Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Palladium-Catalyzed Intramoecular Aerobic Oxidative Alkenlhydroxylation of Allenamides via Molecular Oxygen Activation

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Supporting Information

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I. General Information

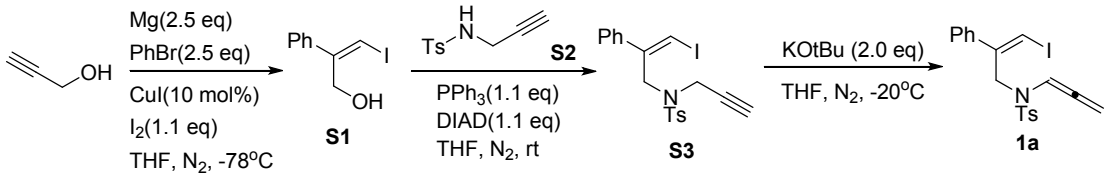
Organic solvents (Aldrich) were used without further purification. Purifications of reactions productswere carried out by flash chromatography using Merck silica gel (40-63 μm).

NMR spectra were recorded on a AVANCE Ⅲ HD 400MHz spectrometer [^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz)]. Chemical shifts for 1H NMR are reported in parts per million (δ) relative to methylbenzenesulfonyl as the internal standard. Coupling constant (*J*) are reported in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. Chemical shifts for ^{13}C NMR are reported in parts per million (δ) relative to the solvent ($CDCl_3$, δ 77.16 and DMSO-d_6 δ 39.6).

All commercially available reagents were bought from Macklin, Aladdin and used without further purification. Dry THF was steamed with metal sodium. Tri-2,4-xylylphosphine and AgF were directly purchased from Aladdin. Structure **1a** and **1p** are known compounds and were prepared according to reported procedures and other substrates are synthesized in same way.

Reactions were conducted in dry solvents under Nitrogen atmosphere unless otherwise stated. The abbreviation “rt” refers to reactions carried out approximately at 23-27ºC. Reaction mixtures were stirred using Teflon-coated Magnetic stirring rotor. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4 or $MgSO_4$. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator, followed by residual solvent removal under high vacuum. The reactions were monitored by tlc or **GC-MS**.

II. The General Synthetic Procedure and Analytical Data for Compounds 1a-1t.



General Procedure:

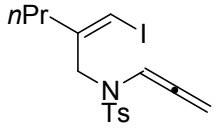
Firstly, prepare phenyl Grignard reagent. In a 250 ml three-necked flask, 3 g magnesium shavings (2.5 equiv, 125 mmol) was added. Anhydrous tetrahydrofuran was added until it just exceeded the magnesium turnings.0.3 ml bromobenzene was injected once with a syringe and heated by a hair dryer until the solution became cloudy and bubbles appeared, indicating that the format reagent was successfully initiated.13 ml (2.5 equiv, 125 mmol) of bromobenzene in 100 ml of THF was slowly added dropwise through a 150 ml dropping funnel, and the reaction solution was kept under reflux by adjusting the dropping rate. After the completion of the dropwise addition, the reaction was stir at room temperature for 2 h until the magnesium turnings exhaust, and a clear solution is obtained. At this time, the Grignard reagent has been prepared, waiting for the next step. In another 500 ml three-necked flask, 2.8 g of propargyl alcohol (1.0 equiv, 50 mmol) was dissolved in 70 ml THF, and 0.95 g of CuI (10 mol%, 5 mmol) was added under stirring, and the whole system was operated under nitrogen atmosphere. The suspension was then cooled to -78 °C. At this time, the freshly prepared Grignard reagent was transferred to a constant pressure dropping funnel under nitrogen protection. With vigorous stirring, the Grignard reagent was added dropwise and the reaction temperature was kept below -60°C. After the completion of the dropwise addition, stir at low temperature for 1 h, warm to room temperature and stir for 18 h. Then, the reaction system was again cooled to -78 °C, and 13 g (1.1 equiv, 55 mmol) I_2 in 40 ml dry THF was added dropwise with vigorous stirring, keeping the temperature below -60 °C. Stir for 0.5 h after the drop, and then stir at room temperature for 1 h. The system was cooled to 0 °C and the reaction was quenched by slow dropwise addition of saturated NH_4Cl solution. After liquid separation, the aqueous phase was extracted with ethyl acetate (3×50 ml) and the organic phases were combined. The organic phase was washed with a saturated $Na_2S_2O_3$ solution. Finally, the organic phase was washed with a saturated NaCl solution and dried over anhydrous Na_2SO_4 .The crude product was purified by column chromatography using petroleum Petroleum ether/ethyl acetate (10:1) as eluent to

afford a yellow liquid(68% yield).

Synthesize material **S3** according to the general operation method of Mitsunobu. In a 100 ml round bottom flask, 2.6 g (1.0 equiv, 10 mmol) of **S1** was dissolved in 30 ml of THF, followed by 2.3 g (1.1 equiv, 11 mmol) of **S2**, 2.9 g (1.1 equiv, 11 mmol) of PPh_3 and 2.2 ml (1.1 equiv, 11 mmol) DIAD. Stir at room temperature overnight. The reaction was followed by TLC. After the material was consumed, ethyl acetate (3 × 50 ml) was combined and the organic phase was combined and purified by column chromatography to give a white solid **S3**(3.74 g, 8.3 mmol).

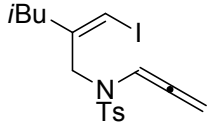
Synthesize material **1a** according to the general operation method of preparation of allene. In a 100 ml round bottom flask, 1.1 g (2.0 equiv, 10 mmol) of potassium tert-butoxide was added under nitrogen atmosphere. Then, 10 ml dry THF was added with vigorous stirring. Next, 2.3 g (1.0 equiv, 5 mmol) of **S3** dissolved in 10 ml of THF. The mixed solution was added dropwise with vigorous stirring, keeping the temperature below -20 °C over 1 hour. The reaction was followed by TLC. After the material **S3** was consumed, the organic phase was directly purified by column chromatography to give a white solid **1a**(2g, 4.5 mmol).

(Z)-N-(2-(iodomethylene)pentyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1b



following the general procedure described above, compound **1b** (2.04 g, 4.5 mmol, Non-white liquid) was obtained in 98 % yield.

(Z)-N-(2-(iodomethylene)-4-methylpentyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1c

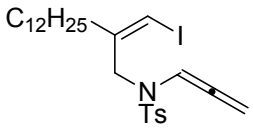


following the general procedure described above, compound **1c** (2.07 g, 4.8 mmol, Non-white liquid) was obtained in 96 % yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.70 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 6.0 Hz, 1H), 6.02 (s, 1H), 5.25 (d, *J* = 6.0 Hz, 2H), 3.78 (s, 2H), 2.45 (s, 3H), 2.13 (d, *J* = 7.2 Hz, 2H), 1.98 (dp, *J* = 13.2, 6.7 Hz, 1H), 0.89 (s, 3H), 0.88 (s, 3H).

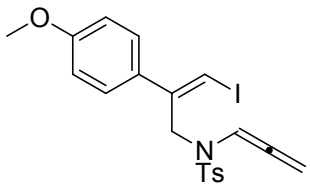
^{13}C NMR (101 MHz, Chloroform-*d*) δ: 201.3, 145.1, 144.0, 134.5, 129.8, 127.4, 99.5, 88.6, 78.0, 53.0, 44.6, 25.7, 22.4, 21.7.

(Z)-N-(2-(iodomethylene)tetradecyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1d



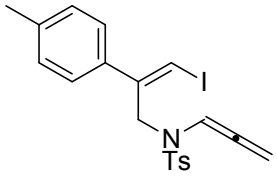
following the general procedure described above, compound **1d** (2.67 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(3-iodo-2-(4-methoxyphenyl)allyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide， 1e



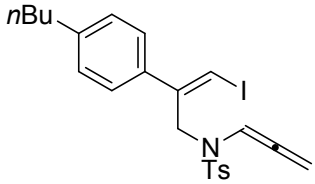
following the general procedure described above, compound **1e** (2.31 g, 4.8 mmol, white amorphous solid) was obtained in 95 % yield.

(Z)-N-(3-iodo-2-(p-tolyl)allyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1f



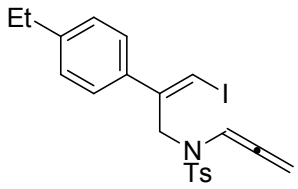
following the general procedure described above, compound **1f** (2.28 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(2-(4-butylphenyl)-3-iodoallyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1g



following the general procedure described above, compound **1g** (2.43 g, 4.8 mmol, white amorphous solid) was obtained in 96 % yield.

(Z)-N-(2-(4-ethylphenyl)-3-iodoallyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1h

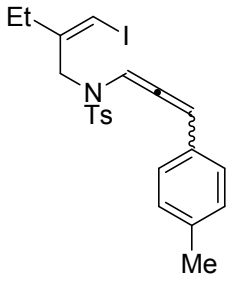


following the general procedure described above, compound **1h** (2.30 g, 4.8 mmol, white amorphous solid) was obtained in 96 % yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.68 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.45 (s, 1H), 6.40 (t, *J* = 6.0 Hz, 1H), 5.25 (d, *J* = 6.0 Hz, 2H), 4.26 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

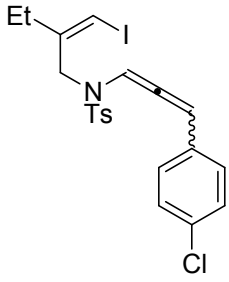
^{13}C NMR (101 MHz, Chloroform-*d*) δ: 201.9, 147.0, 144.3, 143.9, 135.8, 134.5, 129.8, 127.7, 127.4, 127.2, 99.2, 88.2, 81.2, 52.7, 28.6, 21.7, 15.3.

(Z)-N-(2-(iodomethylene)butyl)-4-methyl-N-(3-(p-tolyl)propa-1,2-dien-1-yl)benzenesulfonamide, 1i



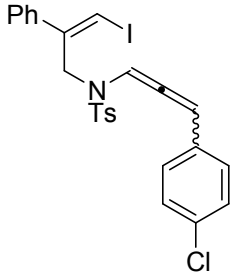
following the general procedure described above, compound **1i** (2.79 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(3-(4-chlorophenyl)propa-1,2-dien-1-yl)-N-(2-(iodomethylene)butyl)-4-methylbenzenesulfonamide, 1j



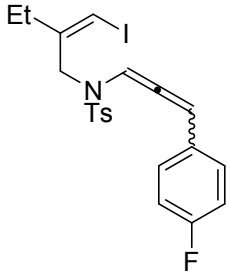
following the general procedure described above, compound **1j** (2.89 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(3-(4-chlorophenyl)propa-1,2-dien-1-yl)-N-(3-iodo-2-phenylallyl)-4-methylbenzenesulfonamide, 1k



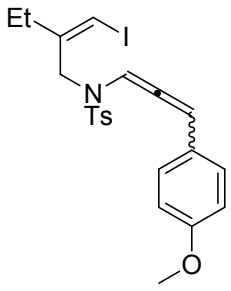
following the general procedure described above, compound **1k** (2.69 g, 4.8 mmol, white amorphous solid) was obtained in 95 % yield.

(Z)-N-(3-(4-fluorophenyl)propa-1,2-dien-1-yl)-N-(2-(iodomethylene)butyl)-4-methylbenzenesulfonamide, 1l



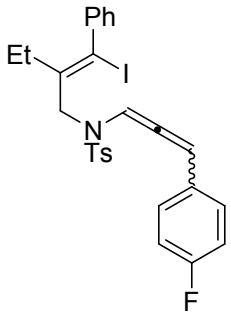
following the general procedure described above, compound **1l** (2.39 g, 4.8 mmol, white amorphous solid) was obtained in 96 % yield.

(Z)-N-(2-(iodomethylene)butyl)-N-(3-(4-methoxyphenyl)propa-1,2-dien-1-yl)-4-methylbenzenesulfonamide, 1m



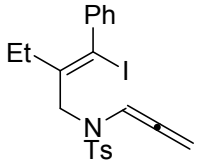
following the general procedure described above, compound **1m** (2.44 g, 4.8 mmol, white amorphous solid) was obtained in 96 % yield.

(Z)-N-(3-(4-fluorophenyl)propa-1,2-dien-1-yl)-N-(2-(iodo(phenyl)methylene)butyl)-4-methylbenzenesulfonamide, 1n



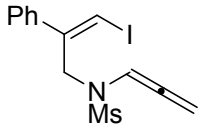
following the general procedure described above, compound **1n** (2.81 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(2-(iodo(phenyl)methylene)butyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1o



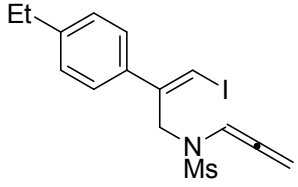
following the general procedure described above, compound **1o** (2.35 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(3-iodo-2-phenylallyl)-N-(propa-1,2-dien-1-yl)methanesulfonamide, 1p



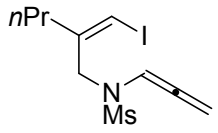
following the general procedure described above, compound **1p** (1.80 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(2-(4-ethylphenyl)-3-iodoallyl)-N-(propa-1,2-dien-1-yl)methanesulfonamide, 1q



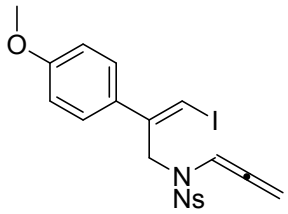
following the general procedure described above, compound **1q** (1.93 g, 4.8 mmol, white amorphous solid) was obtained in 96 % yield.

(Z)-N-(2-(iodomethylene)hexyl)-N-(propa-1,2-dien-1-yl)methanesulfonamide, 1r



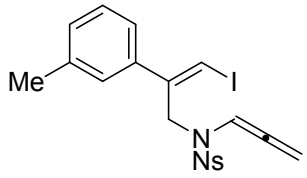
following the general procedure described above, compound **1q** (1.74 g, 4.9 mmol, Non-white liquid) was obtained in 98 % yield.

(Z)-N-(3-iodo-2-(4-methoxyphenyl)allyl)-4-nitro-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1s



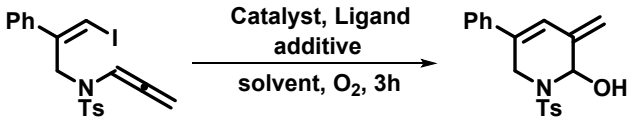
following the general procedure described above, compound **1s** (2.51 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

(Z)-N-(3-iodo-2-(m-tolyl)allyl)-4-nitro-N-(propa-1,2-dien-1-yl)benzenesulfonamide, 1t



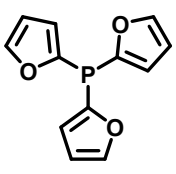
following the general procedure described above, compound **1t** (2.43 g, 4.9 mmol, white amorphous solid) was obtained in 98 % yield.

III. Optimization of reaction conditions.

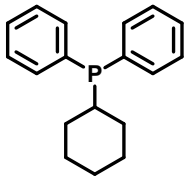


1a 2a

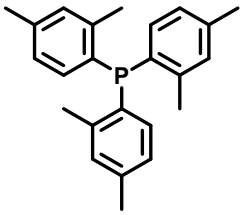
Entry	Catalyst(mol%)	Ligand(mol%)	Additive(equiv)	Solvent	Yield(%)
1	$Pd(OAc)_2$(5)	L_1 (20)		DCM	0
2	$Pd(OAc)_2$(5)	L_1 (20)	$AgNO_3$(1.5)	DCM	12
3	$Pd(OAc)_2$(5)	L_1 (20)	$AgNO_3$(1.5)	THF	22
4	$Pd(dba)_2$(5)	L_1 (20)	$AgNO_3$(1.5)	THF	25
5	$Pd(PPh_3)_4$(5)	L_1 (20)	$AgNO_3$(1.5)	THF	26
6	$Pd_2(dba)_3$(5)	L_1 (20)	$AgNO_3$(1.5)	THF	30
7	$Pd_2(dba)_3$(5)	L_1 (20)	AgOAc(1.5)	THF	34
8	$Pd_2(dba)_3$(5)	L_1 (20)	Ag_2CO_3(1.5)	THF	46
9	$Pd_2(dba)_3$(5)	L_1 (20)	Ag_2SO_4(1.5)	THF	32
10	$Pd_2(dba)_3$(5)	L_1 (20)	Ag_2O(1.5)	THF	0
11	$Pd_2(dba)_3$(5)	L_1 (20)	$AgBF_4$(1.5)	THF	0
12	$Pd_2(dba)_3$(5)	L_1 (20)	AgF(1.5)	THF	48
13	$Pd_2(dba)_3$(5)	PPy_3 (20)	AgF(1.5)	THF	7
14	$Pd_2(dba)_3$(5)	L_2 (20)	AgF(1.5)	THF	57
15	$Pd_2(dba)_3$(5)	L_3 (20)	AgF(1.5)	THF	64
16	$Pd_2(dba)_3$(5)	L_3 (20)	AgF(1.5)	acetone	33
17	$Pd_2(dba)_3$(5)	L_3 (20)	AgF(1.5)	1,4-dioxane	0
18	$Pd_2(dba)_3$(5)	L_3 (20)	AgF(1.5)	benzene	0
19	$Pd_2(dba)_3$(5)	L_3 (20)	AgF(1.5)	toluene	0
20	$Pd_2(dba)_3$(5)	L_4 (20)	AgF(1.5)	THF	59
21	$Pd_2(dba)_3$(5)	L_5 (20)	AgF(1.5)	THF	34
22	$Pd_2(dba)_3$(5)	DPPM (20)	AgF(1.5)	THF	17
23	$Pd_2(dba)_3$(5)	DPPD (20)	AgF(1.5)	THF	56
24	$Pd_2(dba)_3$(5)	L_3 (20)	Cs_2CO_3(1.5)	THF	0
25	$Pd_2(dba)_3$(5)	L_3 (20)	KOtBu(1.5)	THF	0
26	$Pd_2(dba)_3$(5)	L_3 (20)	CsF(1.5)	THF	0
27	**$Pd_2(dba)_3$(5)**	**L_3 (20)**	AgF(1.5)	THF(air)	**88**
28	$Pd_2(dba)_3$(5)	L_3 (20)	AgF(1.5)	THF(N_2)	43



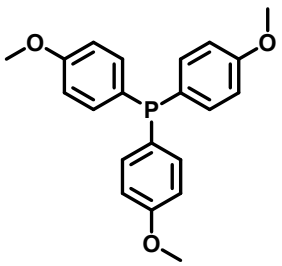
L_1: Tri(2-furyl)phosphine



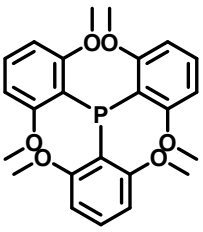
L_2: Cyclohexyldiphenylphosphine



L_3: Tris(2,4-dimethyiphenyl)phosphine

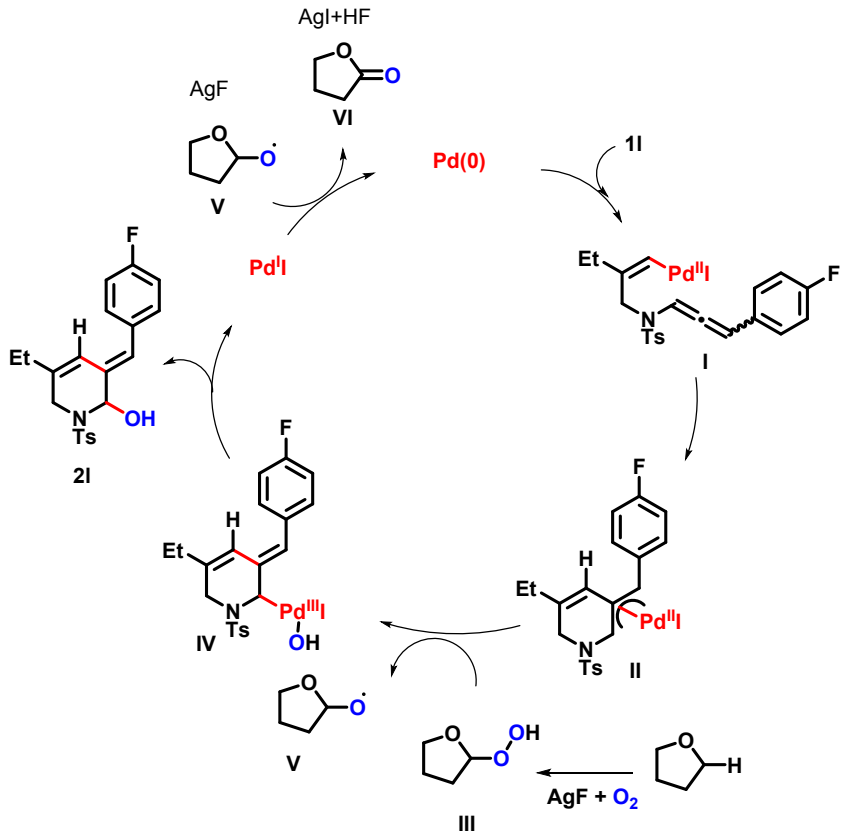


L_4: Tris(4-methoxyphenyl)phosphine



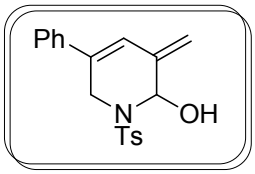
L_5: Tris(2,6-dimethoxyphenyl)phosphine

IV. Another plausible reaction mechanism.



Another plausible mechanism is illustrated above. Firstly,η^3 π-allylpalladium intermediate **II** was formed. Molecular oxygen is acitived by AgF and reacted with THF to give 2-tetrahydrofuryl hydroperoxide **III**. Followed radical addition of hydroperide **III** with intermediate **II** probably generate a tentative intermediate **IV** which give product **2l** *via* reductive elimination. Catalyst Pd(0) is regenerate associated by AgF and radical **V**.

