Copper-catalysed bromine atom transfer cyclisation in SDS micelles

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Supplementary Information

Content

1. General information

All solvents and commercially available reagents were purchased as reagent grade and were used without further purification unless otherwise stated. Thin-layer chromatography (TLC) was performed using silica gel plates (60 F254) which were visualized under short wavelength UV light (254 nm) or by staining with a solution of phosphomolybdic acid in ethanol (95%). Flash Column chromatography was performed using silica gel of 200-300 mesh. HR-MS analysis was performed on a Bruker APEXII FT-ICR mass instrument equipped with an ESI source. NMR spectra were measured at room temperature using a Bruker Avance III-400 MHz spectrometer (400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR). Samples for NMR spectra were dissolved in $CDCl_3$ unless otherwise specified. Chemical shifts in the NMR spectra are referenced to the residual undeuterated solvent (δ = 7.26 for ^{1}H NMR; δ = 77.0 for ^{13}C NMR). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet, multiplet (m) or broad (br). Electrochemical studies were conducted with the three-electrode CHI660D potentio station under an argon atmosphere. Ferrocene/ferrocenium (Fc/Fc^{+}) was used as an internal reference, a glassy carbon electrode was used as the working electrode, a platinum plate was used as the counter electrode, and Ag/0.01 M $AgNO_3$ (0.1 M *n*-Bu_4NClO_4 in CH_3CN solution) was used as the reference electrode. Photocatalytic reactions were performed using a photoreactor equipped with blue LEDs (JIUSHANG® GCH-4 λ= 410–420 nm, 24 W optical power) or a Kessil® LED lamp (Kessil® PR160L λ= 390 nm, maximum 40 W optical power) as the light source. The unsaturated bromides used as the substrates were prepared following the reported methods.[1]

2. Experimental procedures

2.1 Preparation of the SDS solution and carbonate buffer

Solution of sodium dodecyl sulfate (SDS, 0.3 M) in water was prepared by dissolving SDS (8.65 g, 0.03 mol) in distilled water (100 mL).

Preparation of 1.0 M carbonate buffer solution (pH = 10.6):[2]

Solution A (1.0 M $NaHCO_3$) was prepared by dissolving $NaHCO_3$ (8.4 g, 0.1 mol) in distilled water (100 mL); solution B (1.0 M Na_2CO_3) was prepared by dissolving Na_2CO_3 (10.6 g, 0.1 mol) in distilled water (100 mL). The carbonate buffer was prepared by mixing 90 mL of solution B with 10 mL of solution A.

2.2 General procedure for the bromine atom transfer radical cyclisation

Procedure A

A 20 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was charged with an aqueous solution of $CuBr_2$ (0.05 M, 0.2 mL, 5 mol%), an aqueous SDS solution (0.3 M, 1 mL), Me_6-TREN (9.2 mg, 0.04 mmol, 20 mol%), distilled water (0.6 mL) and carbonate buffer (1.0 M, 0.2 mL), (*L*)-ascorbic acid (7 mg, 0.04 mmol) and the bromide precursor (**1**) (0.2 mmol). The resulting mixture was degassed and backfilled with argon for three times. The mixture was irradiated under stirring with a set of 415 nm LEDs (4×6 W) for 24 h. The temperature was maintained at 26–30 °C by cooling with the built-in cooling fan. The reaction mixture was then transferred to a separatory funnel containing 40 mL brine, and the crude product was extracted with

DCM (3×20 mL). The combined organic phases were washed with fresh brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* (on a rotary evaporator). The residual was purified by flash column chromatography on silica gel (with petroleum ether (PE) and ethyl acetate (EA) as the eluent) to afford the pure product (s).

Procedure B

A 20 mL glass tube equipped with a magnetic stirring bar and a rubber stopper was charged with an aqueous solution of $CuBr_2$ (0.05 M, 0.2 mL, 5 mol%), an aqueous SDS solution (0.3 M, 1 mL), Me_6-TREN (9.2 mg, 0.04 mmol, 20 mol%), distilled water (0.6 mL), carbonate buffer (1.0 M, 0.2 mL), (*L*)-ascorbic acid (7 mg, 0.04 mmol) and the bromide precursor (0.2 mmol). The resulting mixture was degassed and backfilled with argon for three times. The mixture was irradiated under stirring with a 390 nm Kessil® LED lamp (at 20 W) for 24 h. The temperature was maintained at 40 °C by heating with a metal bath. The reaction mixture was then transferred to a separatory funnel containing 40 mL brine, and the crude product was extracted with DCM (3×20 mL). The combined organic phases were washed with fresh brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* (on a rotary evaporator). The residual was purified by flash column chromatography on silica gel (with PE and EA as the eluent) to afford the pure product (s).

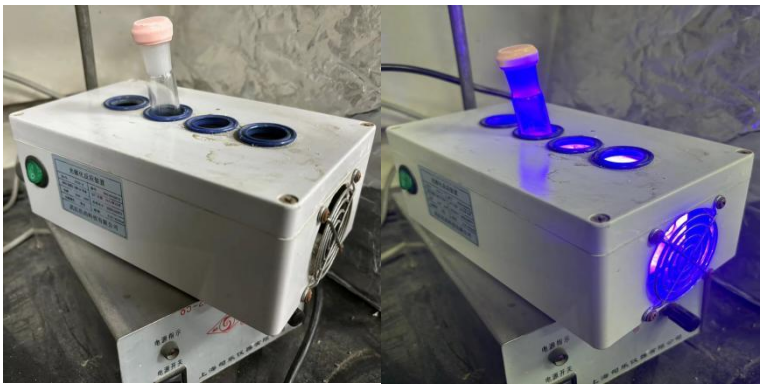
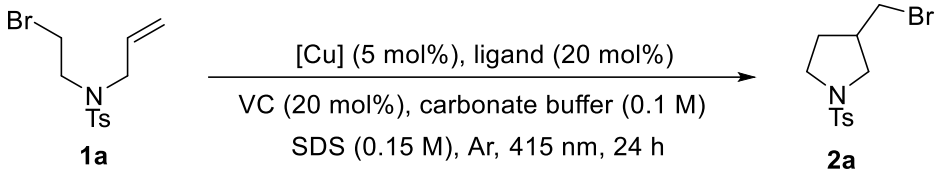


Figure S1. Photoreactor for Procedure A.

Figure S2. Photoreactor for Procedure B.

3. Optimalization of reaction conditions

Table S1 Screening of copper salts and ligands



Entry	Copper salt	Ligand	Yield (%)
1	--	Me_6-TREN	ND[a]
2	CuBr	Me_6-TREN	76
3	$Cu(CH_3CN)_4PF_6$	Me_6-TREN	73
4	$Cu(OTf)_2$	Me_6-TREN	48
5	$CuSO_4$	Me_6-TREN	25
6	$CuBr_2$	--	ND[a]
7	$CuBr_2$	DABCO	ND[a]
8	$CuBr_2$	TMEDA	4
9	$CuBr_2$	PMDETA	7
10	$CuBr_2$	EBEDA	ND[a]
11	$CuBr_2$	TPMA	59
12	CuBr	Me_6-TREN	ND[a,b]

The reaction was conducted on 0.2 mmol scale in 2.0 mL of carbonate-buffered SDS solution at 28-32 °C. Isolated yield. [a]Most of **1a** was recovered. [b]In the absence of VC.

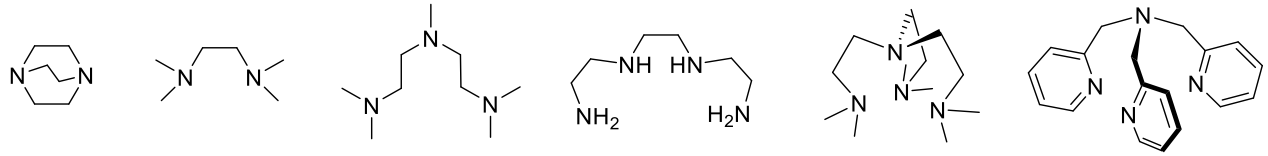
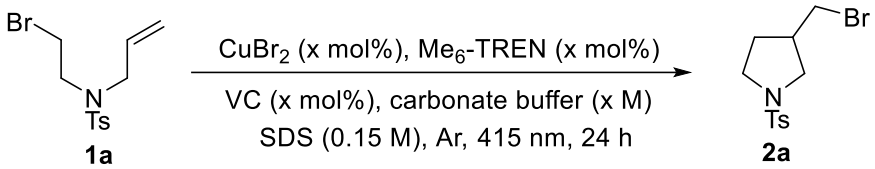


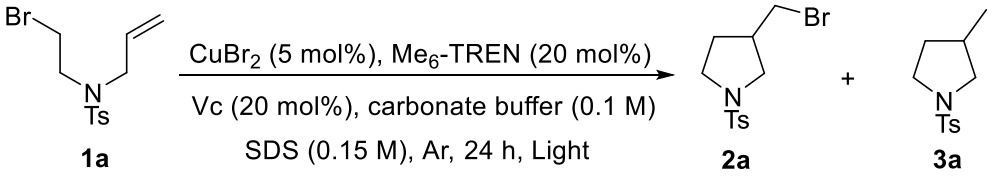
Table S2 Optimization of reaction conditions



Entry	$CuBr_2$ (mol%)	Me_6-TREN (mol%)	VC (mol%)	Carbonate buffer (M)	Conversion (%)	Yield (%)
1	3	20	20	0.1	92	73
2	10	20	20	0.1	97	85
3	5	5	20	0.1	36	14
4	5	10	20	0.1	97	79
5	5	20	10	0.1	95	76
6	5	20	40	0.1	48	32
7	5	20	20	--	12	0
8	5	20	20	0.2	96	77
9	5	20	40	0.2	94	78
10	5	20	100	0.5	100	77

The reaction was conducted on 0.2 mmol scale in 2.0 mL of carbonate-buffered SDS solution at 28-32 °C. Isolated yield.

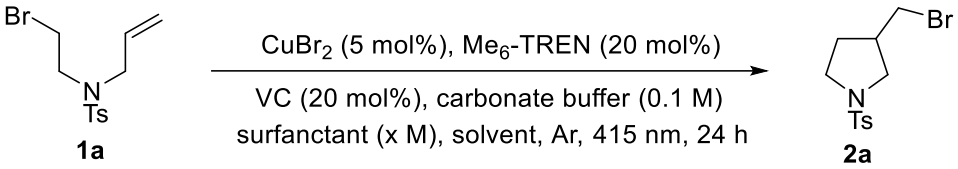
Table S3 Impact of temperature and light on the reaction



Entry	Temperature (°C)	Light source	Yield of **2a** (%)	Yield of **3a** (%)
1	30	--	57	0
2	40	--	81	0
3	50	--	78	3
4	70	--	66	8
5	28–32	455 nm (18 W)	51	0
6	28–32	415 nm (24 W)	80	0
7	28–32	390 nm (20 W)	80	0

The reaction was conducted on 0.2 mmol scale in 2.0 mL of carbonate-buffered SDS solution. Isolated yield.

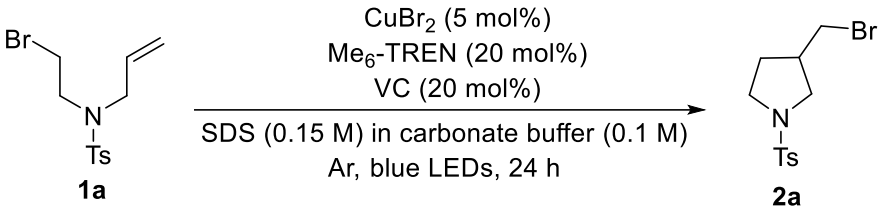
Table S4 Impact of the reaction medium



Entry	Solvent	Surfactant (M)	Yield (%)
1	EtOH (1 mL) + buffer (1 mL)	--	57
2	CH_3CN (1 mL) + Buffer (1 mL)	--	ND[a]
3	buffer (2 mL)	--	ND[a]
4	buffer (2 mL)	CTAB (0.05)	ND[a]
5	buffer (2 mL)	Triton™ X-45 (0.05)	ND[a]
6	buffer (2 mL)	$CH_3(CH_2)_{10}CO_2Na$ (0.05)	4
7	buffer (2 mL)	SDS (0.05)	44
8	buffer (2 mL)	SDS (0.1)	72
9	buffer (2 mL)	SDS (0.15)	77
10	buffer (2 mL)	SDS (0.2)	74
11	buffer (1 mL)	SDS (0.15)	62
12	buffer (3 mL)	SDS (0.15)	74
13	buffer (4 mL)	SDS (0.15)	75

The reaction was conducted on 0.2 mmol scale. 28-32 °C. Isolated yield. [a]Most of **1a** was recovered.

Table S5 Optimal reaction conditions



Entry	Variation of conditions	Yield of **2a**
1	none	80%[a]
2	12 h instead of 24 h	60%
3	no [Cu]	ND[b]
4	no Me_6-TREN	ND[b]
5	no VC	ND[b]
6	H_2O instead of 0.1 M carbonate buffer	ND[b]
7	no SDS	ND[b]
8	no light	57%[c]
9	CTAB instead of SDS	ND[b]
10	Triton™ X-45 instead of SDS	ND[b]
11	$CH_3(CH_2)_{10}CO_2Na$ instead of SDS	ND[b]

The reaction was conducted on 0.2 mmol scale in 2.0 mL of carbonate (Na_2CO_3/$NaHCO_3$)-buffered SDS solution (0.15 M) (pH 10.6) at ambient temperature (28–32 °C). A set of blue LEDs (24 W, 415 nm) was used as the light source unless otherwise specified. Isolated yield. [a]**1a** was completely consumed. [b]Most of **1a** was recovered. [c]37% of **1a** was recovered. No reductive cyclisation product was obtained in all the cases illustrated in this table.

4. Cyclic voltammetry measurements

Cyclic voltammograms of **1o** and **1r** in CH_3CN:

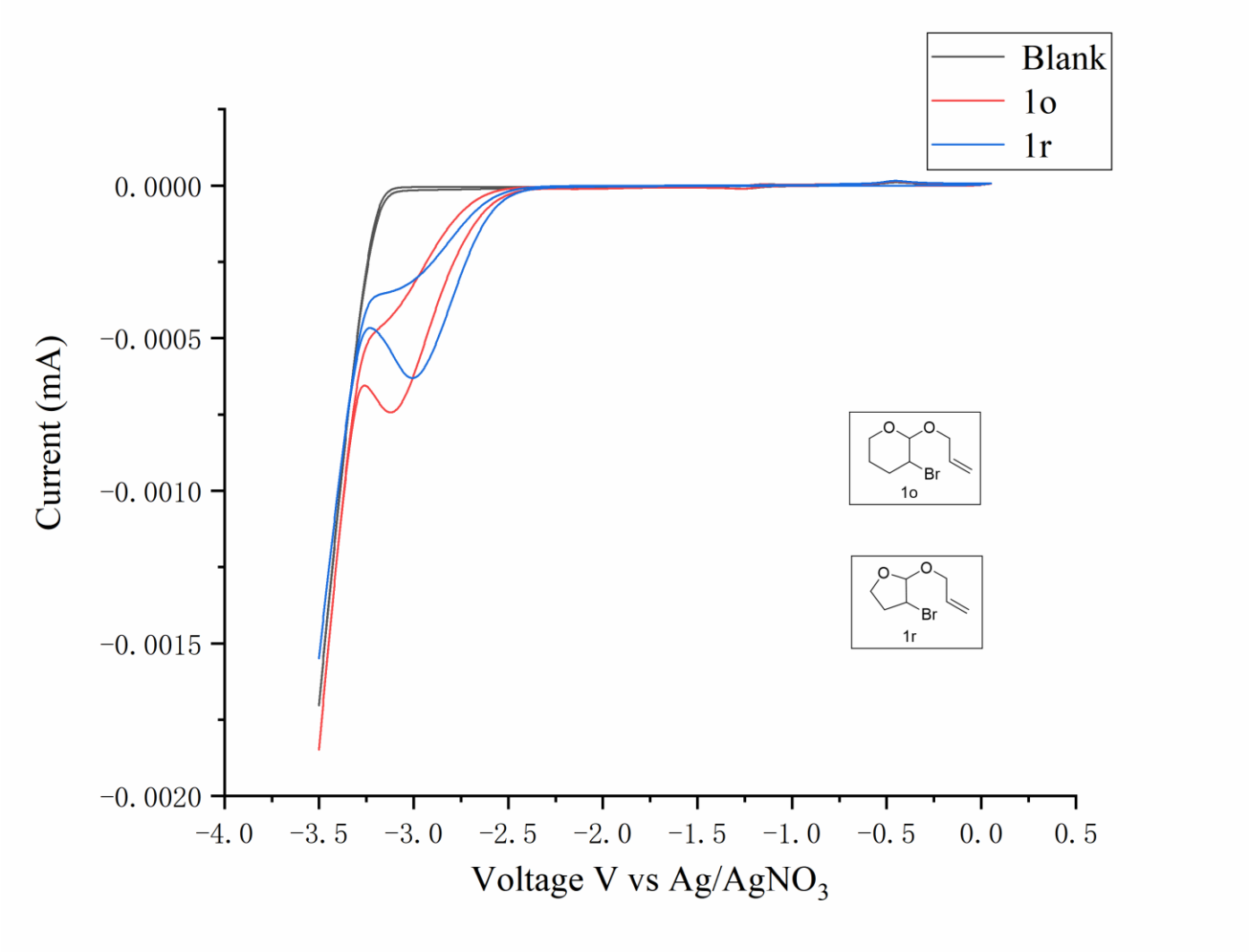


Figure S1 Cyclic voltammograms of 25.0 mM solutions of **1o** and **1r** in CH_3CN with *n*-Bu_4NBF_4 (0.1 M) as supporting electrolyte. All measurements were carried out at room temperature under an argon atmosphere using the GC working electrode and Pt counter electrode at sweep rate of 0.1 V s^{-1}.

The reduction potentials were obtained as the values vs. $Ag/AgNO_3$. These values were converted to the values vs. SCE by adding 0.298 V.[3] The reduction potential of **1o** in CH_3CN was measured to be $E_{1/2}$ = -2.86 V vs. $Ag/AgNO_3$, which corresponds to -2.56 V vs. SCE. The reduction potentials of **1r** in CH_3CN was measured to be $E_{1/2}$ = -2.76 V vs. $Ag/AgNO_3$, which corresponds to -2.46 V vs. SCE.

Cyclic voltammograms of **1o** in EtOH-H_2O (1:1, v/v):

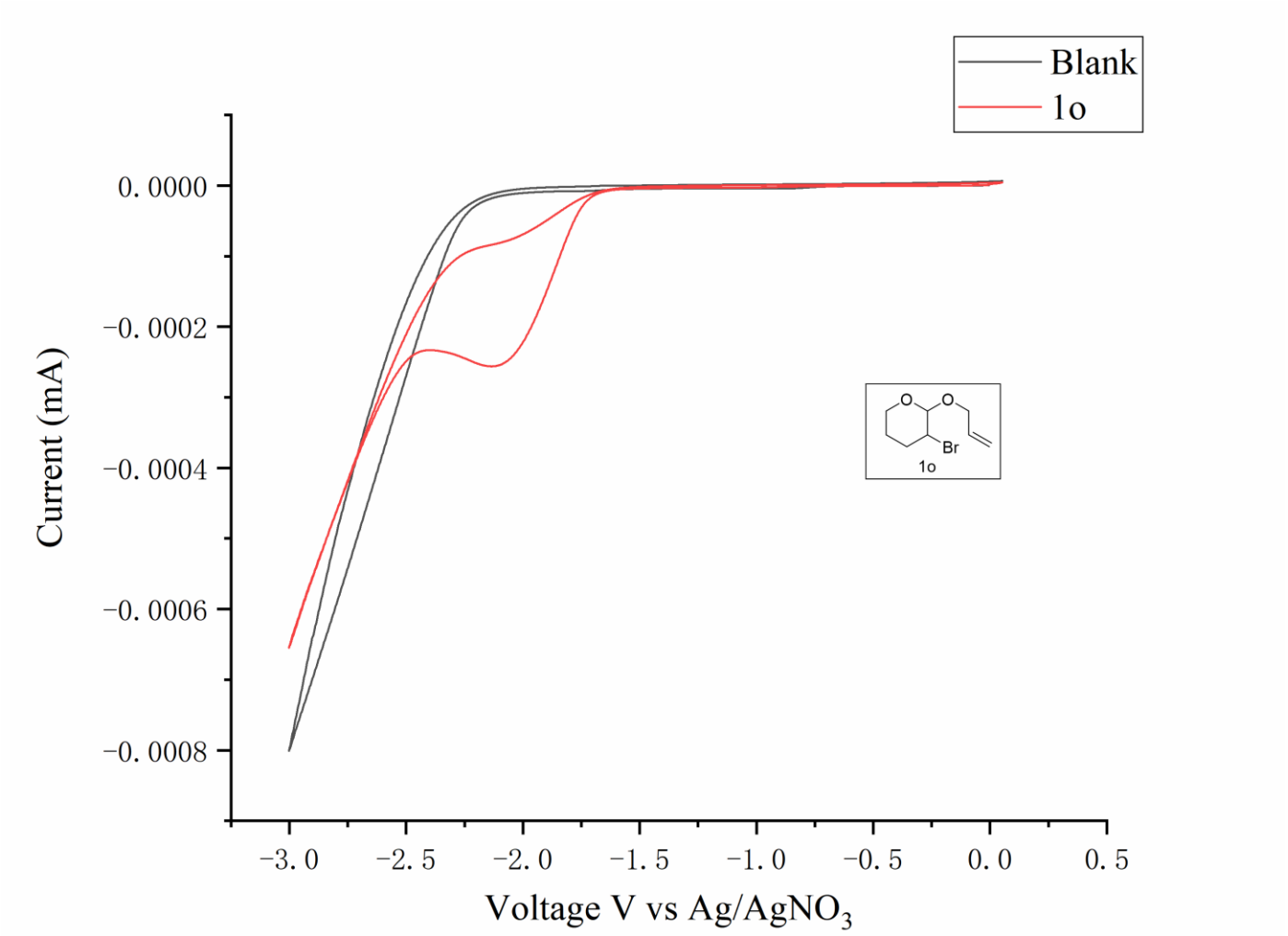


Figure S2 Cyclic voltammograms of 25.0 mM solutions of **1o** in EtOH-H_2O (1:1, v/v) with *n*-Bu_4NBF_4 (0.1 M) as supporting electrolyte. The measurement was carried out at room temperature under an argon atmosphere using the GC working electrode and Pt counter electrode at sweep rate of 0.1 V s^{-1}.

The reduction potentials were obtained as those vs $Ag/AgNO_3$. These values were converted to the values vs SCE by adding 0.298 V.[3] The reduction potential of **1o** in EtOH-H_2O (1:1, v/v) was measured to be $E_{1/2}$ = -1.87 vs. $Ag/AgNO_3$, which corresponds to -1.57 V vs. SCE.

Cyclic voltammograms of **1o** and **1r** in aqueous SDS:

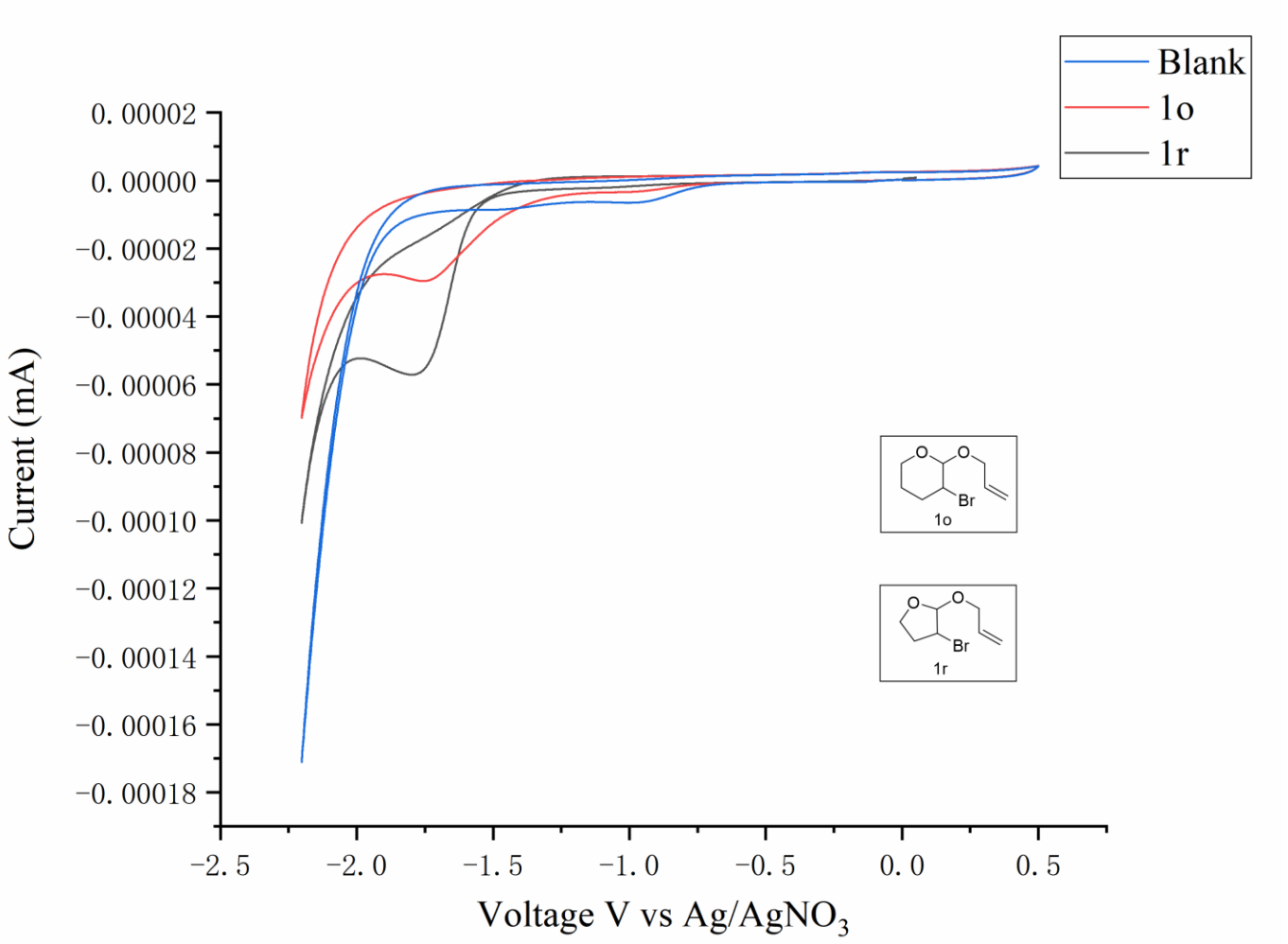
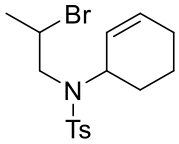


Figure S3 Cyclic voltammograms of 6.0 mM solutions of **1o** and **1r** in aqueous SDS (100 mM), with no additional supporting electrolyte. All measurements were carried out at room temperature under an argon atmosphere using the GC working electrode and Pt counter electrode at sweep rate of 0.1 V s^{-1}.

The reduction potentials were obtained as the values vs. $Ag/AgNO_3$. These values were converted to the values vs. SCE by adding 0.298 V.[3] The reduction potential of **1o** in aqueous SDS solution was measured to be $E_{1/2}$ = -1.58 V vs. $Ag/AgNO_3$, which corresponds to -1.28 V vs. SCE. The reduction potential of **1r** in aqueous SDS solution was measured to be $E_{1/2}$ = -1.66 V, which corresponds to -1.36 V vs. SCE.

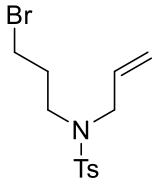
5. Characterization data

***N*-(2-Bromopropyl)-*N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (1n)**



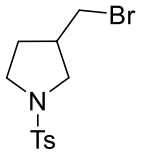
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 2H), 7.35 – 7.26 (m, 2H), 5.92 – 5.84 (m, 0.11H), 5.84 – 5.77 (m, 0.56H), 5.77 – 5.70 (m, 0.48H), 5.24 – 5.17 (m, 0.10H), 5.11 – 5.07 (m, 0.15H), 5.05 – 4.94 (m, 0.94H), 4.61 – 4.50 (m, 0.55H), 4.50 – 4.42 (m, 0.84H), 4.42 – 4.36 (m, 0.60H), 3.89 – 3.80 (m, 0.11H), 3.65 – 3.55 (m, 0.12H), 3.47 – 3.36 (m, 1.07H), 3.32 (dd, *J* = 14.9, 6.5 Hz, 0.50H), 3.18 (dd, *J* = 14.7, 10.2 Hz, 0.44H), 2.47 – 2.38 (m, 3H), 1.94 (s, 2H), 1.86 – 1.78 (m, 1.45H), 1.76 (d, *J* = 6.7 Hz, 3H), 1.74 – 1.71 (m, 0.51H), 1.58 – 1.40 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 143.5, 136.9, 136.4, 136.3, 133.0, 132.4, 129.8, 129.7, 129.5, 127.3, 127.2, 127.0, 126.9, 126.6, 116.4, 55.7, 55.7, 55.3, 52.1, 51.9, 48.5, 47.6, 46.4, 28.8, 28.3, 24.3, 23.5, 22.9, 21.6, 21.6, 21.5. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{16}H_{23}BrNO_2S]^+$: 372.0627, found: 372.0616.

