Supporting Information

Palladium-catalyzed [3+3] annulations of 1-alkyl-indolin-2-imines and dialkyl (2-methylenepropane-1,3-diyl) dicarbonates

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1. General information

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. The reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H NMR and ^{13}C NMR were recorded on JEOL ECS-400 or JEOL ECS-600 spectrometer with $CDCl_3$ as the solvent. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ 7.26 ppm), carbon ($CDCl_3$: δ 77.07 ppm) or tetramethylsilane (TMS δ 0.00). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants *J* are reported in Hz. HRMS data were obtained on Agilent 6520 Q-TOF LC/MS with ESI resource. Chiral HPLC analysis was achieved using an Agilent 1100 Infinity series normal phase HPLC unit and Agilent Chemstation software, UV detection monitored at 254 nm. Single crystal X–ray data were collected on a Bruker APEXII X–ray diffractometer equipped with a CMOS PHOTON 100 detector with a Mo Kα X–ray source (Kα = 0.71073 Å). Melting points were recorded on a Beijing Tech X–4 melting point apparatus.

2. Synthesis of substrates

1-Alkyl-3-alkylindolin-2-imine hydrochlorides (**1**),[1] dialkyl (2-methylenepropane-1,3-diyl) dicarbonates (**2**)[2] and substituted *N*-(1-methylindolin-2-ylidene)benzenesulfonamide (**4**)[3] were synthesized according to the previous procedures.

References

1 H. Tian, F. Peng, P. Zhang, H. Yang and H. Fu, Highly Enantioselective Iridium-Catalyzed Cascade Double Allylation Strategy: Synthesis of Pyrrolidinoindolines with an All-Carbon Quaternary Stereocenter, *Org. Lett.*, 2019, **21**, 8501-8505.

2 A. Lin, Chien, C.-F. Ojima and C.-W. I. Enantioselective Pd-catalyzed tandem allylic alkylation reaction using monodentate phosphoramidite ligands for the formal total synthesis

of huperzine**,** *Org. Chem. Front*., 2014, **1**, 1062-1066**.**

3 Y**.** Tokimizu, S**.** Oishi, N**.** Fujii and H**.** Ohno, Gold-Catalyzed Cascade Cyclization of (Azido)ynamides: An Efficient Strategy for the Construction of Indoloquinolines, *Org. Lett*., 2014, **16**, 3138-3141.

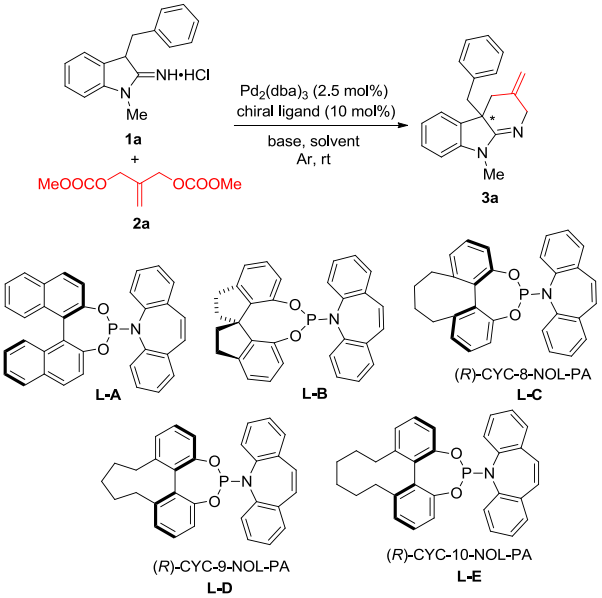
3. Synthesis and characterization data of 3a-3x and 5a-5k

3.1 General procedure for synthesis of 3a-3x

In a sealed tube, $Pd_2(dba)_3$ (2.5% mol, 2.5 μmol, 2.28 mg) and (*Rac*)-**L1** (10% mol, 0.01 mmol, 5.1 mg) were dissolved in anhydrous THF (0.5 mL) under argon atmosphere and vigorously stirred for 15 min, 1-alkyl-3-alkylindolin-2-imine hydrochloride (**1**) (0.1 mmol) and K_2CO_3 (0.3 mmol, 41.5 mg) were added to the solution, then a solution of dimethyl (2-methylenepropane-1,3-diyl) dicarbonate (**2a**) (0.12 mmol, 24.5 mg) in THF (1.0 mL) was added. The resulting mixture was stirred at rt until **1** was consumed completely (monitored by TLC). The reaction mixture was filtered through a celite pad and the filtrate was concentrated in vacuo, and the residue was purified through flash column chromatography (eluent: petroleum ether/ethyl acetate = 1/1) to afford the corresponding cycloaddition product **3**.

3.2 Asymmetric [3+3] annulation of 1a and 2a

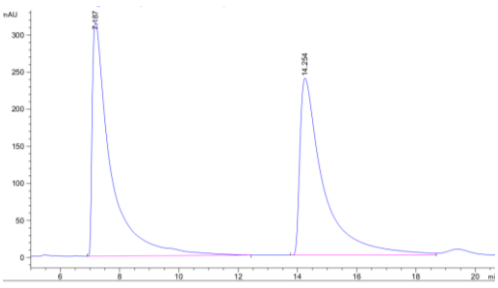
Table S1 Optimization of conditions for enantioselective synthesis of **3a**[a]

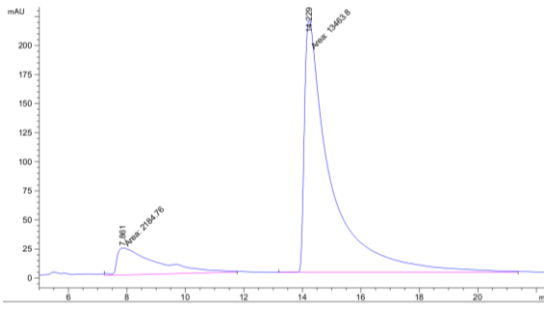


entry	ligand	base	solvent	**3a**

				yield (%)[b]	ee (%)[c]
1	L-A	Cs_2CO_3	THF	70	34
2	L-B	Cs_2CO_3	THF	35	20
3	L-C	Cs_2CO_3	THF	50	31
4	L-D	Cs_2CO_3	THF	54	32
5	L-E	Cs_2CO_3	THF	65	63
6	L-E	Cs_2CO_3	1,4-dioxane	65	54
7	L-E	Cs_2CO_3	DCM	60	46
8	L-E	Cs_2CO_3	DCE	57	38
9	L-E	Cs_2CO_3	MeCN	43	12
10	L-E	Cs_2CO_3	Et_2O	55	70
11	L-E	Cs_2CO_3	toluene	63	70
12	L-E	K_2CO_3	toluene	67	72
13	L-E	Na_2CO_3	toluene	61	64
14	L-E	K_3PO_4	toluene	51	64
15	L-E	DABCO	toluene	50	38
16	L-E	DBU	toluene	34	26
17[d]	L-E	K_2CO_3	toluene	47	69
18[e]	L-E	K_2CO_3	toluene	65	72

[a]Reaction condition: under argon atmosphere, **1b** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), $Pd_2(dba)_3$ (2.5 μmol, 2.5 mol%), other catalyst (5.0 μmol, 5.0 mol%), ligand (0.01 mmol, 10 mol%), base (0.3 mmol, 3 equiv), solvent (1.0 mL), room temperature (~25 °C), time (5 h) in a sealed Schlenk tube. [b]Isolated yield. [c]Enantiomeric excess of the product determined by HPLC analysis using a chiral stationary phase. [d] Reacted at 5 °C. [e]Reacted at 50 °C. dba = dibenzylidene acetone.





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.187	BB	0.5936	1.35676e4	315.38458	50.7539
2	14.254	BV	0.7689	1.31646e4	238.58858	49.2461

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.861	MM	1.5710	2184.75879	23.17857	13.9614
2	14.229	MM	1.0328	1.34638e4	217.27568	86.0386

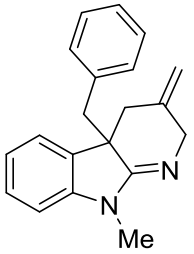
HPLC analysis: **3a** , 72% ee (Chiralpak IB column, ^{i}PrOH/hexane = 10:90, 1.0 mL/min, UV: 254 nm), t_{R1} = 7.7 min (minor), t_{R2} = 14.2 min (major).

3.3 General procedure for synthesis of 5a-5k

Under argon atmosphere, $Pd_2(dba)_3$ (2.5 mol%, 2.5 μmol, 2.28 mg), DPEPHOS (**L7**) (10% mol, 0.01 mmol, 5.4 mg), *N*-(1-methylindolin-2-ylidene)benzenesulfonamide (**4**) (0.1 mmol), di-*tert*-butyl (2-methylenepropane-1,3-diyl) dicarbonate (**2b**) (0.12 mmol, 34.6 mg) and K_2CO_3 (0.3 mmol, 41.5 mg) were added to a Schlenk tube, then 2.0 mL of toluene was added to the tube at room temperature. The mixture was stirred until the reaction completed (monitored by TLC). The resulting solution was concentrated, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to afford the target product **5**.

3.4 Characterization data of 3a-3x and 5a-5k

4*a*-Benzyl-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3a)

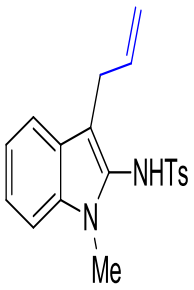


3a

Prepared according to the general procedure (reaction time: 5 h) as described above in 69% yield (19.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.05 (m, 4H), 6.89-6.81 (m, 2H), 6.73-6.71 (m, 2H), 6.45 (d, *J* =7.8 Hz, 1H), 5.16 (s, 1H), 5.09 (s, 1H), 4.56 (s, 2H), 3.02-2.96 (m, 2H), 2.90 (s, 3H), 2.86-2.82 (m, 1H), 2.50 (d, *J* =15.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 146.4, 140.3, 136.2, 132.1, 130.0, 128.3, 127.5, 126.5, 123.1, 119.5, 110.7, 106.3, 51.6, 47.9, 41.7, 37.0, 26.9; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{21}N_2^+$ $[M+H]^+$ 289.1699, found 289.1697.

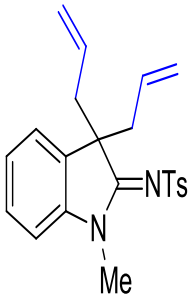
9-Methyl-4*a*-(4-methylbenzyl)-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3b)



A-5

Prepared according to the general procedure (reaction time: 5 h) as described above in 77% yield (23.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.13 (m, 1H), 6.90-6.82 (m, 4H), 6.62 (d, *J* = 7.7 Hz, 2H), 6.48 (d, *J* =7.8 Hz, 1H), 5.16 (d, *J* = 1.0 Hz, 1H), 5.08 (d, *J* = 1.0 Hz, 1H), 4.55 (s, 2H), 2.99 (d, *J* = 15.1 Hz, 1H), 2.93 (s, 3H), 2.89-2.81 (m, 2H), 2.47 (d, *J* =15.1 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 146.5, 140.4, 136.0, 133.0, 132.3, 130.0, 128.2, 123.2, 119.5, 110.6, 106.4, 51.6, 47.9, 41.2, 36.9, 27.0, 21.5; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{23}N_2^+$ $[M+H]^+$ 303.1856, found 303.1856.

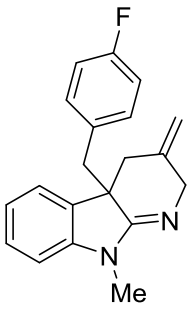
4*a*-(4-Methoxybenzyl)-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3c)



A-6

Prepared according to the general procedure (reaction time: 3 h) as described above in 80% yield (25.5 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light yellow solid. mp = 132-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.11 (m, 1H), 6.86 – 6.80 (m, 2H), 6.64 – 6.59 (m, 4H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 4.53 (s, 2H), 3.71 (s, 3H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.91 (s, 3H), 2.87 (d, *J* = 2.2 Hz, 1H), 2.78 (dd, *J* = 13.3, 2.2 Hz, 1H), 2.46 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 158.3, 146.5, 140.3, 132.3, 131.0, 128.3, 128.2, 123.1, 119.5, 112.9, 110.6, 106.4, 55.2, 51.6, 47.9, 40.8, 36.8, 27.0; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{23}N_2O^+$ $[M+H]^+$ 319.1805, found 319.1809.

4*a*-(4-Fluorobenzyl)-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3d)

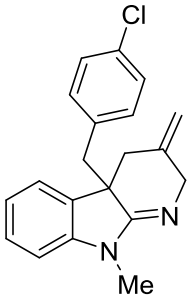


3d

Prepared according to the general procedure (reaction time: 5 h) as described above in 78% yield (24.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* =7.6 Hz 1H), 6.91-6.89 (m, 1H), 6.83 (t, *J* =7.3 Hz, 1H), 6.73 (t, *J* =8.7 Hz, 2H), 6.65-6.61 (m, 2H), 6.43 (d, *J* =7.8 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 4.53 (s, 2H), 2.98-2.93 (m, 2H), 2.88 (s, 3H), 2.77 (d, *J* =13.3 Hz, 1H), 2.49 (d, *J* =15.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 163.0, 160.5, 146.4, 140.1, 132.1 (d, *J* = 2.2 Hz), 131.9, 131.3 (d, *J* = 7.8 Hz), 128.6 (d, *J* = 12.0 Hz), 128.4, 122.9, 119.6, 114.2 (d, *J* = 21.1 Hz), 110.8, 106.4, 51.6, 47.9, 41.1, 37.1, 26.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.6; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}FN_2^+$ $[M+H]^+$ 307.1605, found 307.1606.

4*a*-(4-Chlorobenzyl)-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3e)

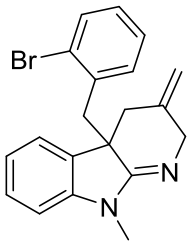


3e

Prepared according to the general procedure (reaction time: 5 h) as described above in 51% yield (16.5 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.13 (m, 1H), 7.04-7.02 (m, 2H), 6.92 (d, *J* =7.3 Hz, 1H), 6.86-6.82 (m, 1H), 6.62 (d, *J* =8.2 Hz, 2H), 6.46 (d, *J* =7.8 Hz, 1H), 5.15-5.09 (m, 2H), 4.54 (s, 2H), 2.99-2.94 (m, 2H), 2.90 (s, 3H), 2.78 (d, *J* =13.3 Hz, 1H), 2.51 (d, *J* =15.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 146.4, 140.0, 134.7, 132.4, 131.7, 131.2, 128.4, 127.6, 122.9, 119.7, 110.8, 106.5, 51.6, 47.8, 41.2, 37.1, 27.0; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}ClN_2^+$ $[M+H]^+$ 323.1310, found 323.1310.

4a-(2-bromobenzyl)-9-methyl-3-methylene-3,4,4a,9-tetrahydro-2H-pyrido[2,3-b]indole (3f)

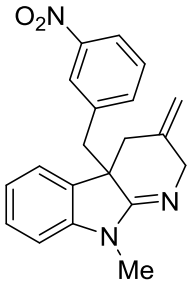


3f

Prepared according to the general procedure (reaction time: 5 h) as described above in 63% yield (23.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.03 – 7.00 (m, 1H), 6.96 – 6.92 (m, 1H), 6.87 – 6.81 (m, 2H), 6.79 – 6.74 (m, 1H), 6.45 (d, *J* = 7.7 Hz, 1H), 5.14 (s, 1H), 5.09 (s, 1H), 4.53 (s, 2H), 3.28 (dd, *J* = 13.4, 2.5 Hz, 1H), 3.04 (d, *J* = 13.4 Hz, 2H), 2.98 (s, 3H), 2.47 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 146.5, 140.3, 136.1, 132.6, 131.6, 131.4, 128.4, 128.2, 126.4, 126.0, 123.5, 119.6, 110.8, 106.3, 51.8, 47.2, 40.3, 37.5, 27.2; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}BrN_2^+$ $[M+H]^+$ 367.0804, found 367.0806.

9-Methyl-3-methylene-4*a*-(3-nitrobenzyl)-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3g)

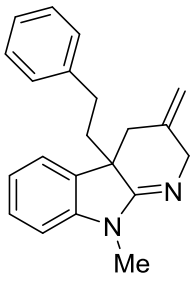


3g

Prepared according to the general procedure (reaction time: 2 h) as described above in 83% yield (27.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* =8.2 Hz, 1H), 7.51 (s, 1H), 7.24 (t, *J* =7.8 Hz, 1H), 7.16 - 7.12 (m, 1H), 7.06 (d, *J* =7.8 Hz, 1H), 6.98 (d, *J* =6.9 Hz, 1H), 6.88 (t, *J* =7.3 Hz, 1H), 6.41 (d, *J* =7.8 Hz, 1H), 5.19 (s, 1H), 5.13 (s, 1H), 4.57 (s, 2H), 3.12 (d, *J* =13.3 Hz, 1H), 2.97 (d, *J* =15.1 Hz, 1H), 2.88 (d, *J* =13.3 Hz, 1H), 2.86 (s, 3H), 2.56 (d, *J* =14.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 147.4, 146.2, 139.7, 138.2, 136.1, 131.0, 128.9, 128.2, 124.6, 122.8, 121.7, 120.0, 111.2, 106.6, 51.7, 47.7, 41.8, 37.3, 26.9; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}N_3O_2^+$ $[M+H]^+$ 334.1550, found 334.1449.

9-Methyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3h)

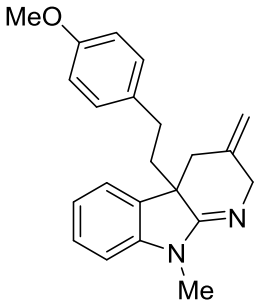


3h

Prepared according to the general procedure (reaction time: 5 h) as described above in 76% yield (23.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.10 (m, 5H), 6.99 (d, *J* =7.3 Hz, 2H), 6.92 (t, *J* =7.3 Hz, 1H), 6.72 (d, *J* =7.8 Hz, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 4.46-4.35 (m, 2H), 3.16 (s, 3H), 2.92 (d, *J* =14.8 Hz, 1H), 2.45 (d, *J* =14.8 Hz, 1H), 2.37 (td, *J* = 12.8, 4.9 Hz, 1H), 2.24 (td, *J* =12.4 Hz, 4.1 Hz, 1H), 2.11 (td, *J* =12.4 Hz, 5.0 Hz, 1H), 1.89-1.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 146.9, 141.6, 140.1, 133.0, 128.4, 128.3, 126.0, 122.3, 120.2, 110.2, 106.7, 51.6, 46.7, 38.3, 38.0, 30.3, 27.4; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}N_2^+$ $[M+H]^+$ 303.1856, found 303.1856.

4*a*-(4-Methoxyphenethyl)-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3i)



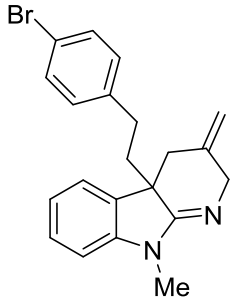
3i

Prepared according to the general procedure (reaction time: 5 h) as described above in 66% yield (22.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* =7.6 Hz, 1H), 7.16 (d, *J* =6.9 Hz, 1H), 6.94 -6.90(m, 3H), 6.75-6.72 (m, 3H), 5.03 (s, 1H), 4.99 (s, 1H), 4.45-4.36 (m, 2H), 3.75 (s, 3H), 3.17 (s, 3H), 2.92 (d, *J* =15.2 Hz, 1H), 2.44 (d, *J* =15.2 Hz, 1H), 2.31 (td, *J* =13.1 Hz, 5.5 Hz, 1H), 2.19 (td, *J* =12.4 Hz, 4.1 Hz, 1H), 2.09 (td, *J* =13.1 Hz, 4.8 Hz, 1H), 1.82 (td, *J* =13.1 Hz, 4.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 157.9, 146.8, 140.1, 133.7, 133.1, 129.2, 128.3, 122.3, 120.2, 113.8, 110.2,

106.7, 55.3, 51.5, 46.7, 38.5, 38.0, 29.4, 27.4; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{23}N_2^+$ $[M+H]^+$ 333.1961, found 333.1961.

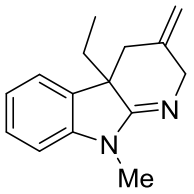
4*a*-(4-Bromophenethyl)-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3j)



3j

Prepared according to the general procedure (reaction time: 5 h) as described above in 61% yield (23.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford an orange oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 4.39 (m, 2H), 3.15 (s, 3H), 2.90 (d, *J* = 14.8 Hz, 1H), 2.44 (d, *J* = 14.8 Hz, 1H), 2.31 (td, *J* = 12.8, 5.1 Hz, 1H), 2.18 (td, *J* = 12.8, 4.4 Hz, 1H), 2.08 (td, *J* = 12.8, 5.1 Hz, 1H), 1.80 (td, *J* = 12.8, 4.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 146.8, 140.5, 139.9, 132.8, 131.4, 130.1, 128.4, 122.2, 120.3, 119.7, 110.3, 106.8, 51.5, 46.6, 38.1, 38.0, 29.8, 27.4; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{22}BrN_2^+$ $[M+H]^+$ 381.0961, found 381.0962.

4*a*-Ethyl-9-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3k)

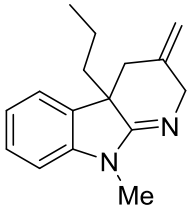


3k

Prepared according to the general procedure (reaction time: 5 h) as described above in 64% yield (15.5 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light yellow solid. mp = 92-94 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 5.01 (s, 1H), 4.96 (s, 1H), 4.41-4.31 (m, 2H), 3.15 (s, 3H), 2.88 (d, *J* =15.1 Hz, 1H), 2.40 (d, *J* =14.7 Hz, 1H), 1.84-1.78 (m, 1H), 1.64-1.58 (m, 1H), 0.64 (t, *J* =6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 146.8, 140.4, 133.2, 128.1,

122.3, 120.0, 110.0, 106.5, 51.5, 47.1, 37.3, 29.1, 27.3, 8.2; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{19}N_2^+$ $[M+H]^+$ 227.1543, found 227.1544.

9-Methyl-3-methylene-4*a*-propyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3l)

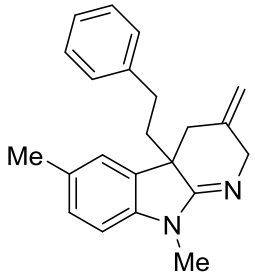


3l

Prepared according to the general procedure (reaction time: 5 h) as described above in 58% yield (13.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.17 (m, 1H), 7.07 (d, *J* =7.3 Hz, 1H), 6.89-6.84 (m, 1H), 6.67 (d, *J* =7.7 Hz, 1H), 5.01 (s, 1H), 4.96 (s, 1H), 4.42-4.30 (m, 2H), 3.14 (s, 3H), 2.86 (d, *J* =15.1 Hz, 1H), 2.38 (d, *J* =14.7 Hz, 1H), 1.78-1.71 (m, 1H), 1.56-1.48 (m, 1H), 1.14-1.04 (m, 1H), 0.99-0.90 (m, 1H), 0.76-0.71 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 146.7, 140.3, 133.6, 128.0, 122.3, 120.0, 110.0, 106.5, 51.5, 46.8, 38.5, 37.8, 27.4, 17.1, 14.2; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{21}N_2^+$ $[M+H]^+$ 241.1699, found 241.1699.

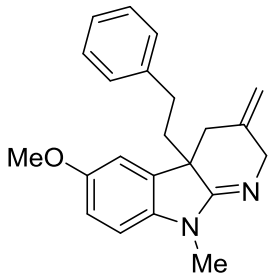
6,9-Dimethyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3m)



3m

Prepared according to the general procedure (reaction time: 5 h) as described above in 67% yield (20.9 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light yellow solid. mp = 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.10 (m, 3H), 7.05-6.97 (m, 4H), 6.63 (dd, *J* =7.8 Hz, 3.2 Hz, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 4.45-4.33 (m, 2H), 3.14 (s, 3H), 2.91 (d, *J* =14.7 Hz, 1H), 2.43 (d, *J* =15.6 Hz, 1H), 2.39-2.36 (m, 1H), 2.34 (s, 3H), 2.27-2.21 (m, 1H), 2.16-2.08 (m, 1H), 1.87-1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 144.6, 141.7, 140.2, 133.1, 129.6, 128.5, 128.4, 128.3, 126.0, 123.2, 110.2, 106.5, 51.5, 46.8, 38.1, 30.3, 27.5, 21.2; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{25}N_2^+$ $[M+H]^+$ 317.2012, found 317.2012.

6-Methoxy-9-methyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3n)

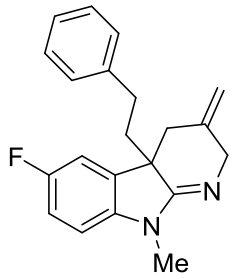


3n

Prepared according to the general procedure (reaction time: 5 h) as described above in 63% yield (21.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* =7.3 Hz, 2H), 7.13-7.10 (m, 1H), 6,99 (d, *J* =6.9 Hz, 2H), 6.79-6.76 (m, 2H), 6.62 (d, *J* =7.8 Hz, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 4.44-4.32 (m, 2H), 3.83 (s, 3H), 3.14 (s, 3H), 2.88 (d, *J* =14.7 Hz, 1H), 2.44 (d, *J* =14.7 Hz, 1H), 2.35 (td, *J* = 12.6, 4.6 Hz, 1H), 2.22 (td, *J* = 12.8, 4.0 Hz, 1H), 2.12 (td, *J* = 12.6, 4.8 Hz, 1H), 1.83 (td, *J* = 12.8, 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 168.9, 154.6, 141.5, 140.6, 139.9, 134.3, 128.4, 128.3, 126.0, 112.1, 110.4, 110.4, 106.8, 56.1, 51.3, 47.2, 38.2, 38.0, 30.3, 27.7; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{25}N_2O^+$ $[M+H]^+$ 333.1961, found 333.1966.

6-Fluoro-9-methyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3o)



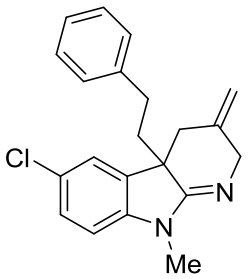
3o

Prepared according to the general procedure (reaction time: 5 h) as described above in 75% yield (24.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.4 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 2H), 6.97-6.90 (m, 2H), 6.62 (dd, *J* = 8.4, 4.1 Hz, 1H), 5.05 (s, 1H), 5.00 (s, 1H), 4.46 – 4.34 (m, 2H), 3.15 (s, 3H), 2.88 (d, *J* = 14.8 Hz, 1H), 2.45 (d, *J* = 14.8 Hz, 1H), 2.37 (td, *J* = 12.6, 4.9 Hz, 1H), 2.24 (td, *J* = 12.6, 4.2 Hz, 1H), 2.13 (td, *J* = 12.6, 4.9 Hz,

1H), 1.83 (td, *J* = 12.8, 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 168.6, 159.2, 156.8, 142.9, 141.3, 139.6, 134.4 (J_{FC} =7.7 Hz), 128.4 (J_{FC} =11.5 Hz), 126.1, 114.3 (J_{FC} = 23.0 Hz), 110.6, 110.5, 110.4, 106.8 (J_{FC} =7.7 Hz), 51.5, 47.0, 38.2, 37.9, 30.3, 27.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.4; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{22}FN_2^+$ $[M+H]^+$ 321.1762, found 321.1760.

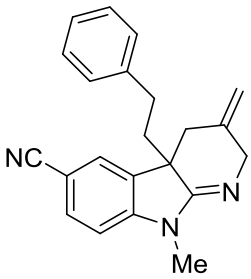
6-Chloro-9-methyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3p)



3p

Prepared according to the general procedure (reaction time: 5 h) as described above in 65% yield (21.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light yellow solid. mp = 156 - 158 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.19 (m, 3H), 7.14-7.12 (m, 1H), 7.11 (d, *J* =8.4 Hz, 1H), 7.00 (d, *J* =6.7 Hz, 2H), 6.62 (d, *J* =8.3 Hz, 1H), 5.04 (s, 1H), 4.99 (s, 1H), 4.44-4.33 (m, 2H), 3.13 (s, 3H), 2.88 (d, *J* =14.5 Hz, 1H), 2.43 (d, *J* =14.5 Hz, 1H), 2.35 (td, *J* =12.4 Hz, 5.5 Hz, 1H), 2.25 (td, *J* =12.4 Hz, 4.8 Hz, 1H), 2.11 (td, *J* =12.4 Hz, 5.5 Hz, 1H), 1.83 (td, *J* =12.4 Hz, 4.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 145.5, 141.2, 139.5, 134.7, 128.4, 128.3, 128.2, 126.1, 125.3, 122.8, 110.6, 107.5, 51.5, 46.8, 38.2, 38.0, 30.3, 27.5; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{22}ClN_2^+$ $[M+H]^+$ 337.1466, found 337.1466.

9-Methyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole-6-carbonitrile (3q)

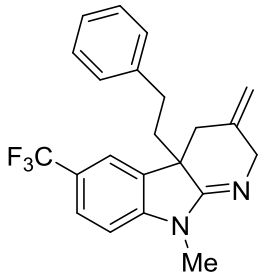


3q

Prepared according to the general procedure (reaction time: 2 h) as described above in 67% yield (21.9 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow solid. mp =

156 - 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.35 (d, *J* = 1.5 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.13 (t, J = 7.3 Hz, *1*H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 5.06 (s, 1H), 5.03 (s, 1H), 4.47–4.33 (m, 2H), 3.16 (s, 3H), 2.91 (d, *J* = 14.8 Hz, 1H), 2.42 (d, *J* = 14.8 Hz, 1H), 2.35–2.21 (m, 2H), 2.14–2.06 (m, 1H), 1.88–1.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 150.5, 140.7, 138.7, 134.0, 133.9, 128.5, 128.2, 126.3, 125.5, 120.0, 111.2, 106.9, 102.6, 51.6, 46.3, 38.1, 37.7, 30.2, 27.4; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{22}N_3^+$ $[M+H]^+$ 328.1808, found 328.1810.

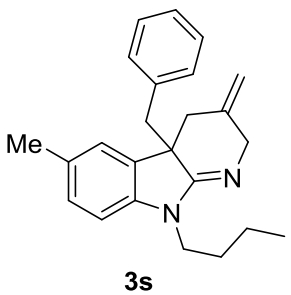
9-Methyl-3-methylene-4*a*-phenethyl-6-(trifluoromethyl)-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3r)



3r

Prepared according to the general procedure (reaction time: 2.5 h) as described above in 54% yield (20.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 1H), 7.35 (s, 1H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.14 – 7.11 (m, 1H), 6.97 (d, *J* = 7.1 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.06 (s, 1H), 5.02 (s, 1H), 4.48 – 4.34 (m, 2H), 3.17 (s, 3H), 2.94 (d, *J* = 14.8 Hz, 1H), 2.45 (d, *J* = 14.8 Hz, 1H), 2.38 – 2.24 (m, 2H), 2.17 – 2.09 (m, 1H), 1.91 – 1.83 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 149.6, 141.0, 139.1, 133.4, 128.4 (d, *J* = 17.8 Hz), 126.3 (d, *J* = 3.7 Hz), 126.2, 123.5, 122.2 (q, J_{FC} =32.6 Hz), 120.8, 119.2 (d, *J* = 3.1 Hz), 110.9, 106.2, 51.5, 46.5, 38.1, 37.8, 30.2, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9; HRMS (ESI): m/z calcd for $C_{22}H_{22}F_3N_2^+$ $[M+H]^+$ 371.1730, found 371.1730.

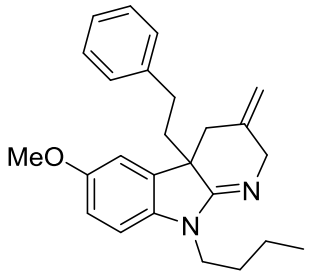
4*a*-Benzyl-9-butyl-6-methyl-3-methylene-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3s)



3s

Prepared according to the general procedure (reaction time: 5 h) as described above in 76% yield (26.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a white solid. Mp = 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.02 (m, 3H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.81 (s, 1H), 6.67 (d, *J* = 6.9 Hz, 2H), 6.33 (d, *J* = 7.9 Hz, 1H), 5.13 (s, 1H), 5.06 (s, 1H), 4.61 – 4.48 (m, 2H), 3.60 (dt, *J* = 14.1, 7.0 Hz, 1H), 3.14 – 3.06 (m, 2H), 2.99 – 2.79 (m, 2H), 2.47 (d, *J* = 15.1 Hz, 1H), 2.30 (s, 3H), 1.23 – 1.15 (m, 2H), 1.12 – 0.98 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 144.1, 140.3, 136.3, 132.4, 129.9, 128.7, 128.3, 127.5, 126.5, 123.8, 110.4, 106.3, 51.6, 48.0, 41.7, 40.6, 37.7, 29.5, 21.1, 20.4, 14.1; HRMS (ESI): m/z calcd for $C_{24}H_{29}N_2^+$ $[M+H]^+$ 345.2325, found 345.2323.

