Supporting Information

Electrochemical Allylation of Aldehydes and Ketones with Allylic Alcohols

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Content

1. Reagents

All commercial materials were used as received unless otherwise noted. Superdry solvents (EtOAc (99.5%), CH_3CN (99.0%), THF (99.5%), DCM, DMF, DMSO, acetone, EtOH) and deuterated solvents were purchased from Energy Chemical. Starting materials for this study were purchased from Energy Chemical, Adamas, Titan, TCI, Leyan.com or were synthesized according to reported procedures.

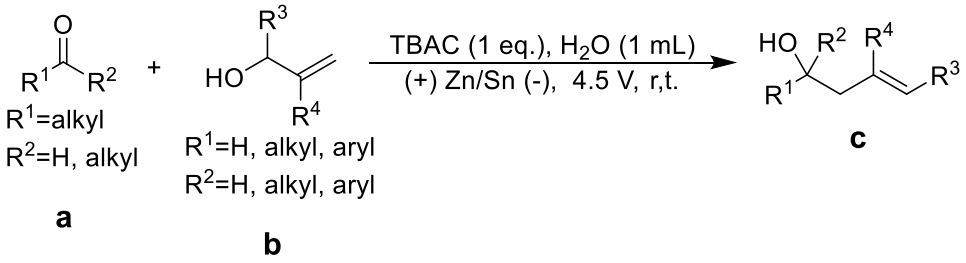
TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed on silica gel (300-400mm) purchased from Qingdao Haiyang Chemical Co. China with ethyl acetate (EtOAc) and Petroleum ether (PE) as eluents unless otherwise indicated.

2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. The manufacturer of the electrochemical workstation is MAISHENG. The model number of the electrochemical workstation is MS152D. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectrometry (HRMS) data were obtained on an LC-MS instrument (ESI-HRMS, Agilent 6520 Q-TOF LC/MS). All reactions were carried out in a 5 mL three-necked heart-shaped flask.

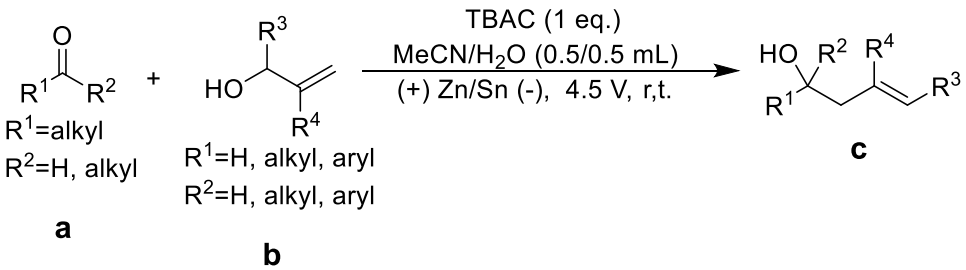
3. General procedure for electrochemical reduction of aldehydes and ketones.

General Procedure A:



A 5 mL three-necked heart-shaped flask was charged with the substrate **a** (1.0 mmol), substrate **b** (2.0 mmol), TBAC (1.0 mmol) and a magnetic stir bar (5 mm*10 mm). The flask was equipped with a rubber stopper, Zinc bar (R=0.8 cm, L=10.0 cm) as anode and Tin Foil (4.0 cm*0.8 cm*0.3 cm) as cathode. The distance between Zinc bar and Tin Foil is 1 cm. These two electrodes were connected to a DC regulated power supply. Then H_2O (1.0 mL) was added. The mixture was electrolyzed using constant voltage conditions at room temperature under magnetic stirring (400 rpm) for proper time in monitored by TLC (3 to 8 hours). The mixture was concentrated under reduced pressure, extracted with DCM for three times (3 × 10.0 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product.

