Supporting Information for

Formal [3+2] Cycloadditions via Indole Activation: A Route to Pyrroloindolines and Furoindolines

Ya-Ni Wang,[†] Tian-Ren Li,[†] Mao-Mao Zhang, Bei-Yi Cheng, Liang-Qiu Lu and Wen-Jing Xiao**

[1]Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China

[2]School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201, China.

[†]These two authors contributed equally to this work.

Table of Contents

1. General Information

3-Methyl indoles **1a**, **1o**, **1p** and **4a**[1] were obtained from comerial soures. Other indoles[2-5] and vinly aziridines[6,7] were prepared according to known procedures.

References:

(1) Kamata, K.; Kotani, M.; Yamaguchi, K.; Hikichi, S.; Mizuno. *Chem. Eur. J.* **2007**, *13*, 639.

(2) Cheng, H.-G.; Lu, L.-Q.; Wang, T.; Yang, Q.-Q.; Liu, X.-P.; Li, Y.; Deng, Q.-H.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2013**, *52*, 3250.

(3) Zhang, Y.; Stephens, D.; Hernandez, G.; Mendoza, R.; Larionov, O. V. *Chem. Eur. J.* **2012**, *18*, 16612.

(4) Yadav, J. S.; Reddy, B. S.; Reddy, P. M.; Srinivas, C. *Tetrahedron Letter* **2002**, *43*, 5185.

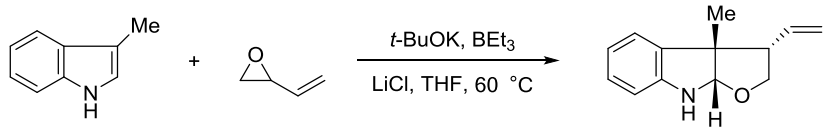
(5) Chen, J.-R.; Li, C.-F.; An, X.-L.; Zhang, J.-J.; Zhu, X.-Y.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2008**, *47*, 2489.

(6) Rodrigo, C.; Dennis G. D.; Fabio S.; Joao, V. C. *Tetrahedron Letter* **2005**, *46*, 2539.

(7) Feng, J.-J.; Lin, T.-Y.; Zhu, C.-Z.; Wang, H.-M.; Wu, H.-H.; Zhang, J.-L. *J. Am. Chem. Soc.* **2016**, *138*, 2178.

2. Details for Condition Optimization

Table S1. Conditions optimization for furoindoline synthsis[a]



1a **4a** **5aa**

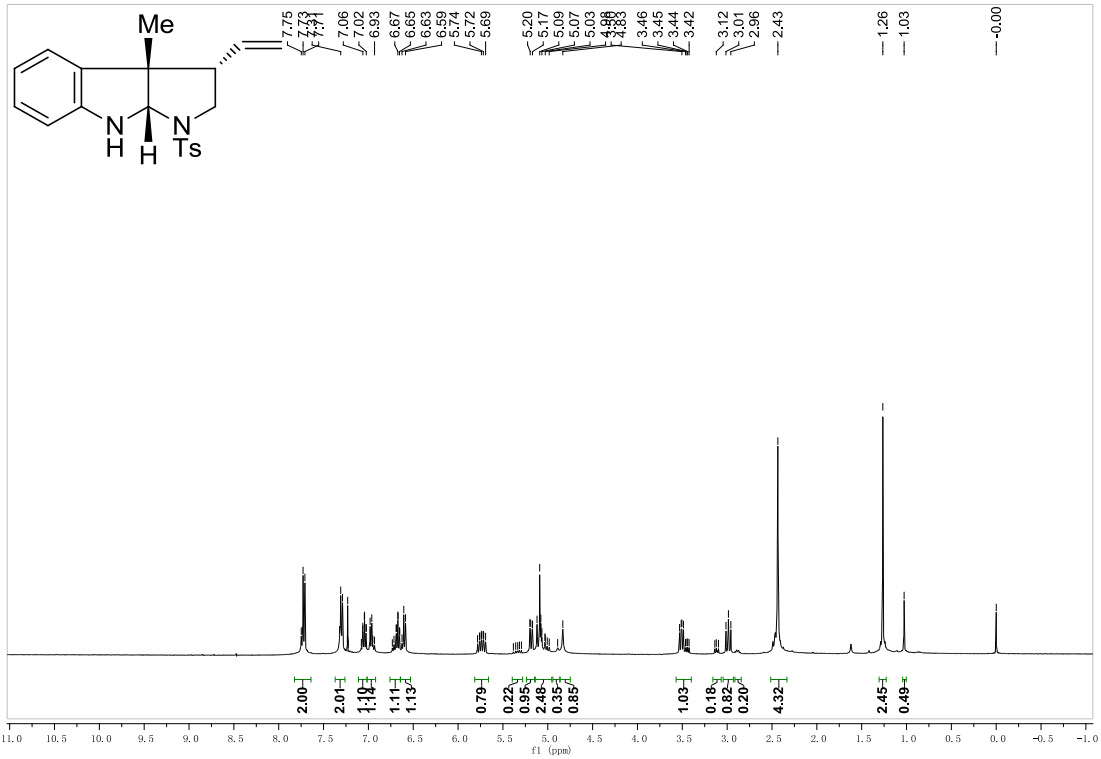
entry	**1a**:**4a** (x:y)	T/^{o}C	solvent	additive	t/h	yield/%[b]
1	2.5:1	25	THF	none	24	n.r.
2	1:1	25	THF	none	24	n.r.
3	1:2.5	25	THF	none	24	n.r.
5	1:2.5	60	THF	none	24	trace
6	1:2.5	80	THF	none	24	>5
7	1:2.5	80	Toluene	none	24	trace

8	1:2.5	80	1,4-dioxane	none	24	trace
9	1:2.5	25	THF	*n*-Bu_4NBr (1 eq.)	24	trace
10	1:2.5	25	THF	*n*-Bu_4NI (1 eq.)	24	trace
11	1:2.5	25	THF	$LiBF_4$ (1 eq.)	24	>10
12	1:2.5	25	THF	LiCl (1 eq.)	24	28
13	1:4	r.t.	THF	LiCl (1 eq.)	24	37
14	1:4	60	THF	LiCl (1 eq.)	12	90

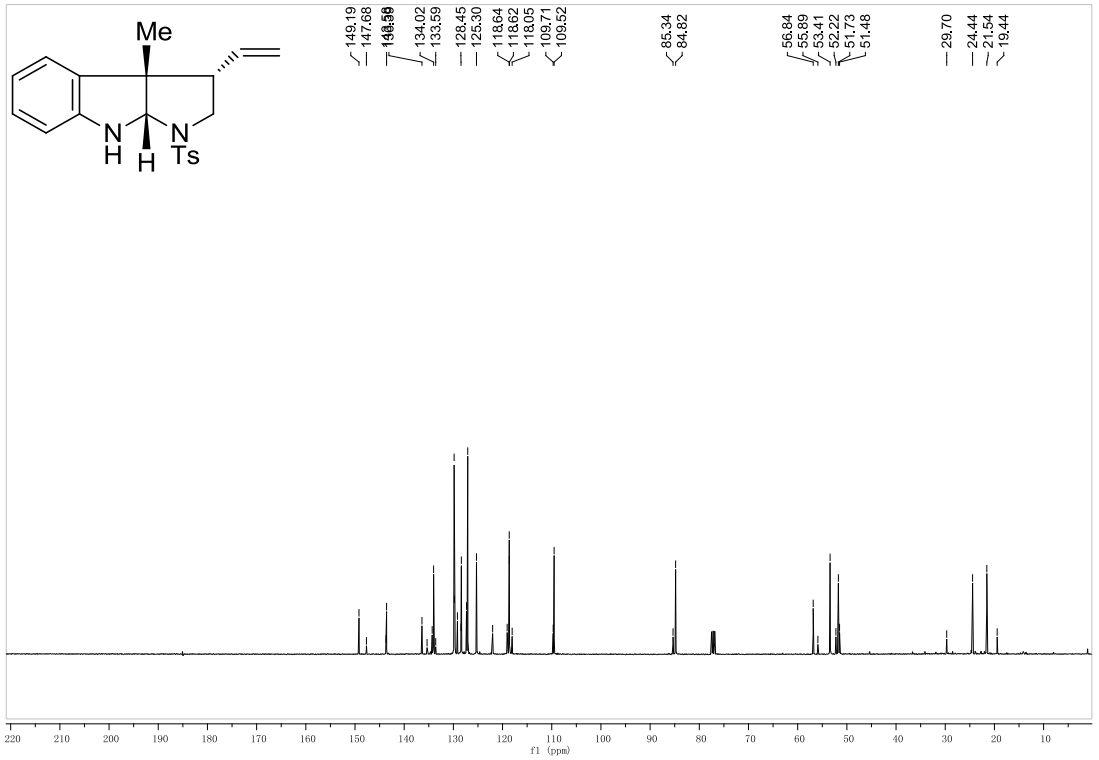
[a] Reaction conditions: **1a** (x mmol.), **4a** (y mmol), BEt_3 (1.1x equiv.), *t*-BuOK (1.1x equiv.), solvent (2.0 ml). [b] Isolated yields based on **2**.

3. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products

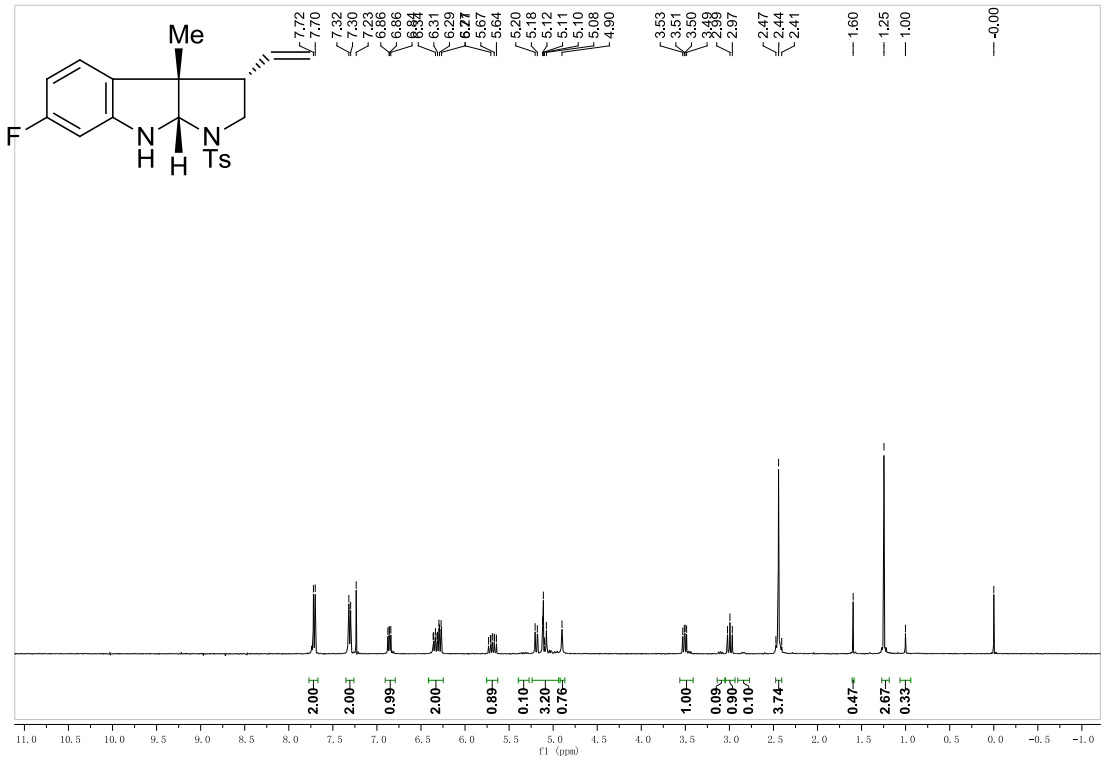
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3aa



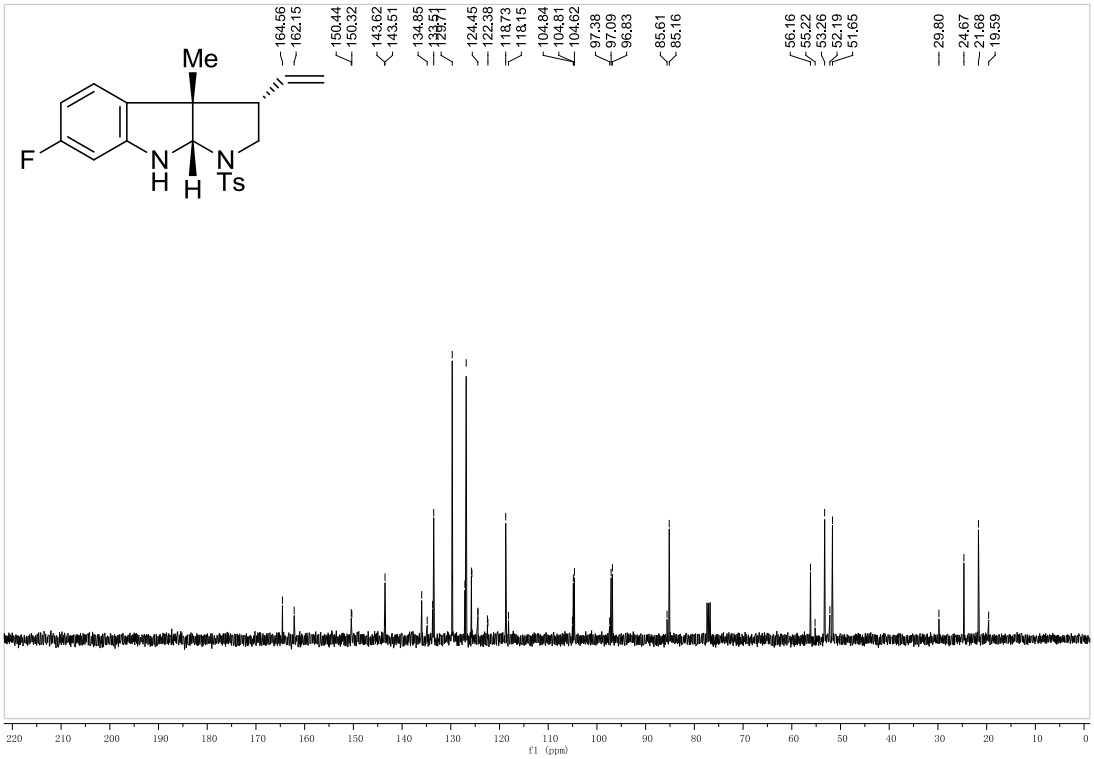
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3aa



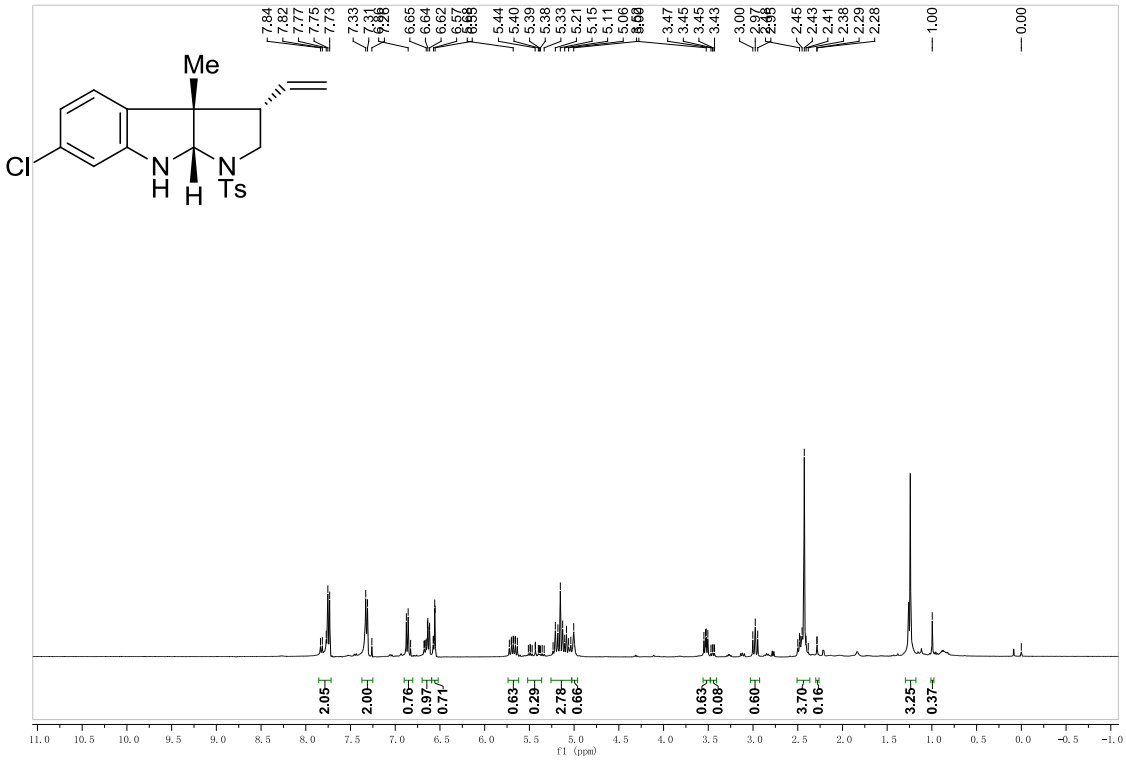
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ba