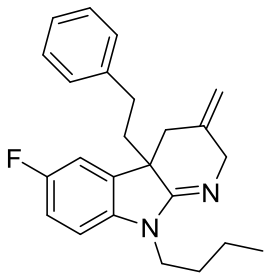
9-Butyl-6-methoxy-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3t)



3t

Prepared according to the general procedure (reaction time: 3 h) as described above in 75% yield (28.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 4.43 – 4.36 (m, 2H), 3.86 – 3.82 (m, 1H), 3.80 (s, 3H), 3.47 – 3.42 (m, 1H), 2.89 (d, *J* = 15.0 Hz, 1H), 2.45 (d, *J* = 15.0 Hz, 1H), 2.38 (td, *J* = 12.9, 4.5 Hz, 1H), 2.22 (td, *J* = 12.9, 4.1 Hz, 1H), 2.13 (td, *J* = 13.0, 4.6 Hz, 1H), 1.82 (td, *J* = 13.0, 4.1 Hz, 1H), 1.71 – 1.59 (m, 2H), 1.44 – 1.38 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H; ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 154.3, 141.7, 140.3, 140.2, 134.4, 128.4, 128.3, 126.0, 112.0, 110.4, 110.1 , 106.8, 56.1, 51.5, 47.0, 41.0, 38.4, 38.1, 30.3, 29.6, 20.5, 14.1; HRMS (ESI): m/z calcd for $C_{25}H_{31}N_2O^+$ $[M+H]^+$ 375.2431, found 375.2432.

9-Butyl-6-fluoro-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3u)

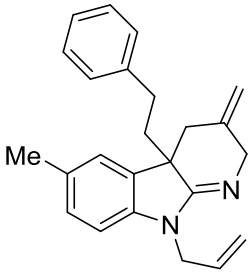


3u

Prepared according to the general procedure (reaction time: 5 h) as described above in 83% yield (30.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light-yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.94 – 6.89 (m, 2H), 6.61 (dd, *J* = 8.4, 4.0 Hz, 1H), 5.04 (s, 1H), 4.99 (s, 1H), 4.44 – 4.36 (m, 2H), 3.86 – 3.80 (m, 1H), 3.47 – 3.42 (m, 1H), 2.88 (d, *J* = 15.0 Hz, 1H), 2.45 (d, *J* = 15.0 Hz, 1H), 2.38 (td, *J* = 12.9, 4.6 Hz, 1H), 2.21 (td, *J* = 12.9, 4.1 Hz, 1H), 2.13 (td, *J* = 13.0, 4.6 Hz, 1H), 1.81 (td, *J* = 13.0, 4.2 Hz, 1H), 1.69 – 1.60 (m, 2H), 1.44 – 1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 158.6, 157.0, 142.5, 141.4, 139.7, 134.5 (d, J_{FC} = 7.3 Hz), 128.4 (d, J_{FC} = 22.5 Hz), 126.1, 114.2 (d, J_{FC} = 23.2 Hz), 110.6, 110.4 (d, J_{FC} = 3.6 Hz), 106.8 (d, J_{FC} = 8.0 Hz), 51.6, 47.0, 41.0, 38.4, 38.0, 30.3, 29.5, 20.5, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1; HRMS (ESI): m/z calcd for $C_{24}H_{28}FN_2^+$ $[M+H]^+$ 363.2231, found 363.2236.

9-Allyl-6-methyl-3-methylene-4*a*-phenethyl-3,4,4a,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3v)



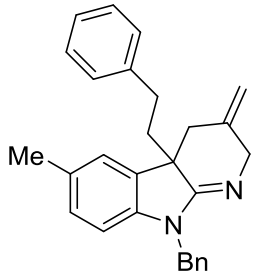
3v

Prepared according to the general procedure (reaction time: 5 h) as described above in 47% yield (16.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 3H), 6.98 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.89 – 5.83 (m, 1H), 5.21 – 5.14 (m, 2H), 5.03 (s, 1H), 4.98 (s, 1H), 4.50 (dd, *J* = 16.8, 4.7 Hz, 1H), 4.43 – 4.36 (m, 2H), 4.09 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.92 (d, *J* = 15.0 Hz, 1H), 2.46 – 2.39 (m, 2H), 2.33 (s, 3H), 2.27 (td, *J* = 13.0, 4.3 Hz, 1H), 2.14 (td, *J* = 13.0, 4.9 Hz, 1H), 1.85 (td, *J* = 13.1, 4.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ

168.1, 143.8, 141.7, 140.2, 133.0, 132.6, 129.6, 128.4, 128.4, 128.3, 126.0, 123.2, 116.4, 110.1, 107.3, 51.6, 46.8, 43.4, 38.3, 38.3, 30.4, 21.1; HRMS (ESI): m/z calcd for $C_{24}H_{27}N_2^+$ $[M+H]^+$ 343.2169, found 343.2168.

9-Benzyl-6-methyl-3-methylene-4*a*-phenethyl-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3w)

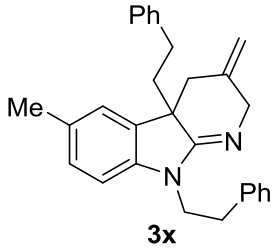


3w

Prepared according to the general procedure (reaction time: 5 h) as described above in 66% yield (26.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.25 – 7.22 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.05 – 7.02 (m, 3H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 5.19 (d, *J* = 16.2 Hz, 1H), 5.07 (s, 1H), 5.03 (s, 1H), 4.65 (d, *J* = 16.2 Hz, 1H), 4.50 – 4.40 (m, 2H), 2.98 (d, *J* = 15.0 Hz, 1H), 2.54 – 2.45 (m, 2H), 2.37 – 2.30 (m, 4H), 2.19 (td, *J* = 13.0, 4.8 Hz, 1H), 1.92 (td, *J* = 13.0, 4.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 143.9, 141.8, 140.3, 137.5, 133.0, 129.8, 128.7, 128.5, 128.5, 128.4, 127.1, 127.1, 126.0, 123.3, 110.2, 107.5, 51.6, 46.9, 44.8, 38.3, 30.5, 21.2; HRMS (ESI): m/z calcd for $C_{28}H_{29}N_2^+$ $[M+H]^+$ 393.2325, found 393.2326.

6-Methyl-3-methylene-4a-phenethyl-9-(3-phenylpropyl)-3,4,4*a*,9-tetrahydro-2*H*-pyrido[2,3-*b*]indole (3x)



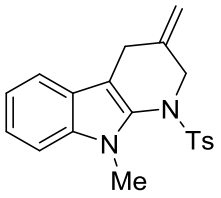
3x

Prepared according to the general procedure (reaction time: 5 h) as described above in 69% yield (28.9 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=1:1) to afford a light-yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.18 (m, 5H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 3H), 6.99 (s, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 5.05 (s, 1H), 5.00 (s, 1H),

4.46 – 4.39 (m, 2H), 3.92 – 3.87 (m, 1H), 3.56 – 3.52 (m, 1H), 2.92 (d, *J* = 15.0 Hz, 1H), 2.73 (t, *J* = 7.9 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.35 (s, 3H), 2.27 (td, *J* = 13.0, 4.2 Hz, 1H), 2.15 (td, *J* = 13.0, 4.8 Hz, 1H), 2.09 – 1.97 (m, 2H), 1.85 (td, *J* = 13.1, 4.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 144.0, 141.8, 141.7, 140.3, 133.1, 129.4, 128.5, 128.4, 128.4, 128.4, 126.0, 126.0, 123.3, 110.1, 106.6, 51.6, 46.7, 40.7, 38.3, 38.2, 33.5, 30.4, 29.0, 21.1; HRMS (ESI): m/z calcd for $C_{30}H_{33}N_2^+$ $[M+H]^+$ 421.2638, found 421.2638.

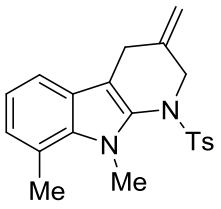
9-Methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5a)



5a

Prepared according to the general procedure (reaction time: 8 h) as described above in 94% yield (33.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. mp = 121 – 123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.24 – 7.22 (m, 2H), 7.21 – 7.16 (m, 1H), 7.07 – 7.00 (m, 3H), 4.68 (d, *J* = 1.7 Hz, 1H), 4.60 (d, *J* = 1.7 Hz, 1H), 4.16 (s, 2H), 3.79 (s, 3H), 2.96 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 137.2, 136.4, 134.2, 133.3, 129.1, 129.0, 125.0, 122.3, 119.6, 118.1, 114.3, 110.0, 104.2, 55.2, 31.2, 25.7, 21.7; HRMS (ESI) calcd for $C_{20}H_{21}N_2O_2S^+$ $[M+H]^+$ 353.1318, found 353.1320.

9-Methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5b)

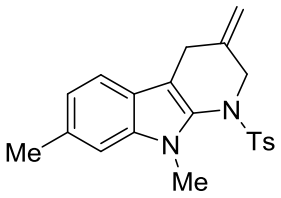


5b

Prepared according to the general procedure (reaction time: 8 h) as described above in 82% yield (30.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light-yellow solid. mp = 192 – 194 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.01 – 7.00 (m, 2H), 4.76 (s, 1H), 4.68 (s, 1H), 4.04 (s, 3H), 2.82 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 137.3, 135.9, 134.3, 133.9, 129.1,

129.0, 126.0, 125.2, 122.1, 119.8, 116.0, 114.3, 104.3, 55.2, 34.2, 25.7, 21.7, 19.9; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_2S^+$ $[M+H]^+$ 367.1475, found 367.1474.

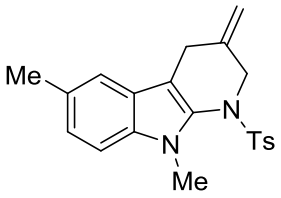
7,9-Dimethyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5c)



5c

Prepared according to the general procedure (reaction time: 8 h) as described above in 90% yield (33.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. mp = 186 – 188 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.18 (s, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 4.76 (s, 1H), 4.66 (s, 1H), 4.23 (s, 2H), 3.83 (s, 3H), 3.01 (s, 2H), 2.53 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 137.4, 136.8, 134.2, 132.7, 132.3, 129.0, 122.8, 121.2, 117.9, 114.2, 111.0, 104.1, 55.2, 31.0, 25.8, 22.1, 21.7; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_2S^+$ $[M+H]^+$ 367.1475, found 367.1475.

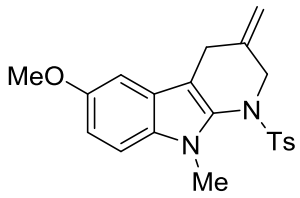
6,9-Dimethyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5d)



5d

Prepared according to the general procedure (reaction time: 6 h) as described above in 97% yield (30.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. mp = 179 – 181 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.18 (s, 1H), 7.12 – 7.07 (m, 3H), 4.76 (d, *J* = 0.7 Hz, 1H), 4.67 (d, *J* = 0.7 Hz, 1H), 4.23 (s, 2H), 3.84 (s, 3H), 3.01 (s, 2H), 2.46 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 137.3, 134.8, 134.3, 133.3, 129.1, 129.0, 128.9, 125.2, 123.9, 117.9, 114.2, 109.7, 103.7, 55.2, 31.1, 25.8, 21.7, 21.6; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_2S^+$ $[M+H]^+$ 367.1475, found 367.1476.

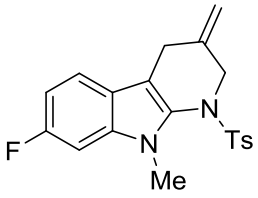
6-Methoxy-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5e)



5e

Prepared according to the general procedure (reaction time: 8 h) as described above in 87% yield (33.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. mp = 207 – 209 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.93 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 4.76 (d, *J* = 0.9 Hz, 1H), 4.67 (d, *J* = 0.7 Hz, 1H), 4.23 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.00 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 144.2, 137.2, 134.3, 133.7, 131.7, 129.1, 129.0, 125.3, 114.3, 112.0, 110.8, 103.8, 100.5, 56.0, 55.2, 31.2, 25.8, 21.7; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3S^+$ $[M+H]^+$ 383.1424, found 383.1424.

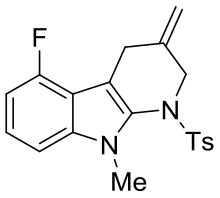
7-Fluoro-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5f)



5f

Prepared according to the general procedure (reaction time: 8 h) as described above in 86% yield (33.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.26 (dd, *J* = 9.0, 3.7 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.04 (dd, *J* = 9.8, 2.3 Hz, 1H), 6.89 – 6.84 (m, 1H), 4.76 (d, *J* = 0.7 Hz, 1H), 4.67 (d, *J* = 0.7 Hz, 1H), 4.21 (s, 2H), 3.81 (s, 3H), 3.00 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 136.9, 136.5 (d, *J* = 12.4 Hz), 134.0, 129.1, 129.0, 127.2, 126.0 , 121.5, 118.9 (d, *J* = 9.9 Hz), 114.5, 108.1 (d, *J* = 24.5 Hz), 104.4, 96.6 (d, *J* = 26.3 Hz), 55.1, 31.3, 25.7, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.4; HRMS (ESI) calcd for $C_{20}H_{20}FN_2O_2S^+$ $[M+H]^+$ 371.1224, found 371.1224.

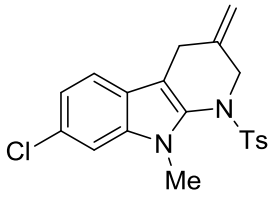
5-Fluoro-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5g)



5g

Prepared according to the general procedure (reaction time: 8 h) as described above in 80% yield (29.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford an orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.08 – 7.04 (m, 4H), 6.71 – 6.66 (m, 1H), 4.67 (d, *J* = 0.8 Hz, 1H), 4.59 (d, *J* = 0.8 Hz, 1H), 4.16 (s, 2H), 3.78 (s, 3H), 3.14 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 155.8, 144.5, 138.8 (d, *J* = 11.6 Hz), 136.9, 134.1, 133.0, 129.2, 129.0, 122.6 (d, *J* = 7.7 Hz), 114.4, 106.0 (d, *J* = 3.5 Hz), 104.8 (d, *J* = 18.9 Hz), 102.7 (d, *J* = 1.4 Hz), 55.0, 31.6, 27.1, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.2; HRMS (ESI) calcd for $C_{20}H_{20}FN_2O_2S^+$ $[M+H]^+$ 371.1224, found 371.1224.

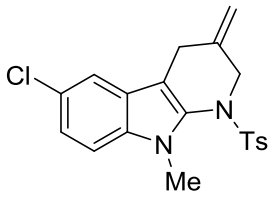
7-Chloro-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5h)



5h

Prepared according to the general procedure (reaction time: 8 h) as described above in 90% yield (34.7 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light-yellow oli; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 1.7 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.10 – 7.06 (m, 3H), 4.77 (s, 1H), 4.68 (s, 1H), 4.22 (s, 2H), 3.82 (s, 3H), 2.99 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 136.7, 134.0, 133.8, 129.1, 129.0, 128.3, 123.5, 120.2, 119.0, 114.5, 110.0, 104.4, 55.1, 31.3, 25.6, 21.7; HRMS (ESI) calcd for $C_{20}H_{20}ClN_2O_2S^+$ $[M+H]^+$ 387.0929, found 387.0930.

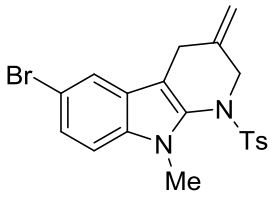
6-Chloro-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5i)



5i

Prepared according to the general procedure (reaction time: 8 h) as described above in 95% yield (36.8 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a light-yellow solid. mp = 181 – 183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 1.8 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.21 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.77 (d, *J* = 0.8 Hz, 1H), 4.68 (d, *J* = 0.8 Hz, 1H), 4.23 (s, 2H), 3.84 (s, 3H), 2.97 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 136.7, 134.7, 134.4, 134.0, 129.1, 128.9, 125.9, 125.4, 122.5, 117.7, 114.6, 111.0, 103.9, 55.1, 31.3, 25.5, 21.7; HRMS (ESI) calcd for $C_{20}H_{20}ClN_2O_2S^+$ $[M+H]^+$ 387.0929, found 387.0923.

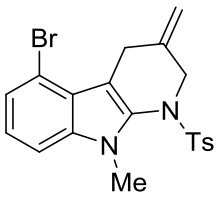
6-Bromo-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-b]indole (5j)



5j

Prepared according to the general procedure (reaction time: 8 h) as described above in 89% yield (38.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. mp = 213 – 215 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.8 Hz, 1H), 7.28 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 4.70 (s, 1H), 4.61 (s, 1H), 4.16 (s, 2H), 3.77 (s, 3H), 2.90 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 136.6, 135.0, 134.3, 134.0, 129.2, 128.9, 126.6, 125.1, 120.8, 114.7, 112.9, 111.5, 103.8, 55.1, 31.3, 25.5, 21.7; HRMS (ESI) calcd for $C_{20}H_{20}BrN_2O_2S^+$ $[M+H]^+$ 431.0423, found 431.0424.

5-Bromo-9-methyl-3-methylene-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (5k)

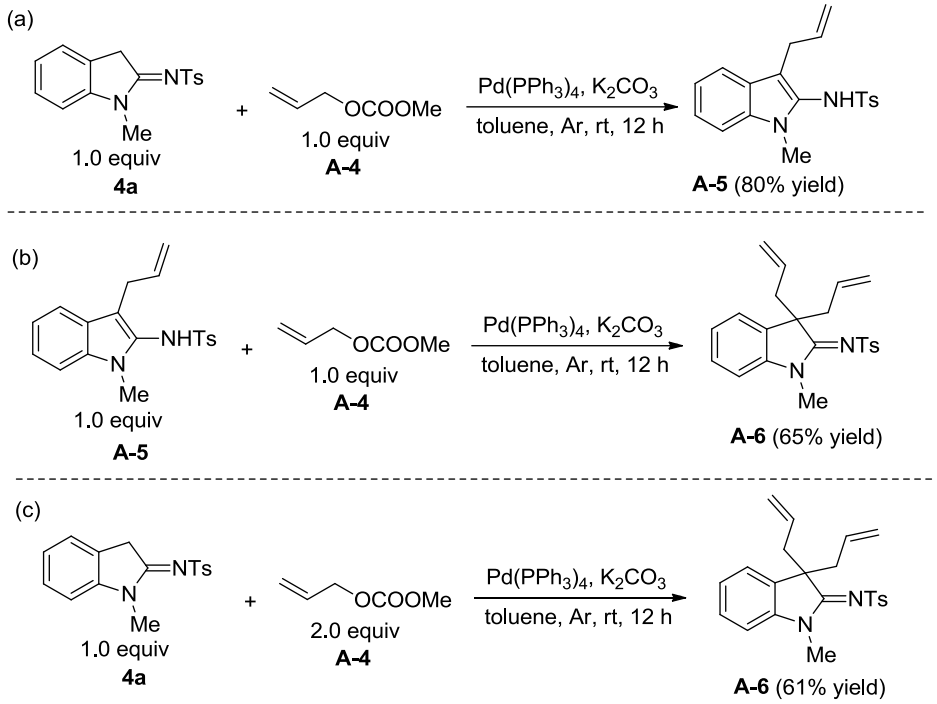


5k

Prepared according to the general procedure (reaction time: 8 h) as described above in 71% yield (30.4 mg). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow solid. mp = 187 – 189 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 6.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.9 Hz, 1H), 4.69 (d, *J* = 0.9 Hz, 1H), 4.66 (d, *J* = 0.9 Hz, 1H), 4.20 (s, 2H), 3.84 (s, 3H), 3.45 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.3, 136.7, 134.2, 134.1, 129.2, 129.0, 124.0, 123.6, 123.0, 114.4, 113.9, 109.2,

104.9, 54.7, 31.6, 27.9, 21.7; HRMS (ESI) calcd for $C_{20}H_{20}BrN_2O_2S^+$ $[M+H]^+$ 431.0423, found 431.0419.

4. Investigations on mechanism for synthesis of 5



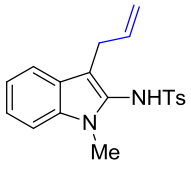
Procedure I: 4a (30.0 mg, 0.1 mmol), $Pd(PPh_3)_4$ (8.6 mg, 5.0 mol%), K_2CO_3 (13.8 mg, 0.1 mmol) were added to a Schlenk tube. Then dry toluene (1 mL) and allyl methyl carbonate **A-4** (11.6 mg, 0.1 mmol) were added to the tube under argon atmosphere. The resulting mixture was stirred at room temperature for 12 h. Upon completion (as determined by TLC), the mixture was diluted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (PE:EA, 5:1) to give product **A-5** in 80% yield (27.2 mg).

Procedure II: A-5 (34.0 mg, 0.1 mmol), $Pd(PPh_3)_4$ (8.6 mg, 5.0 mol%), K_2CO_3 (13.8 mg, 0.1 mmol) were added to a Schlenk tube. Then dry toluene (1 mL) and allyl methyl carbonate **A-4** (11.6 mg, 0.1 mmol) were added to the tube under argon atmosphere. The resulting mixture was stirred at room temperature for 12 h. Upon completion (as determined by TLC), the mixture was diluted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (PE:EA, 10:1) to give product **A-6** in 65% yield (24.7 mg).

Procedure III: 4a (30.0 mg, 0.1 mmol), $Pd(PPh_3)_4$ (8.6 mg, 5.0 mol%), K_2CO_3 (27.6 mg, 0.2

mmol) were added to a Schlenk tube. Then dry toluene (2 mL) and allyl methyl carbonate **A-4** (23.2 mg, 0.2 mmol) were added to the tube under argon atmosphere. The resulting mixture was stirred at room temperature for 12 h. Upon completion (as determined by TLC), the mixture was diluted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (PE:EA, 10:1) to give product **A-6** in 61% yield (23.1 mg).

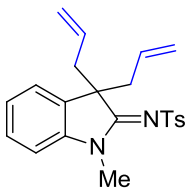
***N*-(3-Allyl-1-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide (A-5)**



A-5

It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a yellow oil. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). Yield: 80% (27.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.42 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.35-7.28 (m, 3H), 7.17 (td, *J* = 7.6, 0.7 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.02 (s, 1H), 5.36-5.26 (m, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 4.95 (dd, *J* = 10.1, 1.7 Hz, 1H), 3.34 (dd, *J* = 13.2, 8.3 Hz, 1H), 3.19 (s, 3H), 3.06 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 143.0, 142.3, 139.7, 131.3, 129.9, 129.8, 129.4, 126.5, 124.6, 123.8, 120.8, 109.2, 81.5, 44.3, 28.4, 21.6; **HRMS (ESI)**: *m/z* calcd for $C_{19}H_{21}N_2O_2S^+$ $[M+H]^+$ 341.1318, found 341.1320.

(*Z*)-*N*-(3,3-Diallyl-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (A-6)



A-6

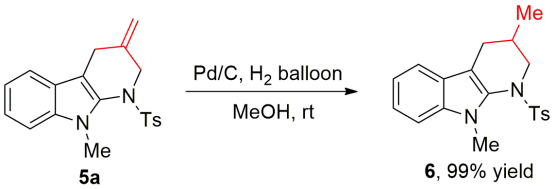
It was purified by flash chromatography (V_{PE}:V_{EA}=10:1) to afford a colorless oil. R_f = 0.6 (petroleum ether/ethyl acetate = 10:1). Yield: 65% (24.7 mg) via **Procedure II**; 61% (23.1 mg) via **Procedure III**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.28-7.22 (m, 4H), 7.14 (td, *J* = 7.5, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.32-5.22 (m, 1H), 5.00-4.95 (m, 2H), 4.84-4.80 (m, 2H), 3.45 (dd, *J* = 13.6, 7.6 Hz, 2H), 3.32 (s, 3H), 2.66 (dd, *J* = 13.6, 7.0 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 143.3, 142.1, 141.5, 133.5, 131.9, 129.2, 128.2, 126.4,

123.9, 122.8, 119.3, 109.0, 57.7, 41.1, 29.6, 21.6; **HRMS (ESI)**: *m/z* calcd for $C_{22}H_{25}N_2O_2S^+$ $[M+H]^+$ 381.1631, found 381.1632.

5. Scaled-up synthesis of the product 5a

Under argon atmosphere, to a mixture of *N*-(1-methylindolin-2-ylidene)benzenesulfonamide **4a** (300.0 mg, 1.0 mmol), di-*tert*-butyl (2-methylenepropane-1,3-diyl) dicarbonate (**2b**) (346.0 mg, 1.2 mmol) , K_2CO_3 (415 mg, 3.0 mmol) and $Pd_2(dba)_3$ (0.025 mmol) /DPEPHOS (**L7**) (0.05 mmol) in a Schlenk tube, 10 mL of toluene was added at room temperature. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and was then concentrated to dryness. The residue was purified through flash column chromatography (petroleum ether/ethyl acetate 5:1) to afford the corresponding cycloadduct **5a** in 90% yield (317 mg) .

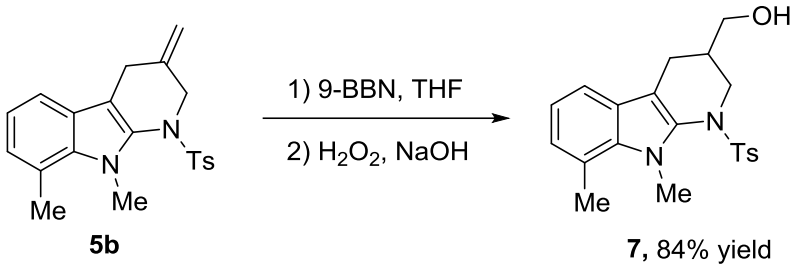
6. Transformations of the product 5.



5a (35.2 mg, 0.10 mmol) and palladium 10% on carbon (20.0 mg) were placed in a 10 mL Schlenk tube. The tube was evacuated and refilled with hydrogen through a hydrogen balloon. After addition of 2.0 mL of MeOH, The resulting mixture was stirred until **5a** was completely consumed in 24 h (monitored by TLC) and was then filtered through Celite and concentrated to dryness. The crude product was purified directly by column chromatography on silica gel with PE/EtOAc mixture as the eluent and **6** was obtained as a colorless oil (35.1 mg, 99% yield).

3,9-Dimethyl-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indole (6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.39 (dd, *J* = 17.4, 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.11 (m, 1H), 4.01 (dd, *J* = 14.1, 4.0 Hz, 1H), 3.84 (s, 3H), 2.95 (dd, *J* = 14.1, 12.3 Hz, 1H), 2.54 (dd, *J* = 16.3, 6.8 Hz, 1H), 2.41 (s, 3H), 2.07 (dd, *J* = 16.3, 10.2 Hz, 1H), 1.32 – 1.27 (m, 1H), 0.83 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 136.9, 135.4, 133.1, 129.8, 128.1, 125.8, 122.1, 119.5, 118.0, 110.0, 104.0, 55.2, 32.3, 27.4, 24.4, 21.8, 19.1; HRMS (ESI) calcd for $C_{20}H_{23}N_2O_2S^+$ $[M+H]^+$ 355.1475, found 355.1476.



To 3 mL of 9-borabicyclo[3.3.1]nonane (9-BBN) (0.5 M in THF) solution at 0 °C under Ar atmosphere, a solution of the **5b** (0.1 M in THF, 0.1 mmol) was added dropwise. The resulting mixture was stirred at rt for 2 h and quenched with 4 mL of 1 N aqueous NaOH solution and 0.60 mL of 30% aqueous H_2O_2 solution. After stirring for 1 h, the aqueous layer was extracted with 15 mL portions of EA three times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel (eluting with PE : EA = 2:1) to afford **7** as a white solid (32.3 mg, 84% yield).

(8,9-Dimethyl-1-tosyl-2,3,4,9-tetrahydro-1H-pyrido[2,3-b]indol-3-yl)methanol (7)

mp = 103 – 105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 3H), 7.02 – 6.97 (m, 2H), 4.29 (dd, *J* = 14.2, 4.1 Hz, 1H), 3.94 (s, 3H), 3.50 (dd, *J* = 10.7, 4.8 Hz, 1H), 3.30 (dd, *J* = 10.7, 7.5 Hz, 1H), 3.05 (dd, *J* = 14.2, 12.3 Hz, 1H), 2.78 (s, 3H), 2.41 – 2.35 (m, 4H), 2.15 (dd, *J* = 16.2, 10.2 Hz, 1H), 1.73 – 1.62 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 136.6, 135.2, 134.2, 129.9, 128.2, 126.9, 125.0, 122.2, 119.9, 115.8, 103.3, 65.0, 51.4, 35.2, 32.1, 21.8, 21.4, 19.9; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3S^+$ $[M+H]^+$ 385.1580, found 385.1583.

7. X-Ray single crystal data of product 5b

Sample preparation for single crystal 5b: Pure **5b** (20 mg) was dissolved in 1.0 mL of ethyl acetate with a 10 mL of test tube, and then 4.0 mL of *n*-hexane was added to the test tube slowly. The test tube was sealed with a parafilm and kept standing for 3-5 days, and the single crystal **5b** appeared at the bottom of the test tube.

