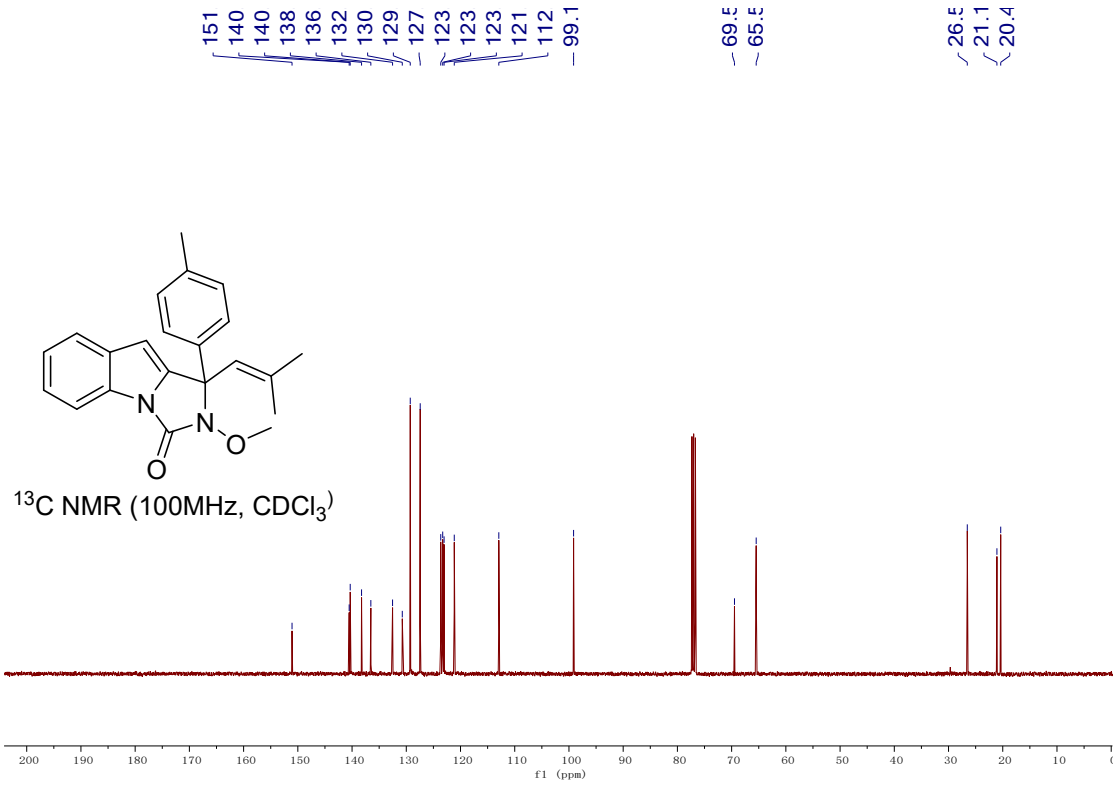
^{13}C NMR spectrum of **3ta**



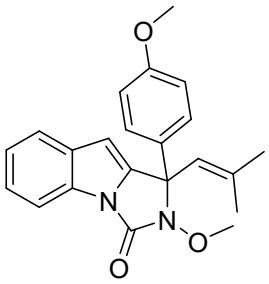
^{1}H NMR spectrum of **3ab**



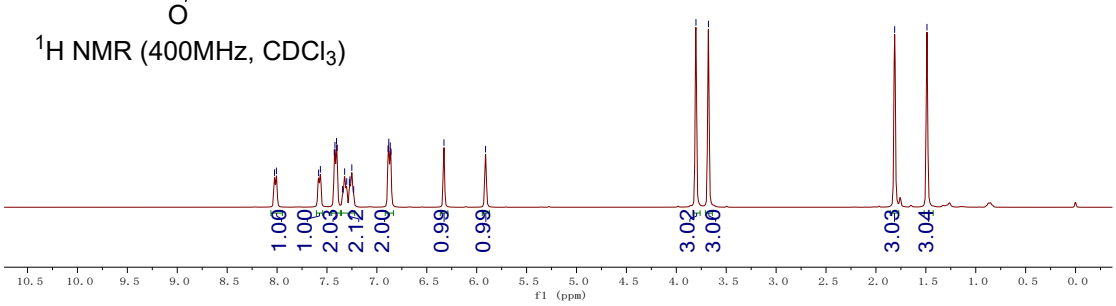
^{13}C NMR spectrum of **3ab**



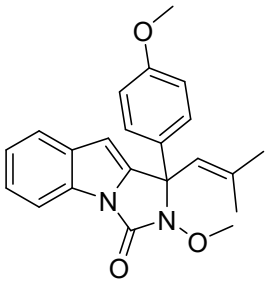
^{1}H NMR spectrum of **3ac**



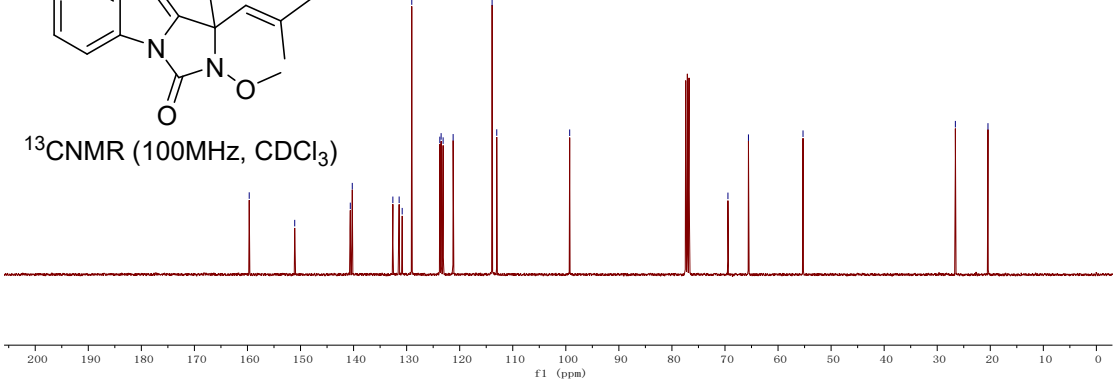
^{1}H NMR (400MHz, $CDCl_3$)



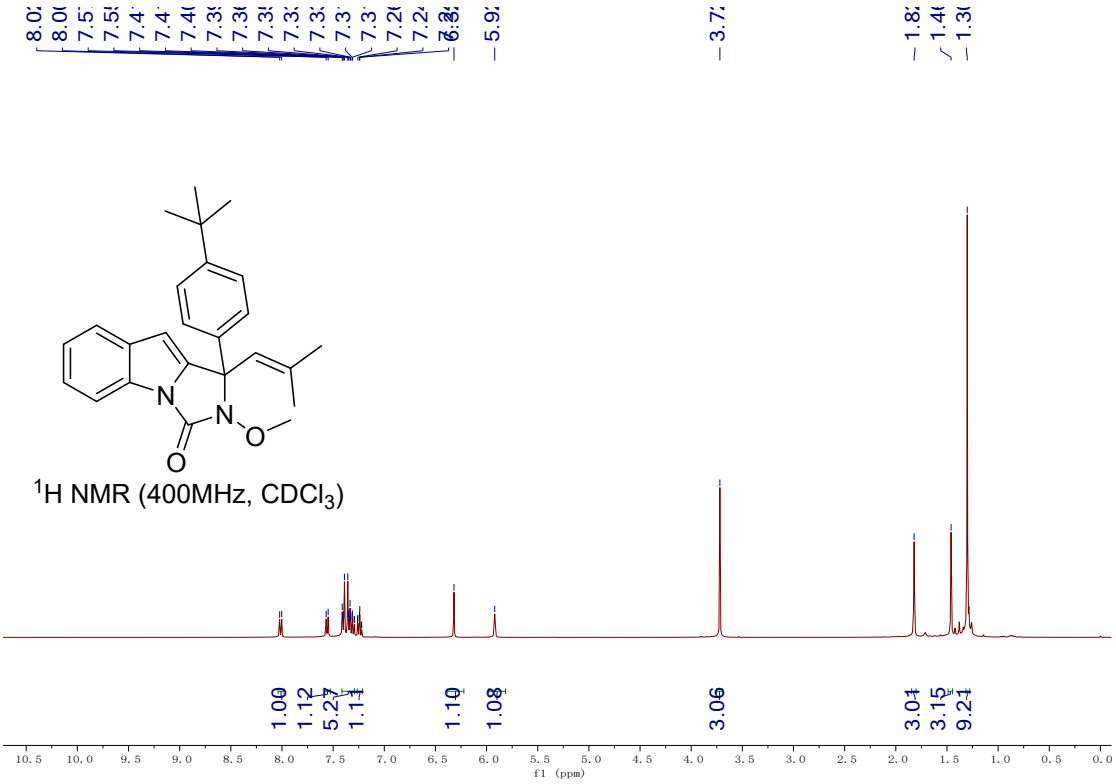
^{13}C NMR spectrum of **3ac**



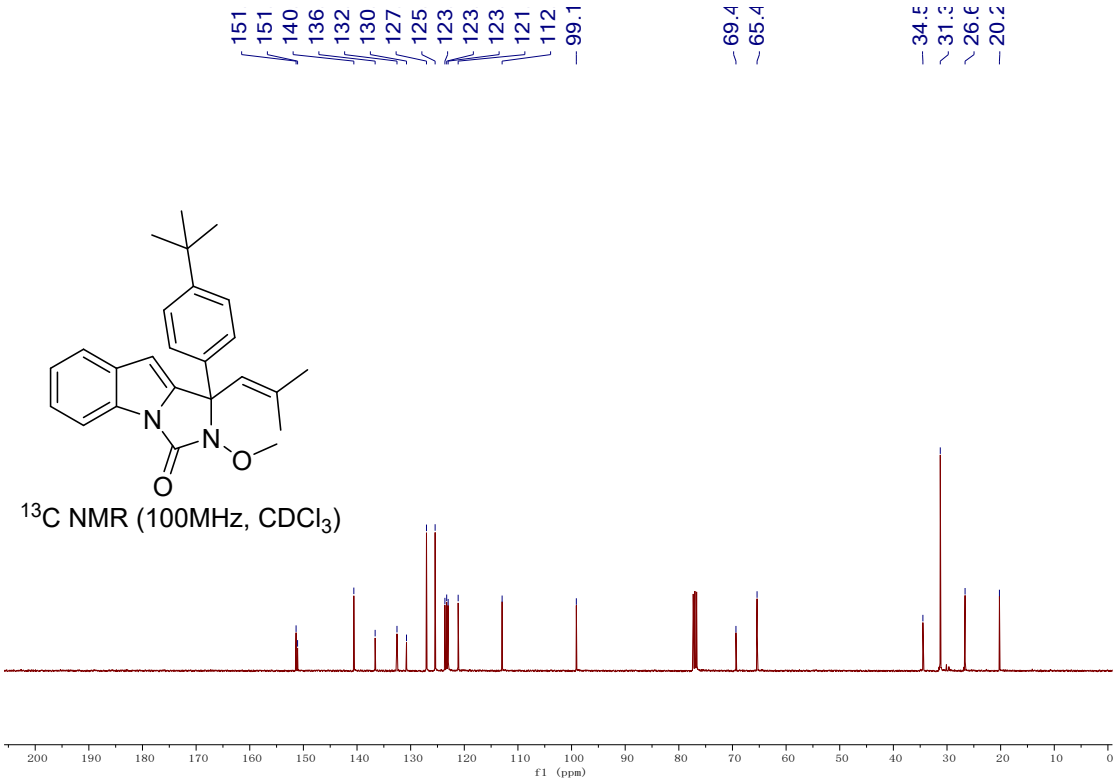
^{13}CNMR (100MHz, $CDCl_3$)