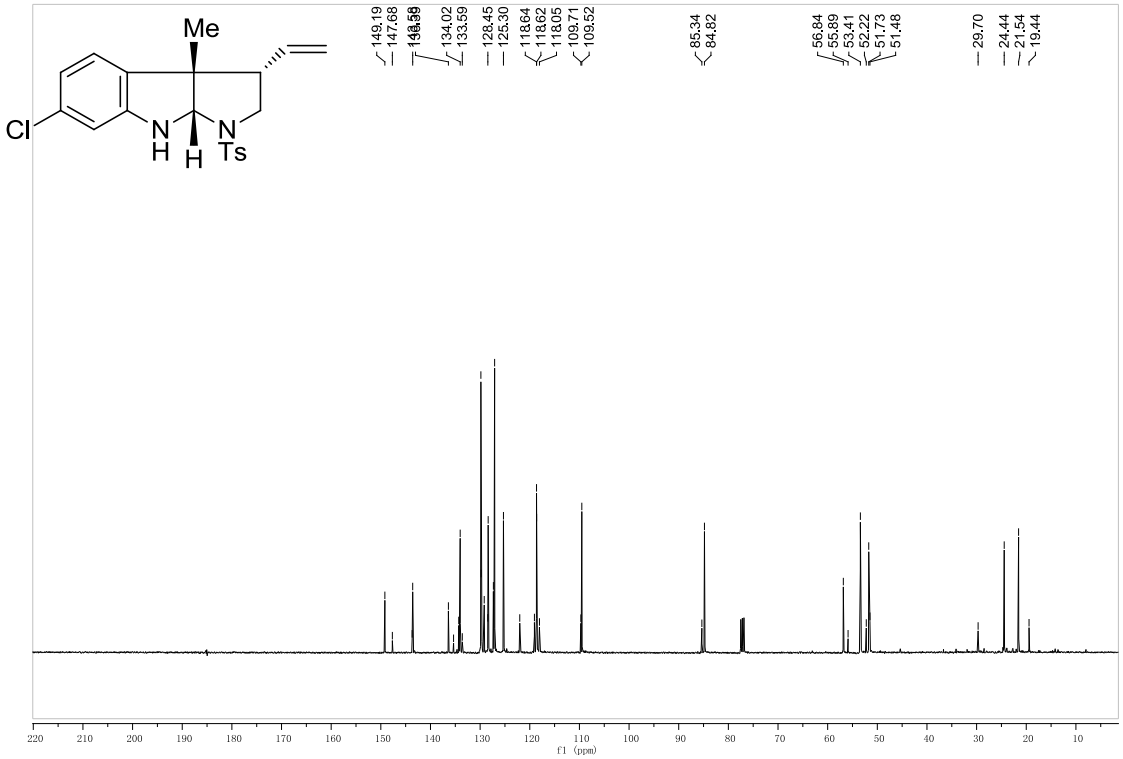
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ba



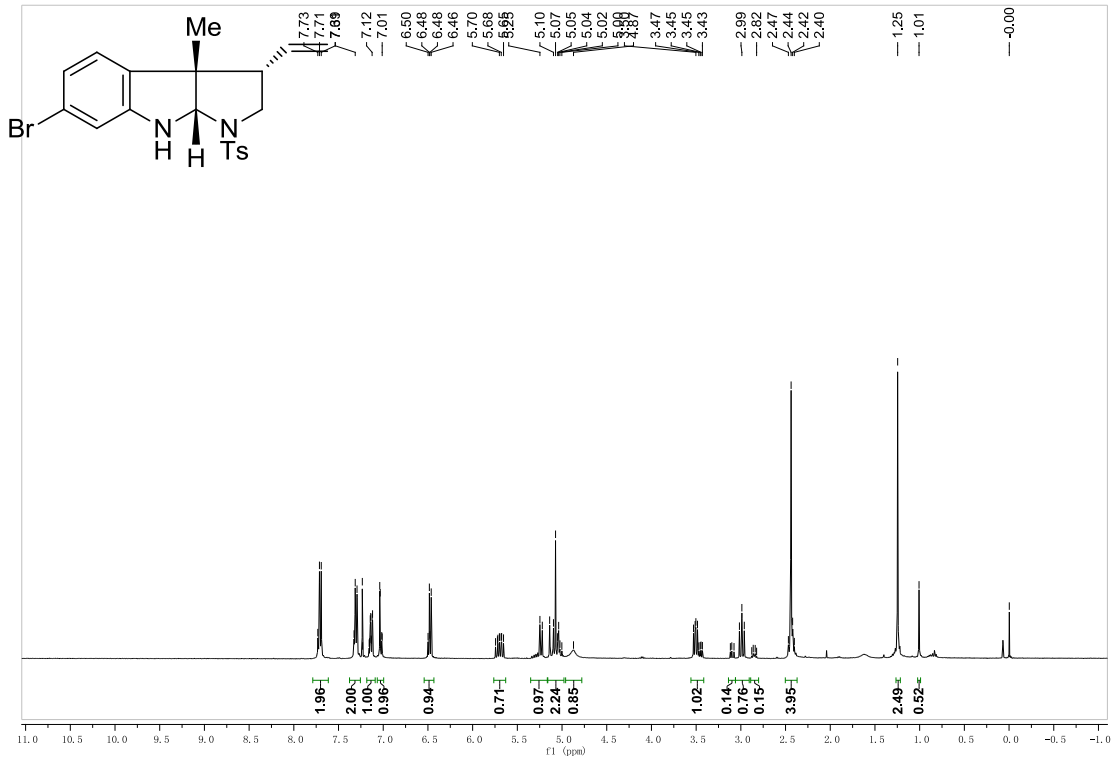
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ca



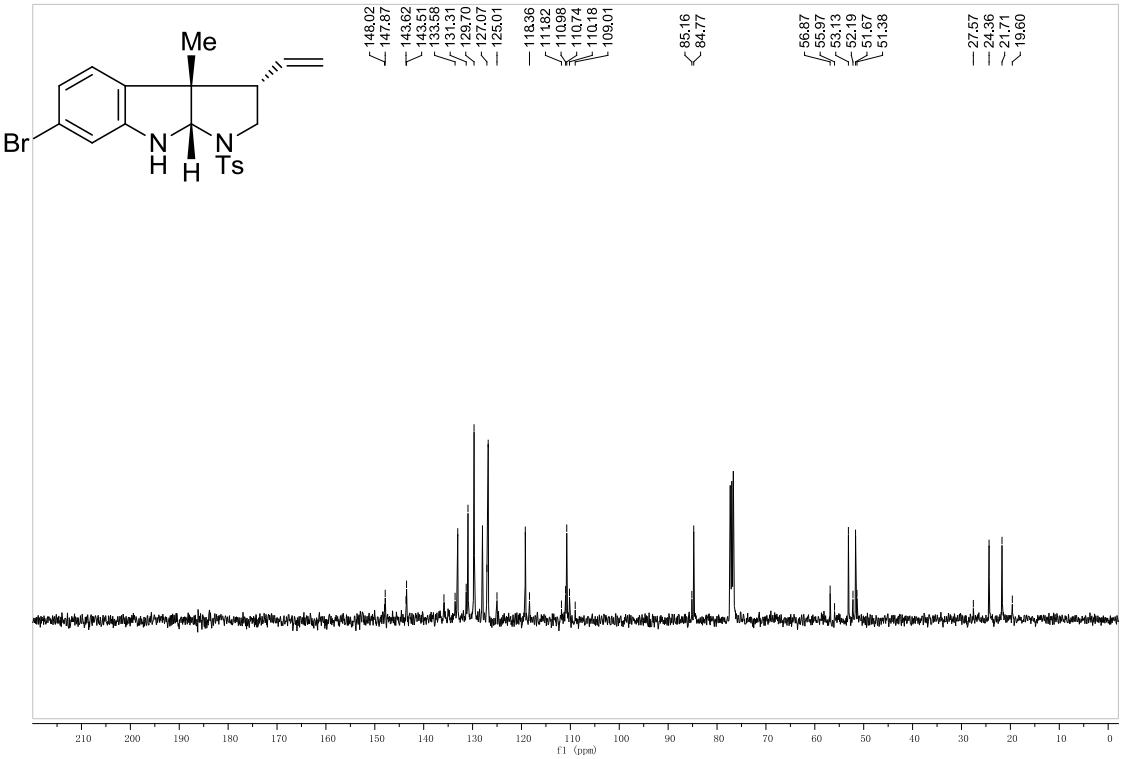
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ca



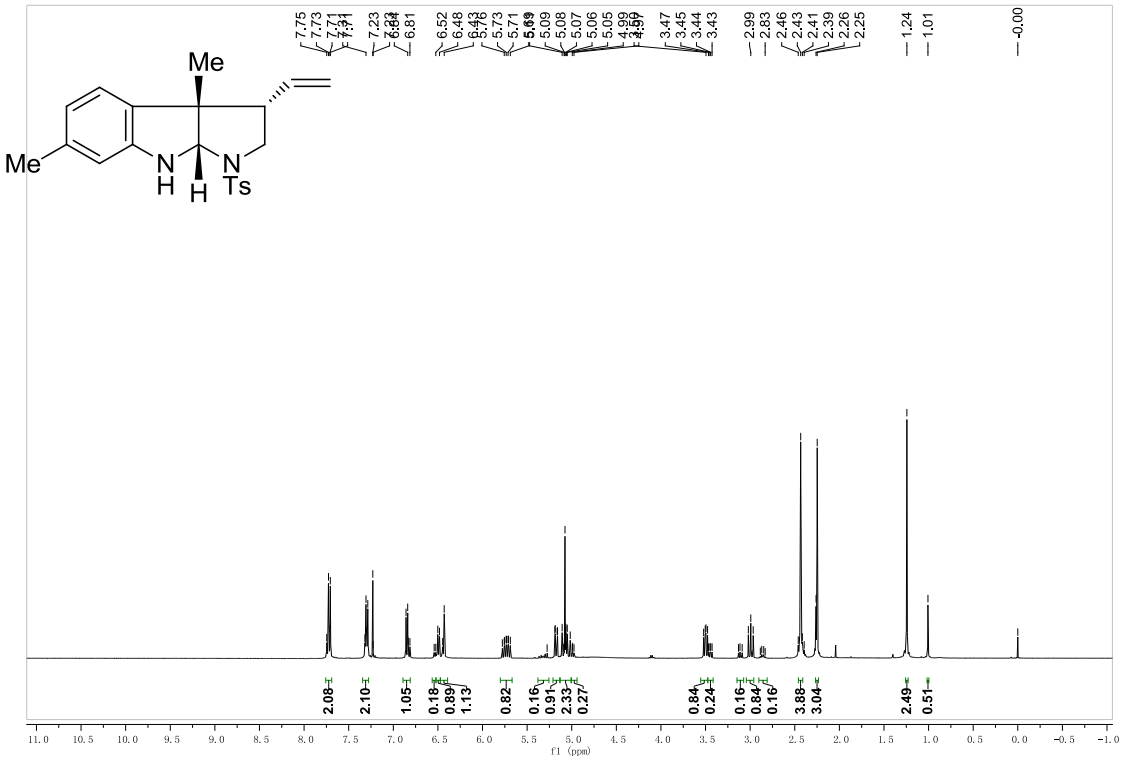
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3da



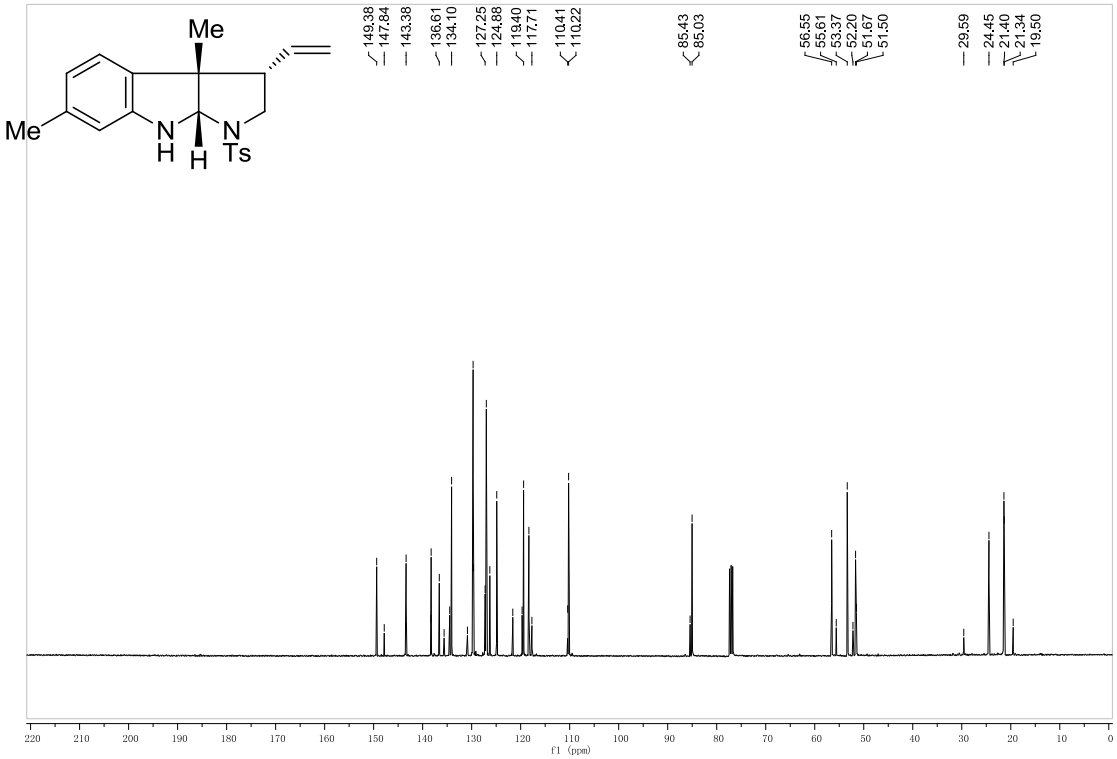
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3da



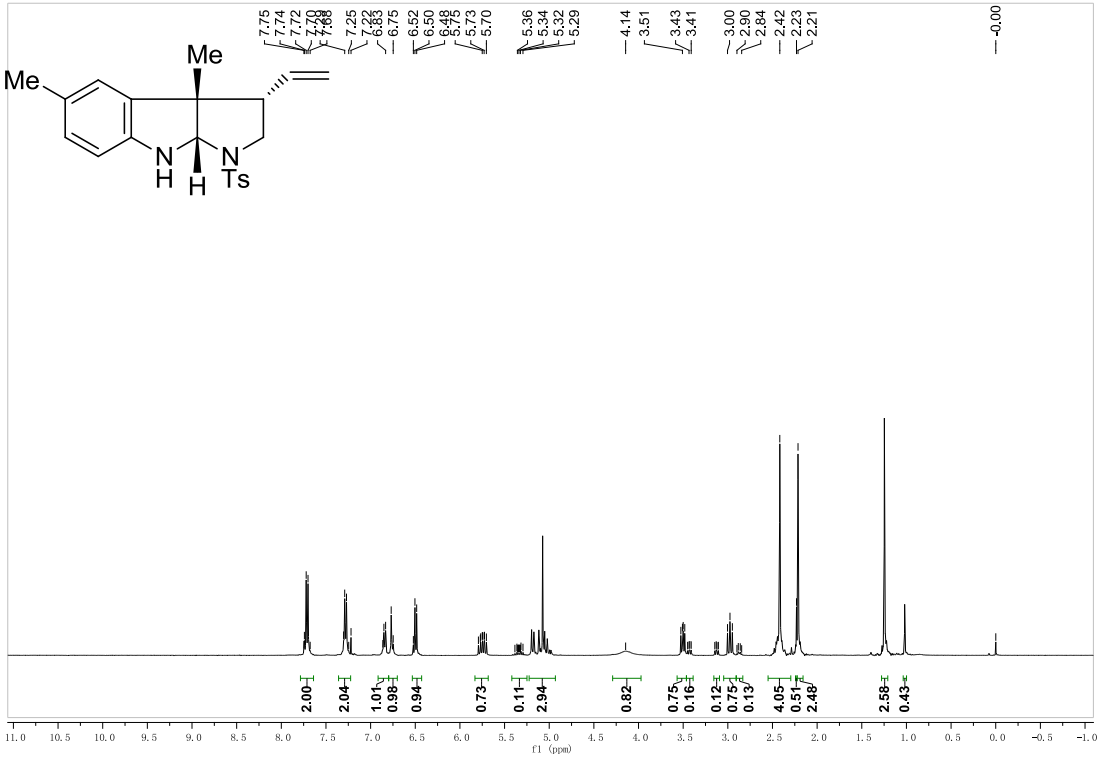
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ea



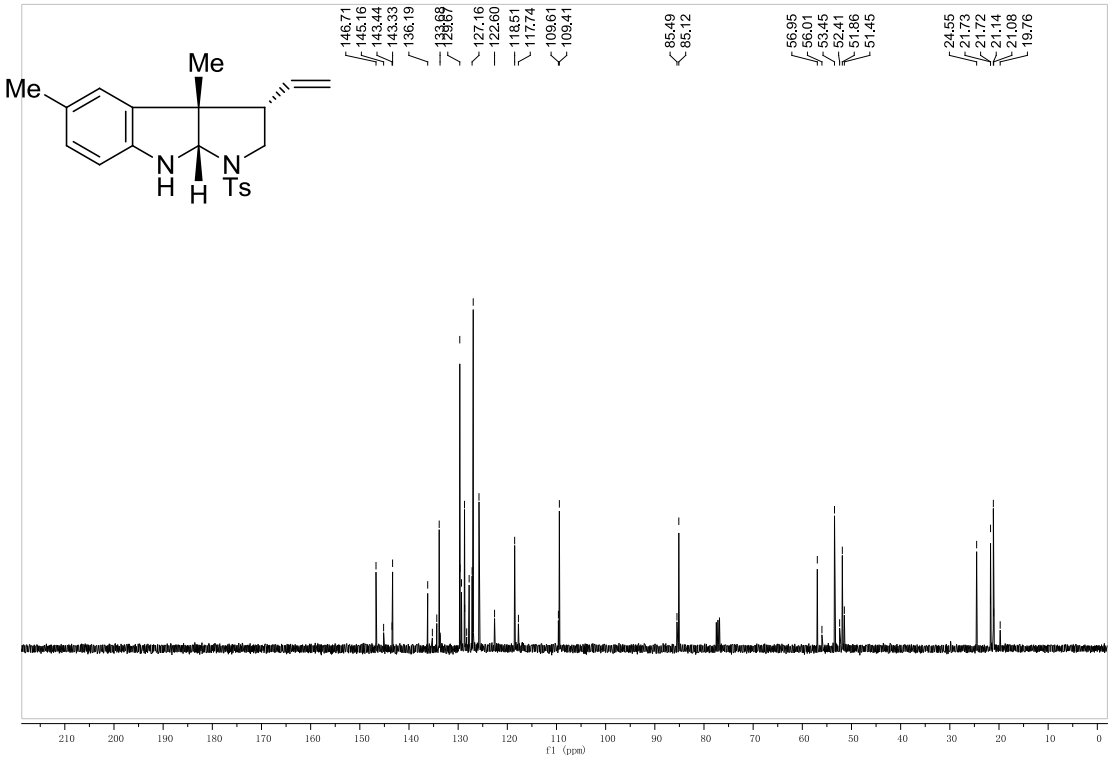
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ea