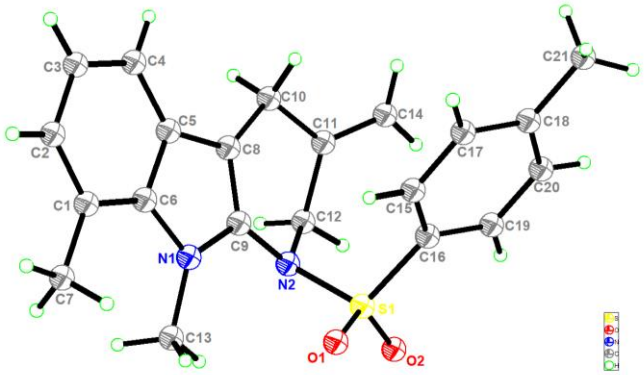


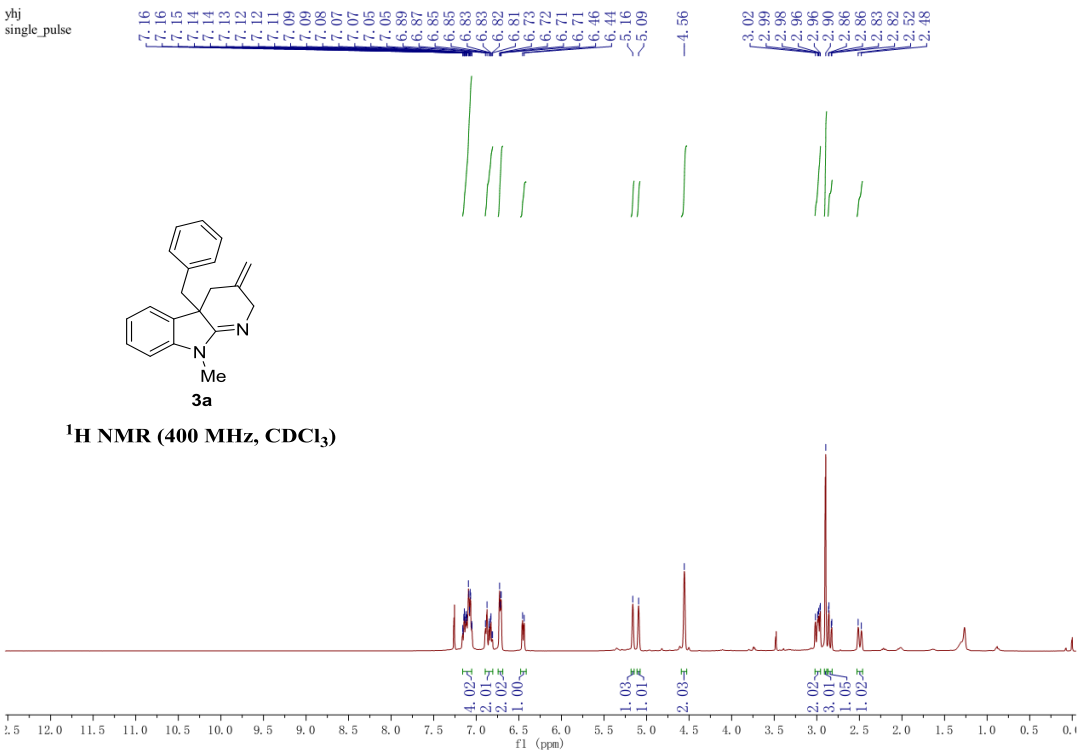
Figure S1. X-Ray structure of **5b** with the ellipsoid contour 80% probability levels

Table S1. Crystal data and structure refinement for 5b

CDC number	2142421
Identification code	**5b**
Empirical formula	$C_{21}H_{22}N_2O_2S$
Formula weight	366.46
Temperature/K	250.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.0562(6)
b/Å	8.7666(6)
c/Å	13.9909(8)
α/°	73.512(6)
β/°	88.716(5)
γ/°	73.406(6)
Volume/Å^3	906.17(11)
Z	2
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	0.197

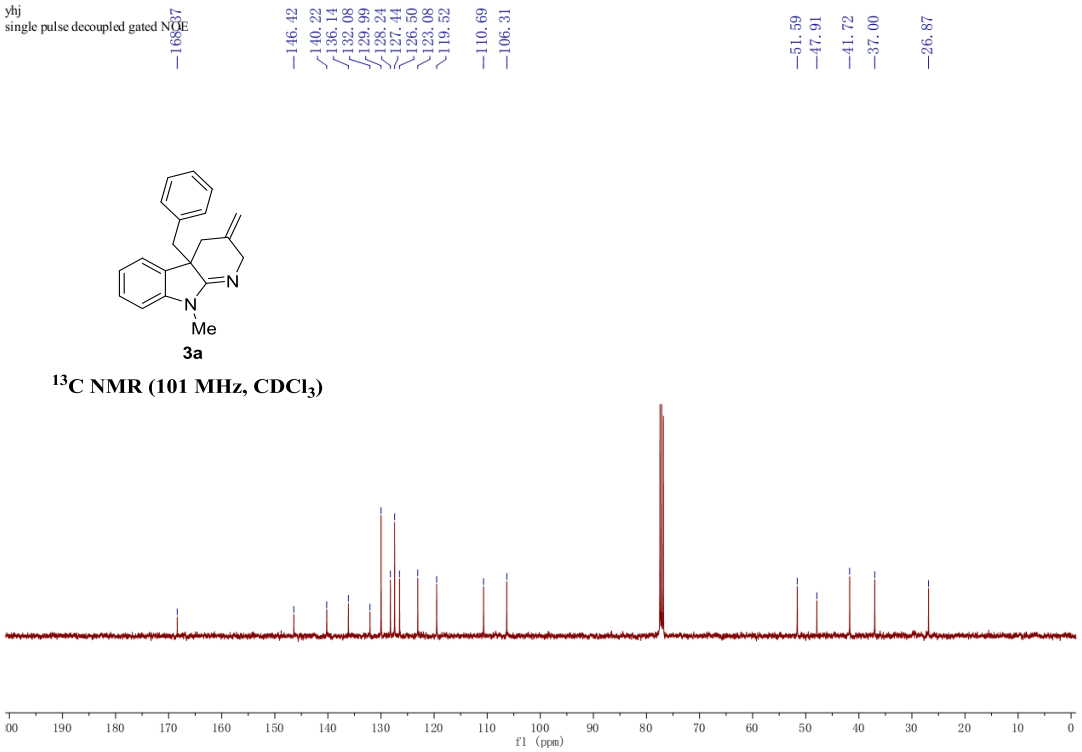
F(000)	388
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.36 to 54
Index ranges	$-7 \leq h \leq 10$, $-7 \leq k \leq 10$, $-14 \leq l \leq 17$
Reflections collected	6647
Independent reflections	3871 [R_{int} = 0.0226, R_{sigma} = 0.0455]
Data/restraints/parameters	3871/0/238
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1116
Final R indexes [all data]	R_1 = 0.0658, wR_2 = 0.1202
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.34

8. NMR spectra of products 3a-3x, 5a-5k, 6 and 7



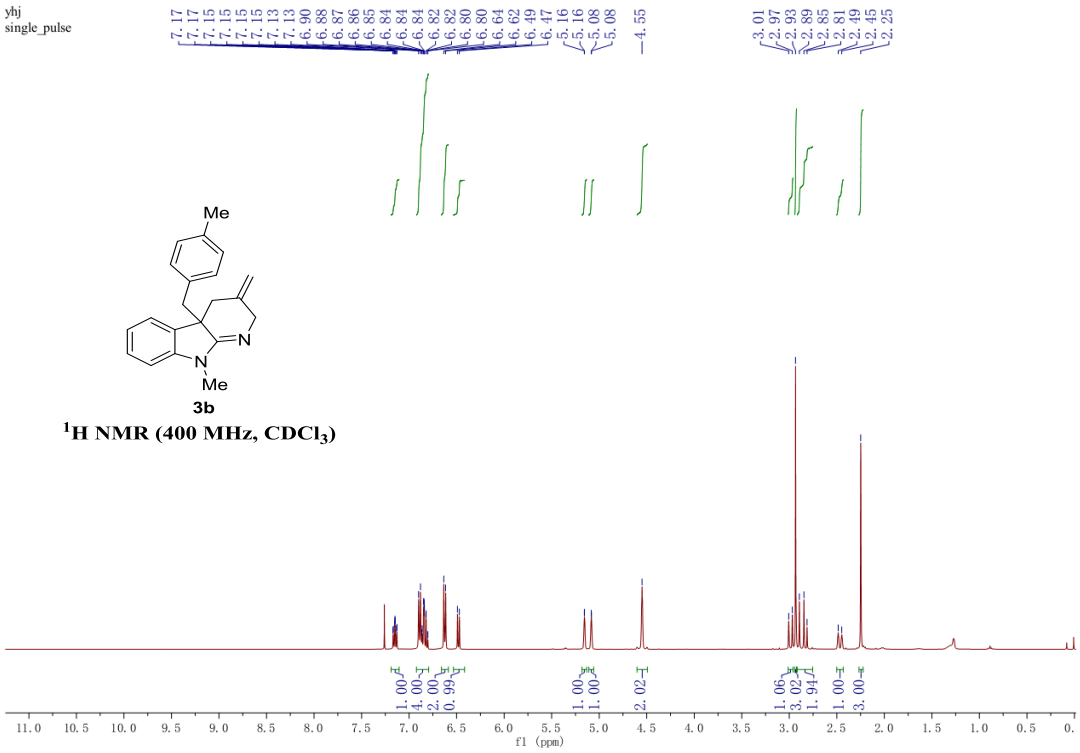
3a

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



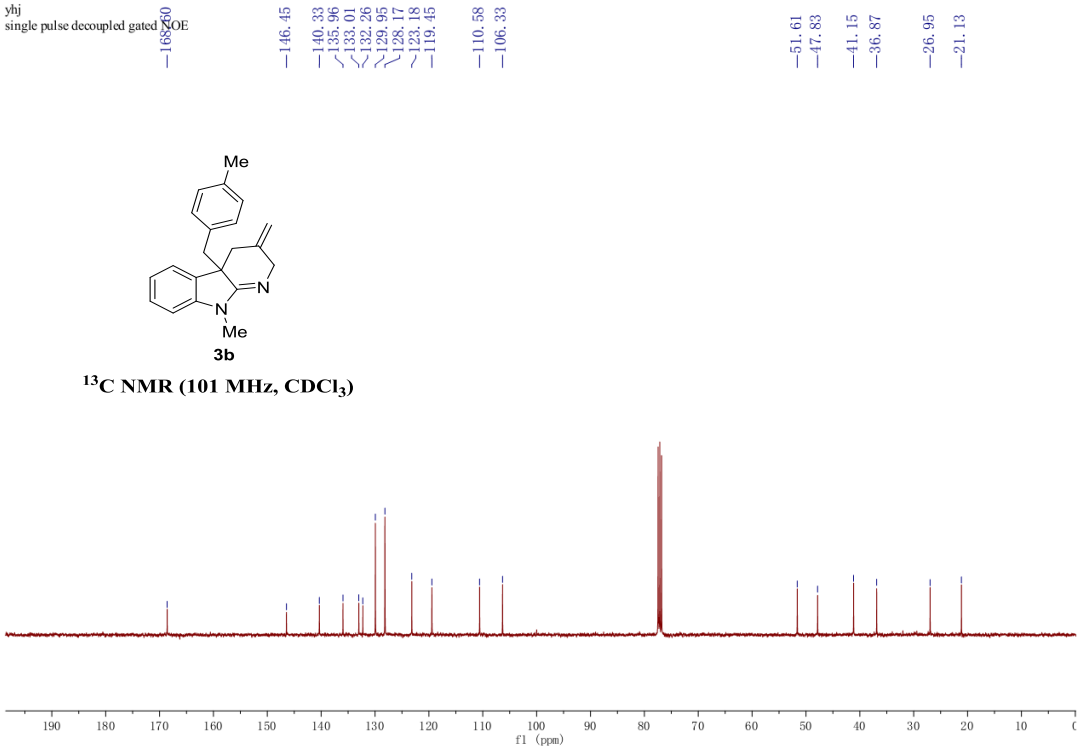
3a

^{13}C NMR (101 MHz, $CDCl_3$)



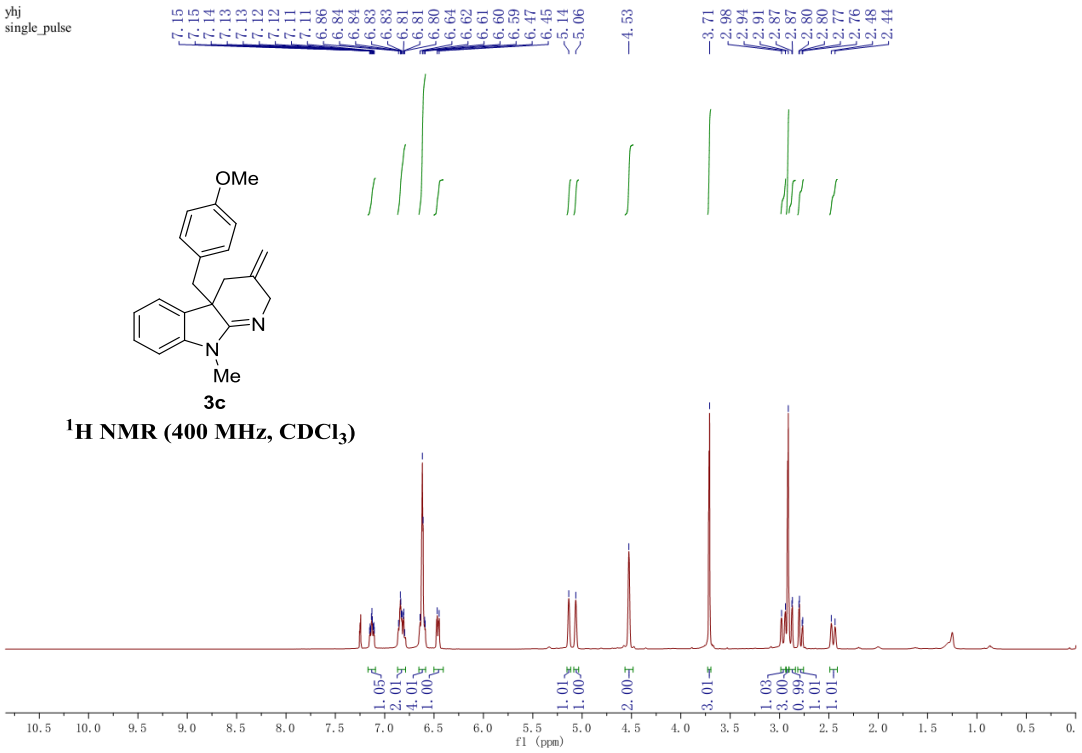
3b

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



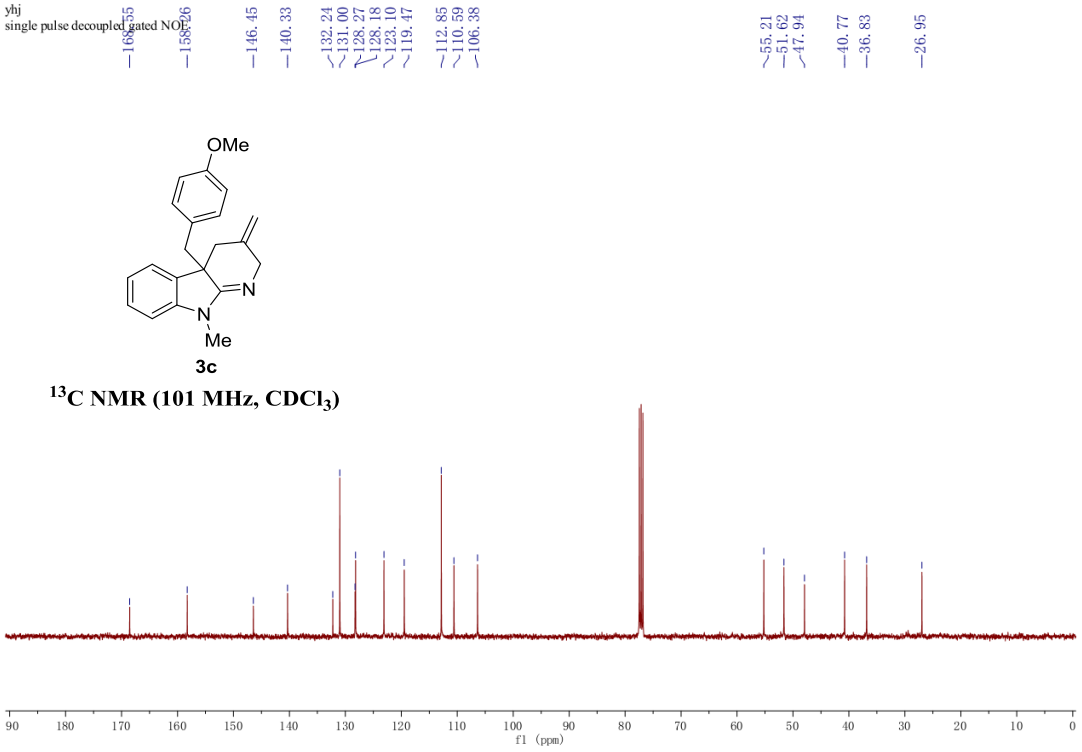
3b

^{13}C NMR (101 MHz, $CDCl_3$)



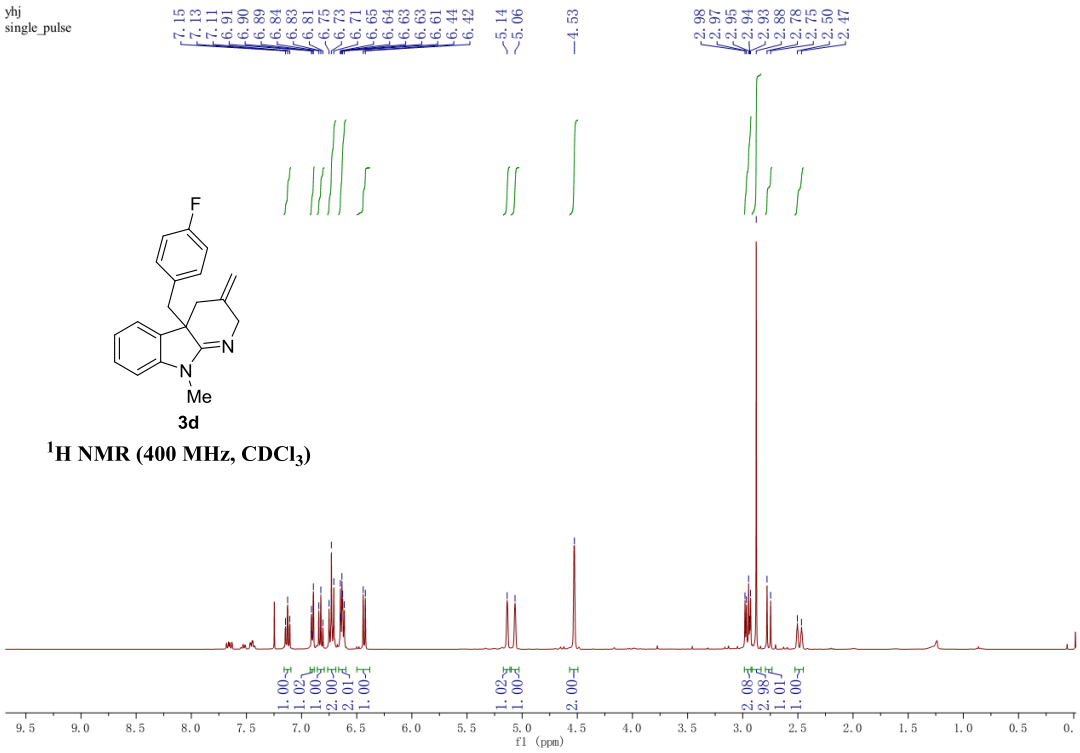
3c

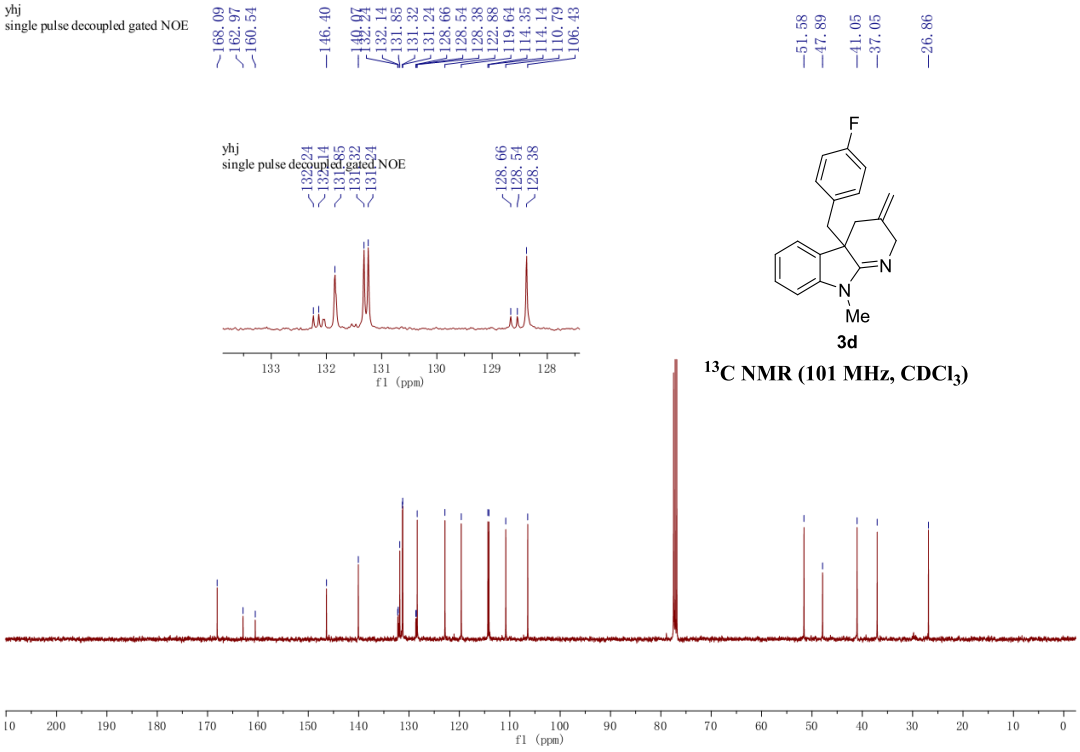
^{1}H NMR (400 MHz, $CDCl_3$)

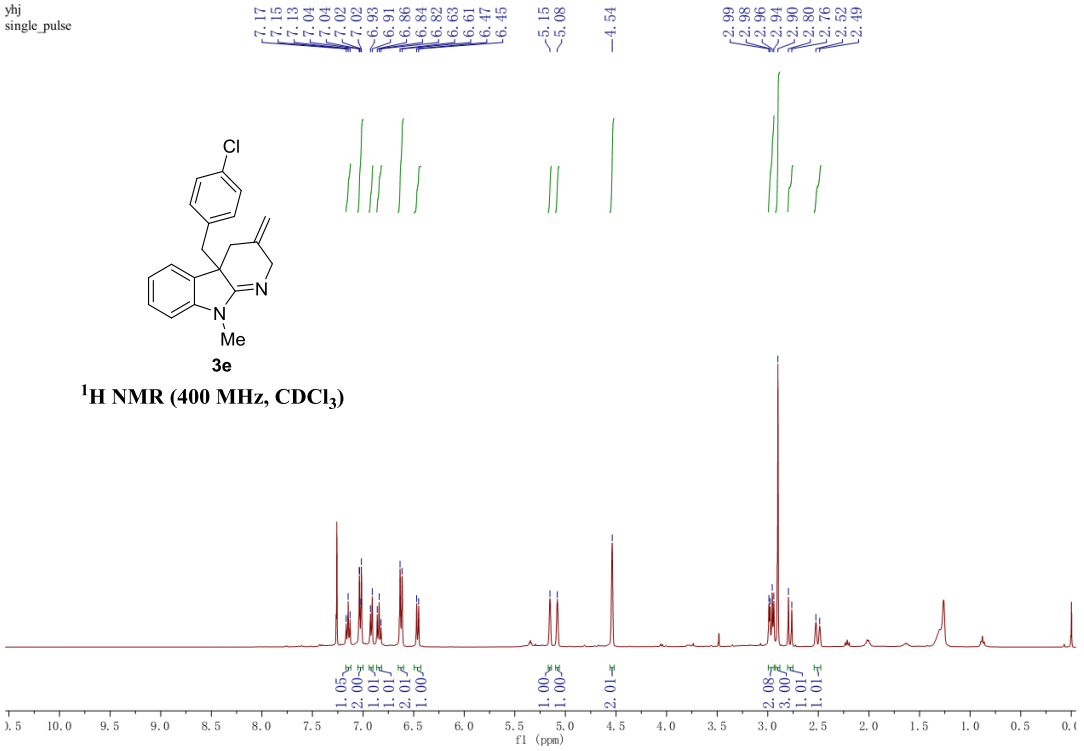


3c

^{13}C NMR (101 MHz, $CDCl_3$)

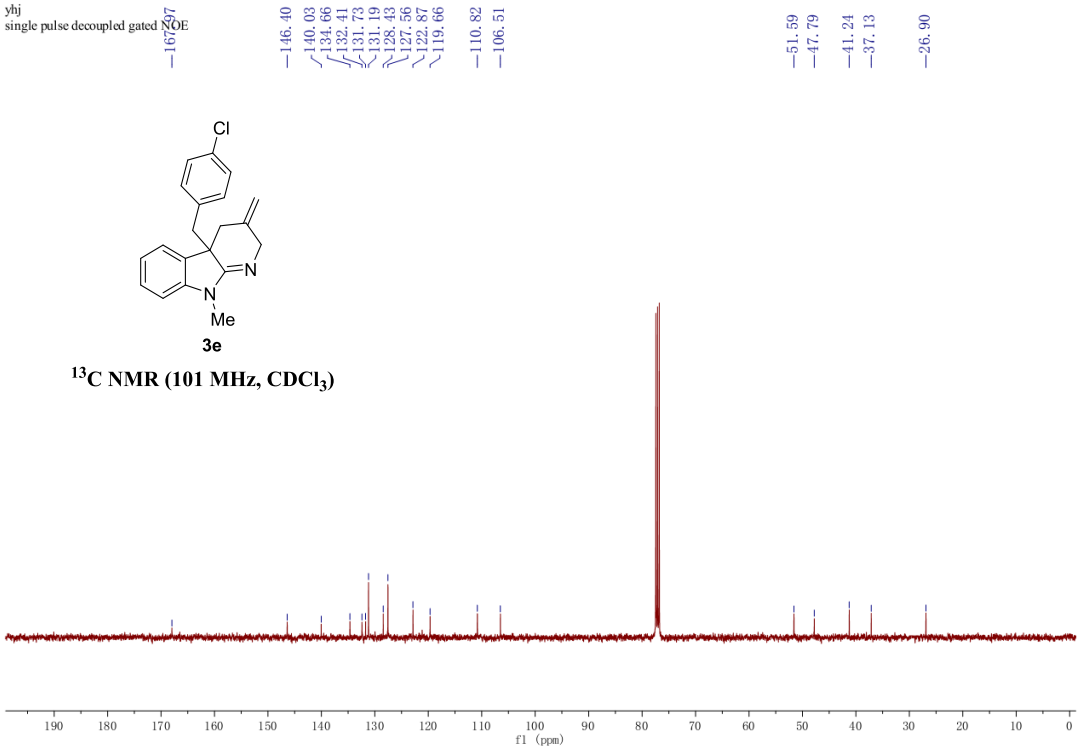

yhj
single_pulse
F
N
N
Me
3d
1H NMR (400 MHz, CDCl3)
f1 (ppm)


yhj
single pulse decoupled gated NOE
yhj
single pulse decoupled gated NOE
F
N
N
Me
3d
13C NMR (101 MHz, CDCl3)
f1 (ppm)



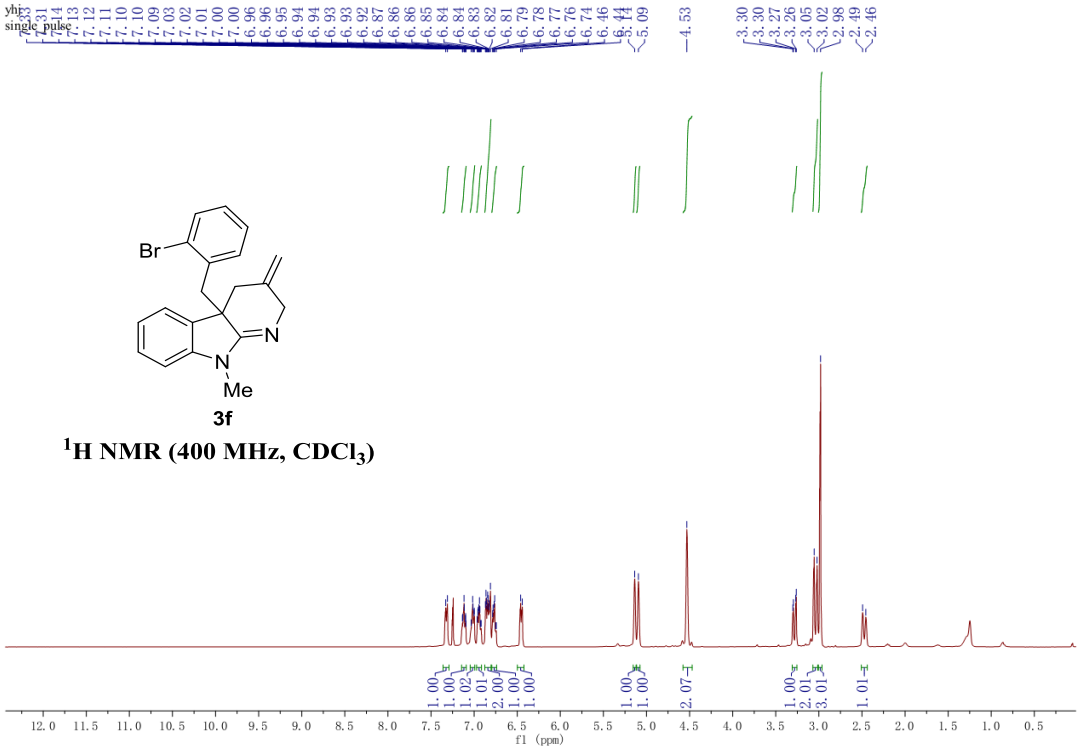
3e

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



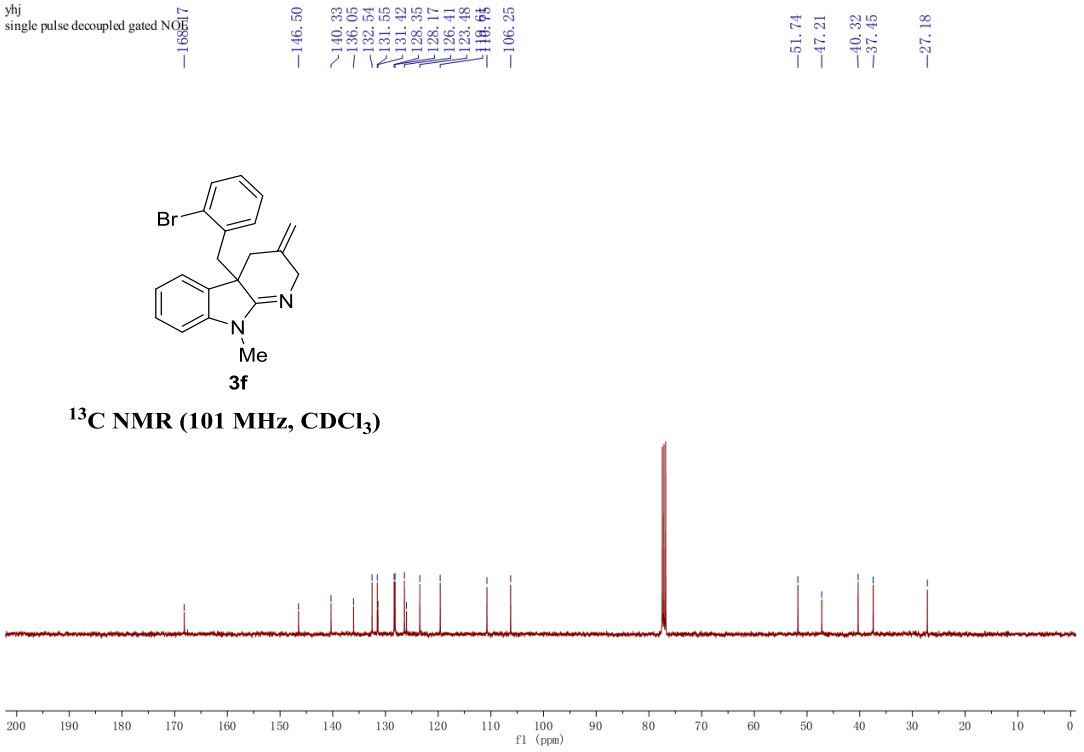
3e

^{13}C NMR (101 MHz, $CDCl_3$)



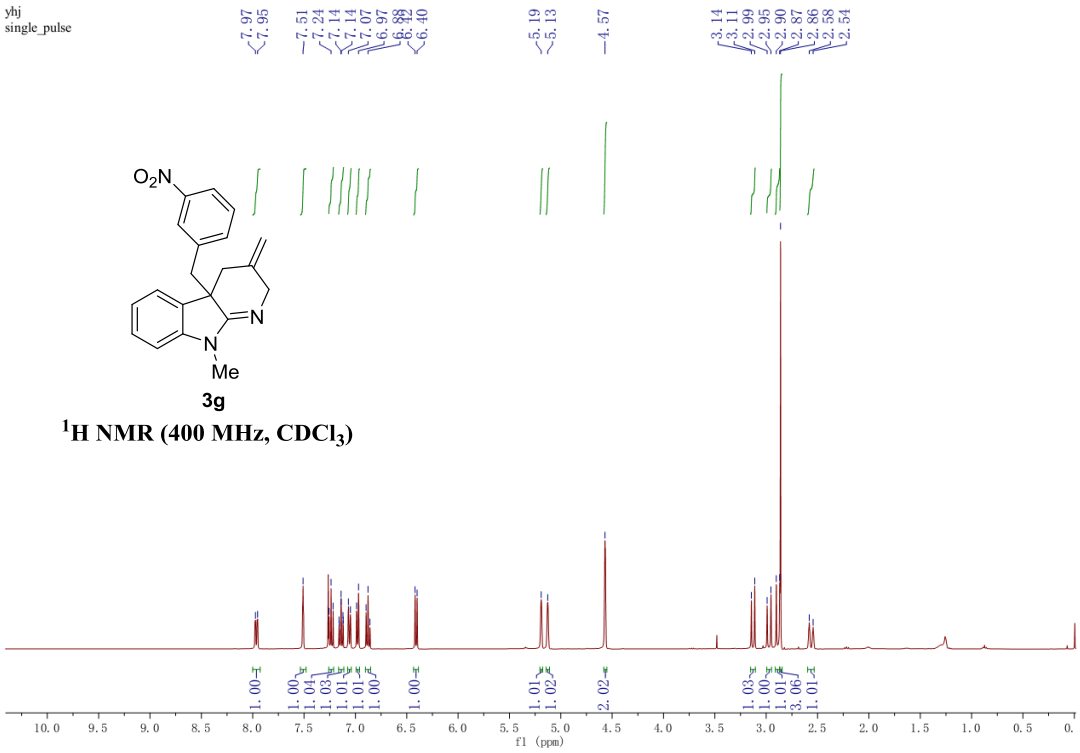
3f

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



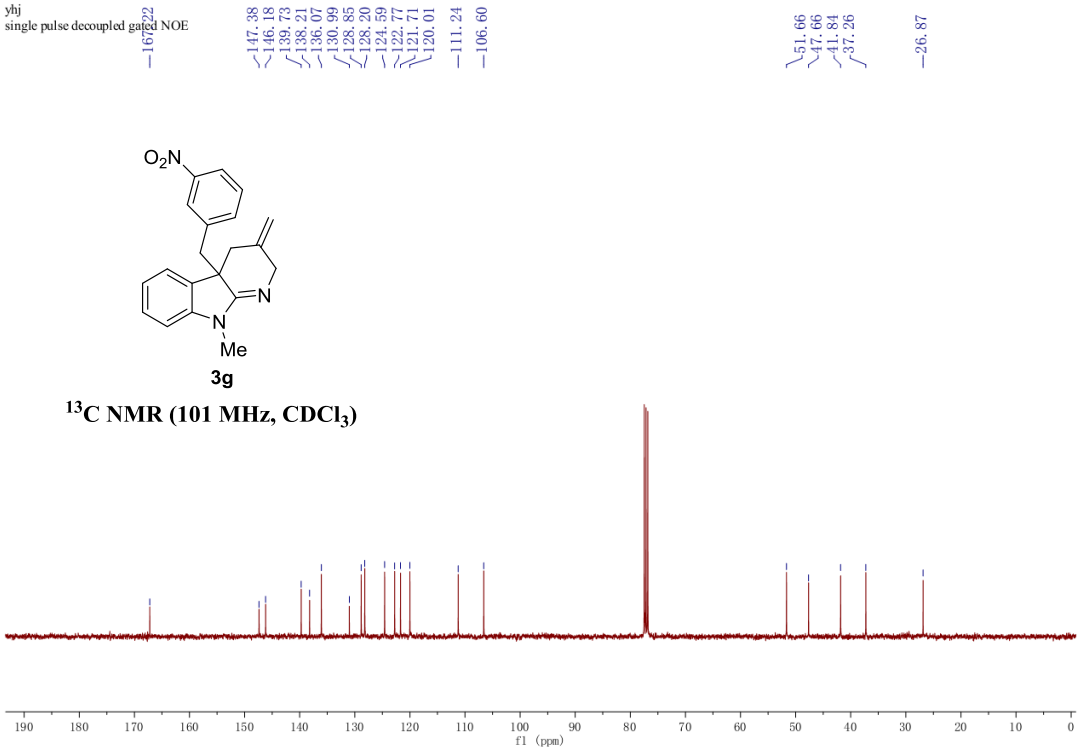
3f

^{13}C NMR (101 MHz, $CDCl_3$)