V. Analytical Data for product 2a-2t



$C_{19}H_{19}NO_3S$

MW：341.42 g • mol^{-1}

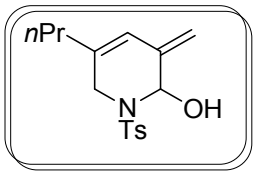
Non-white liquid

Isolated Amount:24.0mg **Yield:**88%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.72 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.31 (dt, *J* = 16.7, 7.3 Hz, 5H), 6.64 (s, 1H), 6.18 (s, 1H), 5.74 (s, 1H), 5.14 (d, *J* = 22.1 Hz, 2H), 4.26 (d, *J* = 16.7 Hz, 1H), 3.76 (d, *J* = 16.8 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.76, 141.79, 137.19, 136.27, 133.69, 129.93, 129.22, 128.72, 128.14, 125.30, 122.15, 115.69, 77.64, 41.26, 21.47.

MS (EI) m/z 341 (M+)； **HRMS (ESI)** Calcd for $C_{19}H_{19}NO_3S$+H 342.1164，Found 342.1165.



$C_{16}H_{21}NO_3S$

MW：307.41 g • mol^{-1}

Non-white liquid

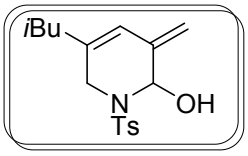
Isolated Amount:13.6mg **Yield:**56%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.92 (s, 2H), 5.01 (d, *J* = 38.5 Hz, 2H), 3.89 (d, *J* = 16.9 Hz, 1H), 3.60 (d, *J* = 16.9 Hz, 1H), 2.42 (s, 3H), 2.24 (d, *J* = 4.3 Hz, 1H), 2.04 (t, *J* = 7.6 Hz, 2H), 1.45 (dtd, *J* = 14.3, 7.2, 2.8 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 143.80, 140.07, 137.49, 135.98, 129.66,

127.68, 119.75, 113.24, 78.38, 42.50, 36.54, 21.60, 20.61, 13.76.

MS (EI) m/z 307 (M+)； **HRMS (ESI)** Calcd for $C_{16}H_{21}NO_3S$+H 308.1320，Found 308.1321.



$C_{17}H_{23}NO_3S$

MW：321.43 g • mol^{-1}

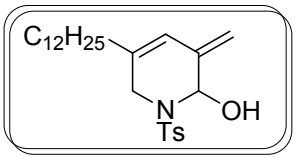
Non-white liquid

Isolated Amount:25.2mg **Yield:**98%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.71 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 6.07 (s, 1H), 5.87 (s, 1H), 5.71 (s, 1H), 4.95 (d, *J* = 43.0 Hz, 2H), 3.75 (d, *J* = 16.9 Hz, 1H), 3.37 (d, *J* = 16.1 Hz, 4H), 2.38 (s, 3H), 1.90 (d, *J* = 5.7 Hz, 2H), 1.68 (dt, *J* = 13.0, 6.4 Hz, 1H), 0.79 (dd, *J* = 13.5, 6.3 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.62, 141.67, 136.64, 136.33, 129.86, 128.03, 121.80, 112.42, 77.83, 43.92, 42.65, 26.55, 22.68, 21.45.

MS (EI) m/z 321 (M+)； **HRMS (ESI)** Calcd for $C_{17}H_{23}NO_3S$+H 322.1477，Found 322.1478.



$C_{25}H_{39}NO_3S$

MW：433.65 g • mol^{-1}

Non-white liquid

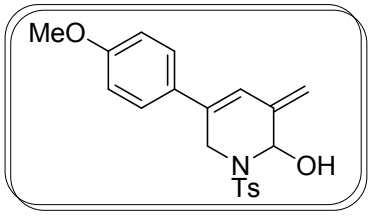
Isolated Amount:32.6mg **Yield:**94%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.76 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.12 (d, *J* = 6.0 Hz, 1H), 5.92 (s, 1H), 5.75 (d, *J* = 5.9 Hz, 1H), 5.04 (s, 1H), 4.93 (s, 1H), 3.80 (d, *J* = 17.0 Hz, 1H), 3.41 (s, 4H), 2.43 (s, 3H), 2.06 (t, *J* = 7.4 Hz,

2H), 1.52-1.13 (m, 20H), 0.91 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.58, 141.68, 137.63, 136.34, 129.82, 128.05, 120.42, 112.31, 77.89, 42.63, 34.10, 31.79, 29.61-29.00 (m), 27.33, 22.59, 21.44, 14.44.

MS (EI) m/z 433 (M+)； **HRMS (ESI)** Calcd for $C_{25}H_{39}NO_3S$+H 434.2729，Found 434.2730.



$C_{20}H_{21}NO_4S$

MW：371.45 g • mol^{-1}

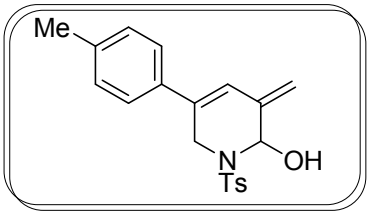
Non-white liquid

Isolated Amount:24.9mg **Yield:**84%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.78 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.60 (s, 1H), 6.22 (s, 1H), 5.79 (s, 1H), 5.15 (d, J = 21.9 Hz, 2H), 4.31 (d, J = 16.7 Hz, 1H), 3.78 (s, 4H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 159.78, 143.73, 141.92, 136.29, 133.26, 129.91, 129.50, 128.13, 126.62, 120.27, 114.66, 114.58, 77.67, 55.64, 41.25, 21.47.

MS (EI) m/z 371 (M+)； **HRMS (ESI)** Calcd for $C_{20}H_{21}NO_4S$+H 372.1270，Found 372.1271.



$C_{20}H_{21}NO_3S$

MW：355.45 g • mol^{-1}

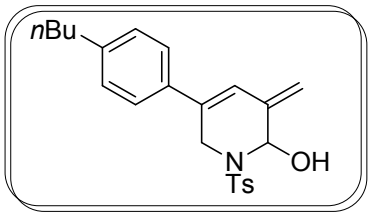
Non-white liquid

Isolated Amount:26.1mg **Yield:**92%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.78 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.66 (s, 1H), 6.23 (d, *J* = 6.3 Hz, 1H), 5.80 (d, *J* = 6.3 Hz, 1H), 5.18 (d, *J* = 21.7 Hz, 2H), 4.31 (d, *J* = 16.7 Hz, 1H), 3.79 (d, *J* = 16.7 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.74, 141.85, 138.19, 136.28, 134.30, 133.54, 129.92, 129.80, 128.12, 125.15, 121.25, 115.23, 77.66, 41.22, 21.47, 21.21.

MS (EI) m/z 355 (M+); **HRMS (ESI)** Calcd for $C_{20}H_{21}NO_3S$+H 356.1320，Found 356.1321.



$C_{23}H_{27}NO_3S$

MW：397.53 g • mol^{-1}

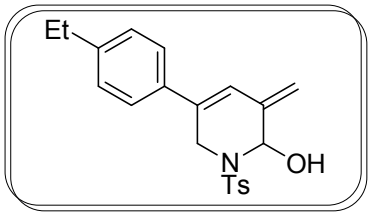
Non-white liquid

Isolated Amount:28.3mg **Yield:**89%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.78 (d, *J* = 8.2 Hz, 2H), 7.39 (dd, *J* = 10.4, 8.3 Hz, 4H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.66 (s, 1H), 5.80 (s, 1H), 5.18 (d, *J* = 22.1 Hz, 1H), 4.31 (d, *J* = 16.7 Hz, 1H), 3.79 (d, *J* = 16.7 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.55 (p, *J* = 7.5 Hz, 2H), 1.35-1.25 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.73, 143.07, 141.88, 136.30, 134.57, 133.63, 129.92, 129.13, 128.12, 125.20, 121.32, 115.21, 77.66, 41.25, 34.91, 33.45, 22.19, 21.47, 14.25.

MS (EI) m/z 397 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{27}NO_3S$+H 398.1790，Found 398.1791.



$C_{21}H_{23}NO_3S$

MW：369.48 g • mol^{-1}

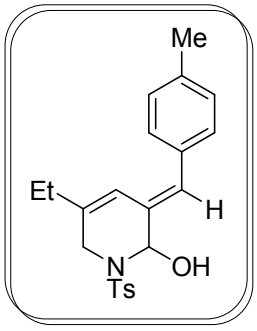
Non-white liquid

Isolated Amount:27.8mg **Yield:**94%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.78 (d, J = 8.2 Hz, 2H), 7.40 (dd, J = 13.4, 8.2 Hz, 4H), 7.23 (d, J = 8.2 Hz, 2H), 6.65 (s, 1H), 6.23 (d, J = 6.3 Hz, 1H), 5.80 (d, J = 6.3 Hz, 1H), 5.18 (d, J = 22.0 Hz, 2H), 4.31 (d, J = 16.7 Hz, 1H), 3.79 (d, J = 16.7 Hz, 1H), 2.61 (q, J = 7.6 Hz, 2H), 2.38 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 144.47, 143.74, 141.85, 136.30, 134.61, 133.64, 129.92, 128.60, 128.12, 125.28, 121.33, 115.23, 77.66, 41.26, 28.29, 21.47, 15.93.

MS (EI) m/z 369 (M+)； **HRMS (ESI)** Calcd for $C_{21}H_{23}NO_3S$+H 370.1477，Found 370.1478.



$C_{22}H_{25}NO_3S$

MW：383.50 g • mol^{-1}

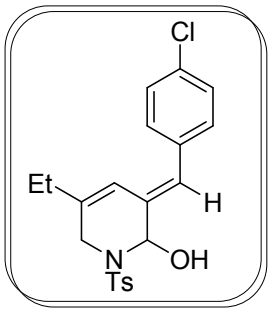
Non-white liquid

Isolated Amount:28.5mg **Yield:**93%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.65 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.29 (s, 1H), 6.11 (s, 2H), 6.08 (d, *J* = 5.6 Hz, 1H), 5.65 (d, *J* = 5.6 Hz, 1H), 3.87 (d, *J* = 17.5 Hz, 1H), 3.44 (d, *J* = 17.5 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H), 2.01 (q, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.64, 140.34, 136.91, 136.10, 133.51, 133.18, 129.81, 129.44, 129.31, 128.05, 125.50, 115.61, 79.85, 43.65, 27.17, 21.45, 21.27, 12.21.

MS (EI) m/z 383 (M+)； **HRMS (ESI)** Calcd for $C_{22}H_{25}NO_3S$+H 384.1633，Found 384.1634.



$C_{21}H_{22}ClNO_3S$

MW：403.92 g • mol^{-1}

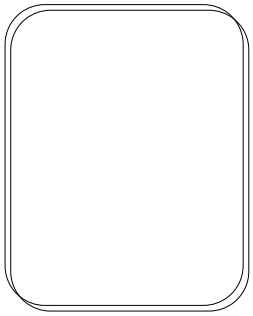
Non-white liquid

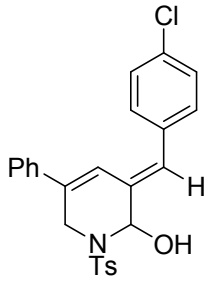
Isolated Amount:23.2mg **Yield:**72%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.77 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.44 (s, 1H), 6.28 (d, *J* = 5.6 Hz, 1H), 6.19 (s, 1H), 5.78 (d, *J* = 5.2 Hz, 1H), 4.02 (d, *J* = 17.7 Hz, 1H), 3.59 (d, *J* = 17.7 Hz, 1H), 2.42 (s, 3H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.02 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.70, 141.54, 136.04, 135.28, 134.36, 132.03, 131.08, 129.82, 128.85, 128.04, 124.16, 115.22, 79.69, 43.66, 27.21, 21.45, 12.22.

MS (EI) m/z 403 (M+)； **HRMS (ESI)** Calcd for $C_{21}H_{22}ClNO_3S$+H 404.1087，Found 404.1088.





$C_{25}H_{22}ClNO_3S$

MW：451.97 g • mol^{-1}

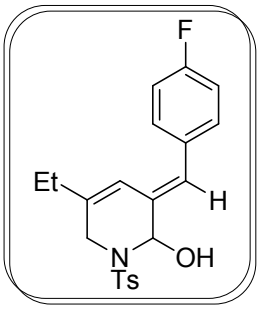
Non-white liquid

Isolated Amount:30.0mg **Yield:**93%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.76 (d, *J* = 8.2 Hz, 2H), 7.47 (dd, *J* = 7.5, 4.4 Hz, 4H), 7.37 (dt, *J* = 21.2, 6 Hz, 4H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.75 (s, 1H), 6.62 (s, 1H), 6.43 (d, *J* = 5.7 Hz, 1H), 5.83 (d, *J* = 5.7 Hz, 1H), 4.51 (d, *J* = 17.6 Hz, 1H), 3.97 (d, *J* = 17.7 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.84, 137.34, 136.00, 135.00, 134.13, 132.46, 131.33, 129.90, 129.31, 129.02, 128.98, 128.02, 127.11, 125.66, 117.76, 79.35, 42.38, 21.45.

MS (EI) m/z 451 (M+)； **HRMS (ESI)** Calcd for $C_{25}H_{22}ClNO_3S$+H 452.1087，Found 452.1088.



$C_{21}H_{22}FNO_3S$

MW：387.47 g • mol^{-1}

Non-white liquid

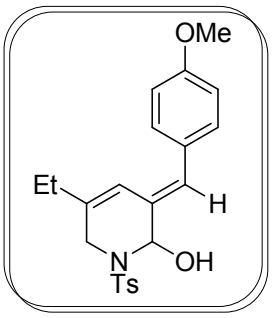
Isolated Amount:29.4mg **Yield:**95%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.71 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27-7.14 (m, 4H), 6.39 (s, 1H), 6.20 (d, *J* = 5.6 Hz, 1H), 6.13 (s, 1H), 5.72 (d, *J* = 5.6 Hz, 1H), 3.96 (d, *J* = 17.6 Hz, 1H), 3.53 (d, *J* = 17.6 Hz, 1H), 2.37 (s, 3H), 2.09 (q, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 162.78, 160.35, 143.68, 141.05, 136.06, 133.65, 132.81, 131.31 (d, *J* = 8.1 Hz), 129.81, 128.04, 124.35, 115.85, 115.64, 115.26, 79.75, 43.64, 27.19, 21.44, 12.23.

^{19}F NMR (377 MHz, DMSO-d_6,δ ppm): -114.59 (ddd, *J* = 14.5, 8.4, 6.2 Hz).

MS (EI) m/z 387 (M+)； **HRMS (ESI)** Calcd for $C_{21}H_{22}FNO_3S$+H 388.1383，Found 388.1384.



$C_{22}H_{25}NO_4S$

MW：399.50 g • mol^{-1}

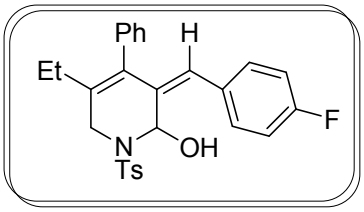
Non-white liquid

Isolated Amount:29.7mg **Yield:**93%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.33 (s, 1H), 6.18 (s, 1H), 6.11 (d, *J* = 5.6 Hz, 1H), 5.70 (d, *J* = 5.6 Hz, 1H), 3.94 (d, *J* = 17.5 Hz, 1H), 3.77 (s, 3H), 3.50 (d, *J* = 17.4 Hz, 1H), 2.37 (s, 3H), 2.08 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 158.81, 143.63, 139.93, 136.09, 132.24, 130.70, 129.80, 128.77, 128.06, 125.25, 115.65, 114.31, 79.92, 55.56, 43.64, 27.18, 21.45, 12.26.

MS (EI) m/z 399 (M+)； **HRMS (ESI)** Calcd for $C_{22}H_{25}NO_4S$+H 400.1583，Found 400.1584.



$C_{27}H_{26}FNO_3S$

MW：463.56 g • mol^{-1}

Non-white liquid

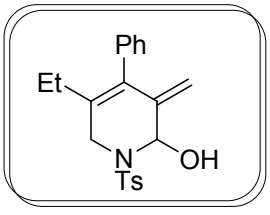
Isolated Amount:34.8mg **Yield:**94%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.61 (d, *J* = 8.1 Hz, 2H), 7.53-7.39 (m, 6H), 7.32 (dt, *J* = 23.4, 8.0 Hz, 3H), 6.83 (d, *J* = 6.3 Hz, 1H), 6.08 (d, *J* = 6.3 Hz, 1H), 5.60 (s, 1H), 4.15 (d, *J* = 18.2 Hz, 1H), 3.86 (d, *J* = 18.3 Hz, 1H), 2.49 (s, 3H), 1.79 (h, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 163.12, 160.68, 143.94, 138.22, 136.08, 135.91, 134.94, 133.13 – 132.53 (m), 132.03, 130.83 (d, *J* = 8.1 Hz), 129.86 (d, *J* = 11.9 Hz), 128.78, 127.91, 127.59 (d, *J* = 14.5 Hz), 115.97 (d, *J* = 21.4 Hz), 74.30, 42.47, 25.34, 21.46, 13.31.

^{19}F NMR (377 MHz, DMSO-d_6,δ ppm): -114.24 (ddd, *J* = 14.4, 9.0, 5.6 Hz).

MS (EI) m/z 463 (M+)； **HRMS (ESI)** Calcd for $C_{27}H_{26}FNO_3S$+H 464.1696，Found 464.1697.



$C_{21}H_{23}NO_3S$

MW：369.48 g • mol^{-1}

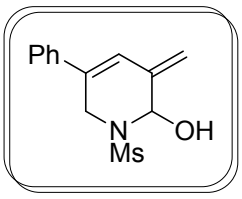
Non-white liquid

Isolated Amount:20.1mg **Yield:**68%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.76 (d, *J* = 8.2 Hz, 2H), 7.51-7.20 (m, 5H), 6.92 (d, *J* = 6.8 Hz, 2H), 6.24 (d, *J* = 5.8 Hz, 1H), 5.79 (d, *J* = 5.8 Hz, 1H), 5.04 (s, 1H), 4.21 (s, 1H), 4.03 (d, *J* = 17.4 Hz, 1H), 3.61 (d, *J* = 17.4 Hz, 1H), 2.42 (s, 3H), 1.77 (dh, *J* = 14.3, 7.3 Hz, 2H), 0.82 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 143.69, 136.06, 135.00, 128.68, 127.45, 113.98, 78.94, 42.71, 25.05, 21.46, 13.29.

MS (EI) m/z 369 (M+)； **HRMS (ESI)** Calcd for $C_{21}H_{23}NO_3S$+H 370.1477，Found 370.1478.



$C_{13}H_{15}NO_3S$

MW：265.33 g • mol^{-1}

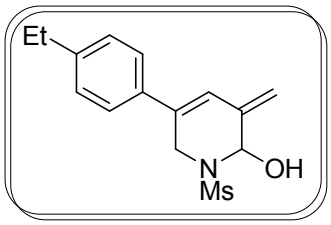
Non-white liquid

Isolated Amount:20.1mg **Yield:**95%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.59 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 6.81 (s, 1H), 6.51 (s, 1H), 5.65 (s, 1H), 5.23 (s, 1H), 4.22 (s, 2H), 3.12 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 141.96, 137.36, 133.95, 129.22, 128.73, 125.30, 121.99, 115.61, 77.38, 41.50, 38.71.

MS (EI) m/z 265 (M+)； **HRMS (ESI)** Calcd for $C_{13}H_{15}NO_3S$+H 266.0851，Found 266.0852.



$C_{15}H_{19}NO_3S$

MW：293.38 g • mol^{-1}

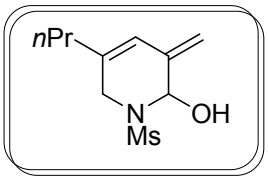
Non-white liquid

Isolated Amount:10.3mg **Yield:**44%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.39 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.60 (s, 1H), 5.90 (d, *J* = 3.9 Hz, 1H), 5.25 (d, *J* = 14.1 Hz, 2H), 4.55 (d, *J* = 16.6 Hz, 1H), 4.15 (d, *J* = 16.2 Hz, 1H), 3.03 (s, 3H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 1H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 145.11, 140.48, 134.70, 134.27, 128.33, 125.23, 120.24, 115.81, 78.12, 41.35, 39.02, 28.58, 15.47.

MS (EI) m/z 293 (M+)； **HRMS (ESI)** Calcd for $C_{15}H_{19}NO_3S$+H 294.1164，Found 294.1167.



$C_{10}H_{17}NO_3S$

MW：231.31 g • mol^{-1}

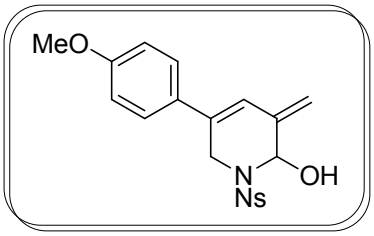
Non-white liquid

Isolated Amount:16.5mg **Yield:**89%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 6.00 (s, 1H), 5.79 (d, *J* = 4.2 Hz, 1H), 5.06 (d, *J* = 30.1 Hz, 2H), 3.95 (d, *J* = 16.7 Hz, 1H), 3.75 (d, *J* = 16.7 Hz, 1H), 2.98 (s, 3H), 2.37-2.31 (m, 1H), 2.12 (t, *J* = 7.6 Hz, 2H), 1.54 (h, *J* = 7.0 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 140.26, 137.62, 119.69, 113.52, 78.33, 42.73, 38.82, 36.62, 20.65, 13.81.