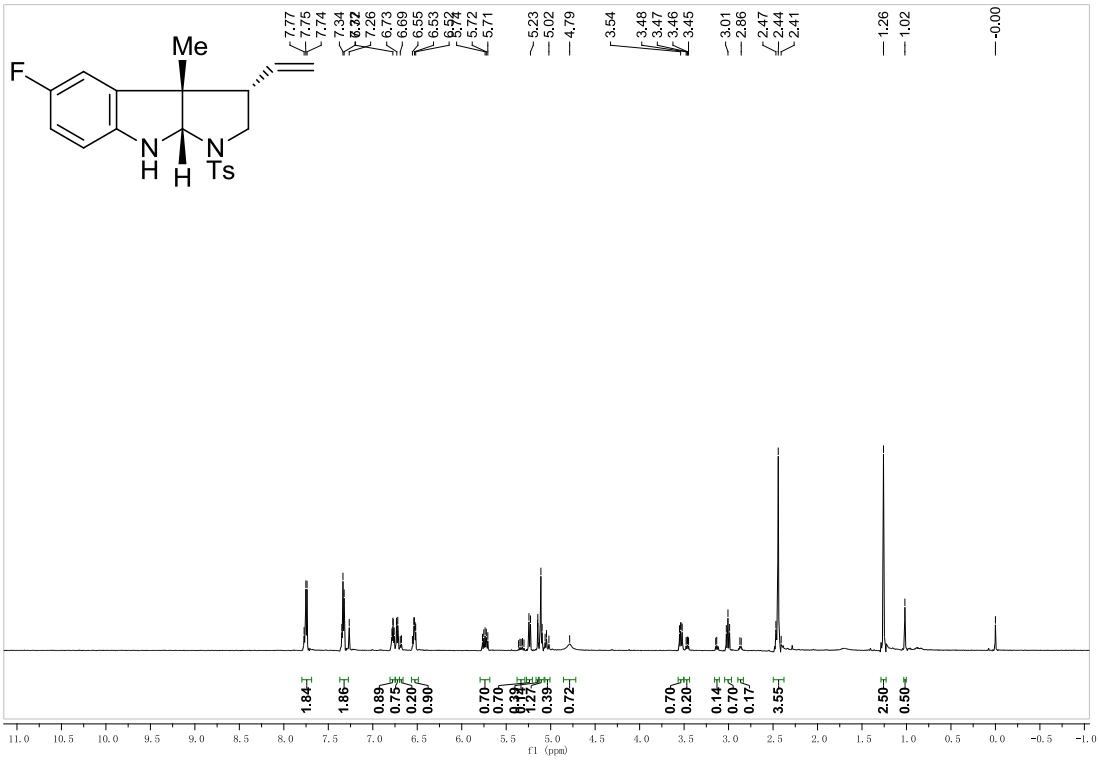
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3fa



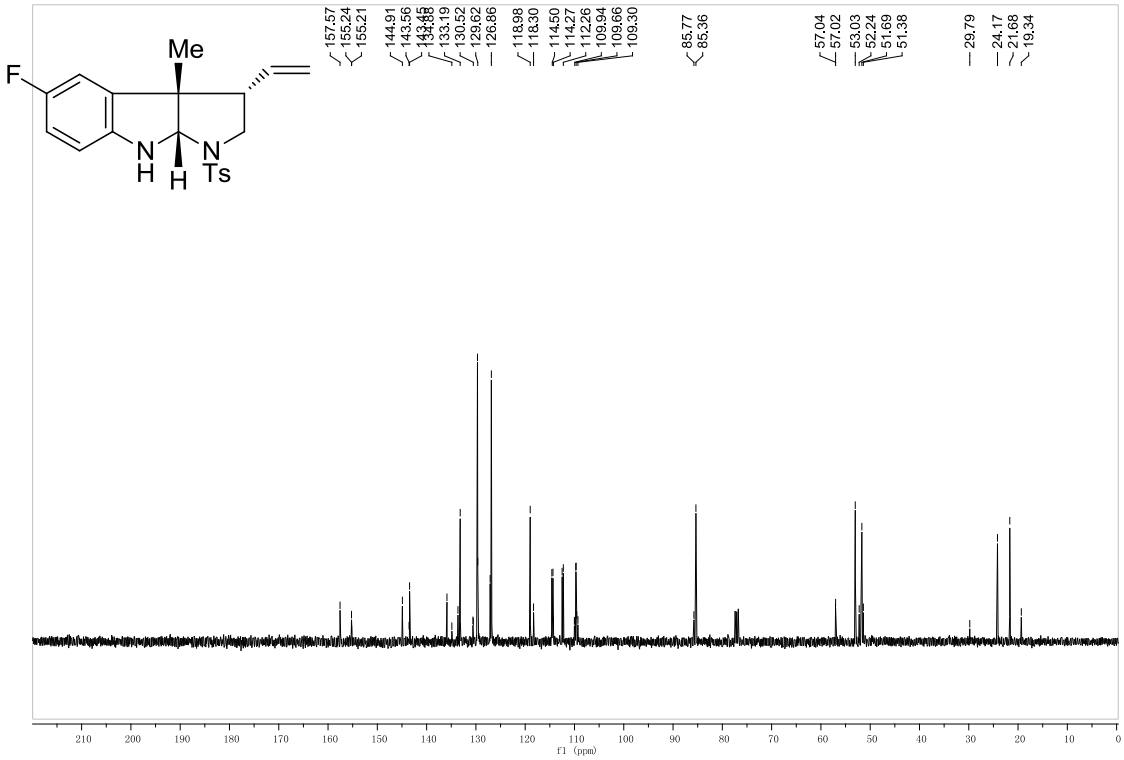
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3fa



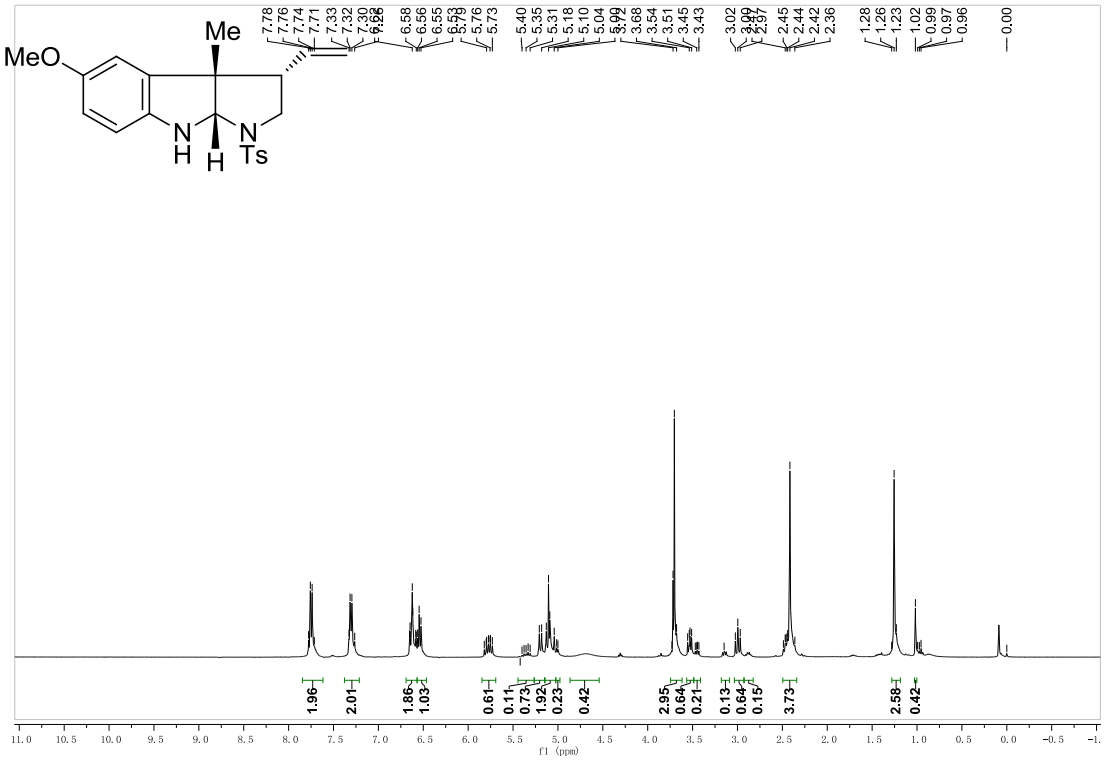
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ga



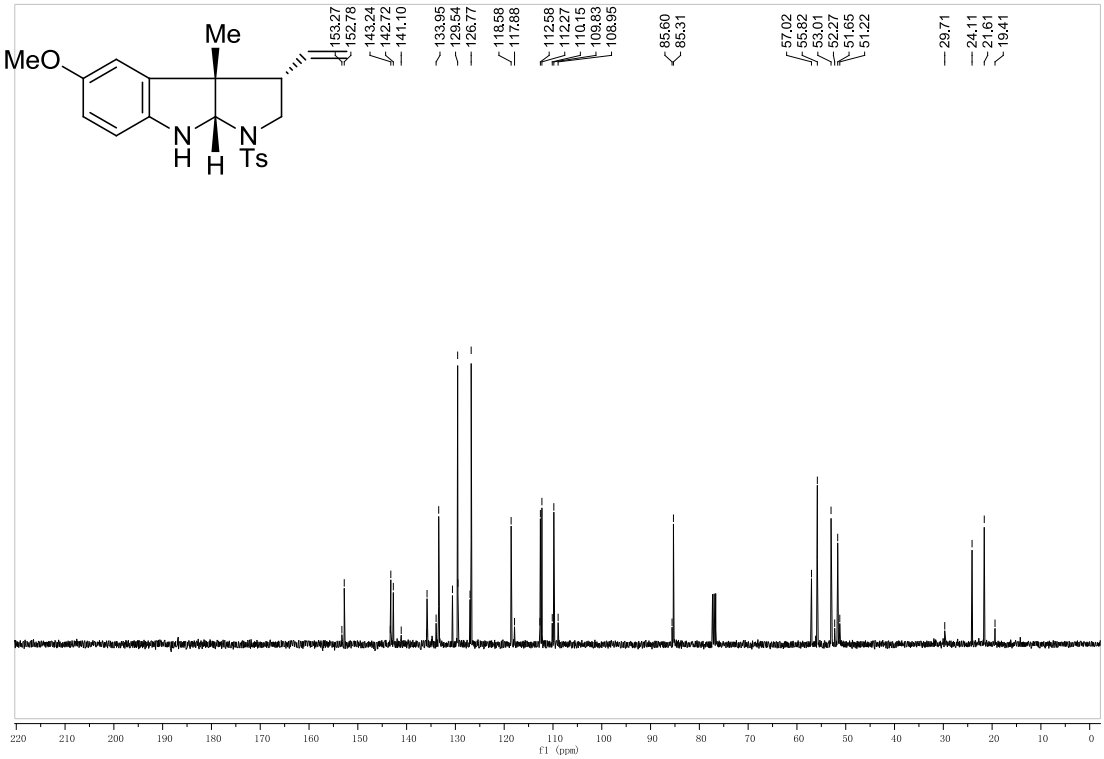
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ga



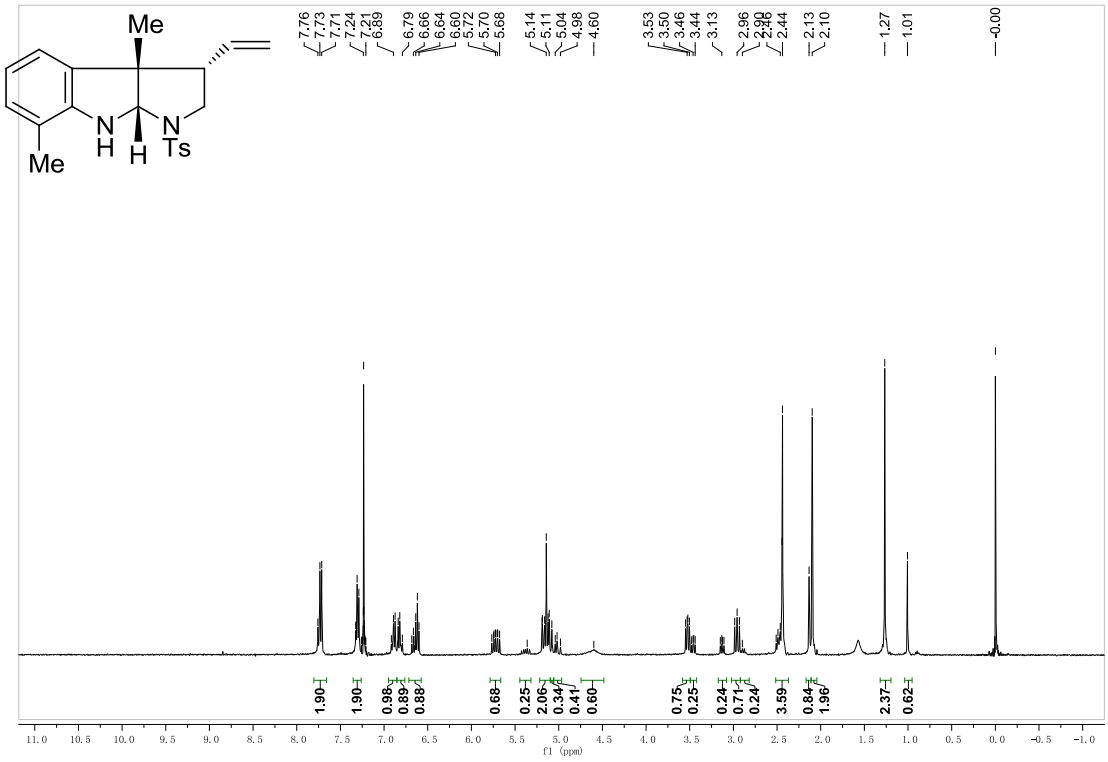
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ha



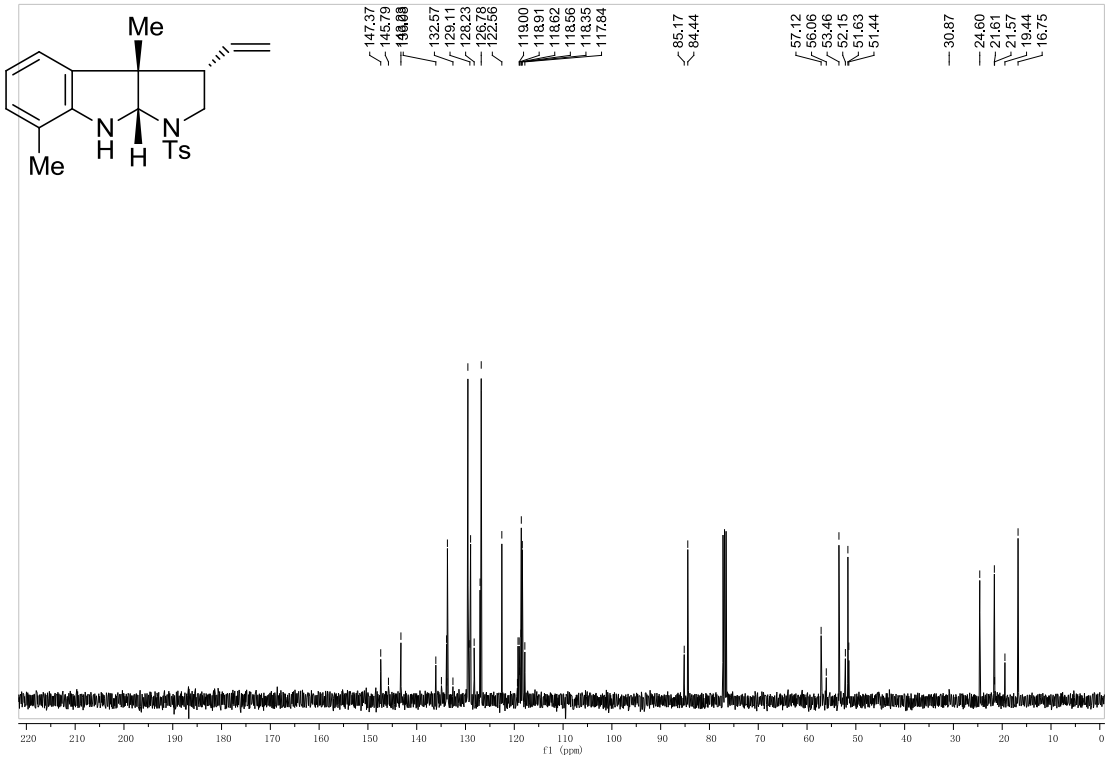
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ha



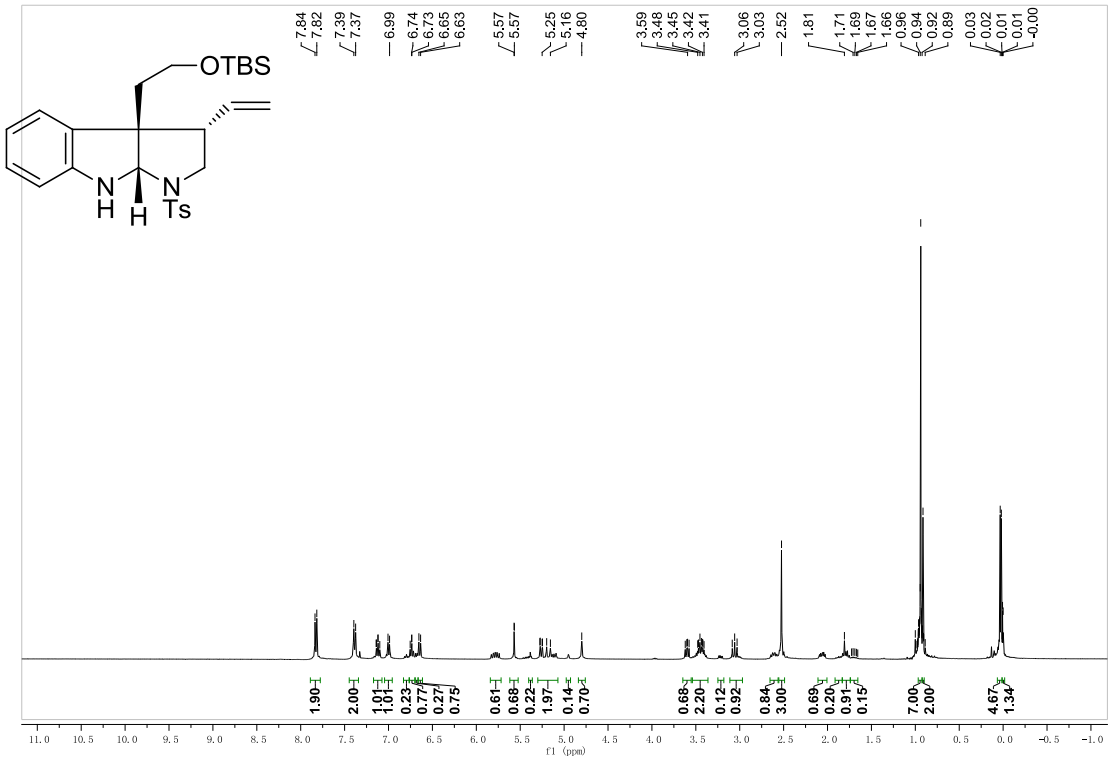
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ia