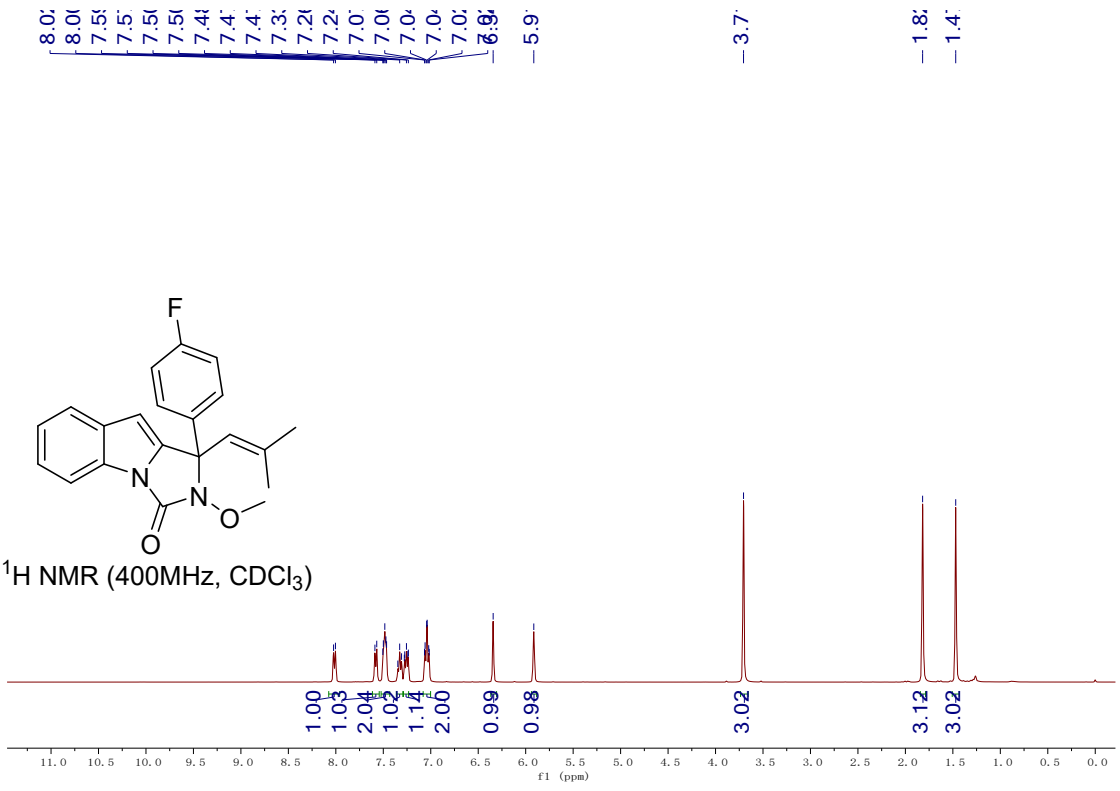
^{1}H NMR spectrum of **3ad**



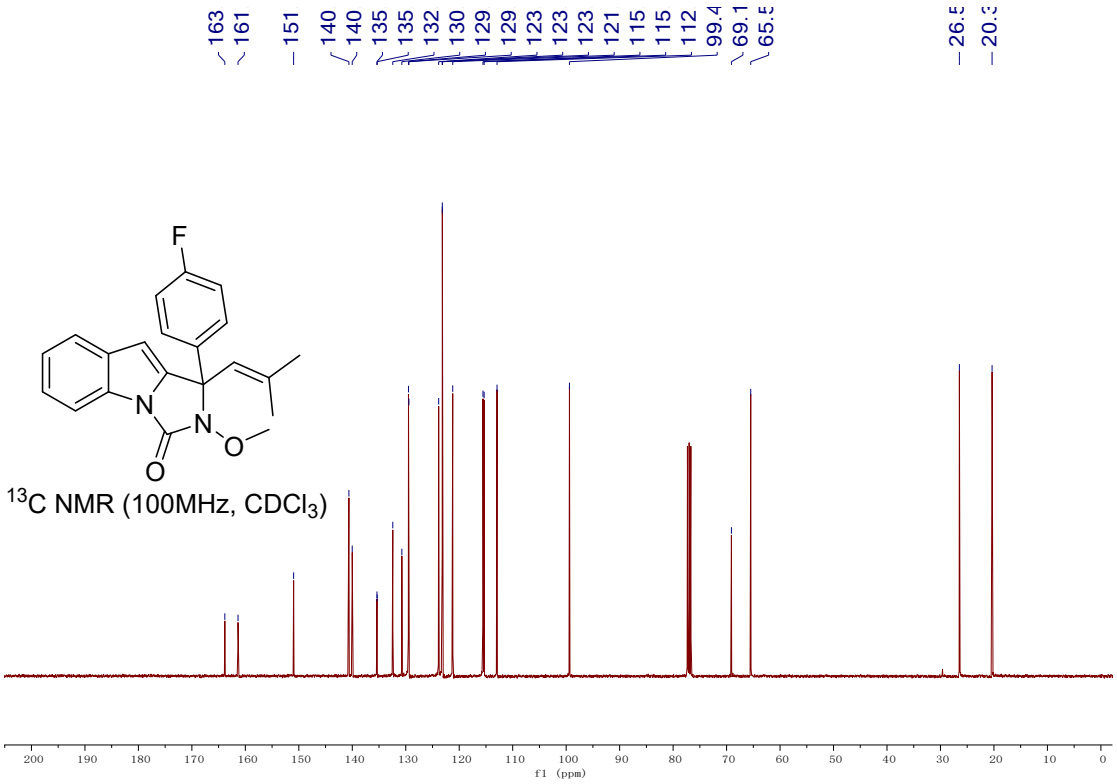
^{13}C NMR spectrum of **3ad**



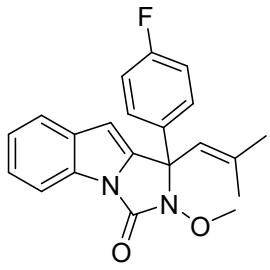
^{1}H NMR spectrum of **3ae**



^{13}C NMR spectrum of **3ae**

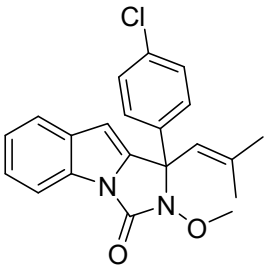


^{19}F NMR spectrum of **3ae**

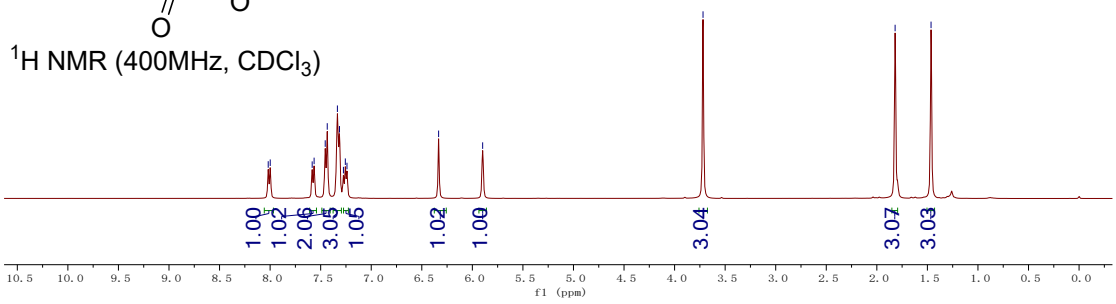


^{19}F NMR (376MHz, $CDCl_3$)

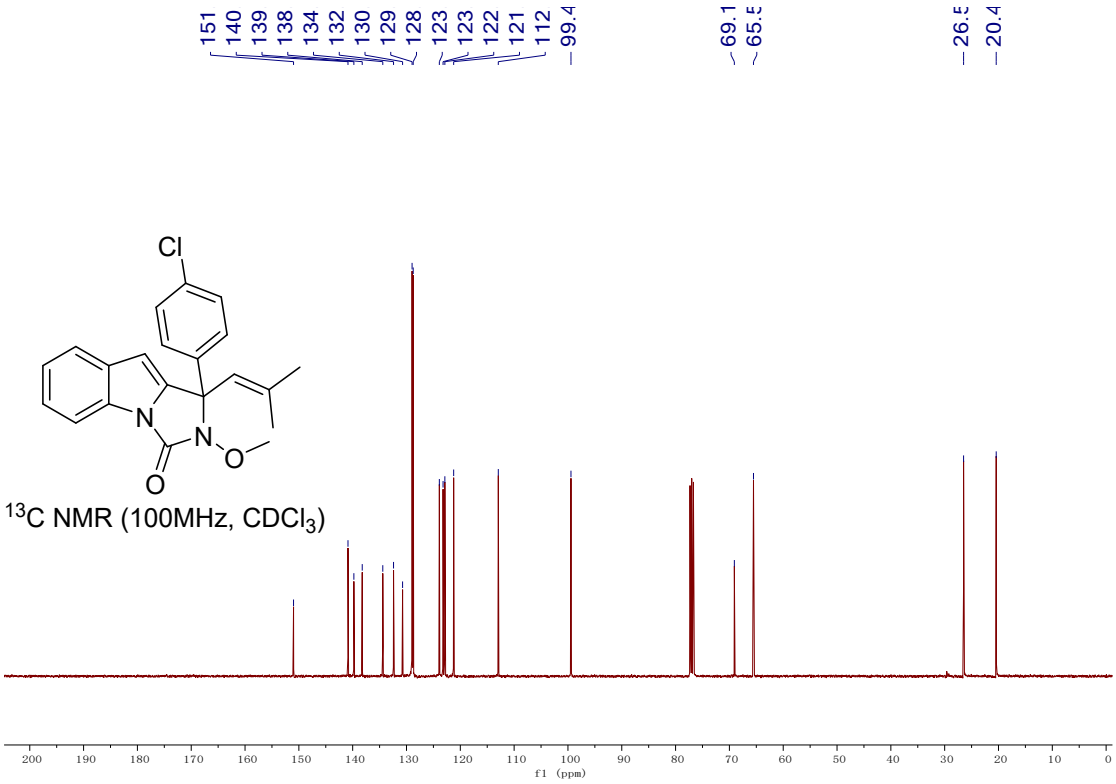
^{1}H NMR spectrum of **3af**



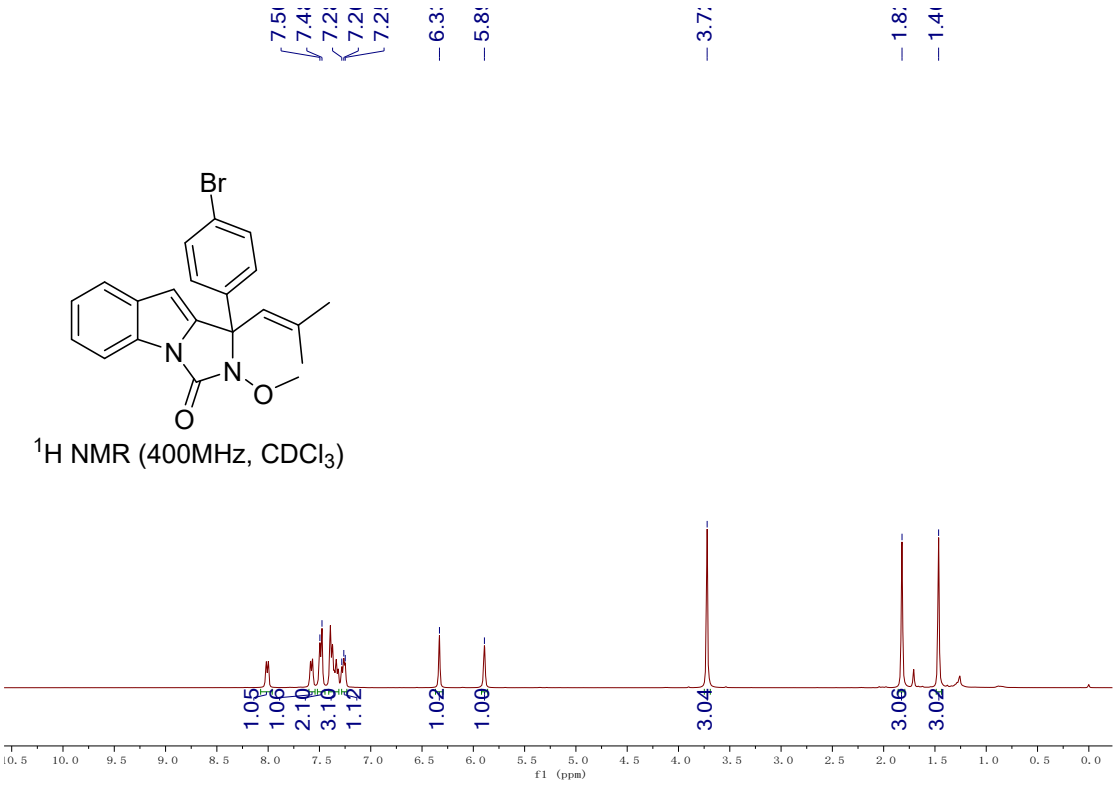
^{1}H NMR (400MHz, $CDCl_3$)