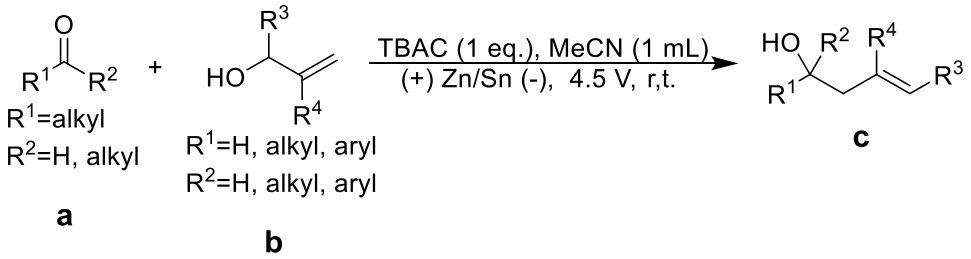
General Procedure B:



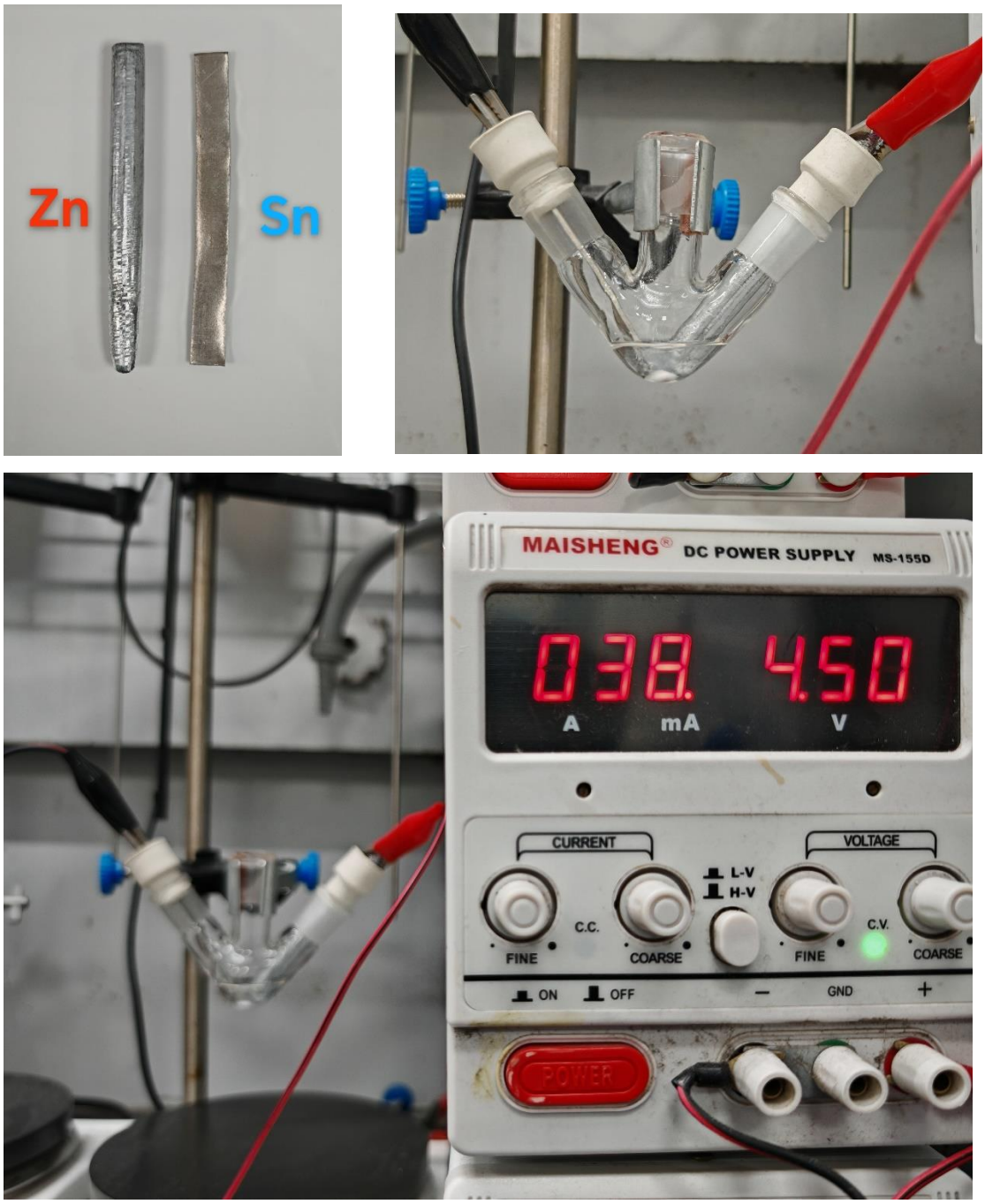
A 5 mL three-necked heart-shaped flask was charged with the substrate **a** (1.0 mmol), substrate **b** (2.0 mmol), TBAC (1.0 mmol) and a magnetic stir bar (5 mm*10