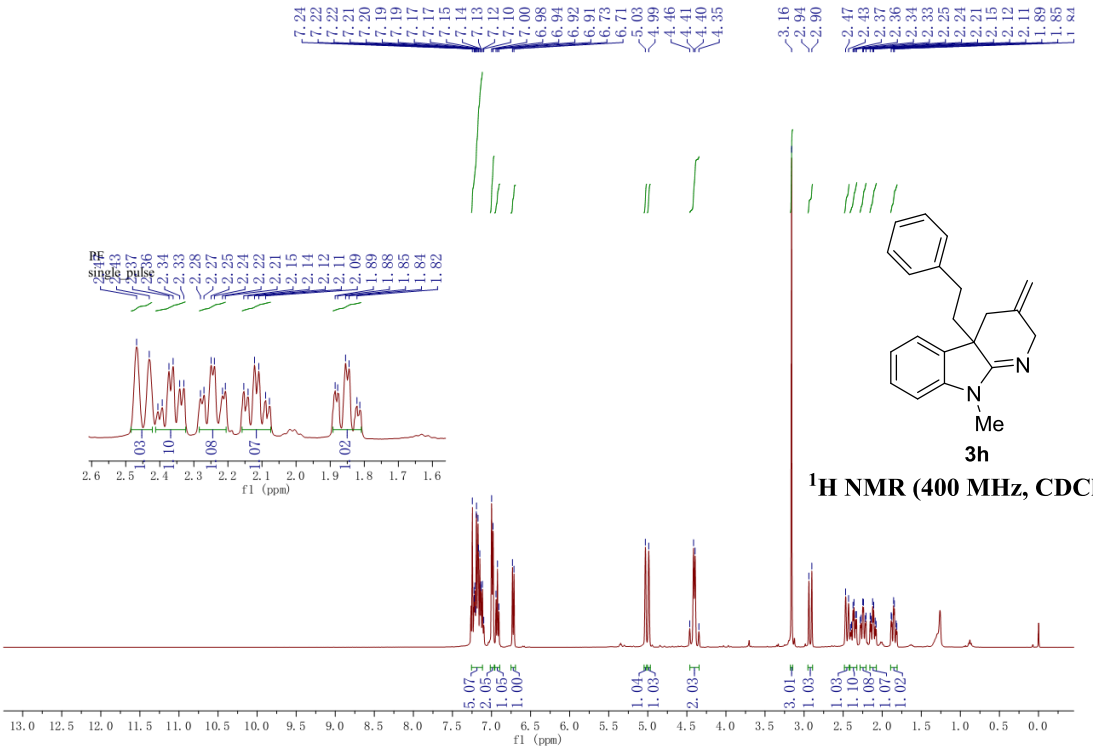
3g

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

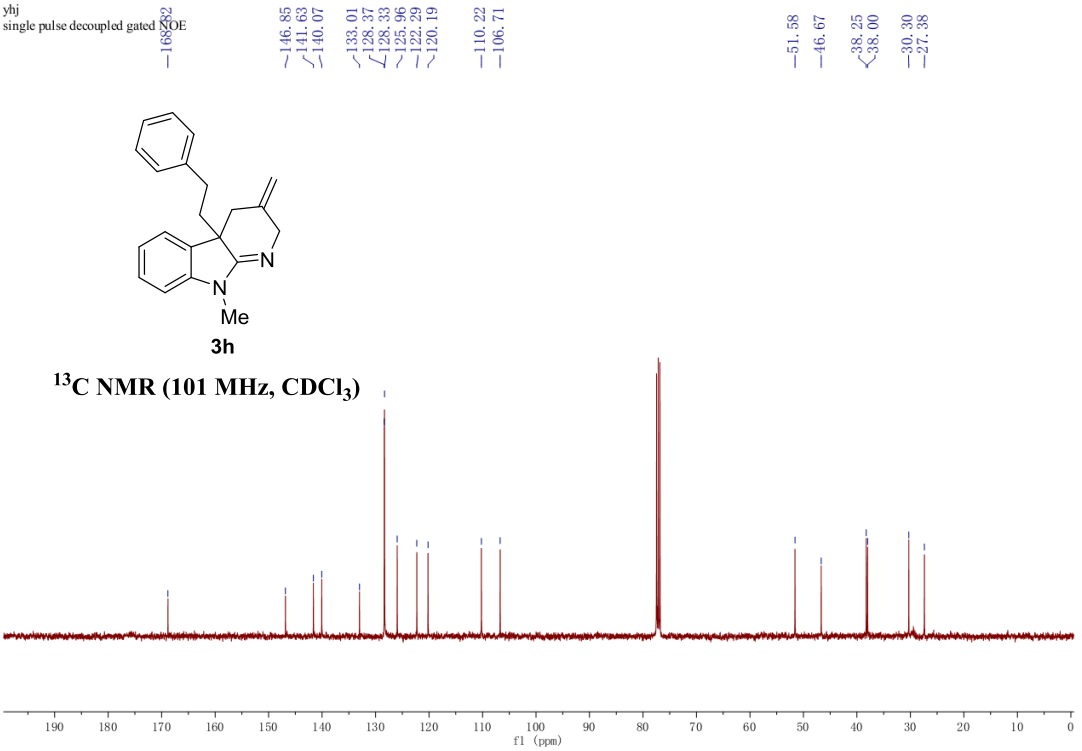


3g

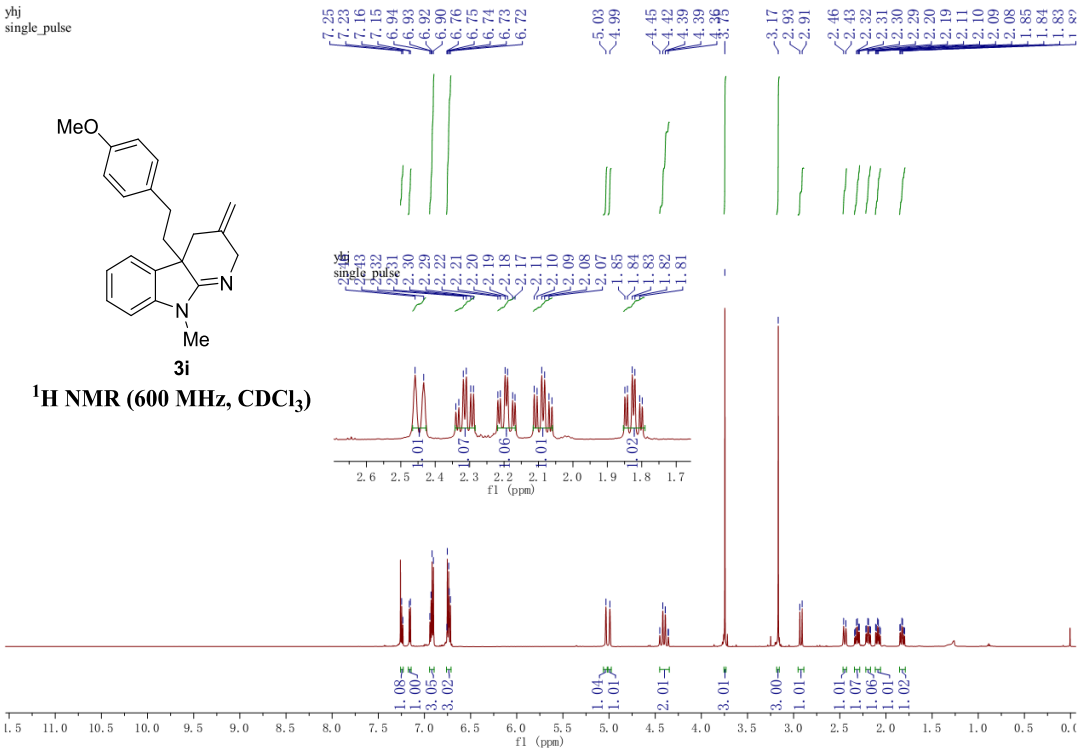
^{13}C NMR (101 MHz, $CDCl_3$)



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

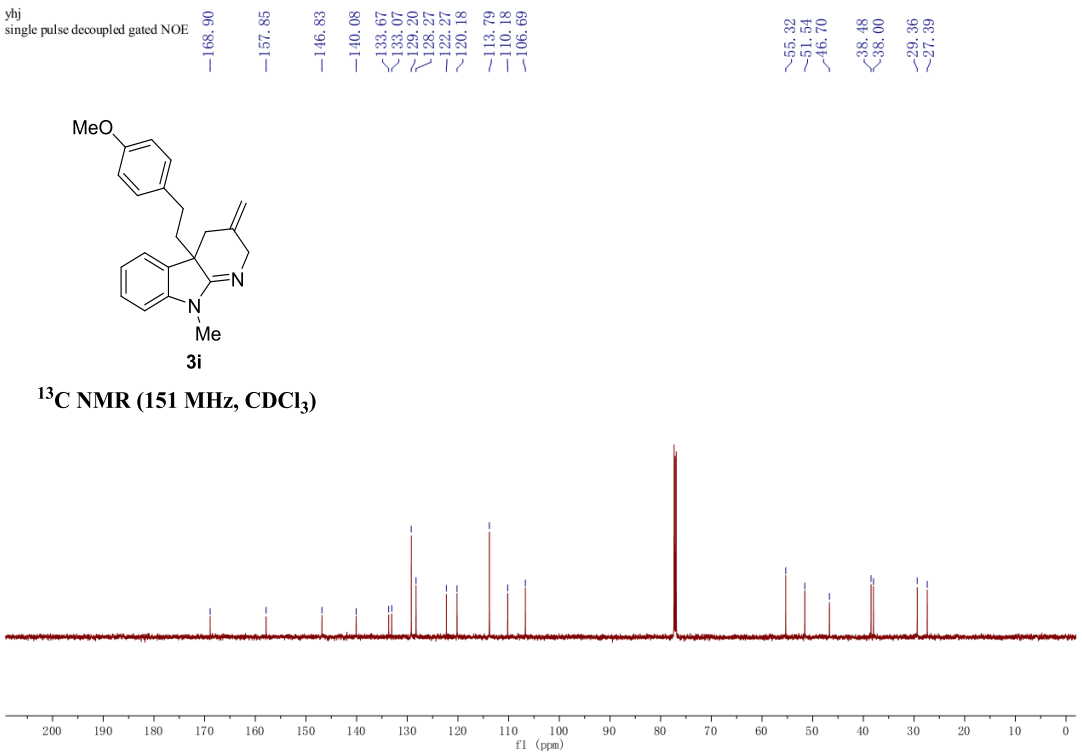


^{13}C NMR (101 MHz, $CDCl_3$)



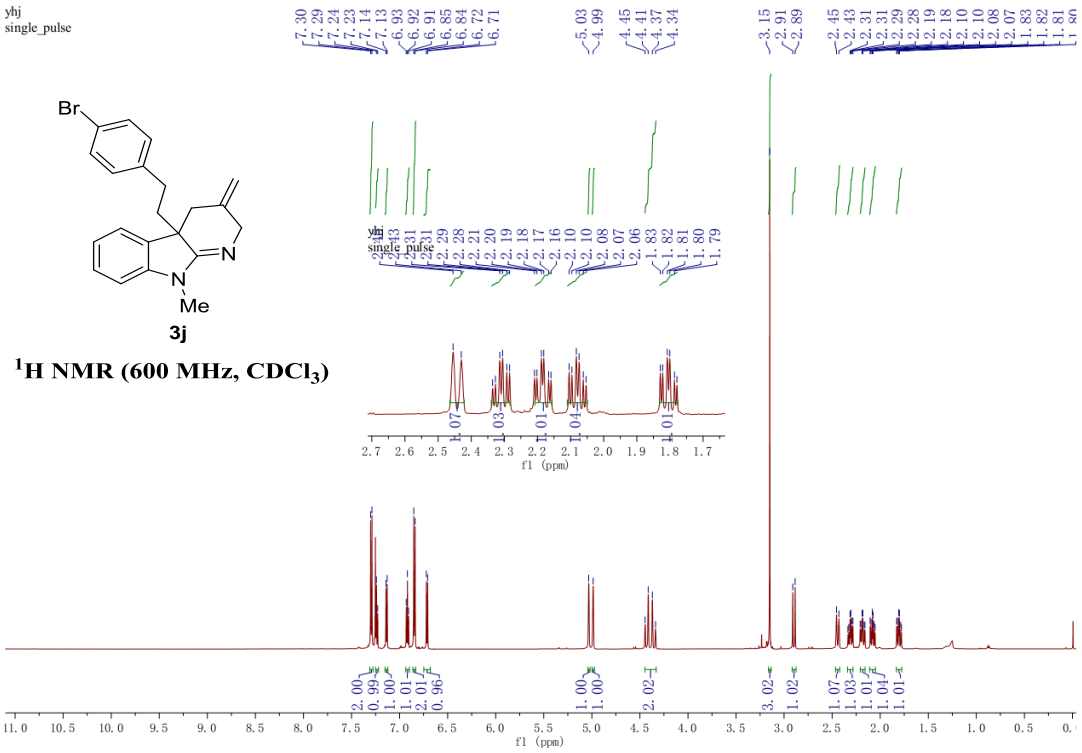
3i

^{1}H NMR (600 MHz, $CDCl_3$)



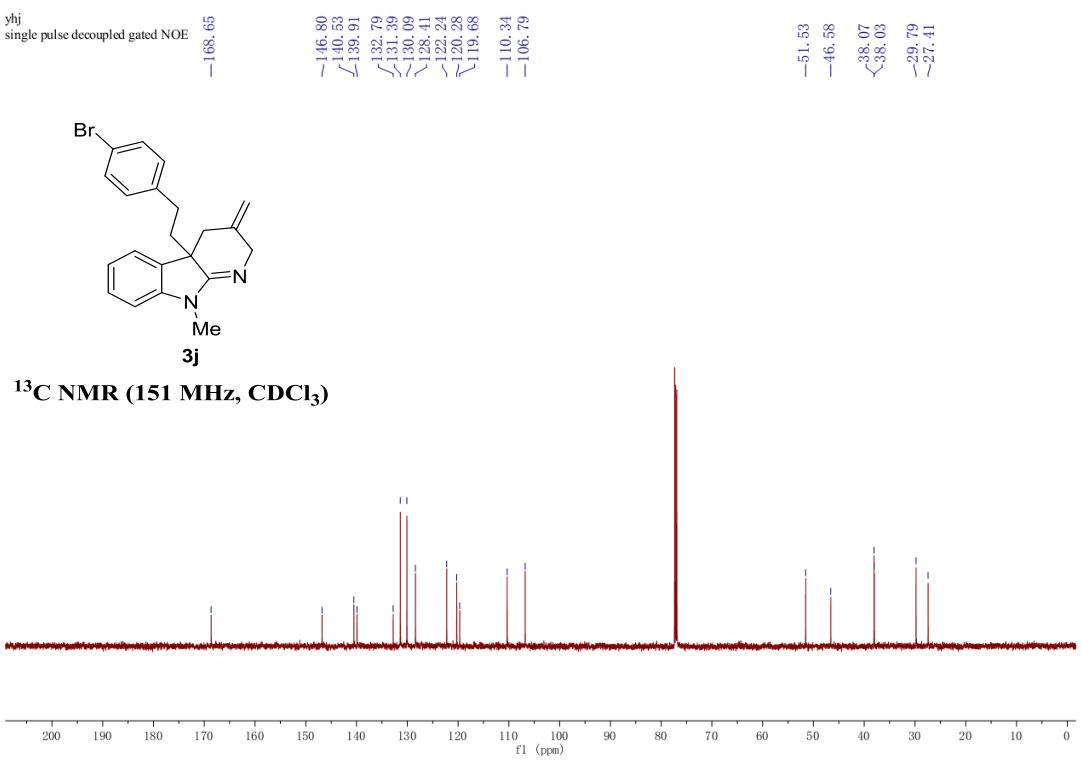
3i

^{13}C NMR (151 MHz, $CDCl_3$)



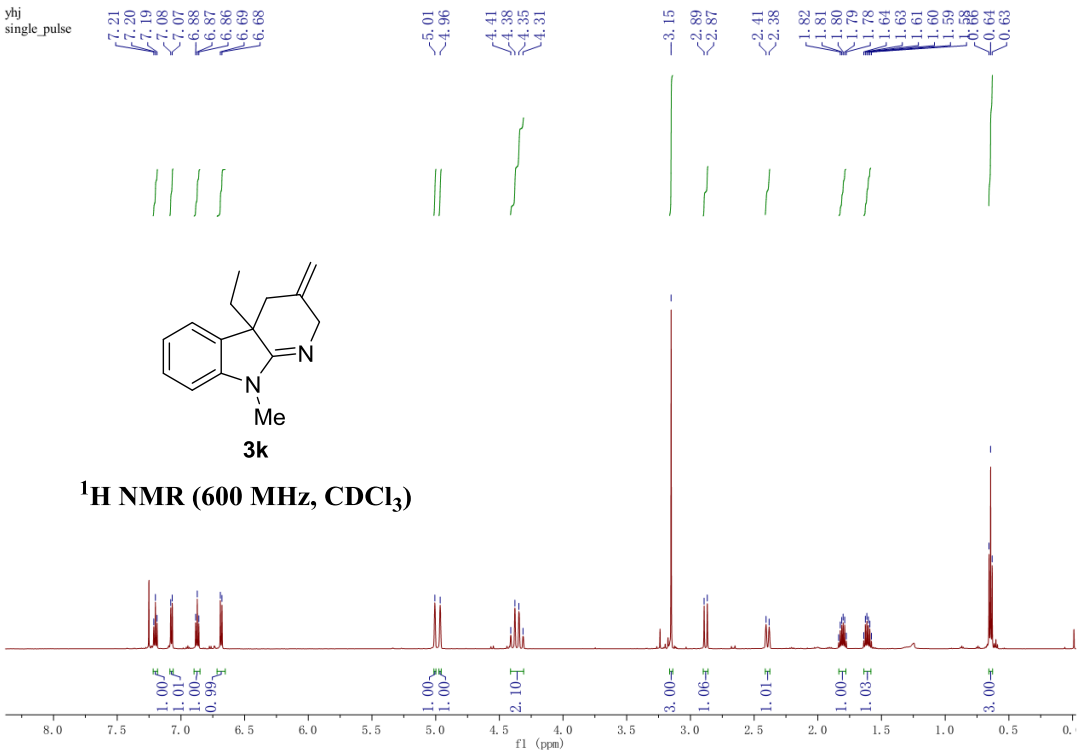
3j

^{1}H NMR (600 MHz, $CDCl_3$)



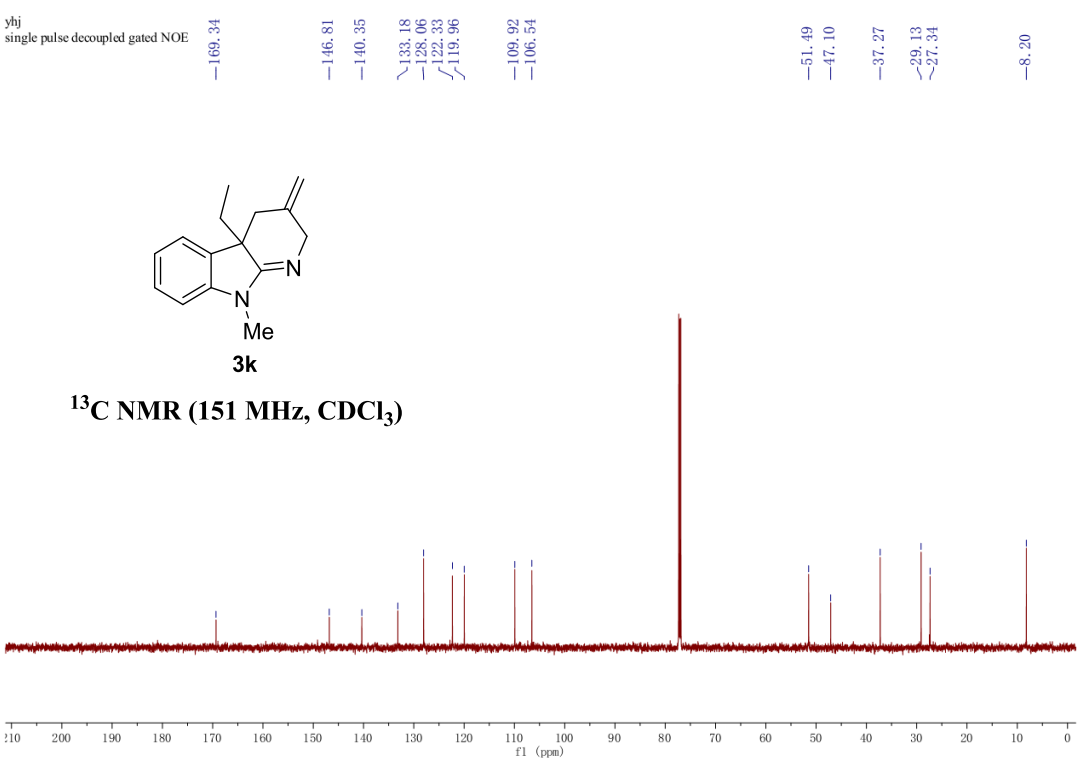
3j

^{13}C NMR (151 MHz, $CDCl_3$)



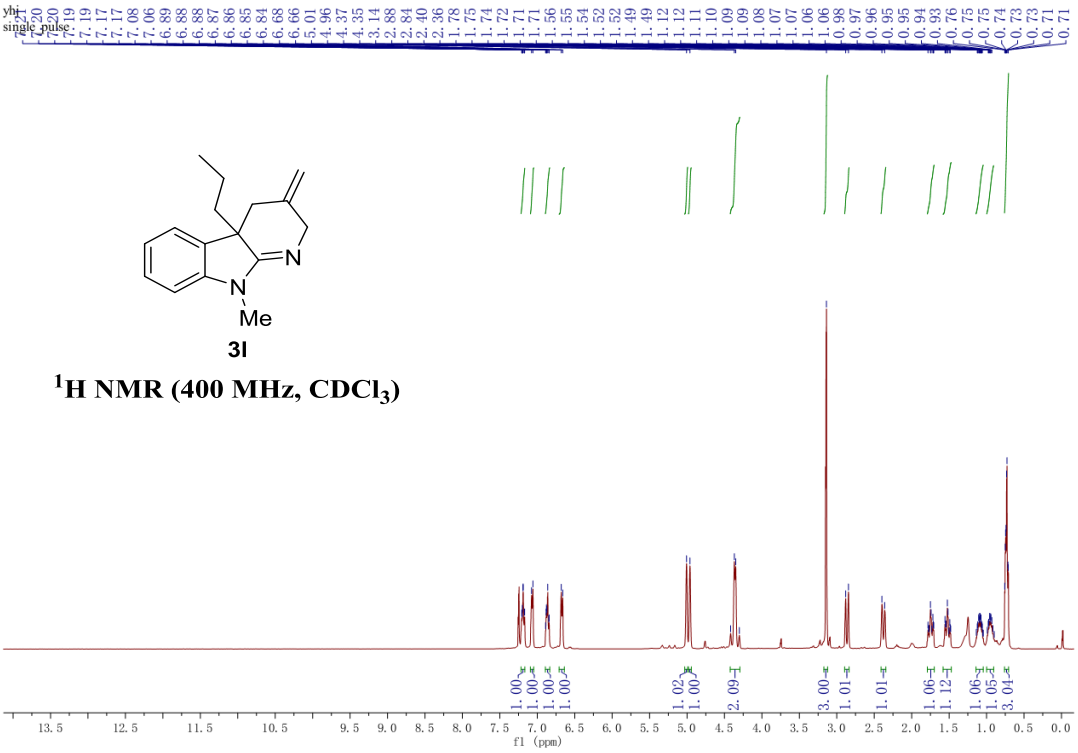
3k

^{1}H NMR (600 MHz, $CDCl_3$)



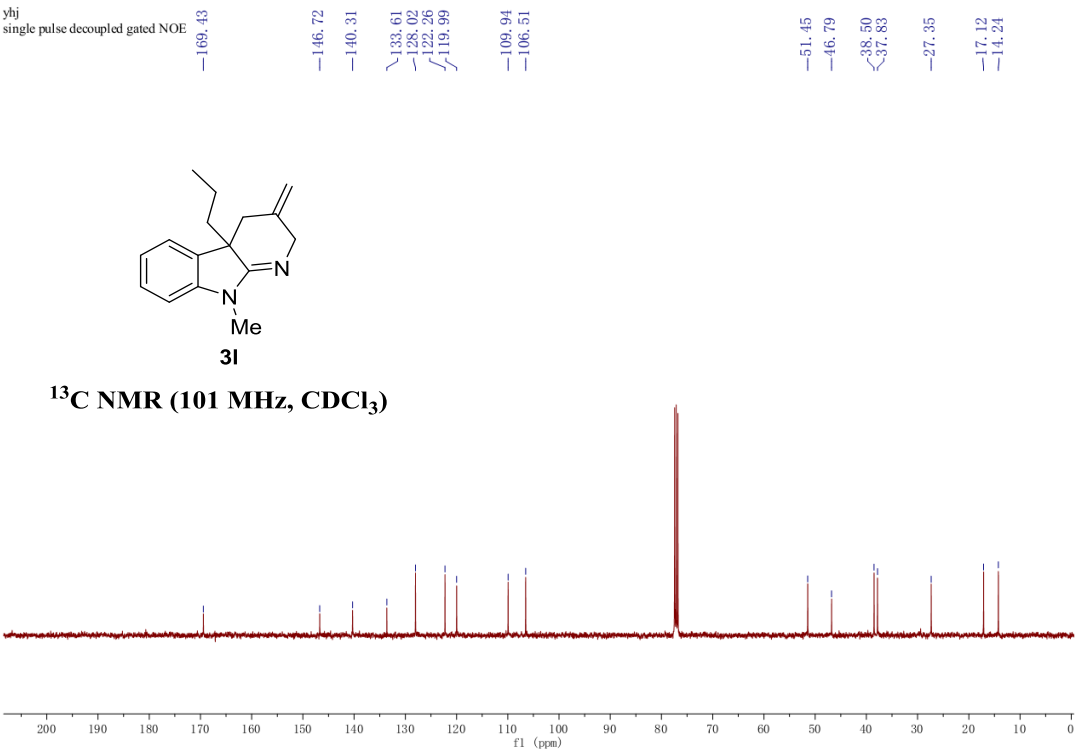
3k

^{13}C NMR (151 MHz, $CDCl_3$)



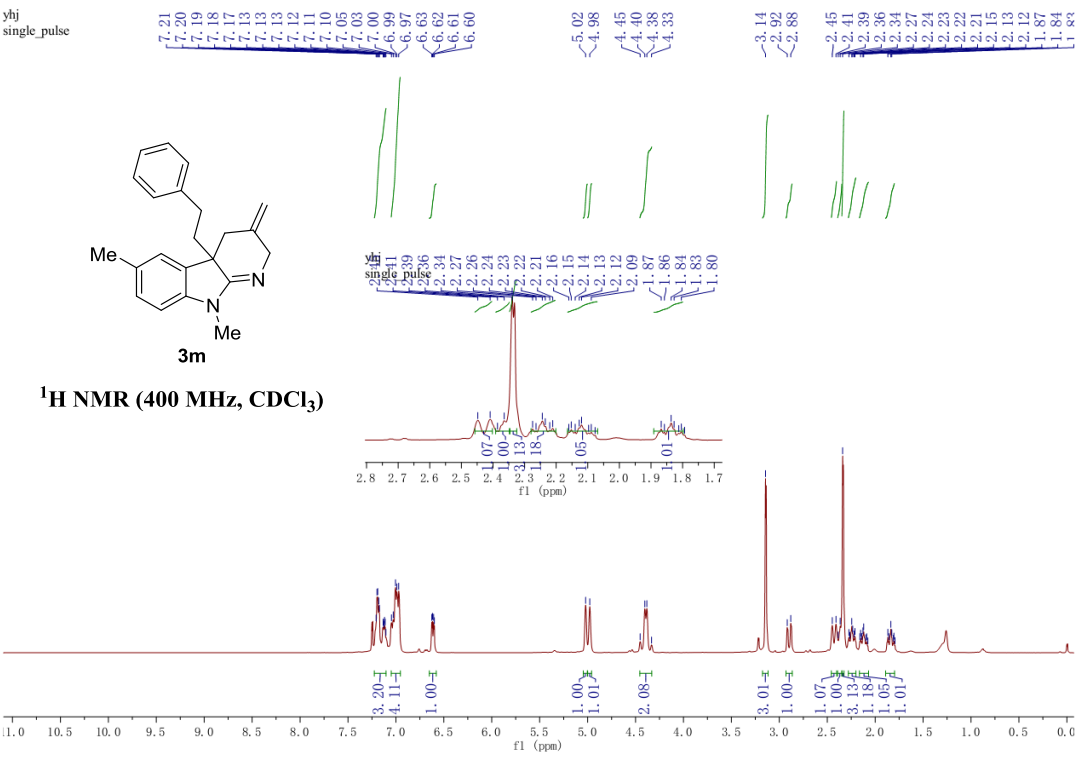
3l

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



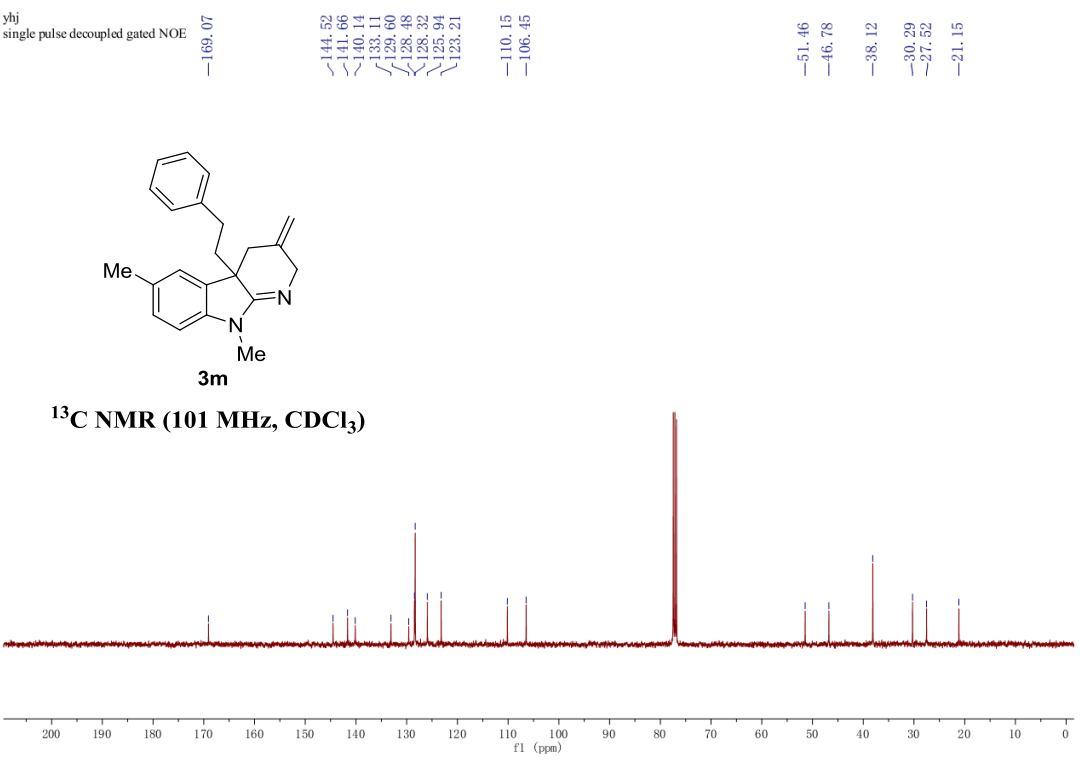
3l

^{13}C NMR (101 MHz, $CDCl_3$)