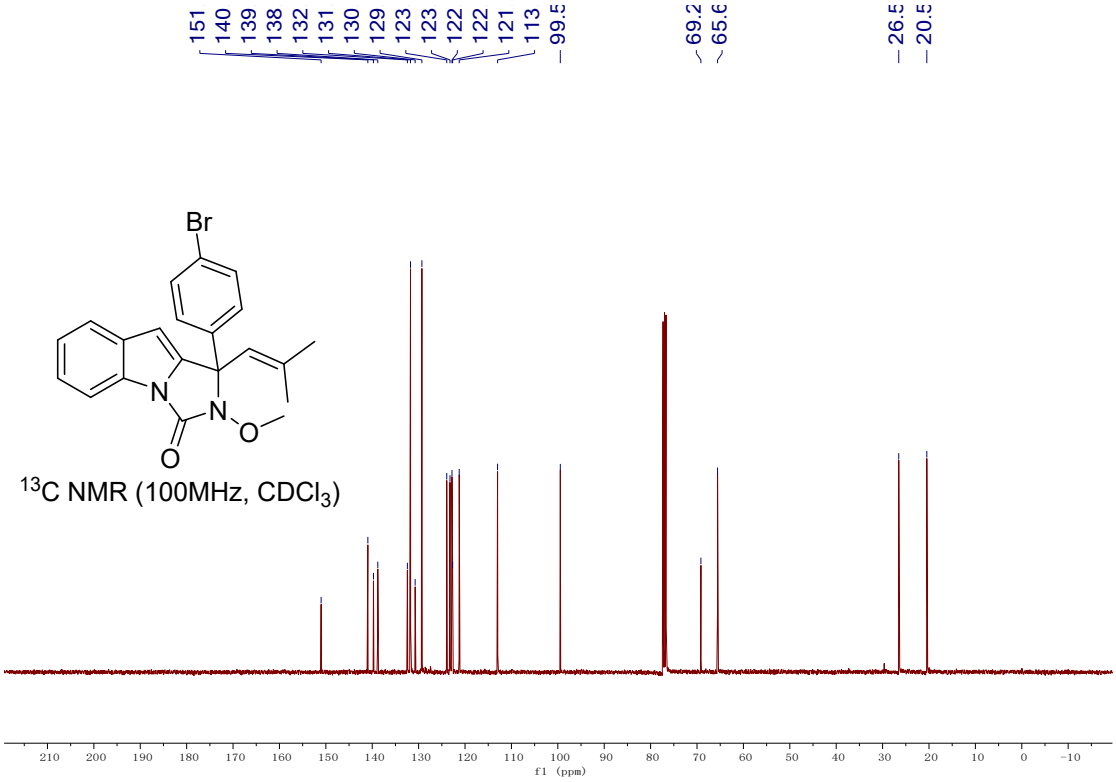
^{13}C NMR spectrum of **3af**



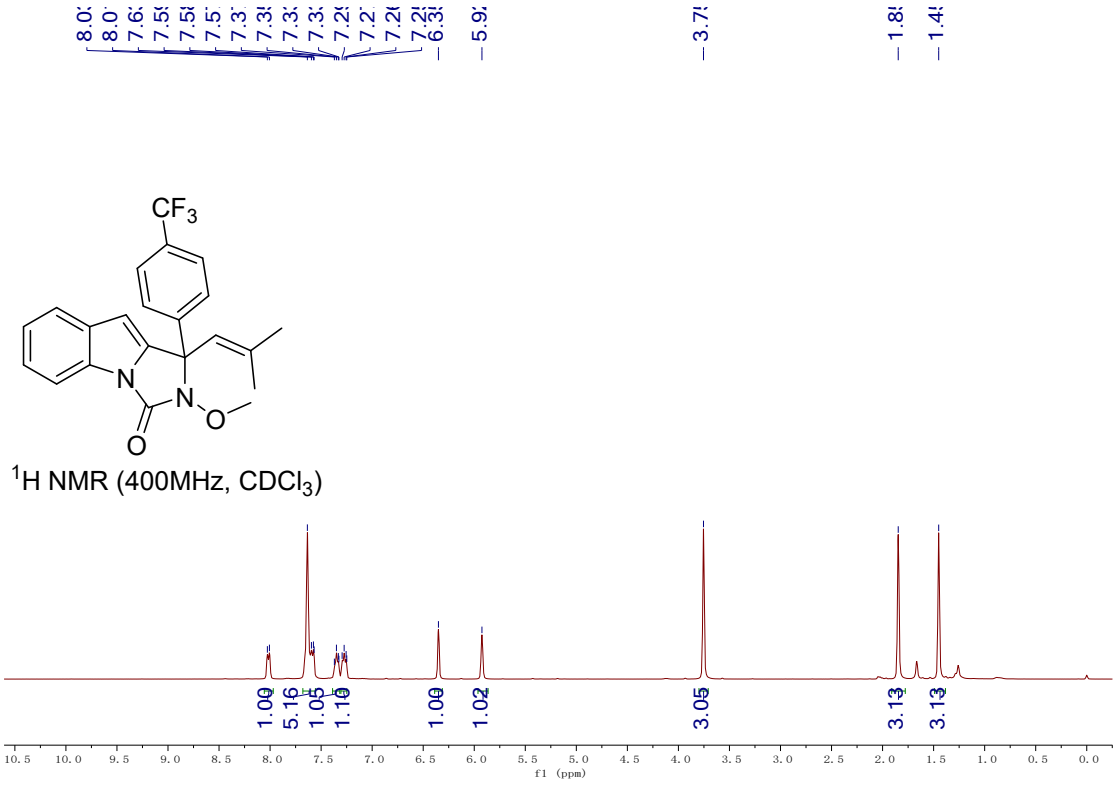
^{1}H NMR spectrum of **3ag**



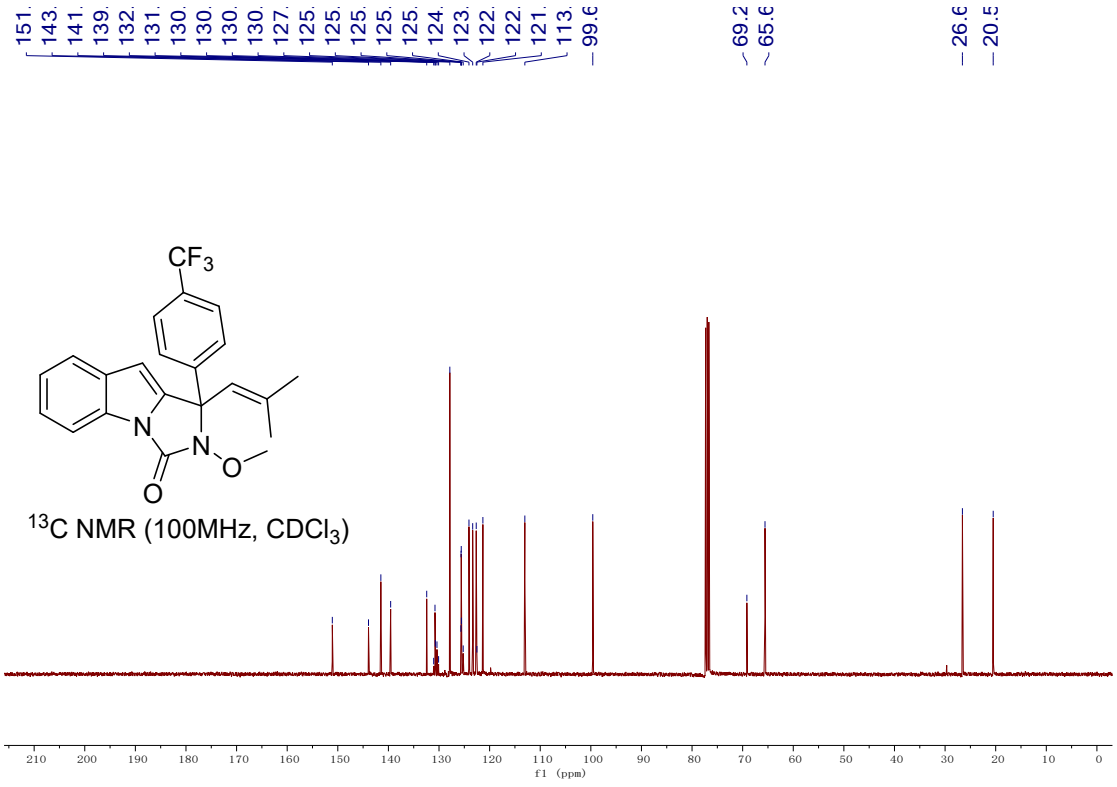
^{13}C NMR spectrum of **3ag**



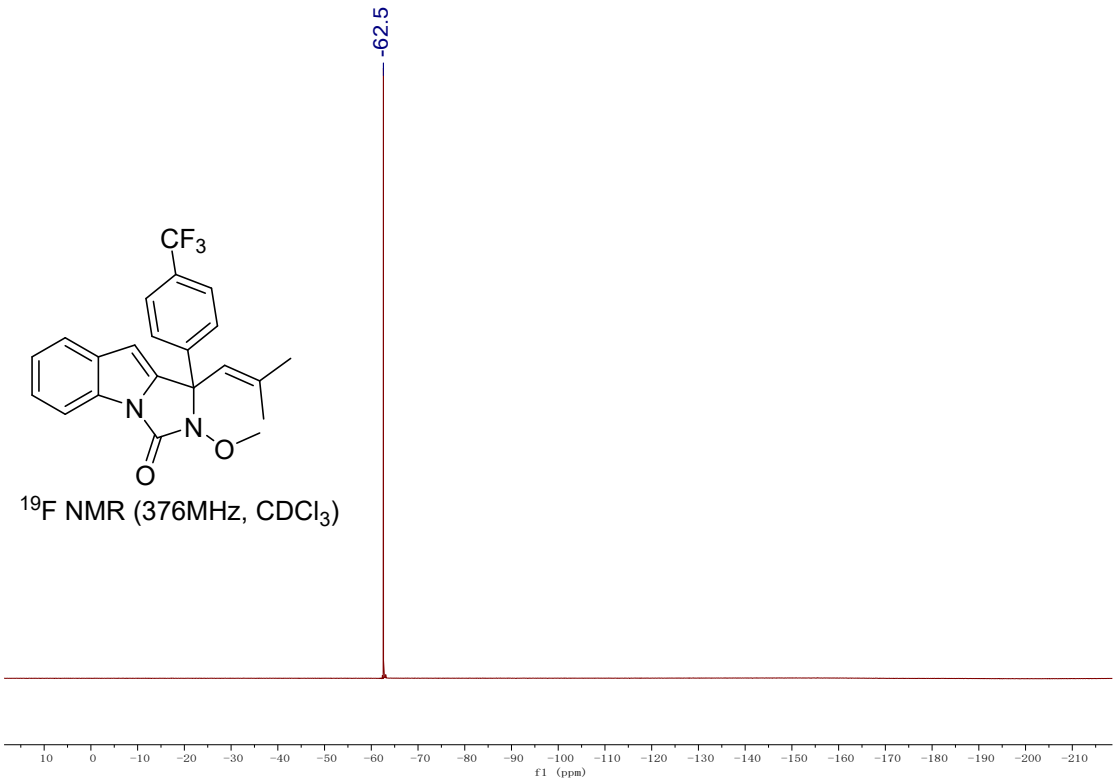
^{1}H NMR spectrum of **3ah**



^{13}C NMR spectrum of **3ah**

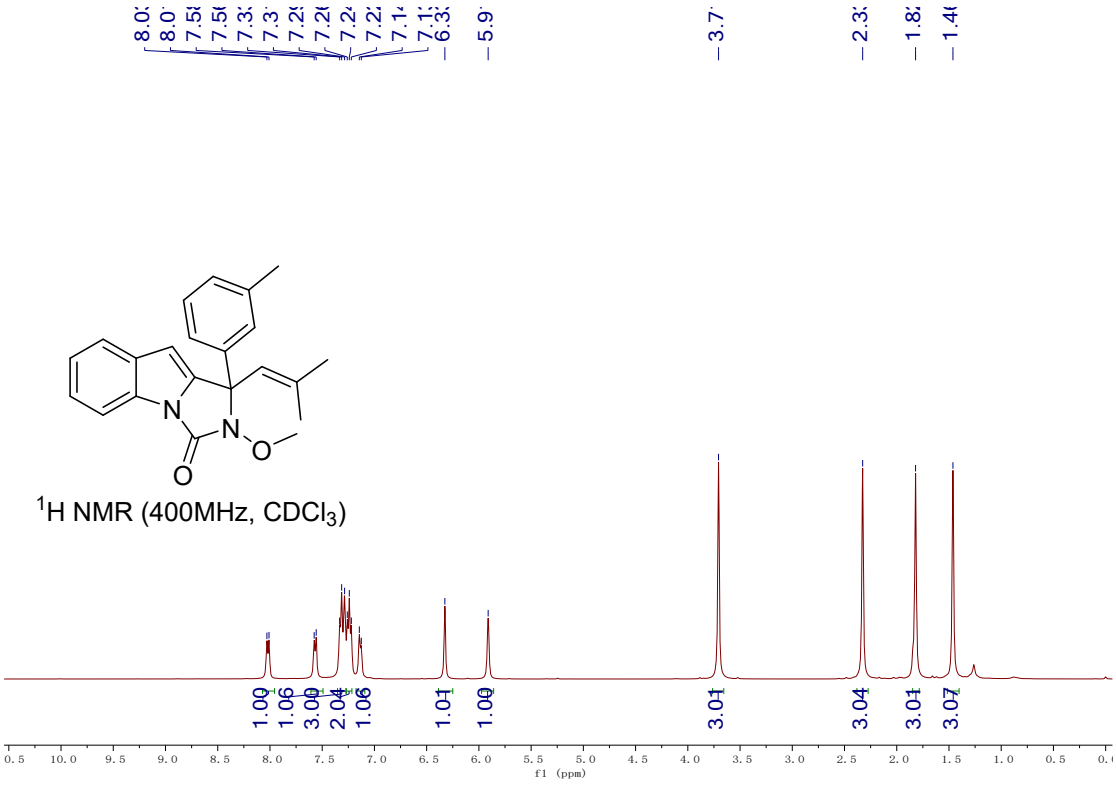