mm). The flask was equipped with a rubber stopper, Zinc bar (R=0.8 cm, L=10.0 cm) as anode and Tin Foil (4.0 cm*0.8 cm*0.3 cm) as cathode. The distance between Zinc bar and Tin Foil is 1 cm. These two electrodes were connected to a DC regulated power supply. Then add MeCN/H_2O (0.5/0.5 mL). The mixture was electrolyzed using constant voltage conditions at room temperature under magnetic stirring (400 rpm) for proper time in monitored by TLC (3 to 8 hours). The mixture was concentrated under reduced pressure, extracted with DCM for three times (3 × 10.0 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product.

General Procedure C:

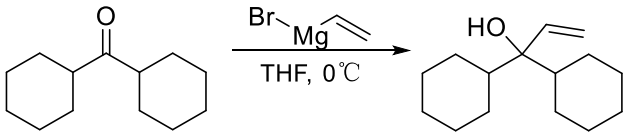


A 5 mL three-necked heart-shaped flask was charged with the substrate **a** (1.0 mmol), substrate **b** (2.0 mmol), TBAC (1.0 mmol) and a magnetic stir bar (5 mm*10 mm). The flask was equipped with a rubber stopper, Zinc bar (R=0.8 cm, L=10.0 cm) as anode and Tin Foil (4.0 cm*0.8 cm*0.3 cm) as cathode. The distance between Zinc bar and Tin Foil is 1 cm. These two electrodes were connected to a DC regulated power supply. Then MeCN (1.0 mL) was added. The mixture was electrolyzed using constant voltage conditions at room temperature under magnetic stirring (400 rpm) for proper time in monitored by TLC (3 to 8 hours). The mixture was concentrated under reduced pressure, extracted with DCM for three times (3 × 10.0 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product.



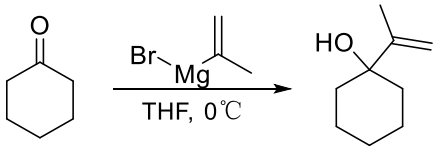
Experimental setup

4. Synthesis of substrates



5b

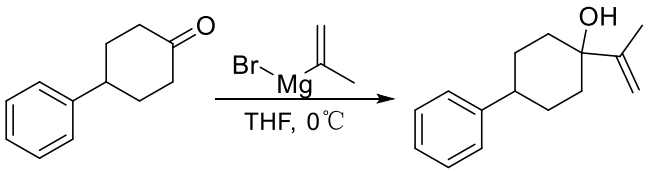
The starting ketone (1.9 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0℃. Add vinylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **5b** (Colorless oil, 1.7 g, 80%). [19]



7b

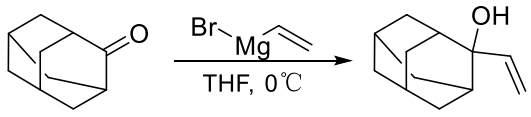
The starting ketone (1.0 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0℃. Add isopropenylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers, and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash

column chromatography (PE: EA 5:1) to afford the desired product **7b** (Colorless oil, 1.3 g, 93%). [20]



8b

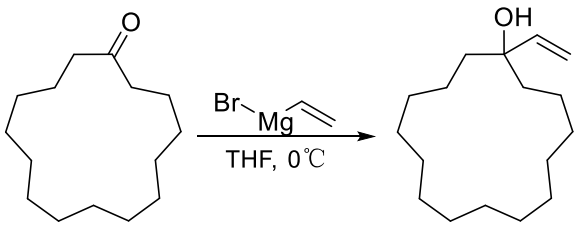
The starting ketone (1.7 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0℃. Add isopropenylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **8b** (White solids, 1.7 g, 84%). [21]



9b

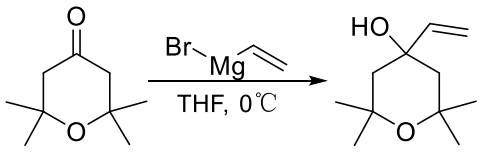
The starting ketone (1.5 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0℃. Add vinylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then

Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **9b** (White solid, 1.6 g, 90%). [22]



10b

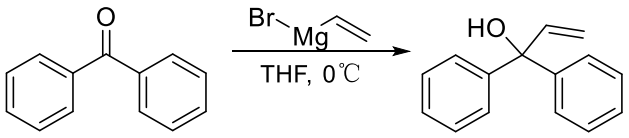
The starting ketone (2.4 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0°C. Add vinylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **10b** (White solid, 2.4 g, 95%).[23]



11b

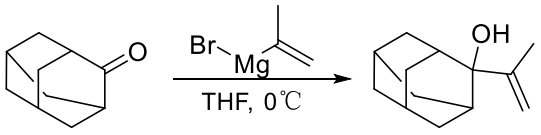
The starting ketone (1.5 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0°C. Add vinylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL)

and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **11b** (Colorless oil, 1.7 g, 96%). [24]



13b

The starting ketone (1.8 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0°C. Add vinylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl (25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **13b** (White solid, 2.1 g, 99%). [25]

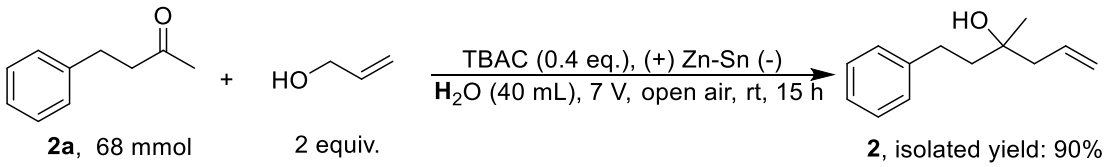


15b

The starting ketone (1.5 g, 10 mmol, 1.0 equiv.) and a magnetic stirrer were added to a 100 ml round-bottomed flask under nitrogen and dissolved in 20 mL of anhydrous THF. Then the flask was placed in an ice bath at 0°C. Add isopropenylmagnesium bromide (12 mL, 1.0 M in THF, 1.2 equiv.) slowly to a cooled (0 °C) solution. Warm the reaction mixture to room temperature. The mixtures react until the ketone was completely consumed by TLC under nitrogen conditions, add saturated aqueous NH_4Cl

(25 mL) and DCM (40 mL) to the reaction mixture. Separate the layers and extract the aqueous layer with DCM (40 mL) twice. Dry the organic layer over anhydrous $NaSO_4$, then Concentrate the organic layer in vacuo. Purify the resulting crude oil by flash column chromatography (PE: EA 10:1) to afford the desired product **15b** (White solid, 1.7 g, 92%). [26]

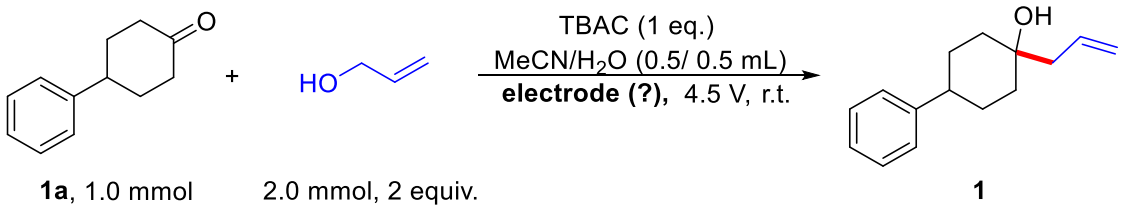
5. Large-Scale Reaction.



A 100 mL beaker was charged with the substrate **2a** (10.0 g, 68 mmol), allyl alcohol (7.9 g, 2 equiv.), TBAC (7.6 g, 0.4 equiv.) and a mechanical stir. The beaker was equipped with a Zinc plate (R=4.0 cm, H= 0.10 cm) as anode and Tin plate (R= 4.0 cm, H= 0.15 cm) as cathode. The Tin plate cathode attached to a copper wire. These two electrodes were connected to a DC regulated power supply. Then H_2O (40.0 mL) was added. The mixture was electrolyzed using constant voltage conditions at room temperature under mechanical stir for proper time in monitored by TLC (15 hours). The mixture was concentrated under reduced pressure, extracted with DCM for five times (5 × 50.0 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product (isolated yield: 90%).