***N*-Allyl-*N*-(3-bromopropyl)-4-methylbenzenesulfonamide (1l)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.70 – 5.54 (m, 1H), 5.25 – 5.09 (m, 2H), 3.78 (d, *J* = 6.5 Hz, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.10 (p, *J* = 6.7 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 136.4, 132.8, 129.7, 127.1, 119.3, 51.5, 46.0, 31.7, 30.4, 21.4. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{13}H_{19}BrNO_2S]^+$: 332.0314, found: 332.0304.

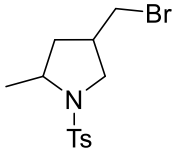
3-(Bromomethyl)-1-tosylpyrrolidine (2a)[4]



Prepared according to **Procedure A**. **Yield**: 80% (51 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.26.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.44 (dd, *J* = 10.3, 7.4 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.27 – 3.15 (m, 3H), 3.05 (dd, *J* = 10.3, 6.8 Hz, 1H), 2.50 (p, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.05 – 1.95 (m, 1H), 1.66 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 133.3, 129.7, 127.6, 52.1, 47.3, 40.9, 34.1, 30.3, 21.5.

4-(Bromomethyl)-2-methyl-1-tosylpyrrolidine (2b)[2]

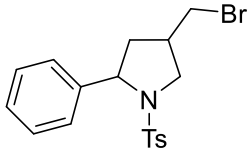


(83/17)

Prepared according to **Procedure A**. **Yield:** 64% (41 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.85 – 3.73 (m, 0.18H), 3.67 – 3.55 (m, 1.89H), 3.32 – 3.21 (m, 1.72H), 3.18 – 3.11 (m, 1H), 3.02 (dd, *J* = 10.2, 7.5 Hz, 0.17H), 2.92 (dd, *J* = 10.1, 8.1 Hz, 0.17H), 2.72 – 2.59 (m, 0.16H), 2.42 (s, 3H), 2.18 – 2.08 (m, 0.86H), 2.06 – 1.92 (m, 0.88H), 1.70 – 1.76 (m, 0.18H), 1.57 – 1.47 (m, 0.2H), 1.39 (d, *J* = 6.2 Hz, 2.55H), 1.35 – 1.28 (m, 1.32H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 143.4, 134.6, 134.4, 129.7, 129.6, 127.4, 56.7, 55.7, 53.5, 52.9, 39.9, 39.8, 39.3, 38.4, 33.7, 33.6, 23.0, 22.7, 21.5.

4-(Bromomethyl)-2-phenyl-1-tosylpyrrolidine (2c)[2]

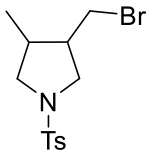


(76/24)

Prepared according to **Procedure B**. **Yield:** 82% (64 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 0.48H), 7.60 (d, *J* = 8.3 Hz, 1.49H), 7.34 – 7.19 (m, 7H), 4.90 (dd, *J* = 8.3, 3.0 Hz, 0.24H), 4.70 (dd, *J* = 8.8, 7.4 Hz, 0.76H), 3.91 (dd, *J* = 10.8, 7.9 Hz, 0.78H), 3.81 (dd, *J* = 10.2, 7.1 Hz, 0.25H), 3.37 – 3.17 (m, 2.82H), 3.13 (dd, *J* = 10.3, 7.4 Hz, 0.26H), 2.75 – 2.59 (m, 0.24H), 2.48 – 2.36 (m, 3.88H), 2.33 – 2.17 (m, 0.86H), 2.00 – 1.93 (m, 0.26H), 1.88 – 1.78 (m, 0.26H), 1.76 – 1.64 (m, 0.8H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 142.3, 142.1, 135.0, 129.6, 129.6, 128.4, 128.4, 127.5, 127.4, 127.4, 126.3, 125.9, 64.1, 62.9, 54.0, 53.0, 42.1, 40.6, 40.4, 39.3, 33.5, 33.2, 21.5.

3-(Bromomethyl)-4-methyl-1-tosylpyrrolidine (2d)[5]

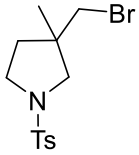


(75/25)

Prepared according to **Procedure A**. **Yield:** 80% (52 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.28.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 3.55 – 3.48 (m, 0.50H), 3.46 (dd, *J* = 10.3, 7.2 Hz, 0.78H), 3.40 – 3.34 (m, 1H), 3.25 (dd, *J* = 10.2, 6.7 Hz, 0.80H), 3.19 – 3.07 (m, 1.31H), 3.07 – 3.00 (m, 1.56H), 2.81 (dd, *J* = 9.8, 8.2 Hz, 0.25H), 2.50 – 2.43 (m, 0.63H), 2.42 (s, 3H), 2.38 – 2.25 (m, 0.83H), 2.04 – 1.96 (m, 0.27H), 1.96 – 1.85 (m, 0.27H), 0.94 (d, *J* = 6.5 Hz, 0.79H), 0.80 (d, *J* = 7.1 Hz, 2.37H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 143.5, 133.6, 133.3, 129.6, 127.5, 127.4, 54.8, 54.4, 52.3, 50.7, 47.5, 44.5, 37.5, 35.4, 33.2, 30.6, 21.5, 16.4, 12.6.

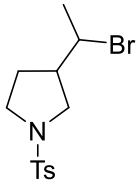
3-(Bromomethyl)-3-methyl-1-tosylpyrrolidine (2e)[6]



Prepared according to **Procedure B**. **Yield:** 32% (21 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.31.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.38 – 3.27 (m, 2H), 3.27 – 3.16 (m, 3H), 3.03 (d, *J* = 10.1 Hz, 1H), 2.44 (s, 3H), 1.84 (dt, *J* = 12.9, 7.2 Hz, 1H), 1.73 – 1.57 (m, 1H), 1.06 (s, 3H).**^{13}C NMR** (101 MHz,$CDCl_3$) δ 143.6, 133.5, 129.7, 127.5, 57.5, 46.7, 43.4, 41.5, 36.2, 23.2, 21.5.

3-(1-Bromoethyl)-1-tosylpyrrolidine (2f)[2]

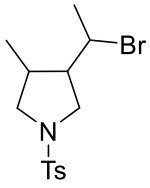


(57/43)

Prepared according to **Procedure B**. **Yield:** 76% (50 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.29, 0.23.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.37 – 7.29 (m, 2H), 3.98 – 3.85 (m, 1H), 3.55 (dd, *J* = 10.2, 7.8 Hz, 0.6H), 3.48 – 3.31 (m, 1.5H), 3.29 – 3.12 (m, 1H), 3.03 (dd, *J* = 10.2, 8.8 Hz, 0.6H), 2.93 (dd, *J* = 10.0, 8.7 Hz, 0.45H), 2.43 (s, 3H), 2.40 – 2.29 (m, 1H), 2.10 – 2.01 (m, 0.46H), 2.00 – 1.91 (m, 0.61H), 1.74 – 1.65 (m, 0.41H), 1.63 (d, *J* = 6.7 Hz, 3H), 1.59 – 1.47 (m, 0.67H).**^{13}C NMR** (101 MHz,$CDCl_3$) δ 143.6, 143.5, 133.5, 133.4, 129.7, 127.9, 127.5, 52.4, 51.5, 51.4, 50.8, 48.1, 47.5, 47.4, 47.2, 30.2, 29.7, 24.8, 24.8, 21.5.

4-(1-Bromoethyl)-4-methyl-1-tosylpyrrolidine (2g)[2]

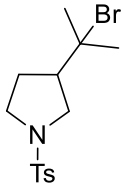


(53/22/14/11)

Prepared according to **Procedure B**. **Yield:** 53% (38 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.37, 0.31. 0.23 .

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.18 – 4.10 (m, 0.11H), 4.08 – 4.00 (m, 0.14H), 3.96 – 3.88 (m, 0.23H), 3.88 – 3.73 (m, 0.54H), 3.67 – 3.57 (m, 0.46H), 3.50 – 3.29 (m, 1.64H), 3.29 – 3.04 (m, 1.52H), 2.92 – 2.73 (m, 0.58H), 2.42 (s, 3H), 2.40 – 2.35 (m, 0.31H), 2.35 – 2.29 (m, 0.25H), 2.29 – 2.18 (m, 0.90H), 2.17 – 2.09 (m, 0.11H), 2.06 – 1.95 (m, 0.27H), 1.89 – 1.79 (m, 0.11H), 1.76 – 1.68 (m, 0.15H), 1.66 – 1.59 (m, 1.75H), 1.48 – 1.39 (m, 1.50H), 1.02 – 0.97 (m, 0.29H), 0.95 (dd, *J* = 6.6, 1.7 Hz, 0.61H), 0.78 – 0.70 (m, 2.16H).**^{13}C NMR** (101 MHz,$CDCl_3$) δ 143.6, 143.5, 143.4, 143.3, 133.9, 129.7, 129.6, 129.6, 127.7, 127.6, 127.4, 127.3, 57.5, 56.9, 56.2, 55.9, 55.6, 55.2, 55.0, 54.9, 53.0, 52.8, 51.4, 51.3, 51.2, 50.9, 50.8, 50.6, 50.4, 49.9, 49.0, 48.1, 48.0, 47.4, 36.9, 35.8, 35.7, 34.7, 34.3, 25.4, 25.1, 24.8, 24.3, 24.0, 23.7, 21.5, 12.8, 12.7, 12.6, 12.5.

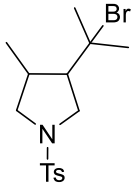
3-(2-Bromopropan-2-yl)-1-tosylpyrrolidine (2h)



Prepared according to **Procedure A**. **Yield:** 35% (0.28 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.28.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.47 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.38 (ddd, *J* = 9.8, 8.6, 3.0 Hz, 1H), 3.21 (td, *J* = 9.5, 6.9 Hz, 1H), 3.12 (t, *J* = 9.5 Hz, 1H), 2.43 (s, 3H), 2.15 (tt, *J* = 10.1, 7.8 Hz, 1H), 1.99 – 1.89 (m, 1H), 1.81 – 1.71 (m, 1H), 1.67 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.4, 129.6, 127.6, 67.7, 51.8, 50.5, 47.9, 33.1, 32.6, 28.4, 21.5. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{14}H_{21}BrNO_2S]^+$: 346.0471, found: 346.0458.

3-(2-Bromopropan-2-yl)-4-methyl-1-tosylpyrrolidine (2i)



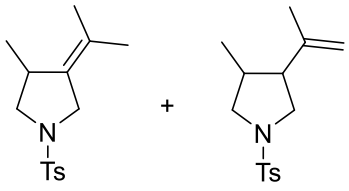
(90/10)

Prepared according to **Procedure A**. **Yield:** 23% (16 mg). **TLC (**EA/PE = 1:5, v/v): R_f = 0.37, 0.26.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.77 – 7.63 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.59 – 3.51 (m, 0.12H), 3.47 – 3.39 (m, 0.95H), 3.37 (d, *J* = 10.3 Hz, 0.07H), 3.33 – 3.29 (m, 0.07H), 3.29 – 3.22 (m, 0.96H), 3.15 (d, *J* = 9.7 Hz, 0.10H), 3.09 (dd, *J* = 10.0, 7.0 Hz, 0.93H), 2.83 (d, *J* = 14.8 Hz, 0.93H), 2.44 (s, 3H), 2.24 (dq, *J* = 13.2, 6.7 Hz, 1H), 1.92 (dd, *J* = 14.1, 7.0 Hz, 1H), 1.76 (s, 0.46H), 1.71 (s, 2.71H), 1.65 (s, 2.80H), 1.10 (d, *J* = 6.8 Hz, 2.75H), 0.88 (d, *J* = 6.9 Hz, 0.38H).**^{13}C NMR** (101 MHz,$CDCl_3$) δ 143.6, 131.9, 129.6, 127.9, 69.2, 58.6, 55.6, 51.7, 36.1, 32.9, 32.2, 21.5, 20.9. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{15}H_{21}BrNO_2S]^+$: 360.0627, found: 360.0618.

3-Methyl-4-(propan-2-ylidene)-1-tosylpyrrolidine (4i-1)[2]

3-Methyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine(4i-2)[2]



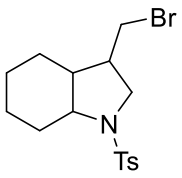
4i-1 **4i-2** (4i-1 : 4i-2 = 57 : 43), 4i-2 (88/12)

Prepared according to **Procedure A**. **Yield:** 22% (16 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.51, 0.45.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.77 – 7.67 (m, 5.30H), 7.32 (d, *J* = 8.3, 2.0 Hz, 5.30H), 4.82 (s, 1H), 4.79 (s, 0.15H), 4.69 (s, 0.14H), 4.54 (s, 1H), 3.94 (d, *J* = 13.5, 1.8 Hz, 1.36H), 3.61 – 3.53 (m, 0.2H), 3.49 (d, *J* = 13.6 Hz, 1.44H), 3.45 – 3.37 (m, 2.37H), 3.28 (t, *J* = 9.6 Hz, 1.21H), 3.22 (d, *J* = 9.0 Hz, 1.37H), 3.18 – 3.08 (m, 1.44H), 3.00 (dd, *J* = 9.1, 6.3 Hz, 1.36H), 2.92 – 2.84 (m, 0.19H), 2.83 – 2.73 (m, 1.51H), 2.59 – 2.50 (m, 1.07H), 2.42 (s, 8H), 2.34 – 2.25 (m, 1.10H), 1.64 (s,3.11H), 1.59 (s, 4.56H), 1.51 (s, 3.93H), 1.04 (d, *J* = 6.9

Hz, 3.92H), 0.90 – 0.79 (m, 1.77H), 0.63 (d, *J* = 7.1 Hz, 0.50H), 0.59 (d, *J* = 7.0 Hz, 2.95H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 143.2, 141.8, 134.2, 133.1, 132.4, 129.6, 129.5, 127.9, 127.4, 127.3, 123.9, 111.7, 55.3, 54.9, 50.0, 48.5, 48.2, 35.5, 34.5, 22.7, 21.5, 20.9, 20.2, 19.4, 13.2.

3-(Bromomethyl)-1-tosyloctahydro-1*H*-indole (2j)[2]

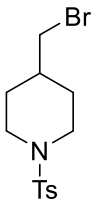


(81/19)

Prepared according to **Procedure A**. **Yield:** 62% (46 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.41.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 12.5, 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.73 – 3.62 (m, 0.38H), 3.58 (dd, *J* = 11.2, 8.3 Hz, 0.82H), 3.34 – 3.28 (m, 1H), 3.27 – 3.17 (m, 2.47H), 3.07 (dd, *J* = 10.5, 8.1 Hz, 0.19H), 2.97 (dd, *J* = 10.3, 8.2 Hz, 0.19H), 2.60 – 2.45 (m, 1H), 2.42 (d, *J* = 5.1 Hz, 3H), 2.11 – 1.89 (m, 1.94H), 1.80 – 1.70 (m, 0.84H), 1.67 – 1.37 (m, 4.87H), 1.29 – 1.10 (m, 2.34H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 143.2, 135.0, 133.5, 129.6, 129.6, 127.5, 127.3, 60.8, 60.0, 52.1, 52.0, 43.0, 41.6, 41.1, 40.9, 33.8, 30.2, 29.9, 28.3, 24.6, 24.1, 23.0, 21.6, 21.5, 21.0, 19.9.

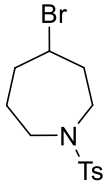
4-(Bromomethyl)-1-tosylpiperidine (2k-1)



Prepared according to **Procedure B**. **Yield:** 38% (25 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.32.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.81 (d, *J* = 11.9 Hz, 2H), 3.24 (d, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 2.25 (td, *J* = 11.9, 2.6 Hz, 2H), 1.88 (d, *J* = 14.2 Hz, 2H), 1.66 – 1.50 (m, 1H), 1.38 (qd, *J* = 12.1, 4.1 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 133.1, 129.6, 126.5, 45.9, 37.9, 37.8, 30.2, 21.5. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{13}H_{19}BrNO_2S]^+$: 332.0314, found: 332.0304.

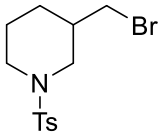
4-Bromo-1-tosylazepane (2k-2)



Prepared according to **Procedure B**. **Yield:** 11% (7 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.38.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.43 (tt, *J* = 7.1, 3.7 Hz, 1H), 3.53 – 3.45 (m, 1H), 3.45 – 3.37 (m, 1H), 3.29 – 3.19 (m, 1H), 3.15 (ddd, *J* = 12.7, 7.2, 5.5 Hz, 1H), 2.42 (s, 3H), 2.39 – 2.30 (m, 1H), 2.26 – 2.07 (m, 3H), 2.05 – 1.93 (m, 1H), 1.81 – 1.68 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 136.1, 129.7, 126.9, 53.5, 47.2, 44.3, 40.5, 35.9, 24.8, 21.5. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{13}H_{19}BrNO_2S]^+$: 332.0314, found: 332.0304.

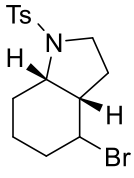
3-(Bromomethyl)-1-tosylpiperidine (11l)



Prepared according to **Procedure B**. **Yield:** 46% (29 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 3.76 – 3.64 (m, 1H), 3.53 (dt, *J* = 11.1, 4.0 Hz, 1H), 3.35 – 3.21 (m, 2H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.29 – 2.19 (m, 1H), 2.07 – 1.94 (m, 1H), 1.83 – 1.70 (m, 2H), 1.70 – 1.56 (m, 1H), 1.18 – 1.05 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 133.2, 129.6, 127.6, 50.2, 46.4, 37.5, 35.4, 28.6, 23.8, 21.5. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{13}H_{19}BrNO_2S]^+$: 332.0314, found: 332.0304.

(3aS,7aS)-4-Bromo-1-tosyloctahydro-1H-indole (2m)[4]

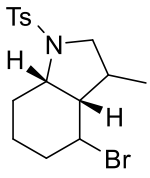


(85/15)

Prepared according to **Procedure B**. **Yield:** 80% (59 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.32, 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.24 – 4.15 (m, 0.87H), 4.08 – 3.97 (m, 0.15H), 3.70 – 3.62 (m, 1H), 3.54 (ddd, *J* = 10.6, 7.8, 5.9 Hz, 1H), 3.27 (ddd, *J* = 10.7, 8.6, 6.1 Hz, 1H), 2.43 (s, 3H), 2.20 (p, *J* = 6.4 Hz, 1H), 2.10 – 1.95 (m, 2H), 1.94 – 1.86 (m, 1H), 1.86 – 1.75 (m, 2H), 1.75 – 1.67 (m, 1H), 1.67 – 1.56 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 134.1, 129.7, 127.4, 58.9, 58.8, 52.8, 48.0, 47.5, 47.1, 33.1, 32.3 28.5, 28.5, 27.7, 26.9, 21.5, 20.3, 19.2.

4-Bromo-3-methyl-1-tosyloctahydro-1H-indole (2n)

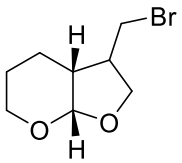


(47/43/10)

Prepared according to **Procedure B**. **Yield:** 32% (24 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.44,0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 2H), 7.37 – 7.28 (m, 2H), 4.31 (q, *J* = 4.5 Hz, 0.42H), 4.26 – 4.15 (m, 0.10H), 4.02 (ddd, *J* = 10.8, 8.9, 4.8 Hz, 0.47H), 3.94 – 3.84 (m, 0.46H), 3.67 (dd, *J* = 10.3, 7.4 Hz, 0.47H), 3.54 (dd, *J* = 7.1, 3.5 Hz, 0.09H), 3.52 – 3.48 (m, 0.44H), 3.45 (dd, *J* = 11.0, 7.5 Hz, 0.54H), 3.32 (d, *J* = 8.3 Hz, 0.09H), 3.20 – 3.09 (m, 0.57H), 2.76 (dd, *J* = 10.3, 7.5 Hz, 0.42H), 2.52 (q, *J* = 7.0 Hz, 0.09H), 2.43 (s, 3H), 2.40 – 2.16 (m, 2H), 1.97 – 1.82 (m, 2H), 1.82 – 1.65 (m, 2H), 1.65 – 1.52 (m, 2H), 1.33 (d, *J* = 7.3 Hz, 0.28H), 1.09 (d, *J* = 7.1 Hz, 1.39H), 0.77 (d, *J* = 6.6 Hz, 1.26H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 143.4, 134.2, 133.4, 129.7, 129.6, 127.6, 127.3, 61.8, 57.9, 54.7, 54.5, 54.1, 52.3, 50.4, 48.9, 37.0, 35.6, 34.2, 31.6, 29.5, 28.7, 21.5, 20.3, 19.7, 16.7, 14.9. **HRMS (ESI-TOF)** m/z $[M+H]^+$ calcd for $[C_{16}H_{23}BrNO_2S]^+$: 372.0627, found: 372.0614.

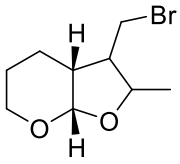
(3aR,7aS)-3-(Bromomethyl)hexahydro-4H-furo[2,3-b]pyran (2o)[4]



Prepared according to **Procedure A**. **Yield:** 41% (18 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (d, *J* = 3.7 Hz, 1H), 4.04 (t, *J* = 8.3 Hz, 1H), 3.85 – 3.70 (m, 2H), 3.62 (dtd, *J* = 11.3, 3.9, 1.5 Hz, 1H), 3.48 – 3.37 (m, 2H), 2.83 (dq, *J* = 16.5, 8.1 Hz, 1H), 1.84 – 1.73 (m, 1H), 1.84 – 1.74 (m, 1H), 1.61 – 1.54 (m, 2H), 1.55 – 1.46 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 101.7, 69.3, 61.4, 43.8, 37.6, 30.7, 22.8, 19.0.

(3aS,7aR)-3-(Bromomethyl)-2-methylhexahydro-4*H*-furo[2,3-b]pyran (2p)[2]

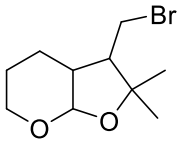


(51/49)

Prepared according to **Procedure A**. **Yield:** 59% (27 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.4, 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (d, *J* = 3.7 Hz, 0.5H), 4.94 (d, *J* = 3.7 Hz, 0.51H), 4.09 – 3.97 (m, 1.16H), 3.92 – 3.85 (m, 0.6H), 3.81 – 3.74 (m, 0.62H), 3.65 – 3.57 (m, 0.74H), 3.52 (dd, *J* = 10.5, 4.1 Hz, 0.64H), 3.45 – 3.34 (m, 2.24H), 2.37 – 2.29 (m, 0.58H), 2.27 – 2.18 (m, 1.17H), 2.10 – 2.02 (m, 0.57H), 1.90 – 1.77 (m, 1.86H), 1.68 – 1.61 (m, 0.58H), 1.60 – 1.52 (m, 1.41H), 1.43 (d, *J* = 6.2 Hz, 1.68H), 1.29 (d, *J* = 6.1 Hz, 1.74H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 101.4, 100.4, 80.7, 76.5, 64.3, 61.4, 51.4, 46.5, 43.6, 38.3, 33.5, 30.2, 22.8, 22.5, 22.3, 21.3, 20.6, 19.4.

3-(Bromomethyl)-2,2-dimethylhexahydro-4H-furo[2,3-b]pyran (2q)[2]

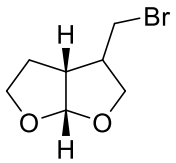


(54/30/16)

Prepared according to **Procedure A**. **Yield:** 64% (33 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.45, 0.36.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (t, *J* = 4.2 Hz, 0.3H), 4.87 (d, *J* = 3.6 Hz, 0.16H), 4.85 (d, *J* = 3.5 Hz, 0.55H), 3.92 – 3.77 (m, 1.1H), 3.68 – 3.52 (m, 0.68H), 3.49 (dd, *J* = 10.5, 4.5 Hz, 0.76H), 3.46 – 3.25 (m, 1.91H), 2.63 – 2.46 (m, 1H), 2.25 – 2.15 (m, 0.34H), 1.97 – 1.68 (m, 3.78H), 1.62 – 1.54 (m, 0.97H), 1.50 (s, 1.74H), 1.38 – 1.32 (m, 0.89H), 1.31 (s, 1.23H), 1.30 (s, 0.8H), 1.20 (s, 2.17H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 100.3, 100.2, 98.4, 98.1, 84.7, 84.6, 78.9, 64.5, 61.1, 60.9, 52.3, 52.1, 47.7, 44.2, 43.7, 43.1, 41.6, 39.0, 38.6, 31.5, 31.4, 31.3, 31.2, 29.3, 24.8, 23.5, 23.4, 23.1, 22.2, 20.2, 19.7, 19.4.

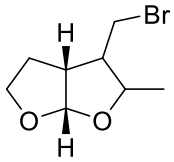
(3aS,6aR)-3-(Bromomethyl)hexahydrofuro[2,3-b]furan (2r)[4]



Prepared according to **Procedure A**. **Yield:** 62% (25 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.26.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (d, *J* = 5.0 Hz, 1H), 4.04 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.90 (dd, *J* = 7.6, 6.1 Hz, 2H), 3.50 (dd, *J* = 11.0, 8.6 Hz, 1H), 3.38 (dd, *J* = 8.0, 1.9 Hz, 2H), 2.94 (ddt, *J* = 9.7, 7.9, 5.1 Hz, 1H), 2.82 (ddt, *J* = 15.2, 11.1, 7.8 Hz, 1H), 1.99 – 1.80 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 109.8, 71.3, 69.1, 45.6, 44.8, 29.2, 24.7.

(3aS,6aR)-3-(Bromomethyl)-2-methylhexahydrofuro[2,3-b]furan (2s)[2]

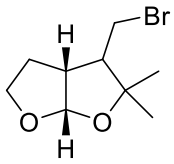


(53/26/21)

Prepared according to **Procedure A**. **Yield:** 70% (30 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.28.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (d, *J* = 4.4 Hz, 0.21H), 5.69 (d, *J* = 5.1 Hz, 0.26H), 5.61 (d, *J* = 5.5 Hz, 0.53H), 4.38 – 4.24 (m, 0.24H),4.11 – 4.02 (m, 0.29H), 4.01 – 3.92 (m, 0.88H), 3.91 – 3.80 (m, 1.29H), 3.79 – 3.67 (m, 0.93H), 3.50 – 3.35 (m, 1.81H), 3.24 (t, *J* = 10.7 Hz, 0.3H), 3.07 – 2.98 (m, 0.33H), 2.98 – 2.88 (m, 0.39H), 2.69 (td, *J* = 7.3, 4.8 Hz, 0.61H), 2.28 (ddt, *J* = 16.0, 7.8, 5.0 Hz, 0.31H), 2.06 – 1.93 (m, 1.14H), 1.93 – 1.73 (m, 1.97H), 1.32 (d, *J* = 6.1 Hz, 1.78H), 1.26 (dd, *J* = 5.9, 2.7 Hz, 0.97H), 1.22 (dd, *J* = 6.8, 2.6 Hz, 0.7H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 109.2, 107.7, 107.5, 78.1, 76.5, 68.8, 67.8, 66.3, 52.8, 51.9, 49.4, 46.7, 46.3, 46.1, 33.3, 32.3, 29.4, 29.2, 25.2, 25.1, 19.5, 19.3, 17.4.

(3aS,6aR)-3-(Bromomethyl)-2,2-dimethylhexahydrofuro[2,3-b]furan (2t)[2]

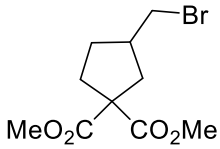


(57/43)

Prepared according to **Procedure A**. **Yield:** 86% (45 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (d, *J* = 5.5 Hz, 0.43H), 5.59 (d, *J* = 5.4 Hz, 0.57H), 4.13 – 4.03 (m, 0.43H), 3.95 (t, *J* = 8.1 Hz, 0.60H), 3.91 – 3.78 (m, 1H), 3.45 – 3.34 (m, 2H), 3.12 – 3.00 (m, 0.42H), 2.65 – 2.53 (m, 1H), 2.07 – 1.83 (m, 2.76H), 1.36 (s, 1.76H), 1.29 (s, 1.28H), 1.18 (s, 1.29H), 1.07 (s, 1.75H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 107.6, 106.5, 83.2, 82.8, 67.5, 66.0, 54.6, 52.8, 50.1, 47.3, 32.4, 32.0, 30.6, 29.5, 27.8, 25.0, 23.9, 22.1.