^{19}F NMR spectrum of **3ah**



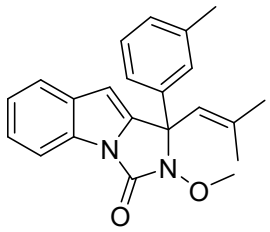
^{19}F NMR (376MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ai**

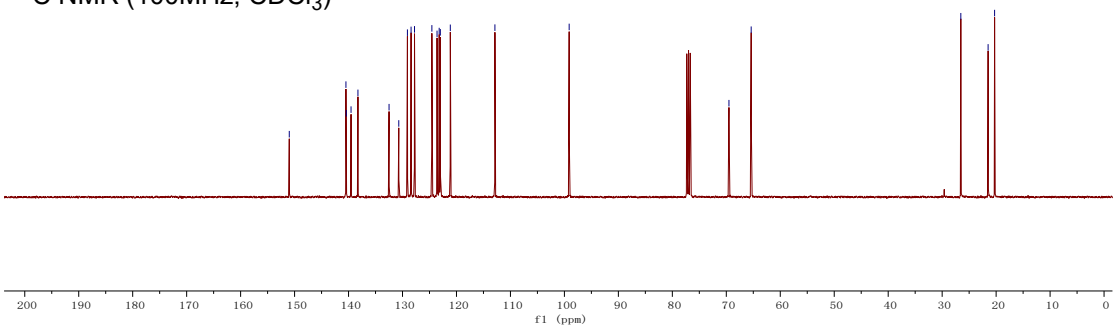


^{1}H NMR (400MHz, $CDCl_3$)

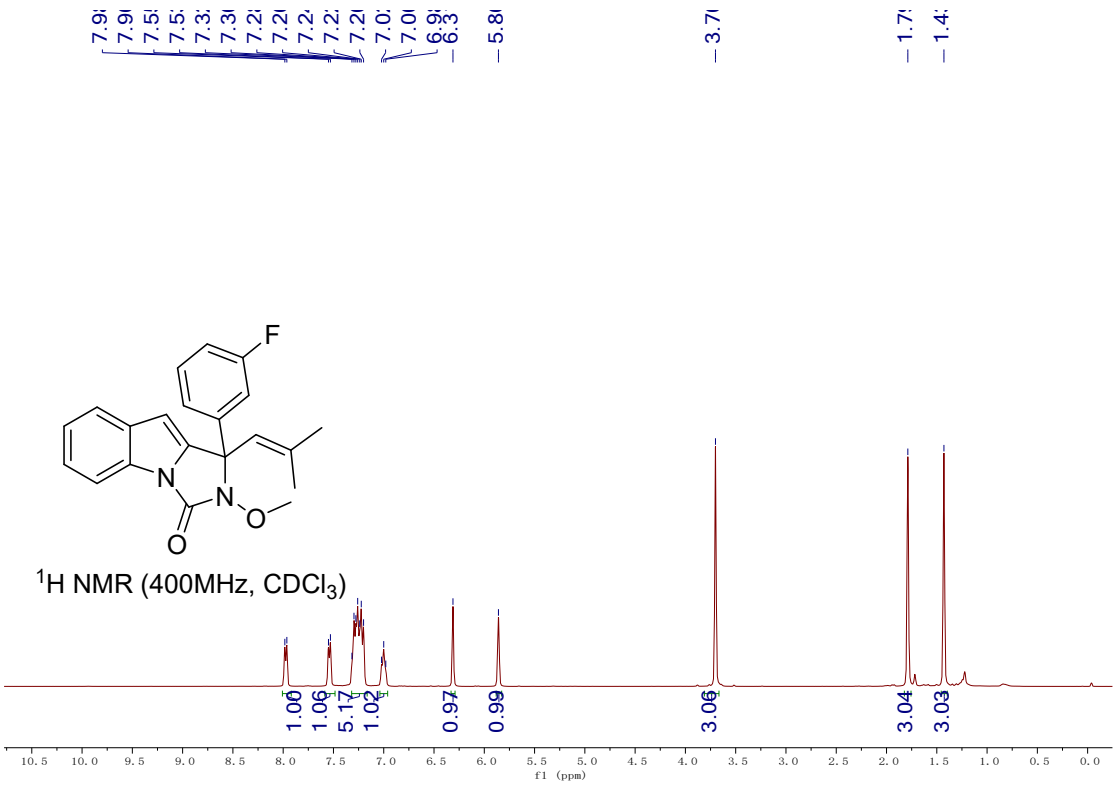
^{13}C NMR spectrum of **3ai**



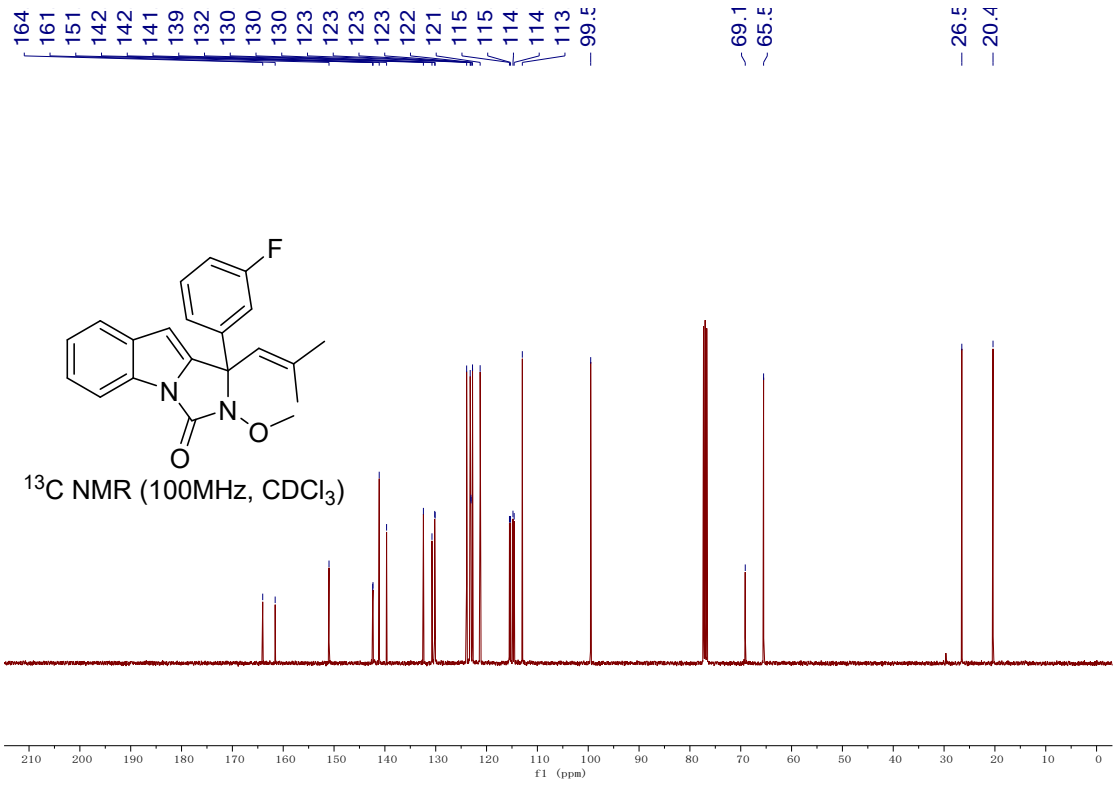
^{13}C NMR (100MHz, $CDCl_3$)