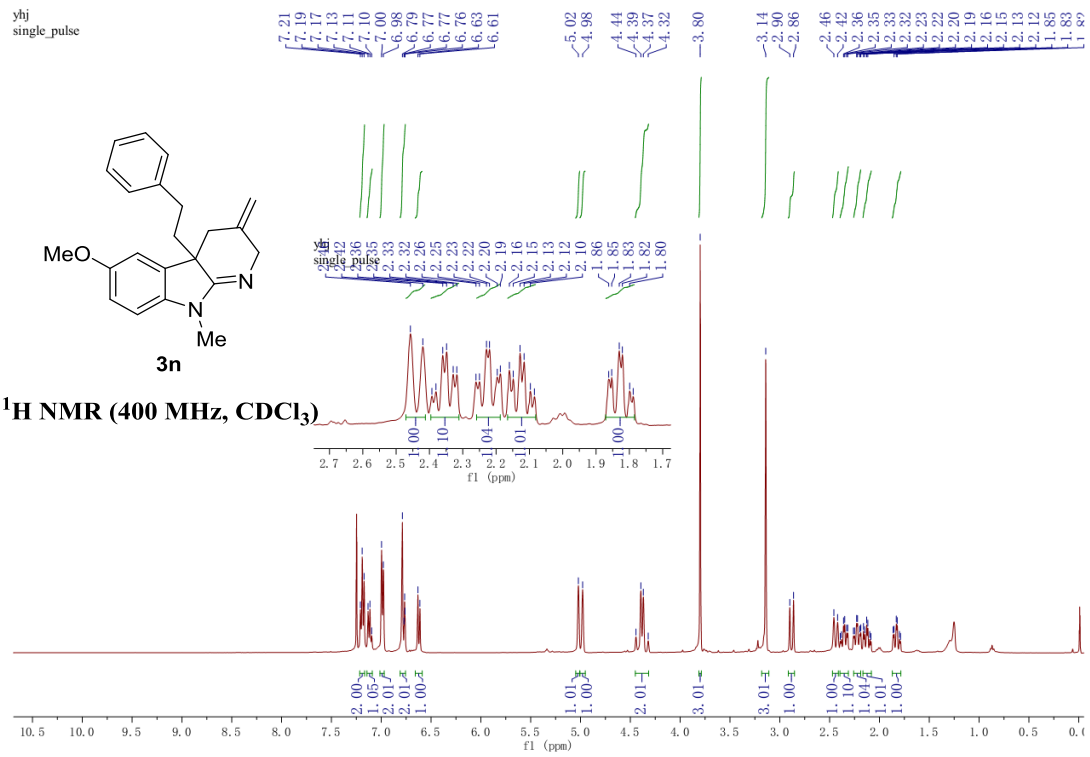
3m

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

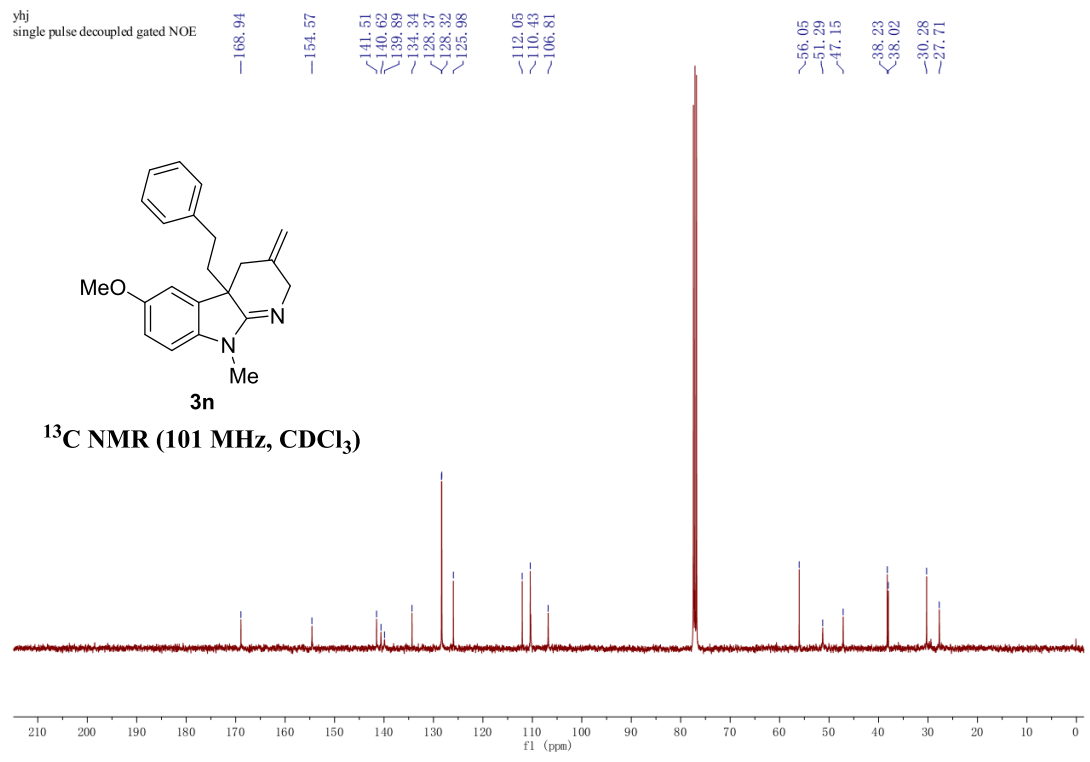


3m

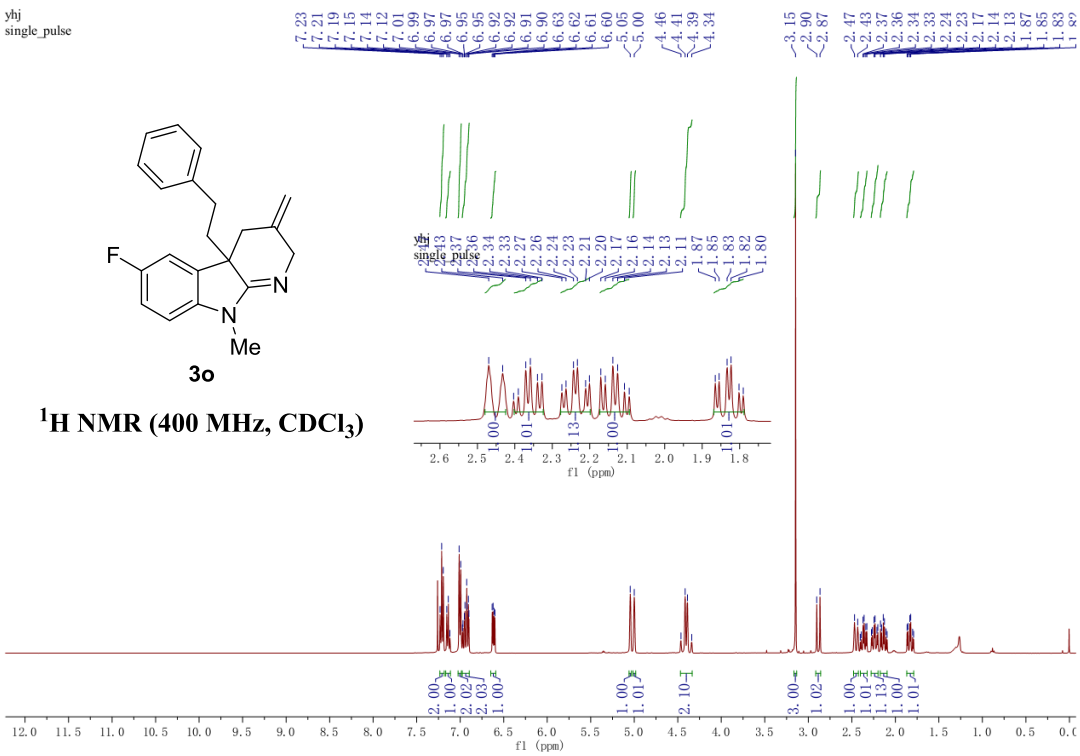
^{13}C NMR (101 MHz, $CDCl_3$)



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

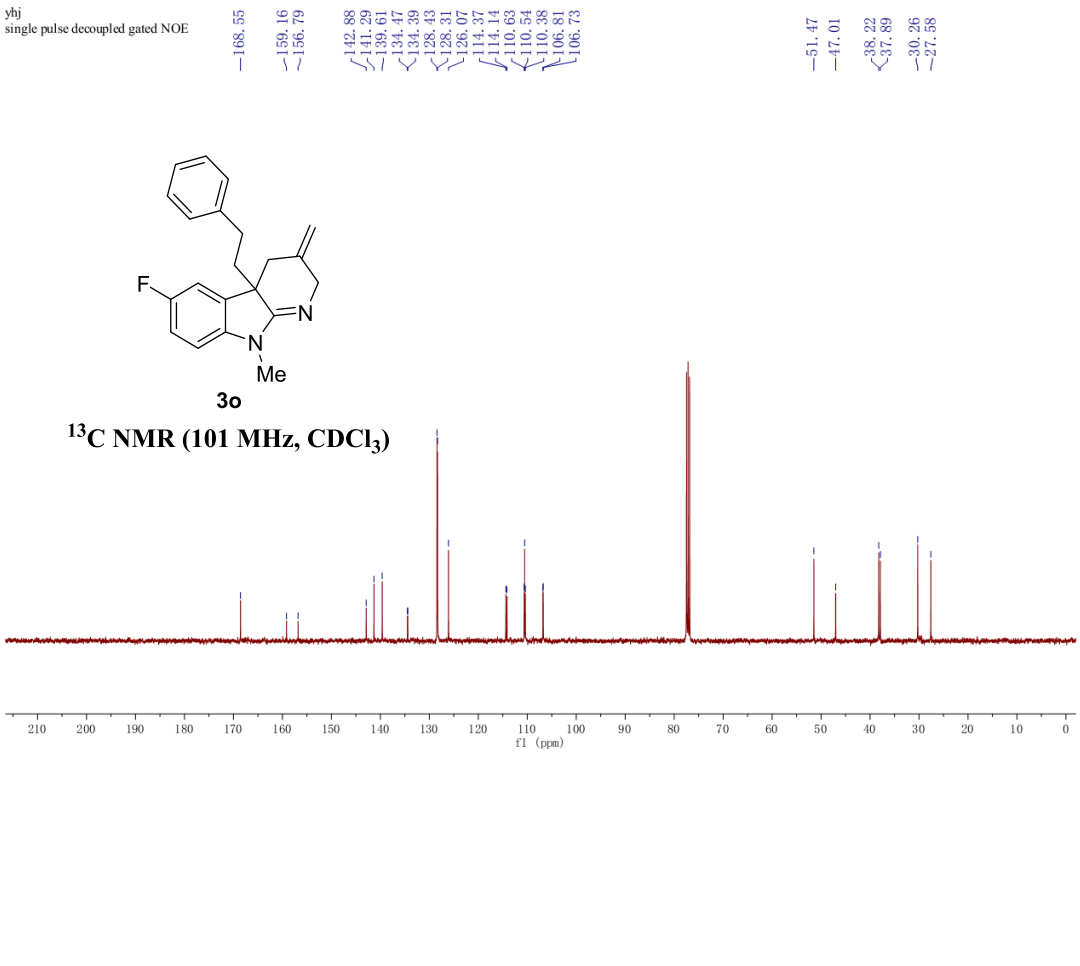


^{13}C NMR (101 MHz, $CDCl_3$)



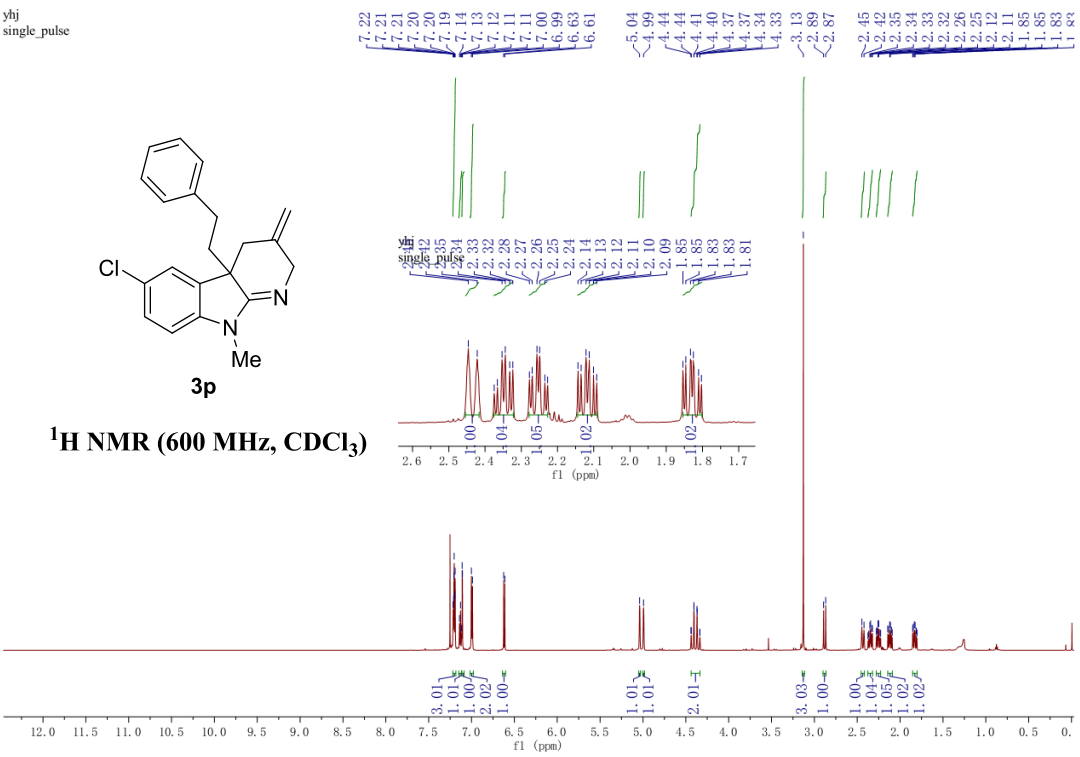
3o

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



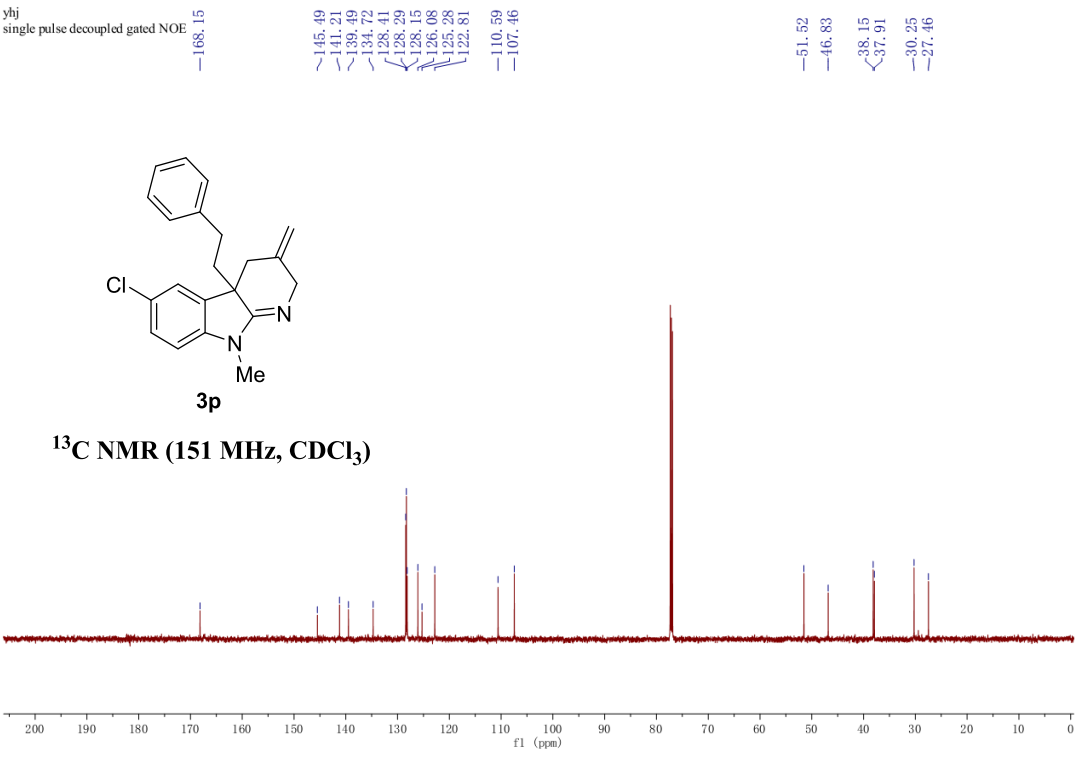
3o

^{13}C NMR (101 MHz, $CDCl_3$)



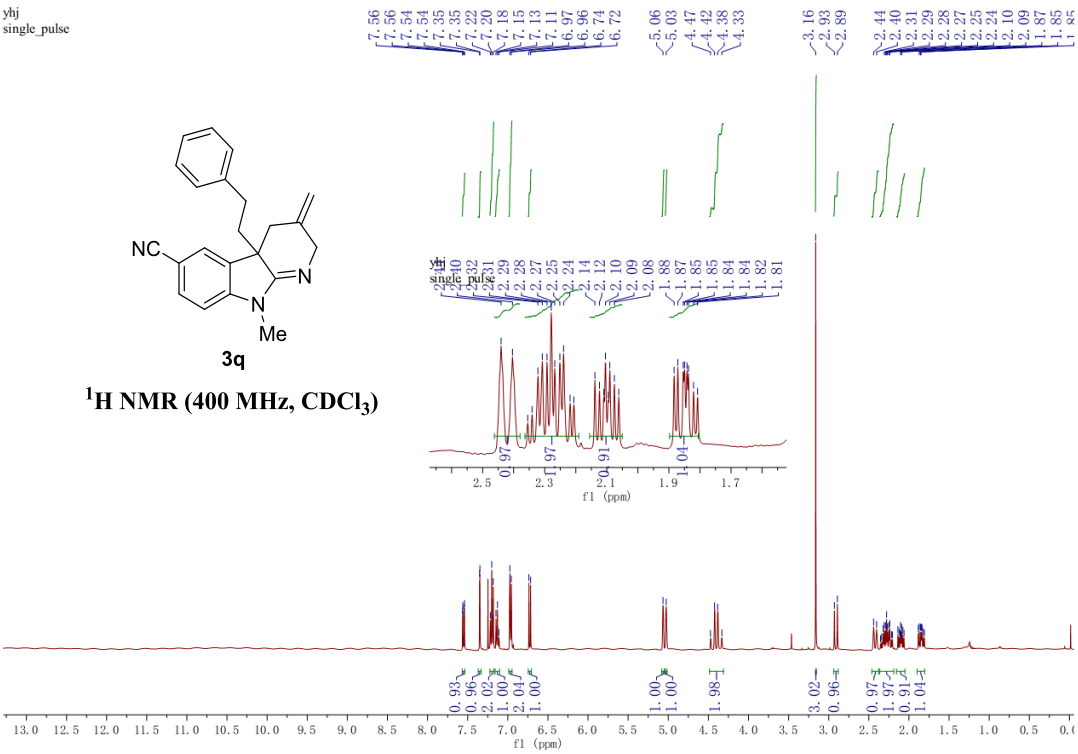
3p

^{1}H NMR (600 MHz, $CDCl_3$)



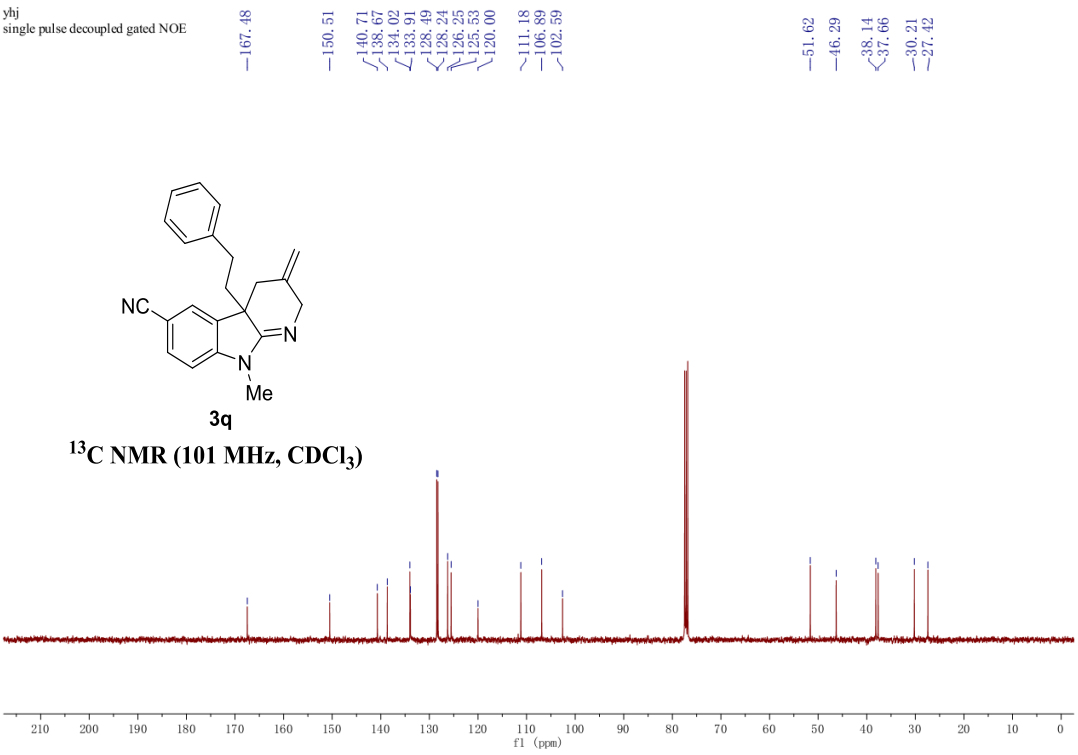
3p

^{13}C NMR (151 MHz, $CDCl_3$)



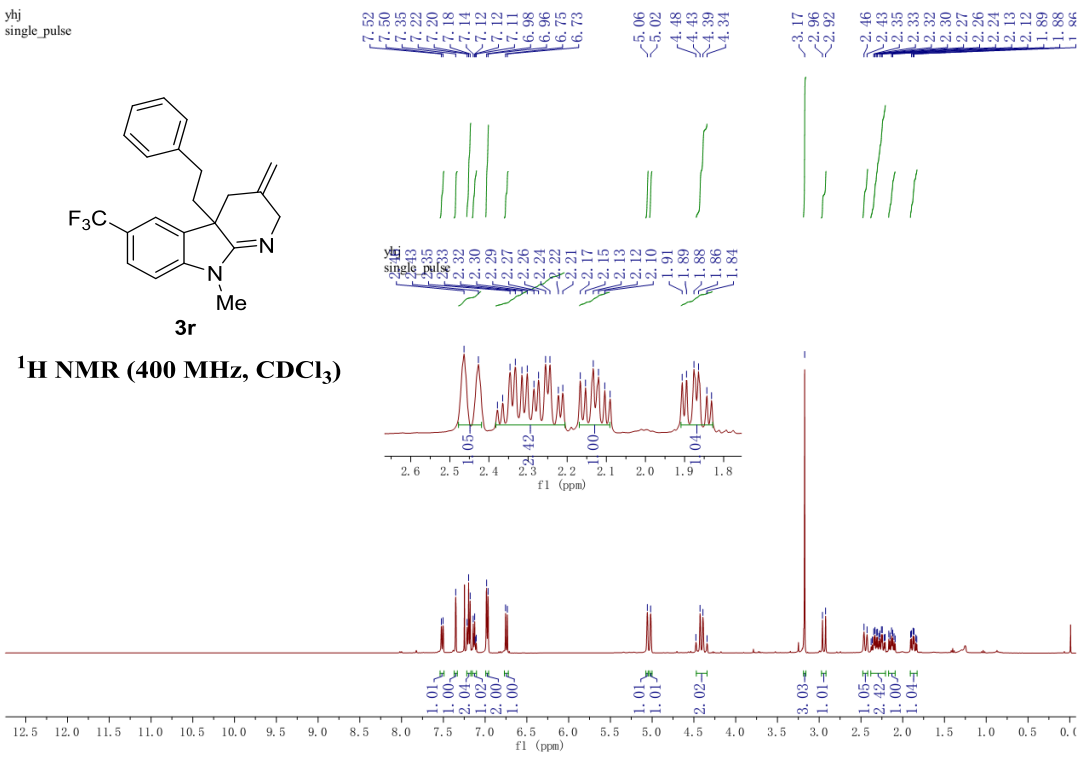
3q

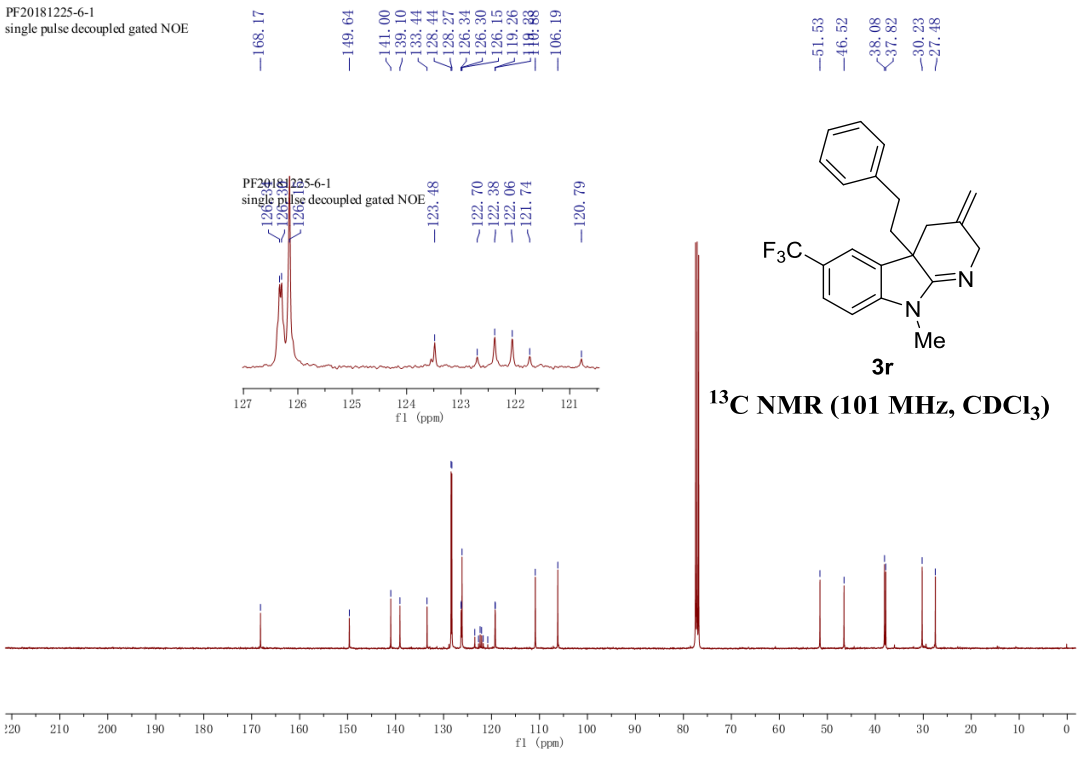
^{1}H NMR (400 MHz, $CDCl_3$)

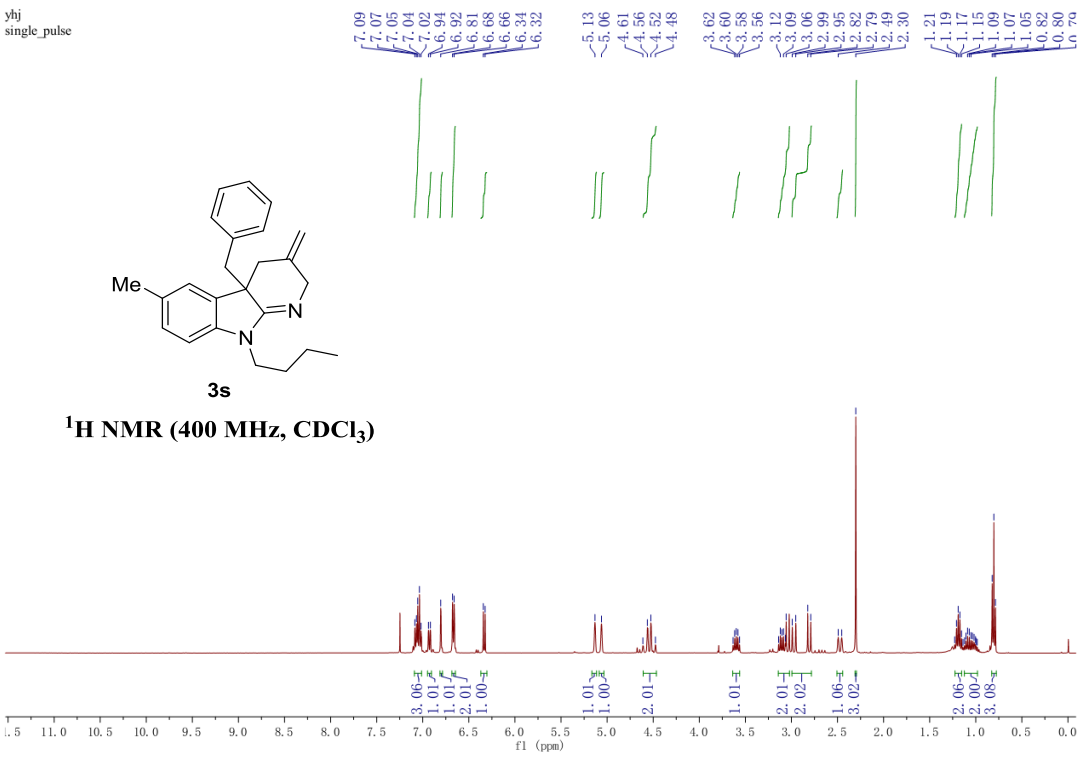


3q

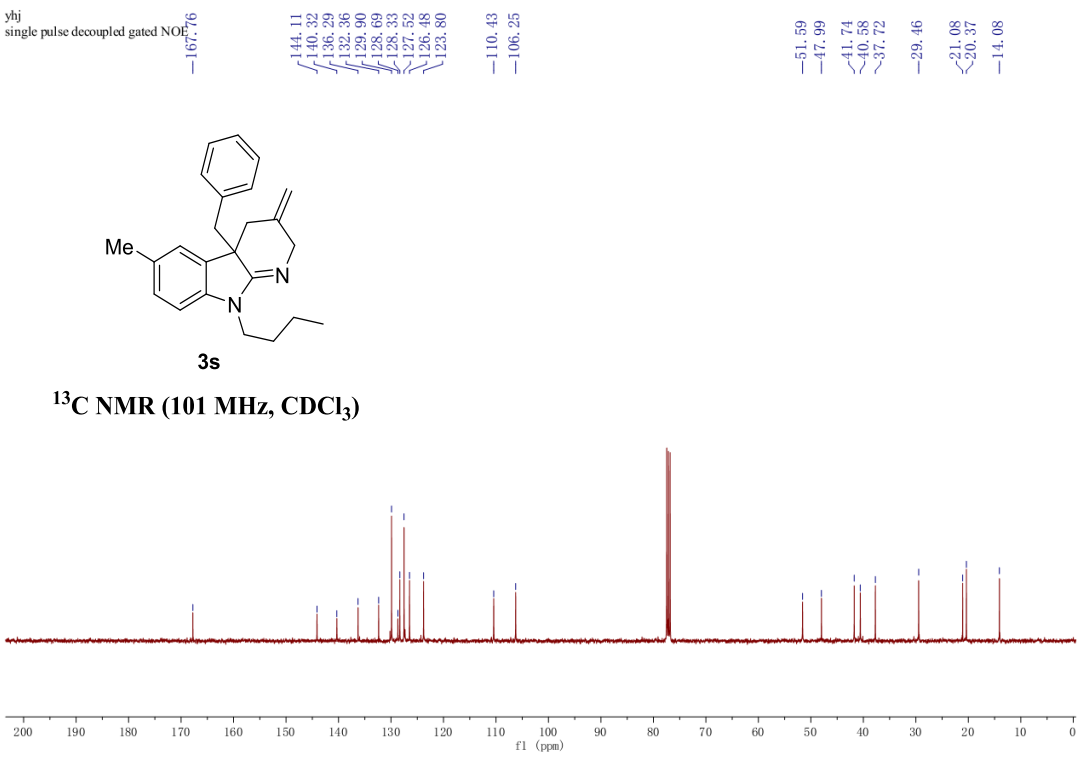
^{13}C NMR (101 MHz, $CDCl_3$)


yhj
single_pulse
F3C
N
N
Me
3r
1H NMR (400 MHz, CDCl3)