Dimethyl 3-(Bromomethyl)cyclopentane-1,1-dicarboxylate (2u)[4]



Prepared according to **Procedure A. Yield:** 80% (47 mg). **TLC** (EA/PE = 1:5, v/v): R_f = 0.51.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 6H), 3.37 (d, *J* = 5.0 Hz, 2H), 2.53 – 2.39 (m, 2H), 2.32 (ddd, *J* = 13.5, 8.5, 4.8 Hz, 1H), 2.20 (dt, *J* = 13.6, 8.1 Hz, 1H), 1.94 (td, *J* = 13.1, 7.5 Hz, 2H), 1.47 (dq, *J* = 13.0, 8.5 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5, 60.0, 52.7, 41.5, 39.3, 37.1, 33.7, 30.8.

6. References

1. M. Giedyk, R. Narobe, S. Weiß, D. Touraud, W. Kunz and B. König, *Nature Catal.*, 2020, **3**, 40–47.
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3. V. V. Pavlishchuk, A. W. Addison, *Inorganica Chimica Acta.*, 2000, **298**, 97–102.
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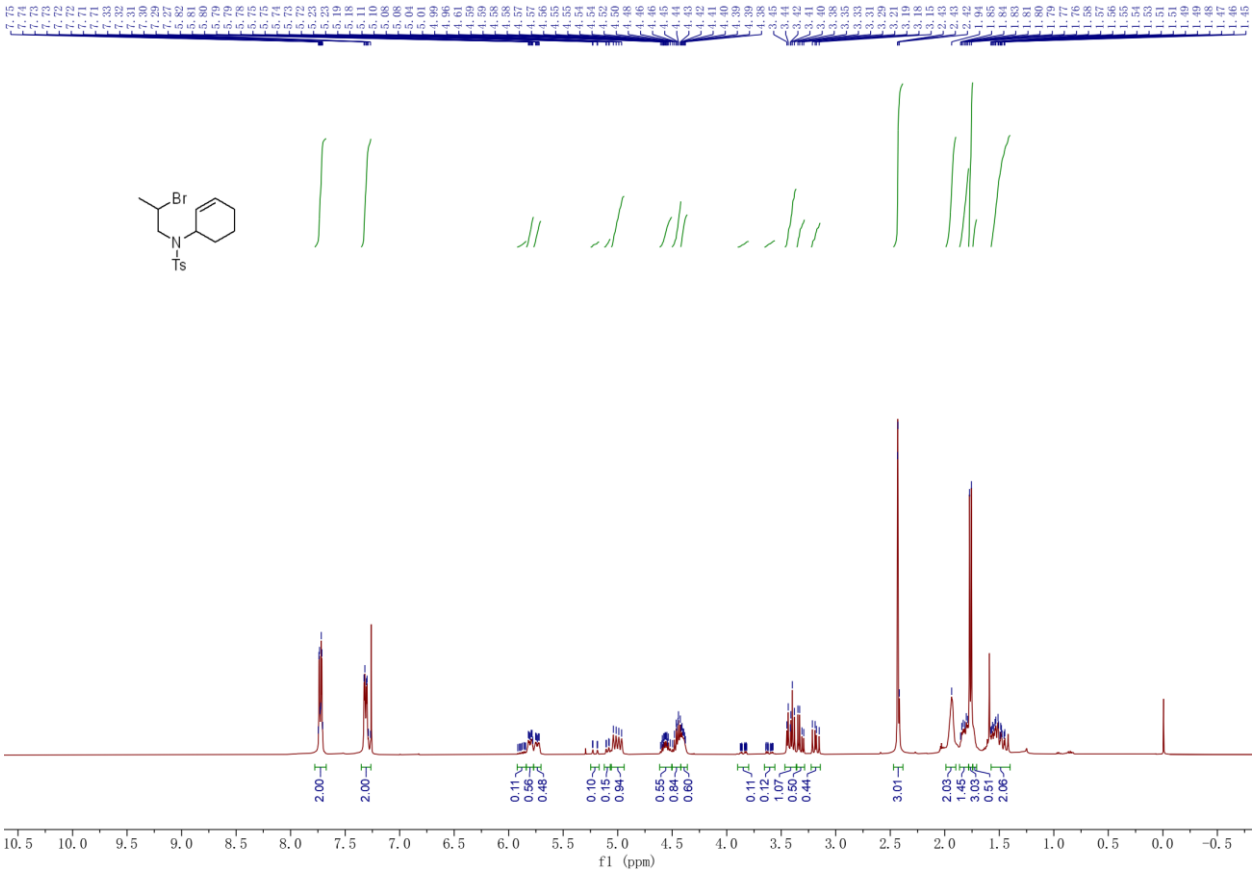
7. ^{1}H and ^{13}C NMR spectra

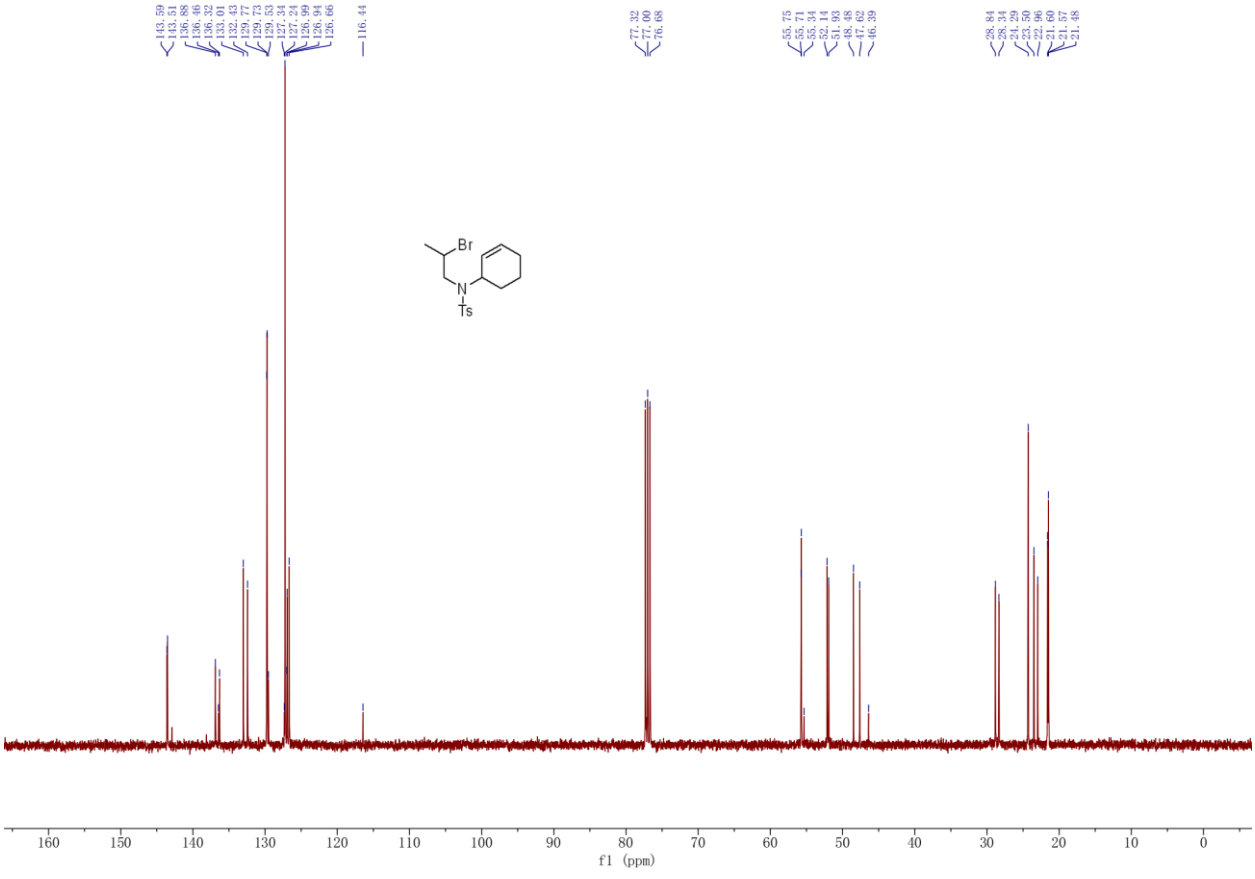
6.1 Substrates

1n

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

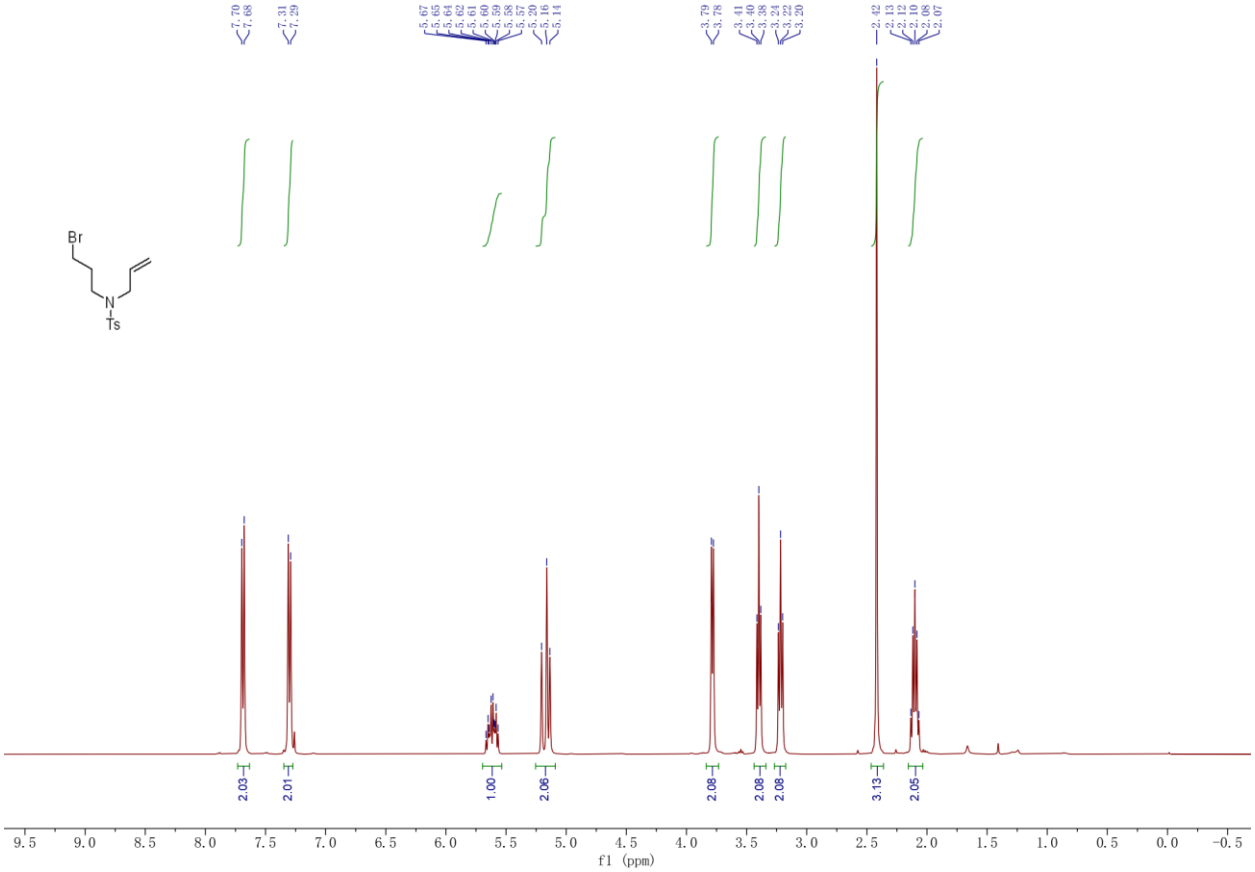


^{13}C NMR ($CDCl_3$, 101 MHz)

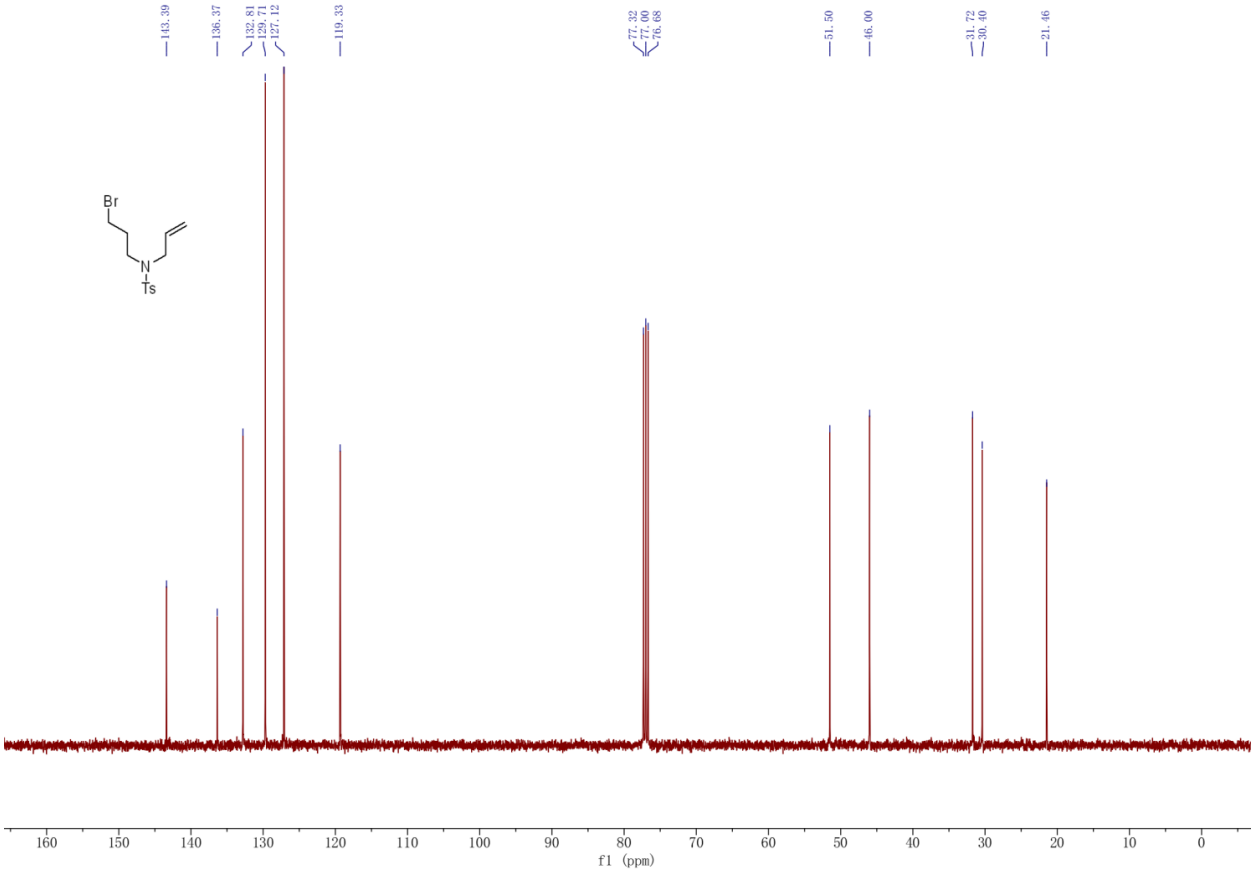


1l

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



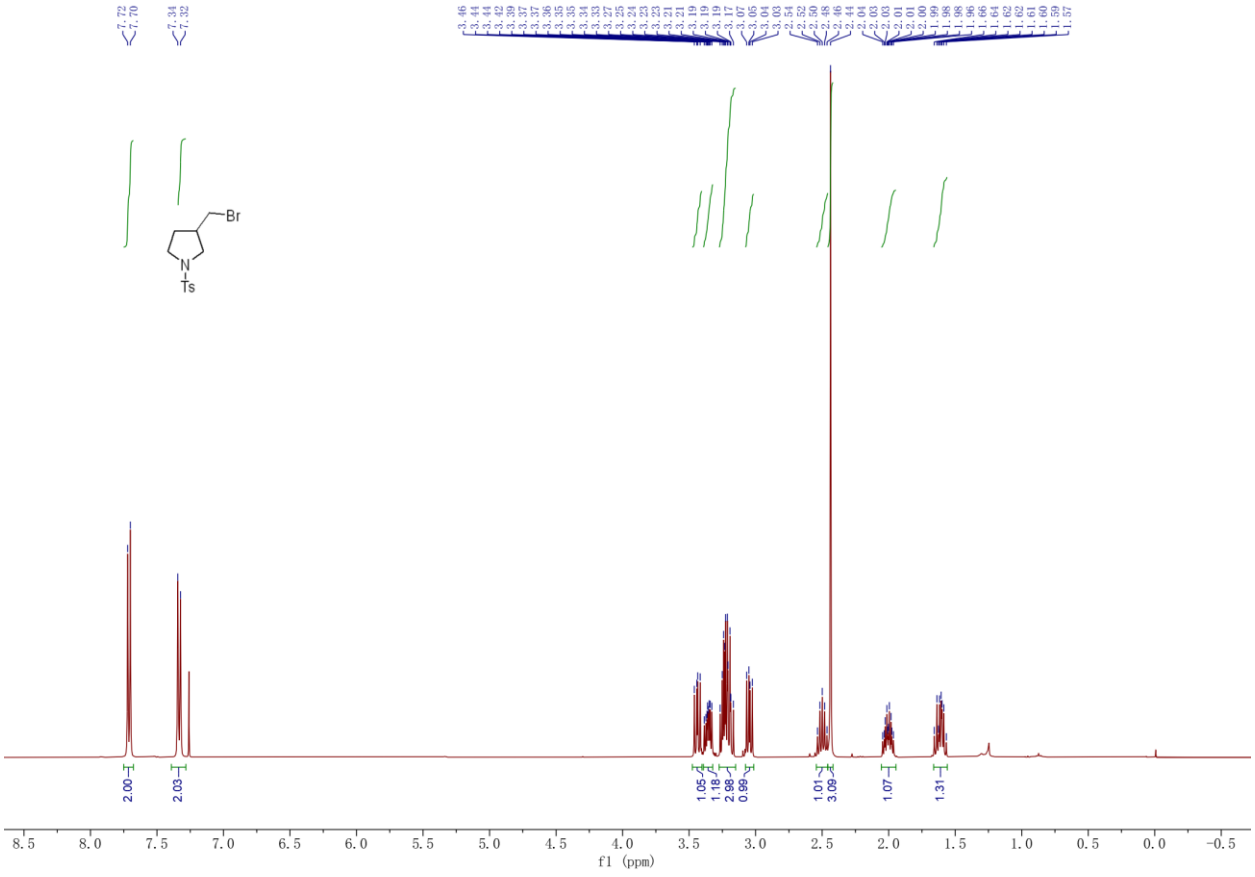
^{13}C NMR ($CDCl_3$, 101 MHz)



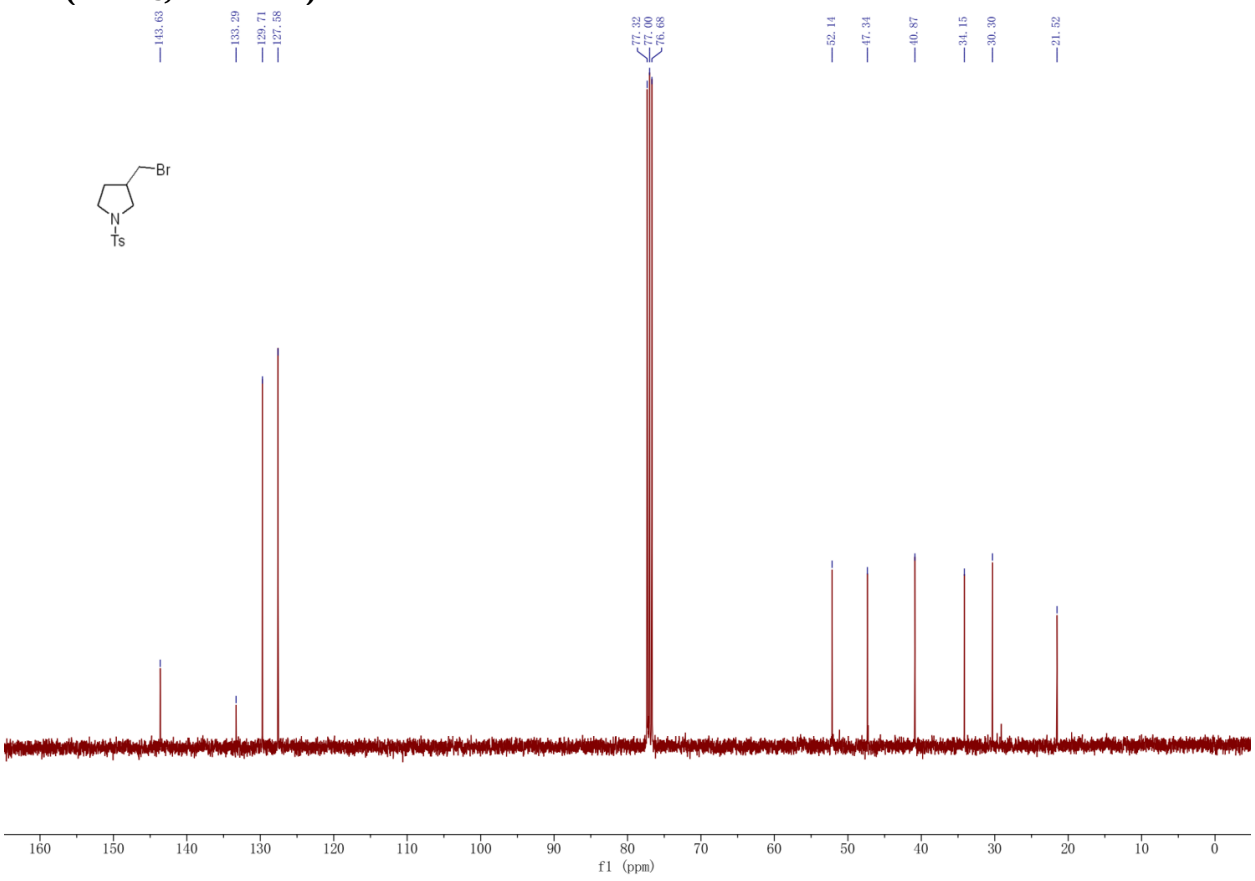
6.2 Products

2a

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

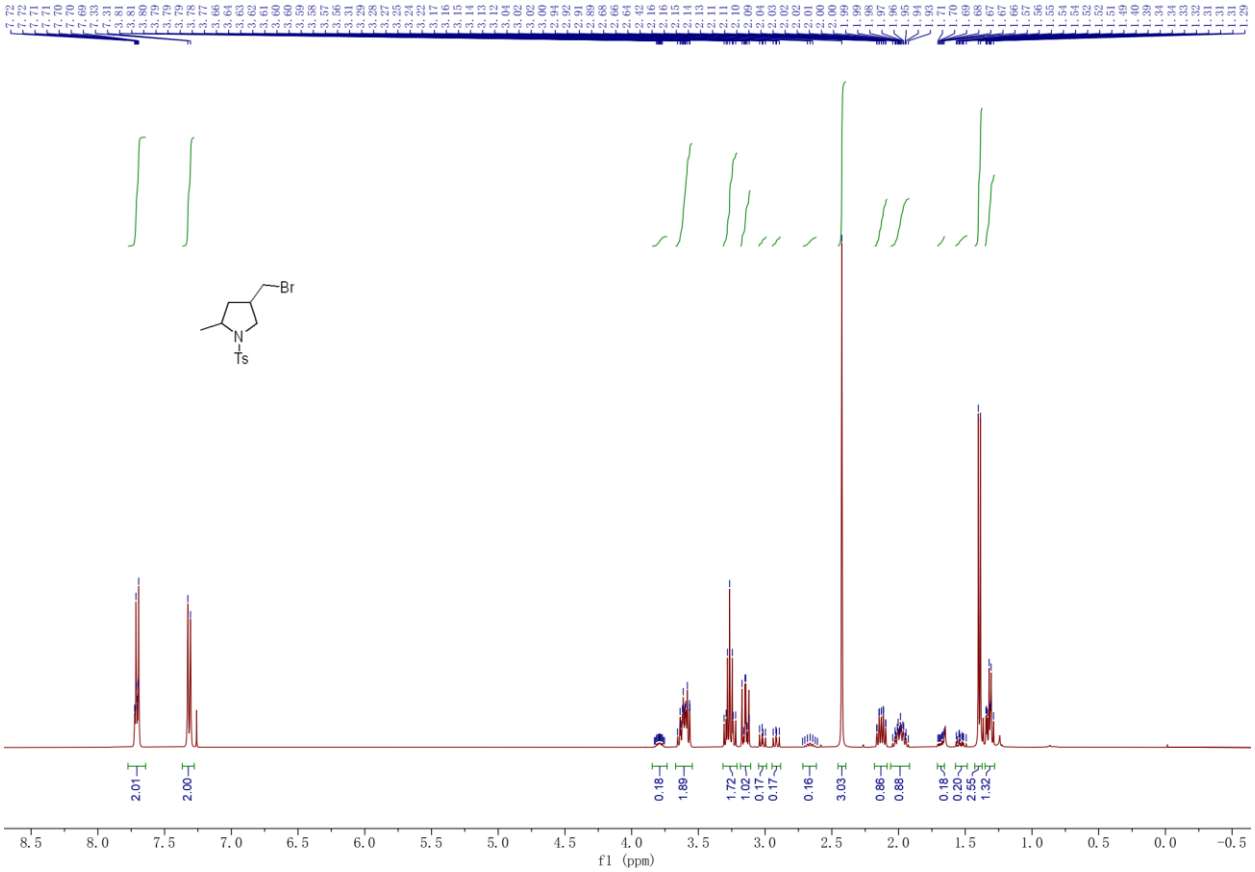


^{13}C NMR ($CDCl_3$, 101 MHz)