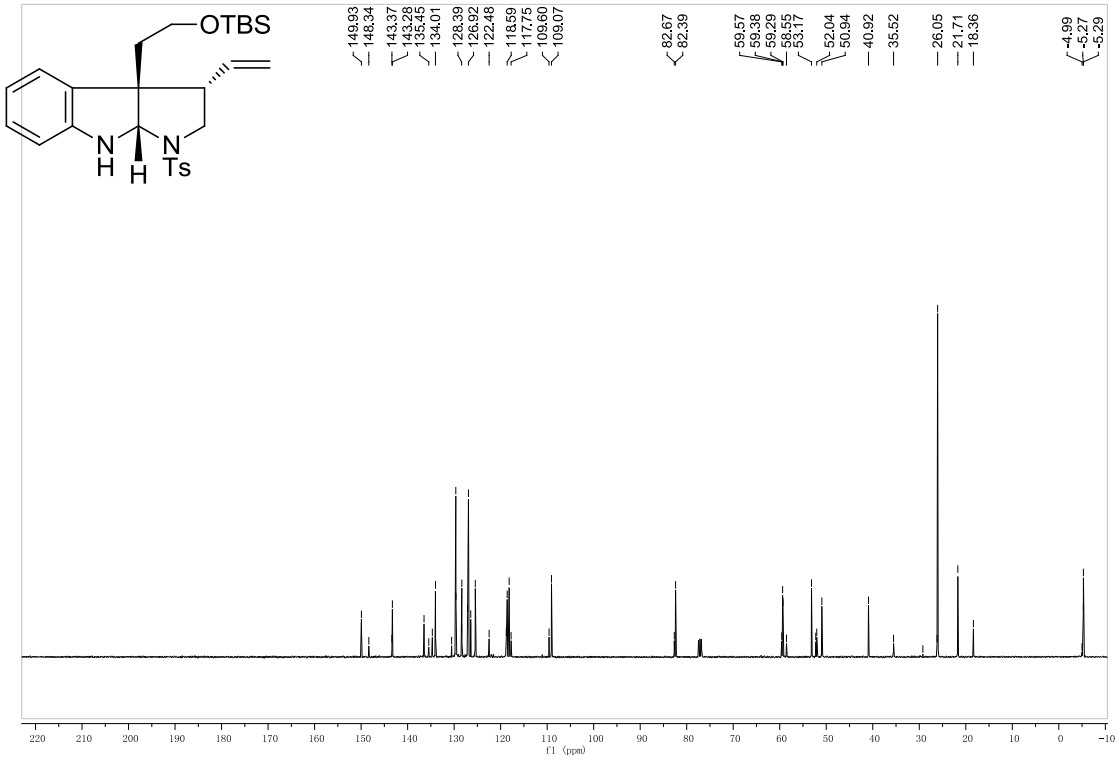
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ia



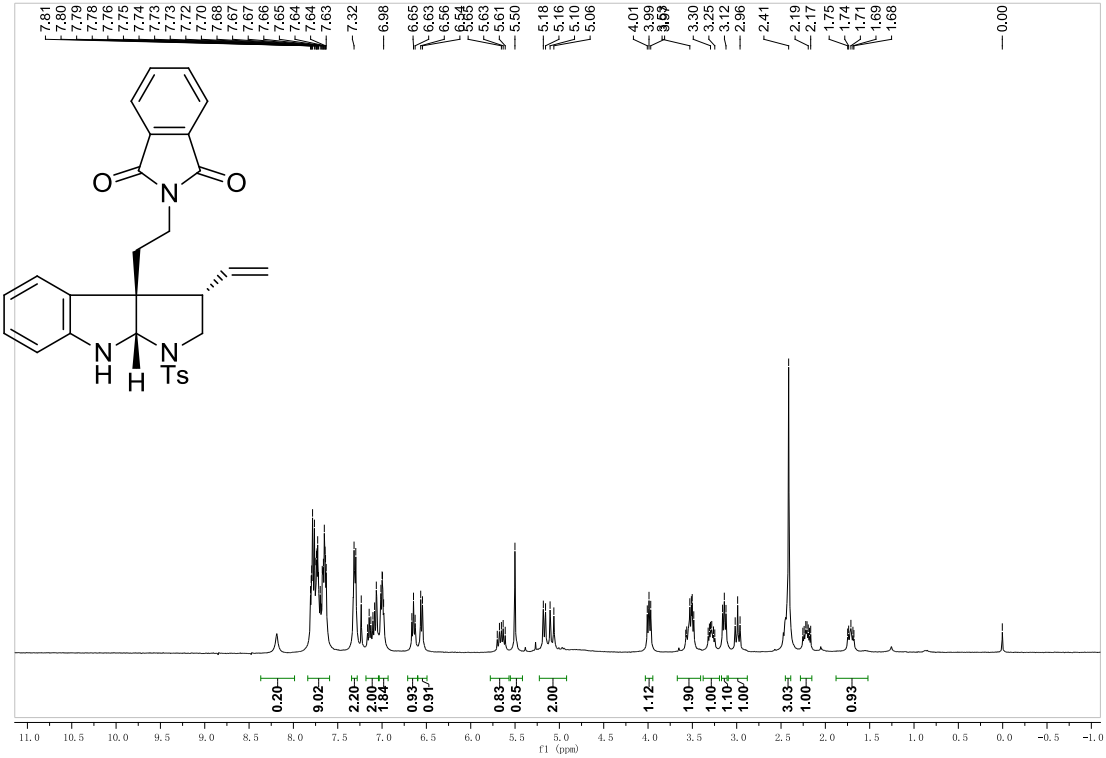
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ja



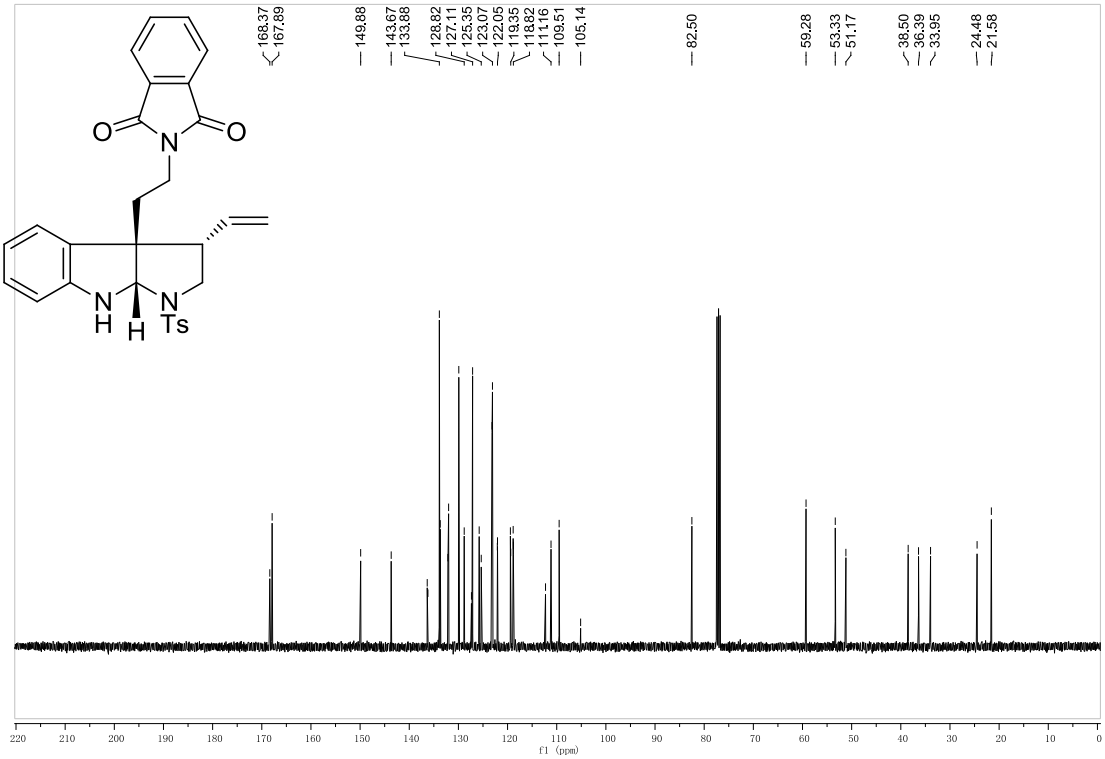
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ja



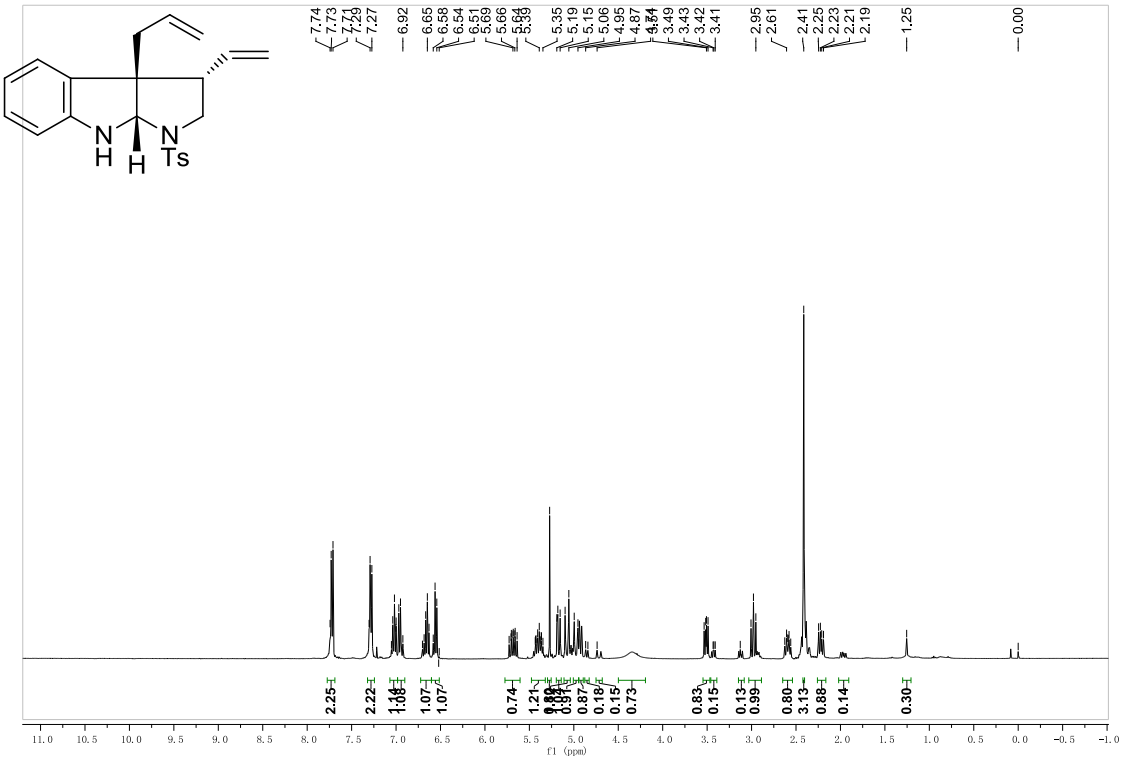
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ka



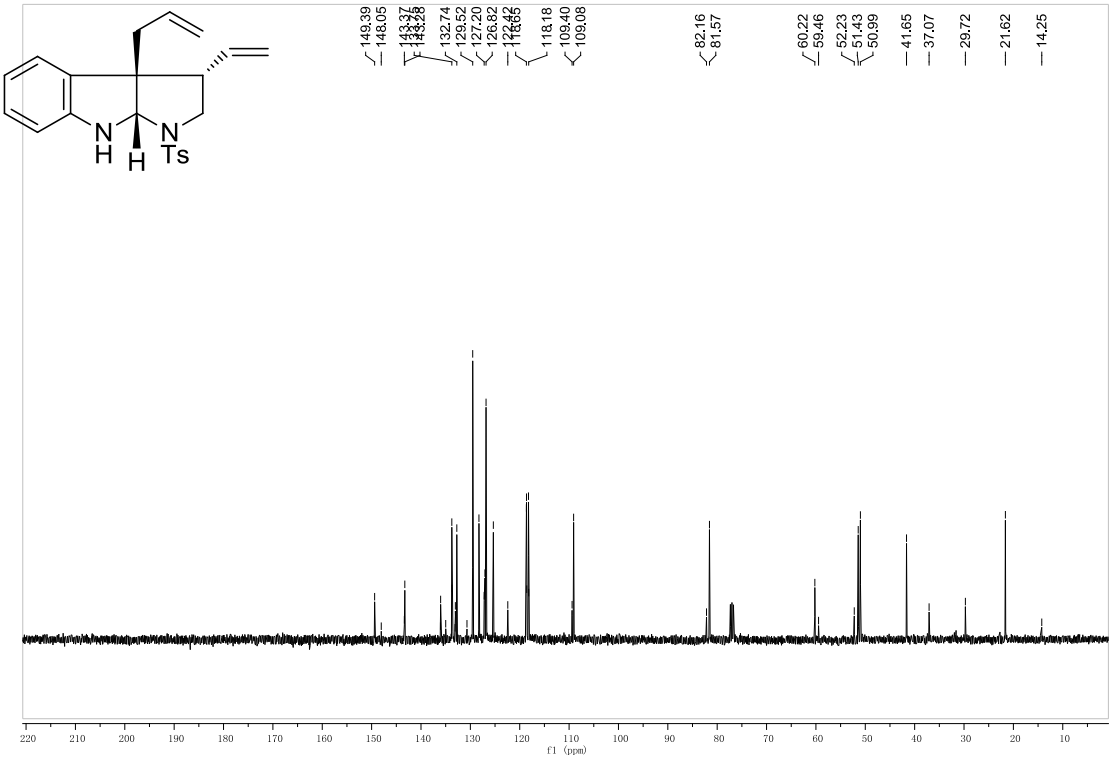
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ka



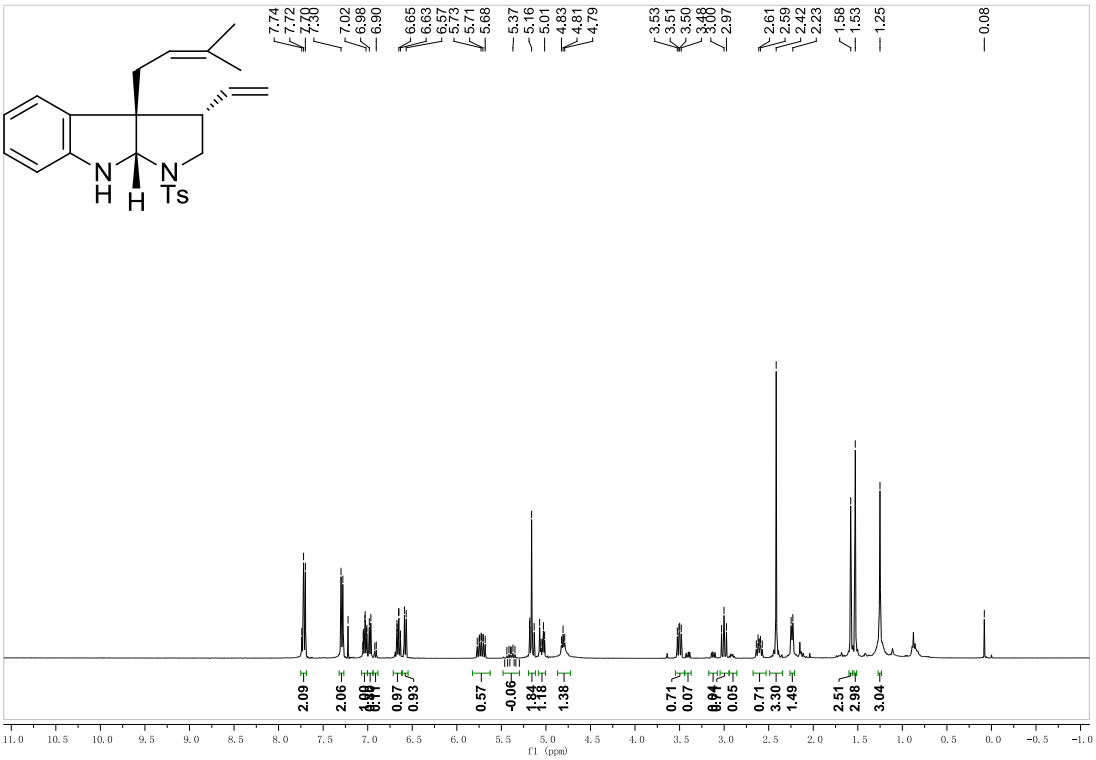
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3la



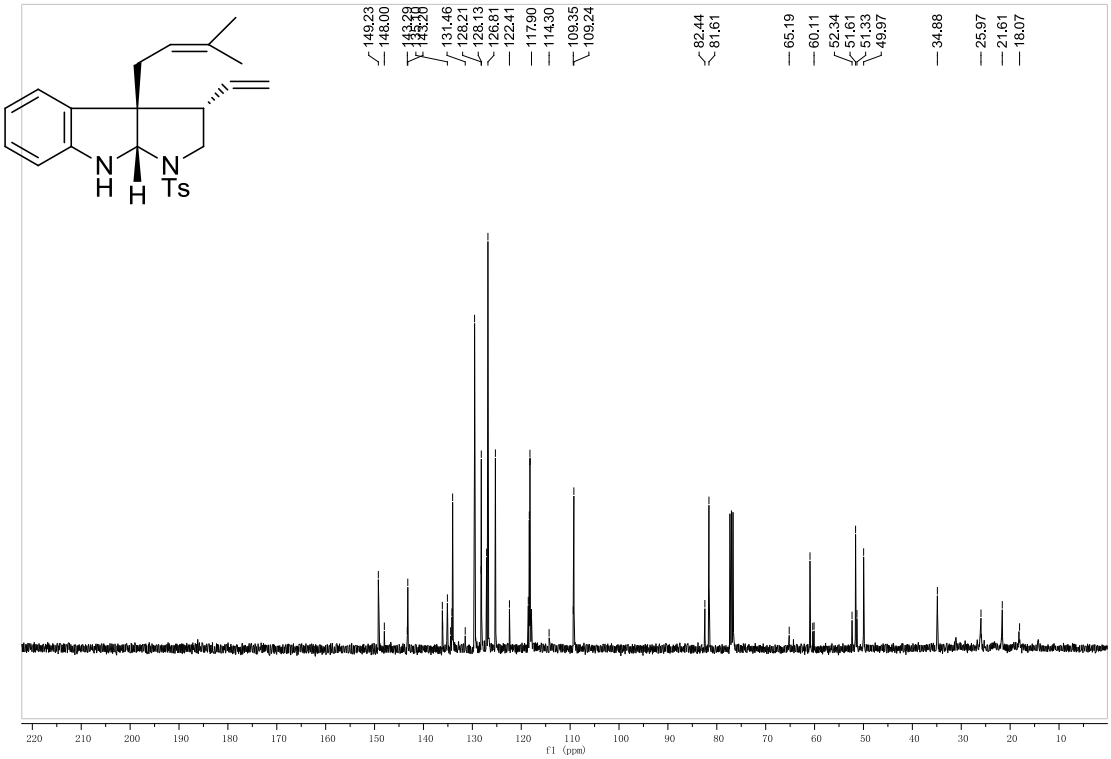
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3la