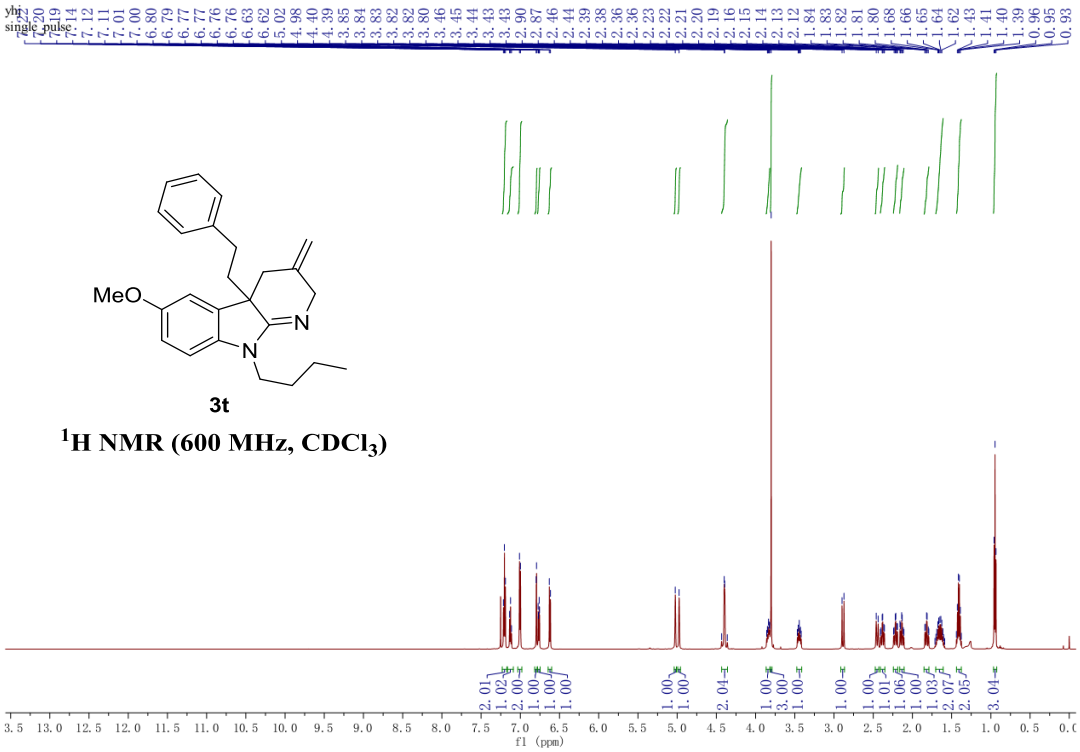

PF20181225-6-1
single pulse decoupled gated NOE
F3C
N
N
Me
3r
13C NMR (101 MHz, CDCl3)



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

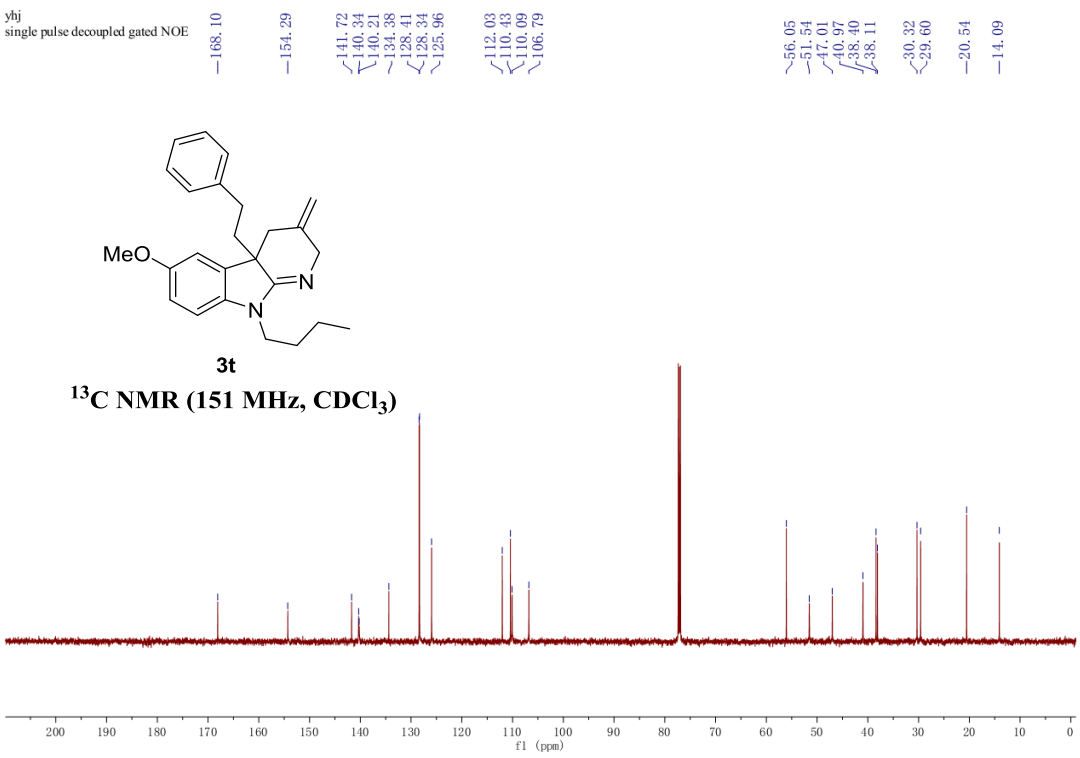


^{13}C NMR (101 MHz, $CDCl_3$)



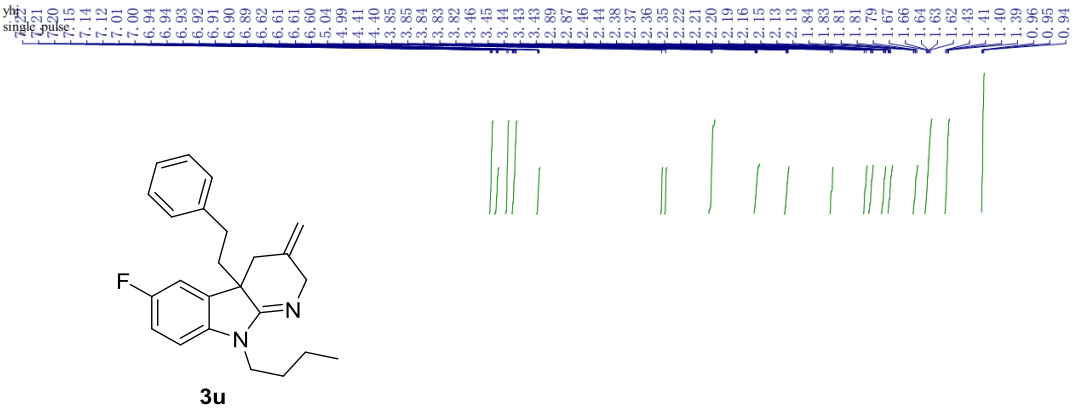
3t

^{1}H NMR (600 MHz, $CDCl_3$)



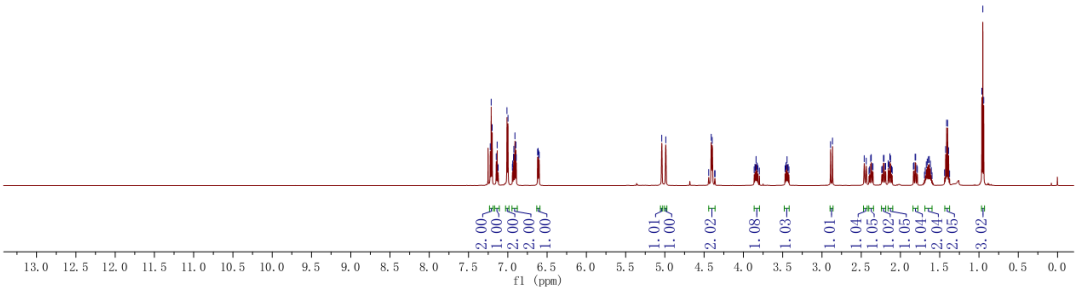
3t

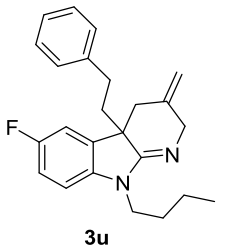
^{13}C NMR (151 MHz, $CDCl_3$)



3u

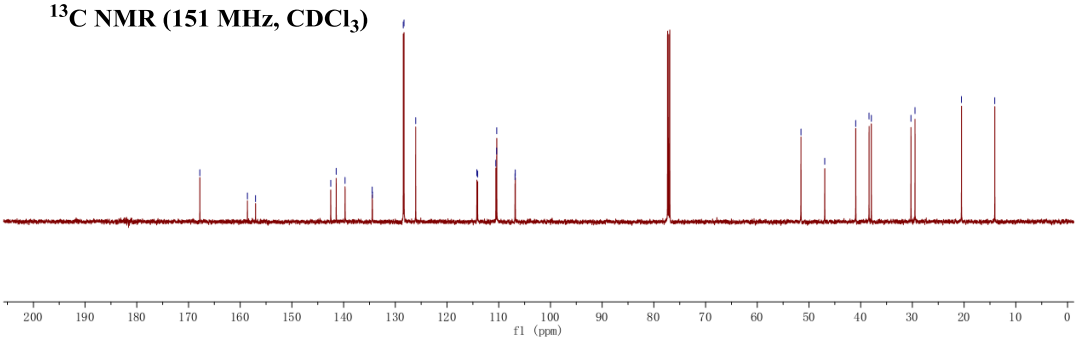
^{1}H NMR (600 MHz, $CDCl_3$)

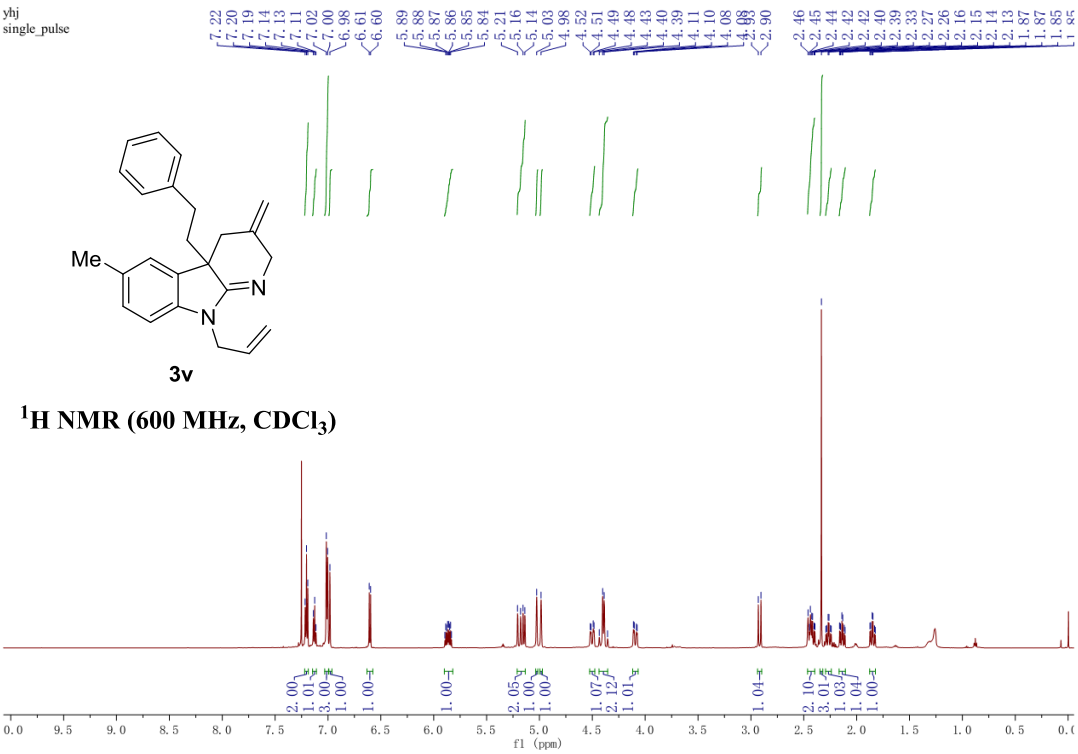




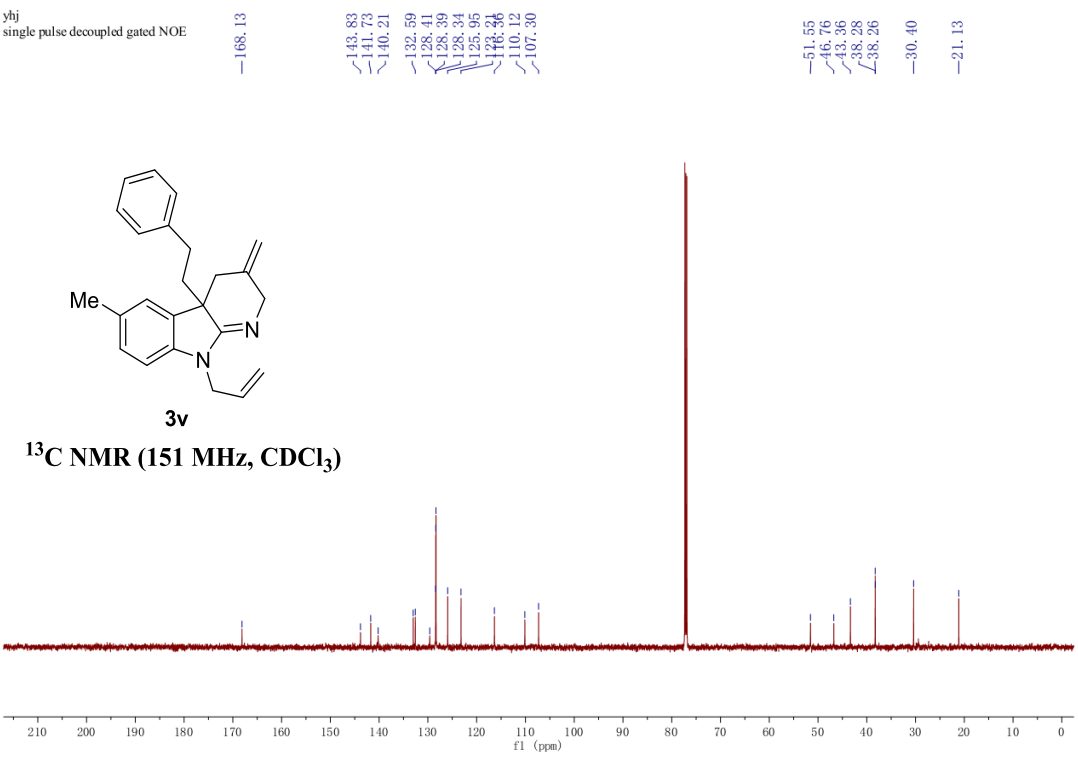
3u

^{13}C NMR (151 MHz, $CDCl_3$)

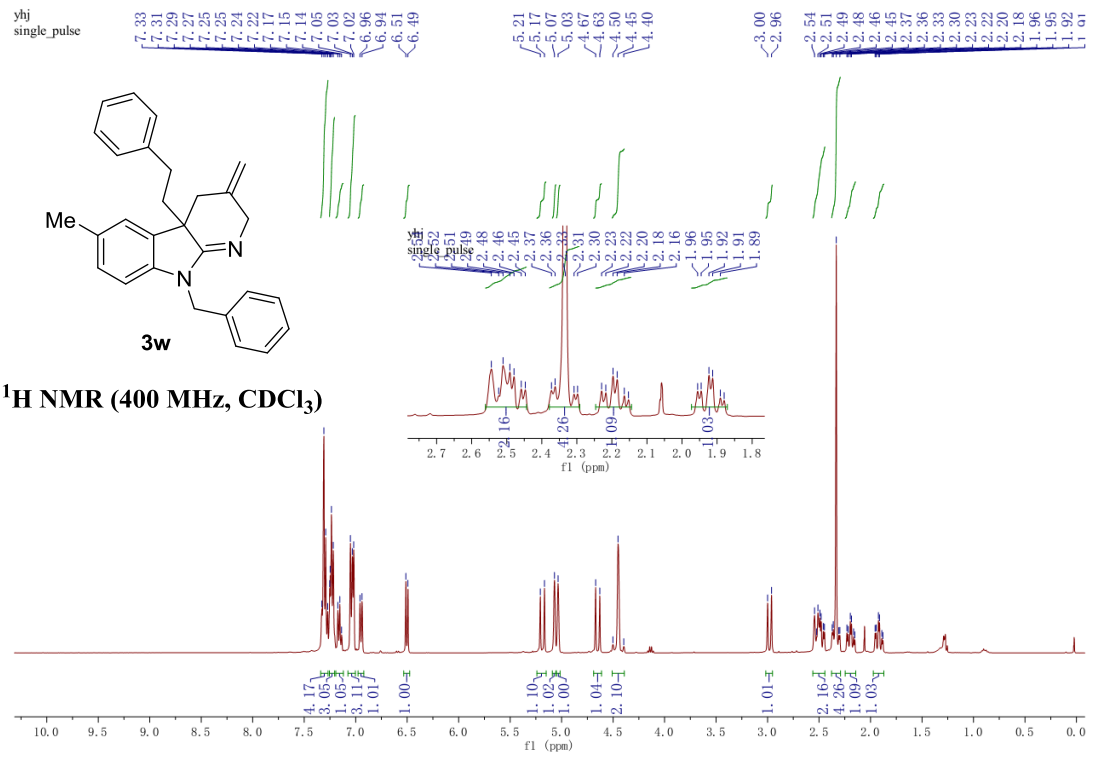




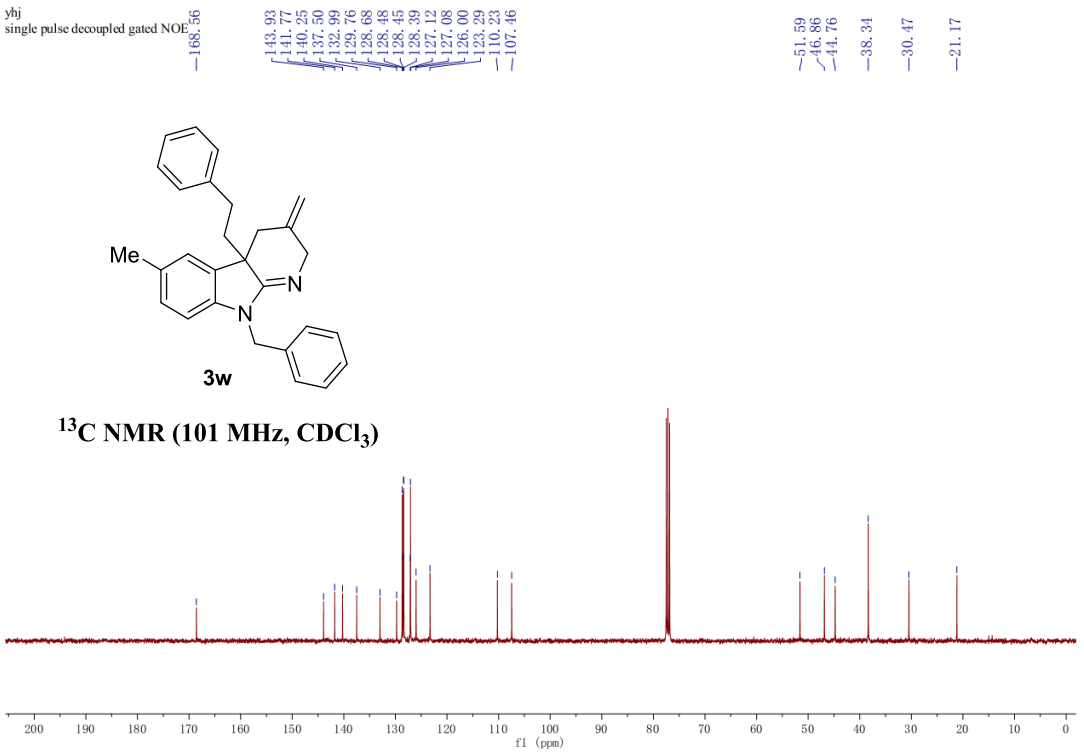
^{1}H NMR (600 MHz, $CDCl_3$)



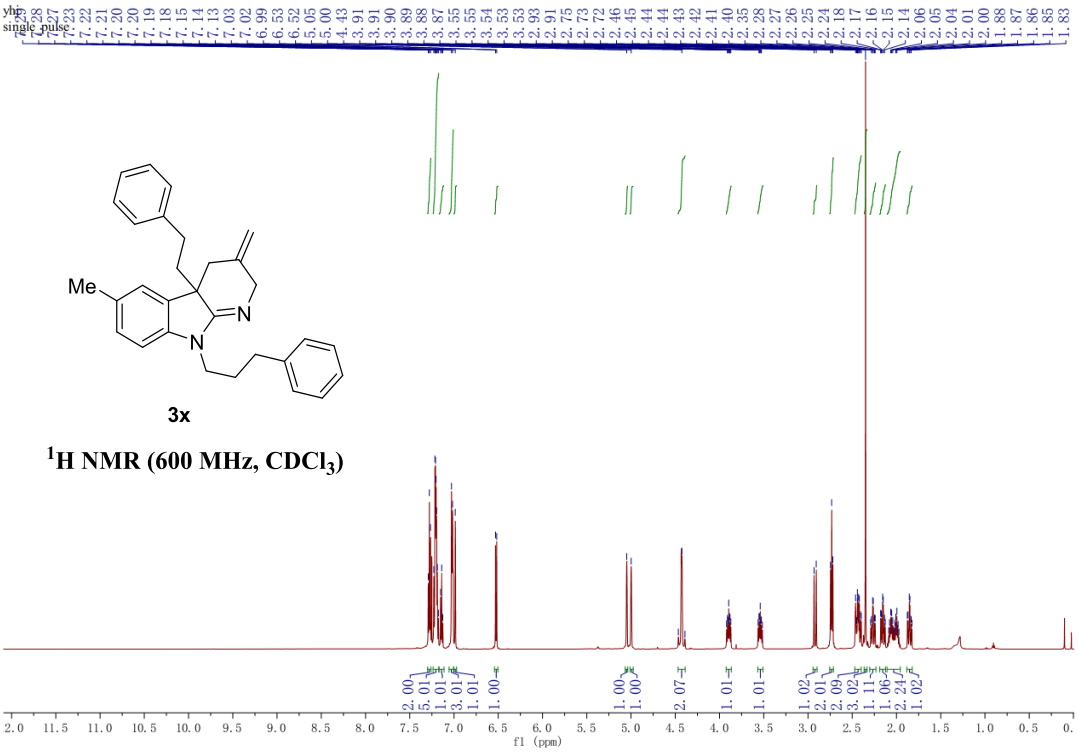
^{13}C NMR (151 MHz, $CDCl_3$)



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

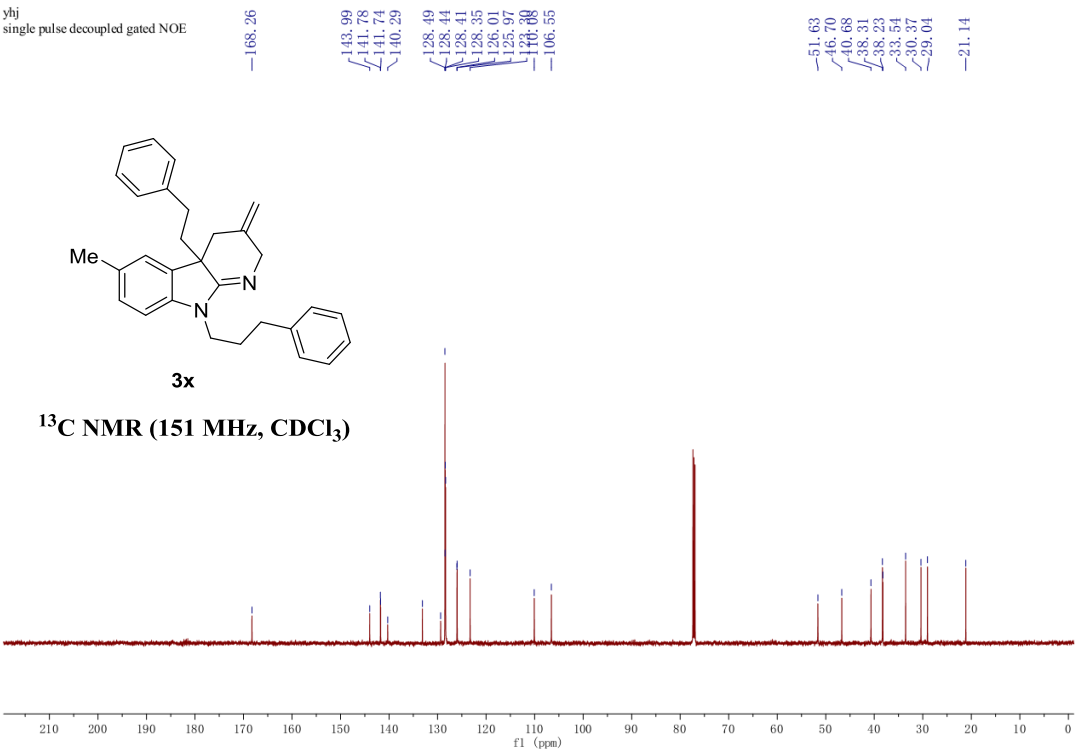


^{13}C NMR (101 MHz, $CDCl_3$)



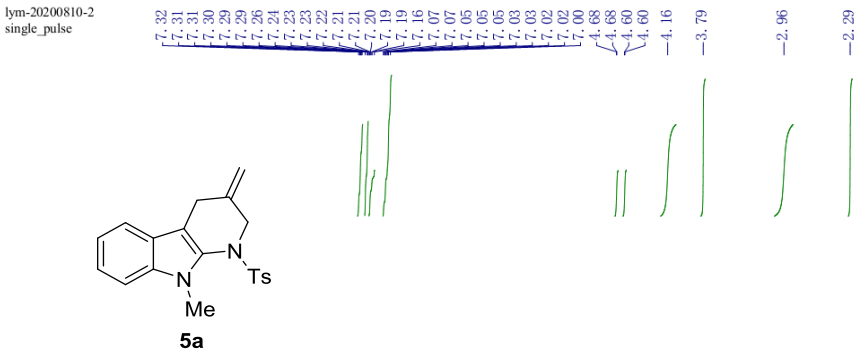
3x

^{1}H NMR (600 MHz, $CDCl_3$)



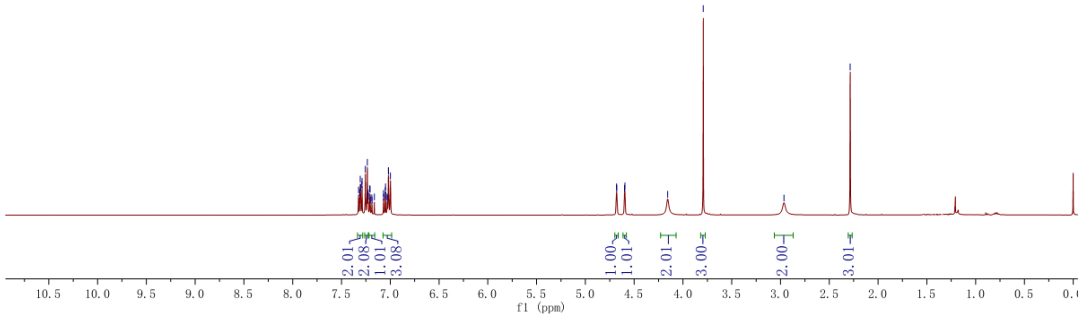
3x

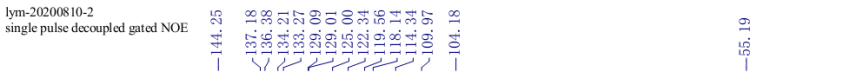
^{13}C NMR (151 MHz, $CDCl_3$)



5a

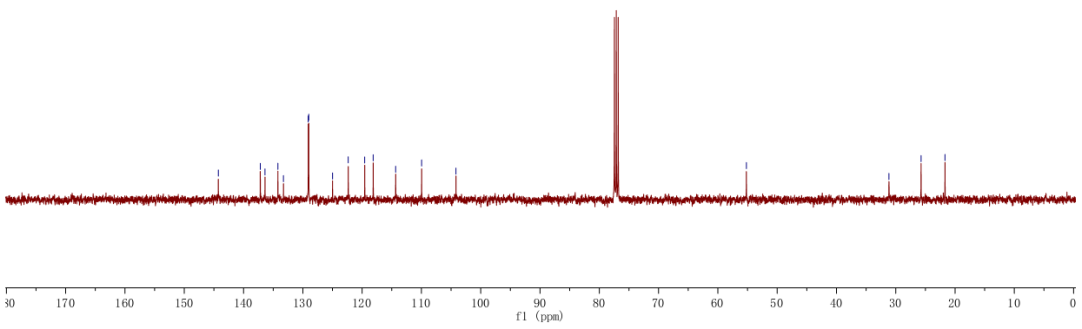
^{1}H NMR (400 MHz, $CDCl_3$)





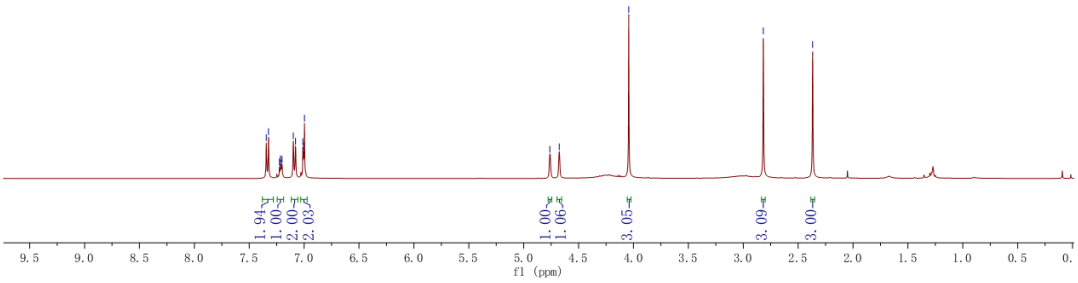
5a

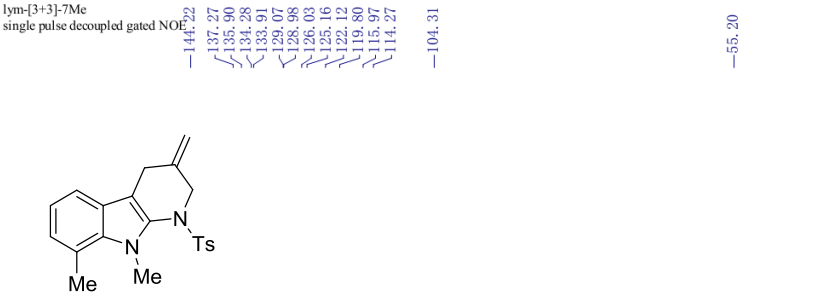
^{13}C NMR (101 MHz, $CDCl_3$)



5b

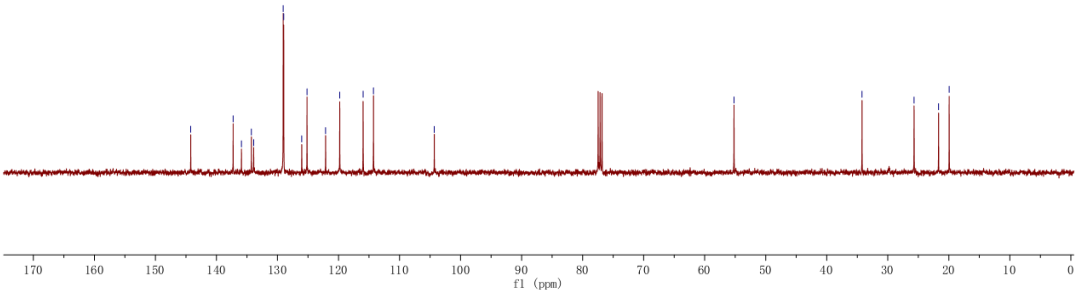
^{1}H NMR (400 MHz, $CDCl_3$)

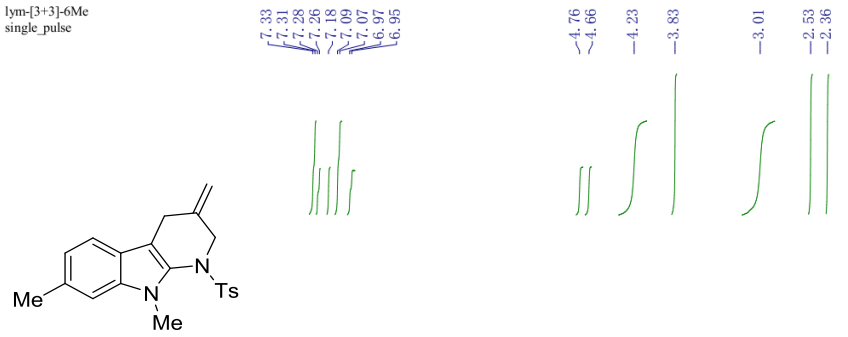




5b

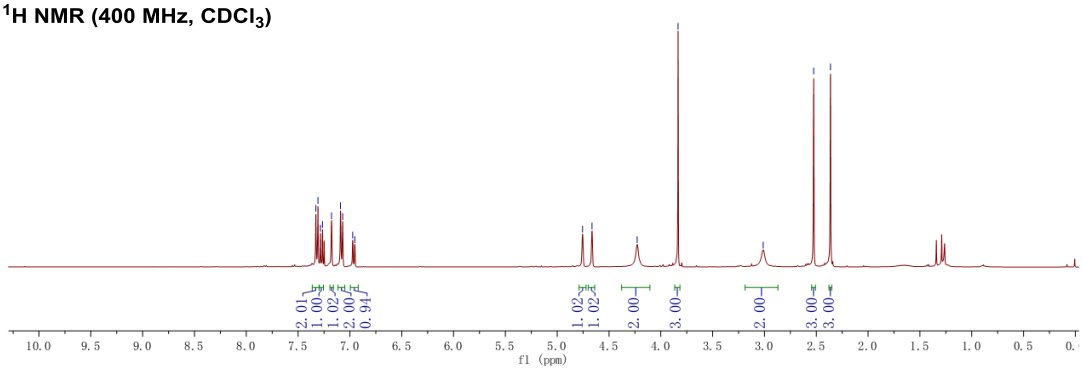
^{13}C NMR (101 MHz, $CDCl_3$)