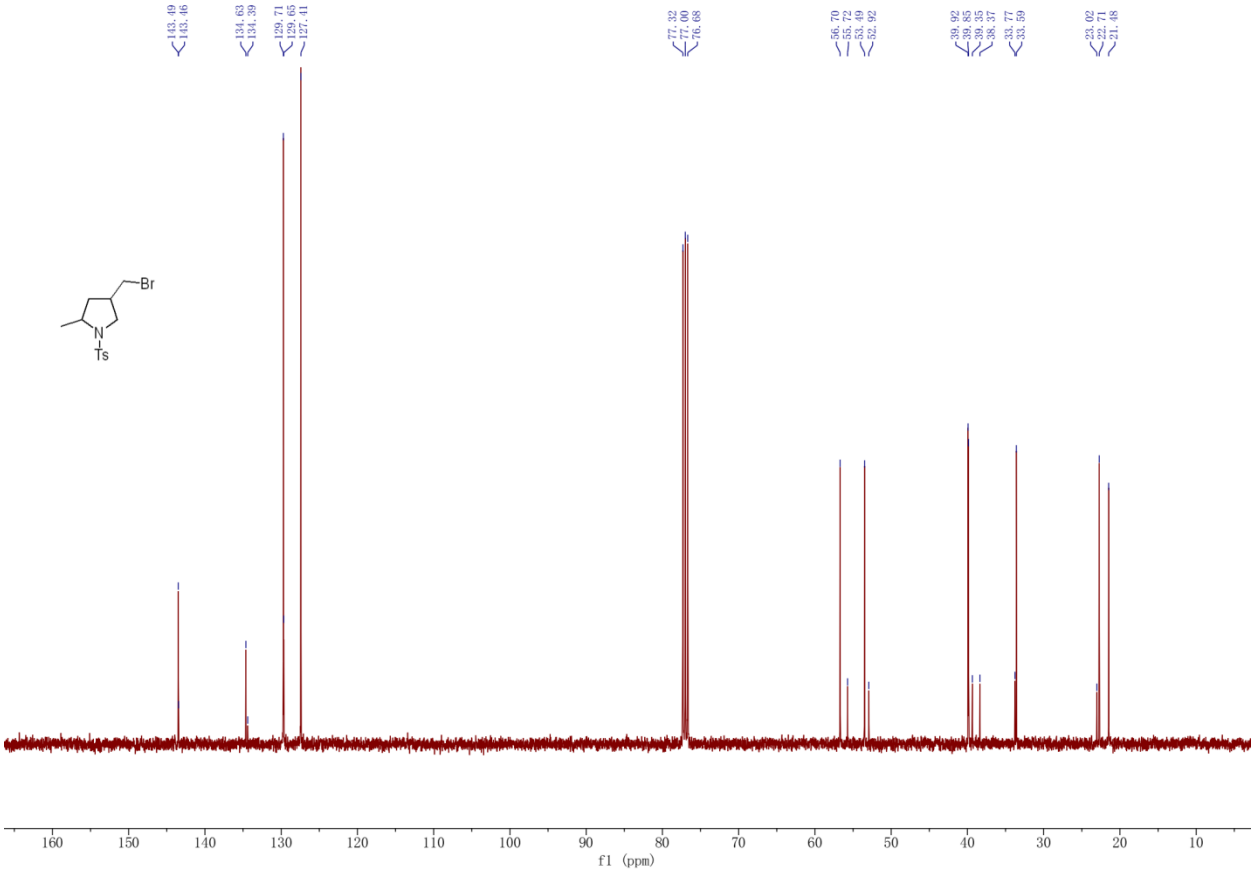


2b

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

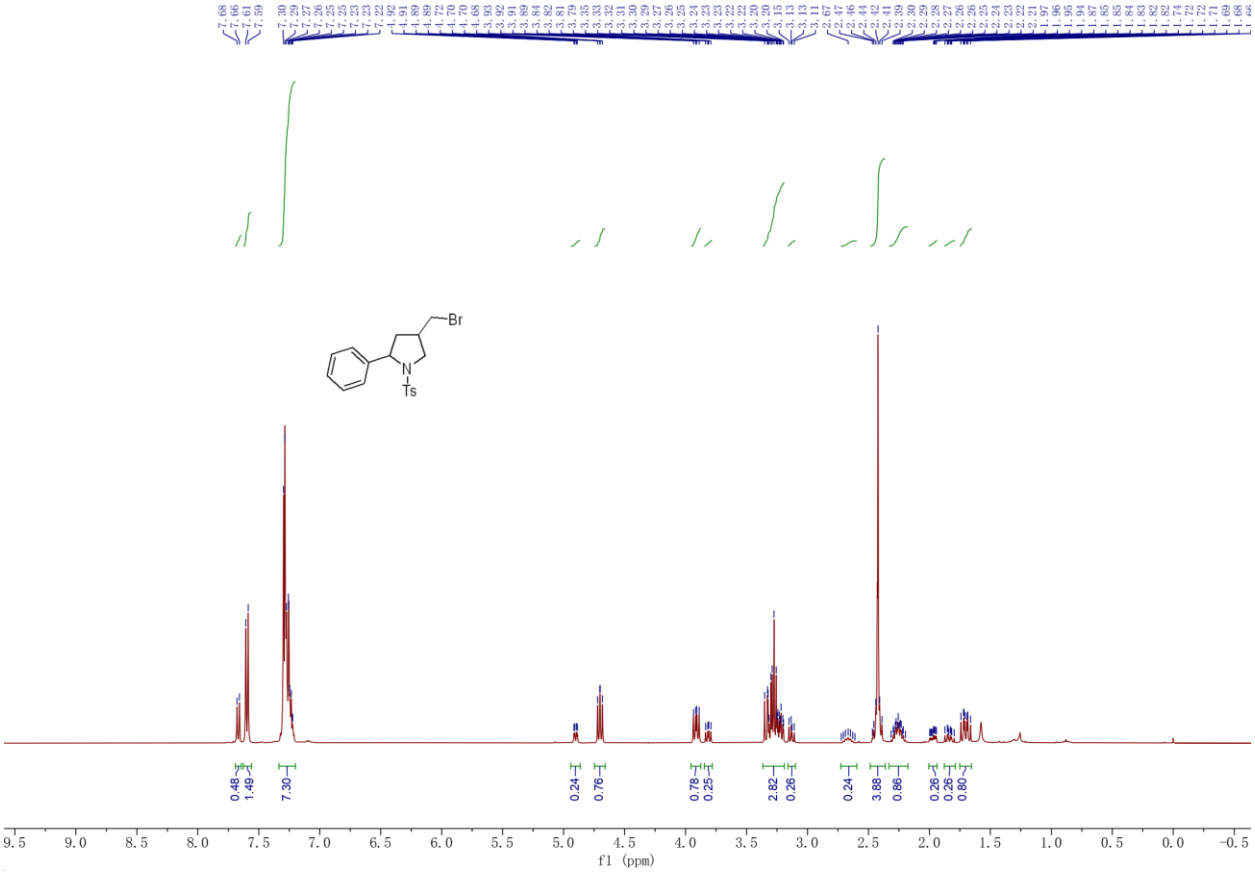


^{13}C NMR ($CDCl_3$, 101 MHz)

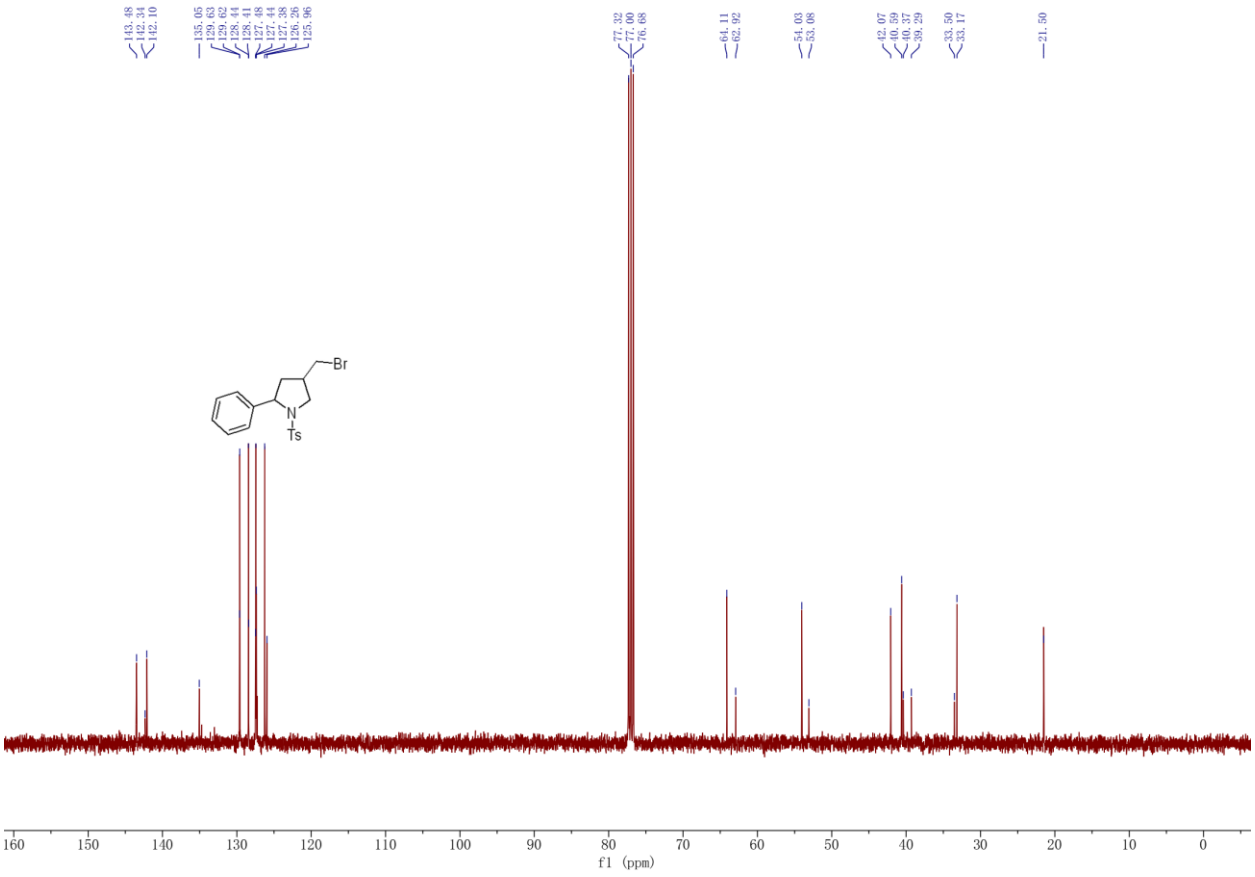


2c

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

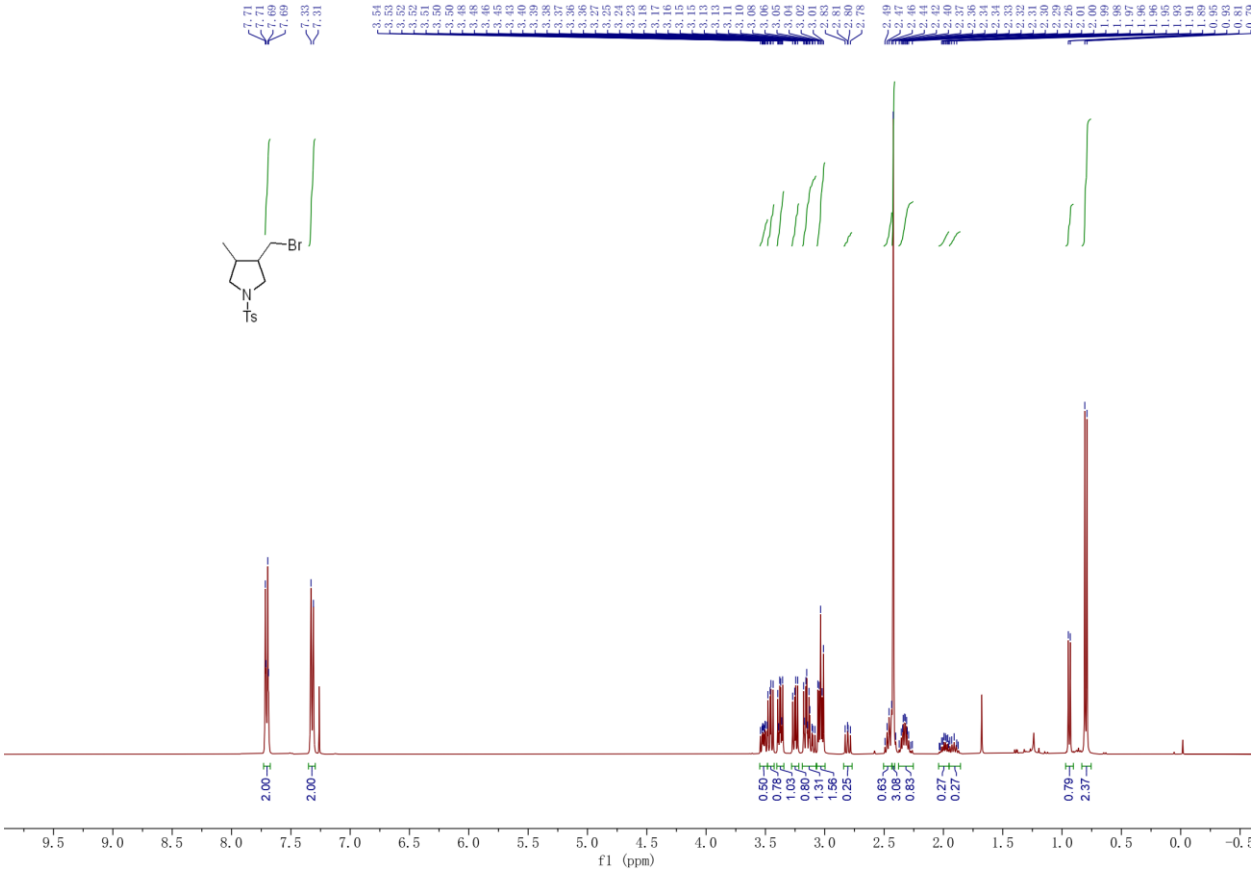


^{13}C NMR ($CDCl_3$, 101 MHz)

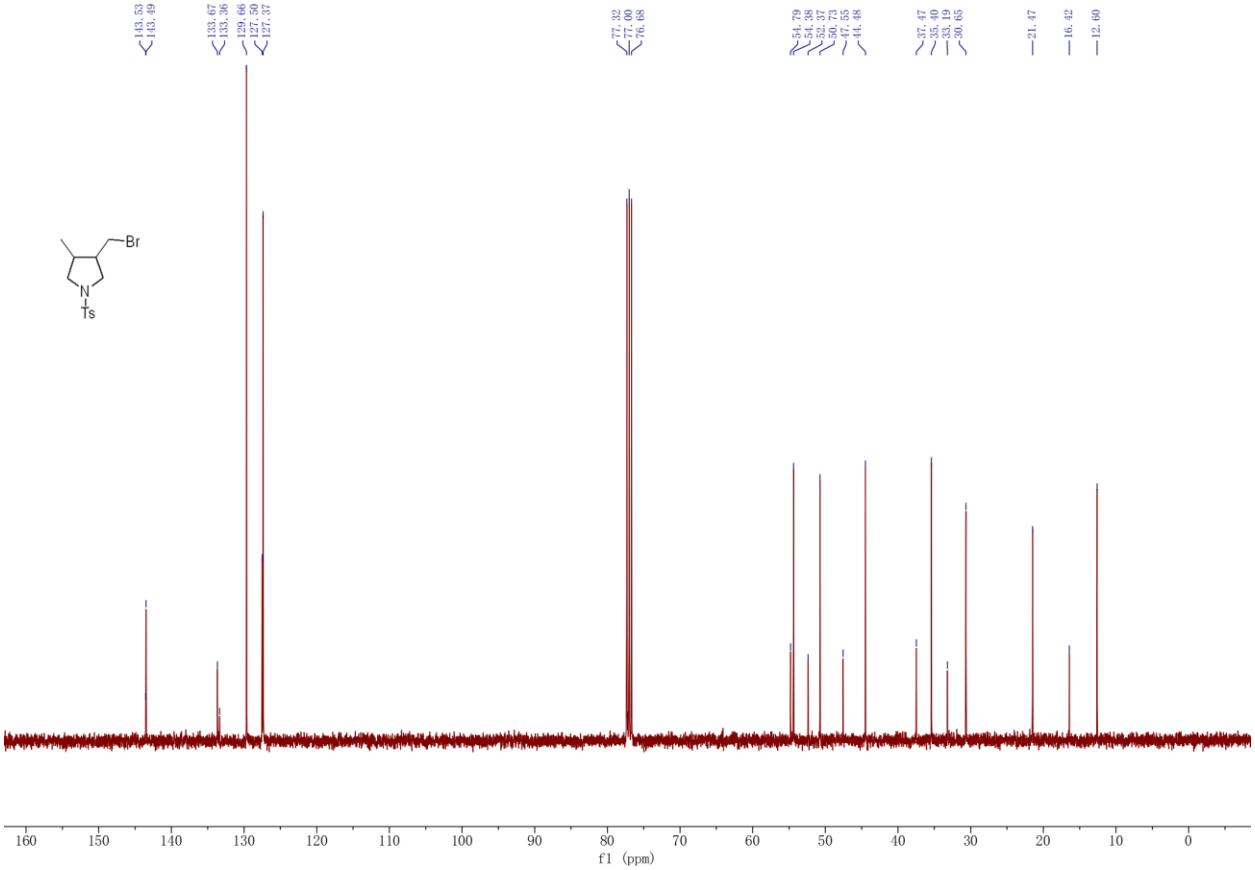


2d

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

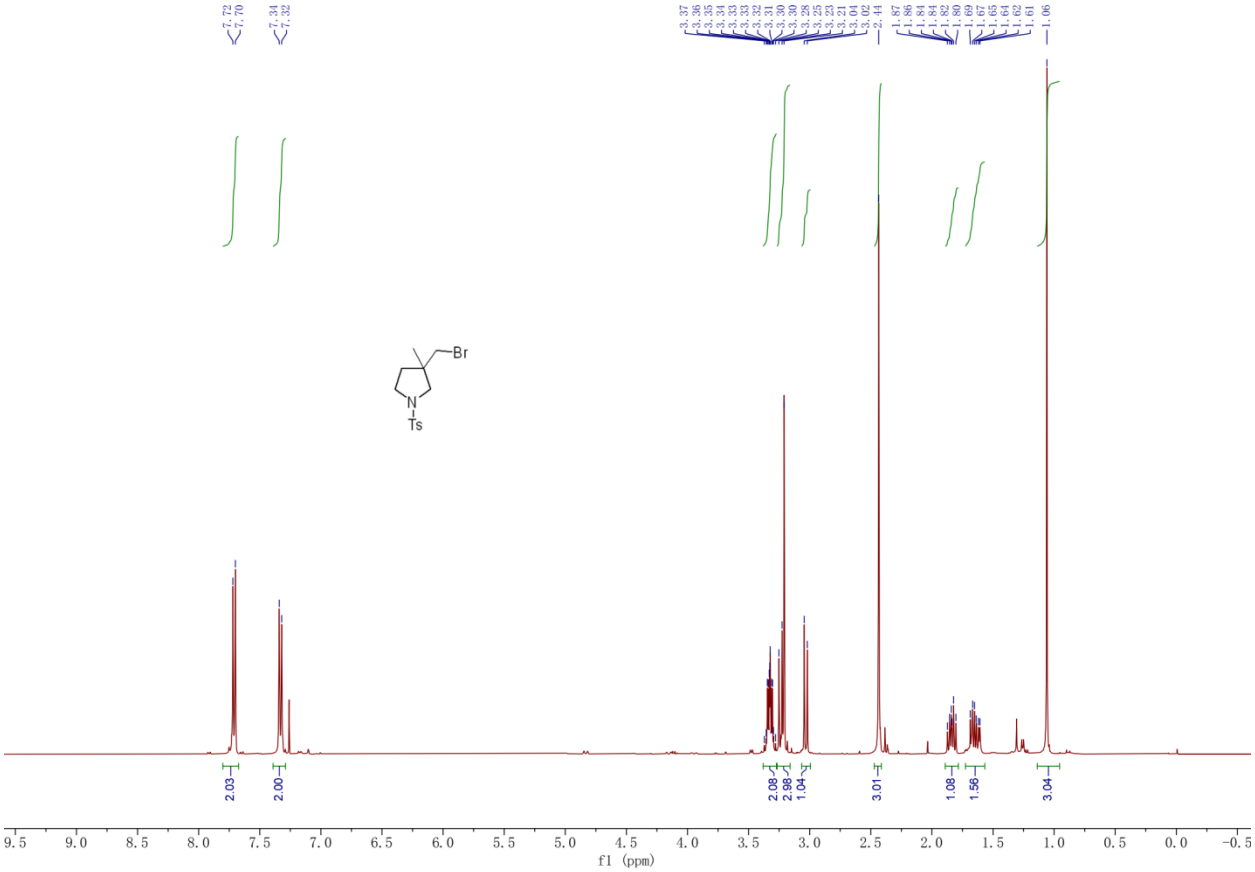


^{13}C NMR ($CDCl_3$, 101 MHz)

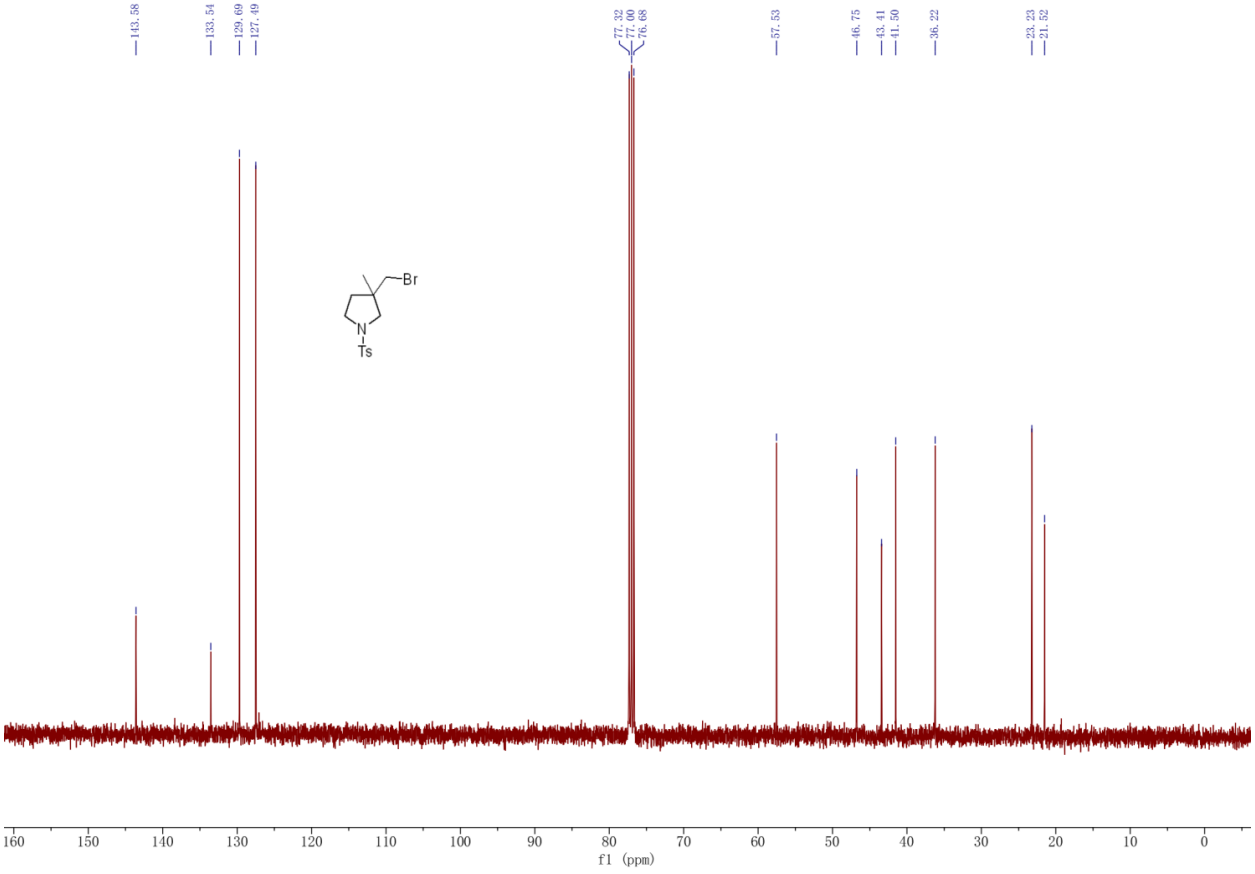


2e

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

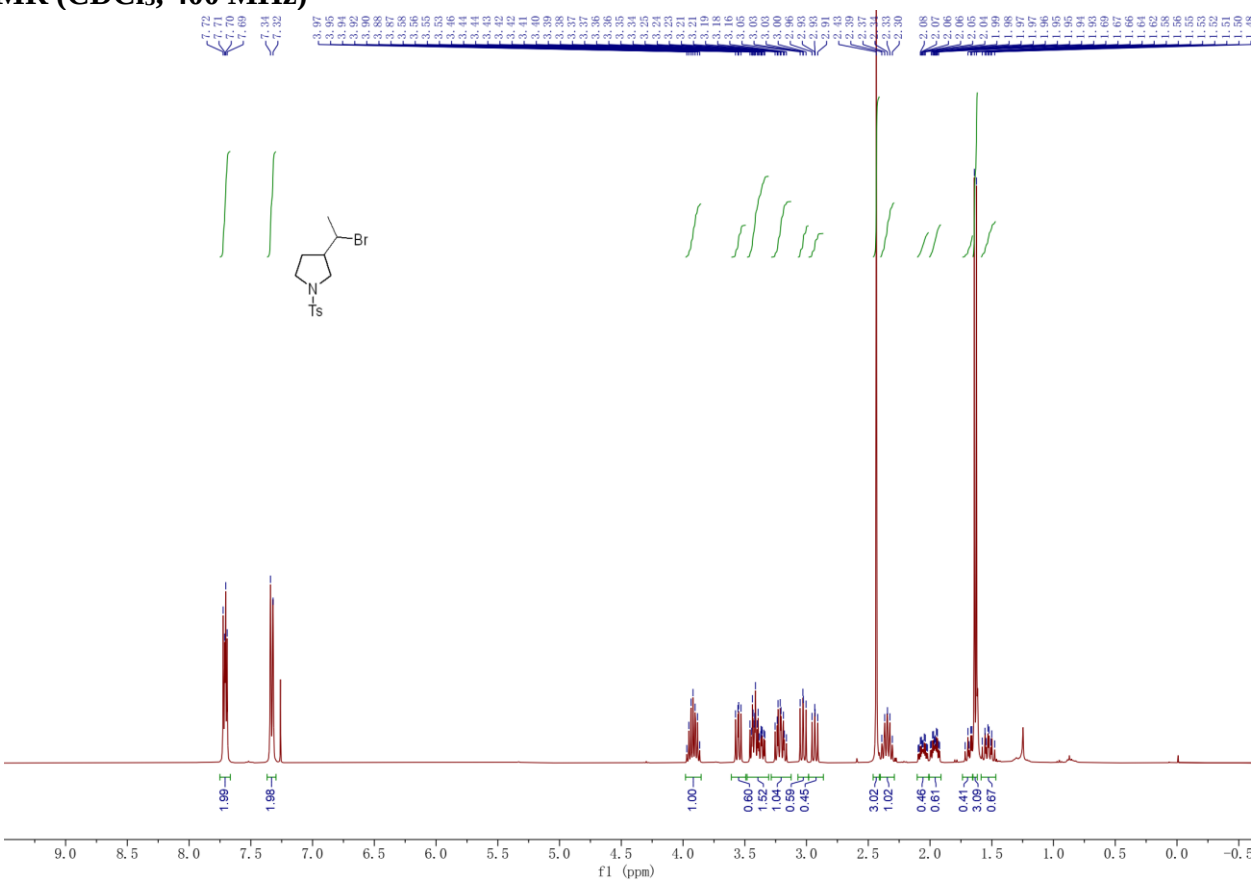


^{13}C NMR ($CDCl_3$, 101 MHz)

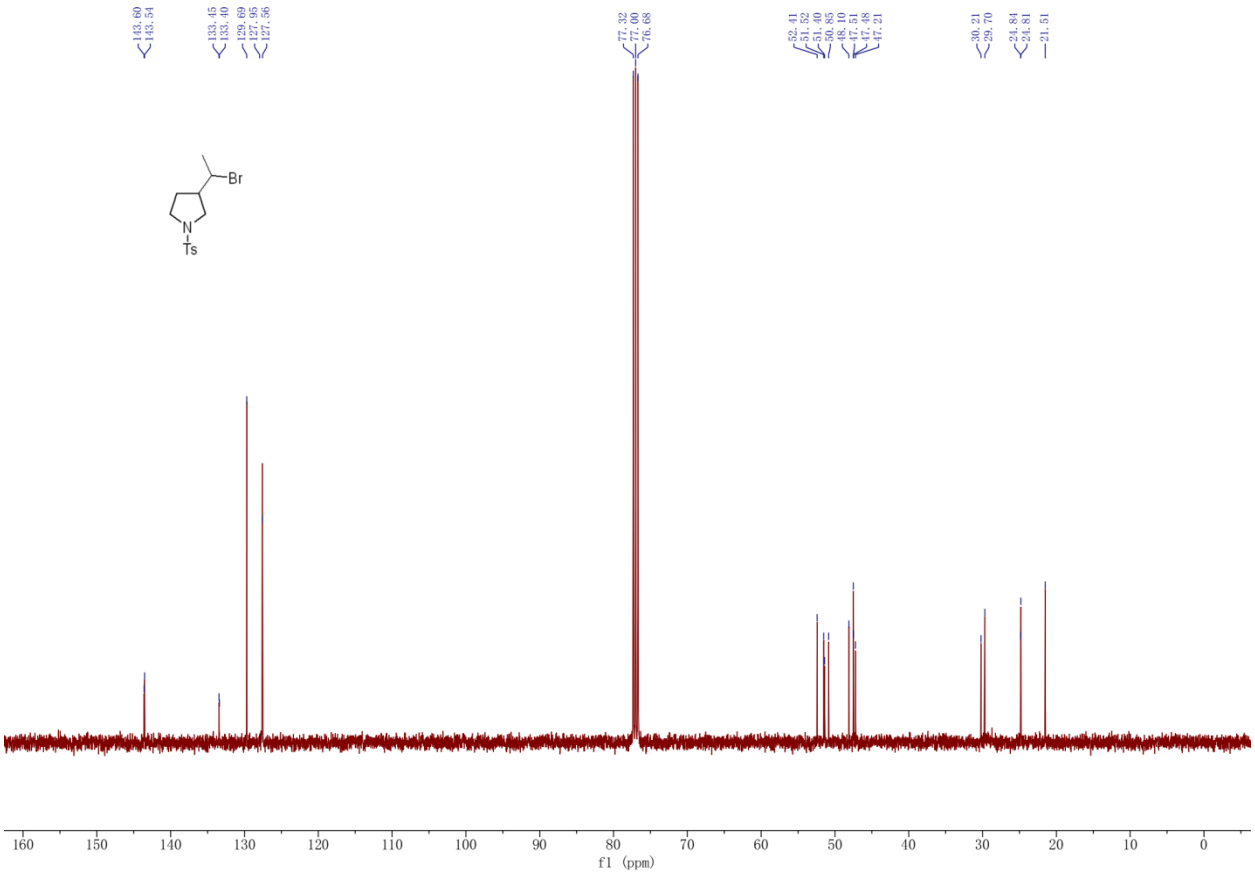


2f

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

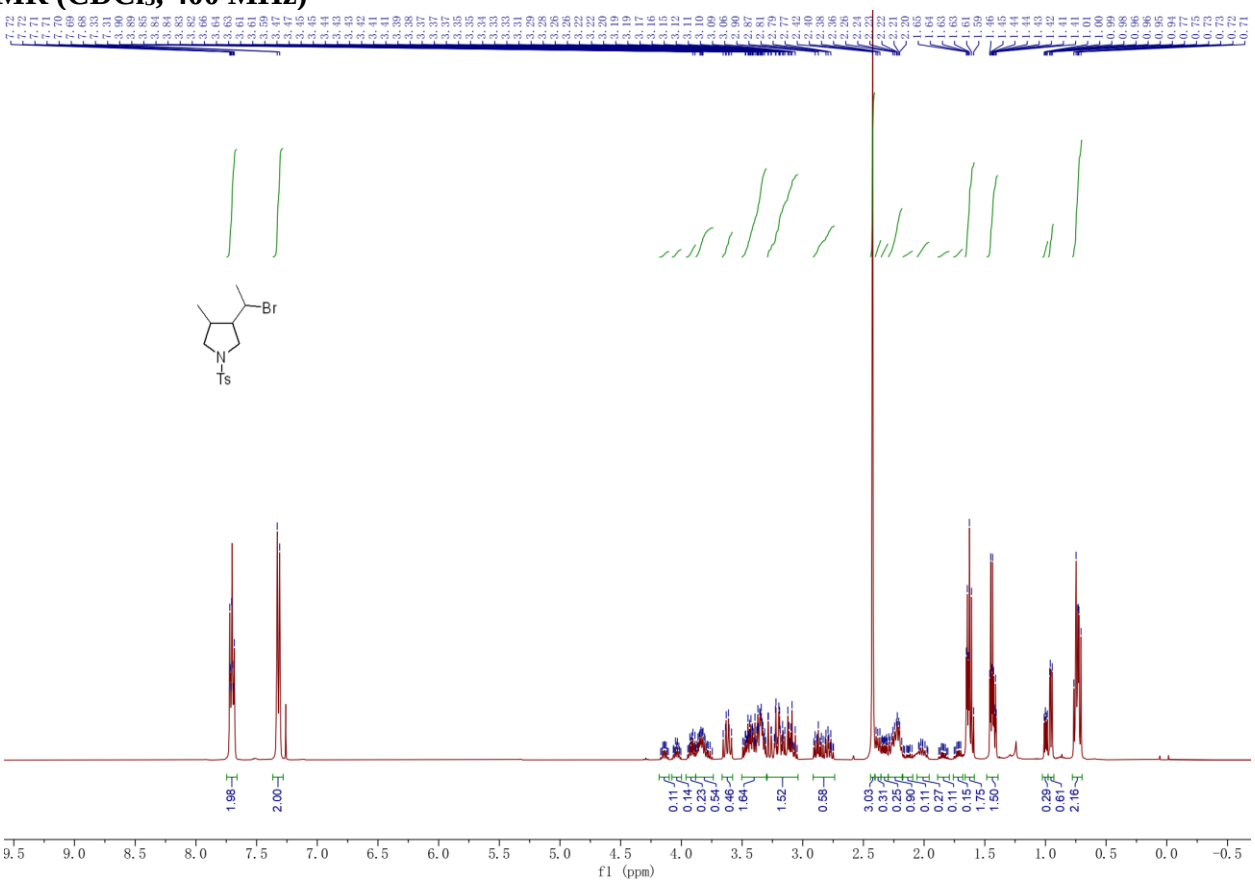


^{13}C NMR ($CDCl_3$, 101 MHz)