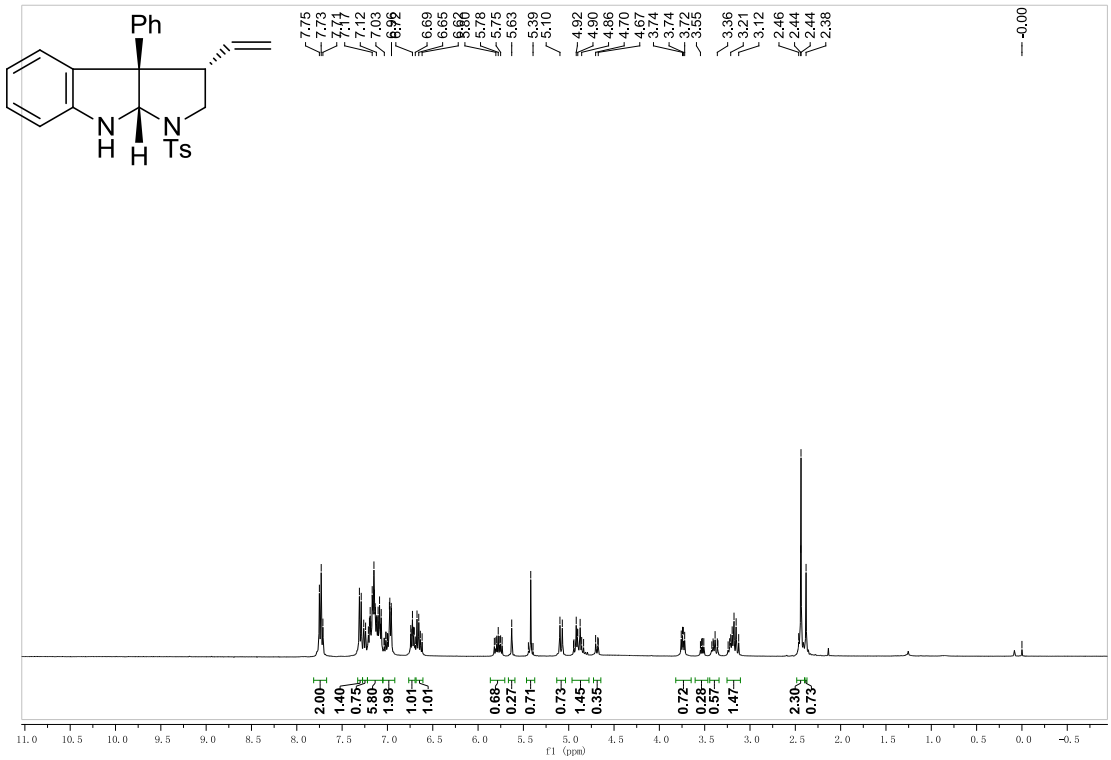
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ma



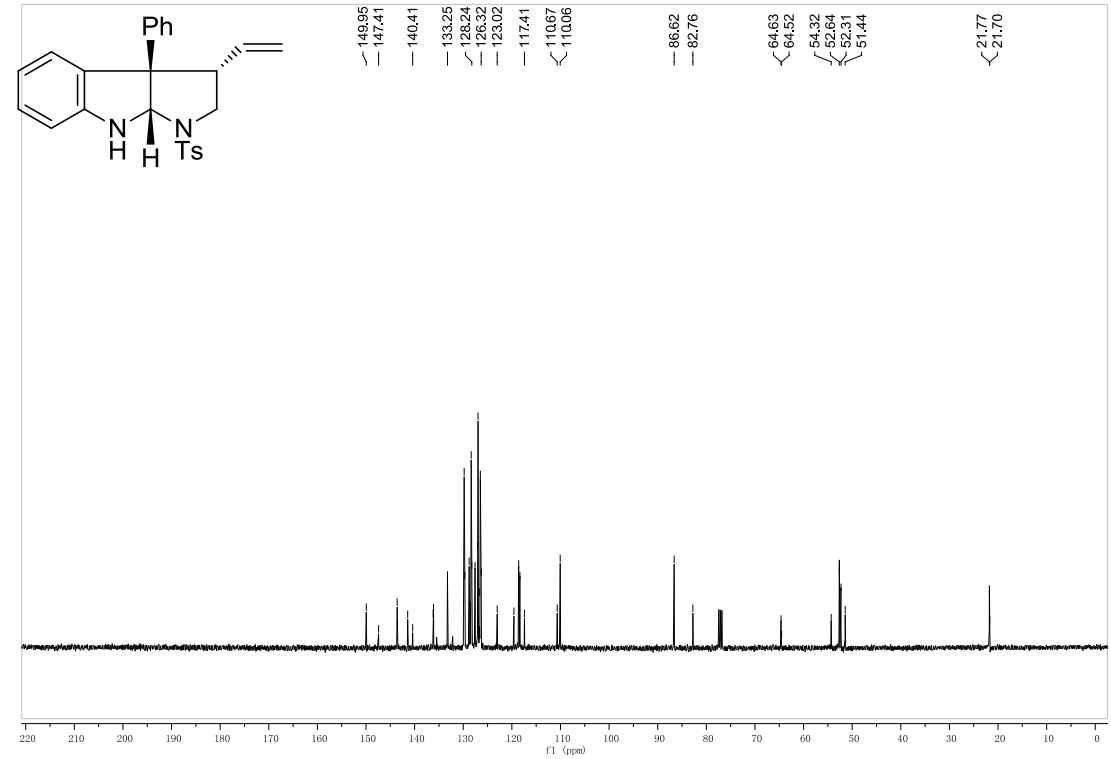
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ma



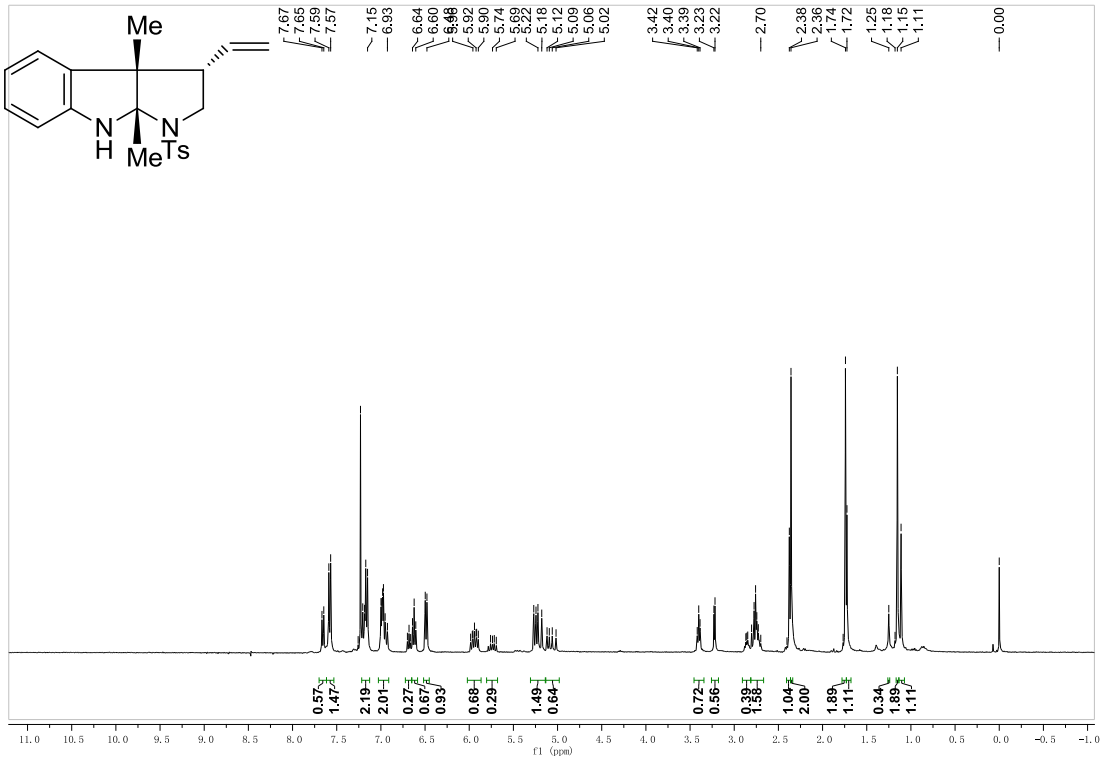
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3na



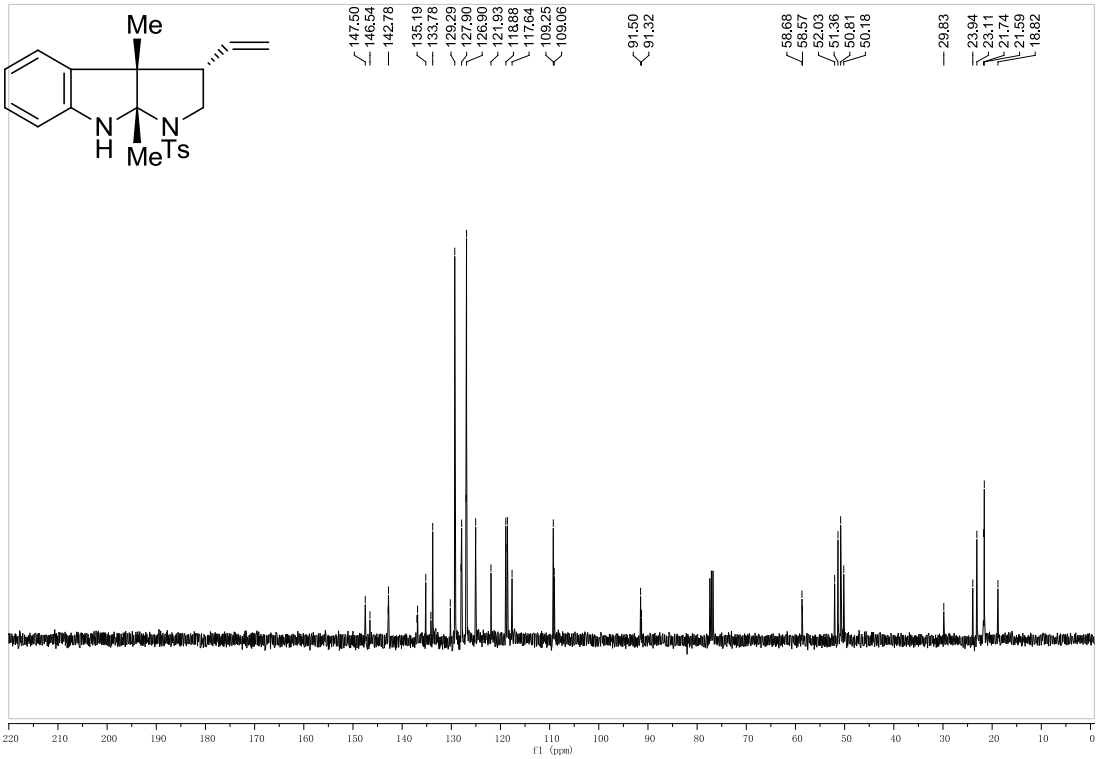
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3na



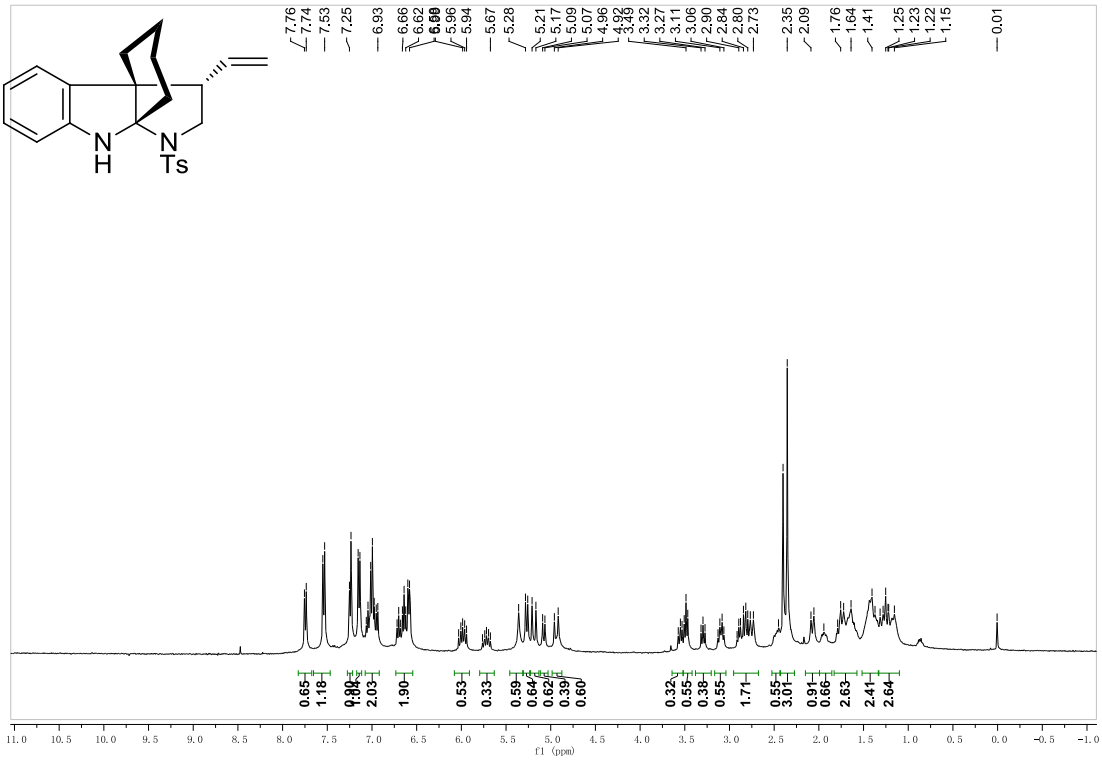
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3oa



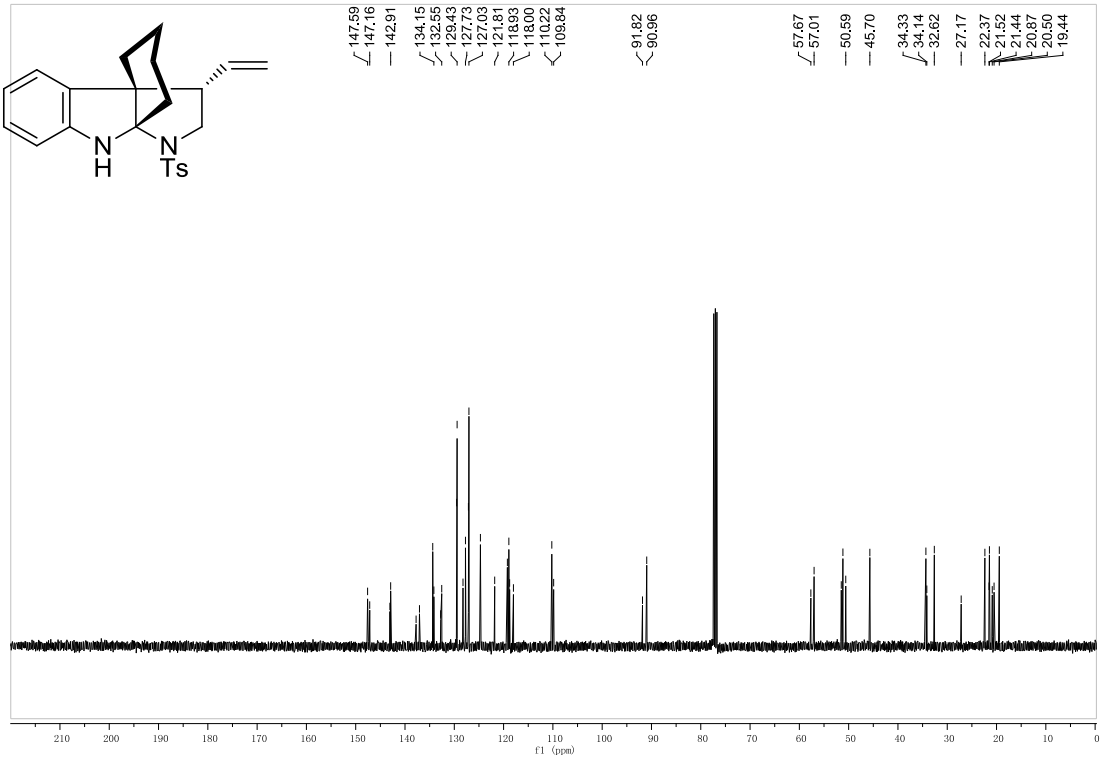
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3oa



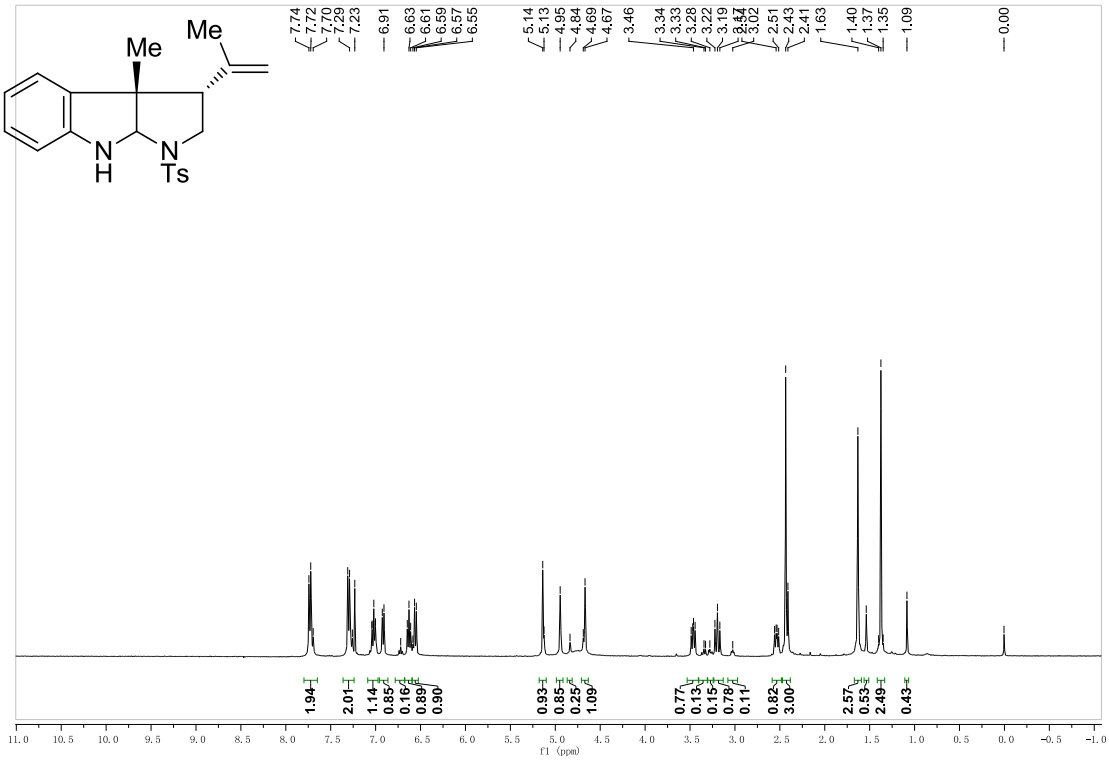
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3pa