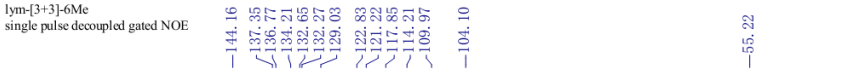


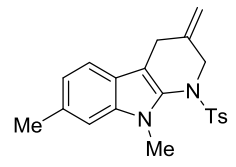


5c

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

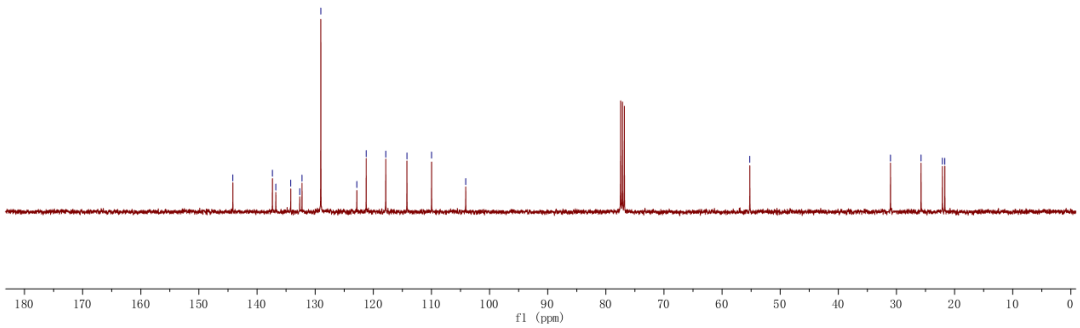




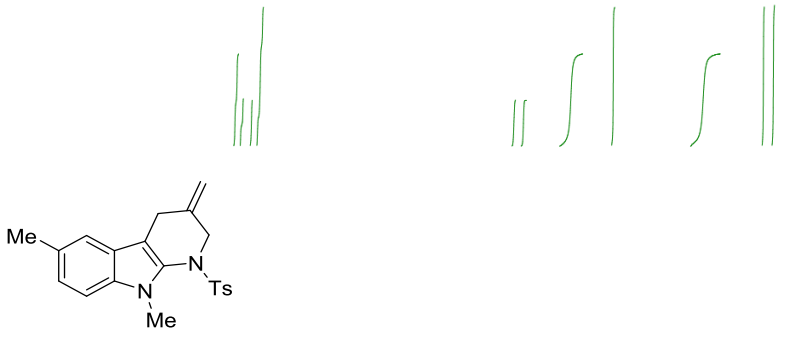


5c

^{13}C NMR (101 MHz, $CDCl_3$)

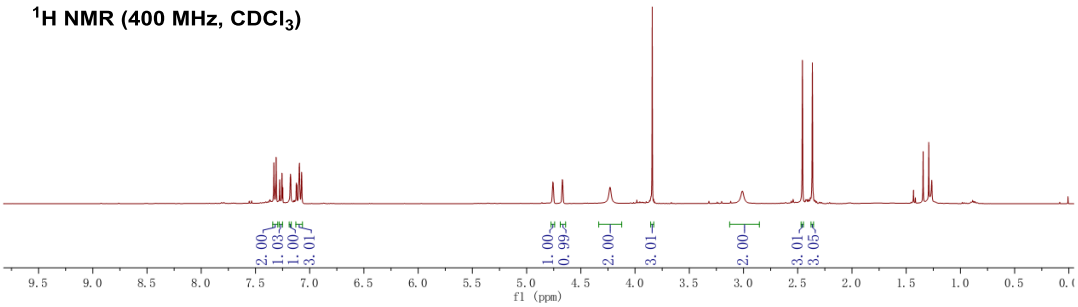


lym-[3+3]-5Me
single_pulse



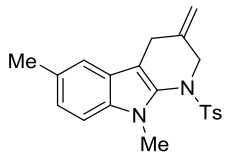
5d

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



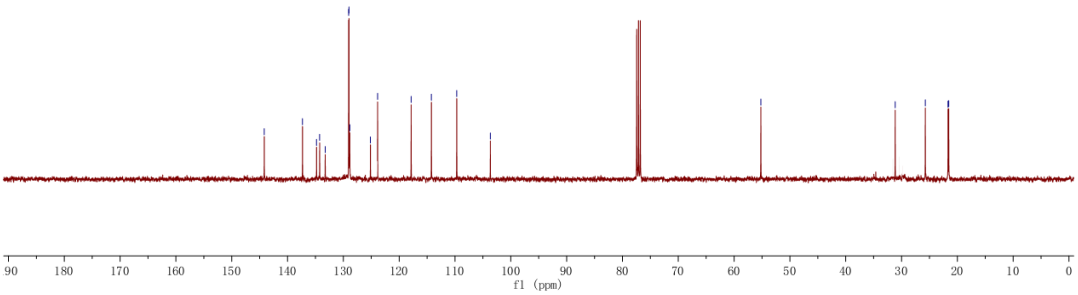
lym-[3+3]-5Me
single pulse decoupled gated NOE

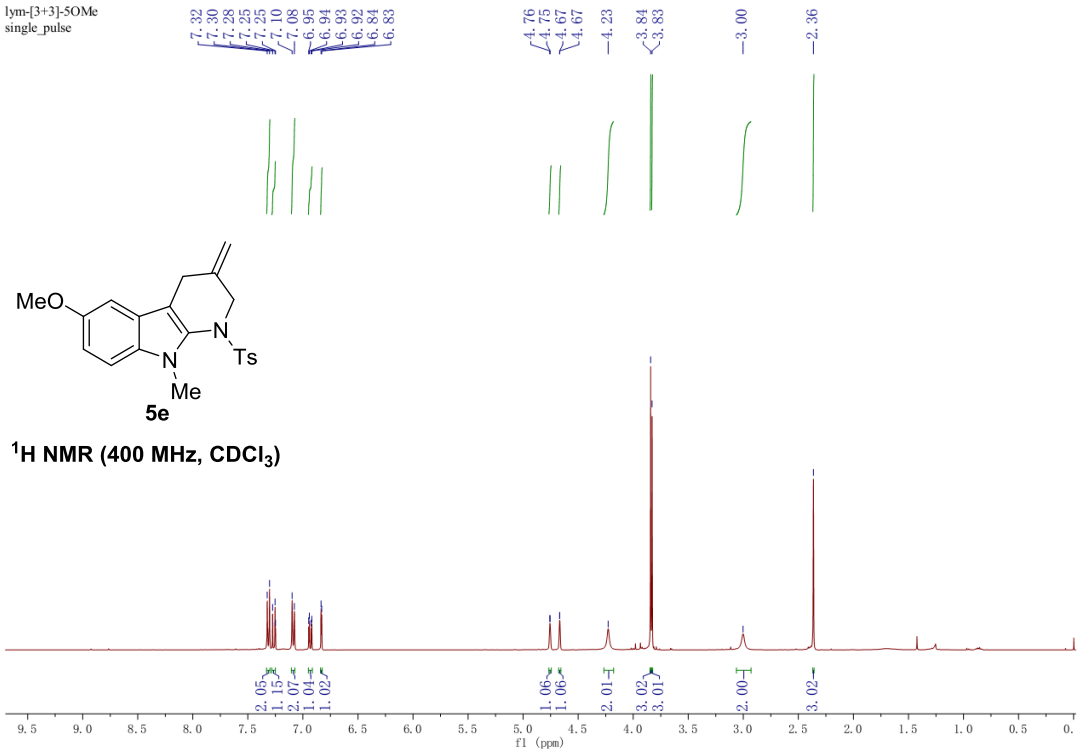
144.17
137.32
134.80
134.25
129.05
128.99
128.85
125.16
114.23
109.69
103.67
55.20
31.14
25.75
21.67
21.55



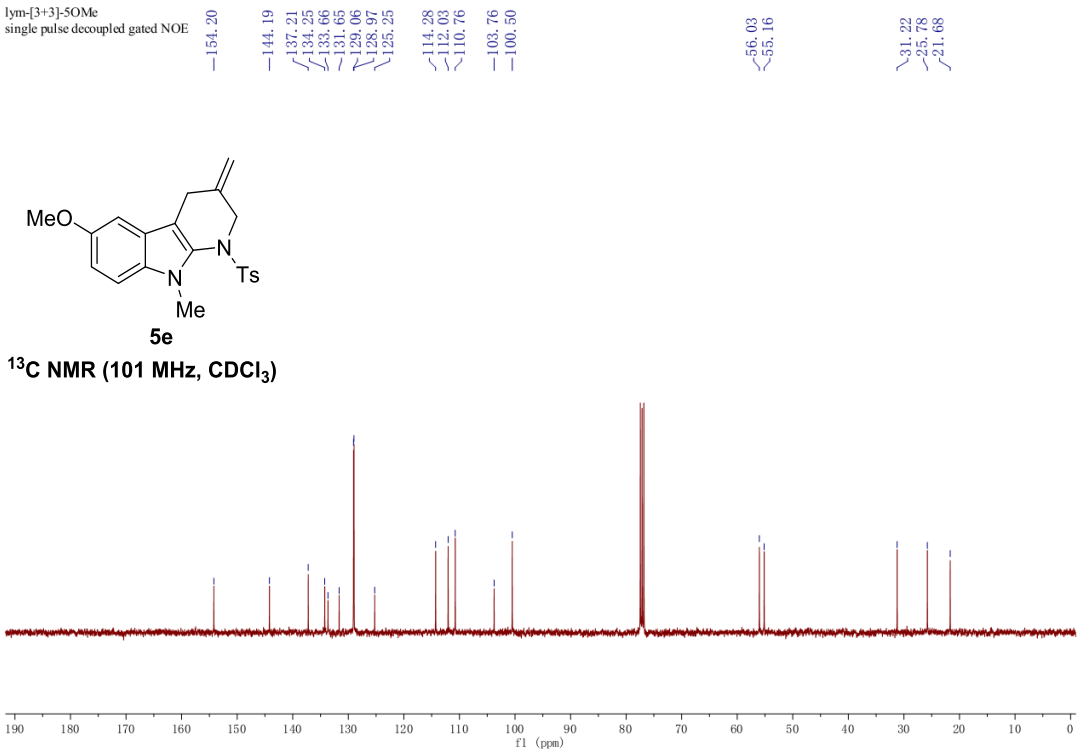
5d

^{13}C NMR (101 MHz, $CDCl_3$)

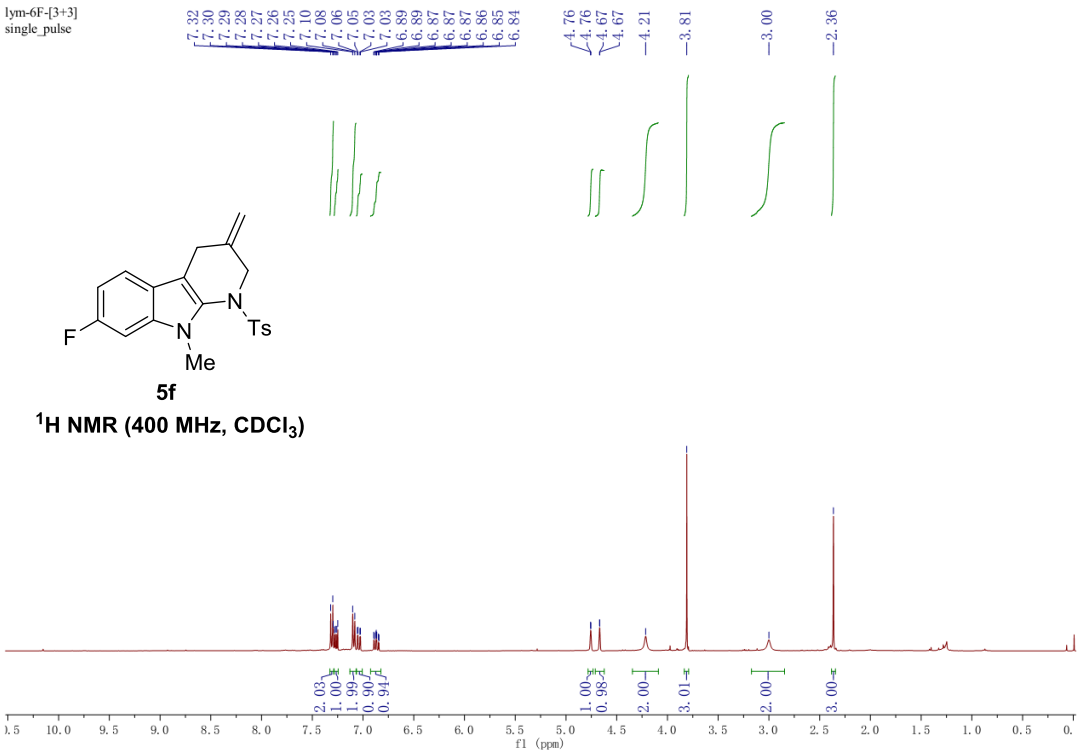




^{1}H NMR (400 MHz, $CDCl_3$)

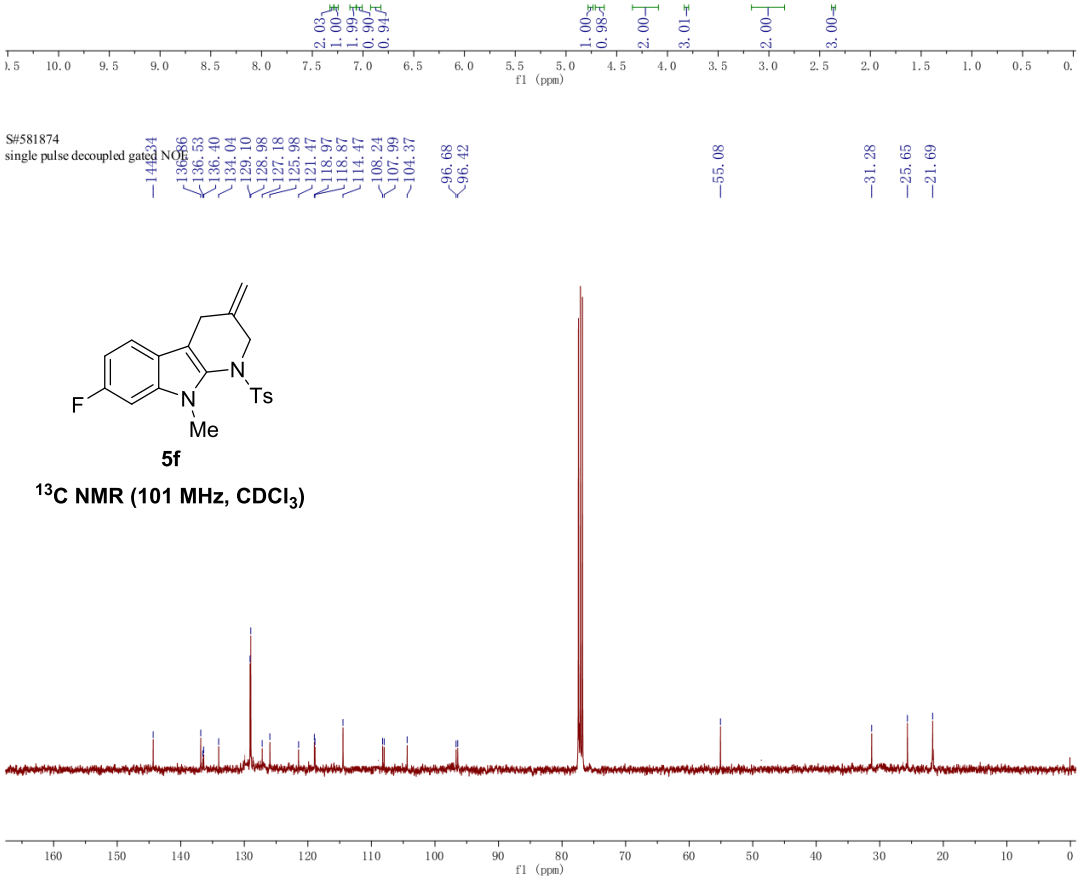


^{13}C NMR (101 MHz, $CDCl_3$)



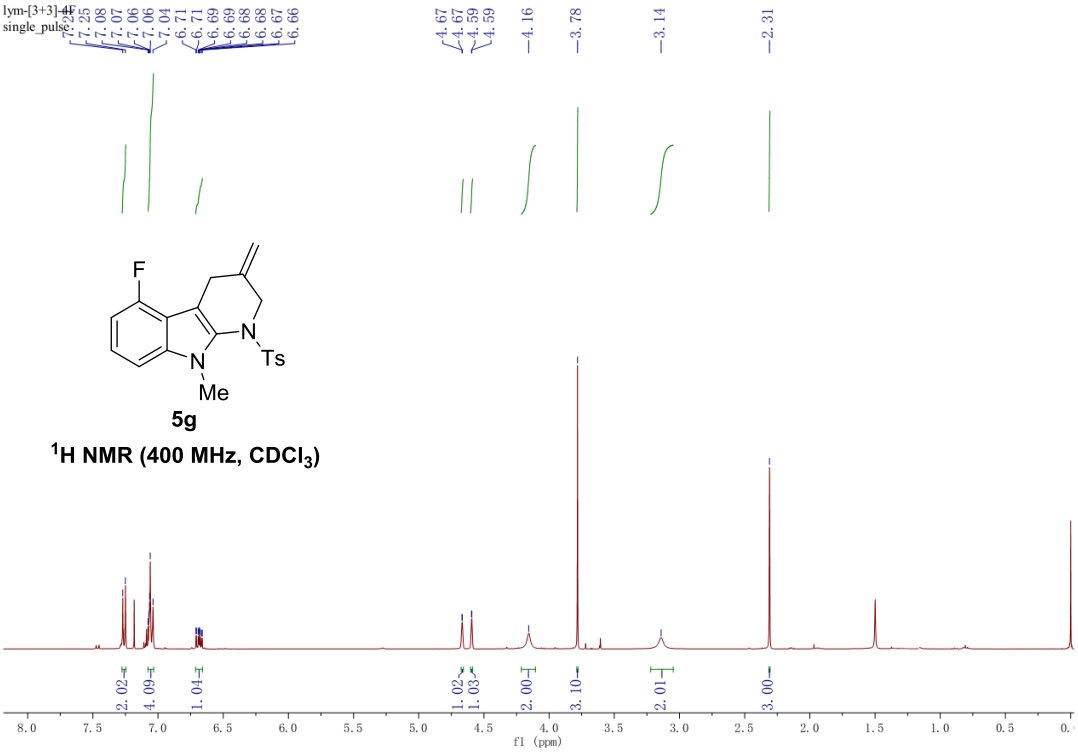
5f

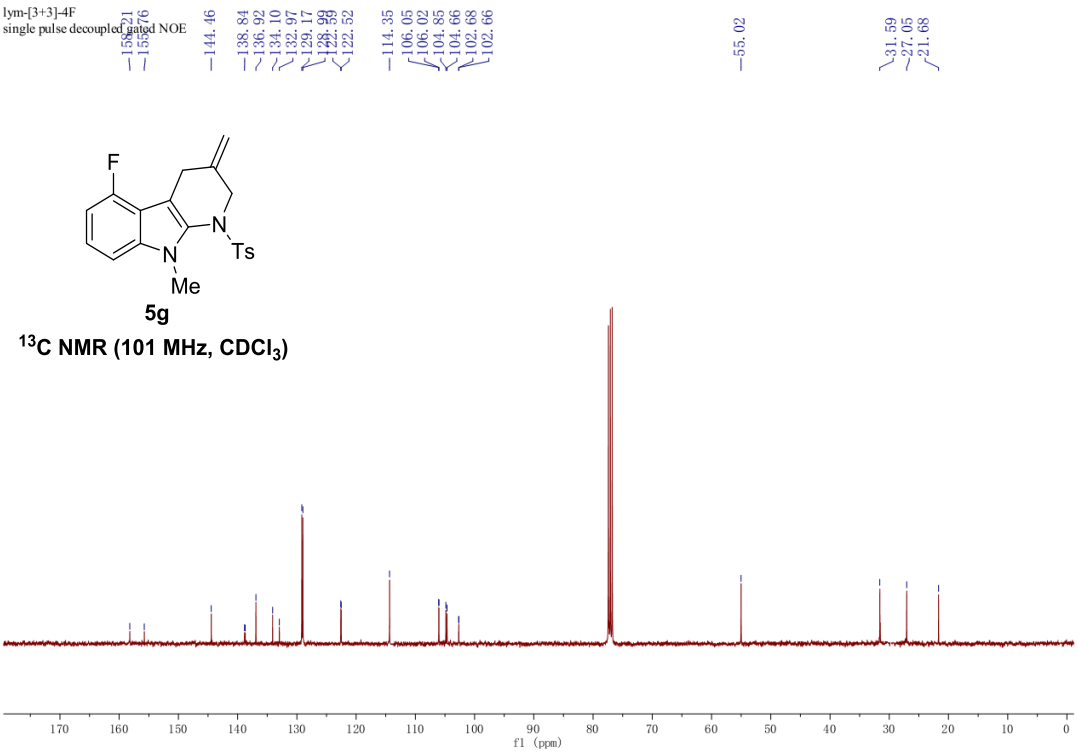
^{1}H NMR (400 MHz, $CDCl_3$)

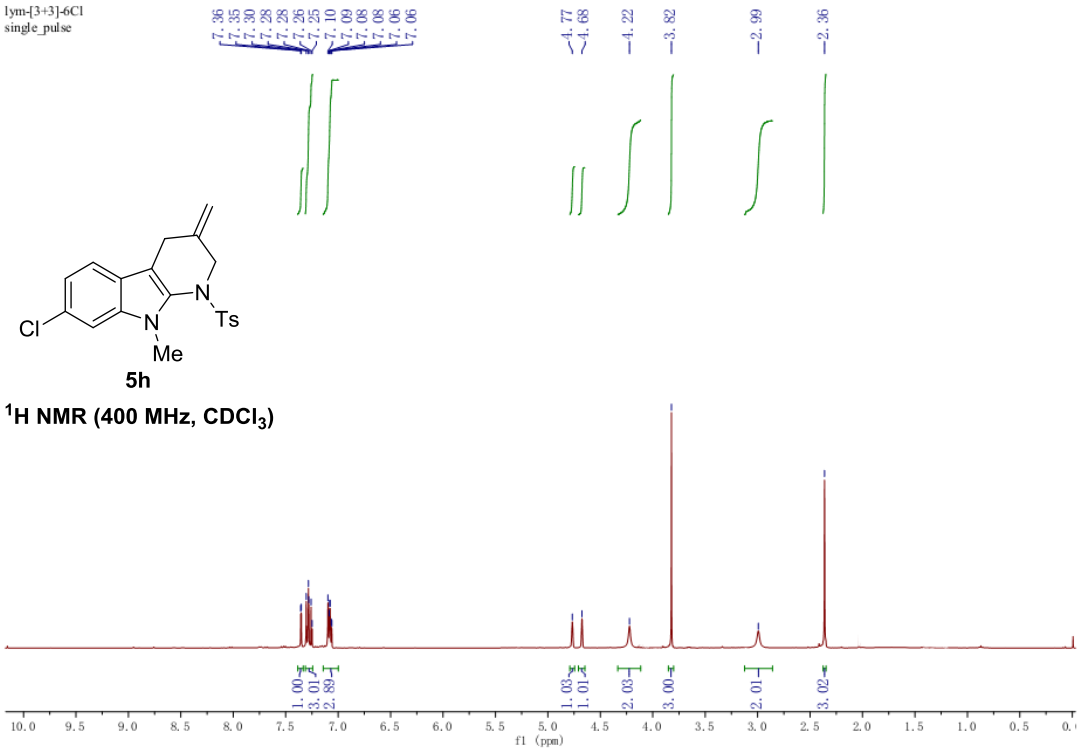


5f

^{13}C NMR (101 MHz, $CDCl_3$)

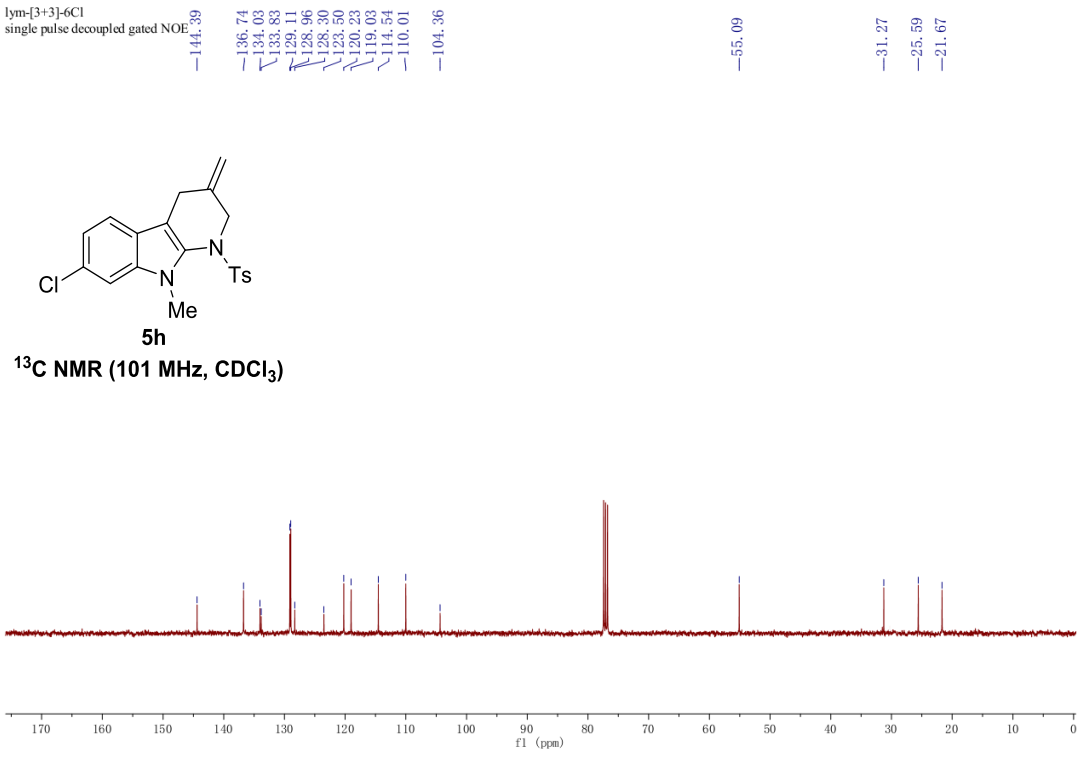

lym-[3+3]-4F
single_pulse
F
N
Ts
N
Me
5g
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


lym-[3+3]-4F
single pulse decoupled gated NOE
F
N
Ts
N
Me
5g
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)



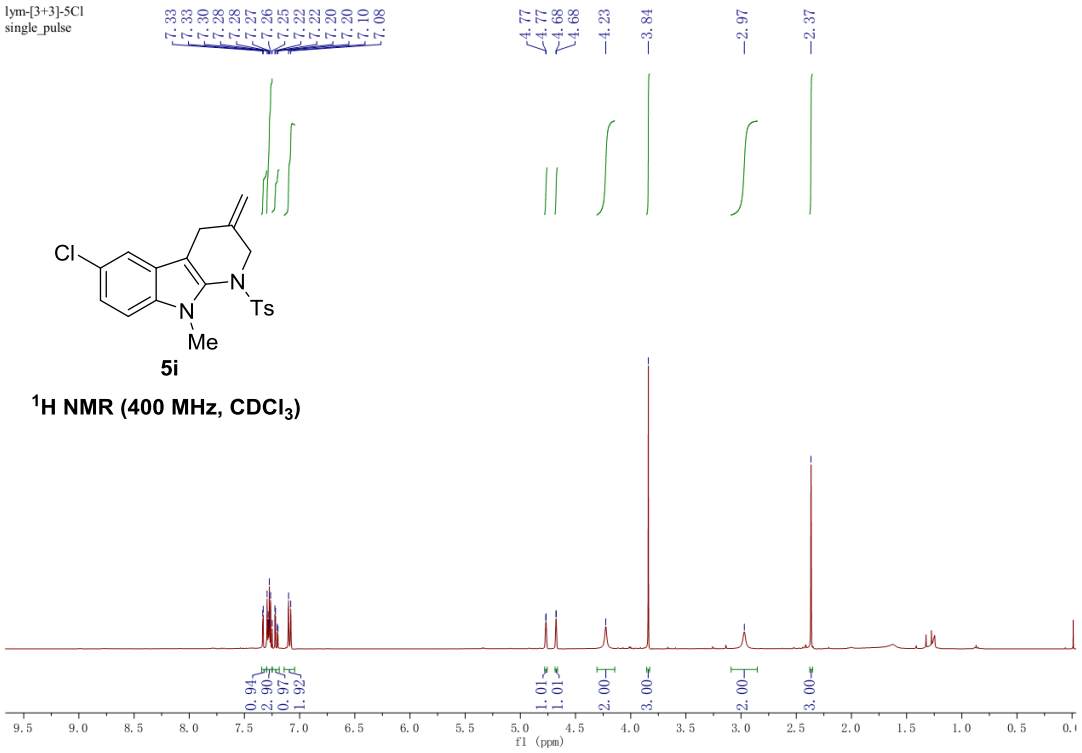
5h

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



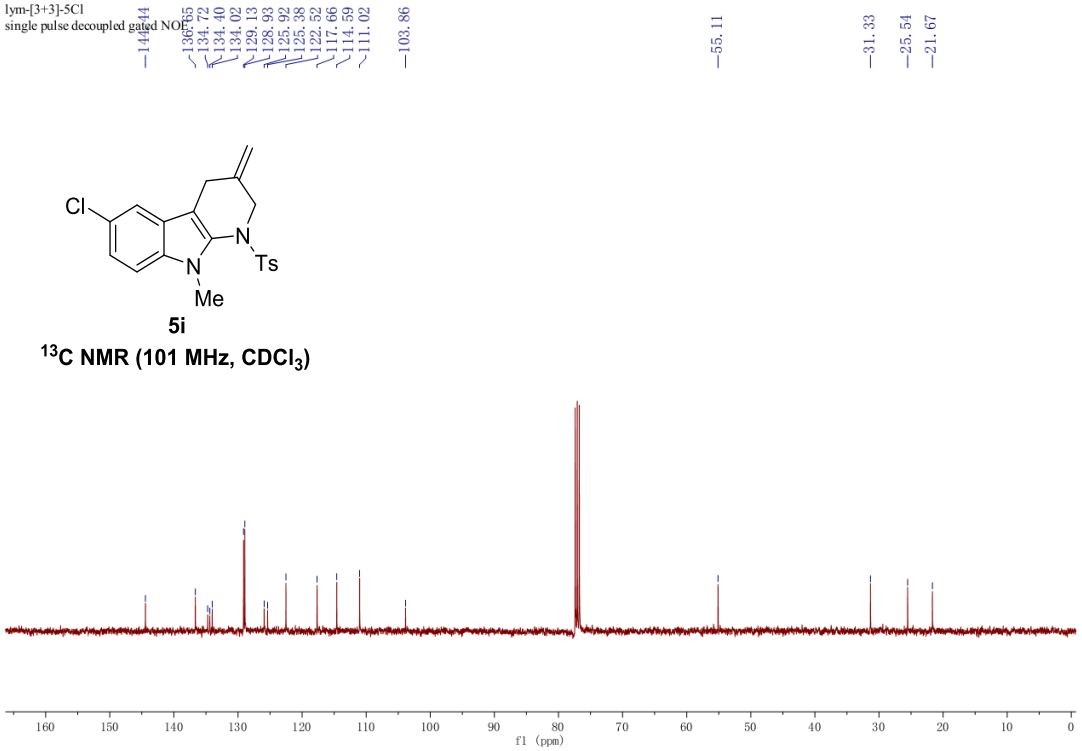
5h

^{13}C NMR (101 MHz, $CDCl_3$)