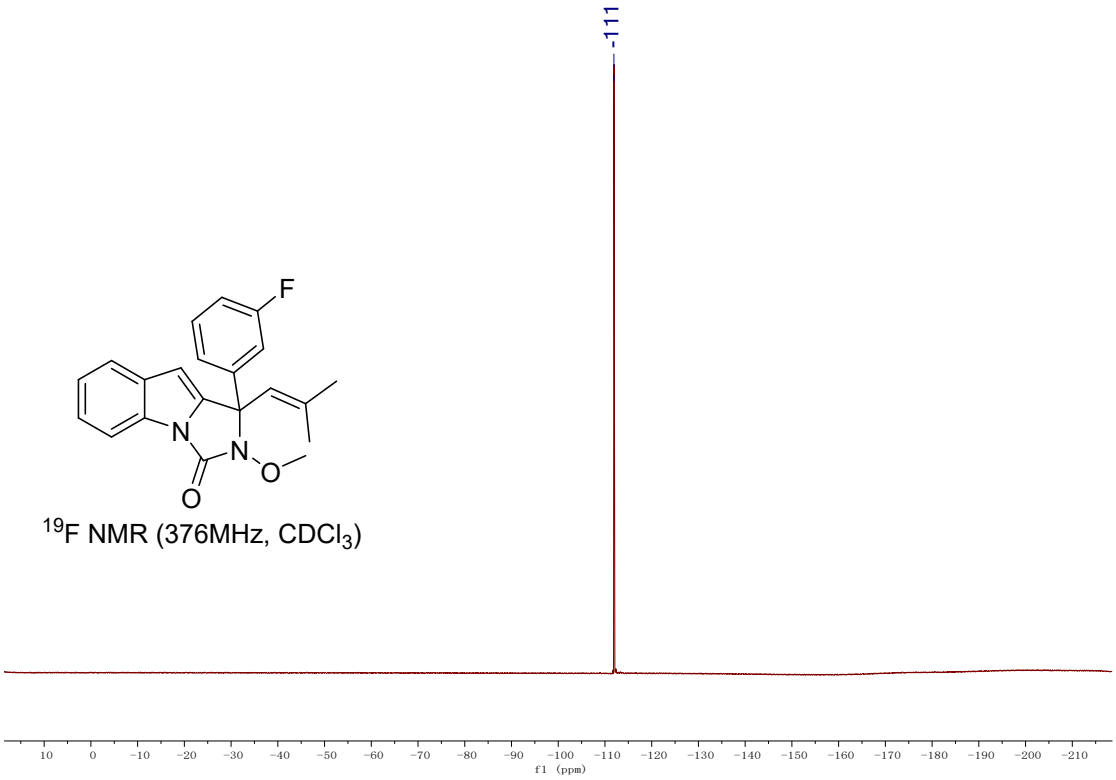
^{1}H NMR spectrum of **3aj**



^{13}C NMR spectrum of **3aj**

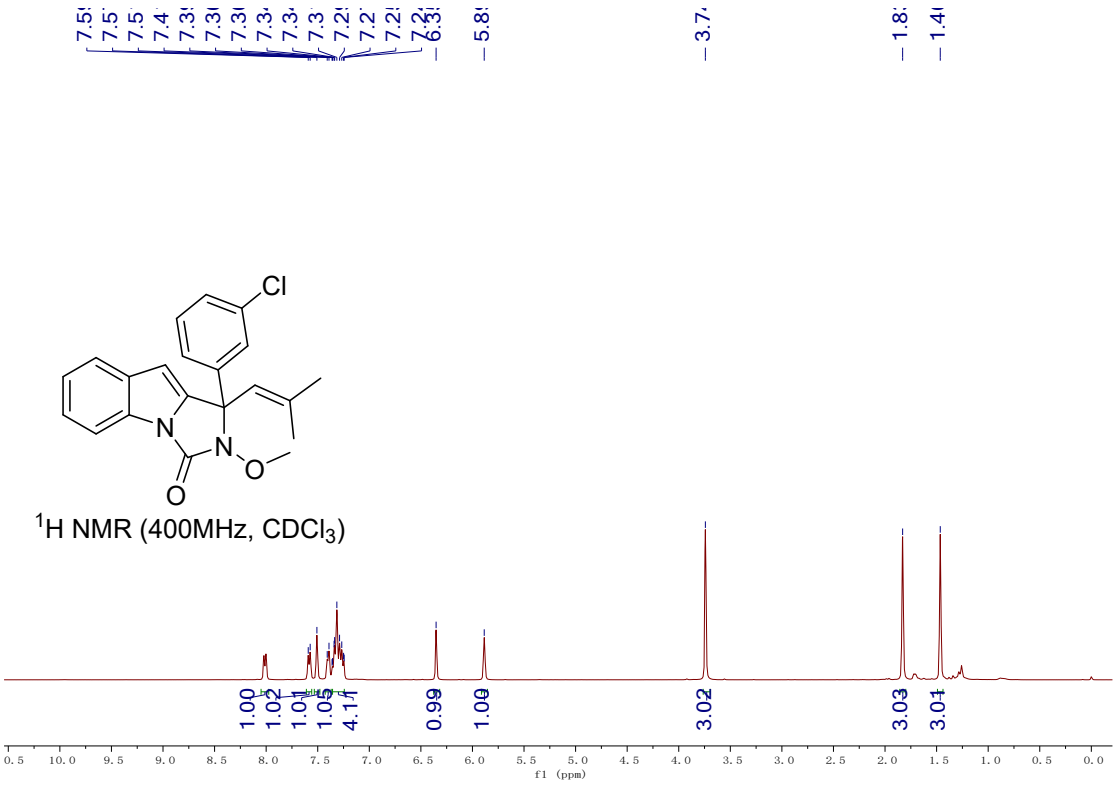


^{19}F NMR spectrum of **3aj**



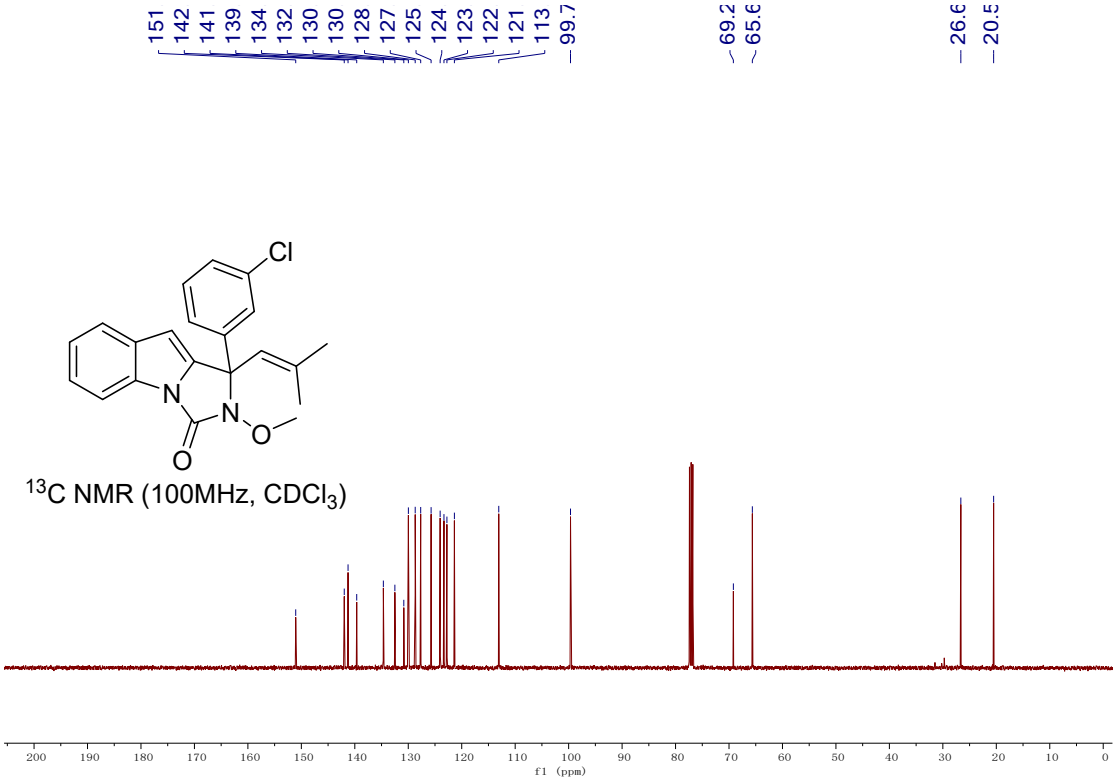
^{19}F NMR (376MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ak**

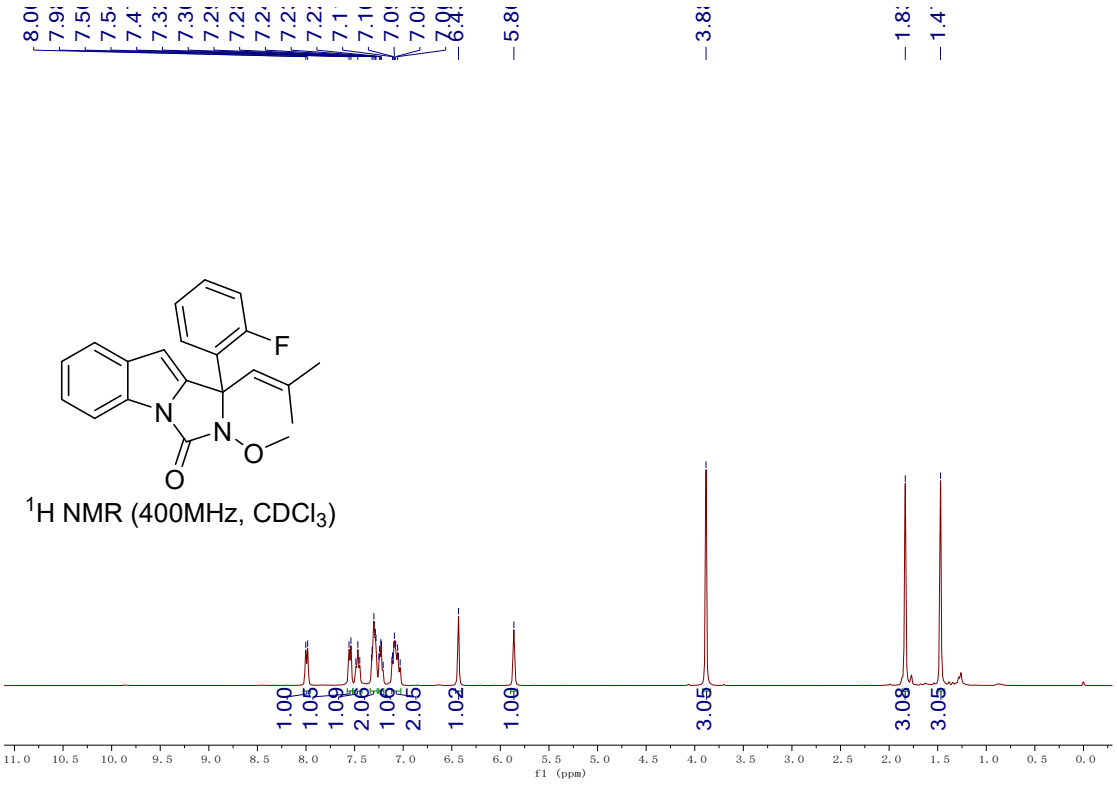


^{1}H NMR (400MHz, $CDCl_3$)

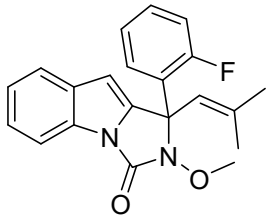
^{13}C NMR spectrum of **3ak**



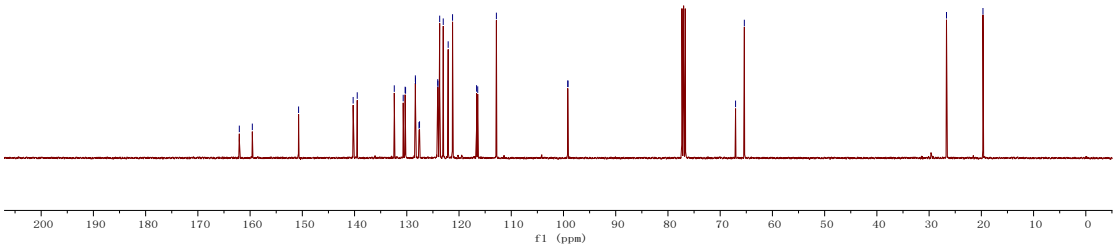
^{1}H NMR spectrum of **3al**



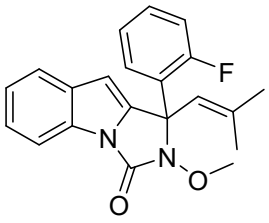
^{13}C NMR spectrum of **3al**



^{13}C NMR (100MHz, $CDCl_3$)

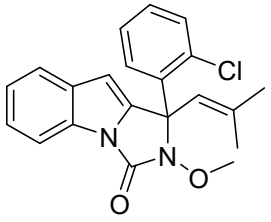


^{19}F NMR spectrum of **3al**

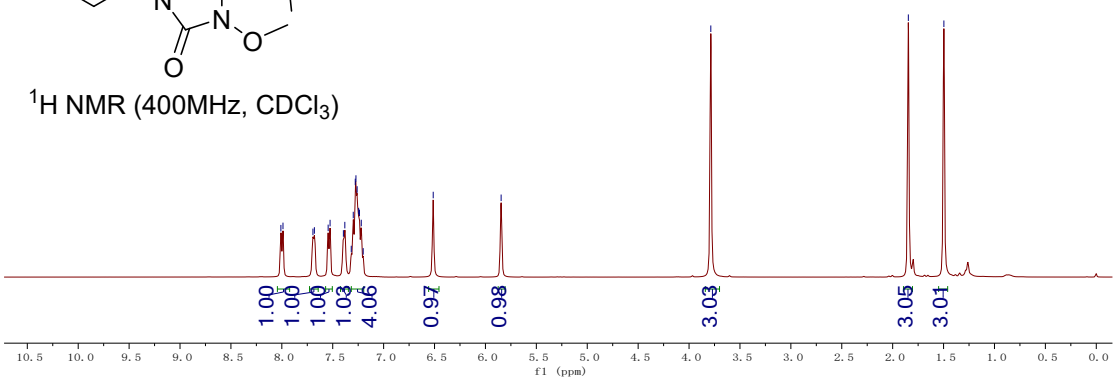


^{19}F NMR (376MHz, $CDCl_3$)