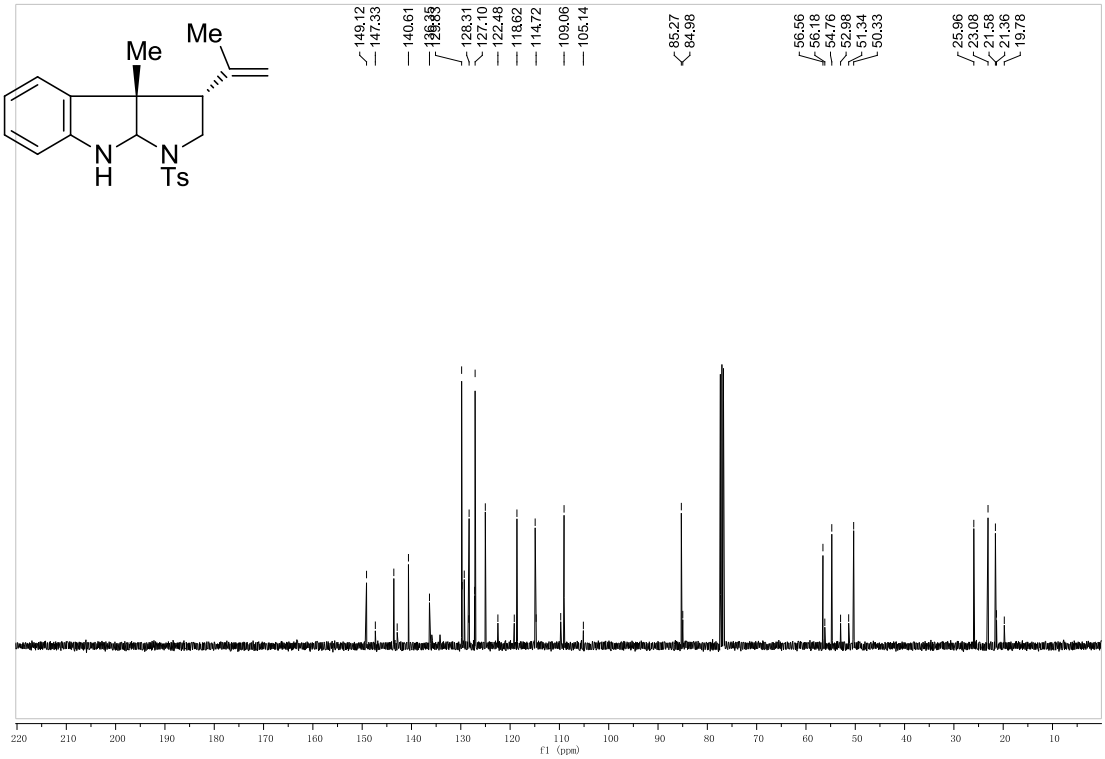
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3pa



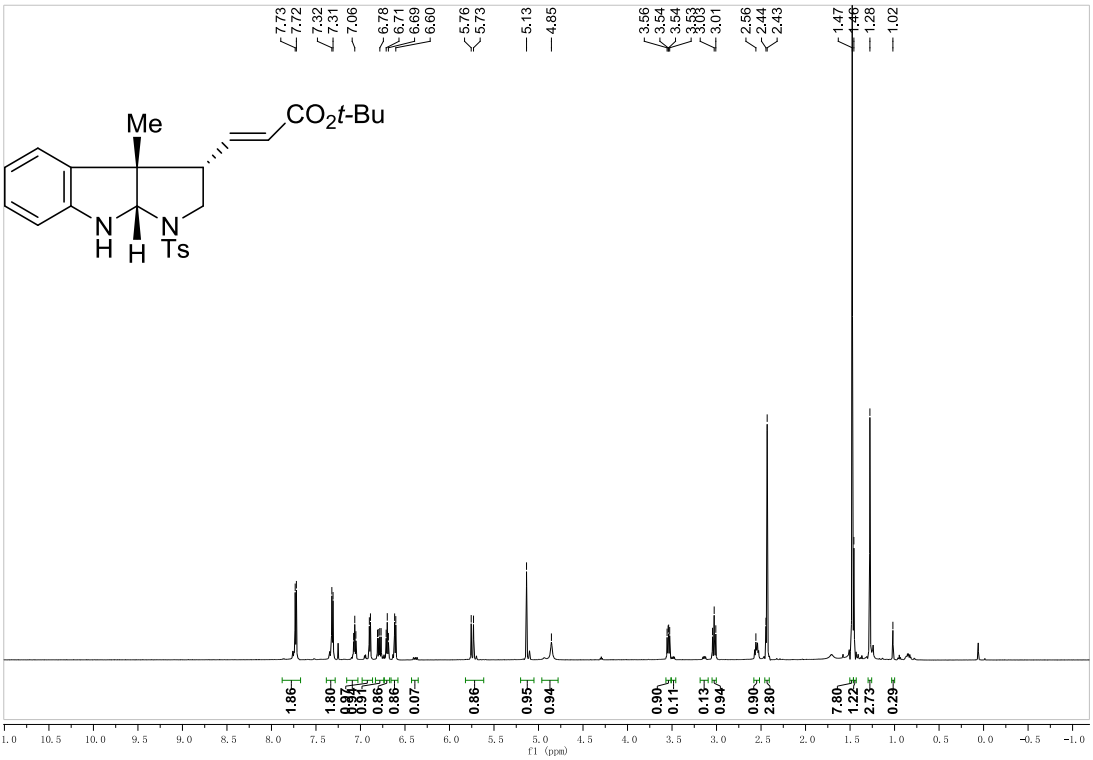
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ab



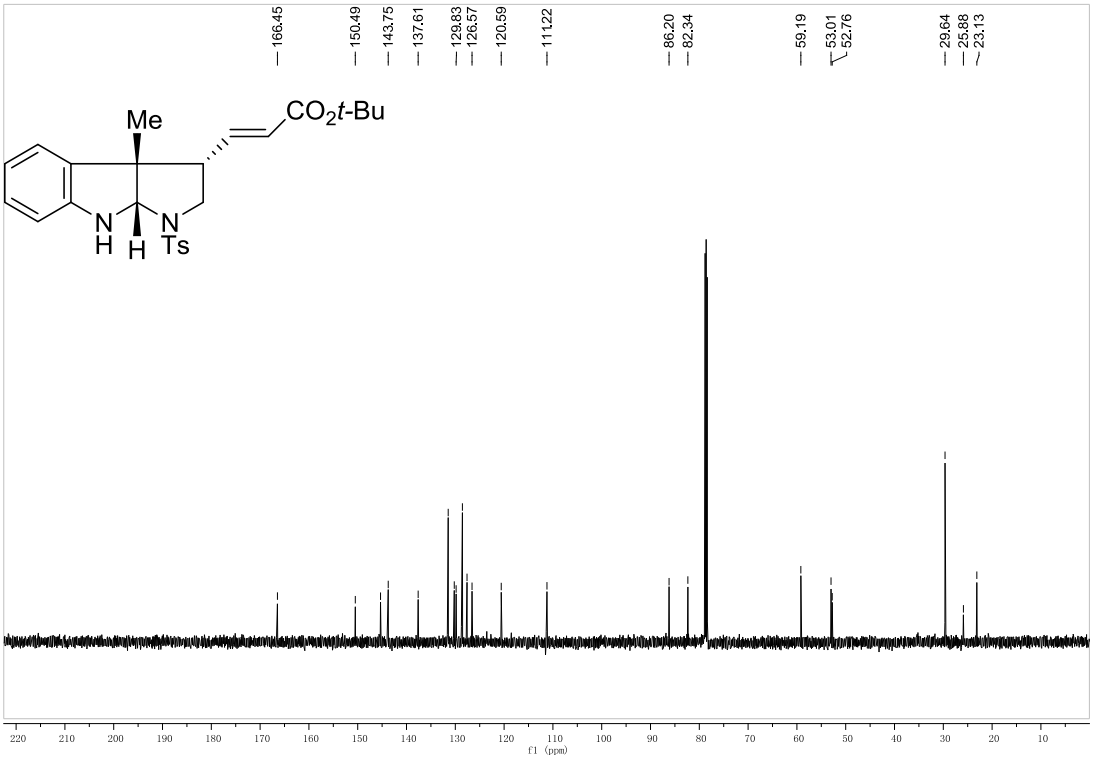
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ab



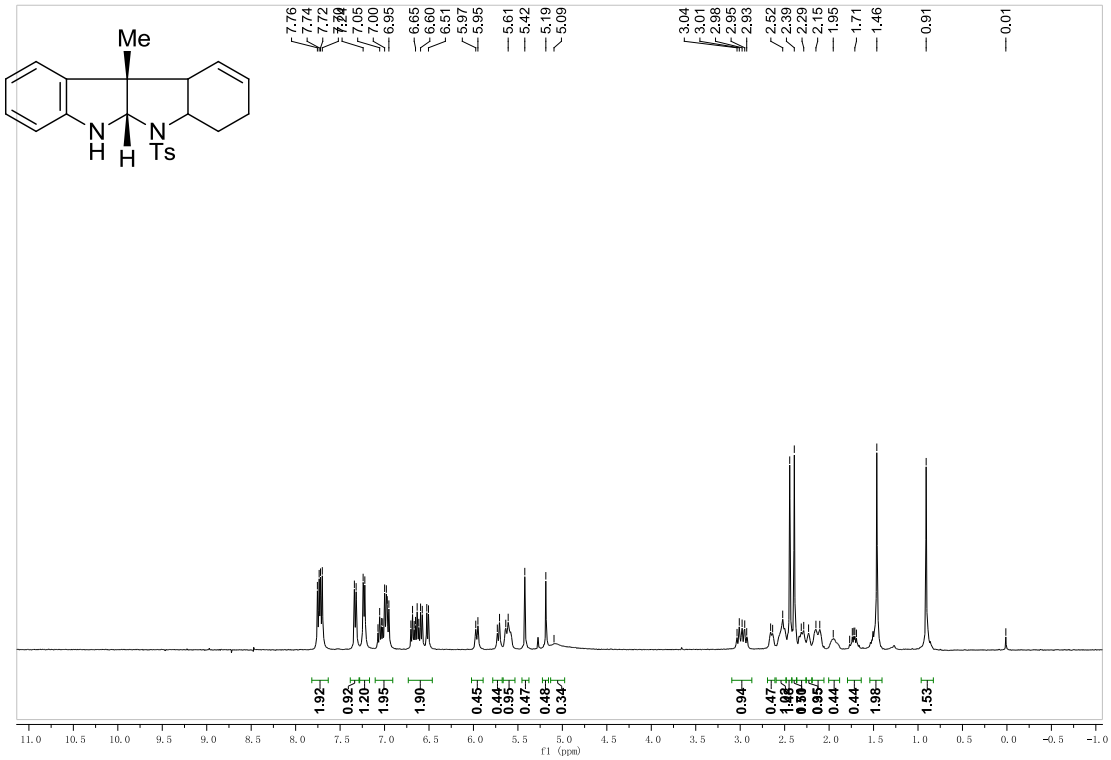
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ac



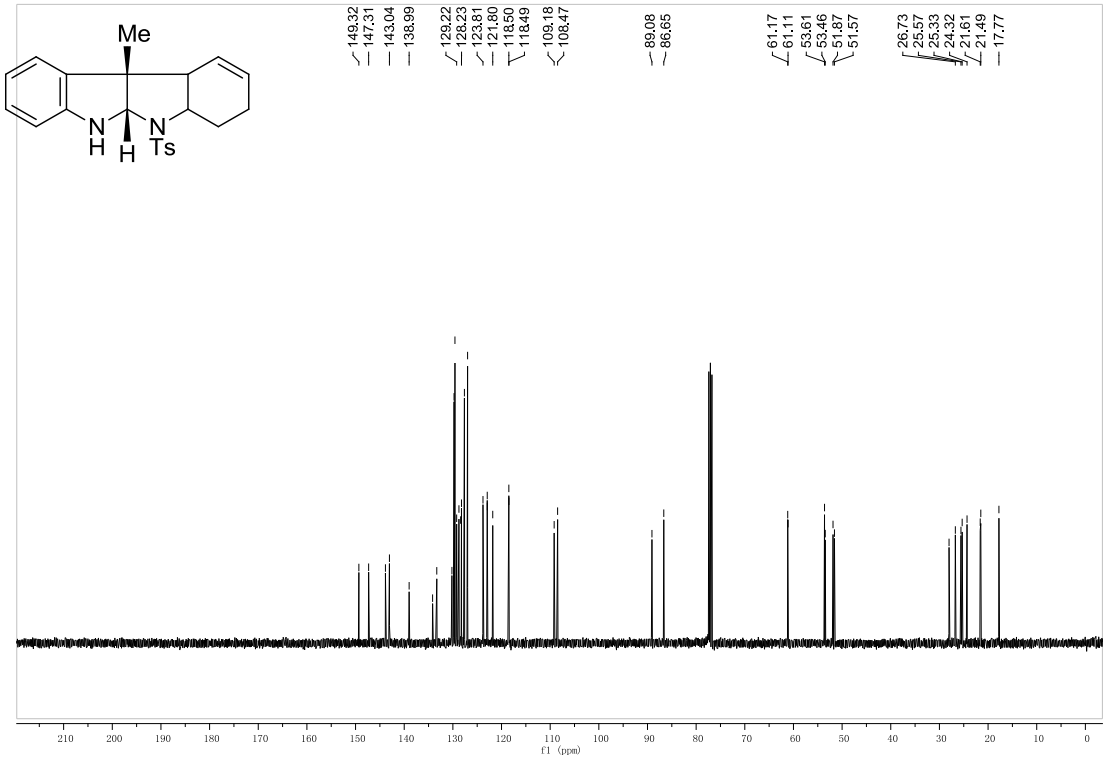
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ac



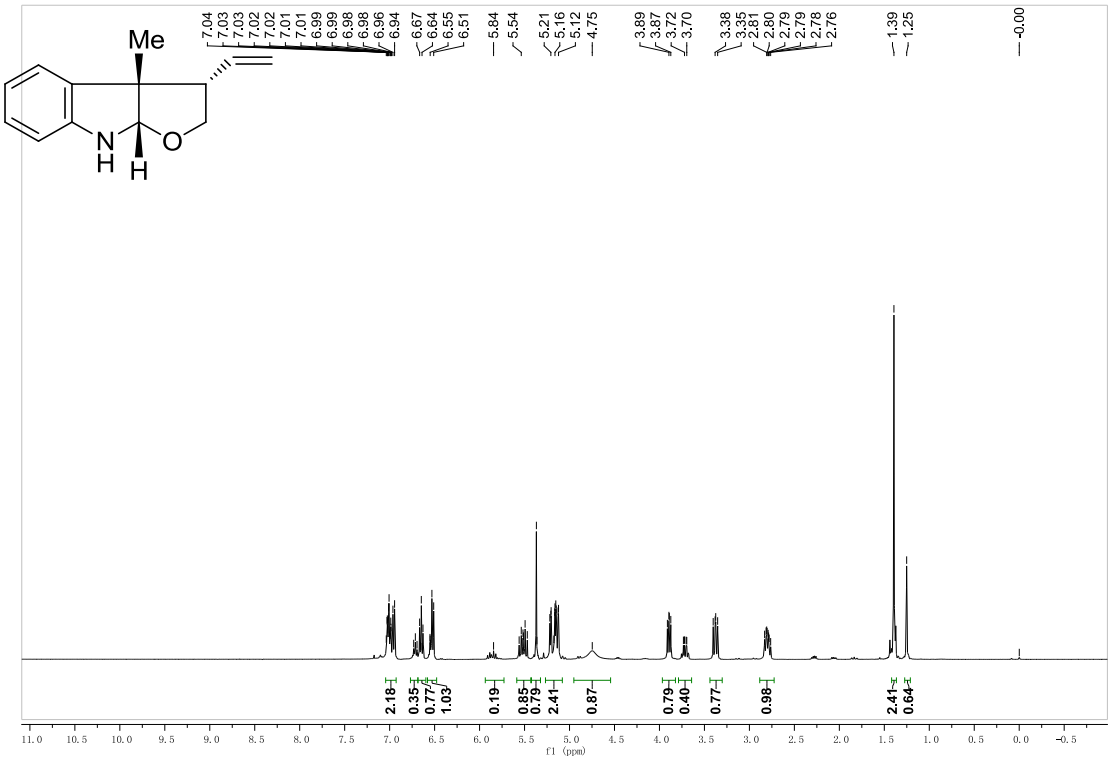
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3ae



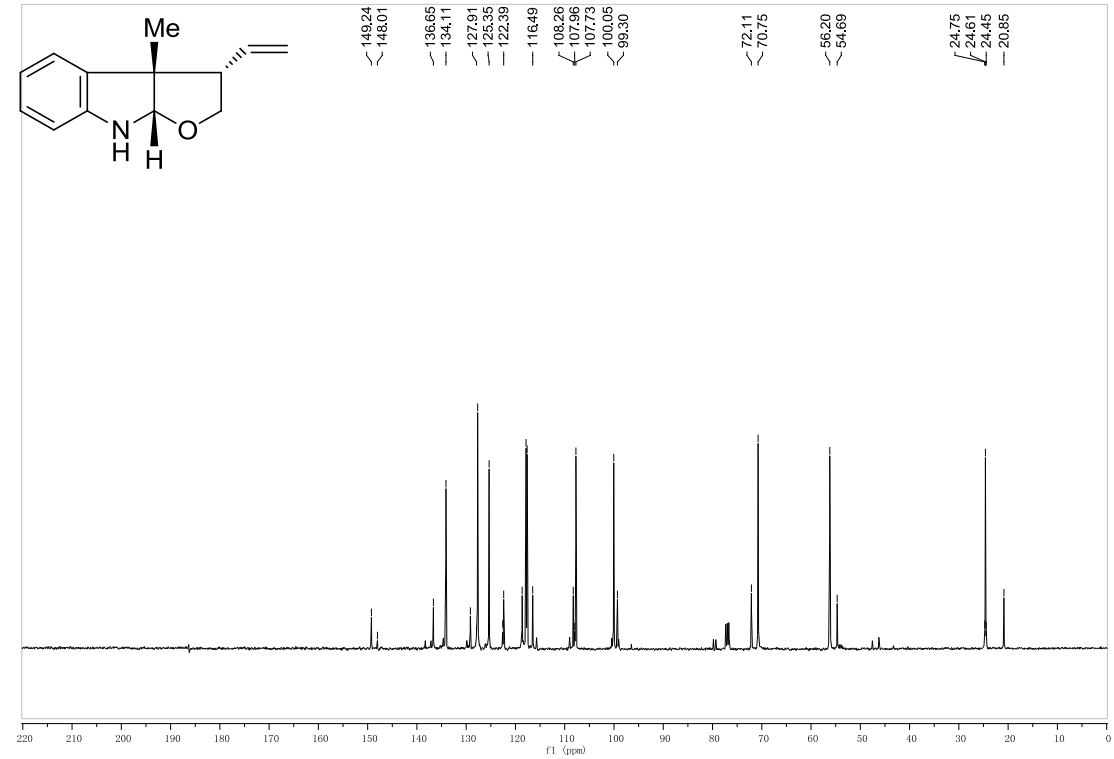
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 3ae