MS (EI) m/z 231 (M+)； **HRMS (ESI)** Calcd for $C_{10}H_{17}NO_3S$+H 232.1007，Found 232.1008.



$C_{19}H_{18}N_2O_6S$

MW：402.42 g • mol^{-1}

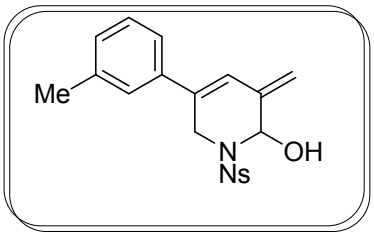
Non-white liquid

Isolated Amount:27.3mg **Yield:**85%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 8.34 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.44 (s, 1H), 6.04 (d, *J* = 4.6 Hz, 1H), 5.23 (d, *J* = 27.6 Hz, 1H), 4.53 (d, *J* = 16.6 Hz, 1H), 3.97 (d, *J* = 16.7 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 160.10, 150.20, 144.65, 139.90, 133.84, 129.12, 126.43, 124.16, 119.39, 115.83, 114.23, 78.31, 55.39, 41.35.

MS (EI) m/z 402 (M+)； **HRMS (ESI)** Calcd for $C_{19}H_{18}N_2O_6S$+H 403.0964，Found 403.0964.



$C_{19}H_{18}N_2O_5S$

MW：386.42 g • mol^{-1}

Non-white liquid

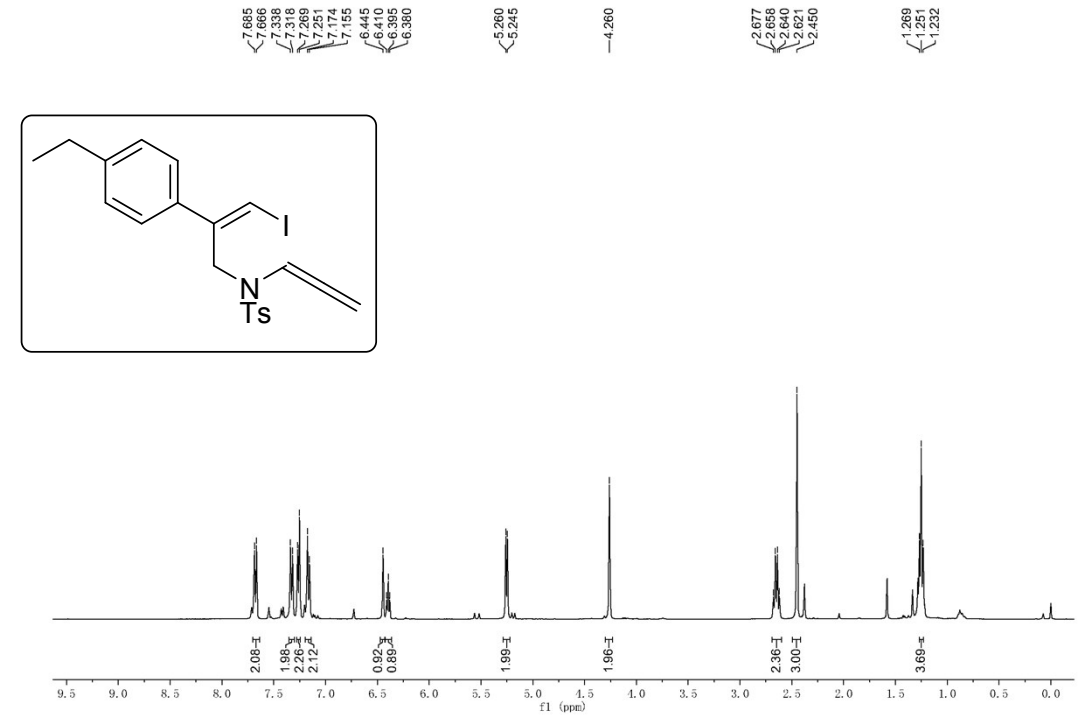
Isolated Amount:27.2mg **Yield:**88%

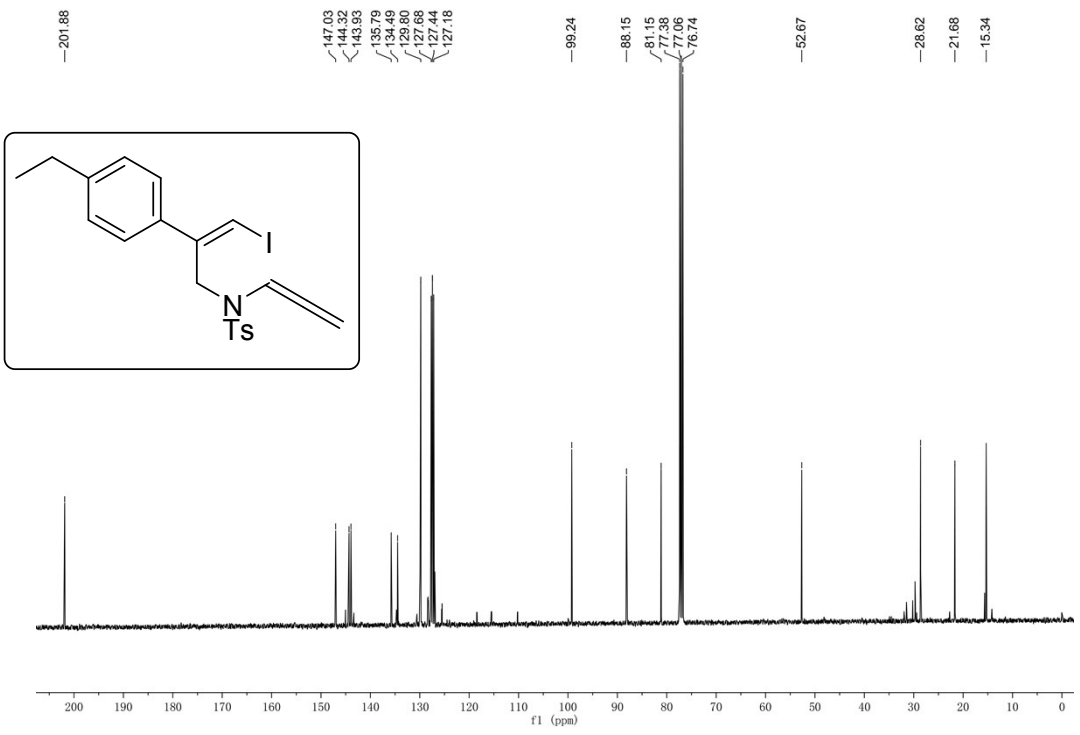
^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 8.39 (d, *J* = 8.7 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 7.43-7.24 (m, 3H), 7.16 (d, *J* = 6.9 Hz, 1H), 6.70 (s, 1H), 6.42 (d, *J* = 6.3 Hz, 1H), 5.83 (d, *J* = 6.3 Hz, 1H), 5.24 (d, *J* = 23.3 Hz, 2H), 4.42 (d, *J* = 16.7 Hz, 1H), 3.90 (d, *J* = 16.9 Hz, 1H), 2.34 (s, 3H).

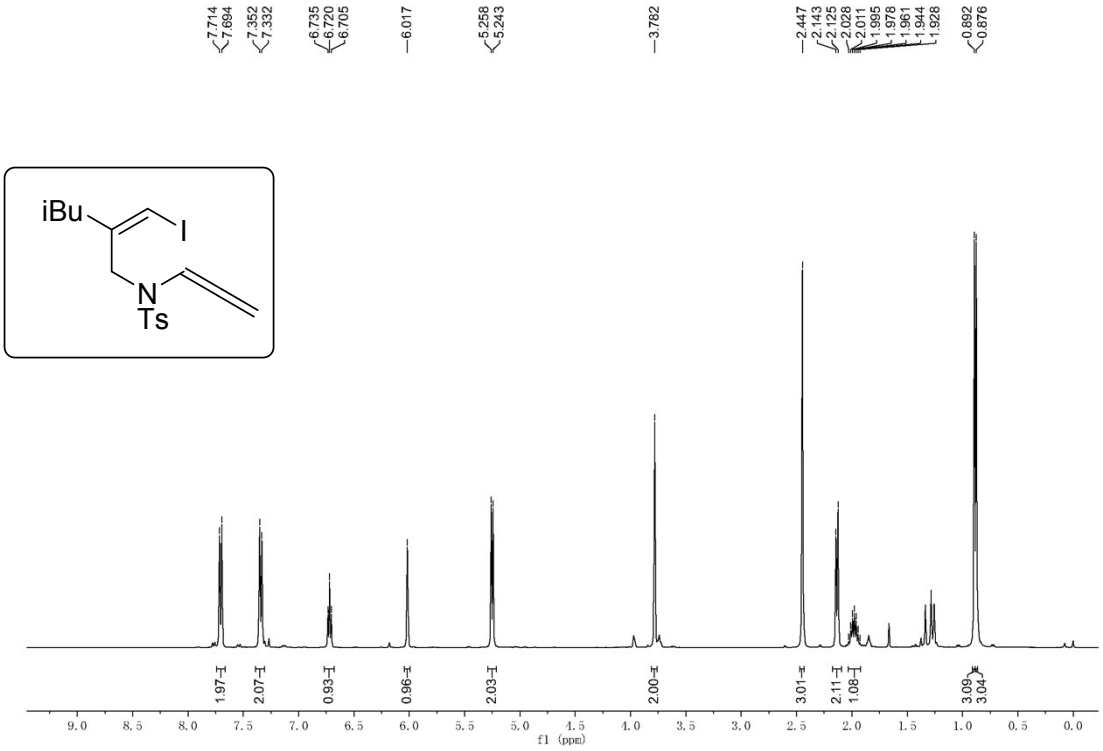
^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 150.37, 144.56, 141.28, 138.39, 137.04, 133.59, 129.76, 129.50, 129.08, 125.92, 124.76, 122.56, 121.99, 116.17, 77.88, 41.46, 21.51.

MS (EI) m/z 386 (M+)； **HRMS (ESI)** Calcd for $C_{19}H_{18}N_2O_5S$+H 387.1015，Found 387.1016.

VI Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR



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6.720
6.705
6.017
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5.243
3.782
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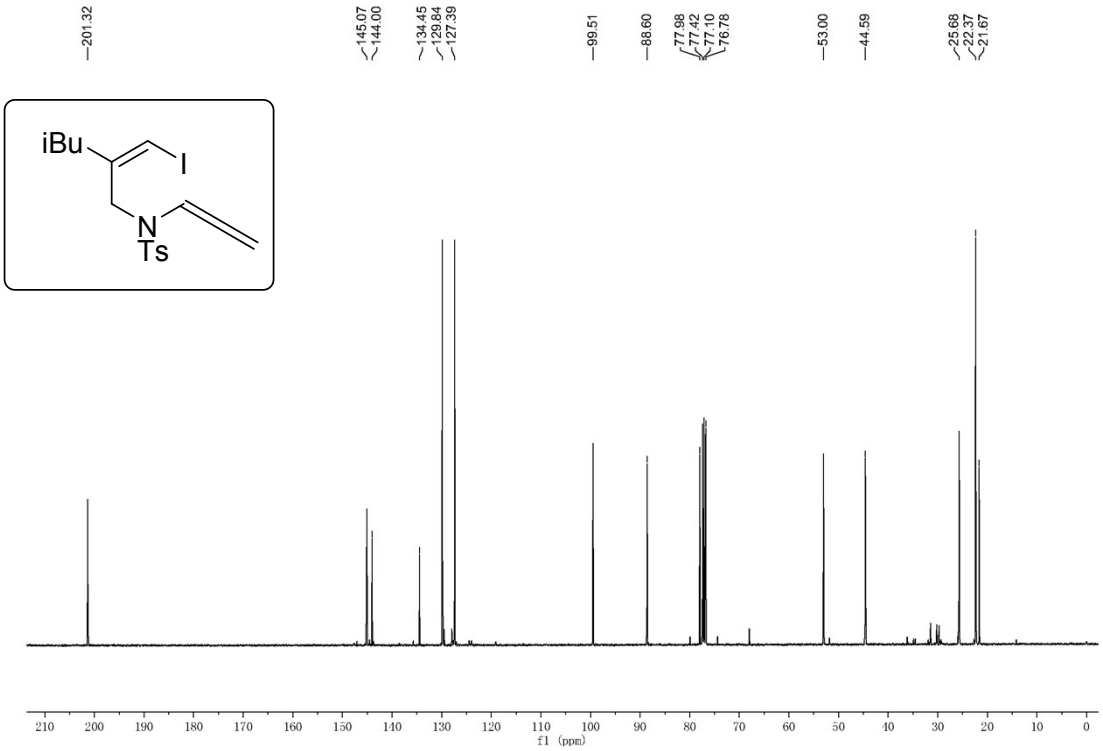
2.125
2.028
2.011
1.995
1.978
1.961
1.944
1.928
0.892
0.876
iBu
I
N
Ts
1.97
2.07
0.93
0.96
2.03
2.00
3.01
2.11
1.08
3.09
3.04
f1 (ppm)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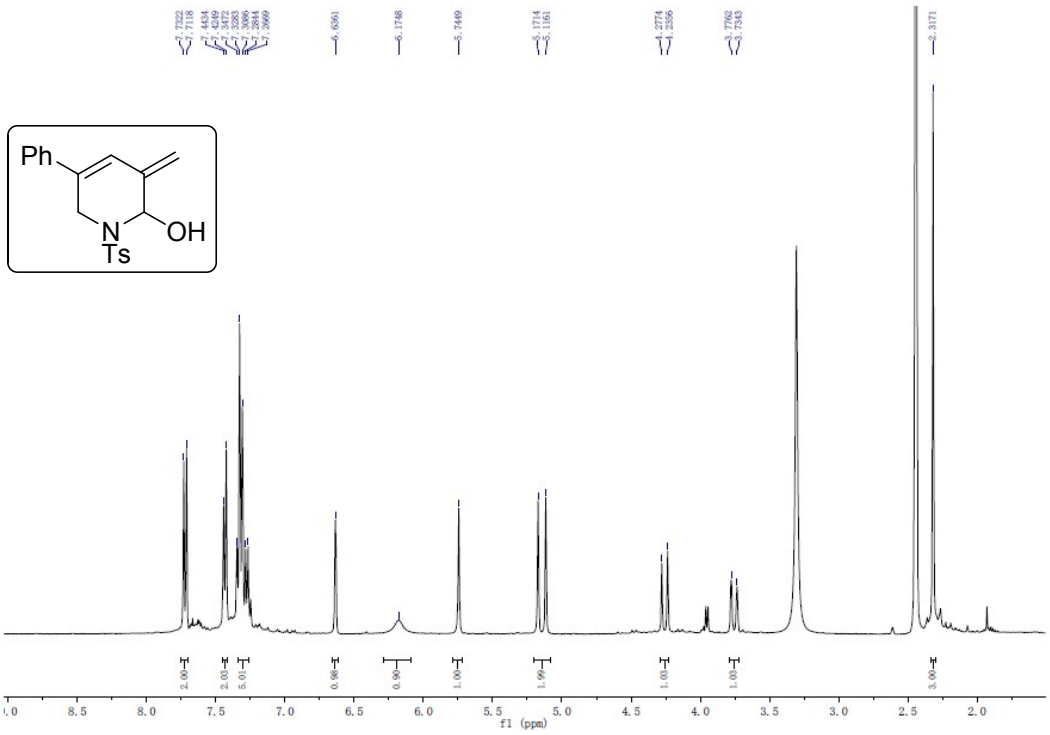
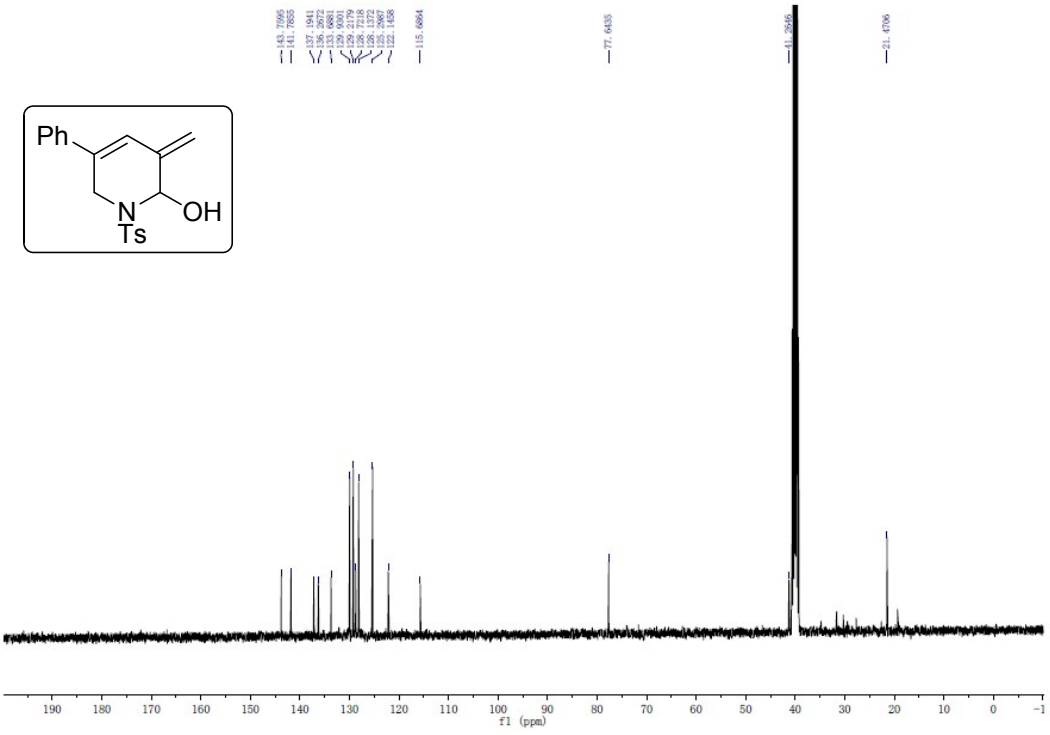
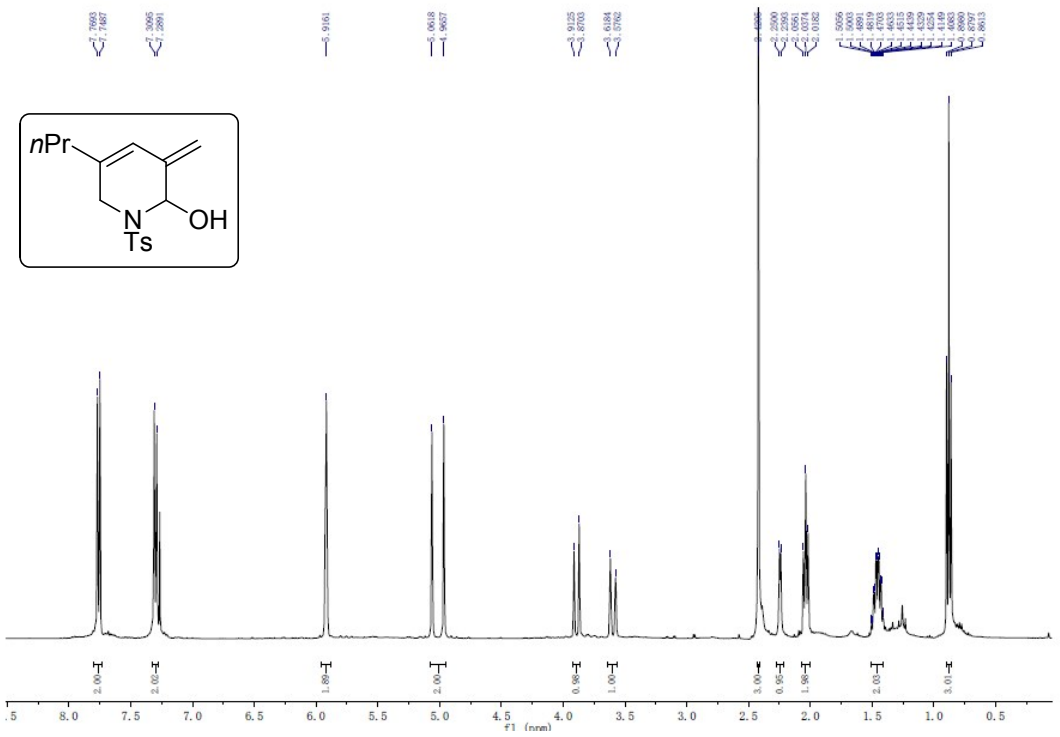
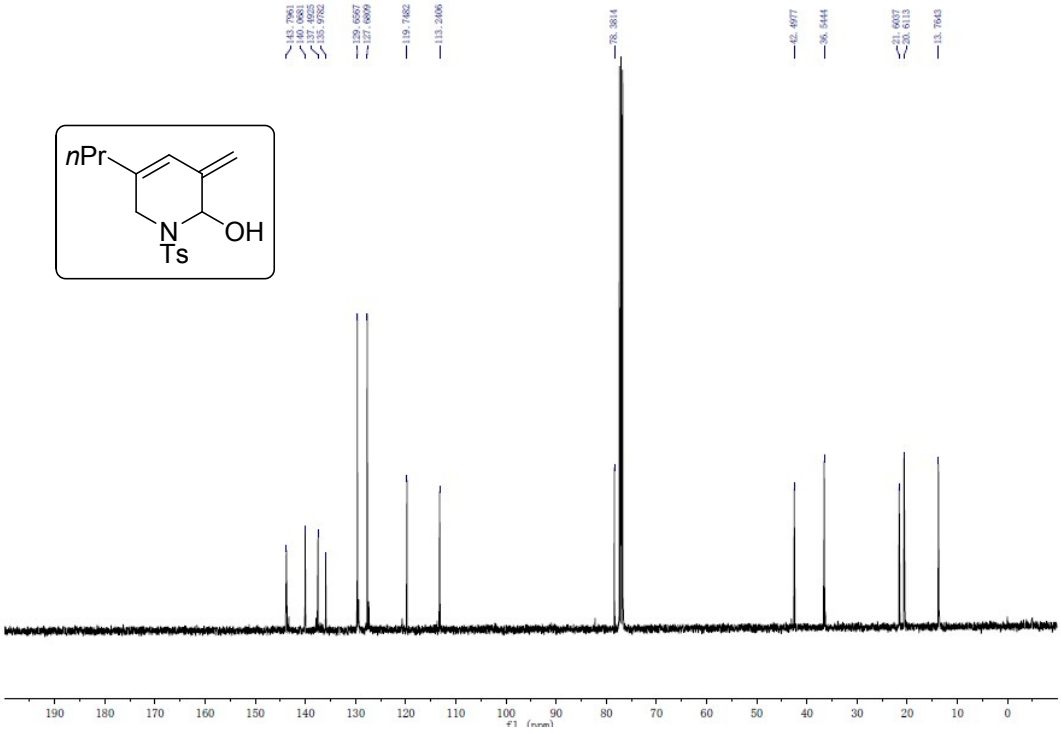
144.00
134.45
129.84
127.39
99.51
88.60
77.98
77.42
77.10
76.78
53.00
44.59
25.68
22.37
21.67
iBu
I
N
Ts
f1 (ppm)