6. Optimization Studies

Optimization of electrode:

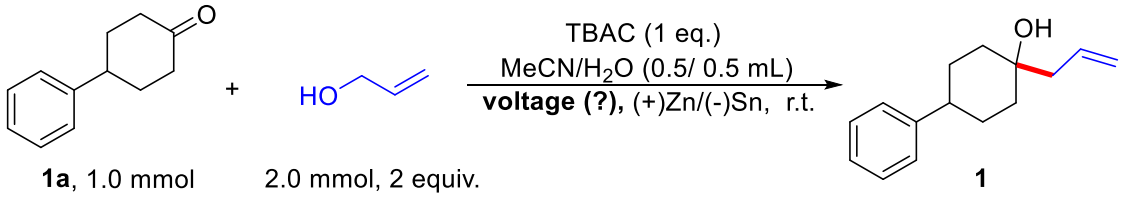


1a, 1.0 mmol 2.0 mmol, 2 equiv. **1**

Entry	Electrode	Voltage (V)	RSM (%)	Yield (%)	Time (h)
1	(+)Zn/(-)GF	4.5	76	16	5
2	**(+)Zn/(-)Sn**	**4.5**	**<5%**	**75**	**5**
3	(+)Zn/(-)Pt	4.5	53	21	5
4	(+)Ni/(-)Sn	4.5	<5%	63	5
5	(+)GF/(-)Sn	4.5	17	70	5

Table S1. Optimization of electrode

Optimization of voltage:

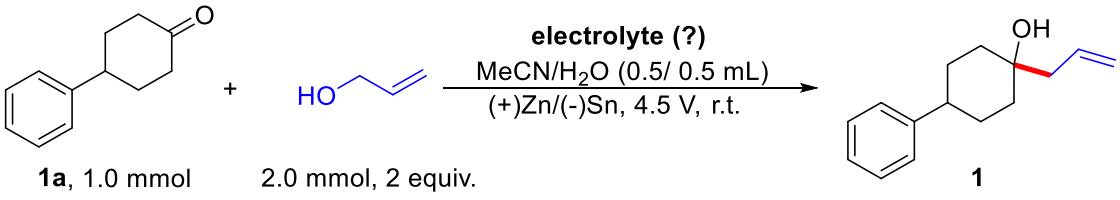


1a, 1.0 mmol 2.0 mmol, 2 equiv. **1**

Entry	Electrode	Voltage (V)	RSM (%)	Yield (%)	Time (h)
1	(+)Zn/(-)Sn	1	99	-	5
2	(+)Zn/(-)Sn	2	99	-	5
3	(+)Zn/(-)Sn	3	<5%	73	9
4	(+)Zn/(-)Sn	4	<5%	73	6
5	**(+)Zn/(-)Sn**	**4.5**	**<5%**	**75**	**5**
6	(+)Zn/(-)Sn	5	<5%	74	5

Table S2. Optimization of voltage

Optimization of electrolyte:

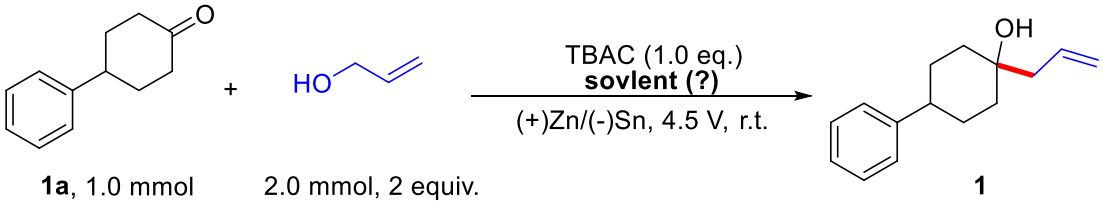


1a, 1.0 mmol 2.0 mmol, 2 equiv. **1**

Entry	Electrode	electrolyte	RSM (%)	Yield (%)	Time (h)
1	(+)Zn/(-)Sn	Et_4NBF_4 (1.0eq)	32	58	5
2	(+)Zn/(-)Sn	NH_4Cl (1.0 eq.)	98	-	5
3	(+)Zn/(-) Sn	CF_3SO_3Na (1.0 eq.)	50	38	5
4	(+)Zn/(-) Sn	Bu_4NBr (1.0 eq.)	<5%	74	5
5	**(+)Zn/(-) Sn**	**Bu_4NCl (1.0 eq.)**	**<5%**	**75**	**5**
6	(+)Zn/(-) Sn	NaCl (1.0 eq.)	98	-	5