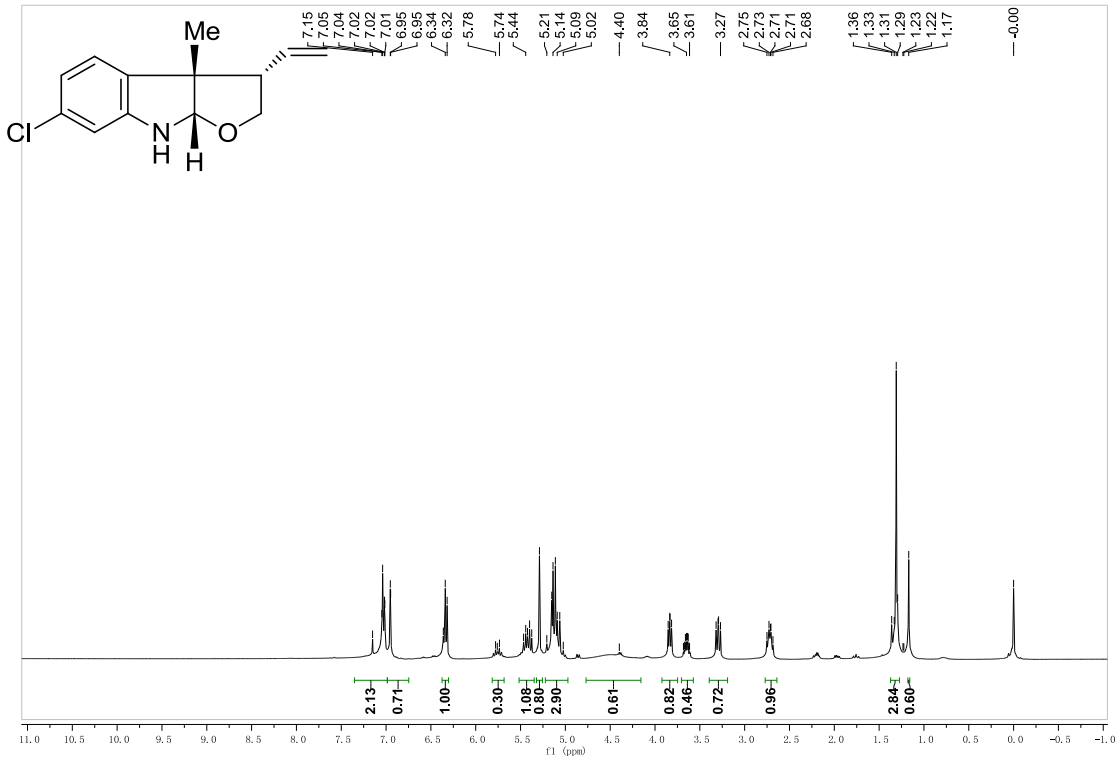
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 5aa



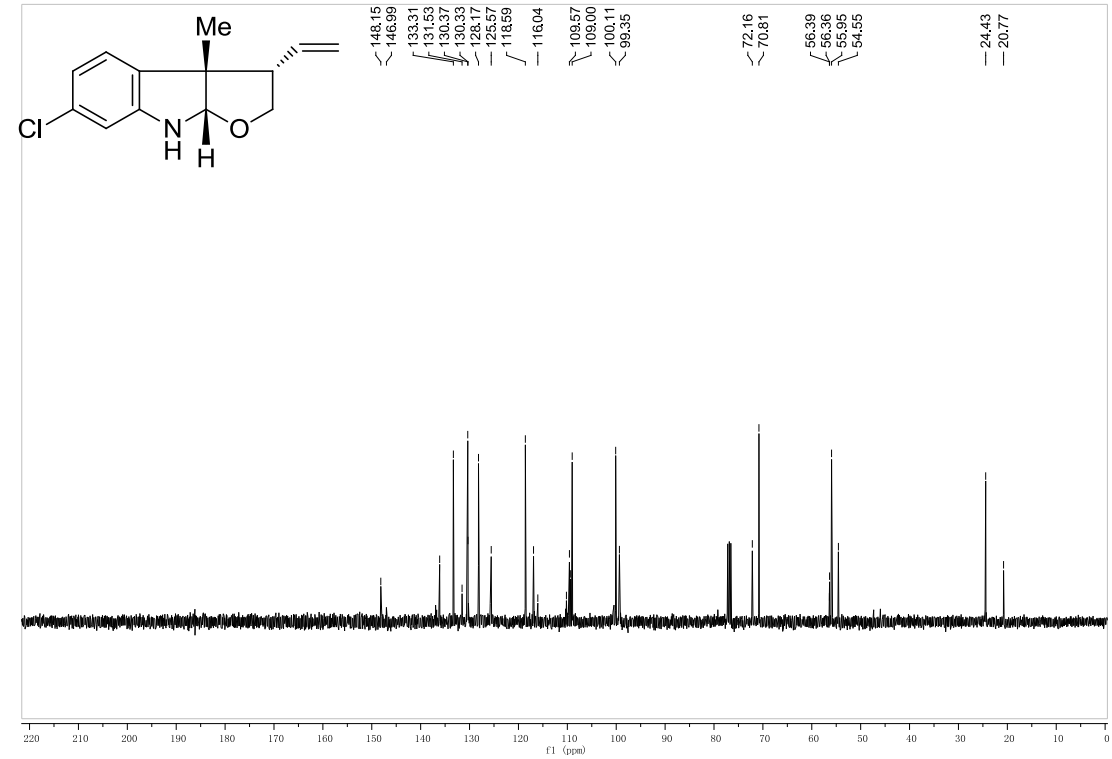
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 5aa



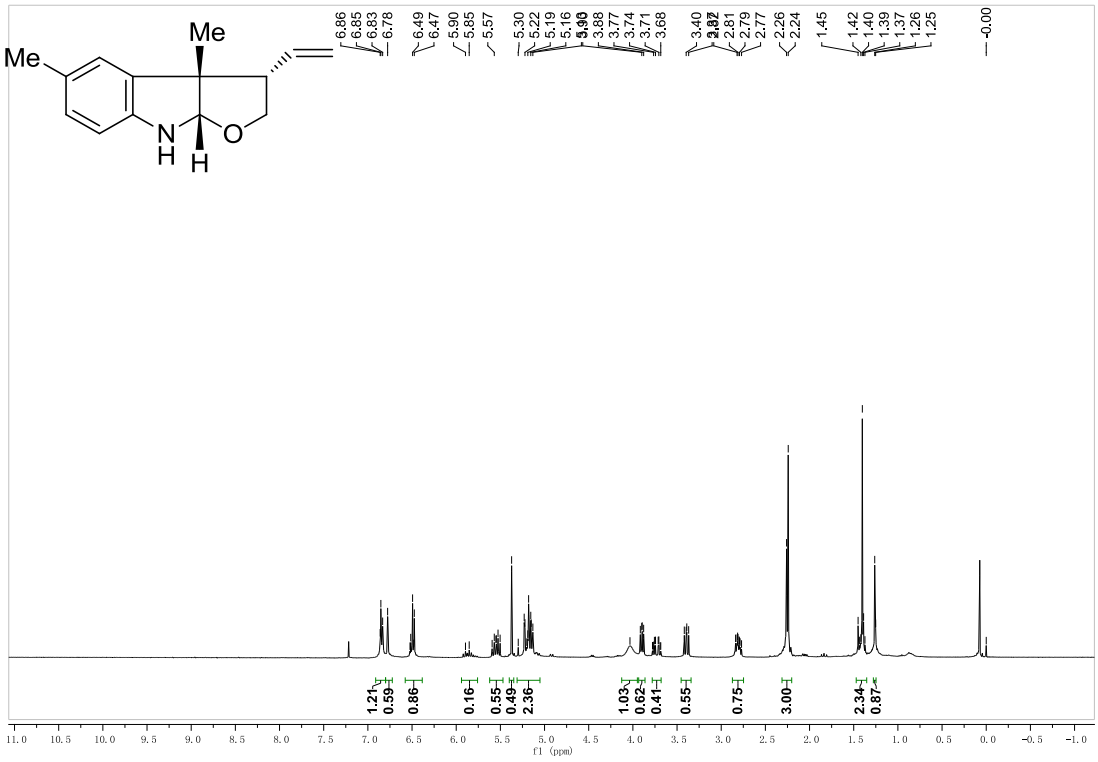
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 5ba



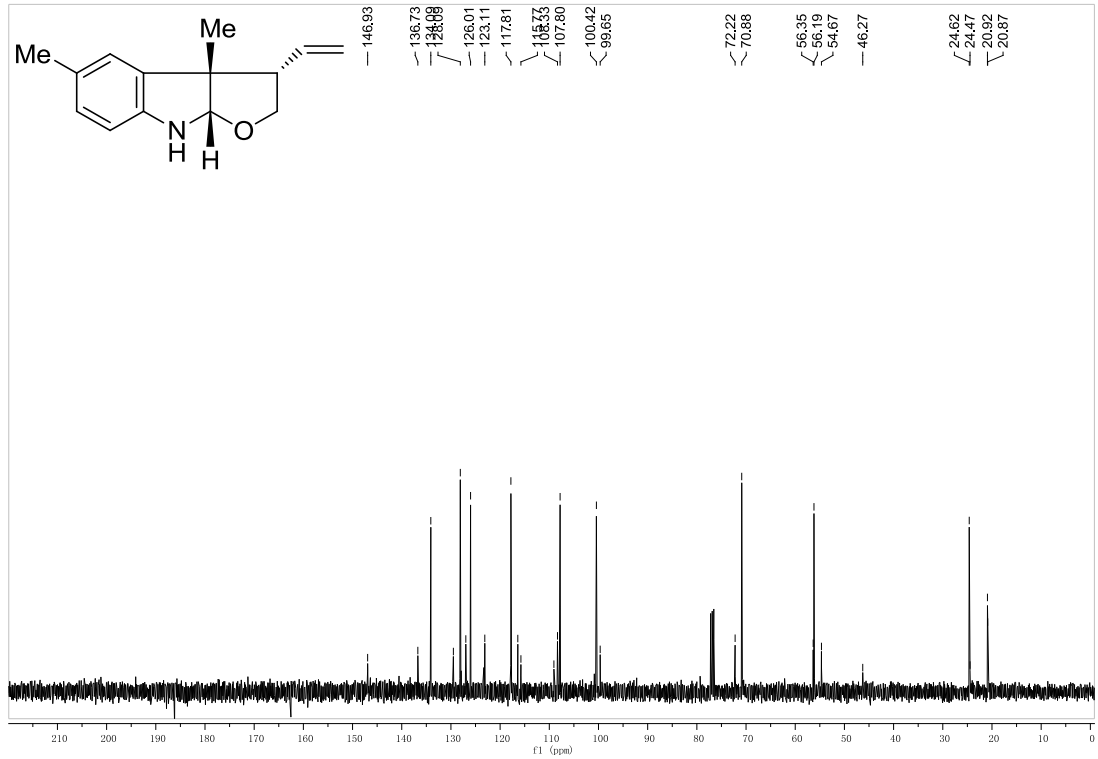
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 5ba



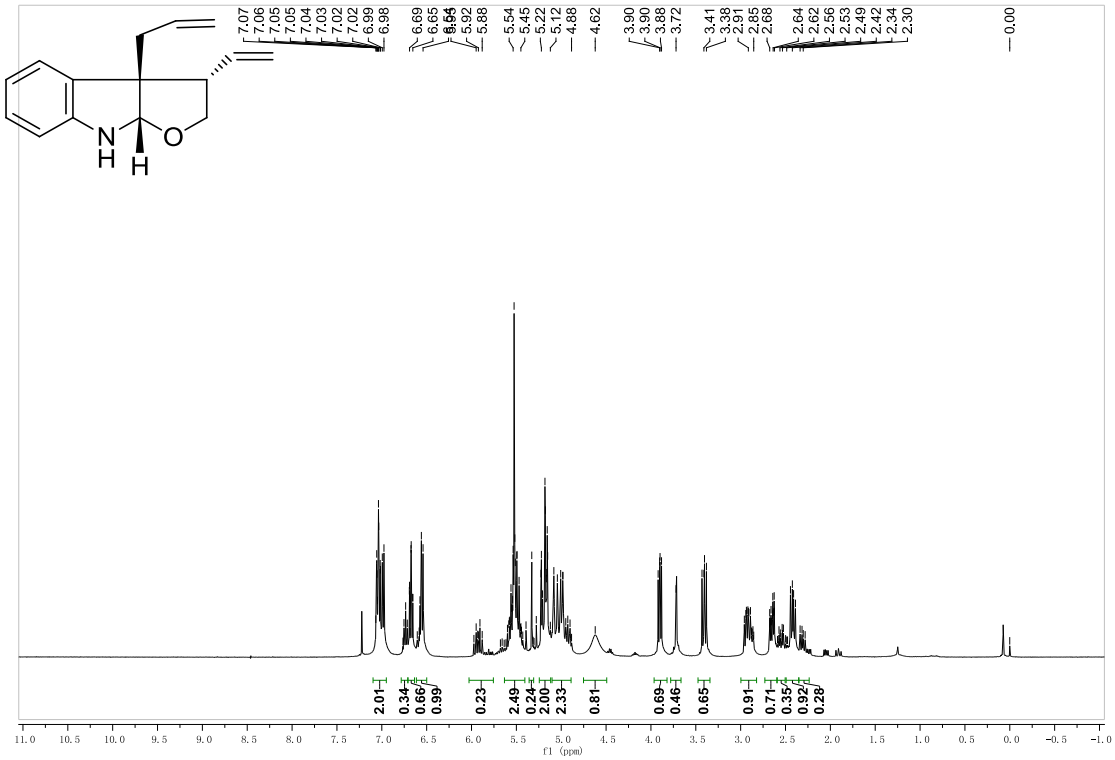
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 5fa



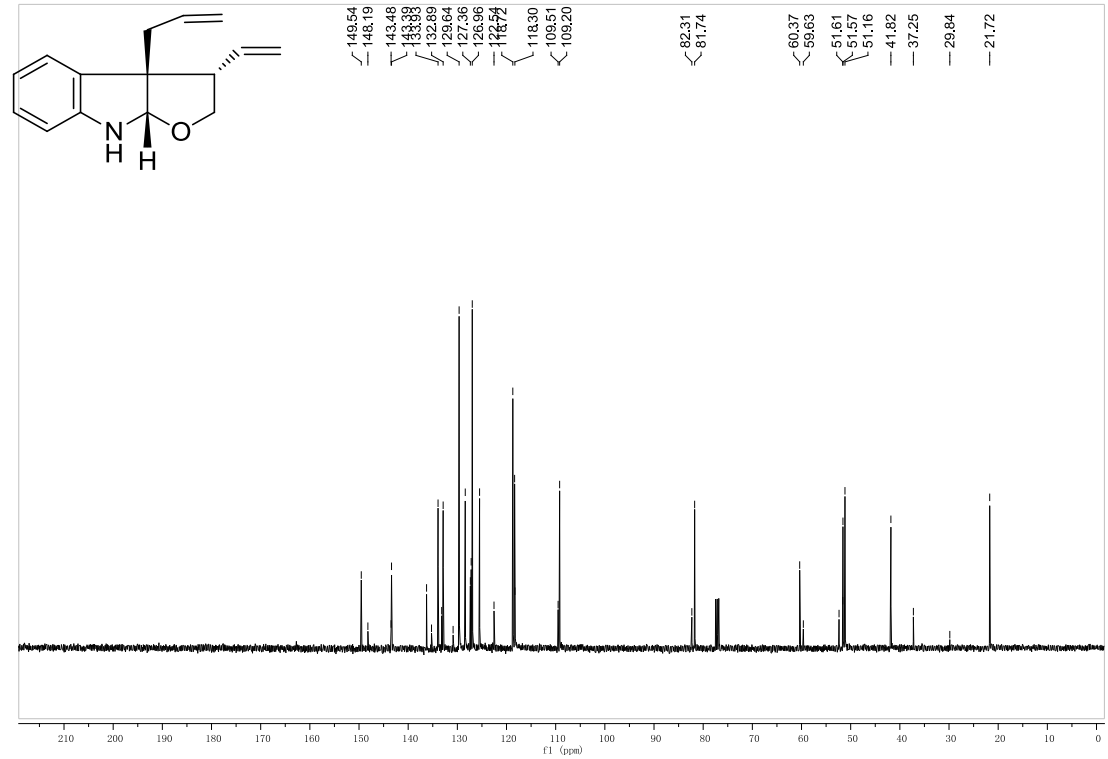
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 5fa