Ph
N
OH
Ts
f1 (ppm)


Ph
N
OH
Ts
f1 (ppm)


nPr
N
Ts
OH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Ts
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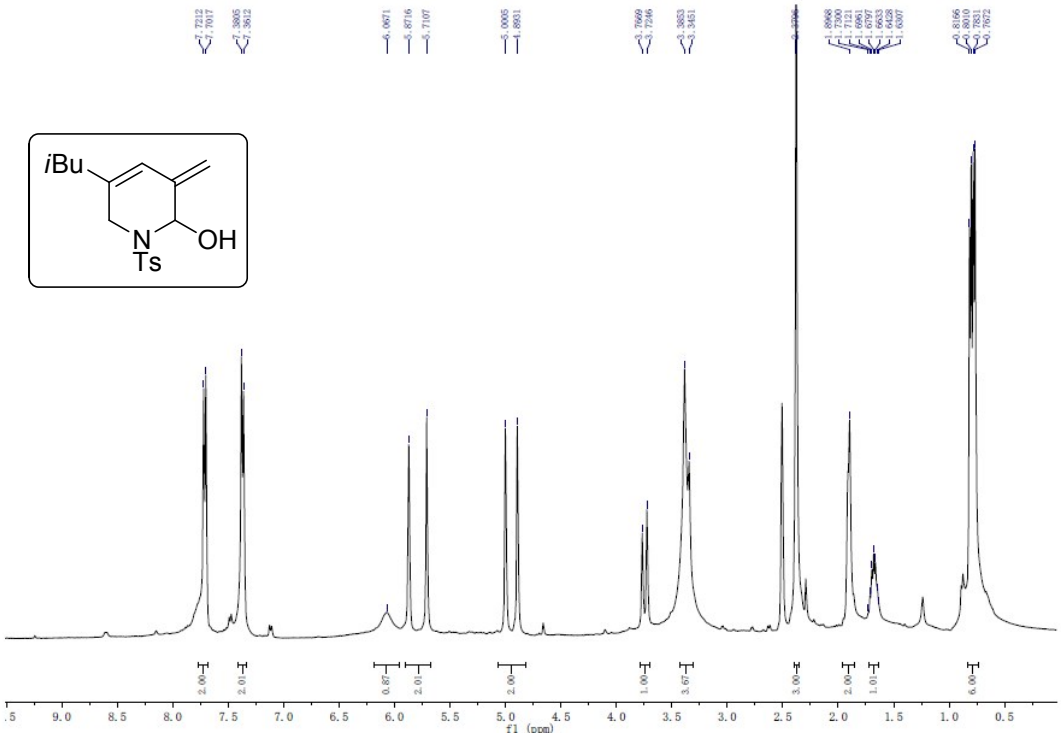
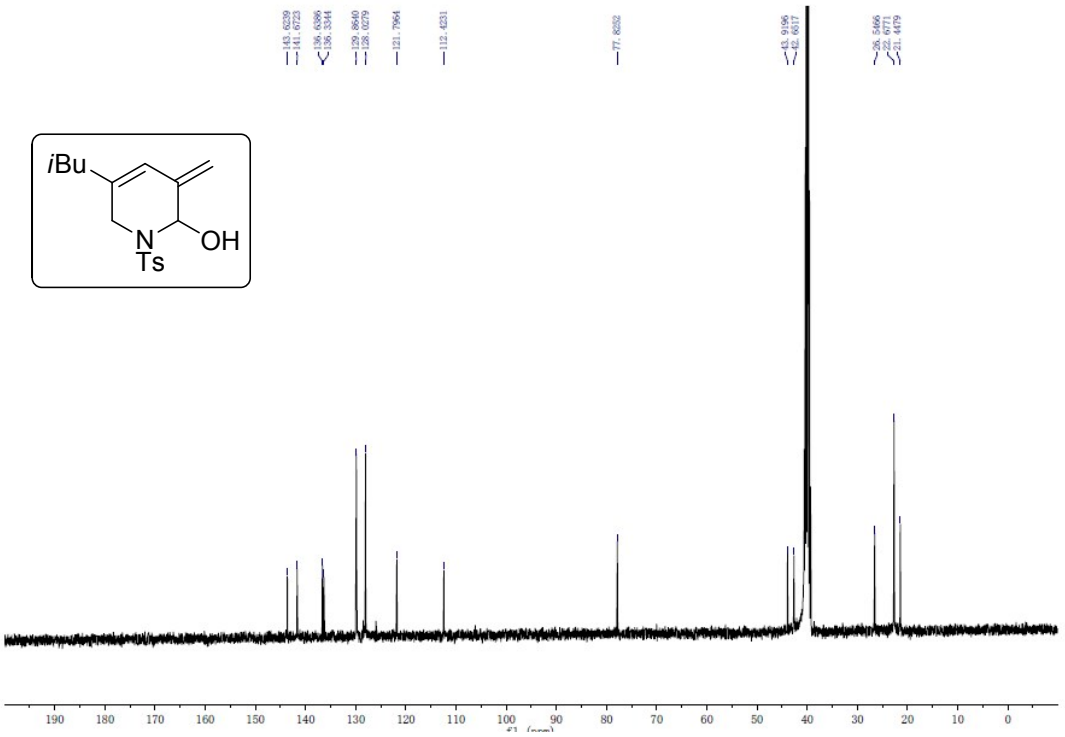

iBu
N
Ts
OH
f1 (ppm)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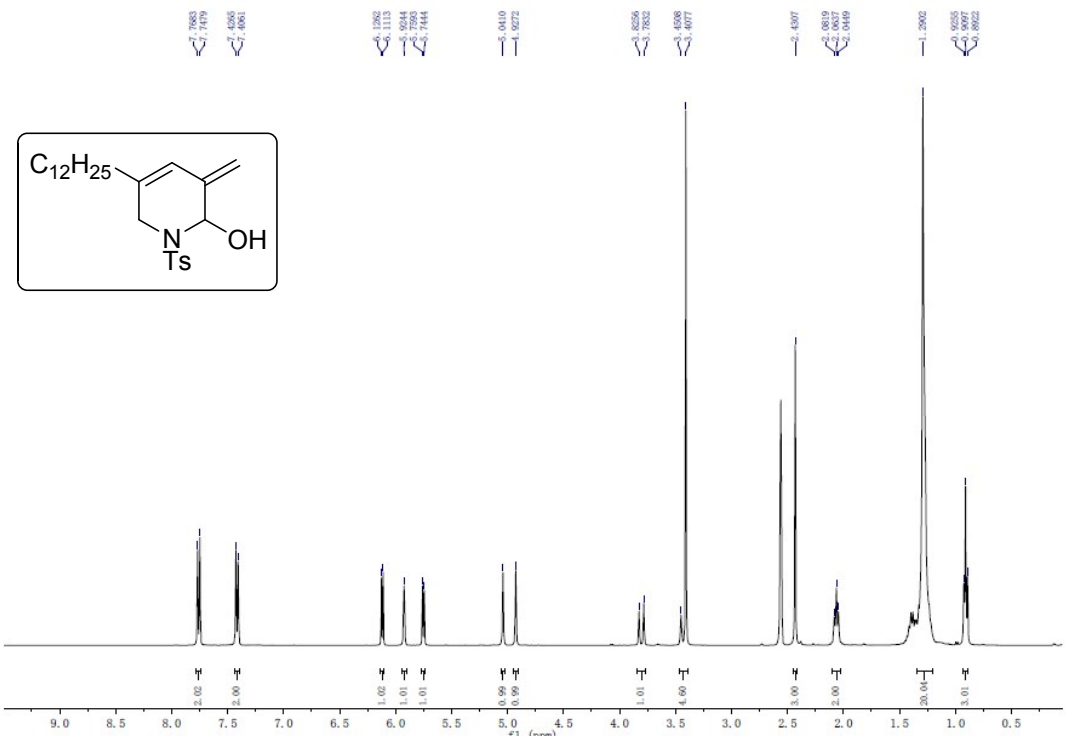
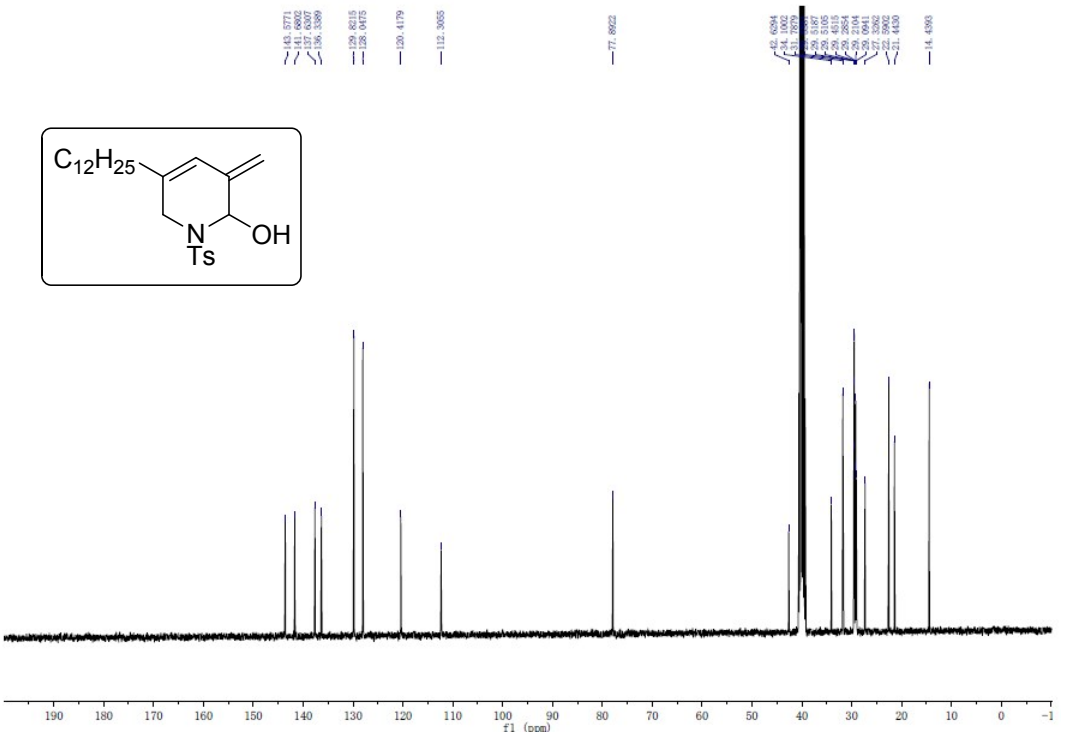
N
Ts
OH
f1 (ppm)


C12H25
N
Ts
OH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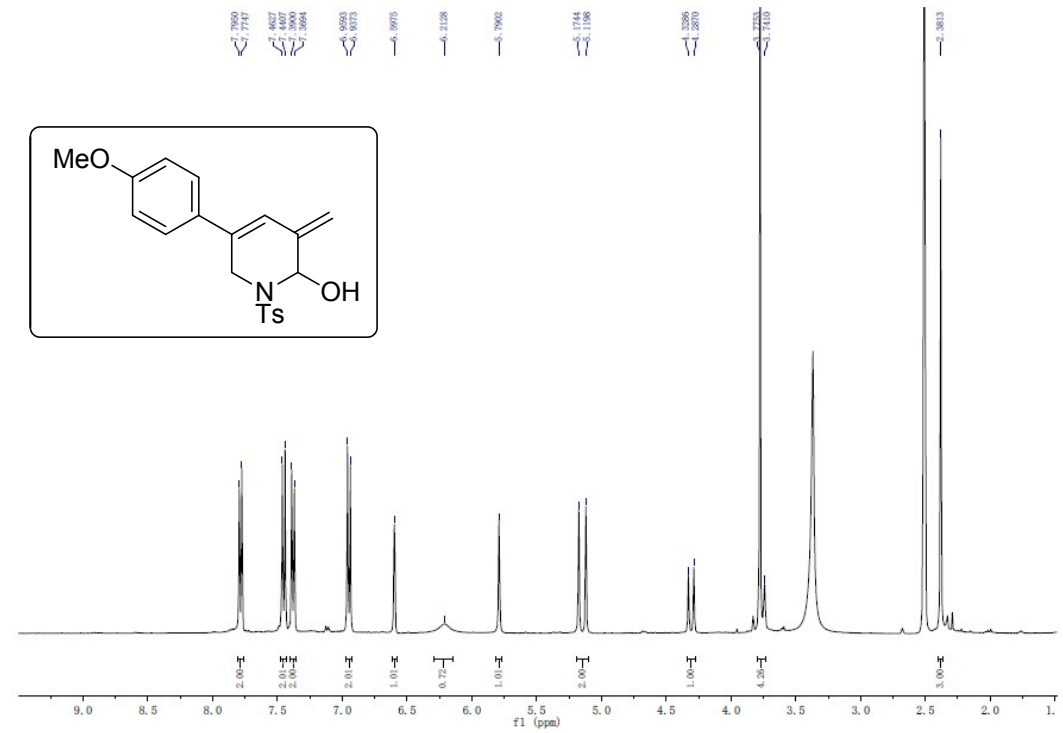
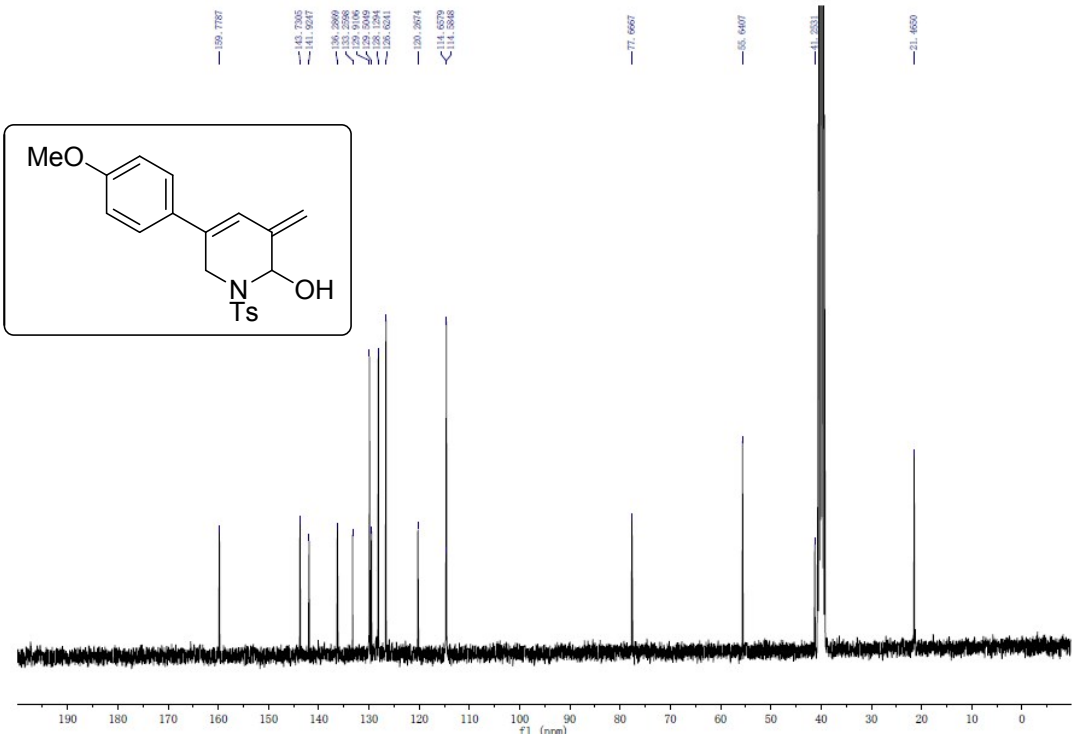
N
Ts
OH
f1 (ppm)