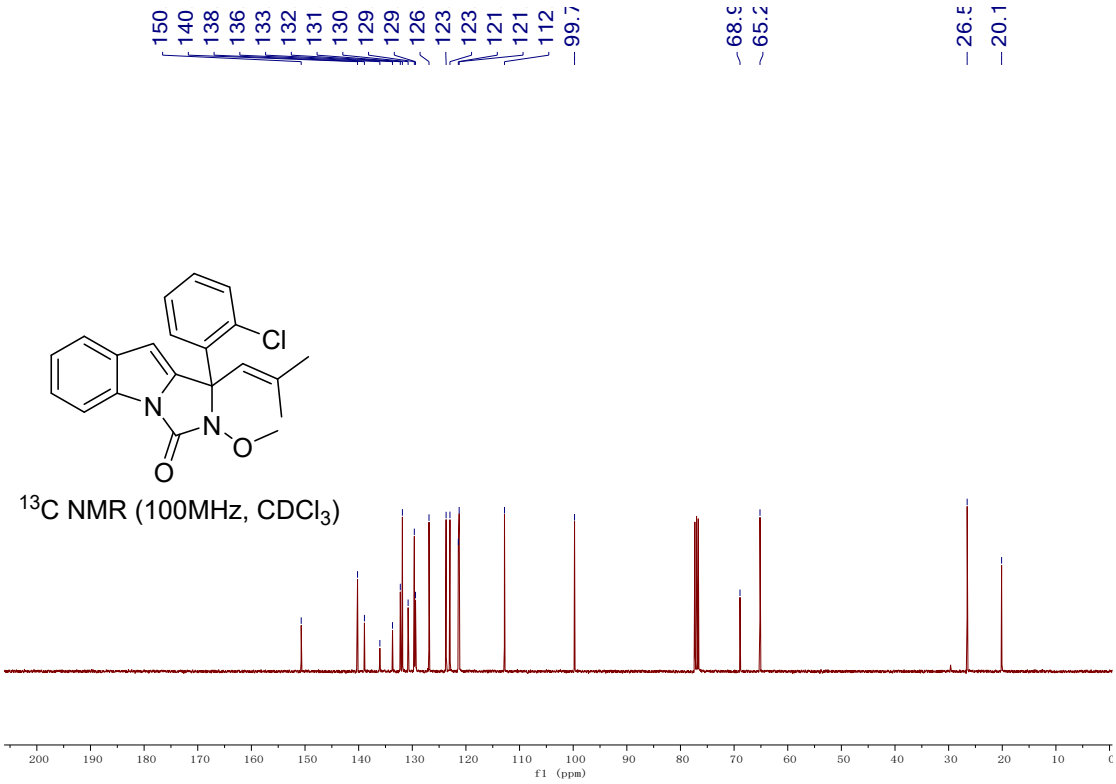
^{1}H NMR spectrum of **3am**



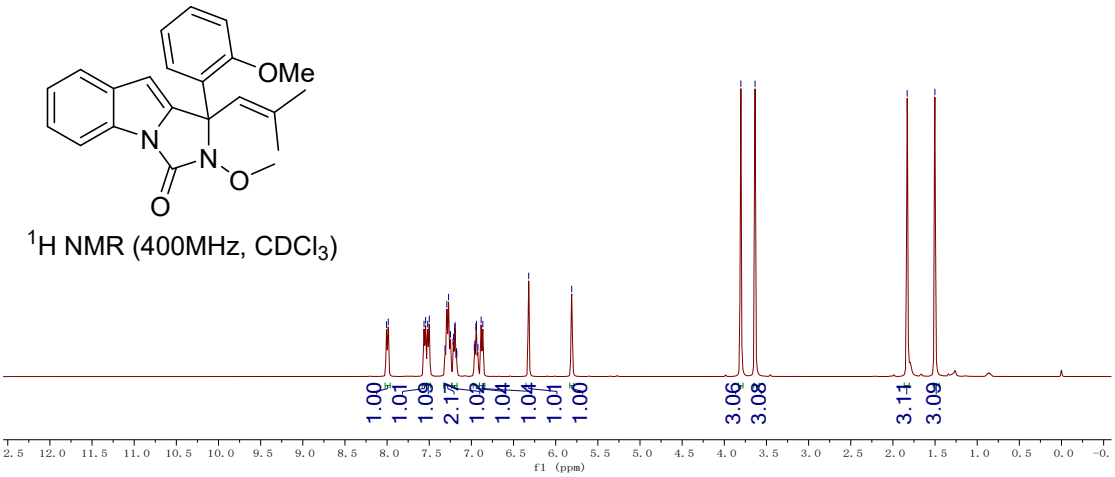
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR spectrum of **3am**

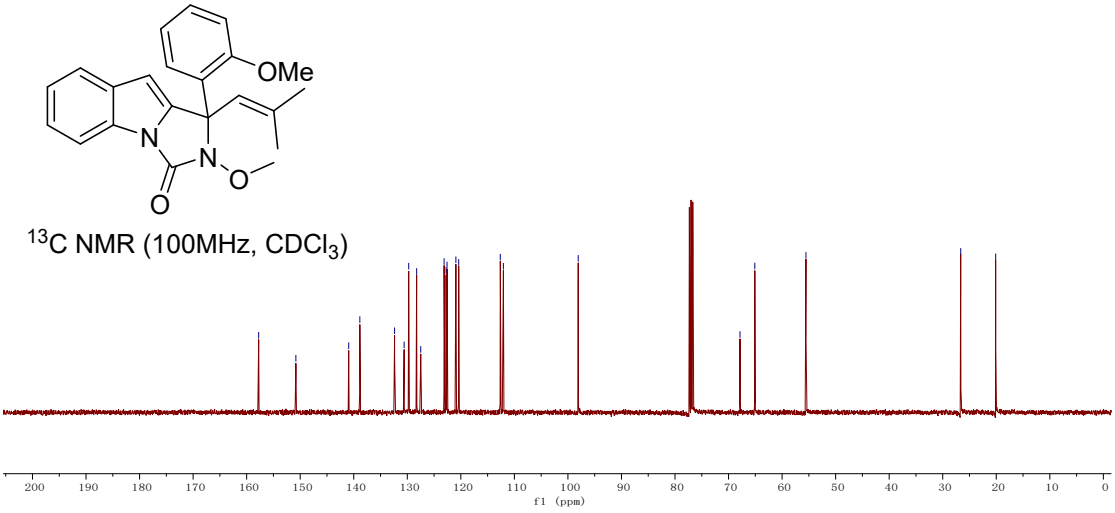


^{1}H NMR spectrum of **3an**



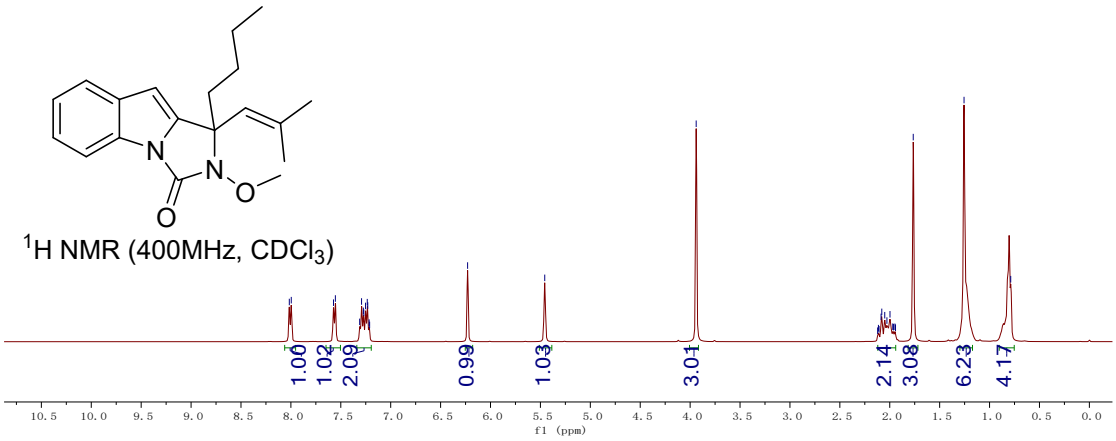
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3an**

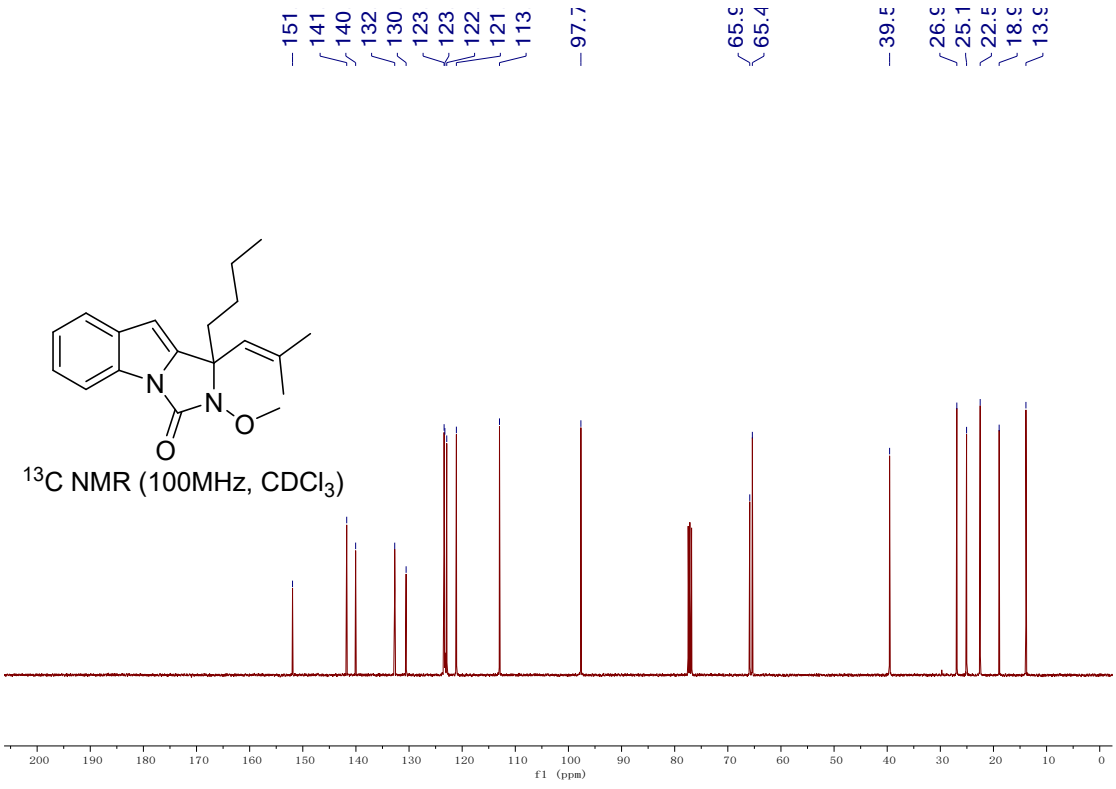


^{13}C NMR (100MHz, $CDCl_3$)