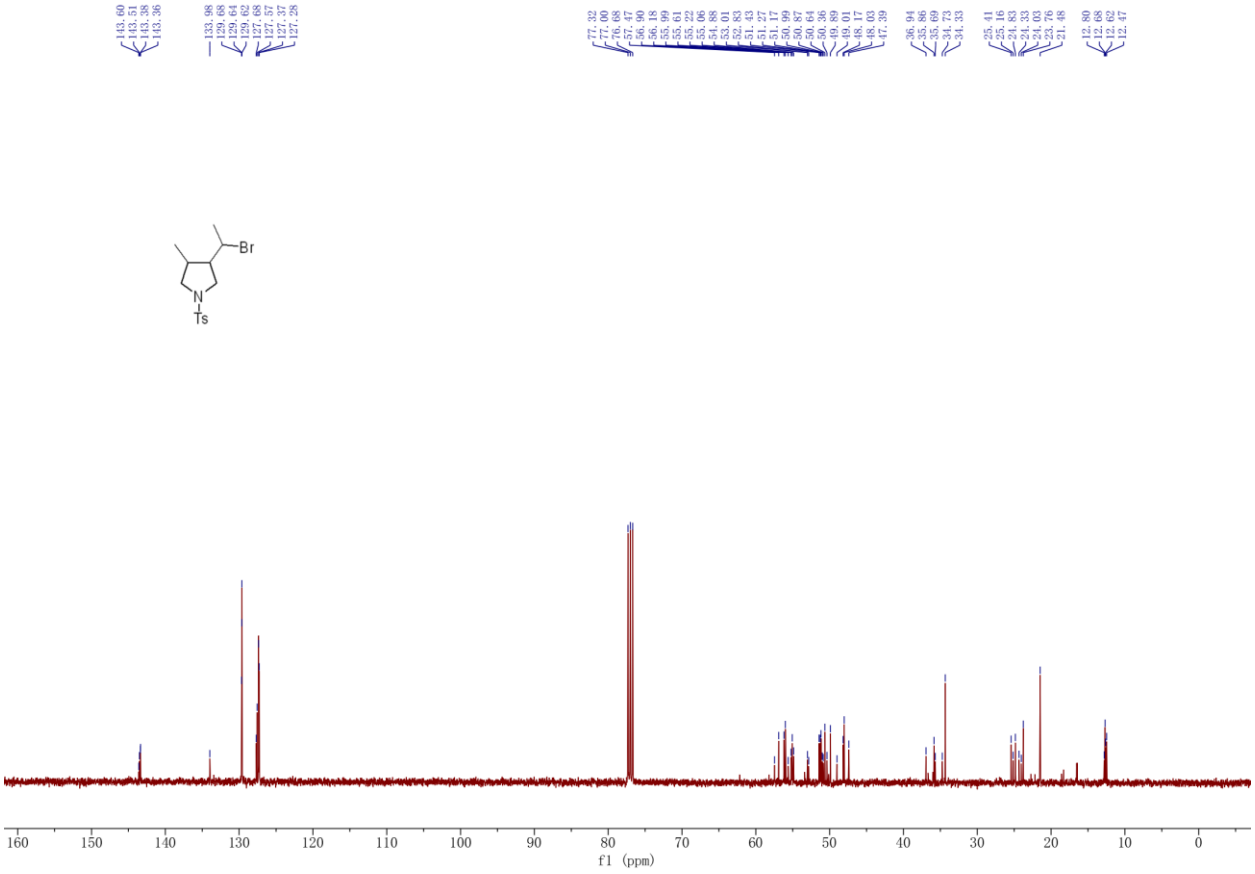


2g

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

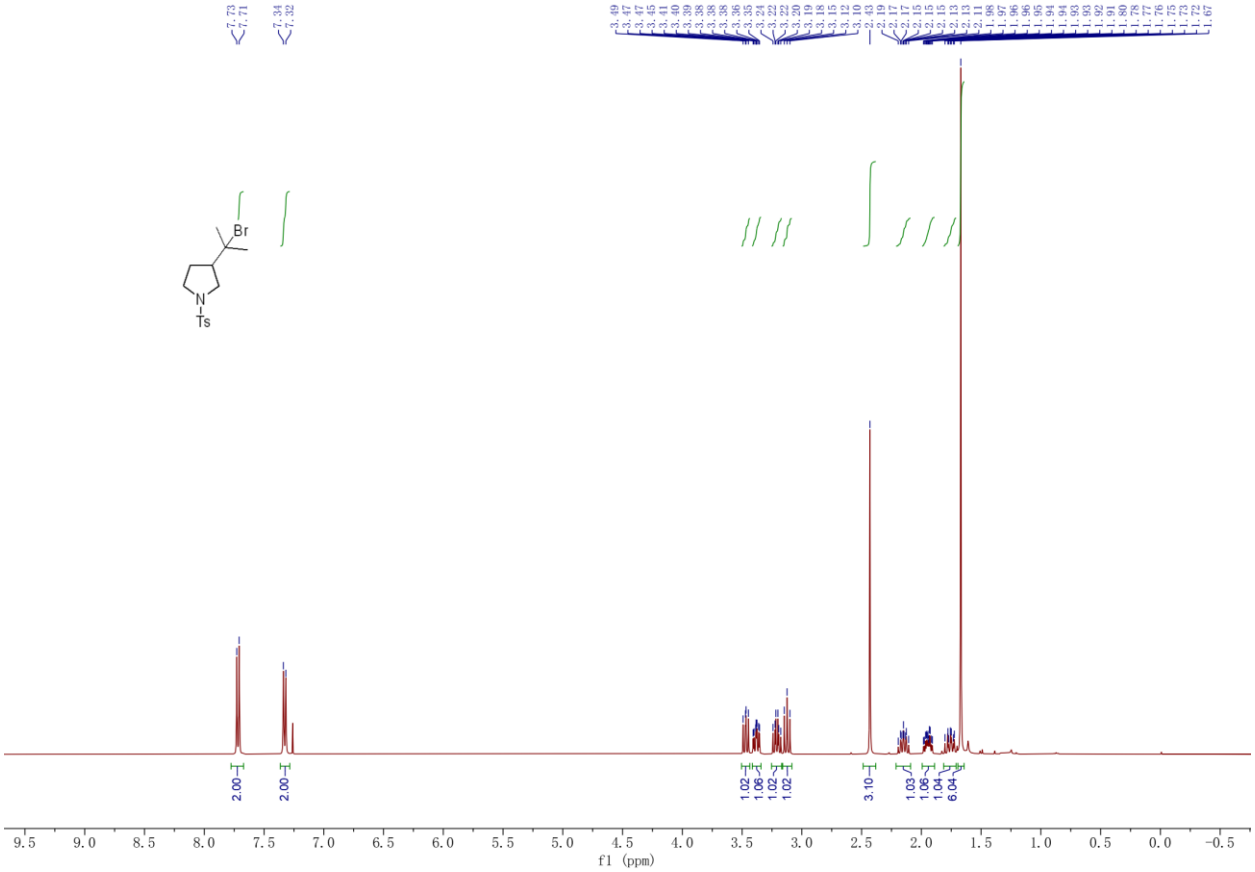


^{13}C NMR ($CDCl_3$, 101 MHz)

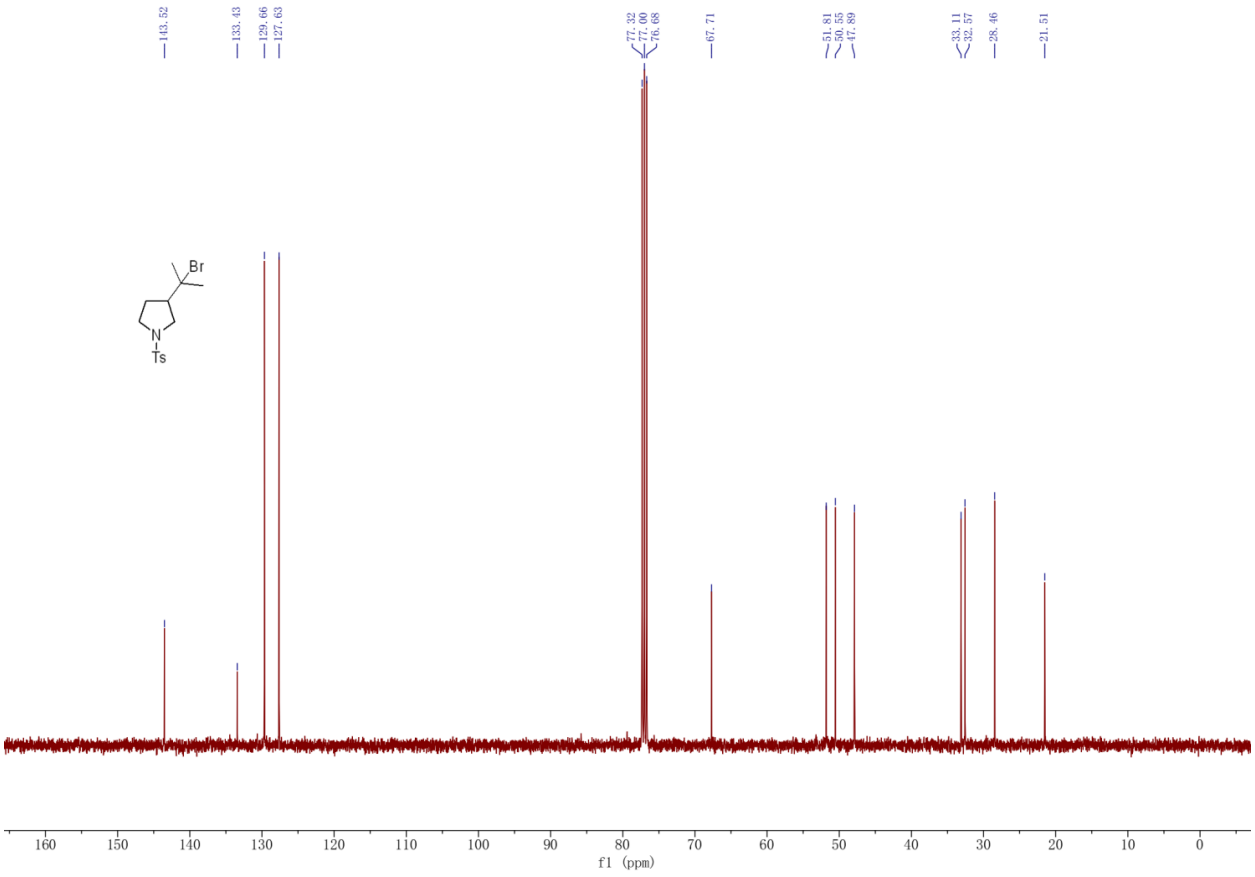


2h

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

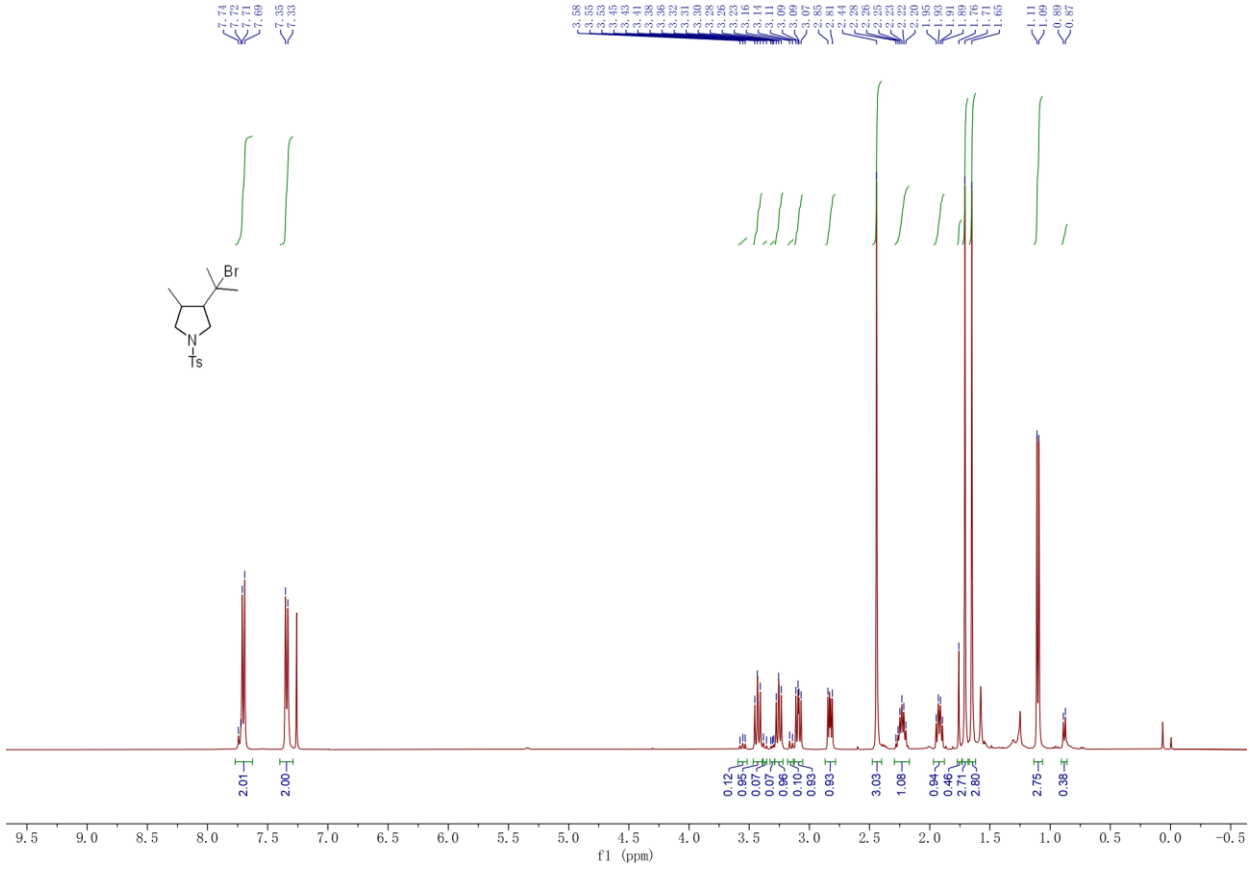


^{13}C NMR ($CDCl_3$, 101 MHz)

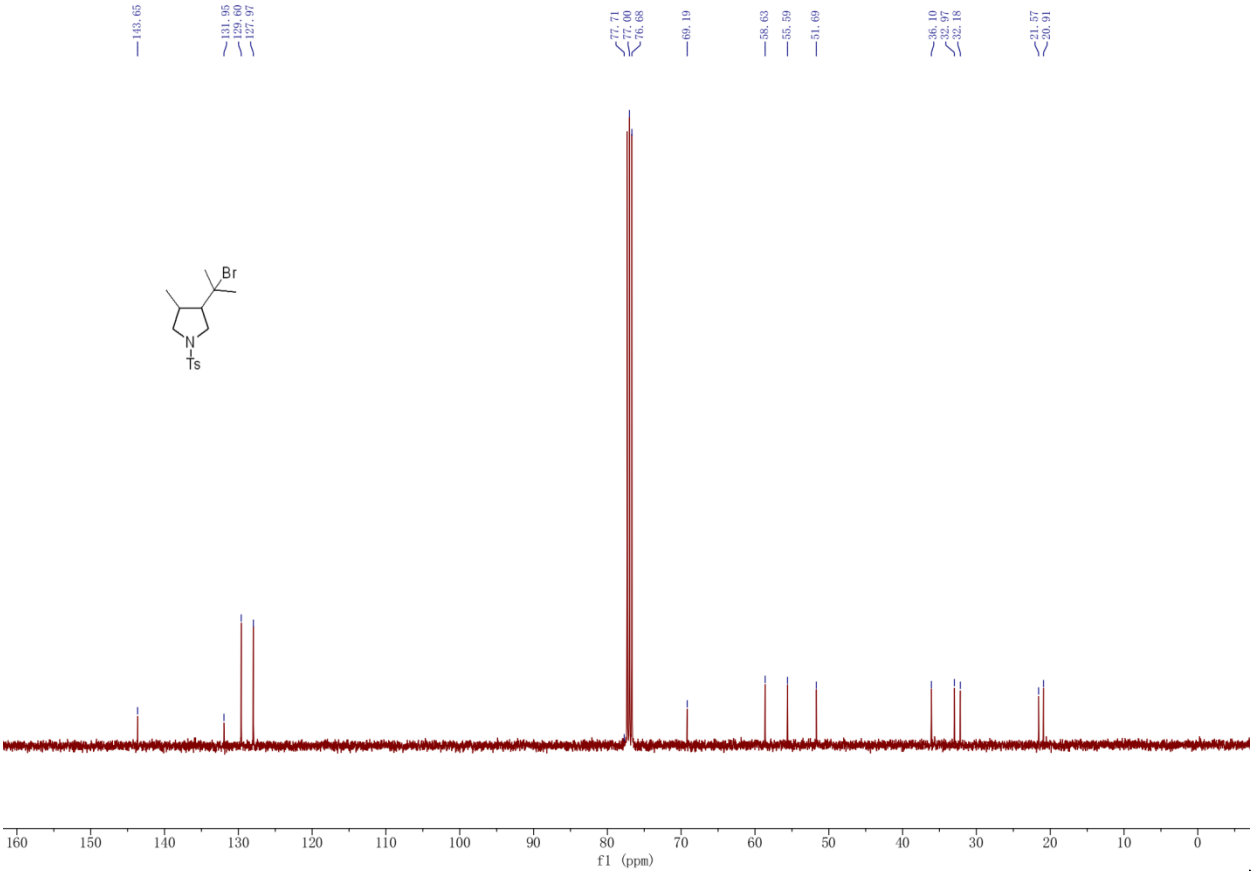


2i

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

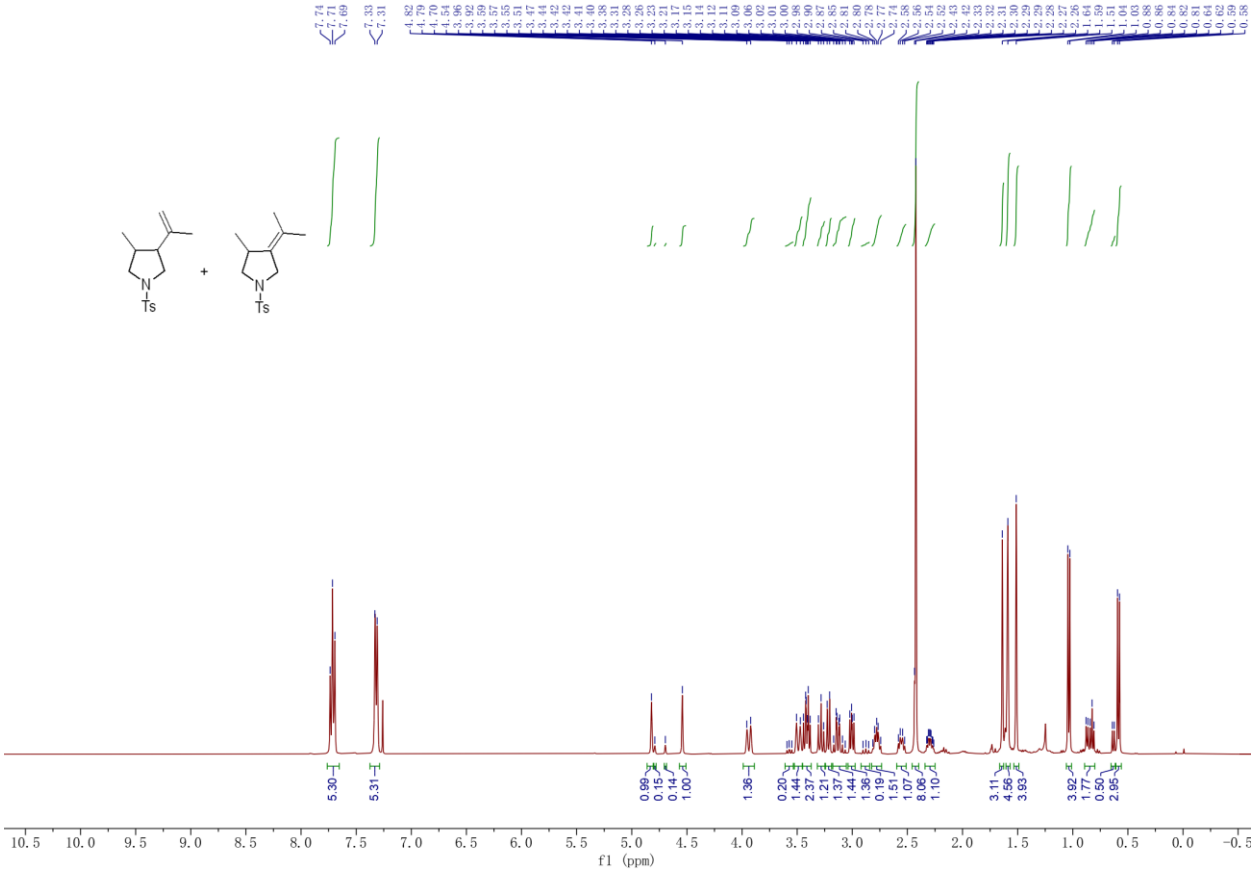


^{13}C NMR ($CDCl_3$, 101 MHz)

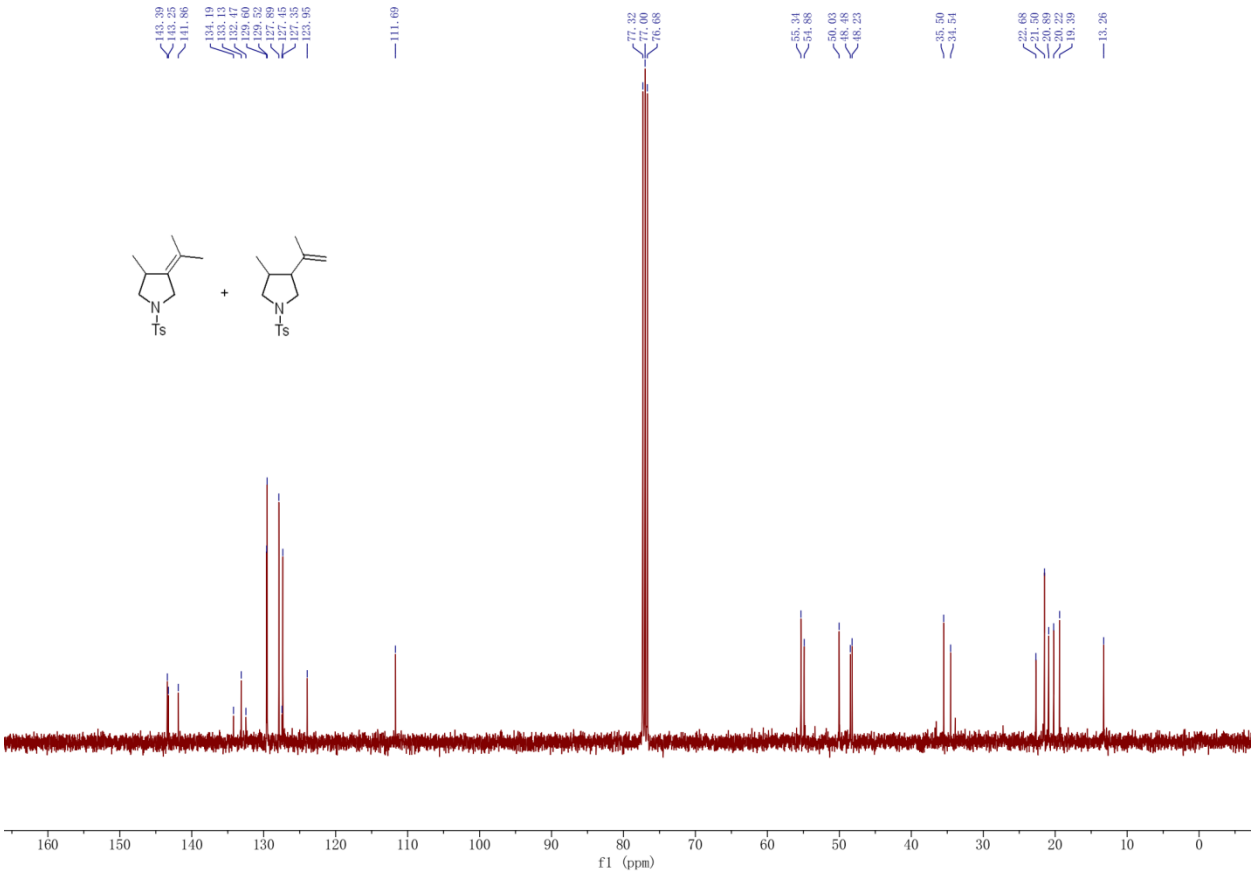


4i-1 and 4i-2

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

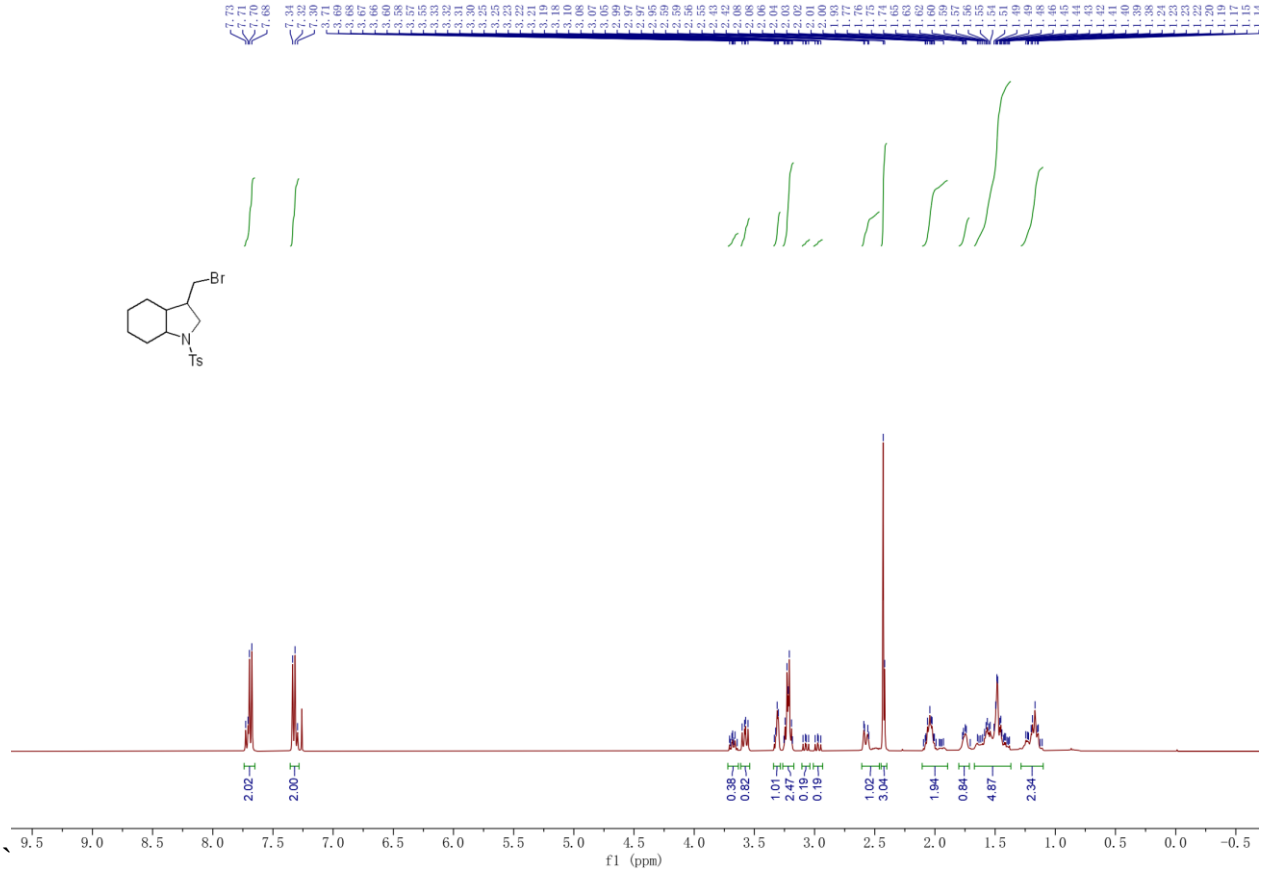


^{13}C NMR ($CDCl_3$, 101 MHz)