MeO
N
Ts
OH
f1 (ppm)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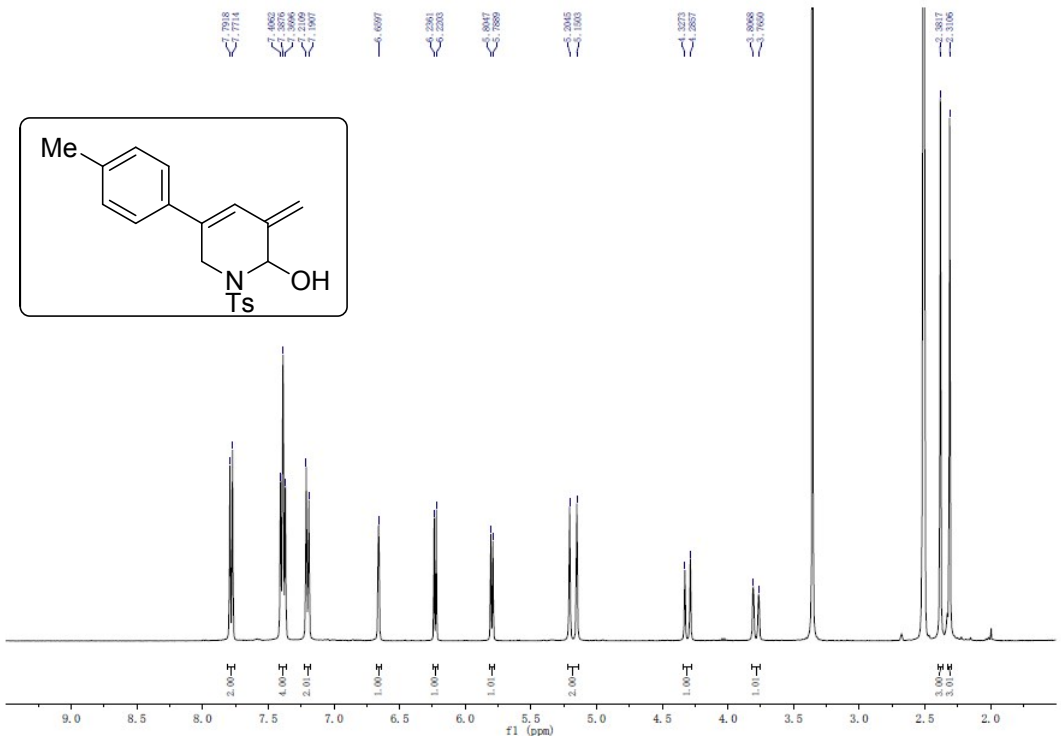
N
Ts
OH
f1 (ppm)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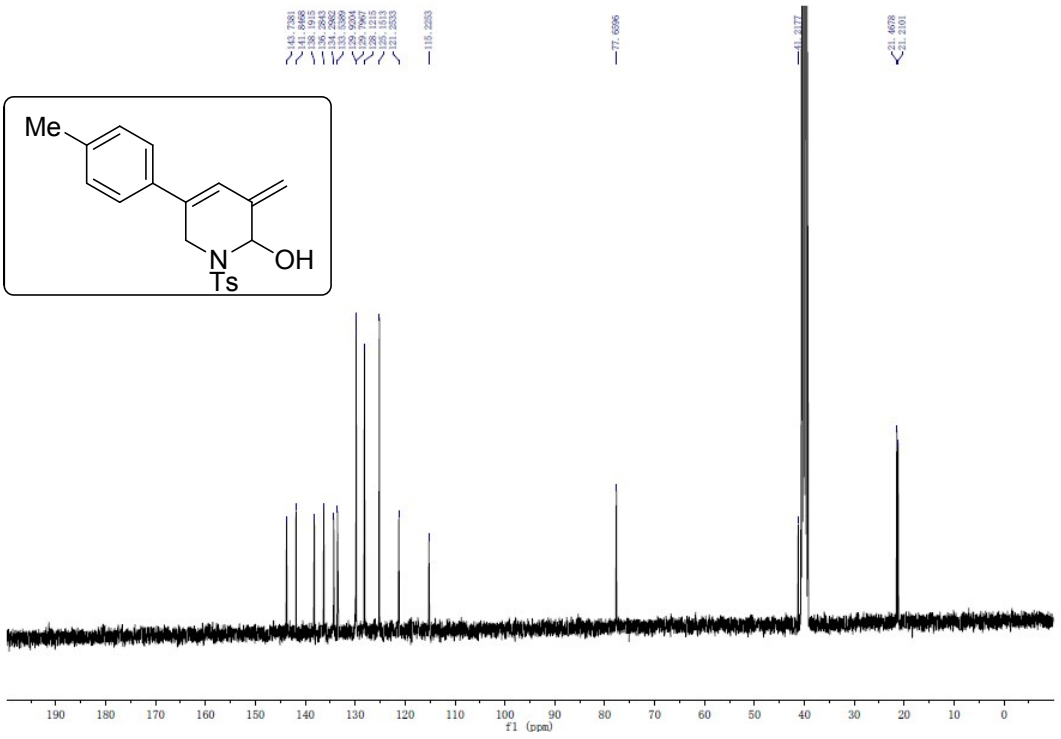
N
Ts
OH
f1 (ppm)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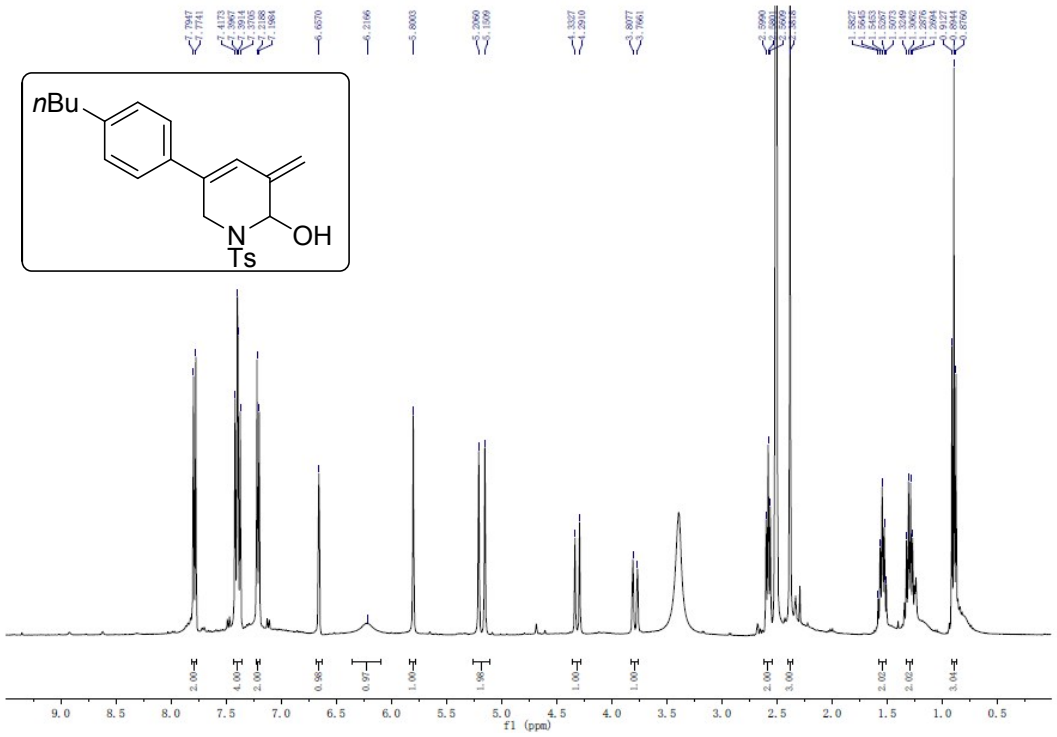
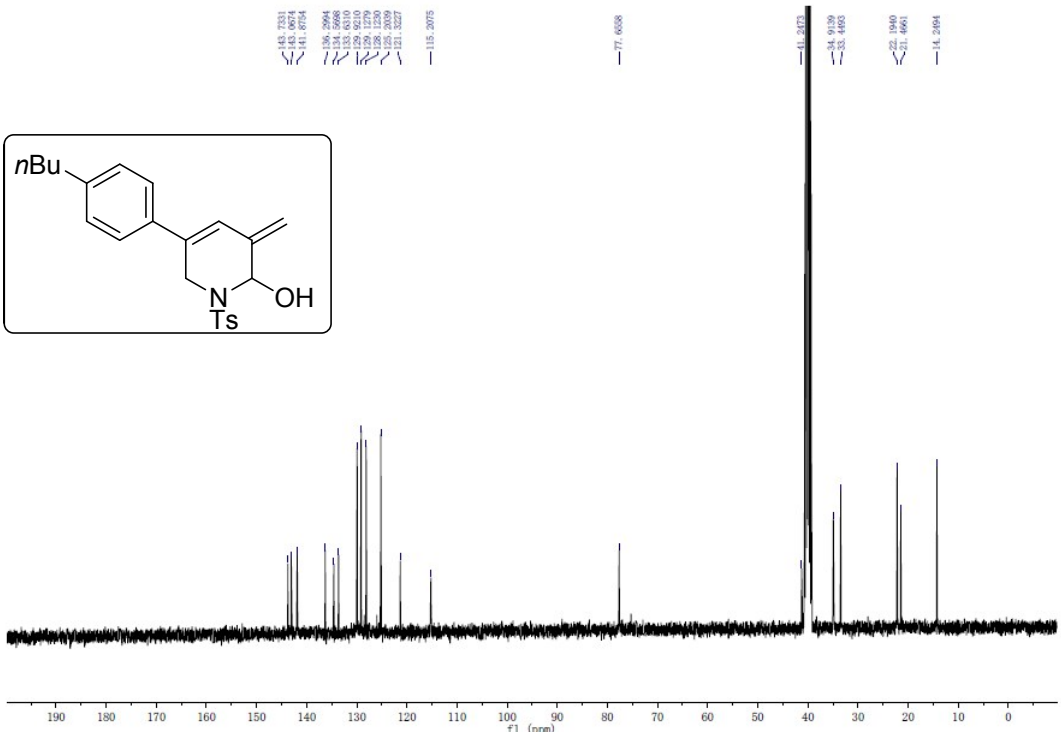
N
Ts
OH
f1 (ppm)