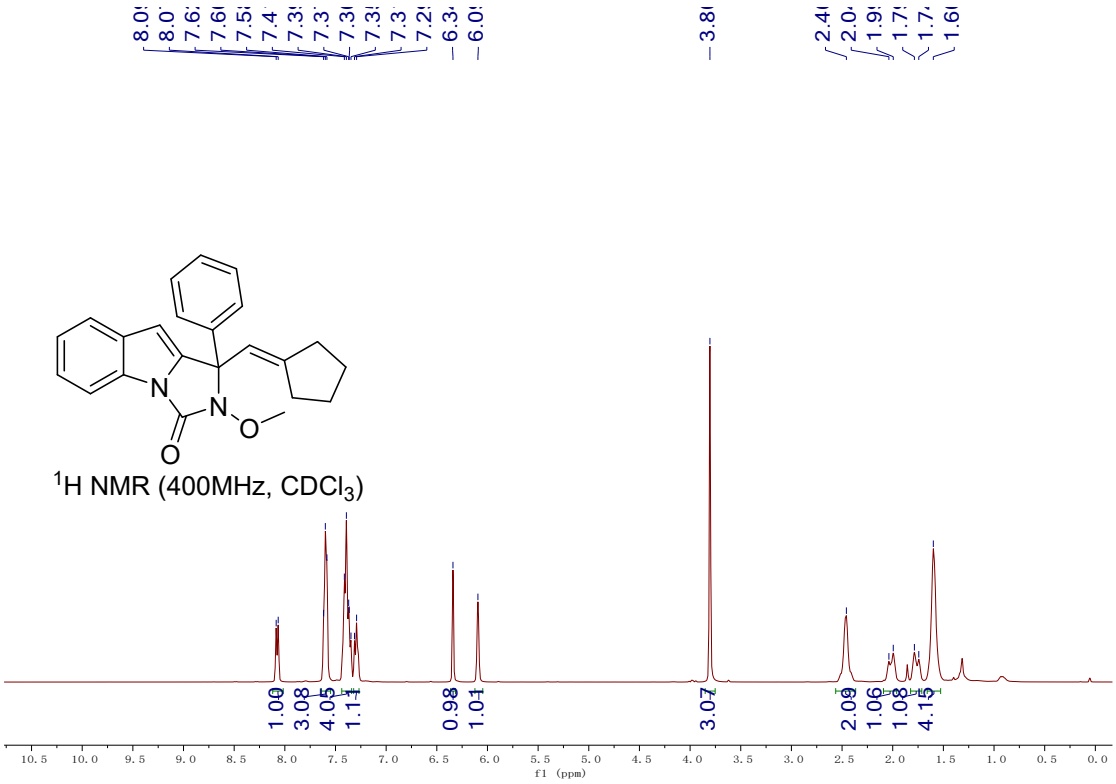
^{1}H NMR spectrum of **3ao**



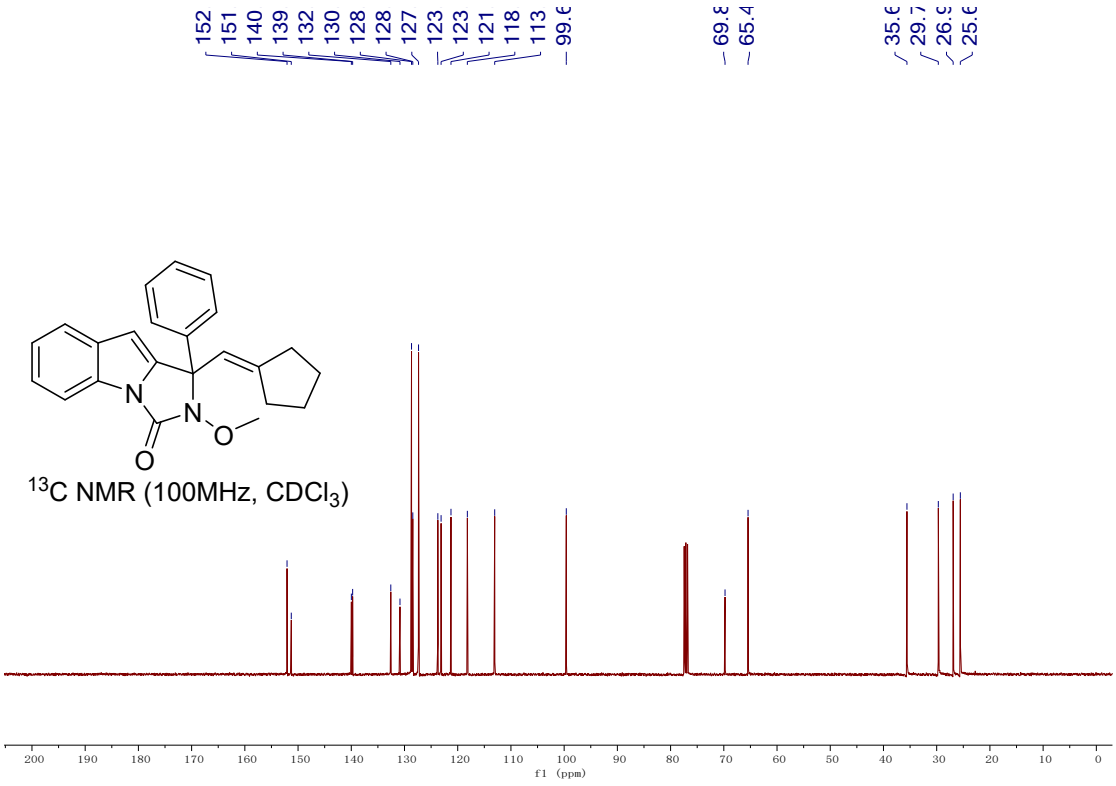
^{13}C NMR spectrum of **3ao**



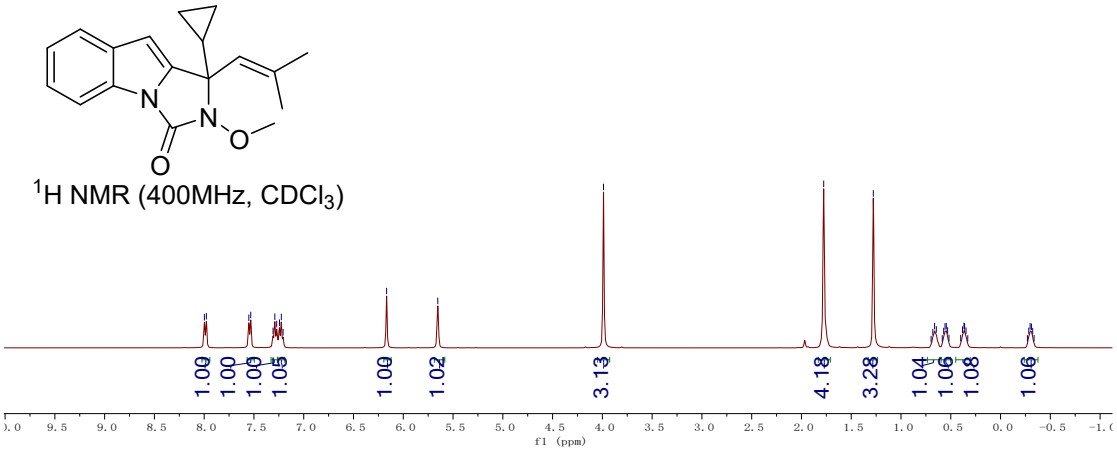
^{1}H NMR spectrum of **3ap**



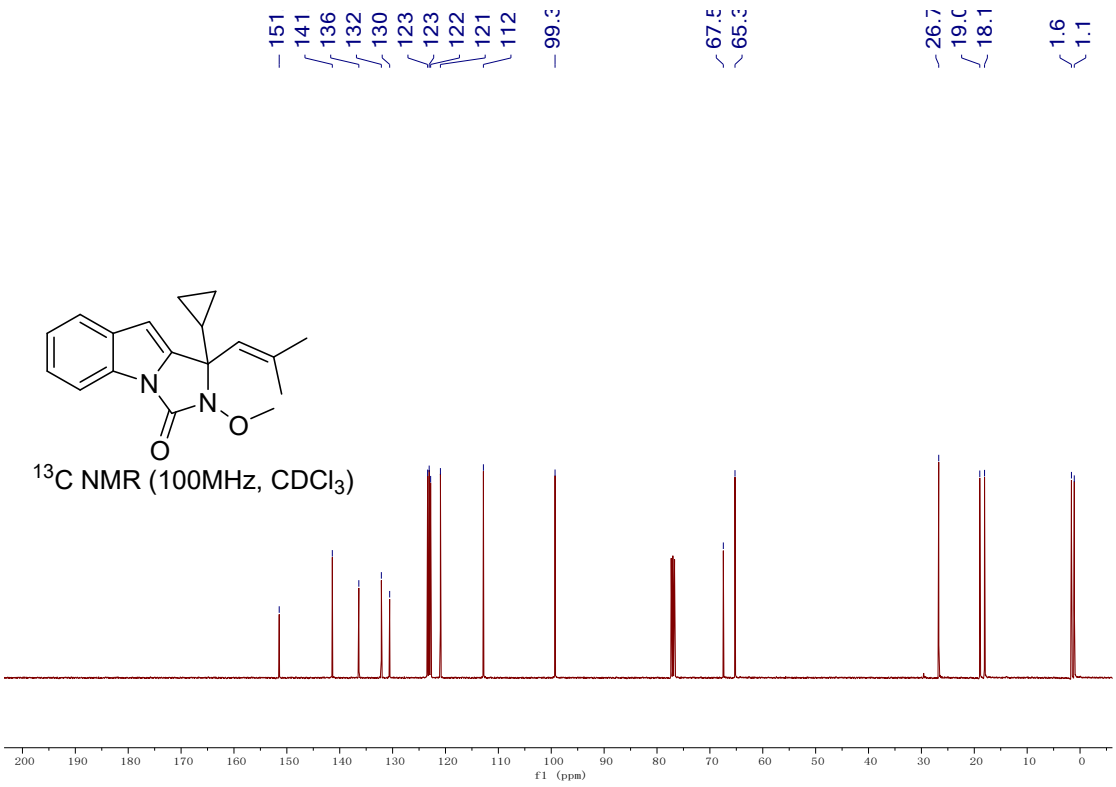
^{13}C NMR spectrum of **3ap**



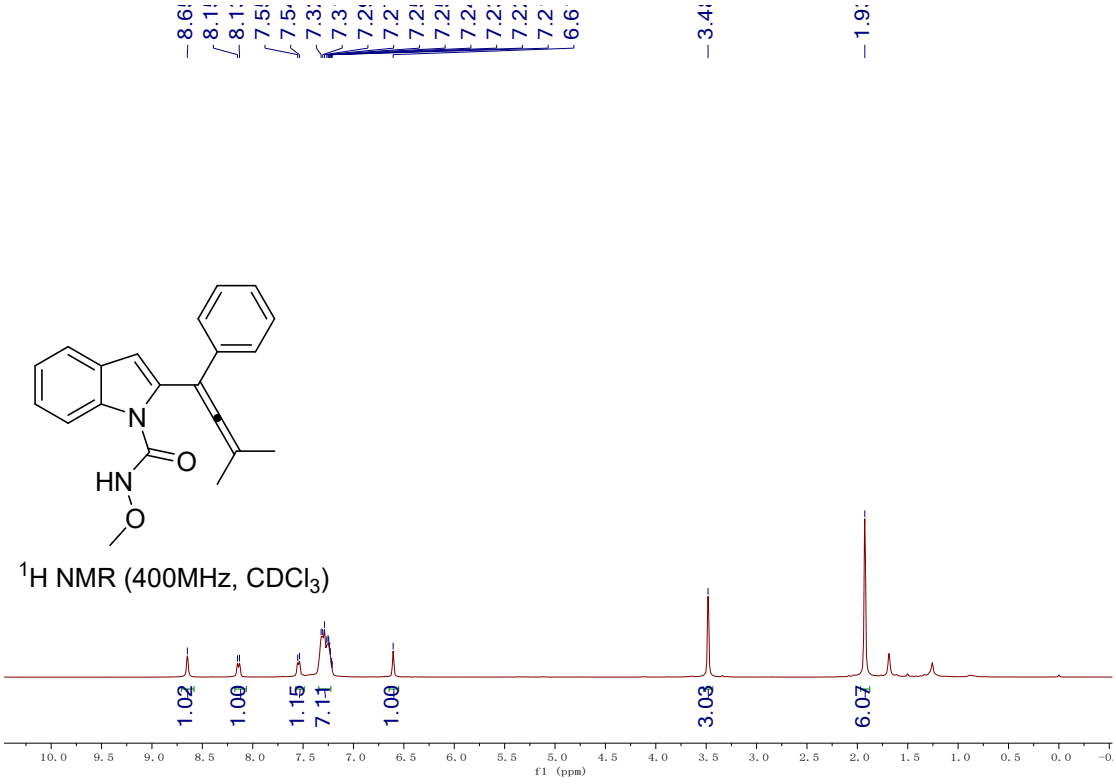
^{1}H NMR spectrum of **3aq**



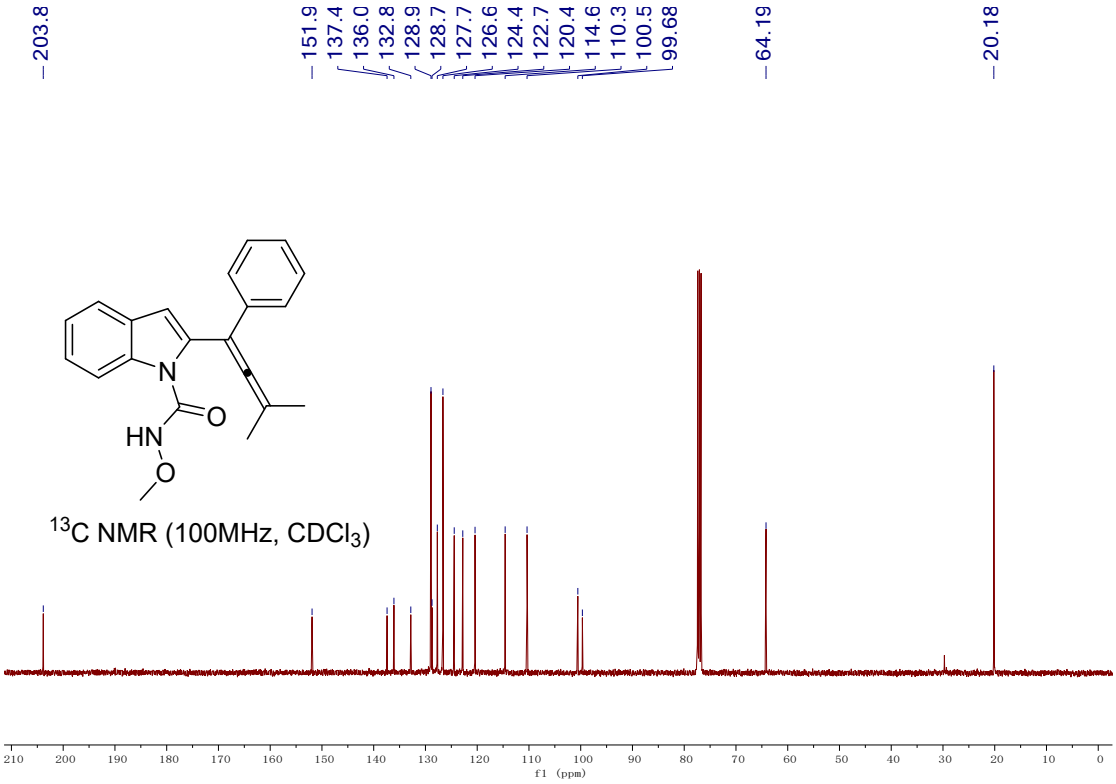
^{13}C NMR spectrum of **3aq**