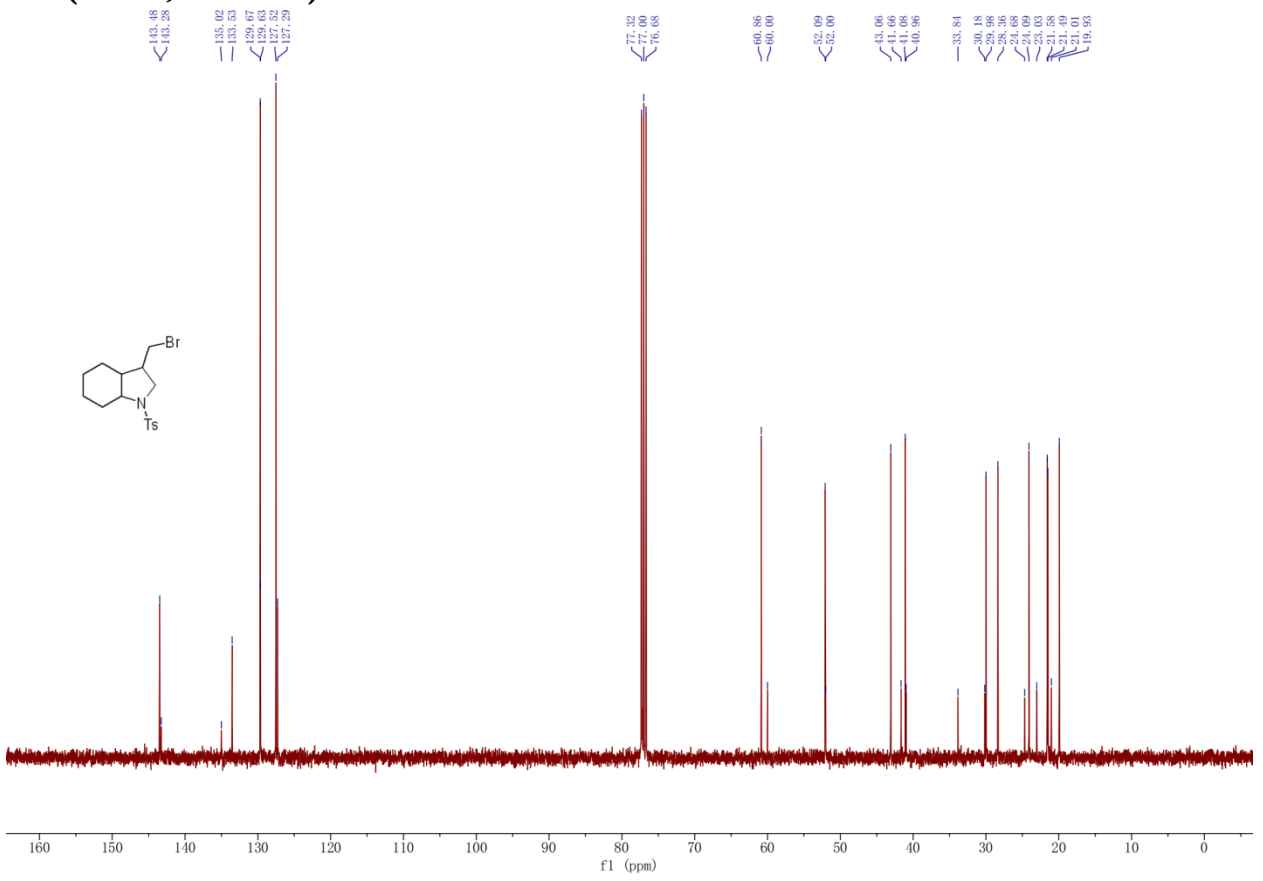


2j

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

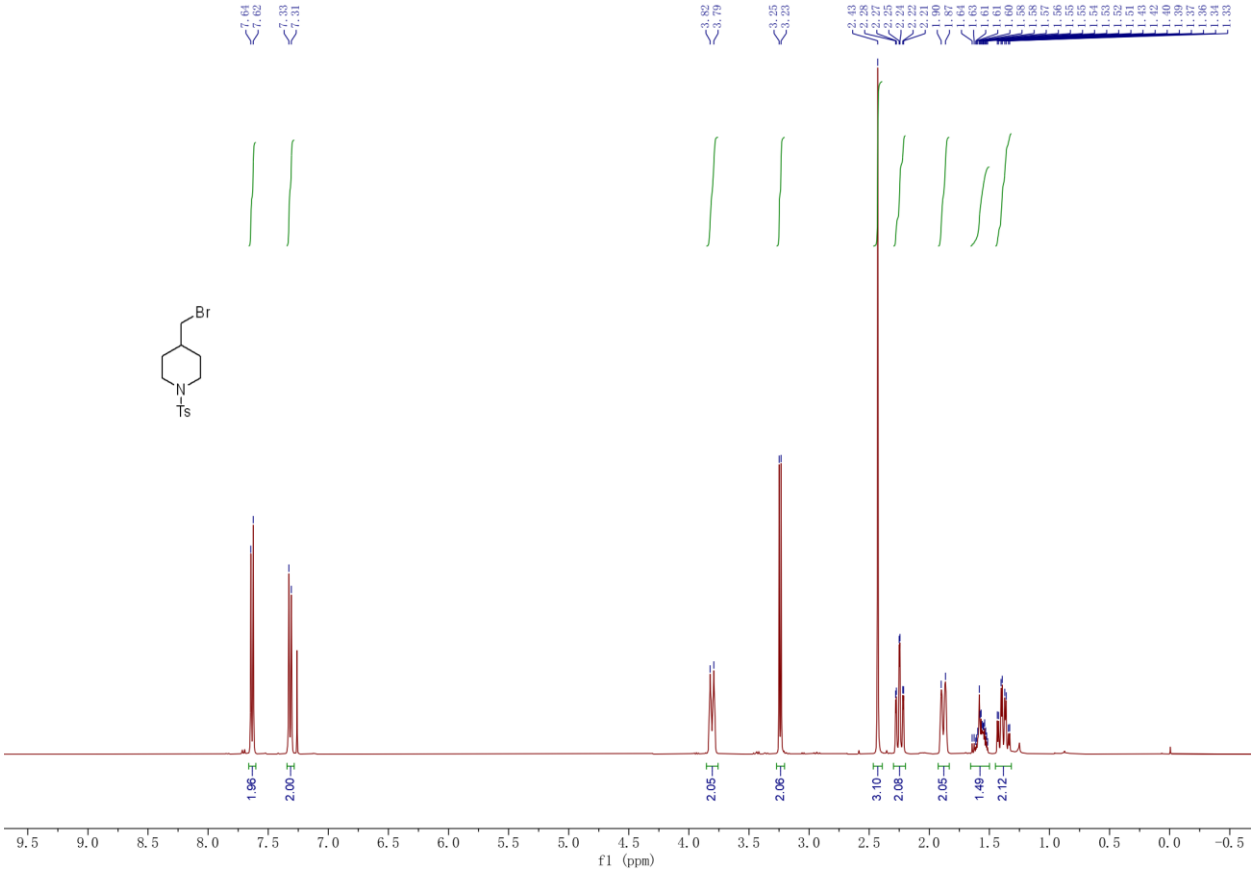


^{13}C NMR ($CDCl_3$, 101 MHz)

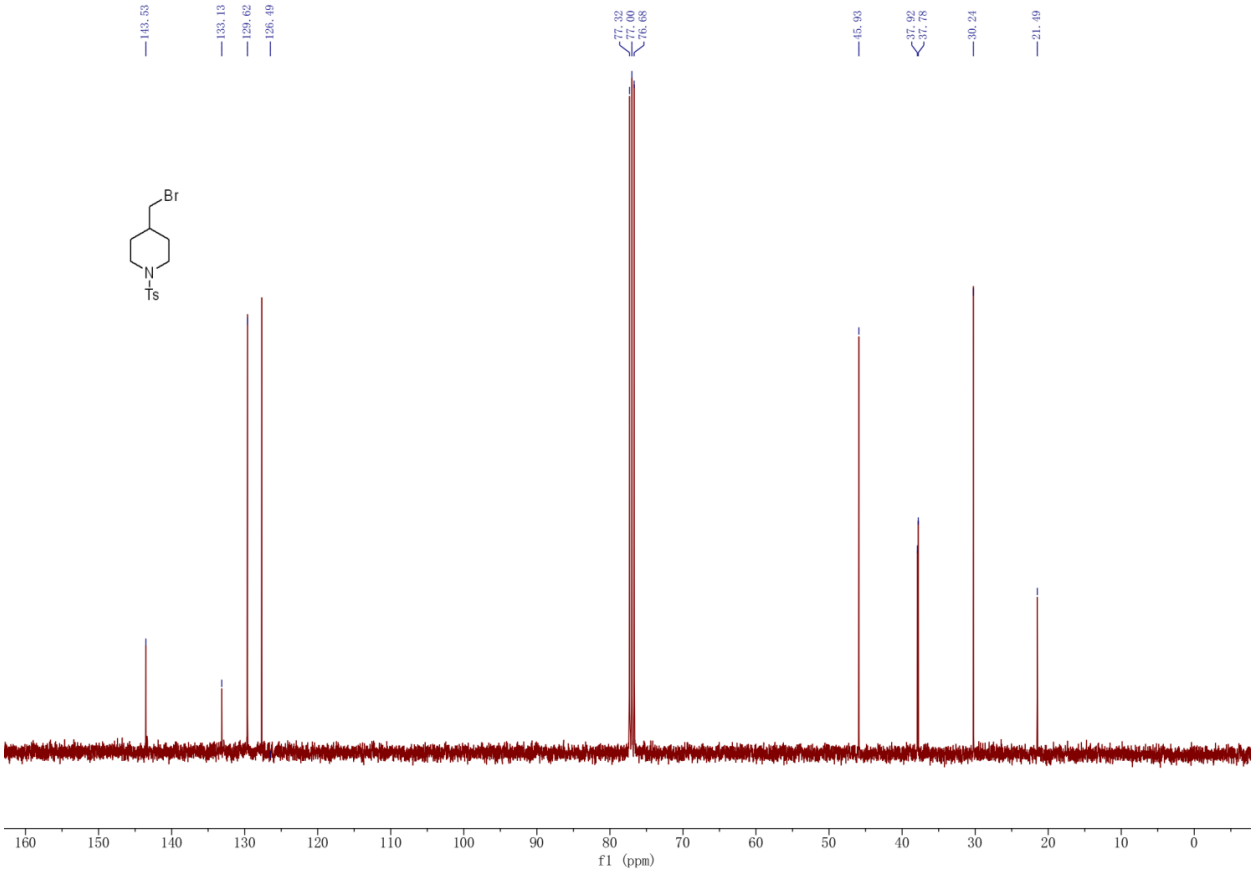


2k-1

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

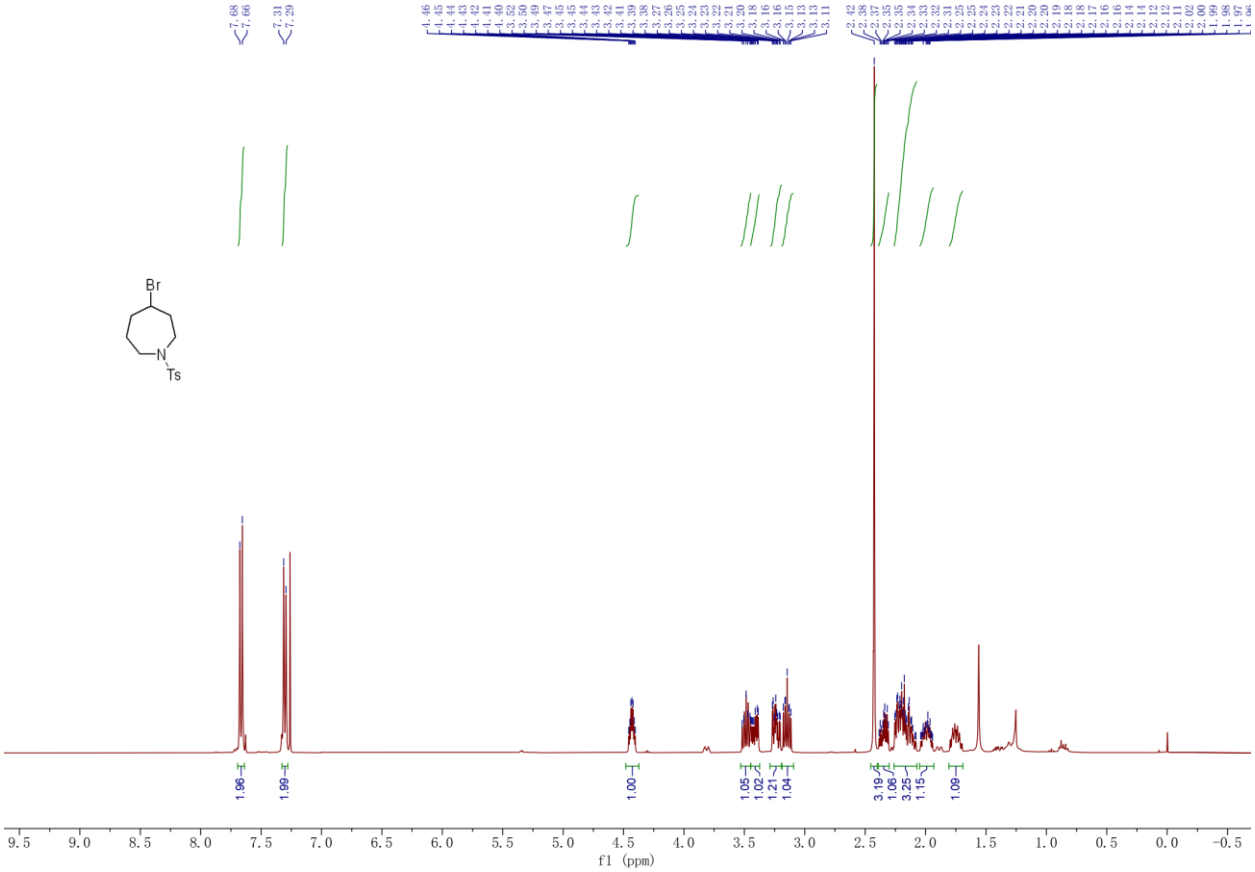


^{13}C NMR ($CDCl_3$, 101 MHz)

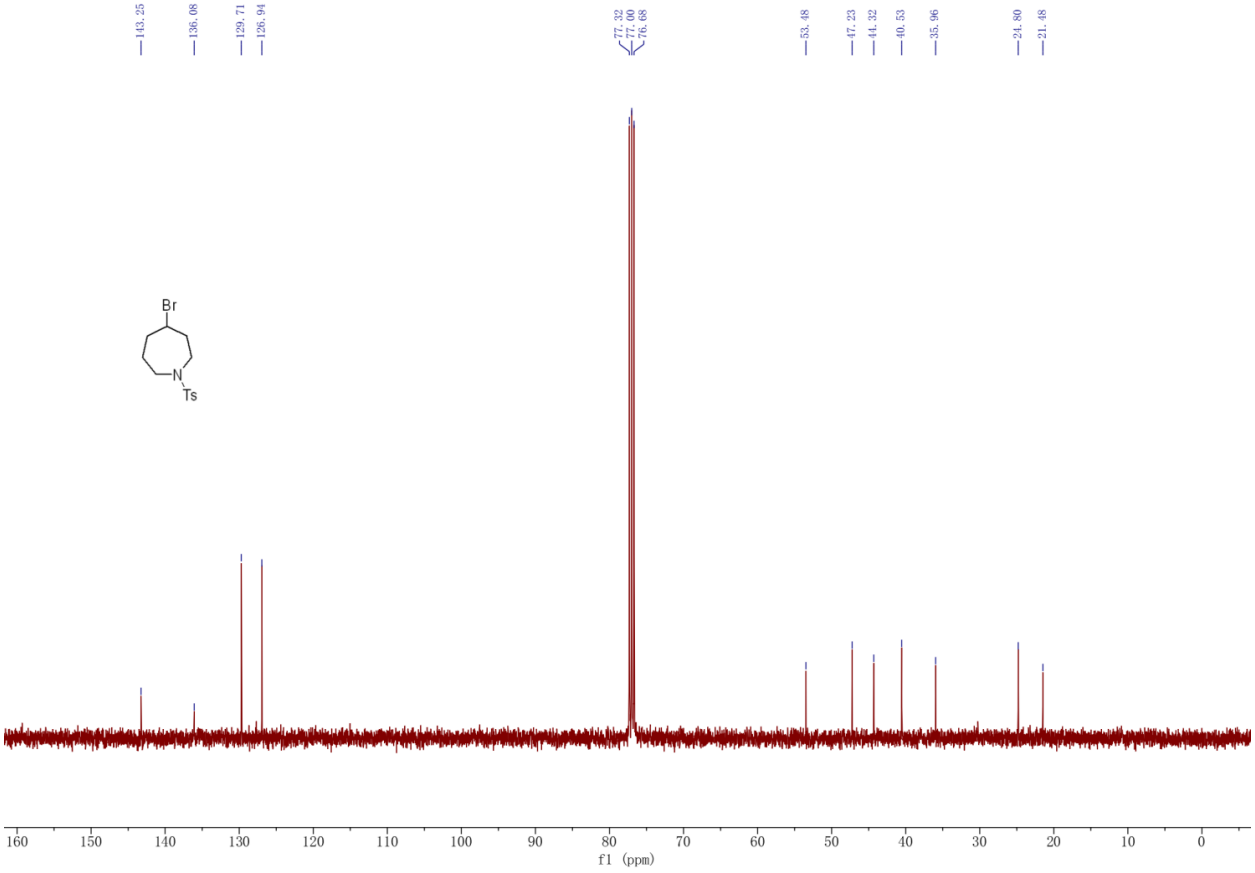


2k-2

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

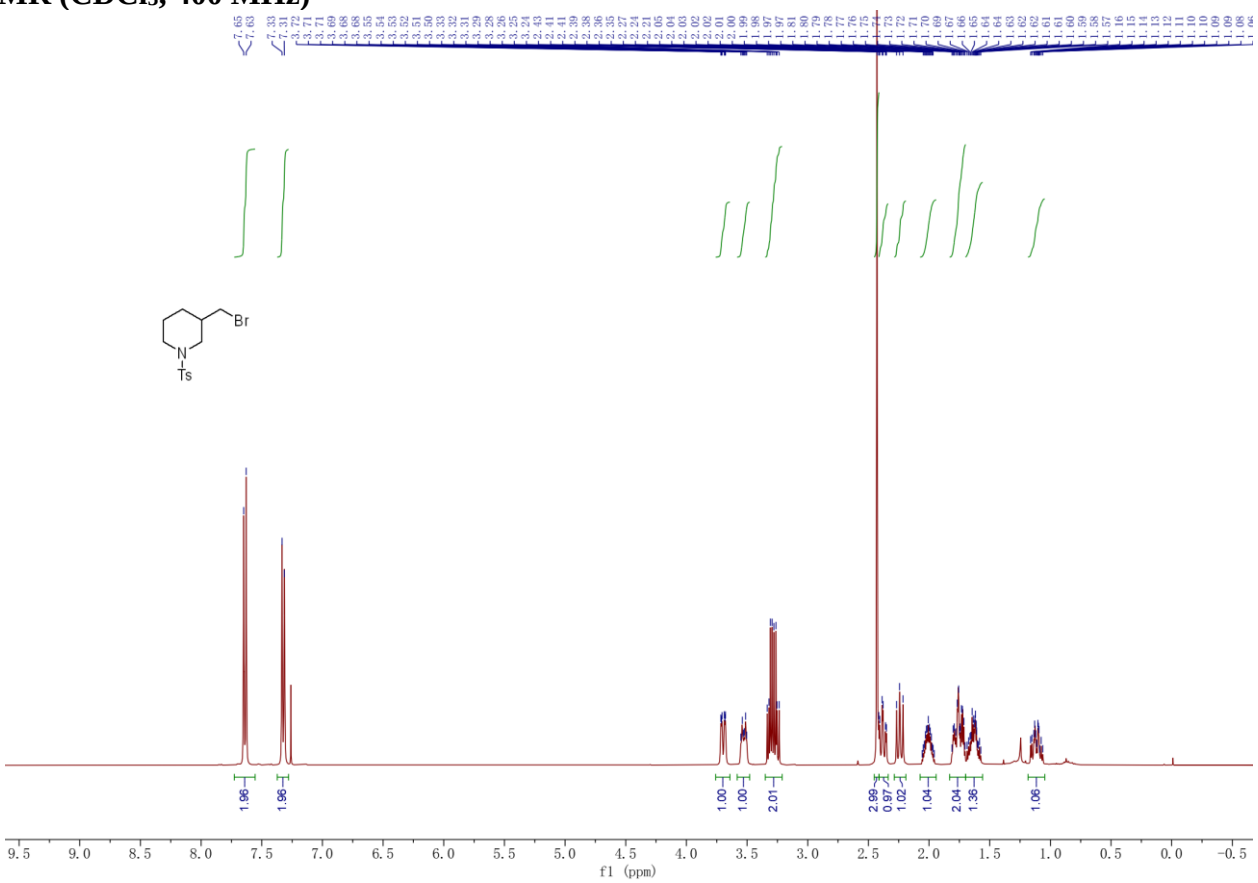


^{13}C NMR ($CDCl_3$, 101 MHz)

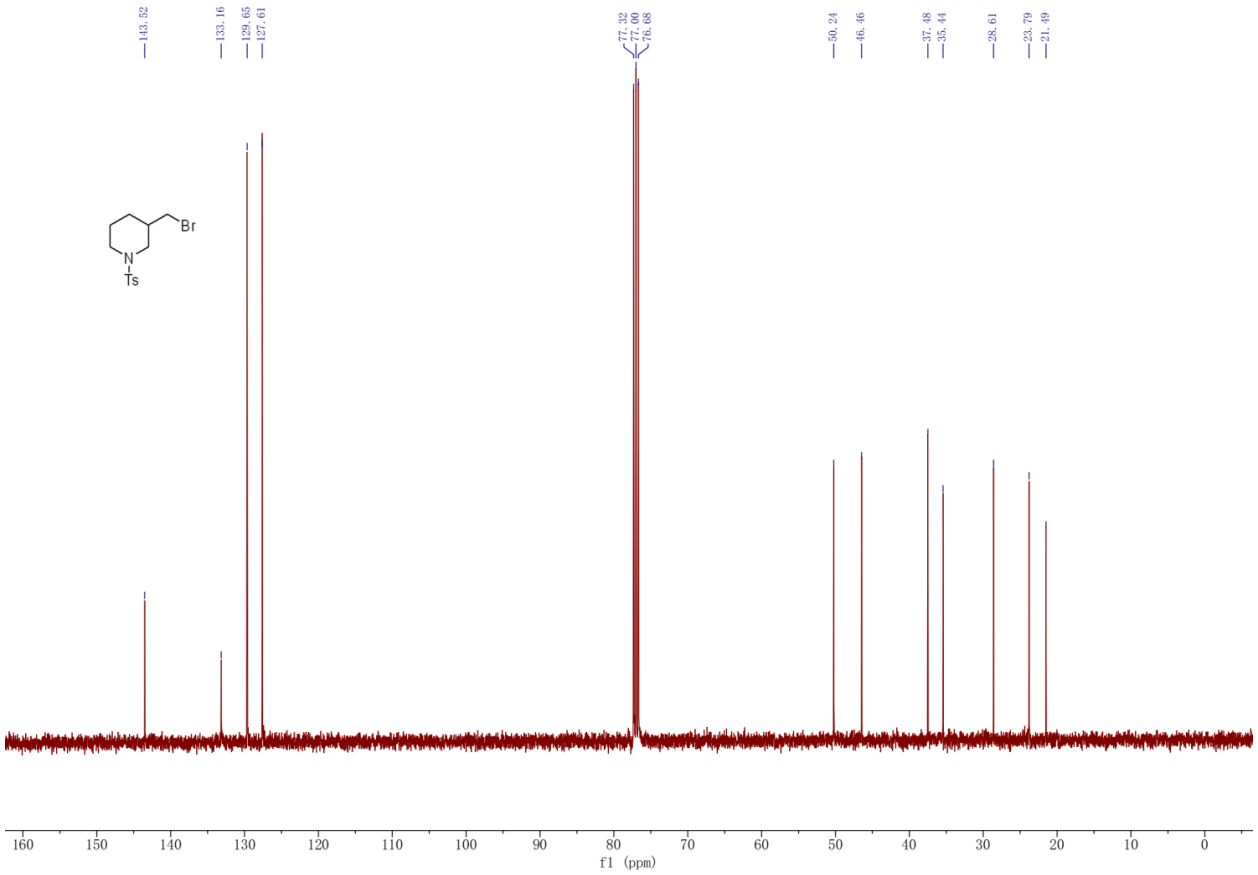


2i

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

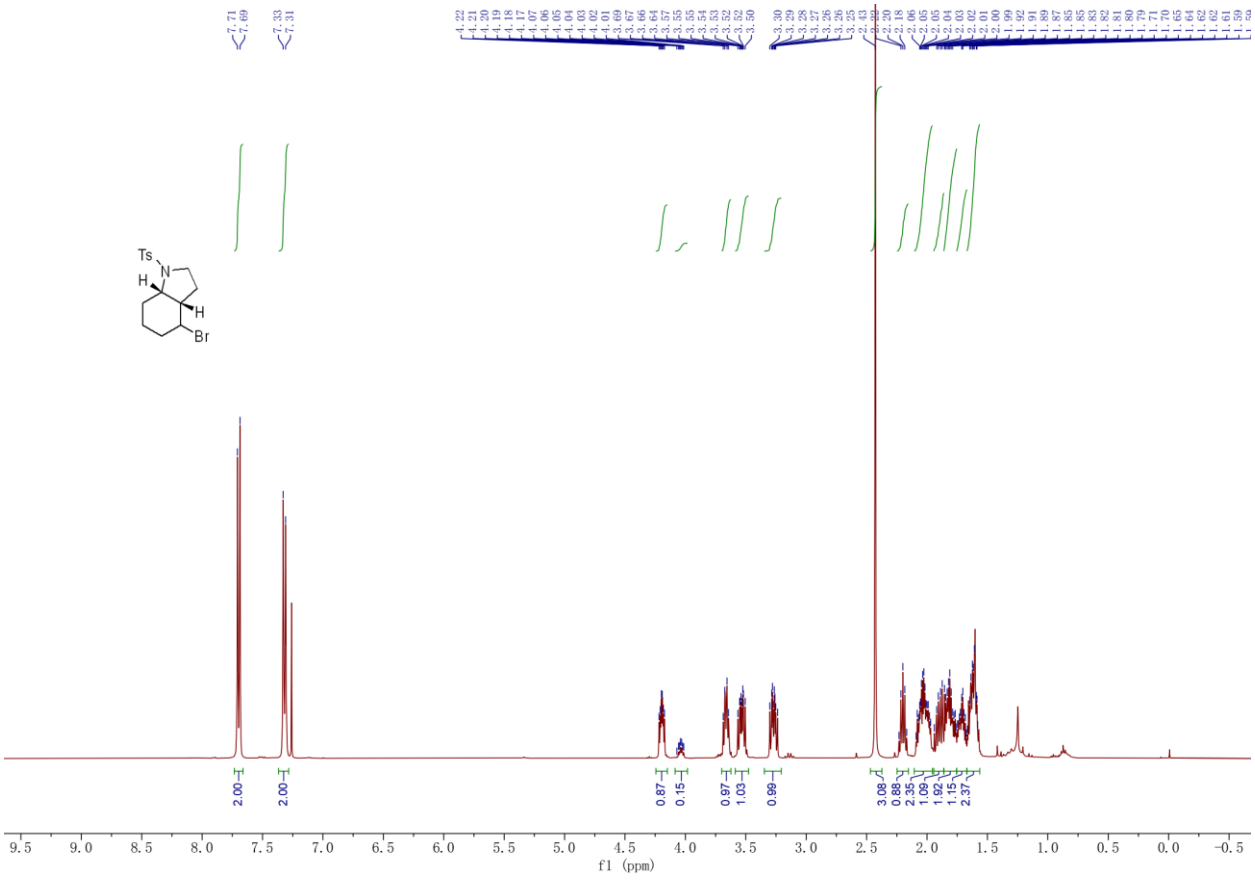


^{13}C NMR ($CDCl_3$, 101 MHz)