nBu
N
Ts
OH
f1 (ppm)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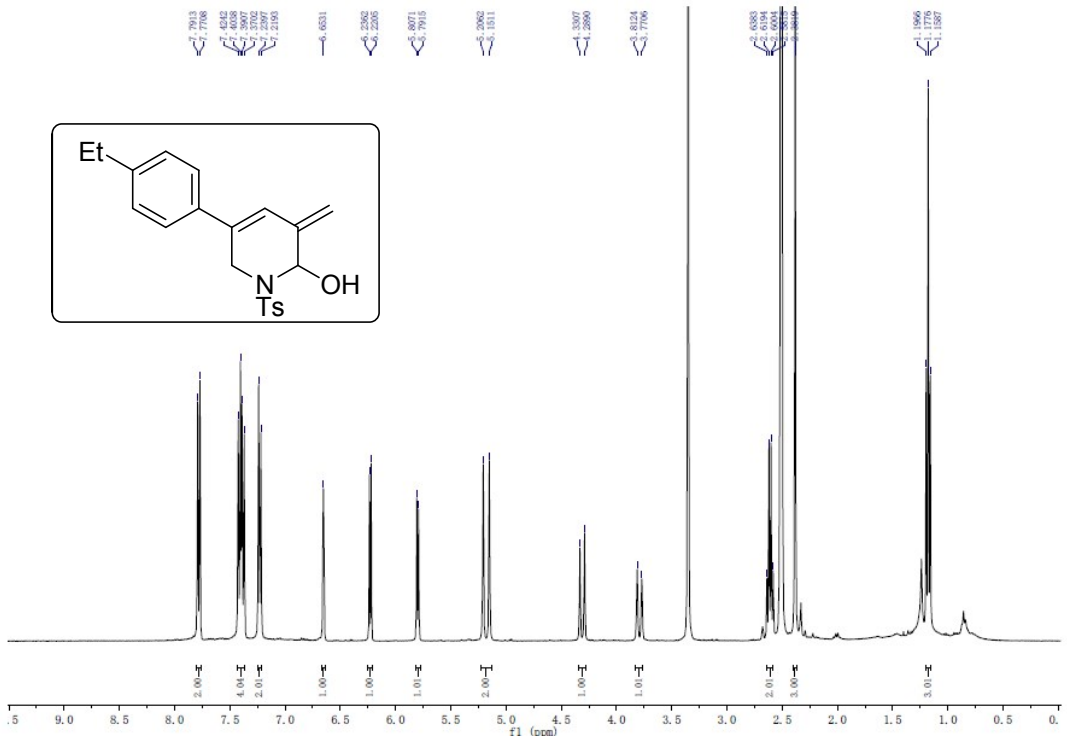
N
Ts
OH
f1 (ppm)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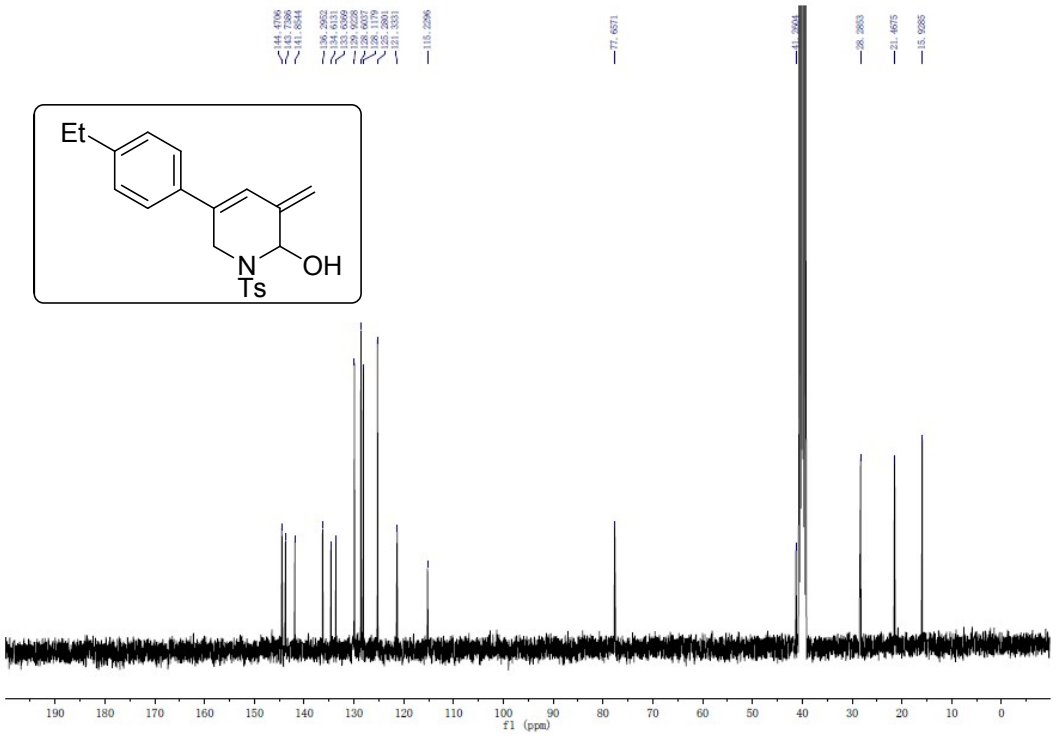
N
Ts
OH
f1 (ppm)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Ts
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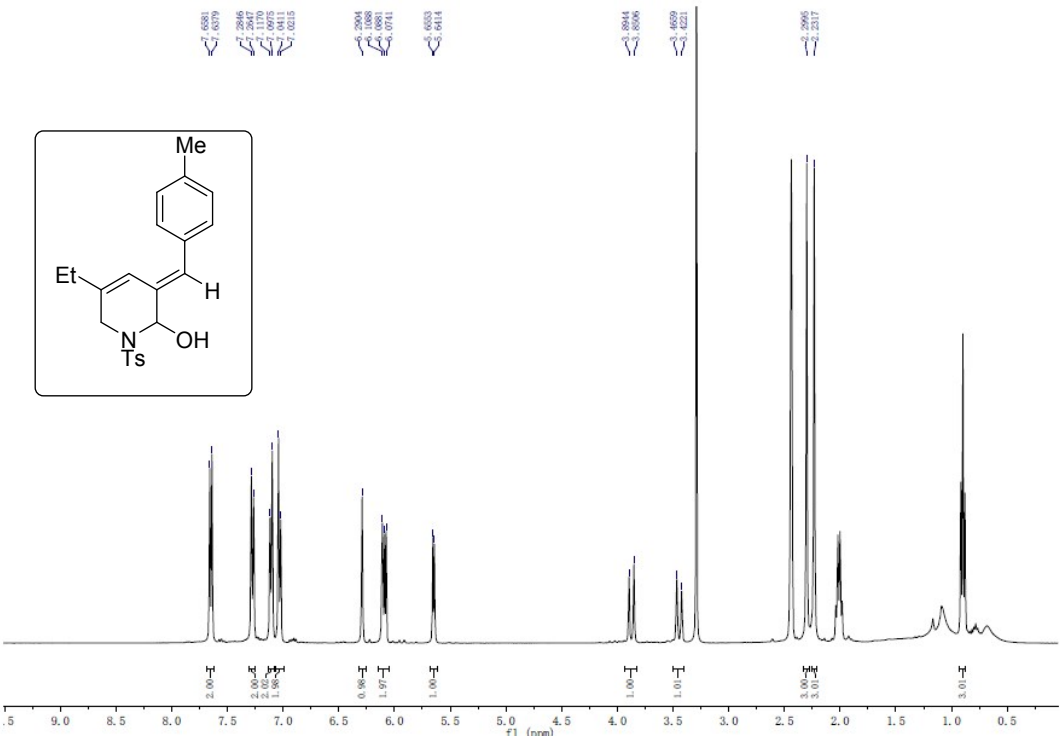
f1 (ppm)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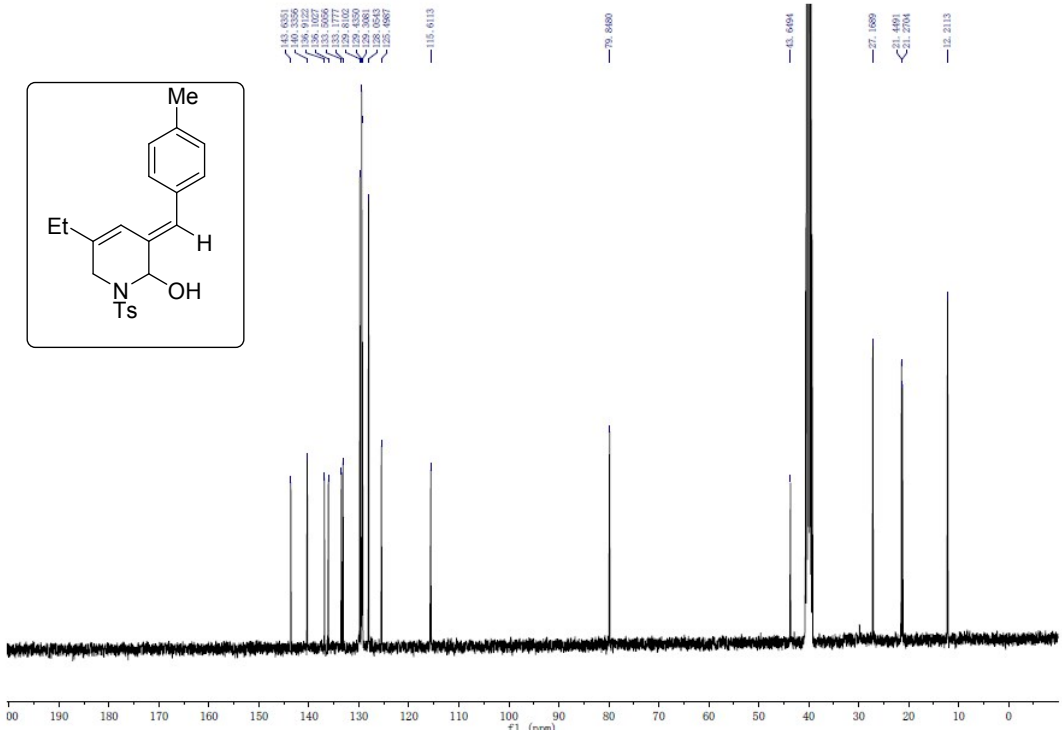
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Ts
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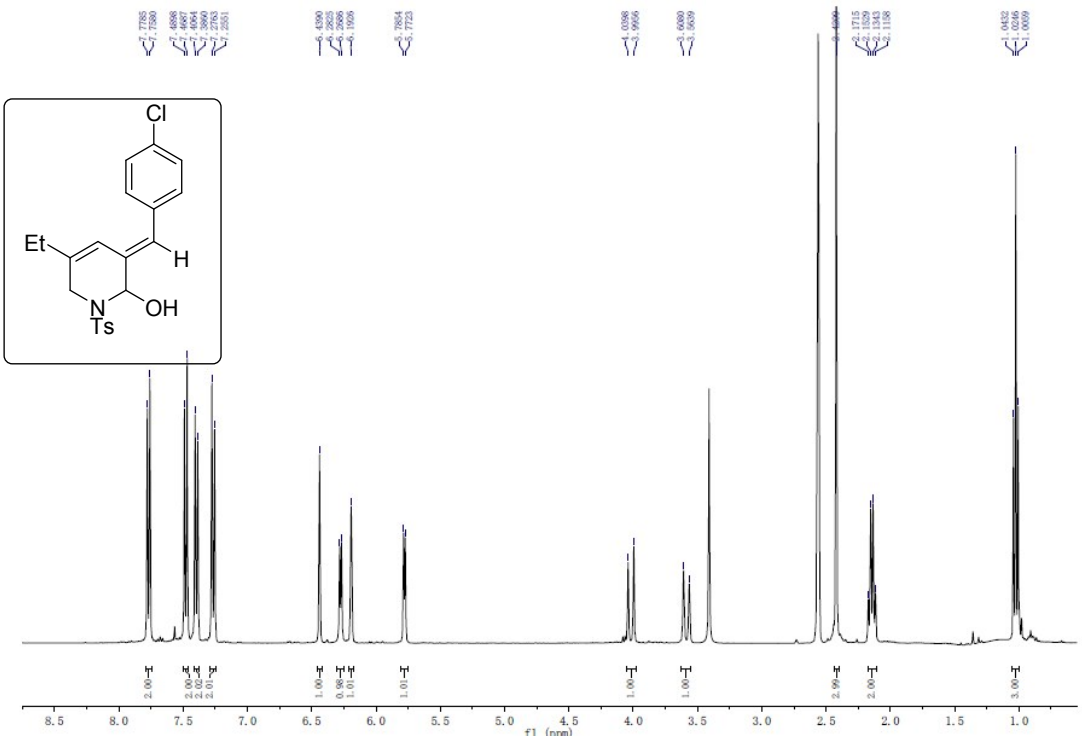
Cl
Et
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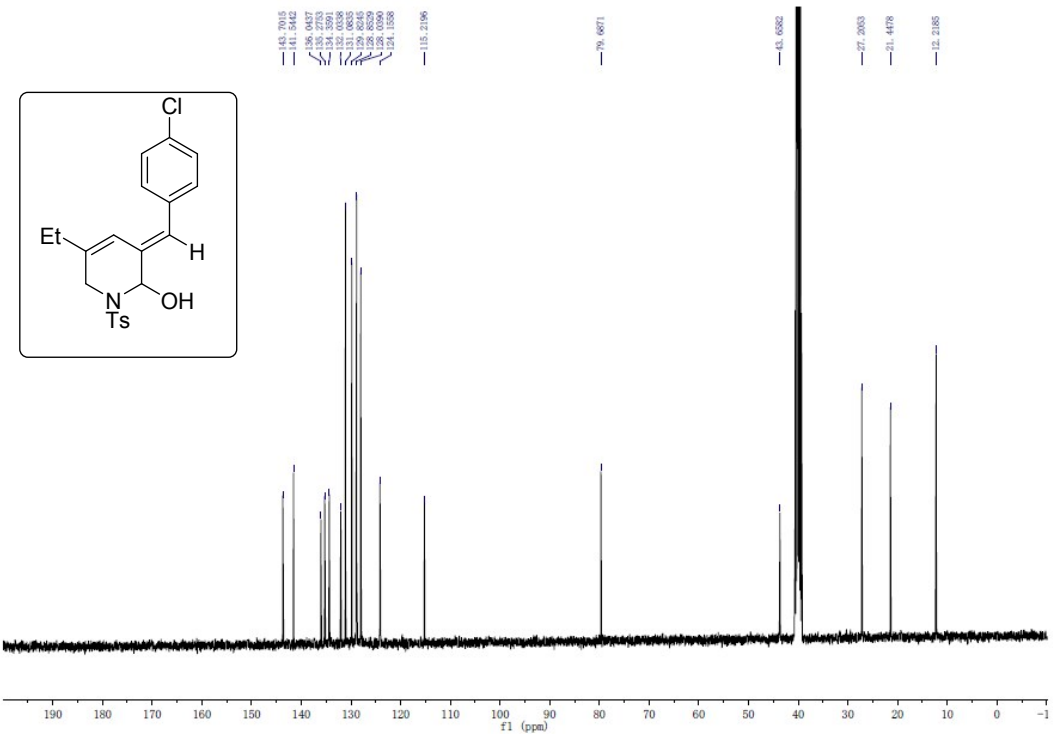
N
OH
Ts
f1 (ppm)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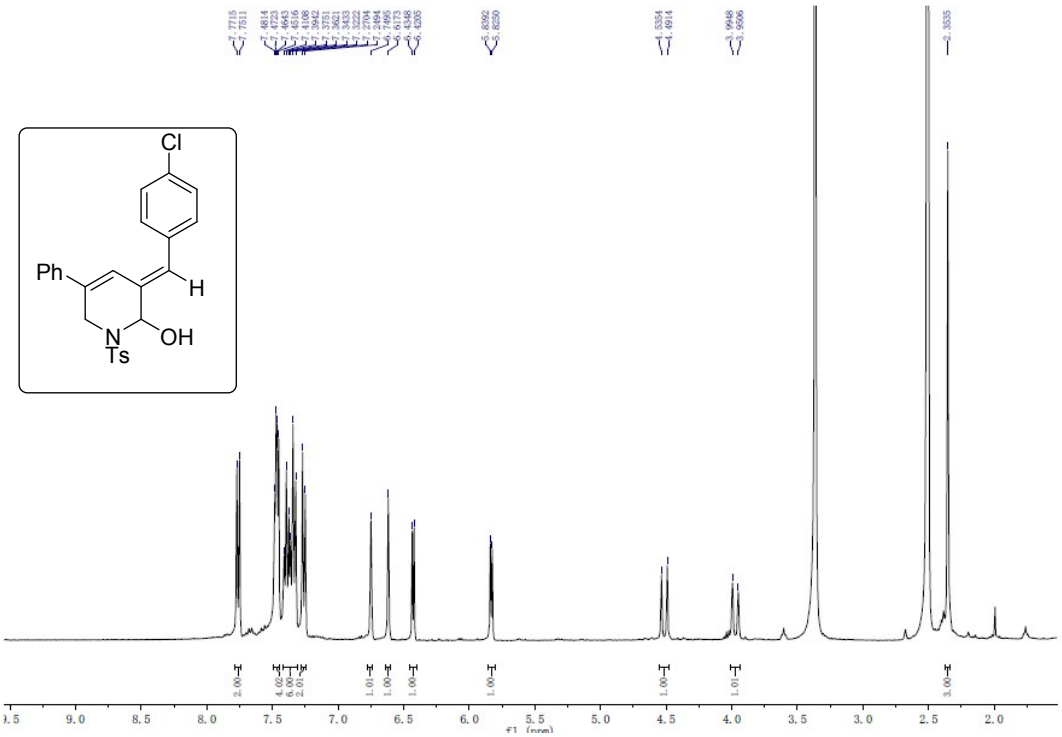
Ts
f1 (ppm)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Ph
H
N
Ts
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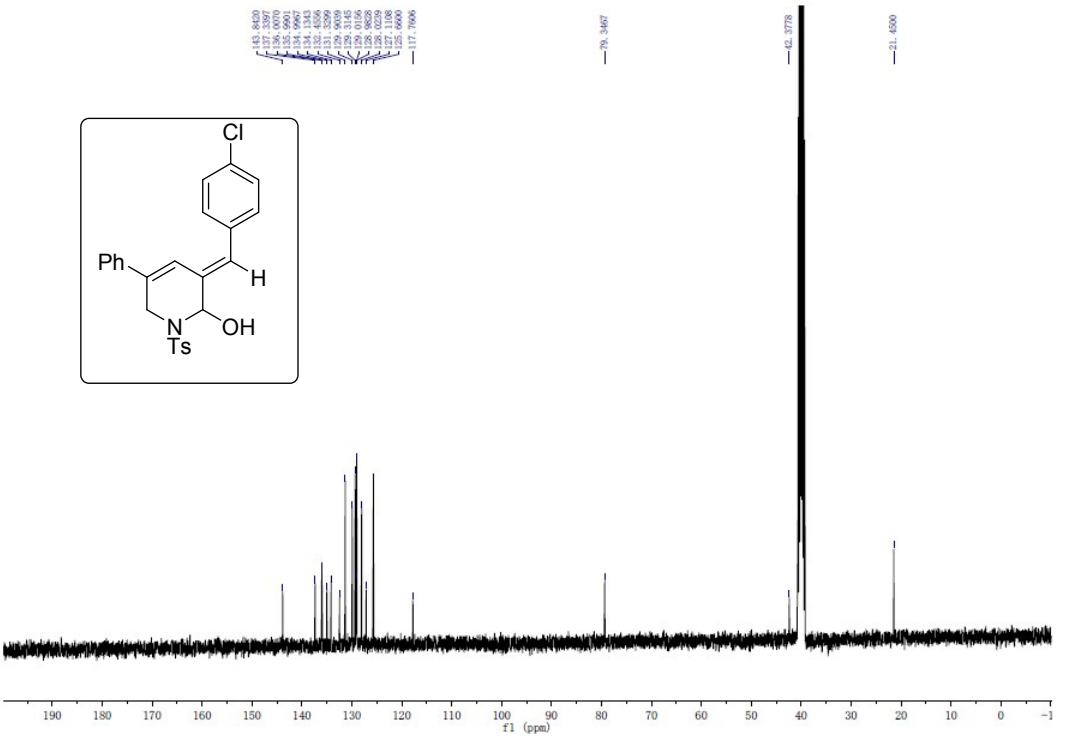
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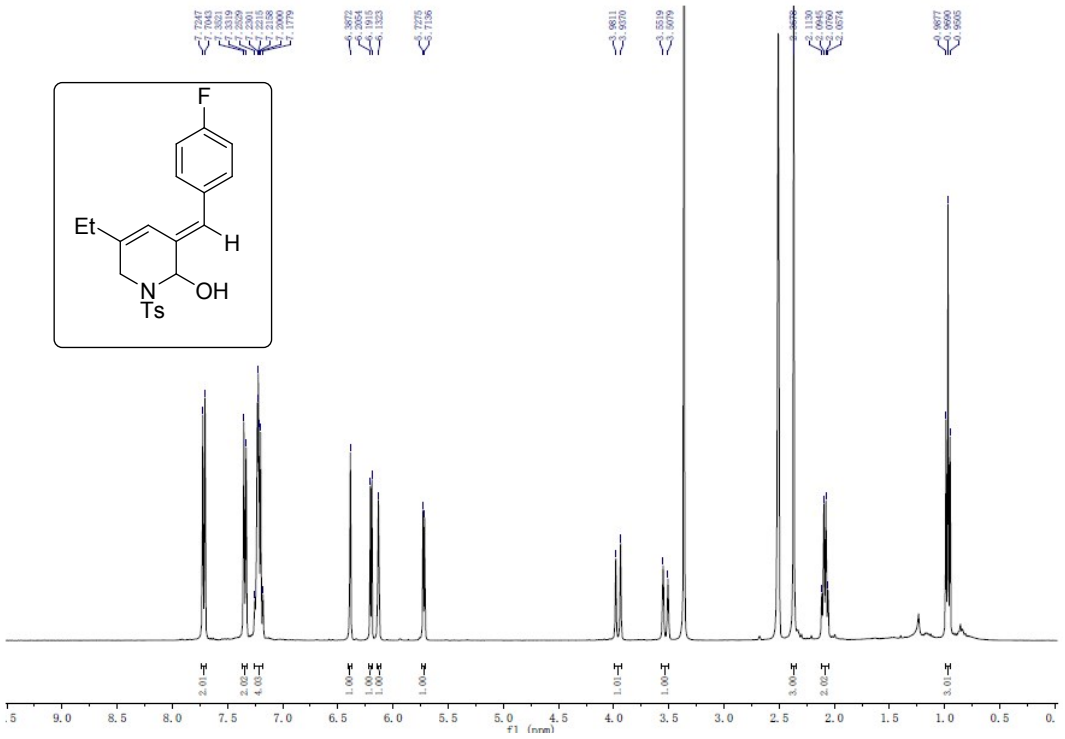
Ph
H
N
Ts
OH
f1 (ppm)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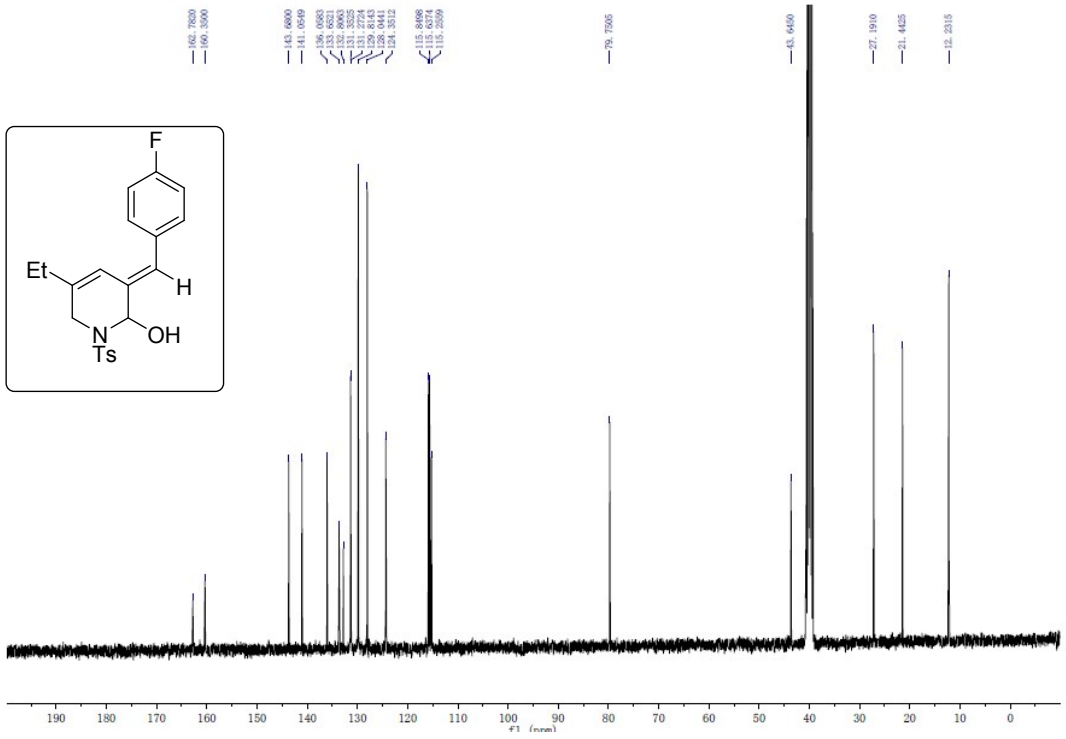
OH
Ts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OH
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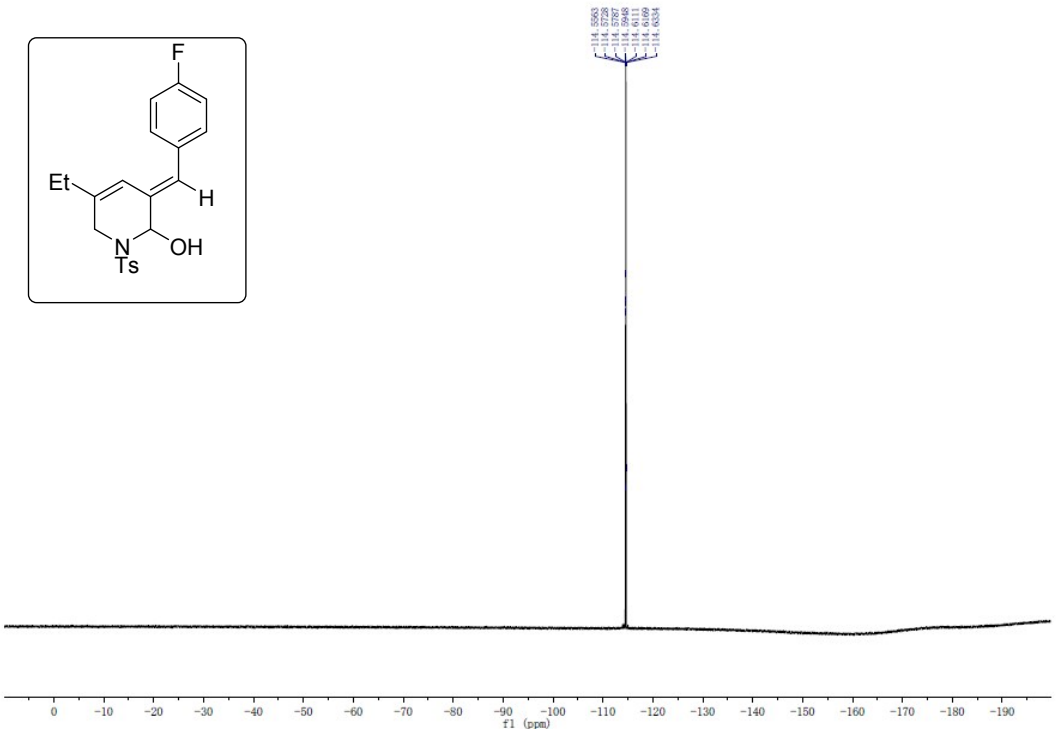
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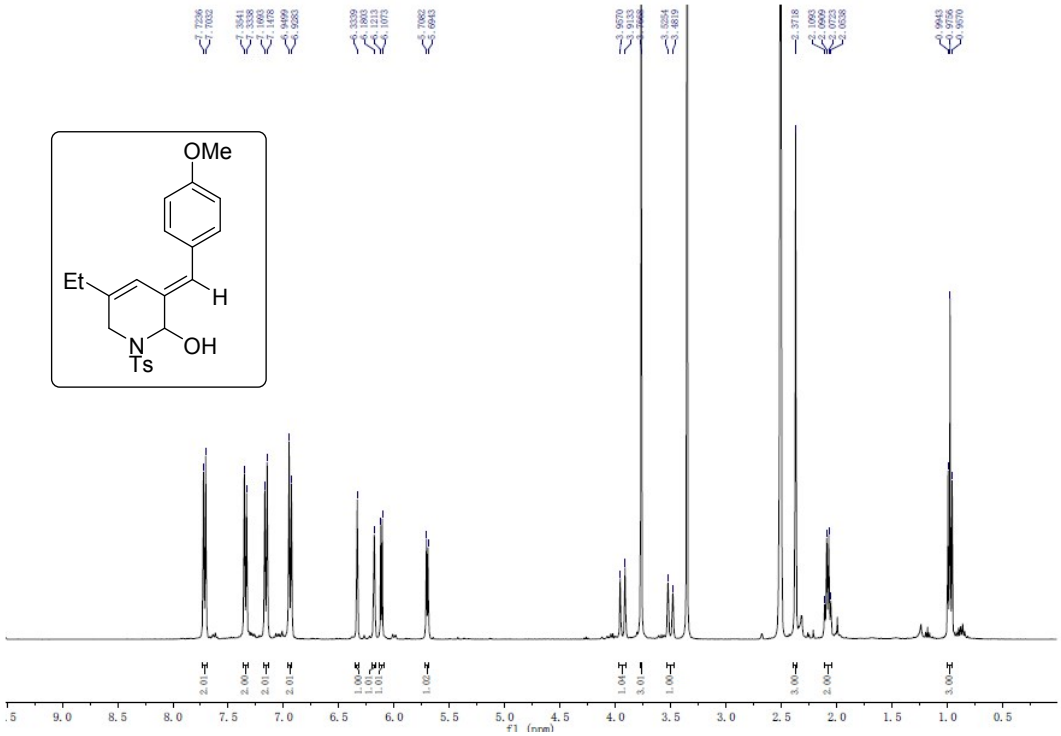
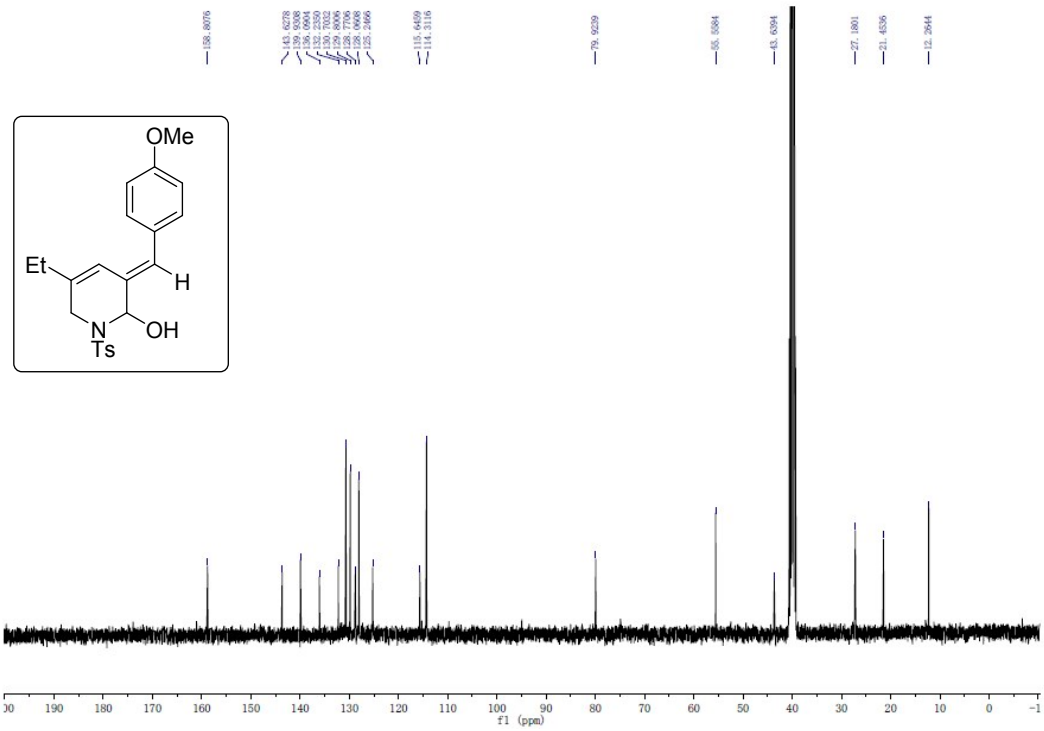
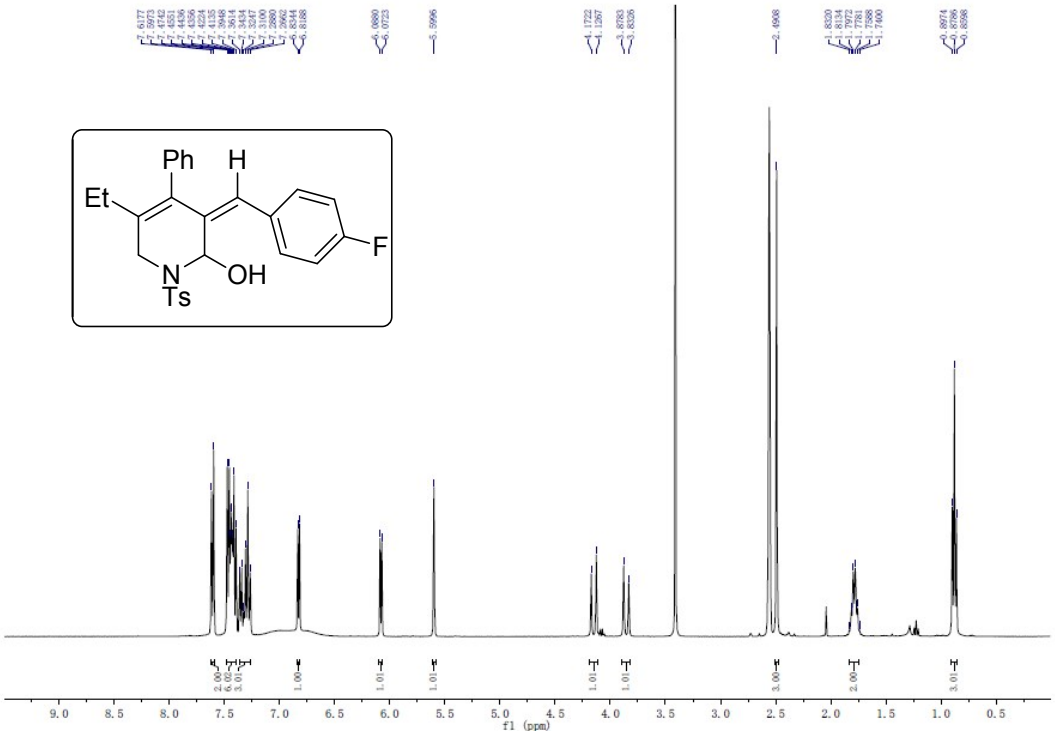
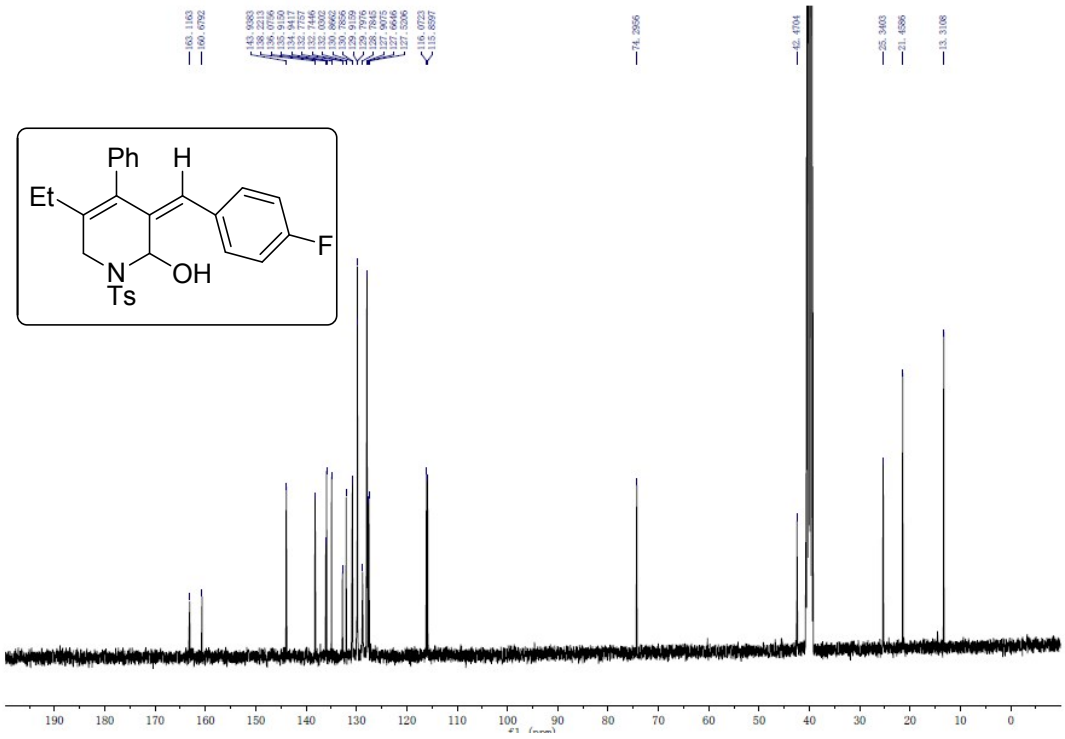
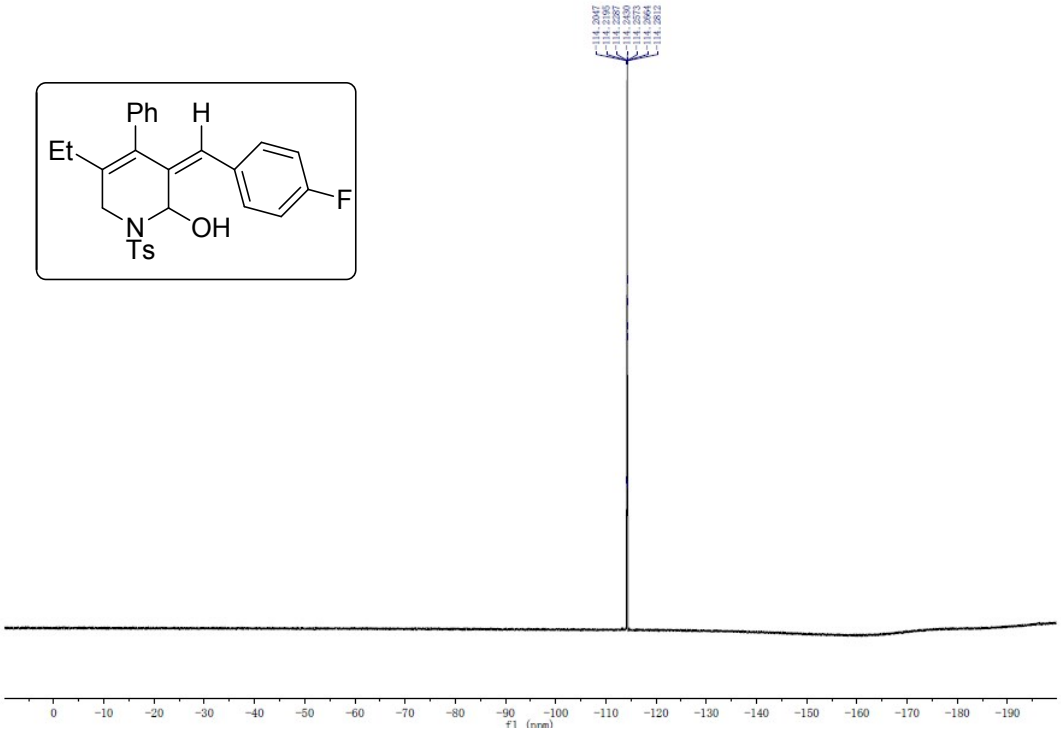
H
N
Ts
OH
f1 (ppm)