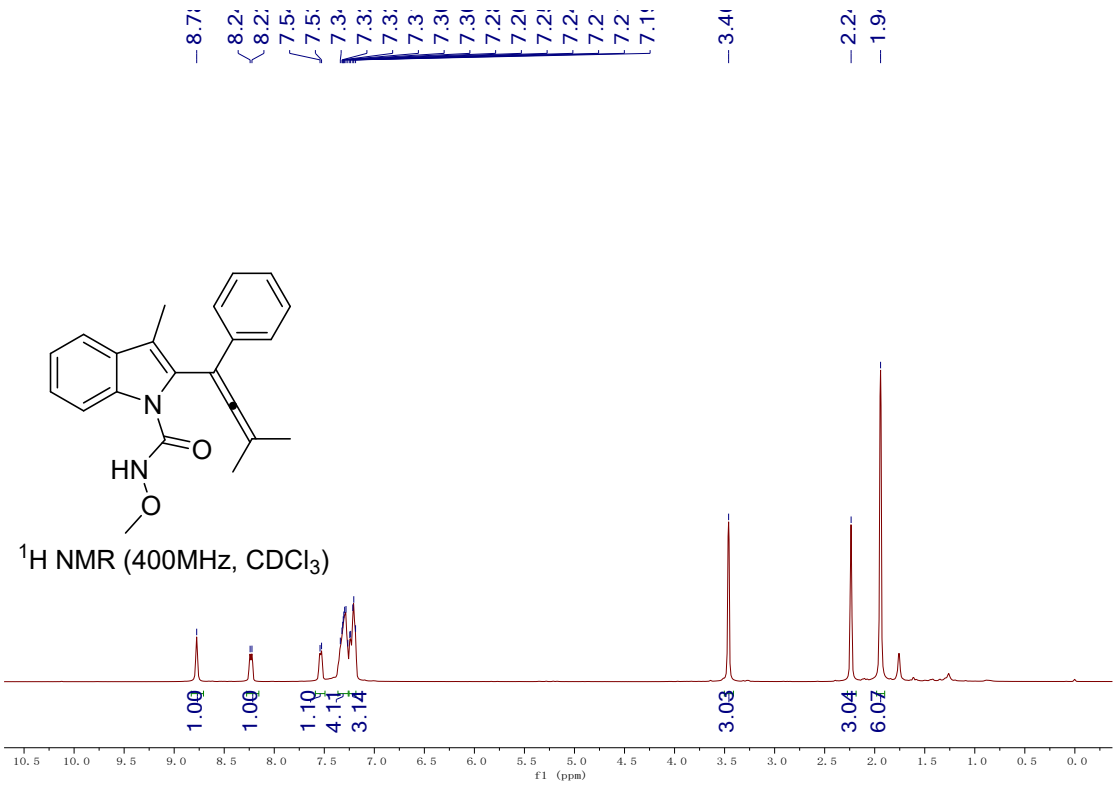
^{1}H NMR spectrum of **4aa**



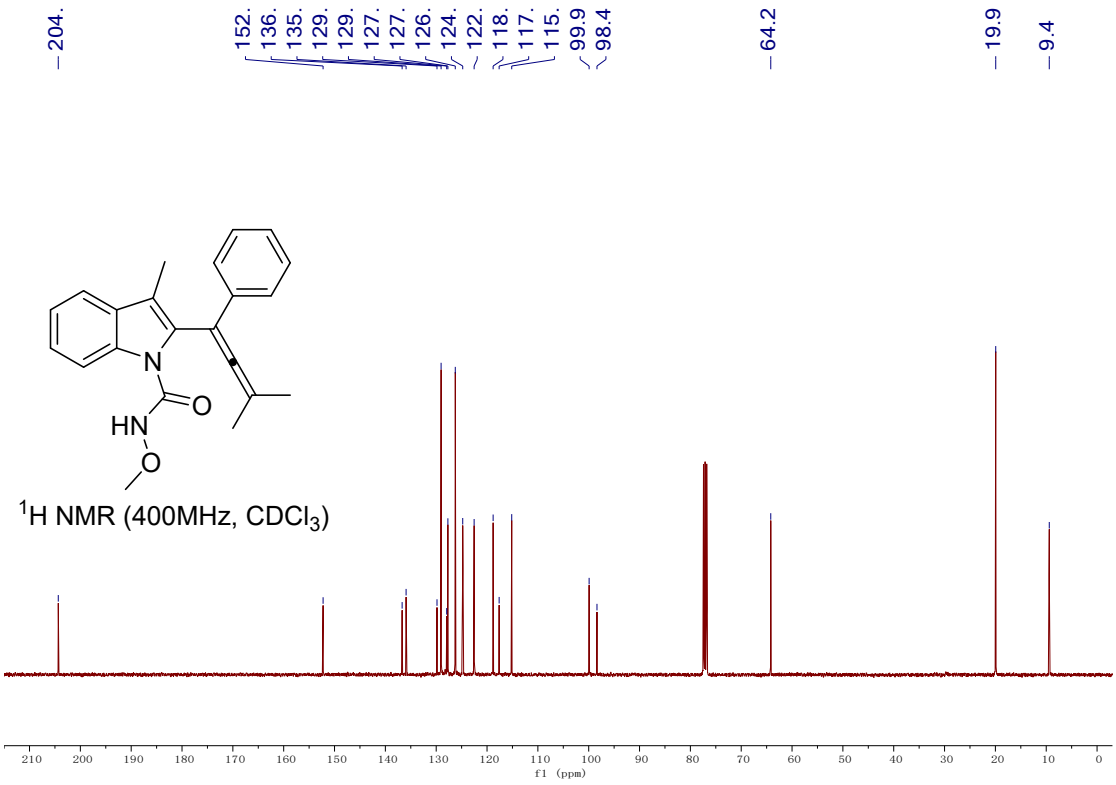
^{13}C NMR spectrum of **4aa**



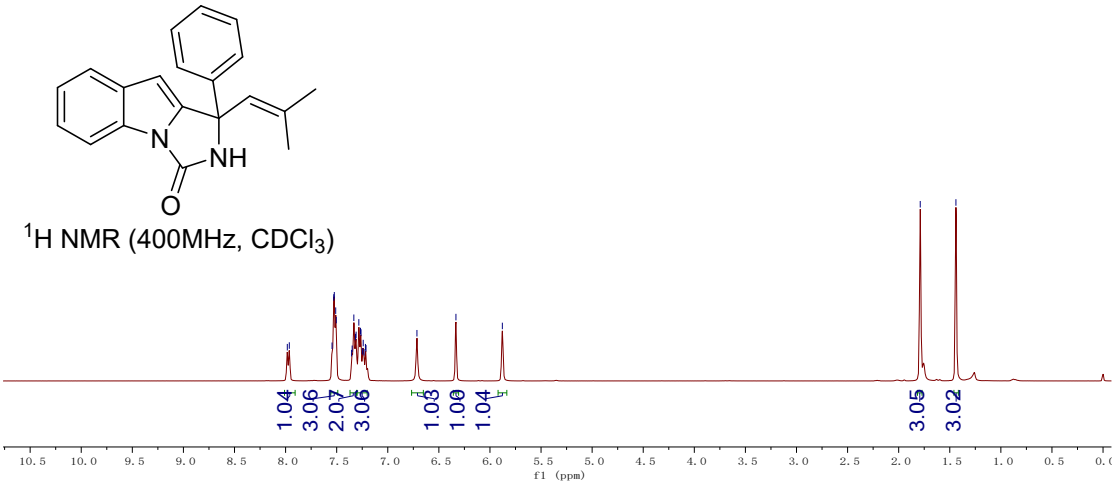
^{1}H NMR spectrum of **4ba**



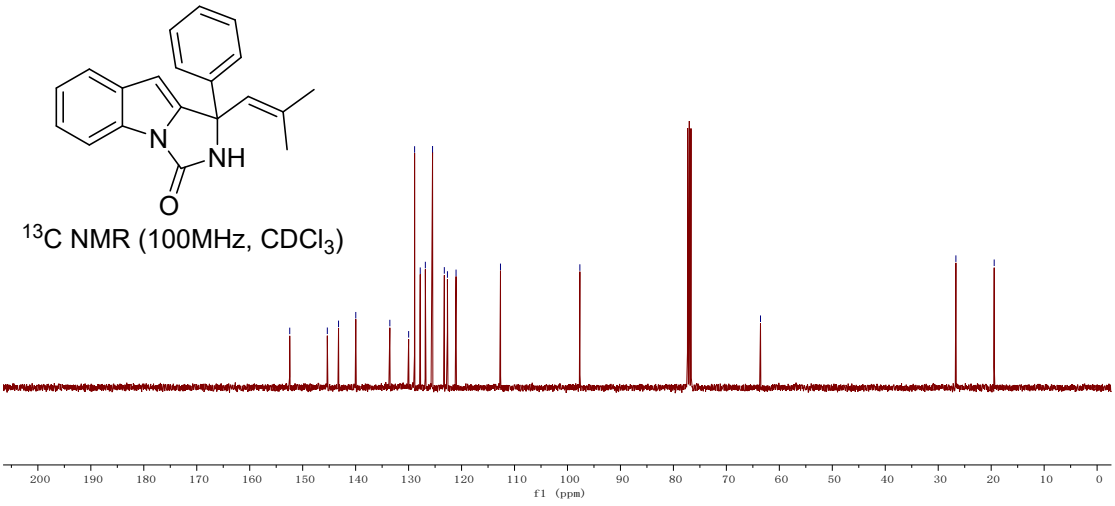
^{13}C NMR spectrum of **4ba**



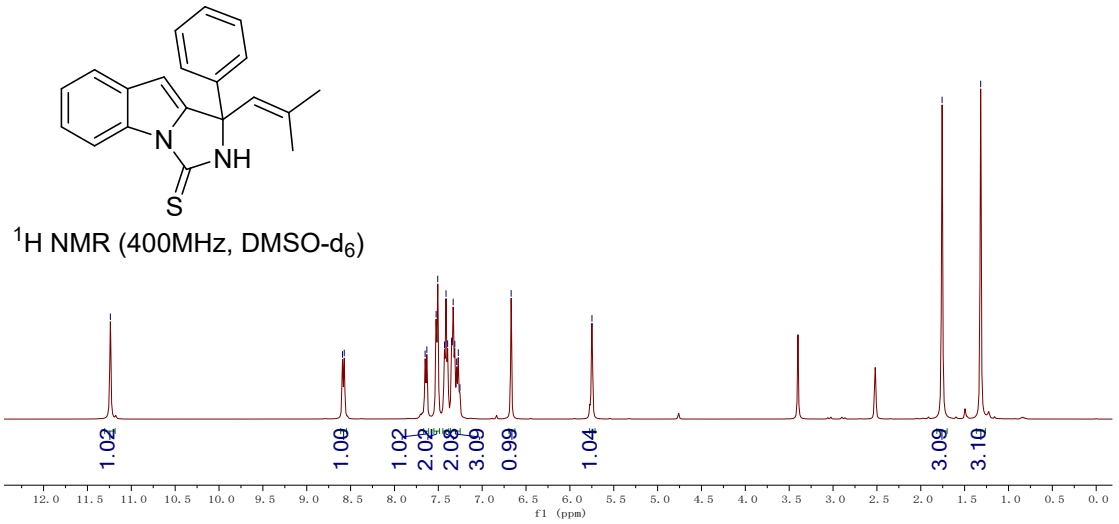
^{1}H NMR spectrum of **5**



^{13}C NMR spectrum of **5**



^{1}H NMR spectrum of **6**



^{13}C NMR spectrum of **6**