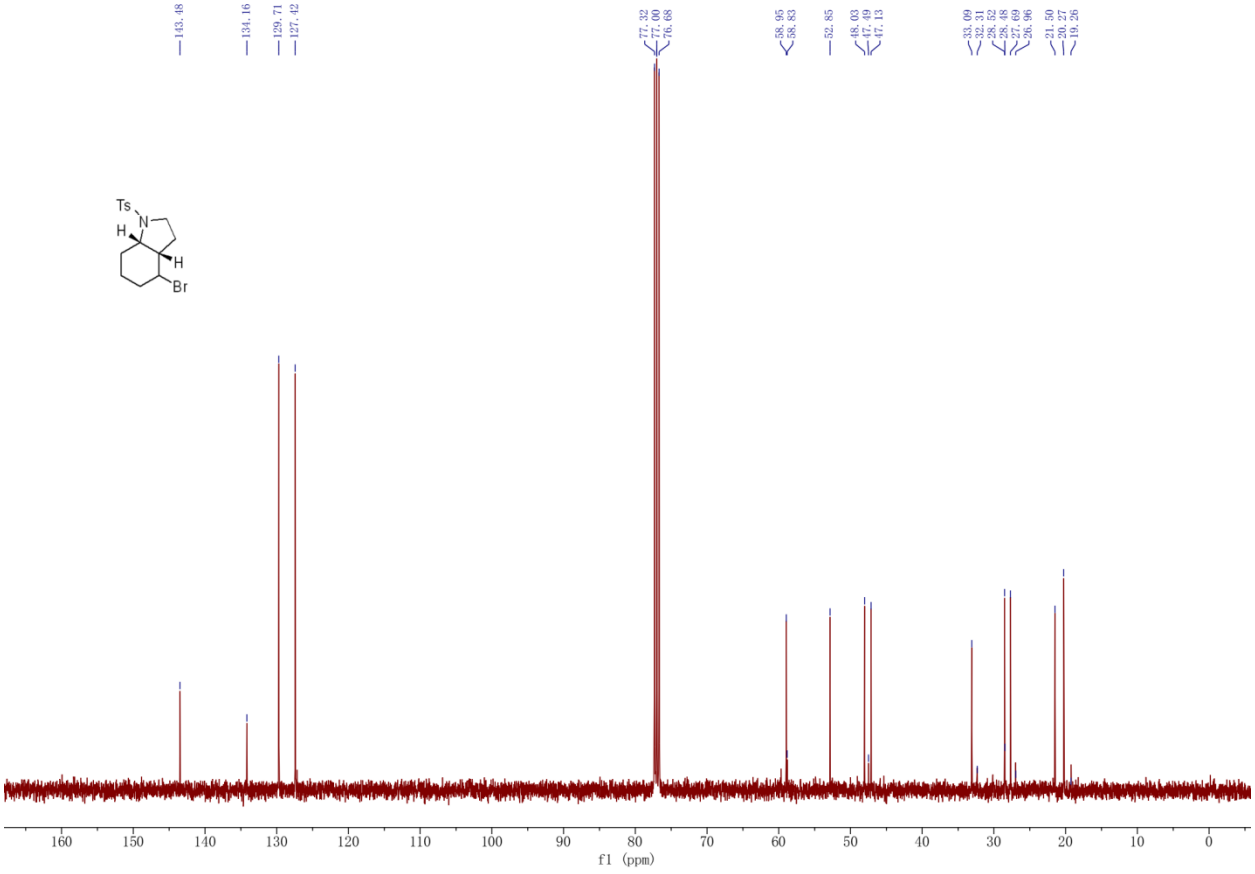


2m

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

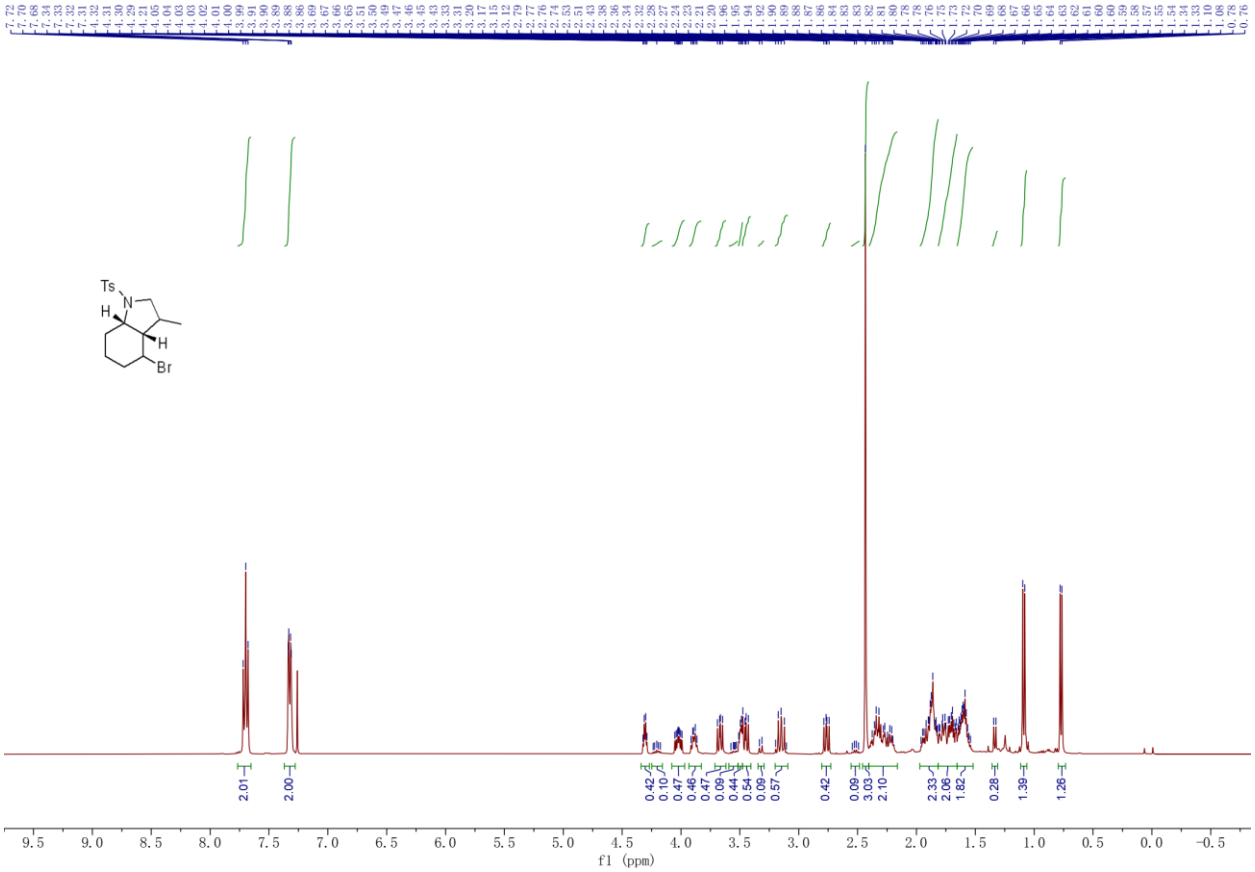


^{13}CNMR ($CDCl_3$, 101 MHz)

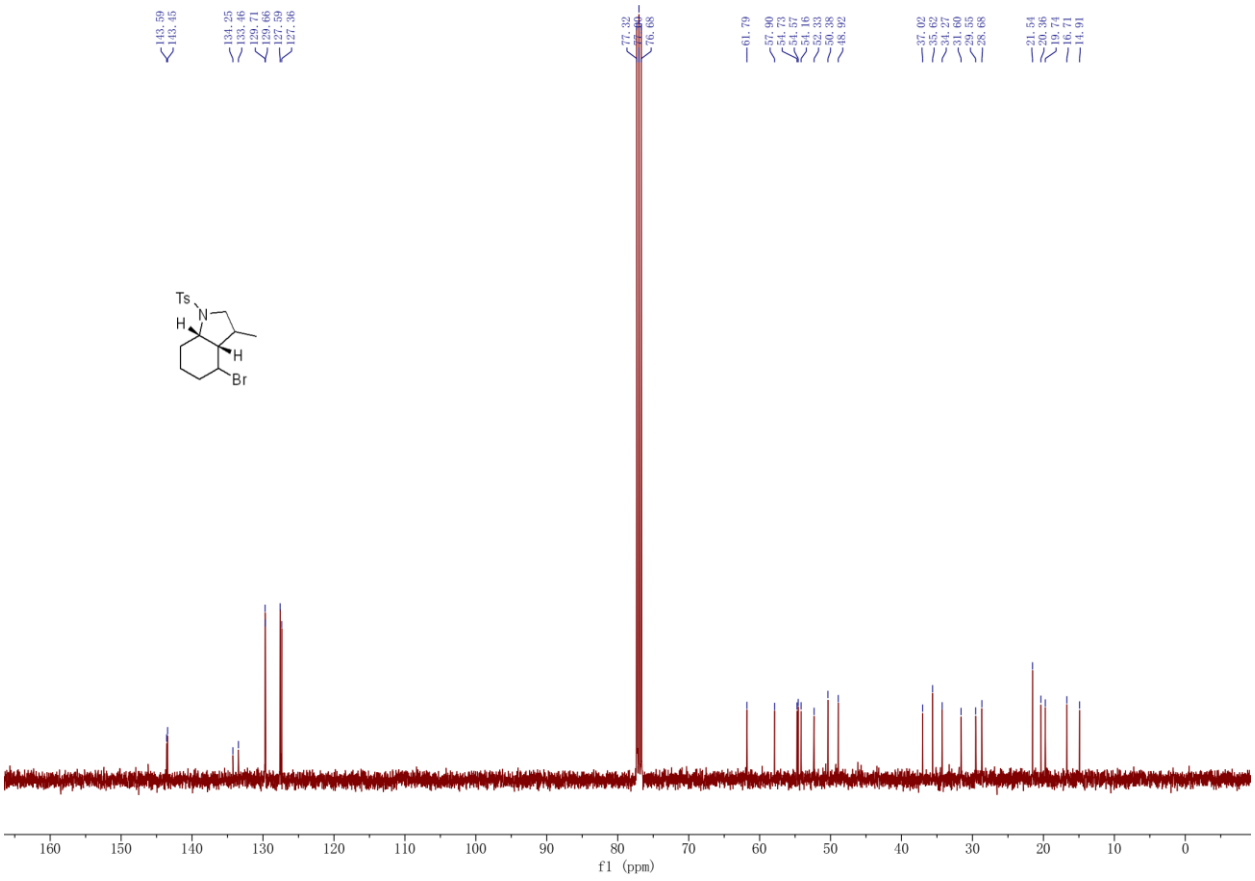


2n

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

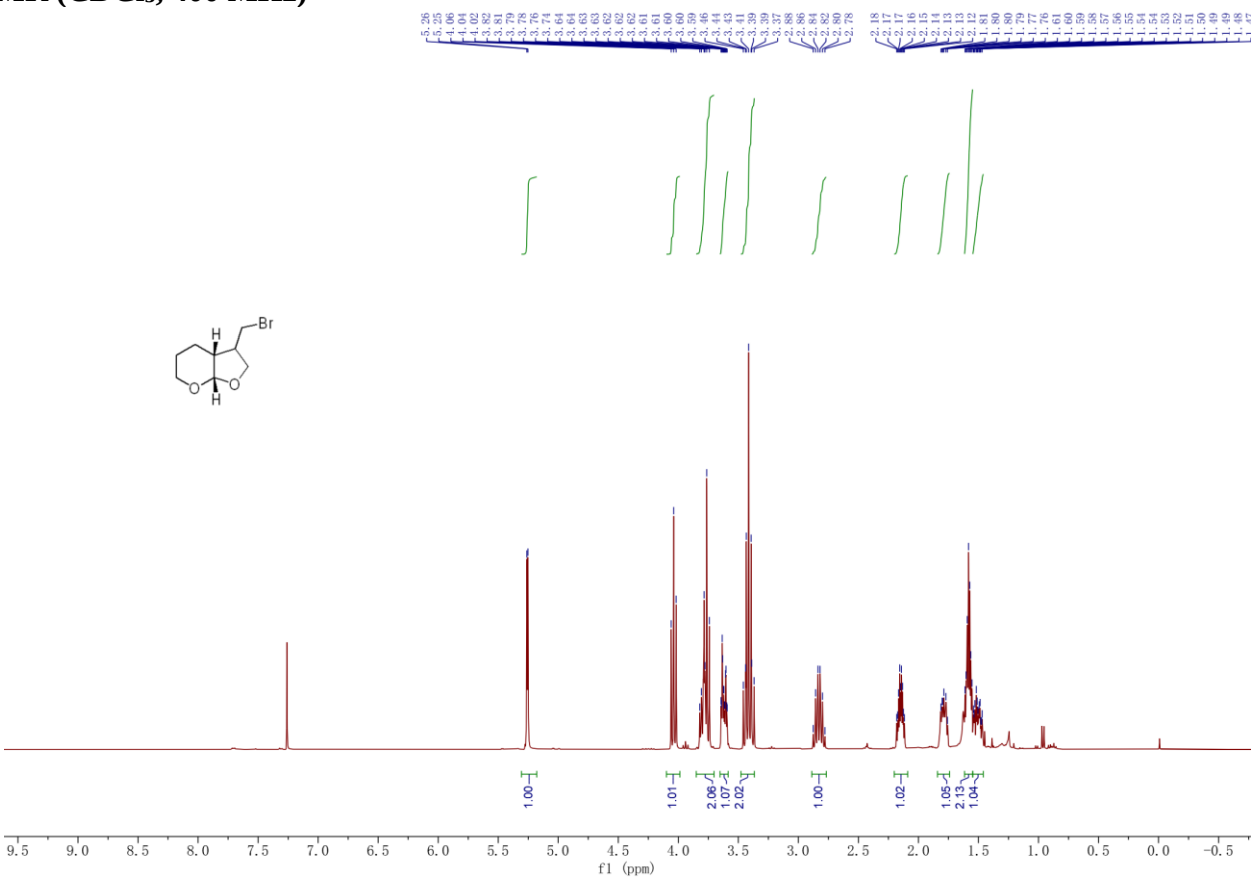


^{13}C NMR ($CDCl_3$, 101 MHz)

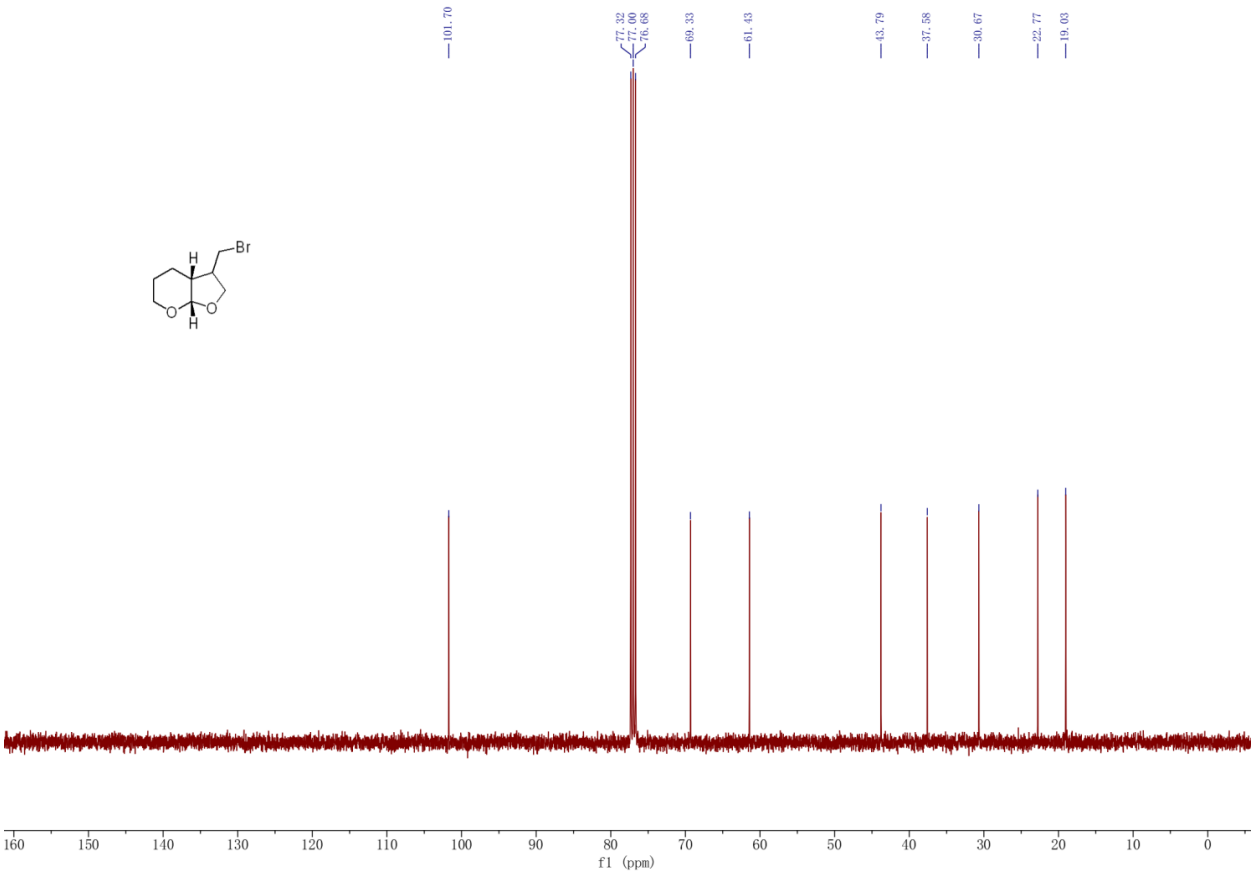


2o

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

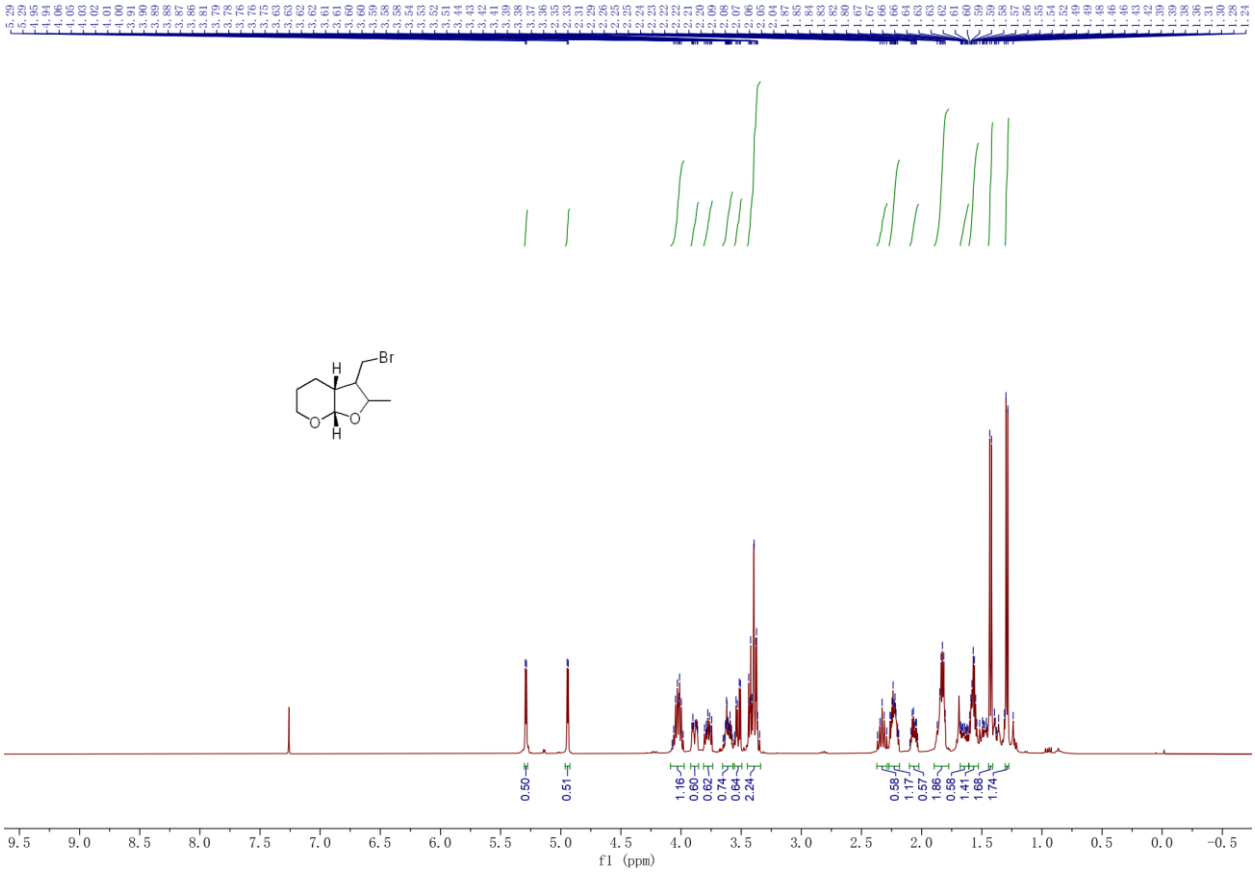


^{13}C NMR ($CDCl_3$, 101 MHz)

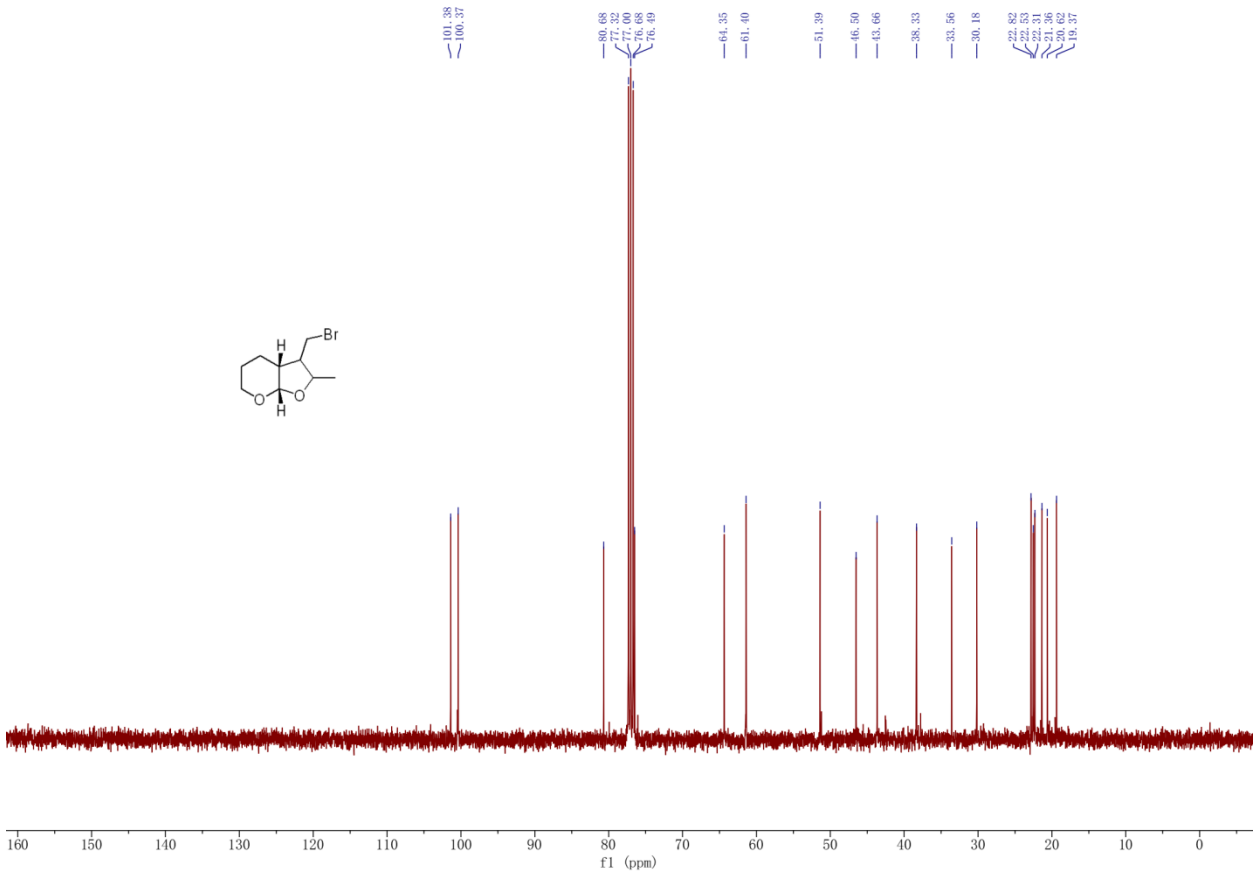


2p

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

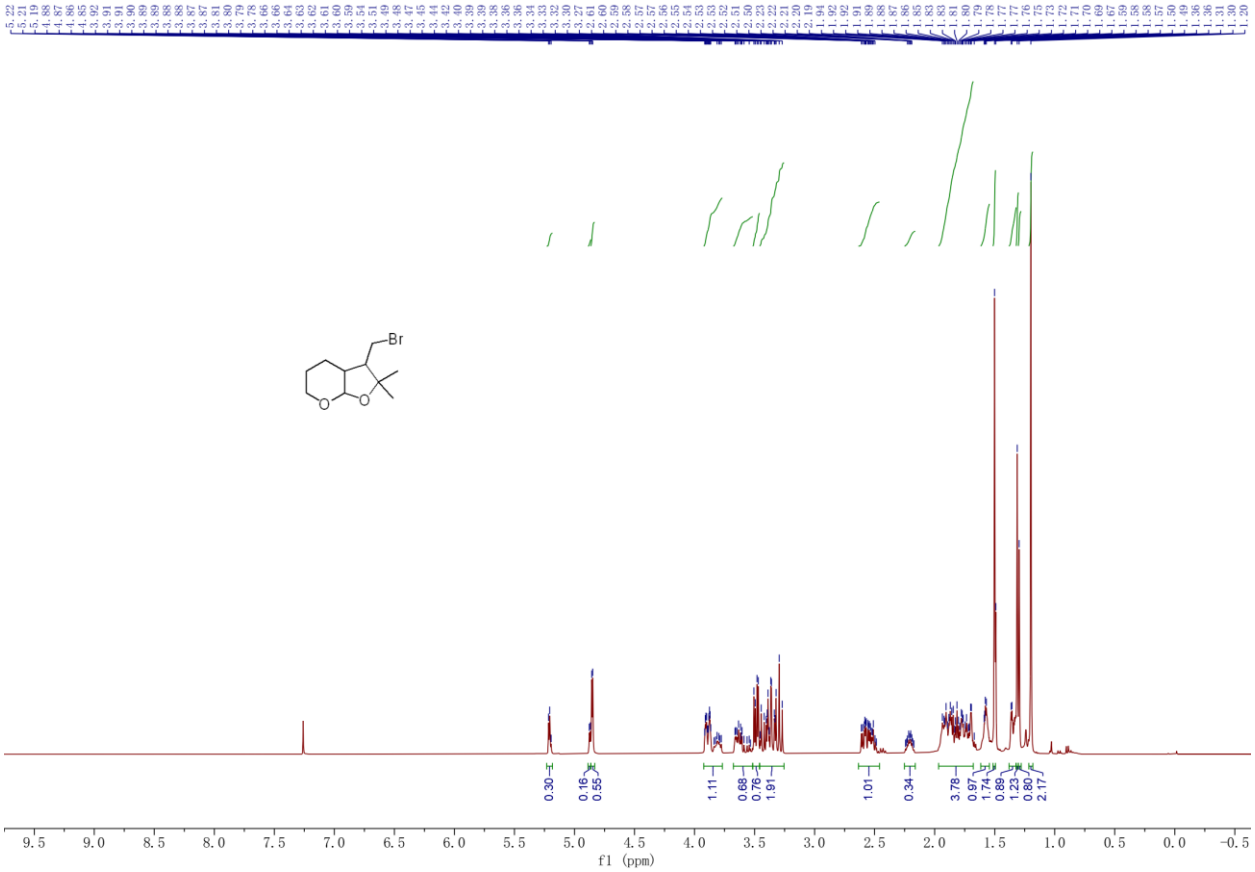


^{13}C NMR ($CDCl_3$, 101 MHz)