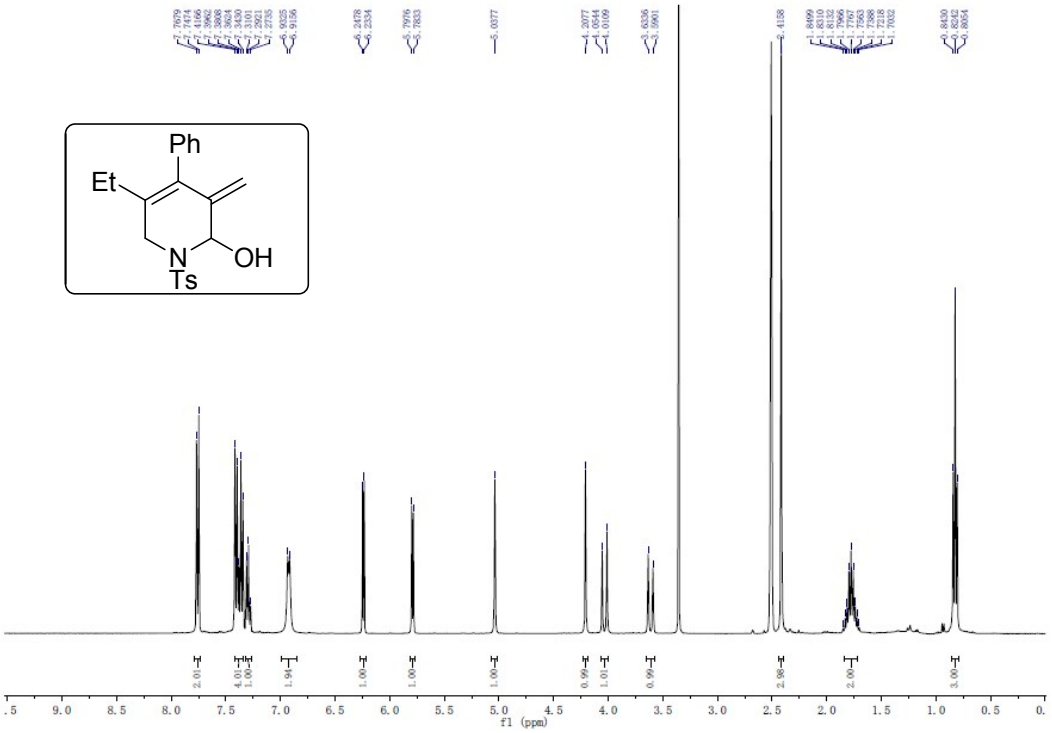

OMe
Et
H
N
Ts
OH
f1 (ppm)

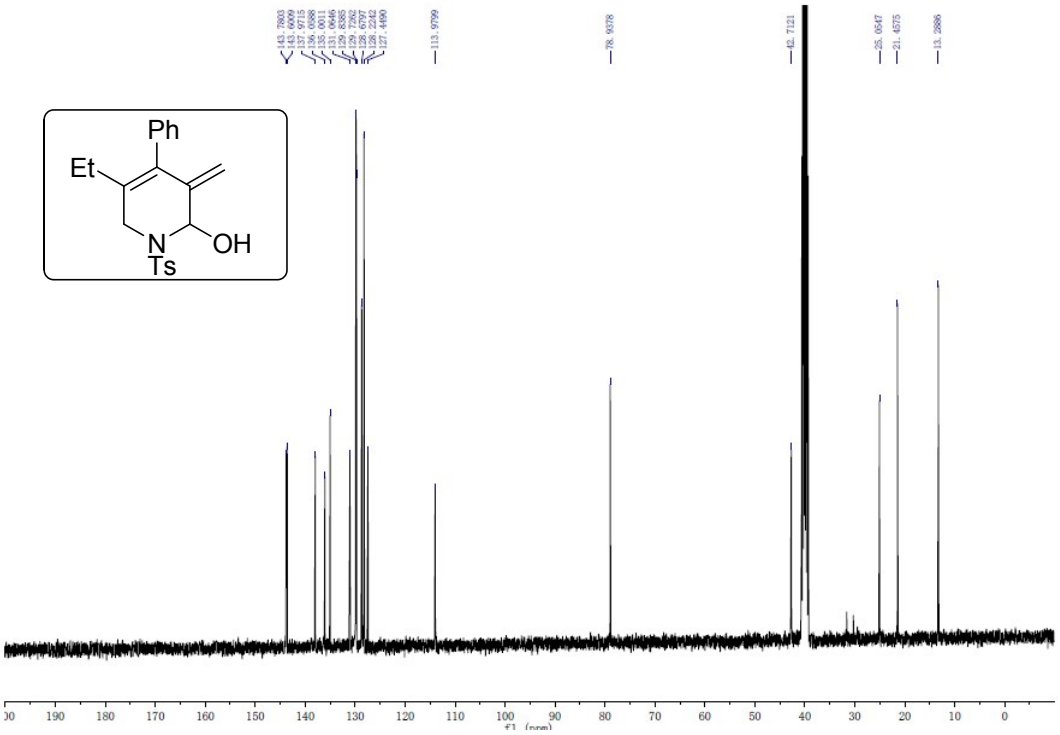

OMe
Et
H
N
OH
Ts
f1 (ppm)

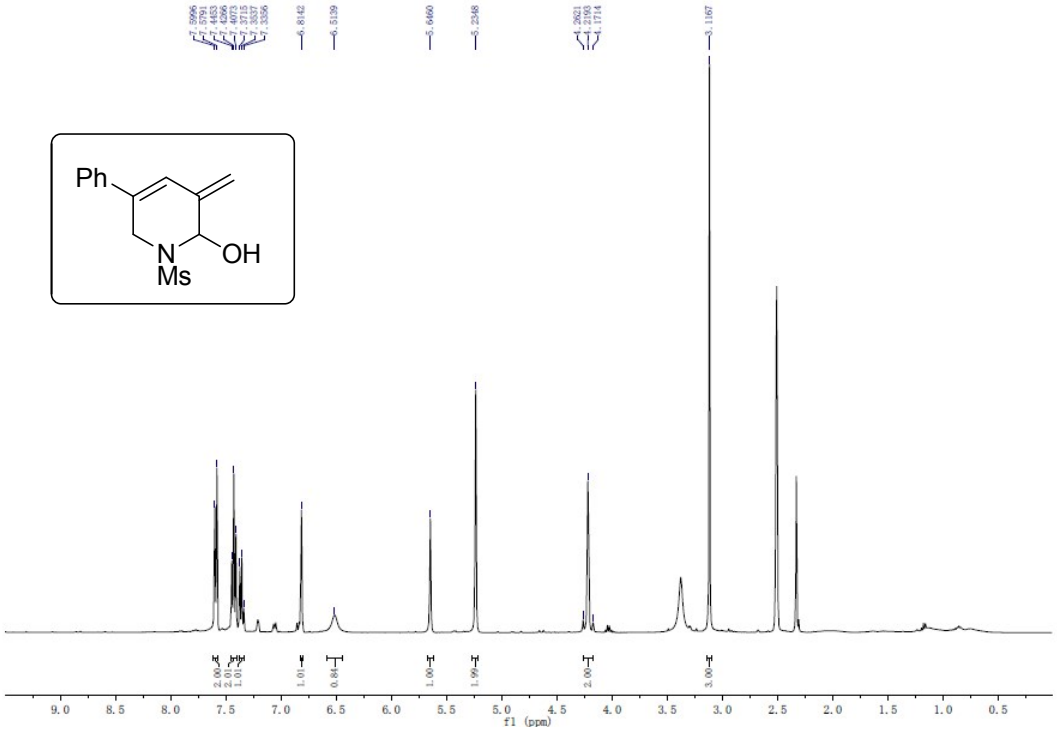

Ph
H
Et
F
N
OH
Ts
f1 (ppm)

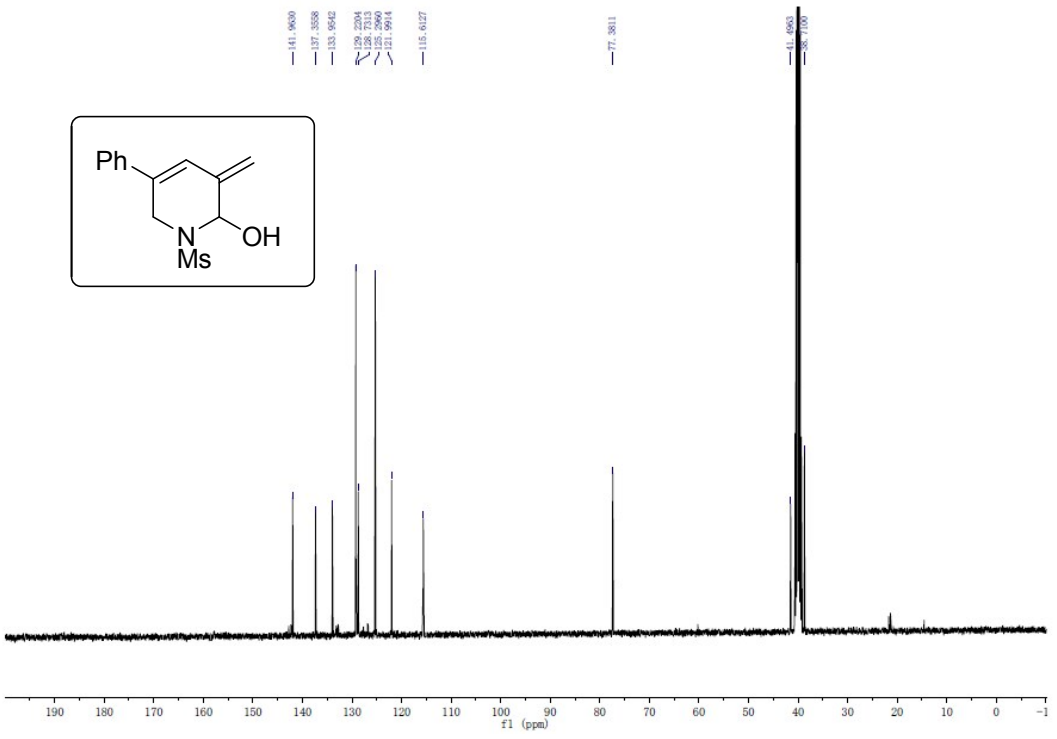

Ph
H
Et
F
N
OH
Ts


Ph
H
Et
F
N
OH
Ts

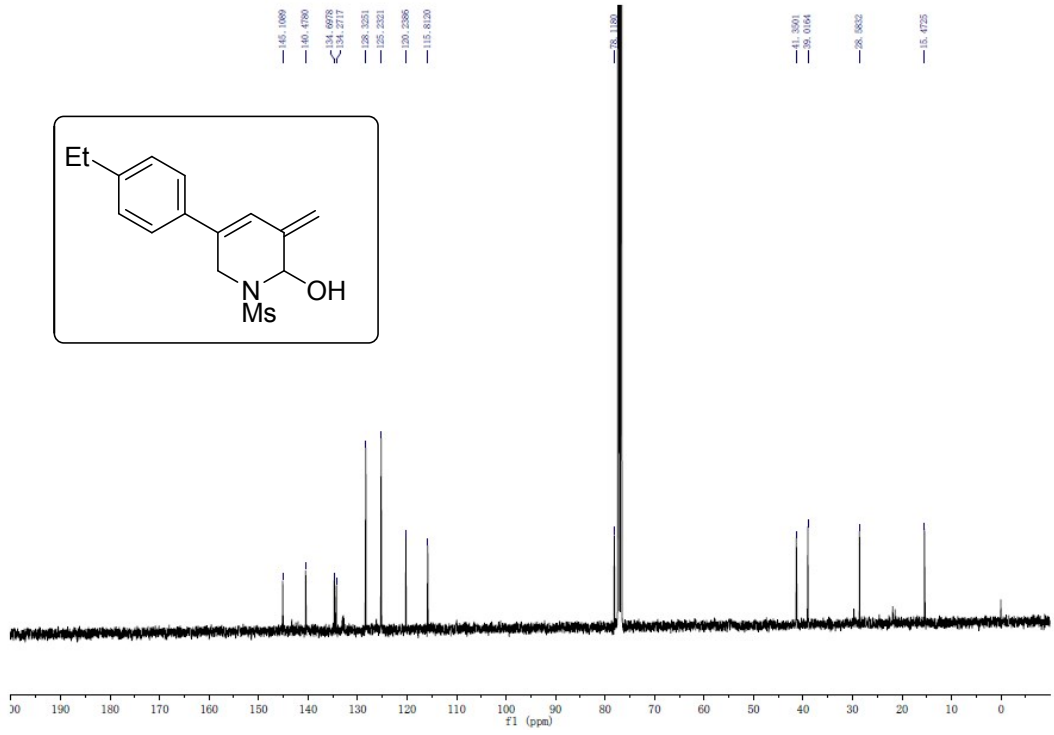

Ph
Et
N
Ts
OH
f1 (ppm)

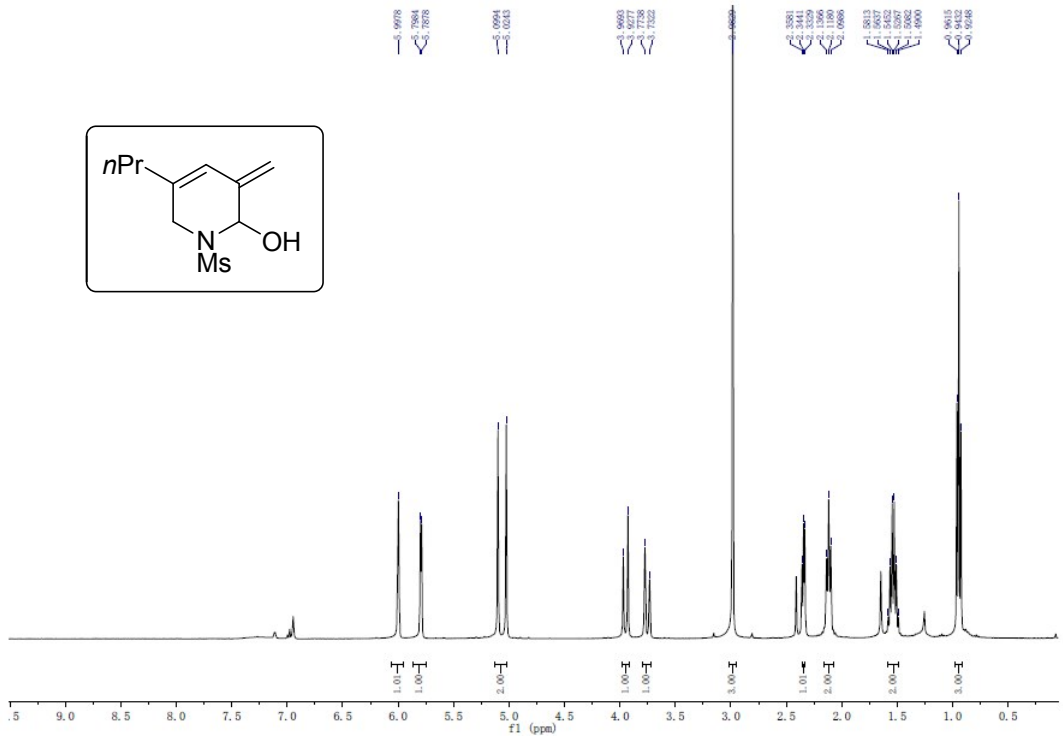

Ph
Et
N
Ts
OH
f1 (ppm)

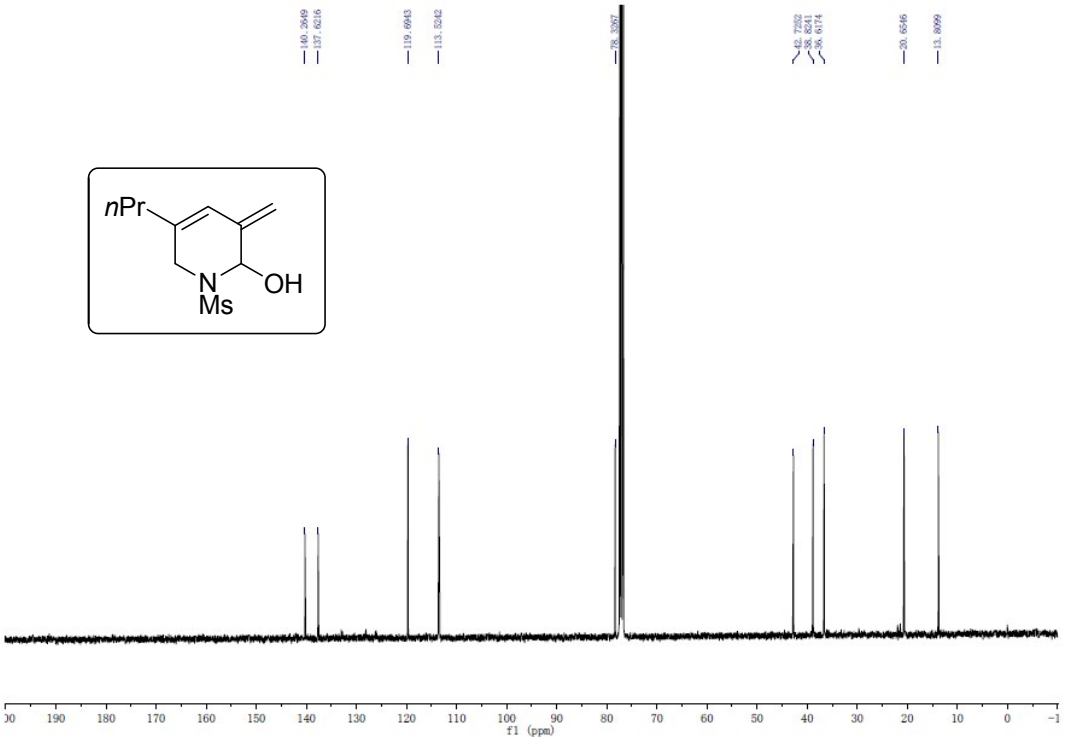

Ph
N
Ms
OH
f1 (ppm)