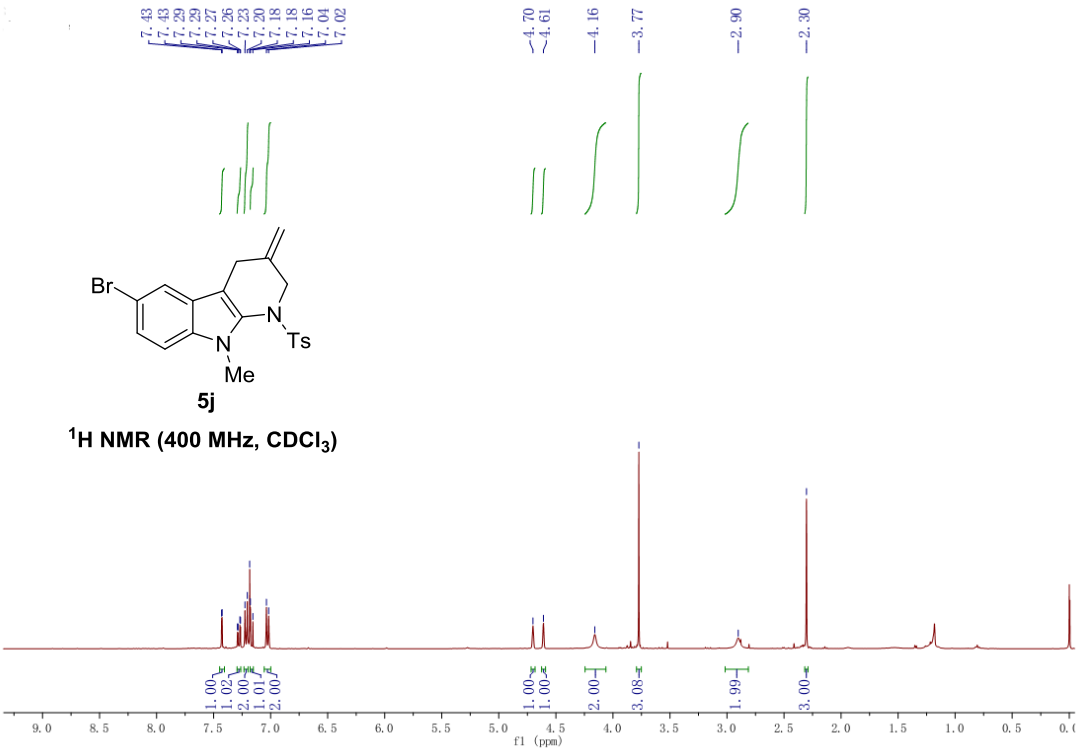
5i

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



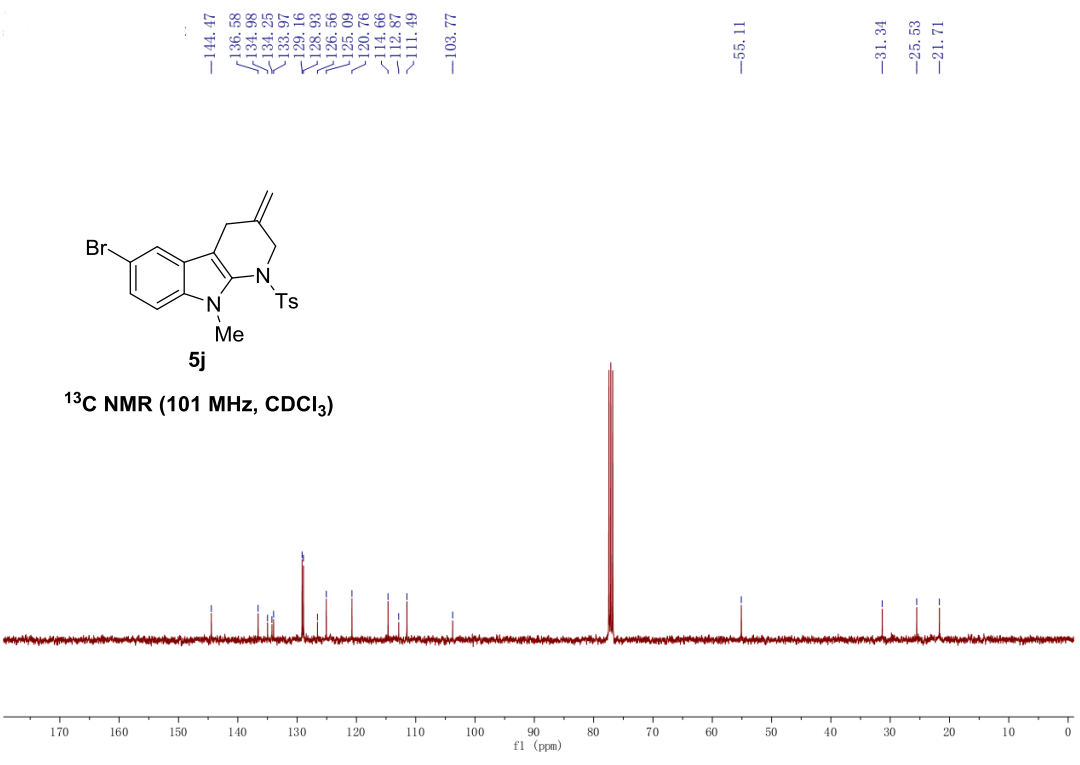
5i

^{13}C NMR (101 MHz, $CDCl_3$)



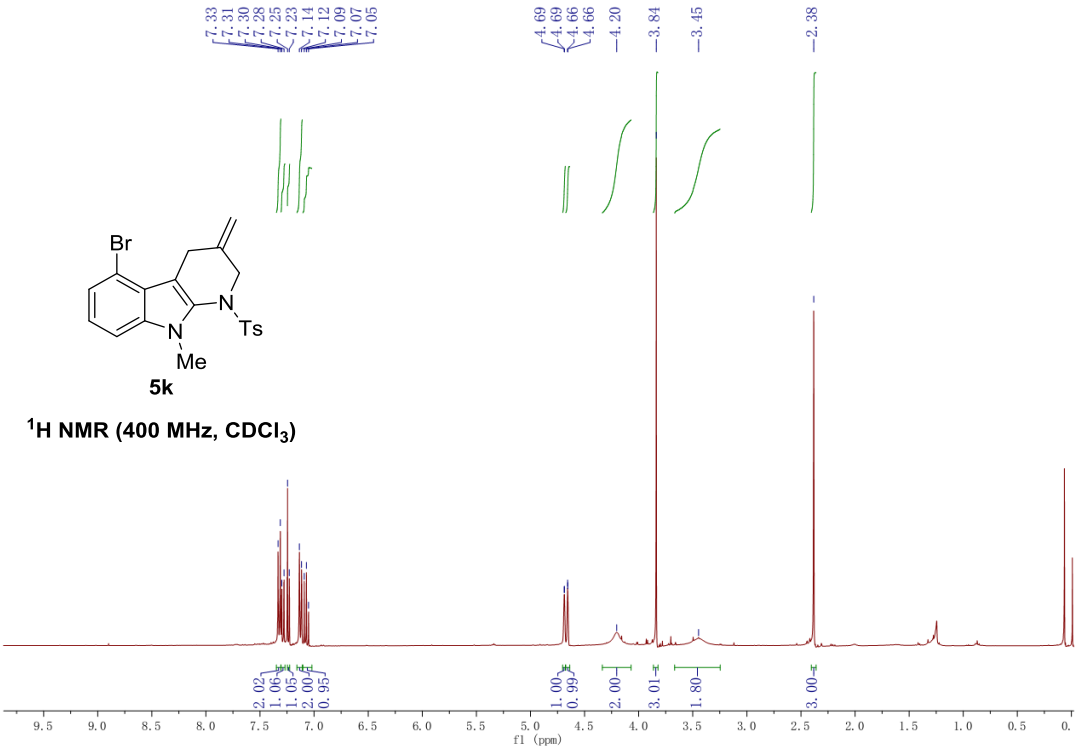
5j

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



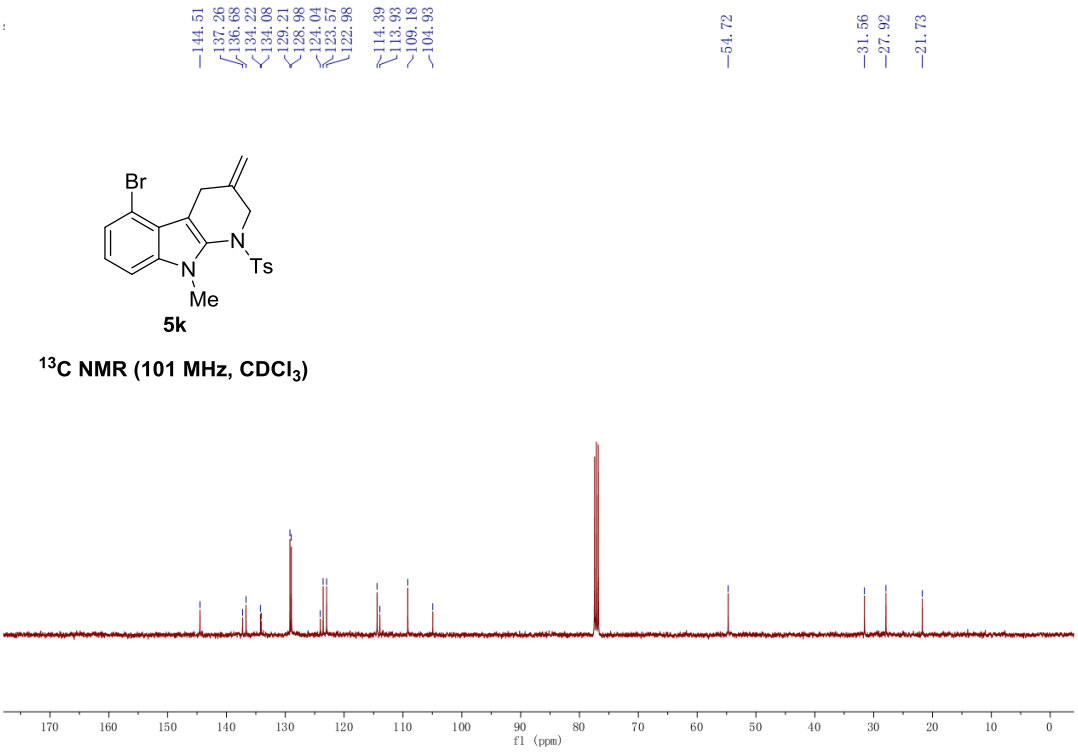
5j

^{13}C NMR (101 MHz, $CDCl_3$)



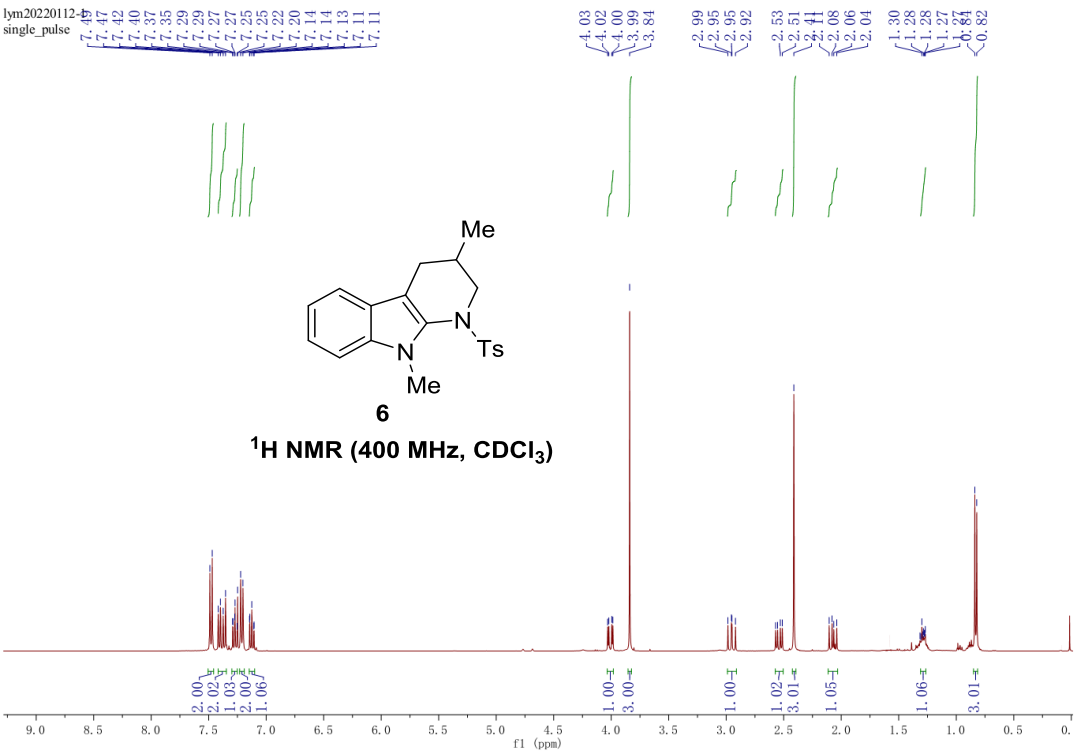
5k

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



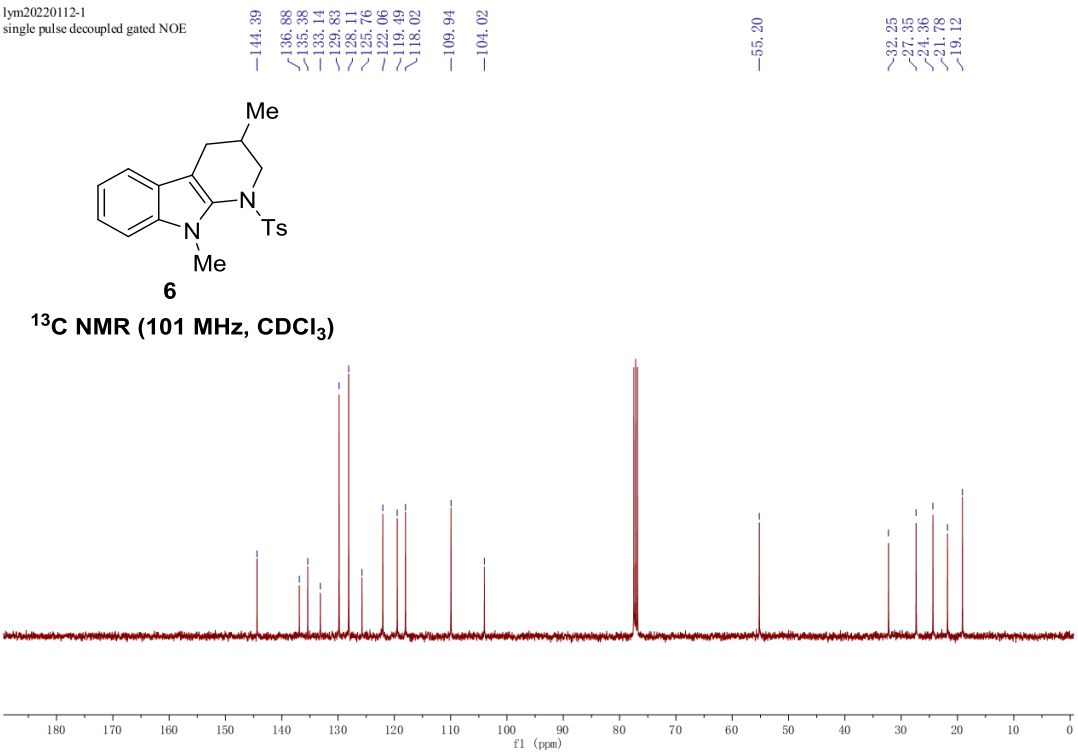
5k

^{13}C NMR (101 MHz, $CDCl_3$)



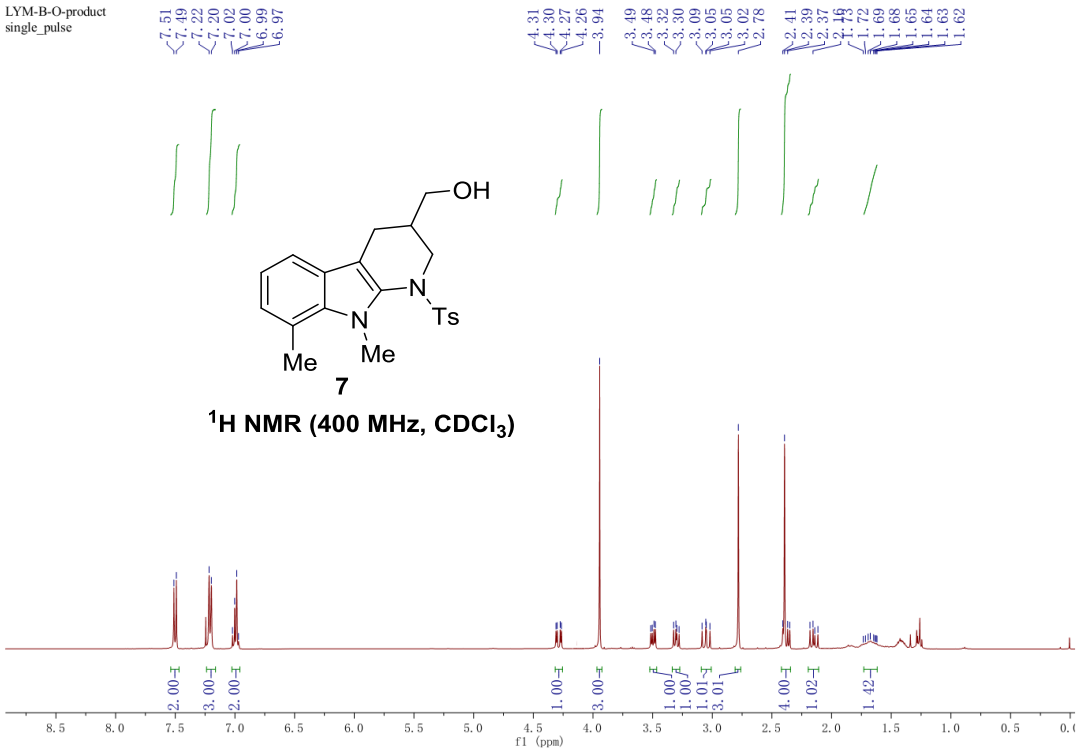
6

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



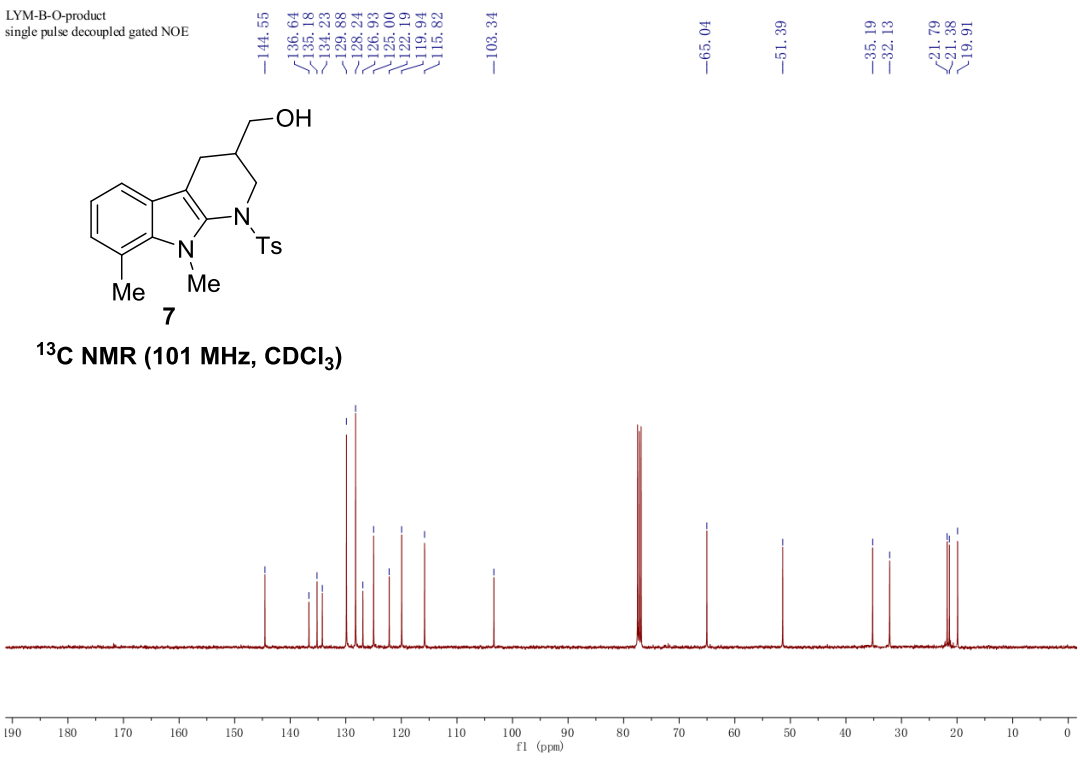
6

^{13}C NMR (101 MHz, $CDCl_3$)



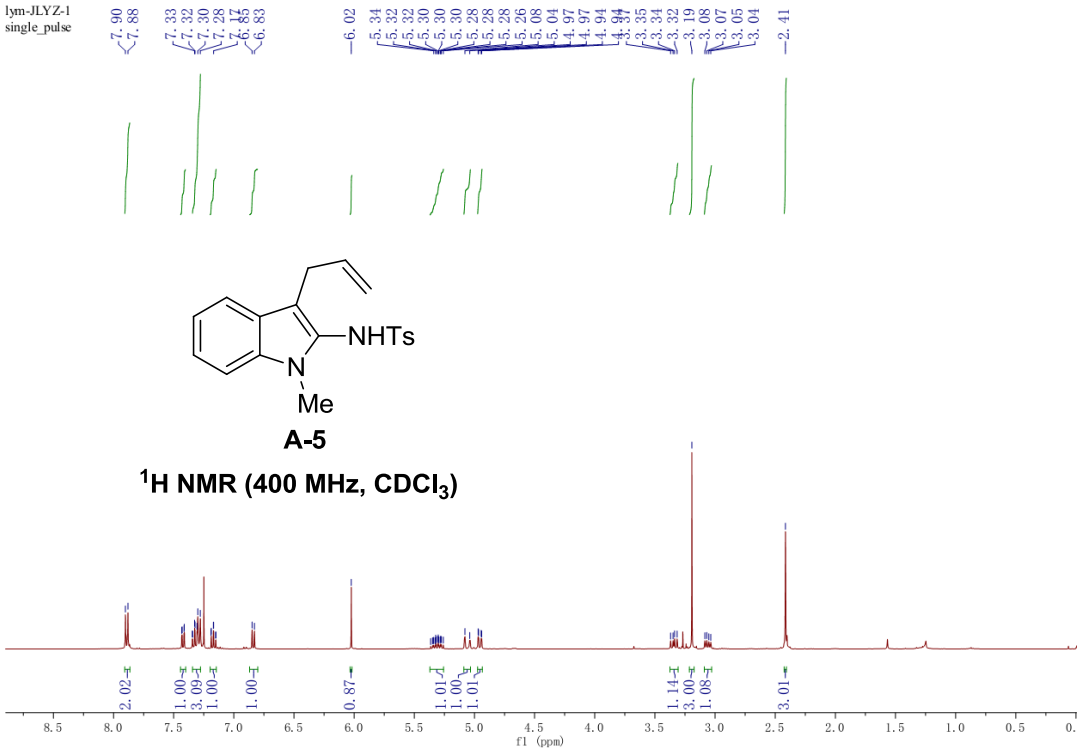
7

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



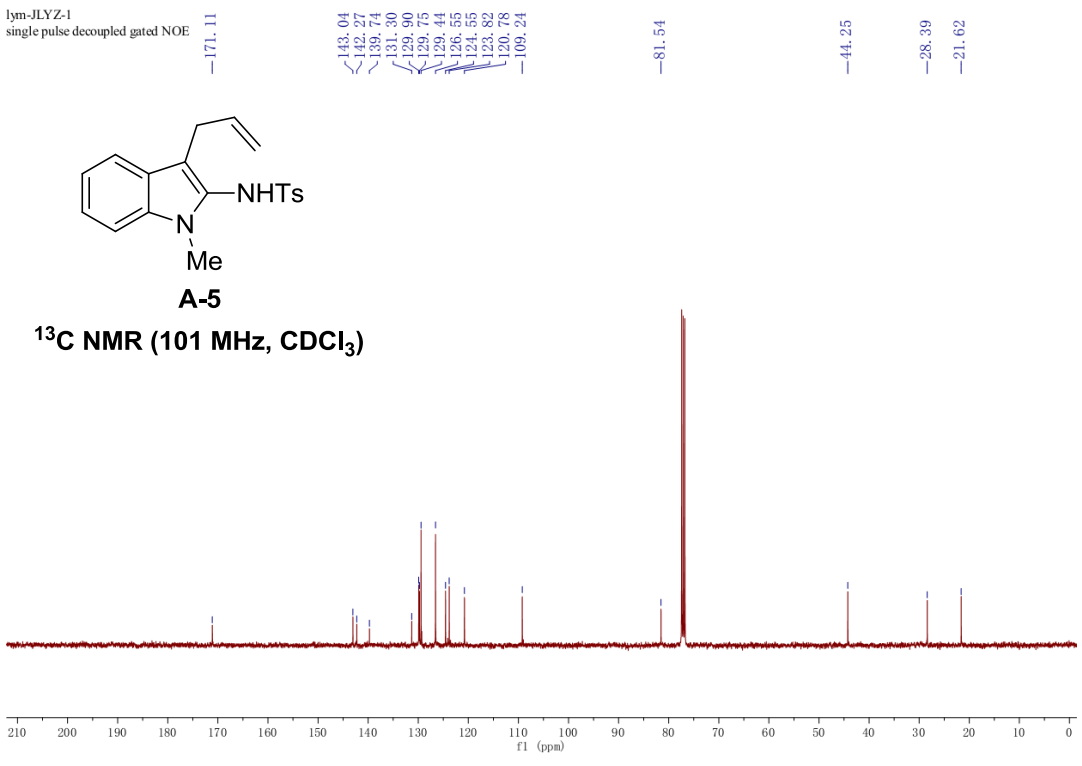
7

^{13}C NMR (101 MHz, $CDCl_3$)



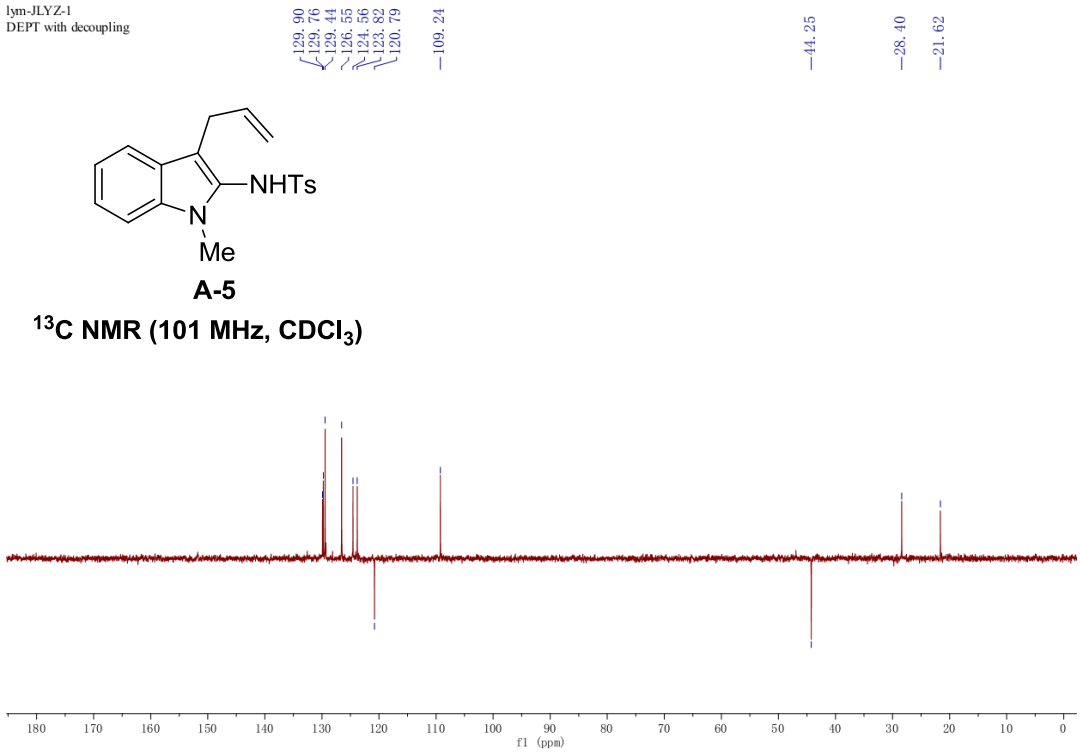
A-5

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



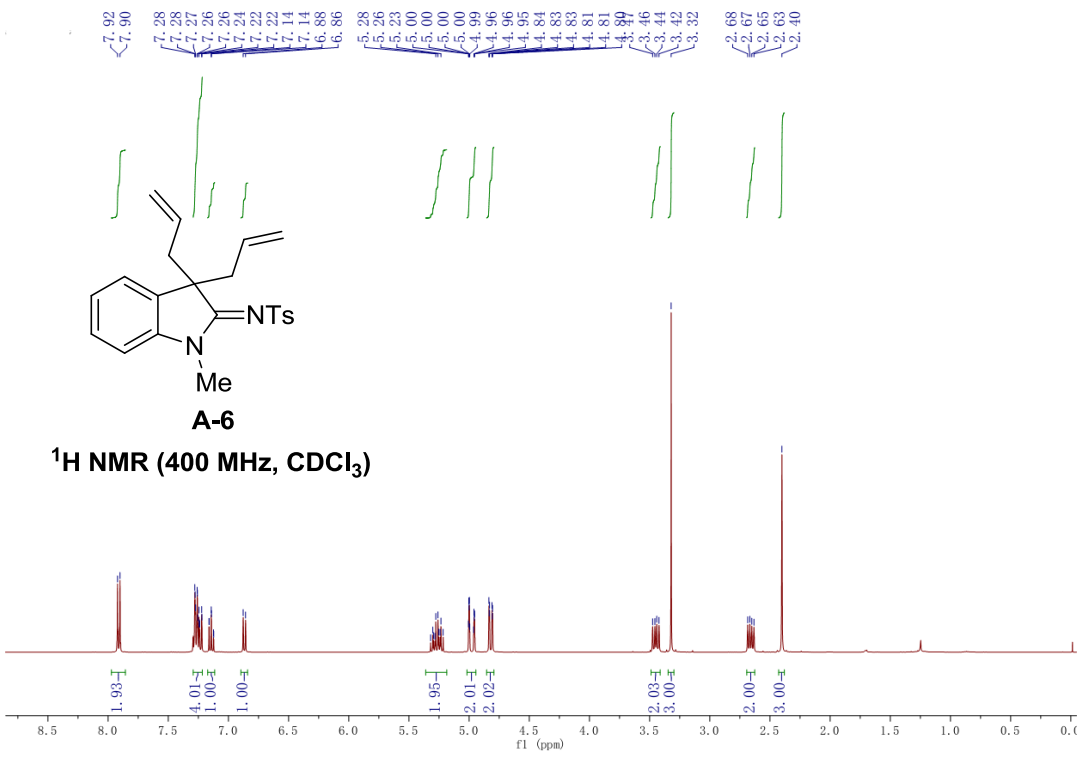
A-5

^{13}C NMR (101 MHz, $CDCl_3$)



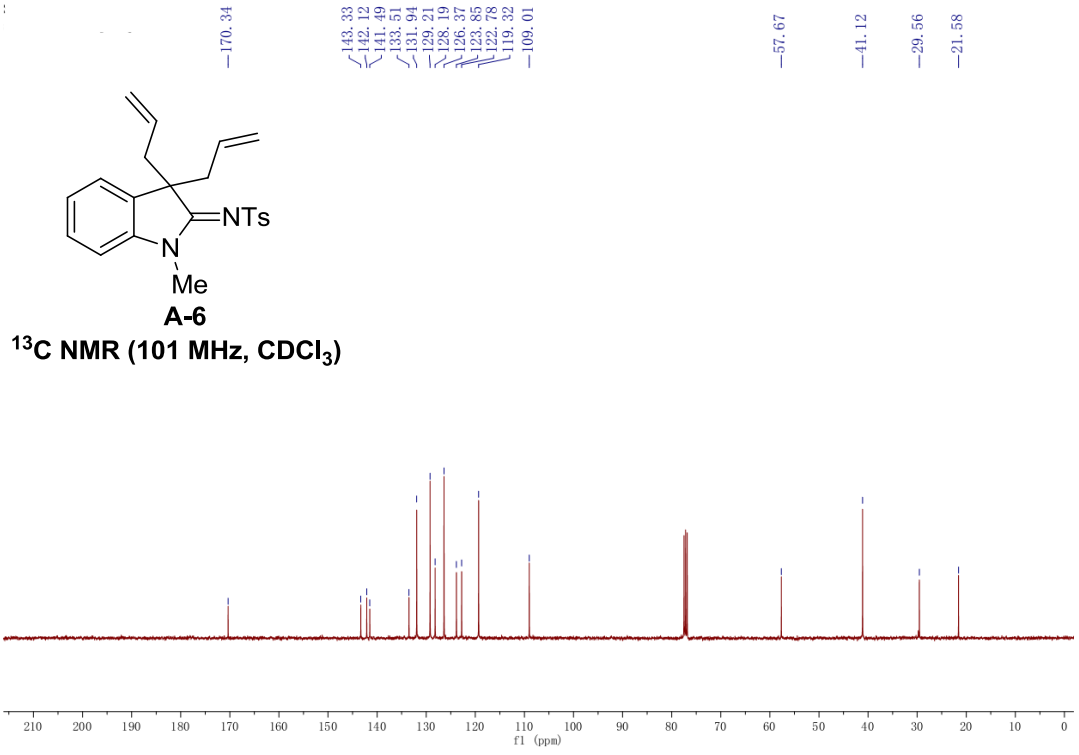
A-5

^{13}C NMR (101 MHz, $CDCl_3$)



A-6

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



A-6

^{13}C NMR (101 MHz, $CDCl_3$)