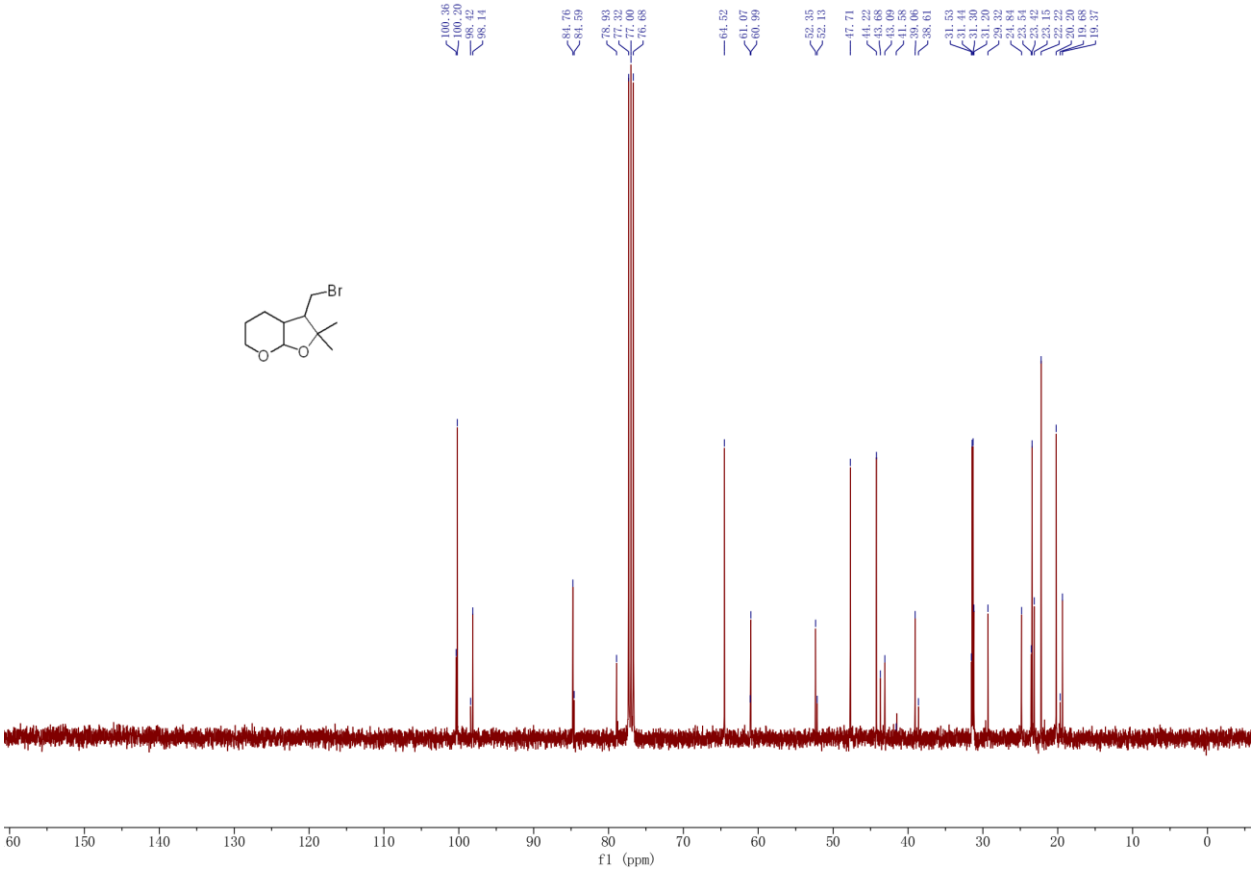


2q

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

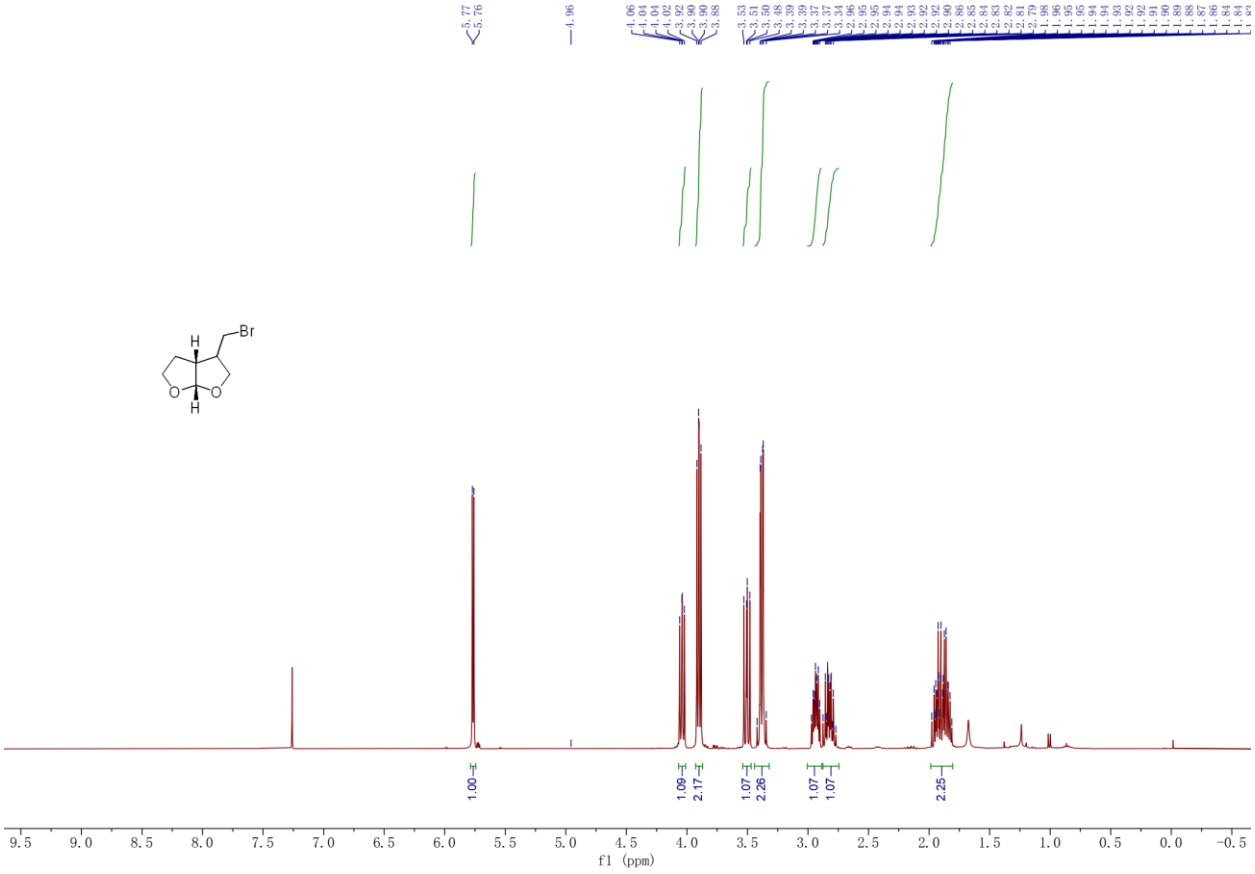


^{13}C NMR ($CDCl_3$, 101 MHz)

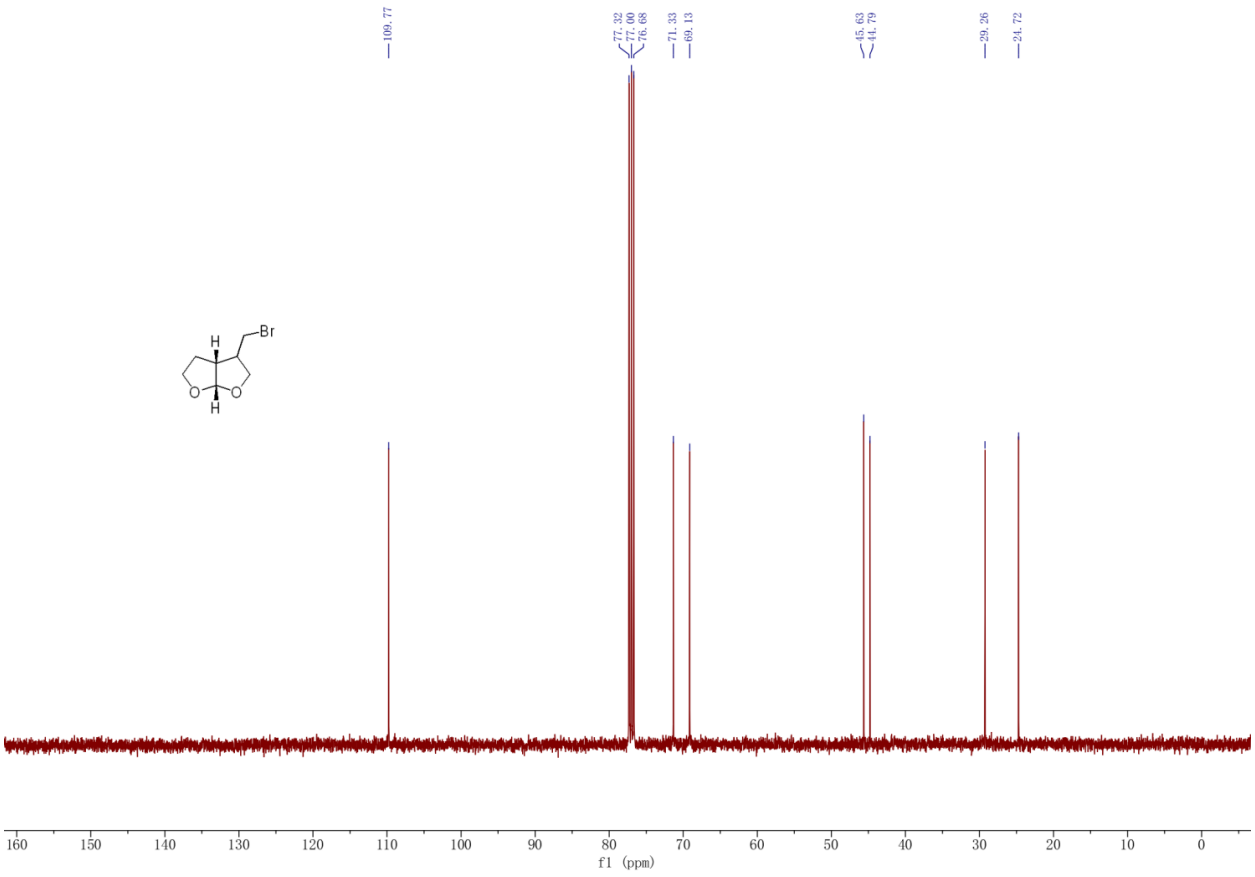


2r

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

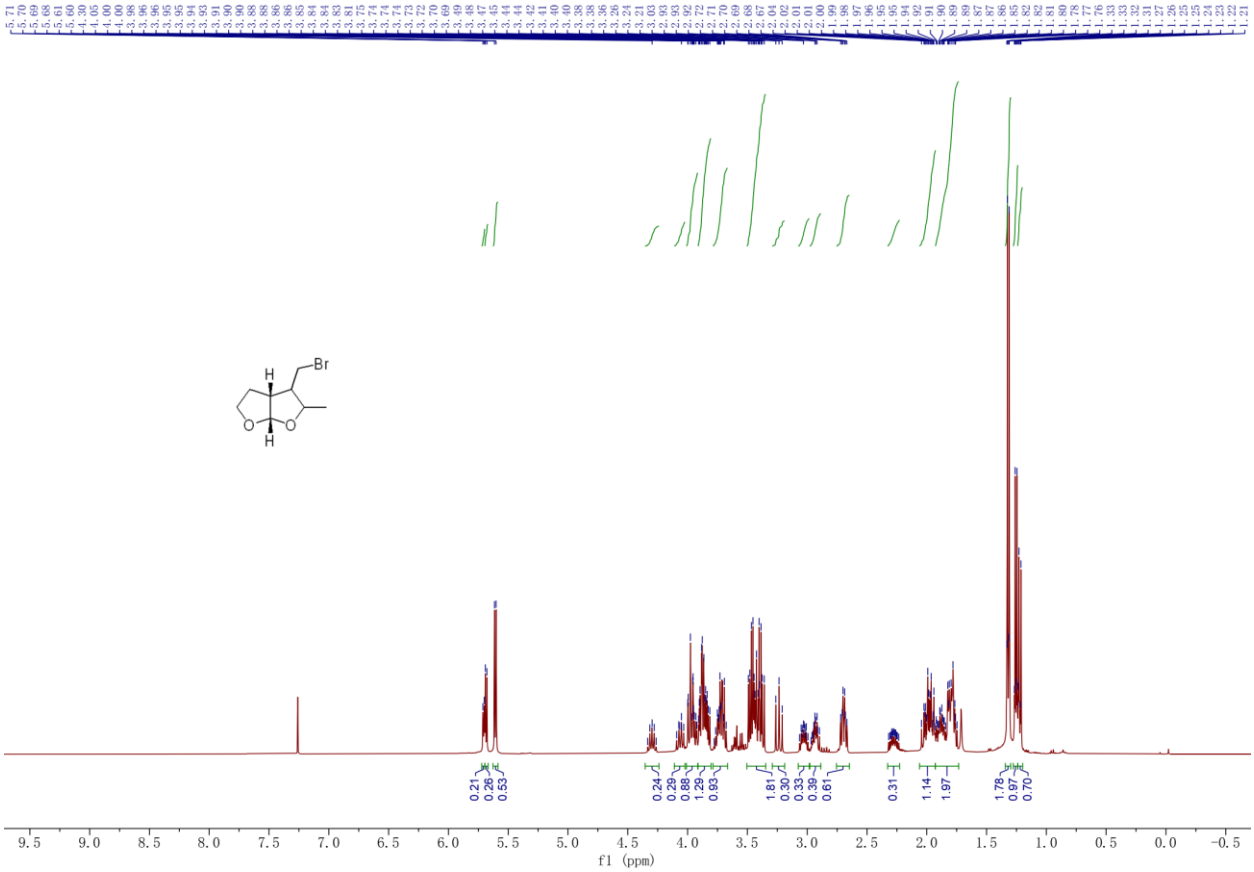


^{13}C NMR ($CDCl_3$, 101 MHz)

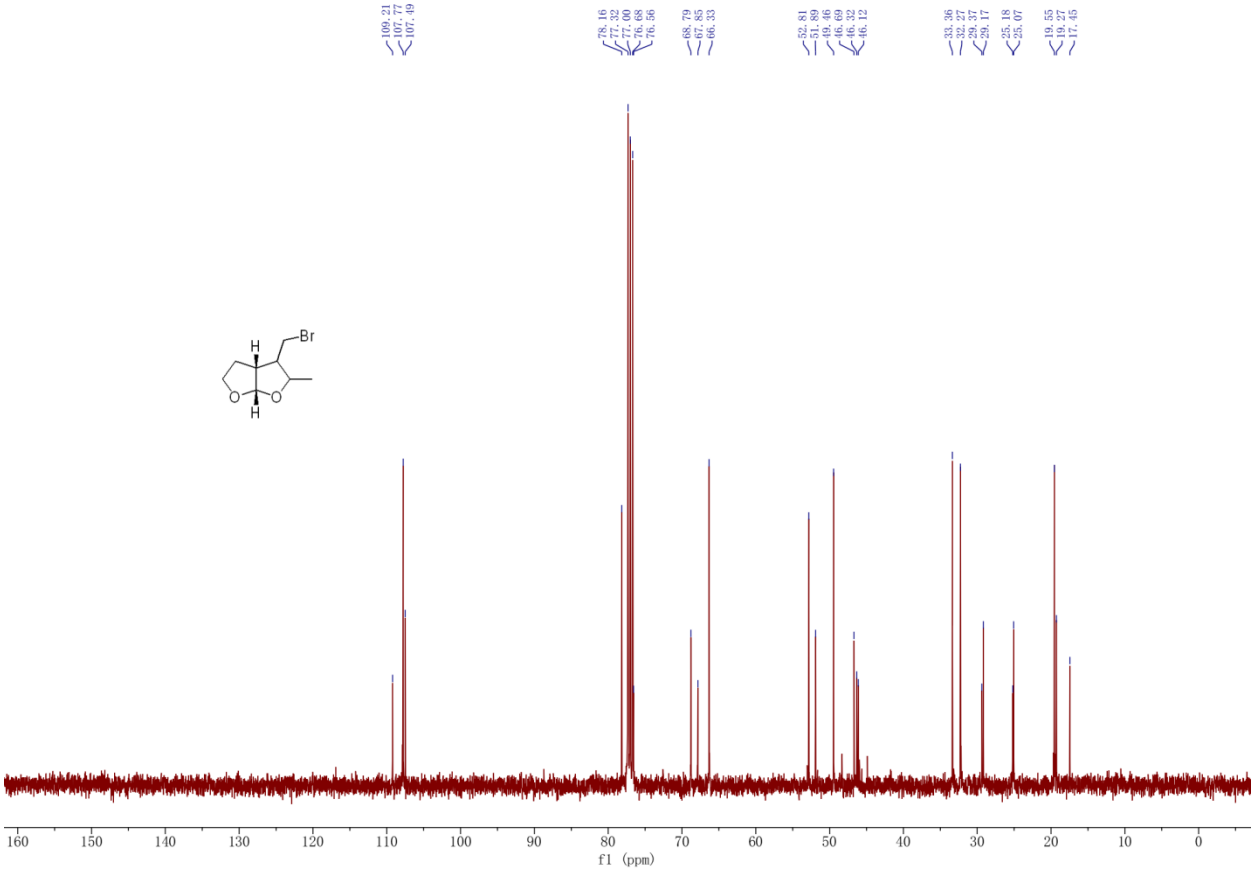


2s

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

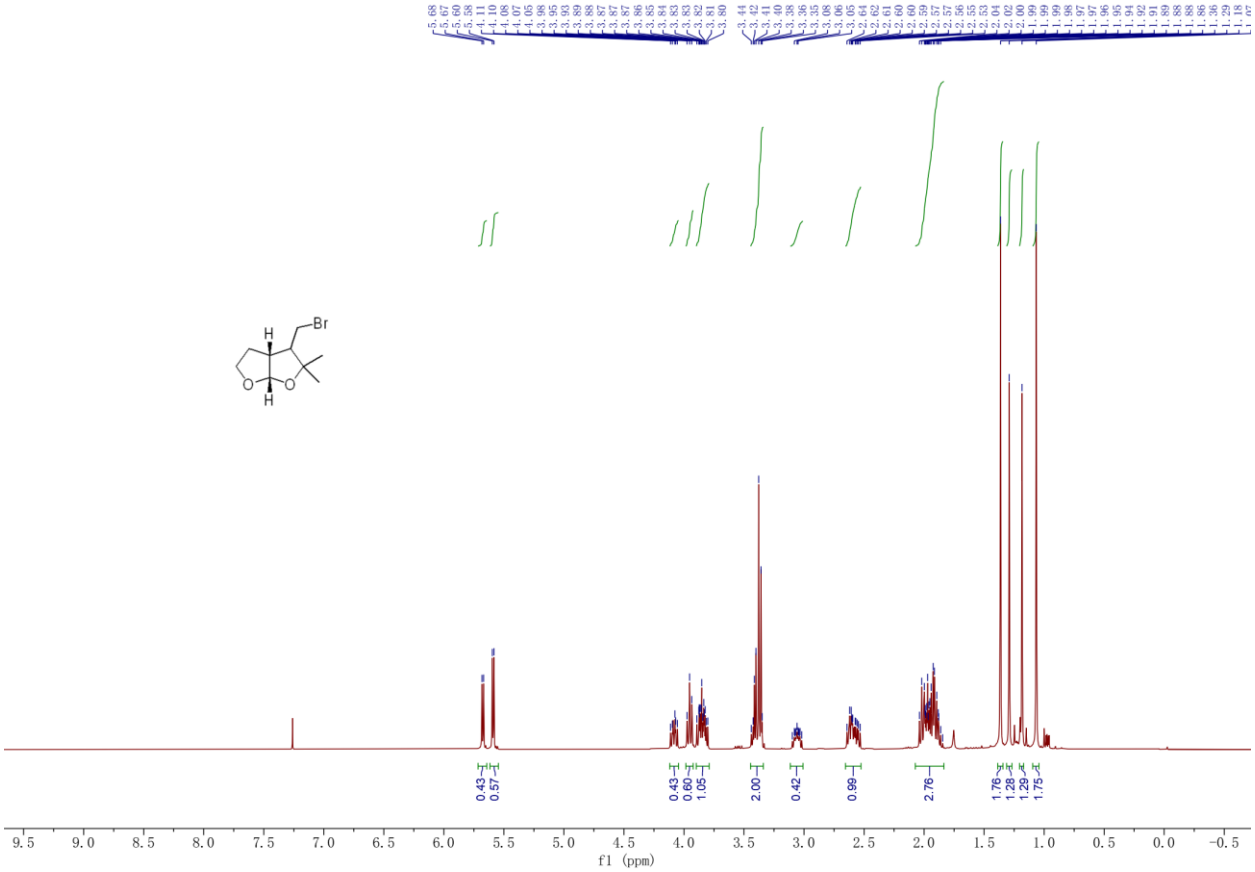


^{13}C NMR ($CDCl_3$, 101 MHz)

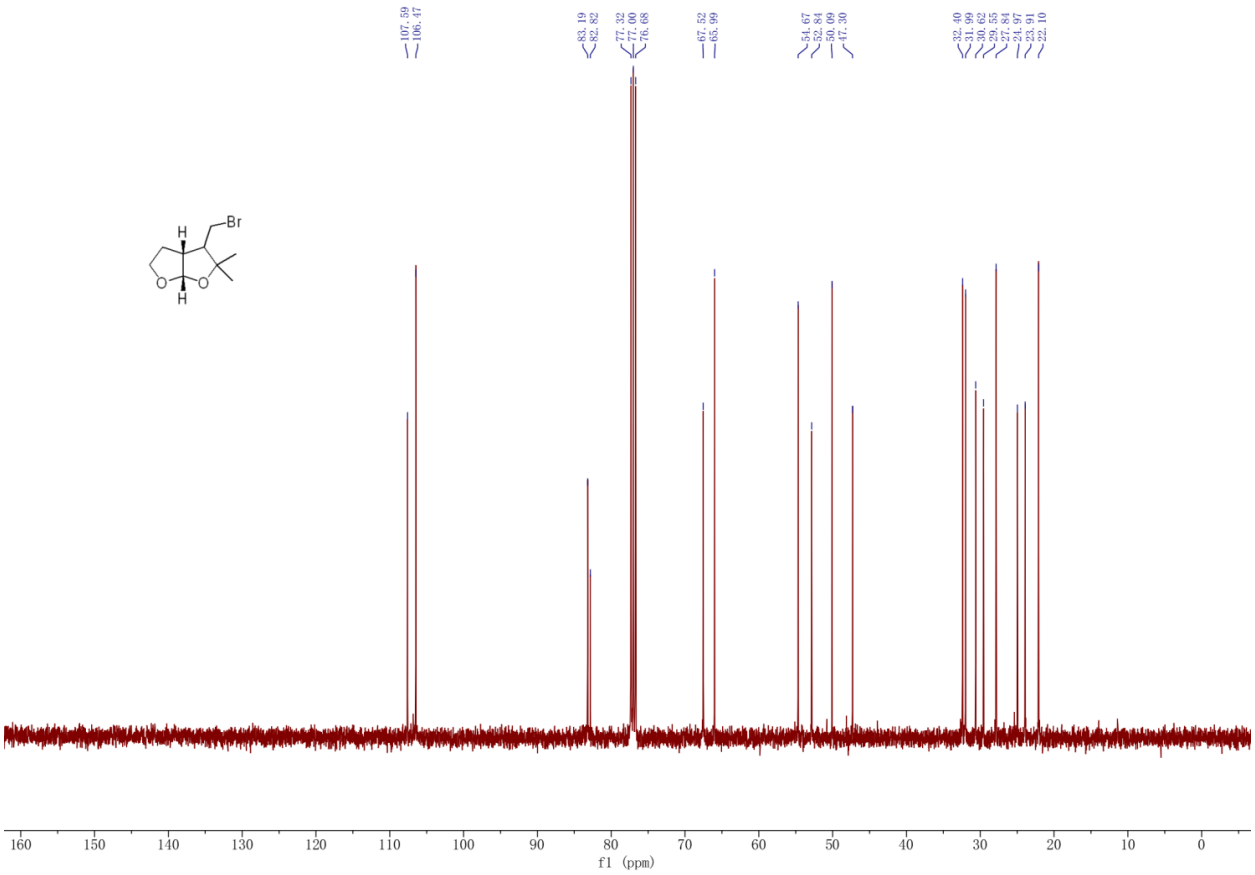


2t

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

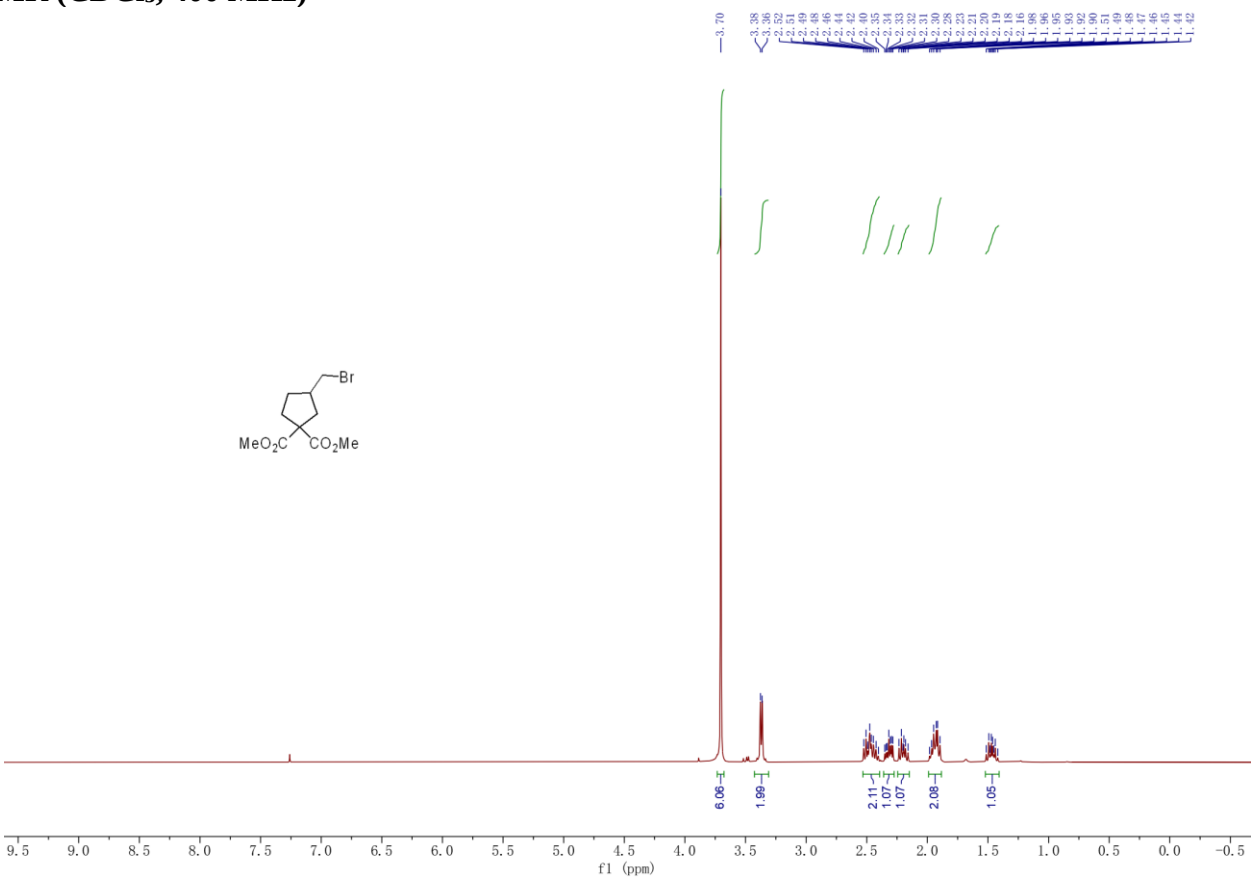


^{13}C NMR ($CDCl_3$, 101 MHz)



2u

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



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