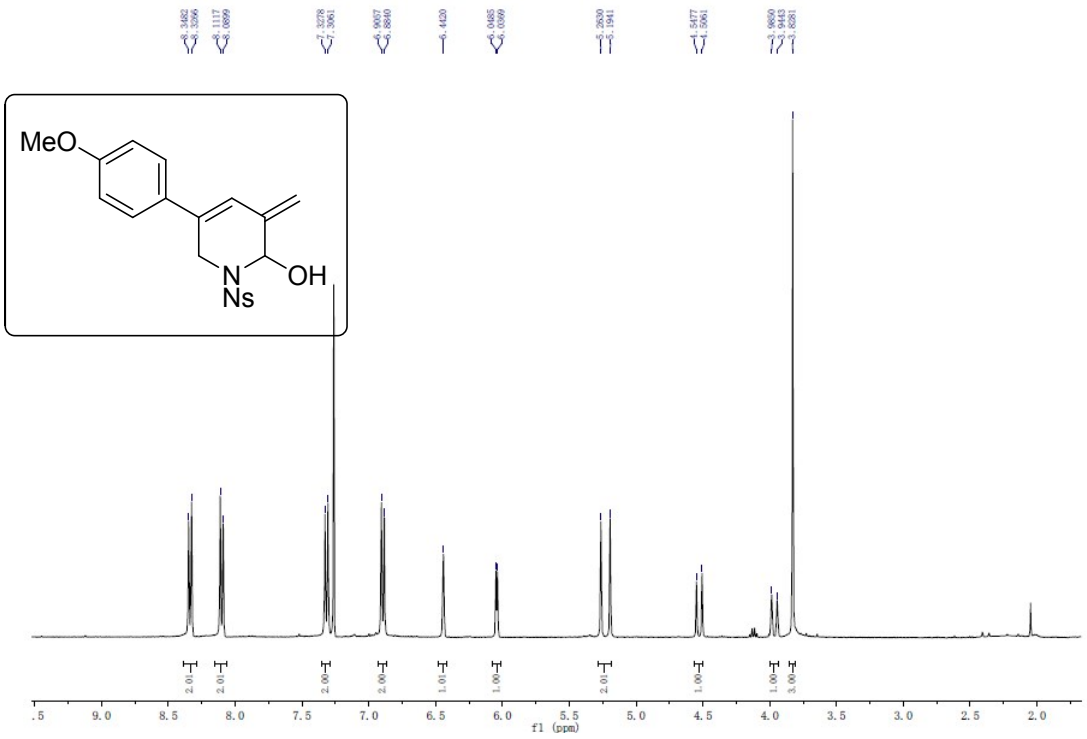

Ph
N
Ms
OH
f1 (ppm)

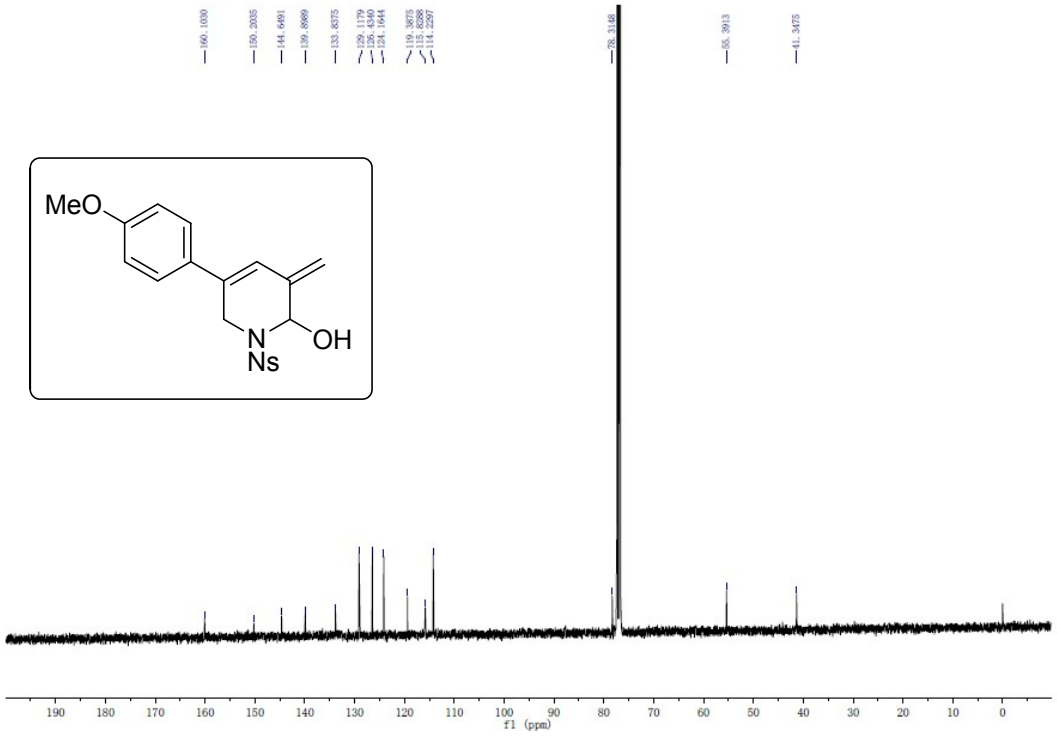

Et
N
Ms
OH
f1 (ppm)

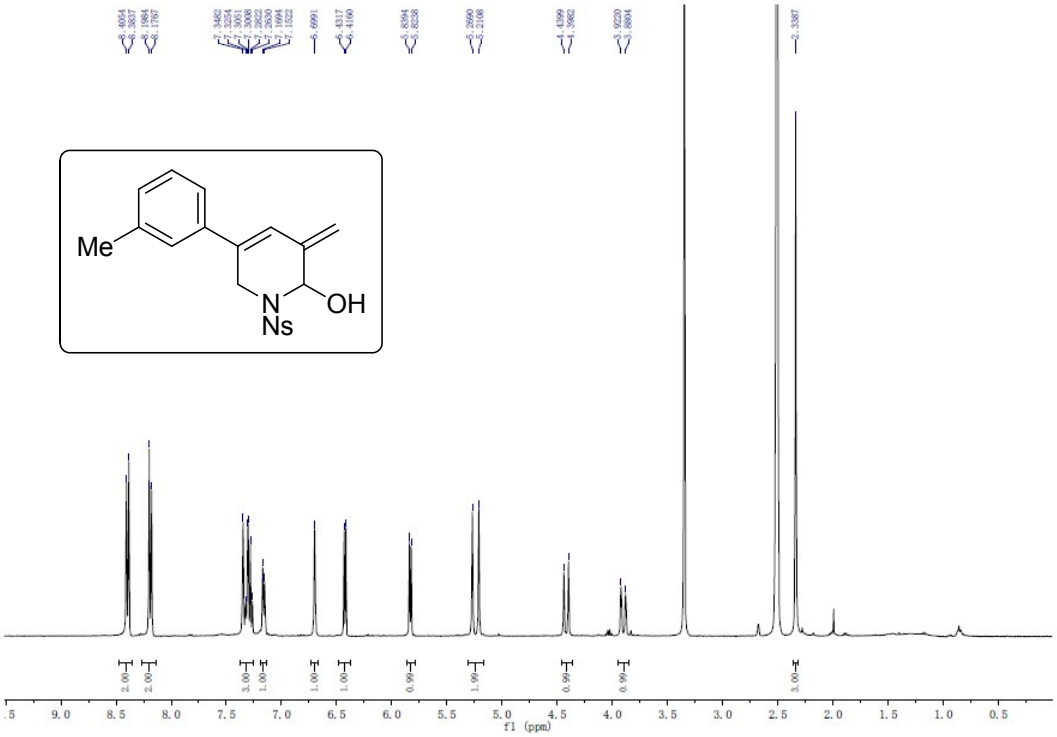

Et
N
Ms
OH
f1 (ppm)

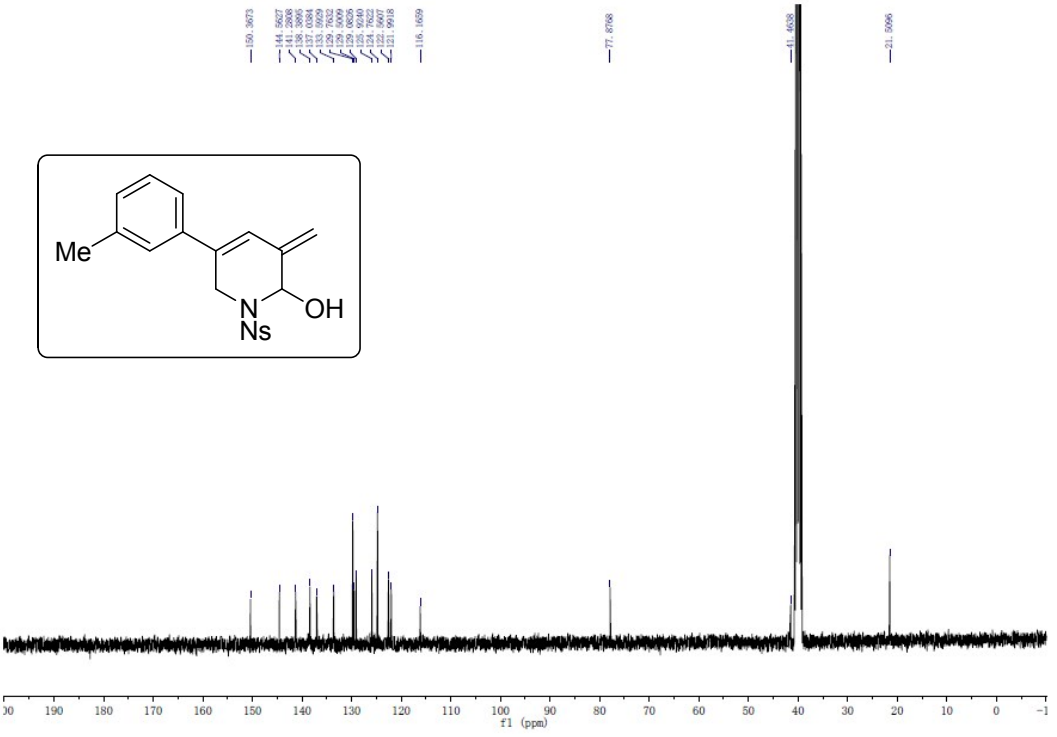

nPr
N
Ms
OH
f1 (ppm)


nPr
N
Ms
OH
f1 (ppm)

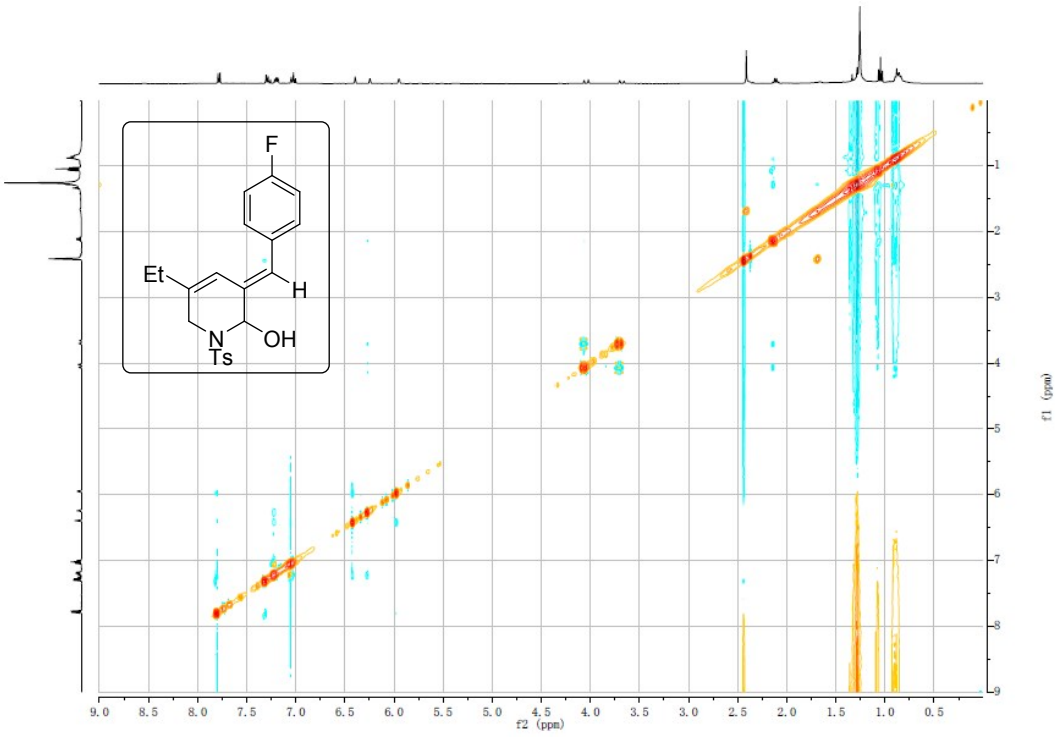

MeO
N
Ns
OH
f1 (ppm)

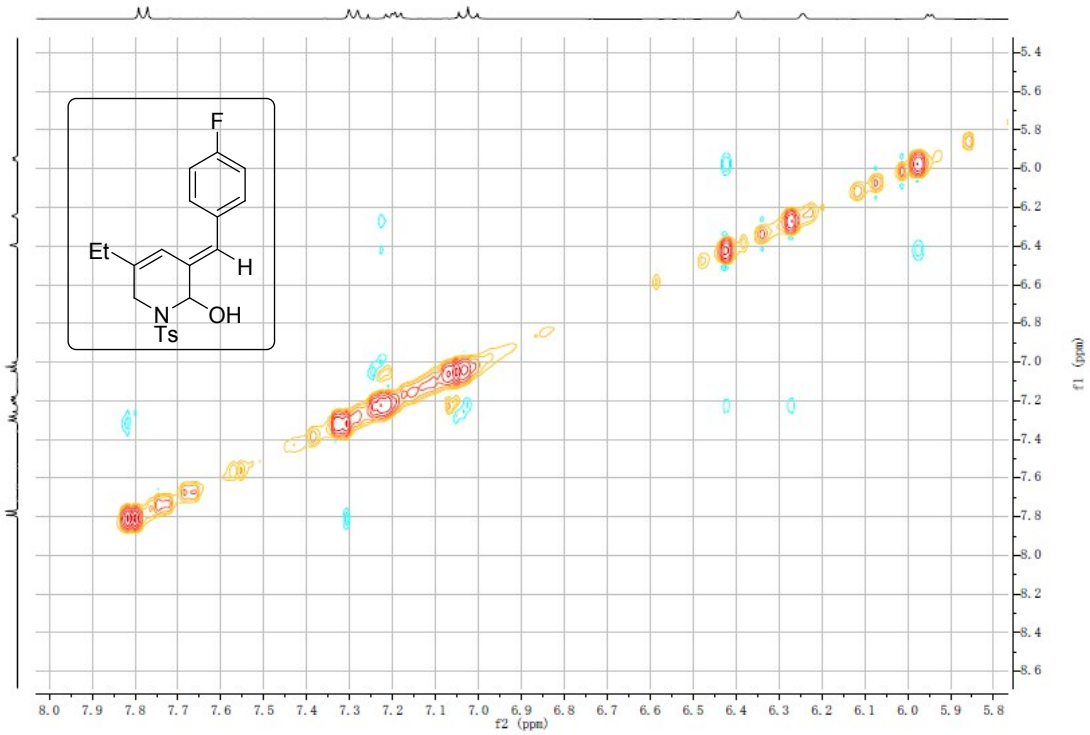

MeO
N
Ns
OH
f1 (ppm)

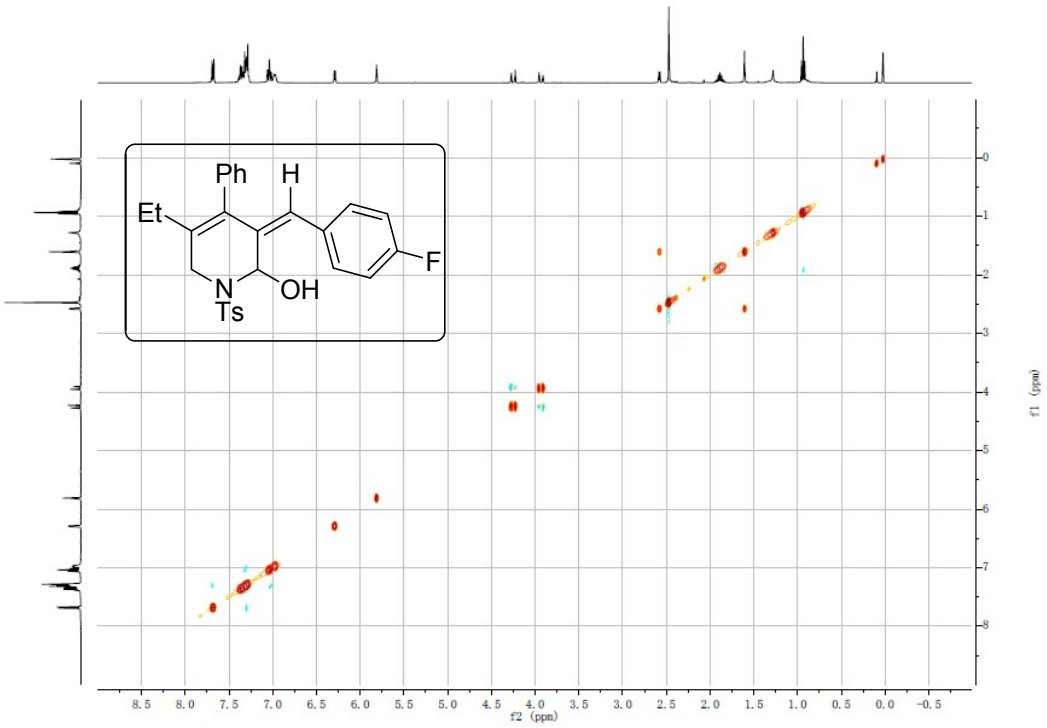

Me
N
Ns
OH
f1 (ppm)


Me
N
Ns
OH
f1 (ppm)

VII ^{1}H NOE of product **2l** and **2n**.

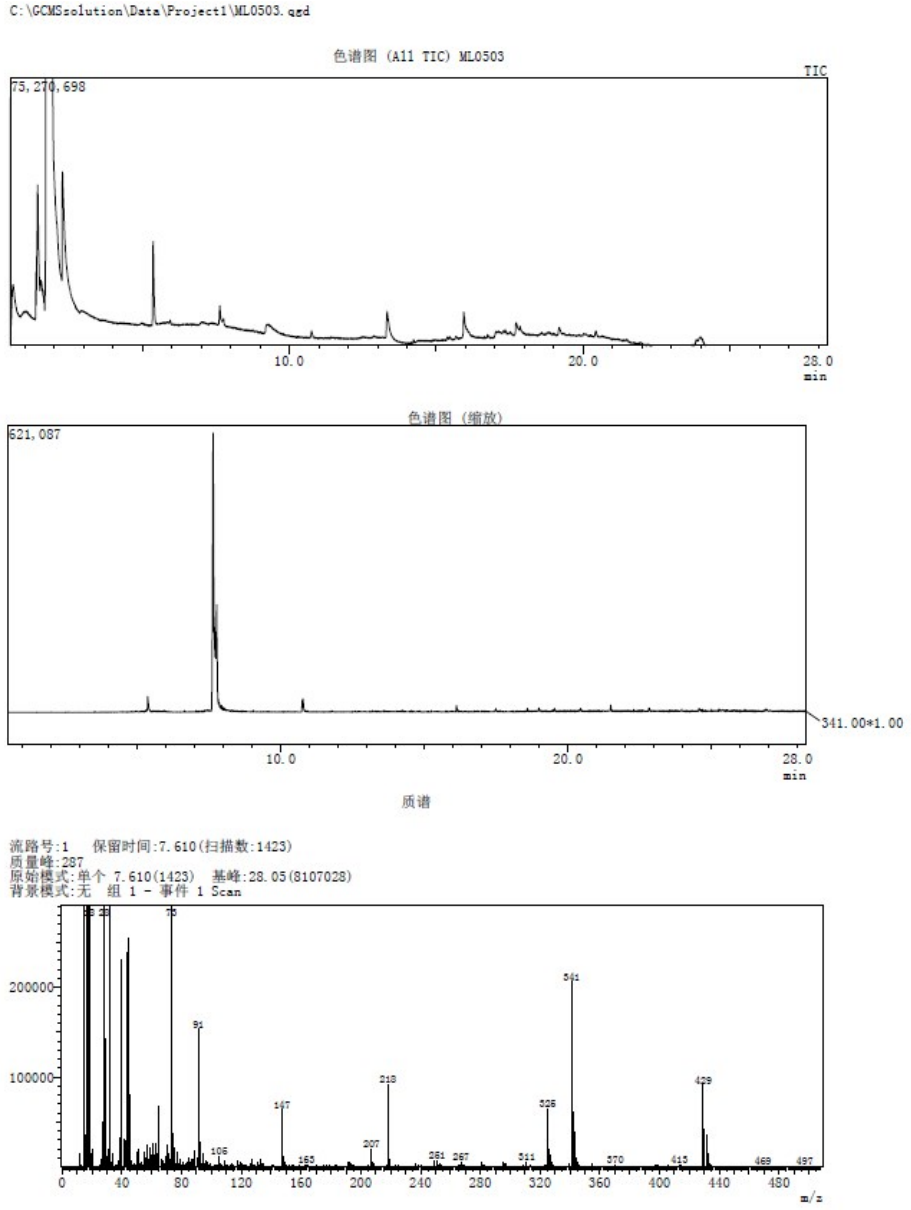





Ph
H
Et
F
N
OH
Ts
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)

VIII Isotope tracking experiment

GCMS of **2a** in presence of H_2O^{18}



1H NMR of **2b** in D-THF