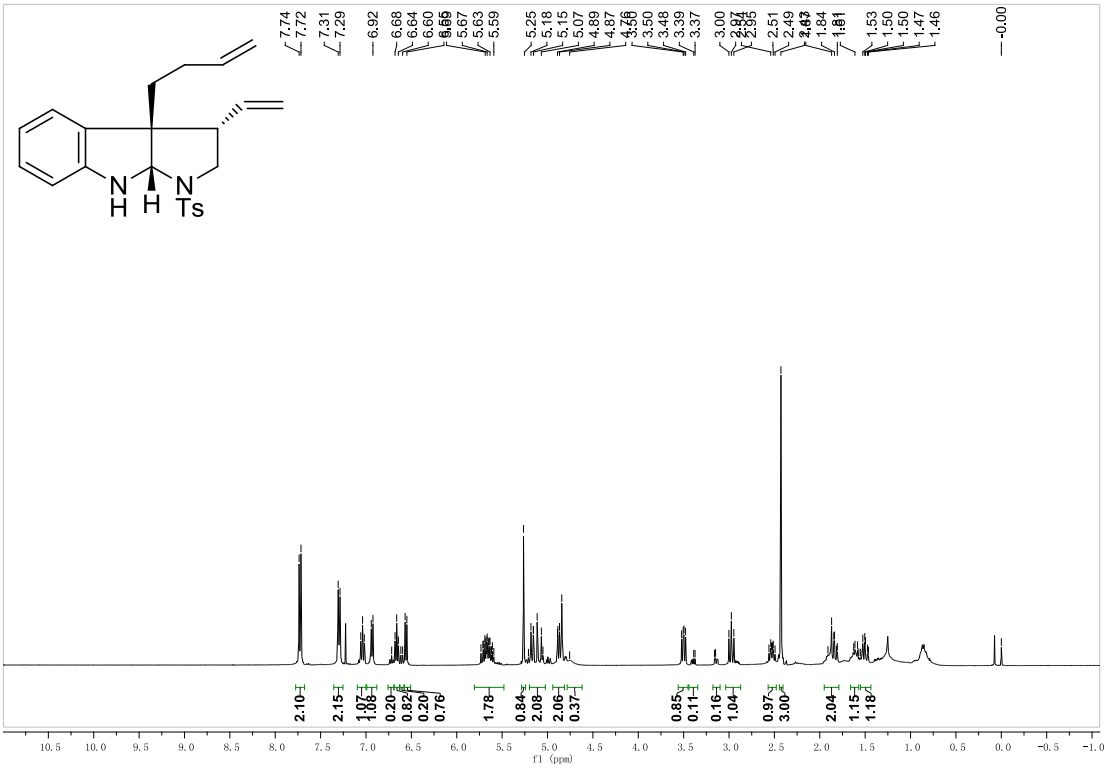
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 5ma



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 5ma

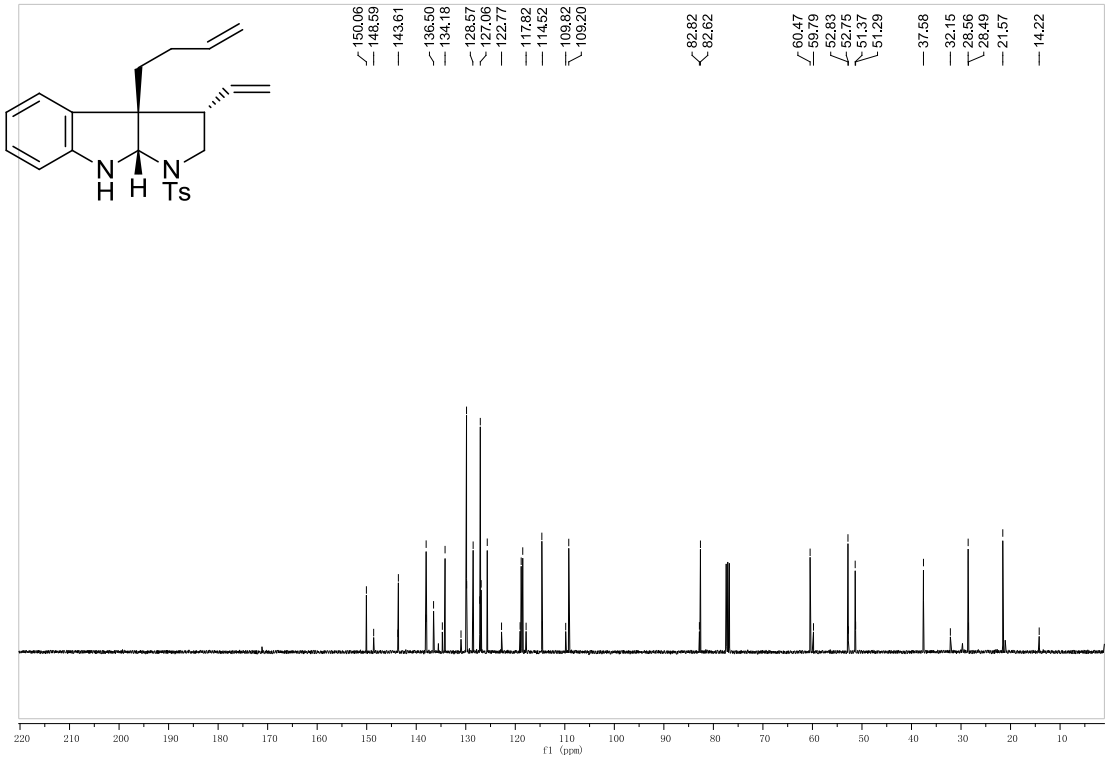


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 3qa

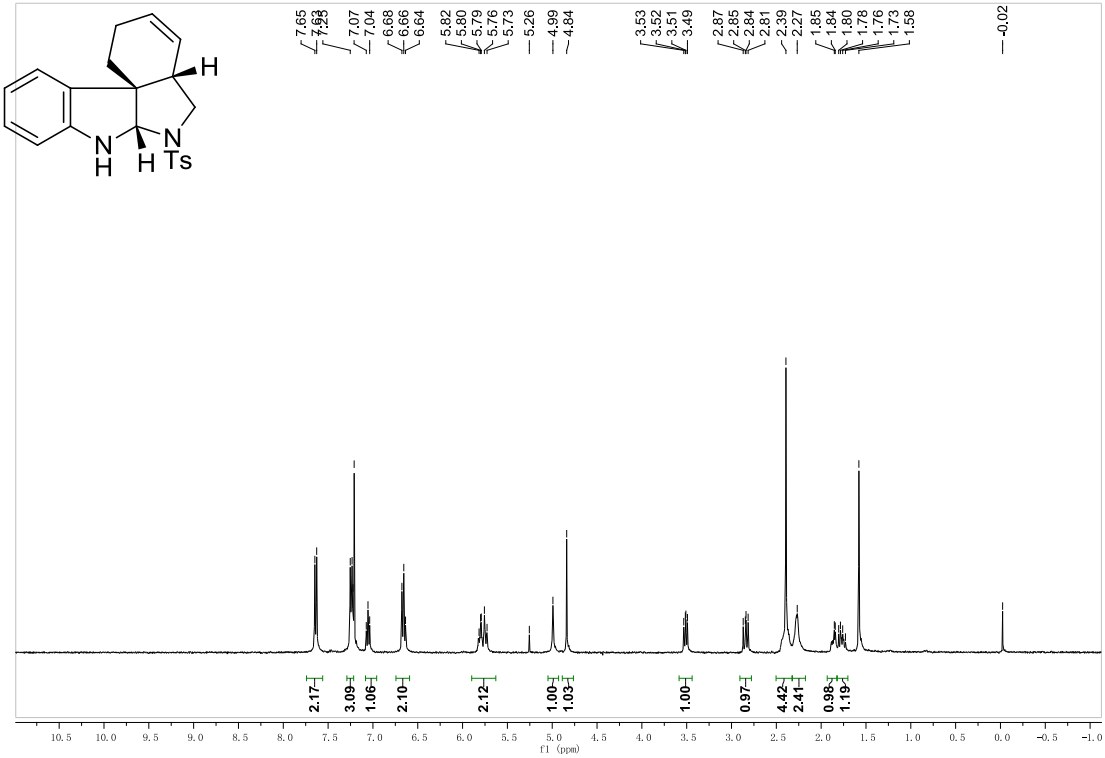


13

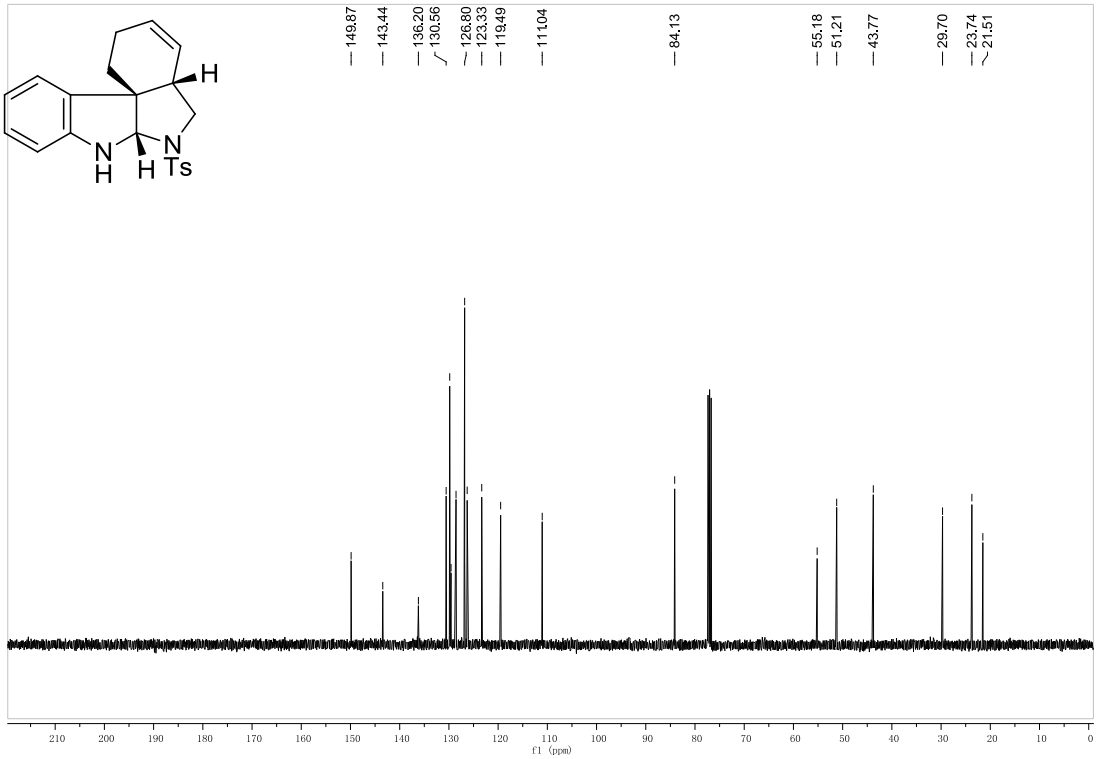
C NMR spectrum (100 MHz, $CDCl_3$) of product 3qa



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of product 6



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of product 6



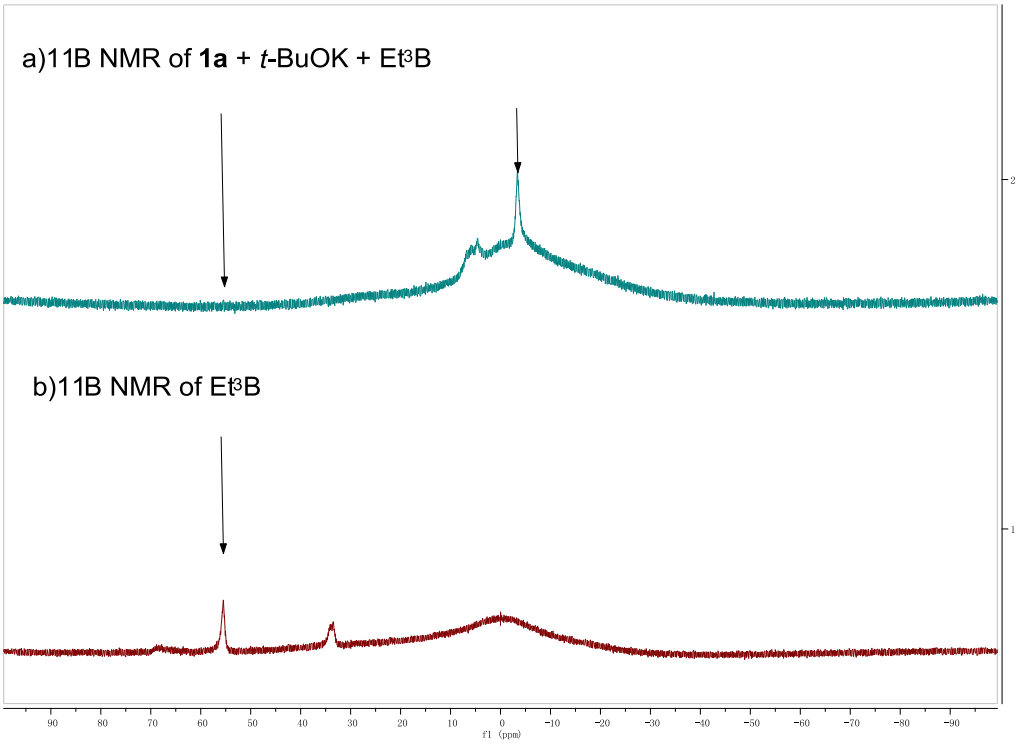
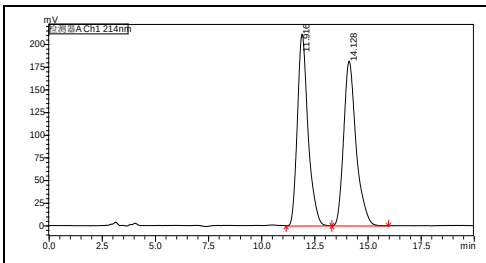
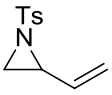


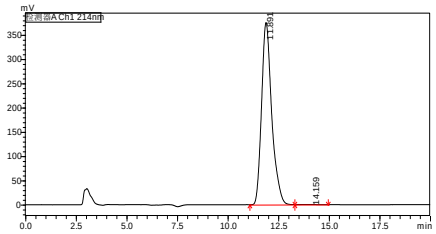
Figure S1. a) ^{11}B NMR of 1a, t-BuOK and Et_3B. b) ^{11}B NMR of Et_3B.

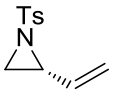
4. Copies of HPLC Spectra



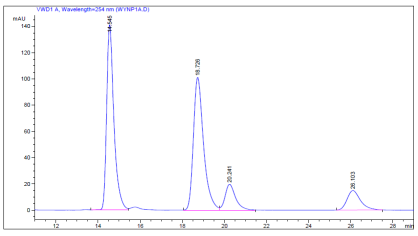


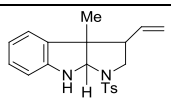
Peak#	Ret. Time	Area	Area%	T.Plate#	Tailing.F	Resolution
1	11.916	7379076	49.950	2866	1.297	---
2	14.128	7393837	50.050	3008	1.322	2.304





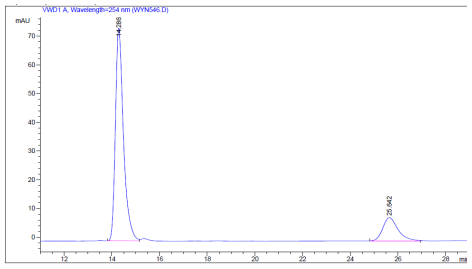
Peak#	Ret. Time	Area	Area%	T.Plate#	Tailing.F	Resolution
1	11.891	13150971	99.831	2842	1.297	---
2	14.159	22305	0.169	4071	---	2.549

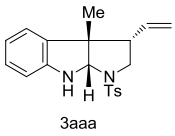




3aa

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.545	VV	0.3621	3390.49097	140.99174	41.7426
2	18.726	BV	0.5073	3384.28687	101.02232	41.6662
3	20.241	VB	0.5222	680.22534	19.70200	8.3747
4	26.103	BB	0.6707	667.37567	14.91090	8.2165

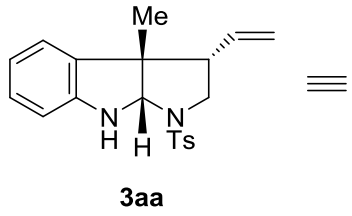




3aaa

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.286	BV	0.3559	1741.32068	74.05688	82.9780
2	25.642	BB	0.6829	357.21301	8.06153	17.0220

5. X-Ray Structure of Product 3aa



3aa

≡

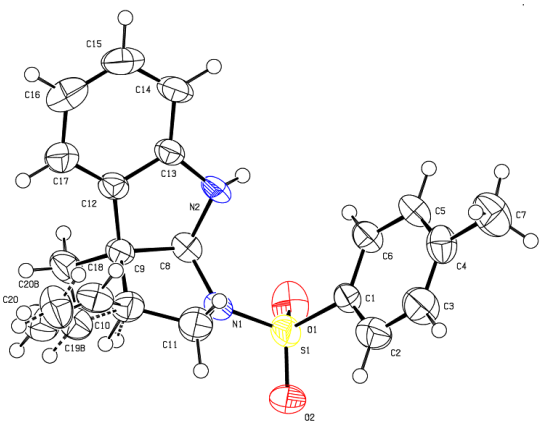


Figure S2. The thermal ellipsoid was drawn at the 50% probability level.

Crystals of the compound **3aa** were obtained by diffusing petroleum ether to the ethyl acetate solution containing **3aa**. The data were collected at 100 K with a diffractometer using graphite-monochromatized Mo-*K*α (λ=0.71073Å) radiation. *SAMRT* (v6.45, Bruker 2003) was used for data collection and *SAINT* (v7.68A, Bruker 2009) was used for data processing. No absorption correction was applied to the intensities due to its weak absorption nature. The structure was solved by Direct method with *SHELXS*[1] and refined by full-matrix least-squares methods using the *OLEX2*,[2] which utilizes the *SHELXL-2013* module.[3] The vinyl group was observed disordered over two parts with the fixed ratio of 0.8:0.2. The bond distances for the two parts were restrained to be the same by "SADI" command with the default deviation, and the anisotropic displacement parameters fot he minor part were strictly restrained by "ISOR 0.01 0.02" command. All non-hydrogen atoms in the structure were refined with anisotropic thermal parameters. All the hydrogen atoms except the H bound to N were introduced to their ideal positions

using riding modes with U_{eq}(H) of 1.5U_{eq}(parent) for terminal methyl groups, and 1.2 U_{eq}(parent) for others. The hydrogen bound to N2 was located from the difference Fourier map, whose coordinates and the isotropic vibration parameter were refined freely. The information concerning crystal data, data collection and refinement results have been documented in the following.

Crystal data **3aa:** 0.12×0.15×0.20 mm, $C_{20}H_{22}N_2O_2S$, M = 354.45, monoclinic, space group $P2_1/n$, a = 13.764 (3) Å, b = 8.3813(18) Å, c = 15.703 (3) Å, , β = 95.075(4) °, V = 1804.4(7) Å^3, Z = 4, ρ = 1.305 g cm^{-3}, μ = 0.195 mm^{-1}, F(000) = 752, 8869 reflections (θ_{max} = 25.25 °) measured (3136 unique, R_{int} = 0.1029 completeness = 96.3%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0811, wR_2 = 0.1757, R indices (all data): R_1= 0.1292, wR_2 = 0.1911. GOF = 1.121 for 250 parameters and 14 restraints, largest diff. peak and hole 0.506/–0.227 eÅ^{-3}.

References:

1. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
3. G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.