Table S3. Optimization of electrolyte

Optimization of solvent:



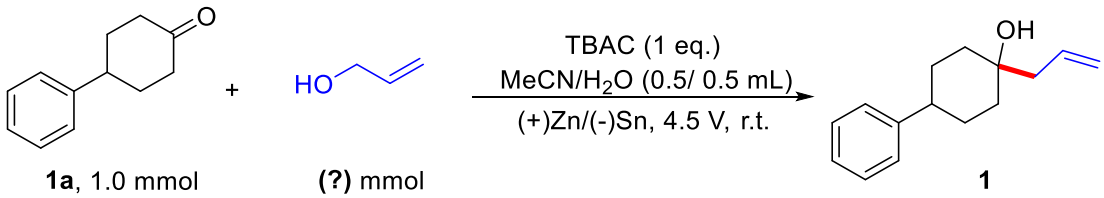
1a, 1.0 mmol 2.0 mmol, 2 equiv. **1**

Entry	Electrode	Solvent	RSM (%)	Yield (%)	Time(h)
1	(+)Zn/(-)Sn	HFIP (1 mL)	98	-	5
2	(+)Zn/(-)Sn	MeCN (1 mL)	<5%	74	5
3	(+)Zn/(-)Sn	DMF (1 mL)	<5%	72	5
4	(+)Zn/(-)Sn	DMSO (1mL)	<5%	74	5
5	(+)Zn/(-)Sn	H_2O (1 mL)	<5%	67	7
6	(+)Zn/(-)Sn	MeCN/H_2O (3/3 mL)	32	56	5
7	(+)Zn/(-)Sn	MeCN/H_2O (2/2 mL)	30	60	5
8	(+)Zn/(-)Sn	MeCN/H_2O (1/1 mL)	11	66	5
9	**(+)Zn/(-)Sn**	**MeCN/H_2O (0.5/0.5 mL)**	**<5%**	**75**	**5**

10	(+)Zn/(-)Sn	DMSO/H_2O (0.5/0.5 mL)	<5%	74	5

Table S4. Optimization of solvent

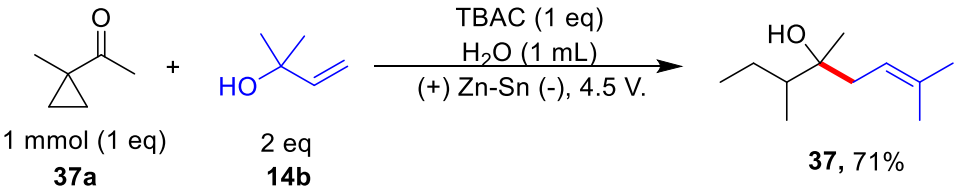
Optimization of allyl alcohol:



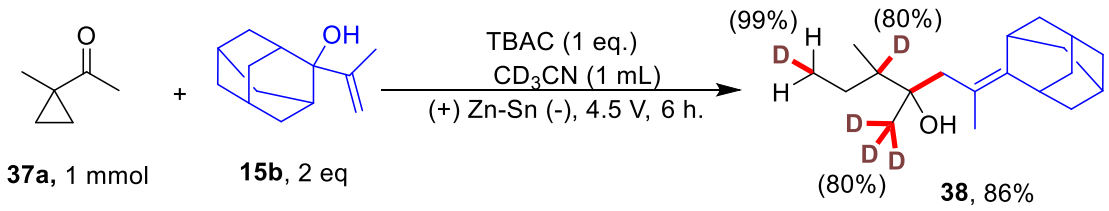
Entry	Electrode	allyl alcohol	RSM (%)	Yield (%)	Time (h)
1	(+)Zn/(-)Sn	1.0 eq.	<5%	68	5
2	(+)Zn/(-)Sn	1.2 eq.	<5%	70	5
3	**(+)Zn/(-) Sn**	**2.0 eq.**	**<5%**	**75**	**5**
4	(+)Zn/(-) Sn	4.0 eq.	<5%	74	5

Table S5. Optimization of allyl alcohol

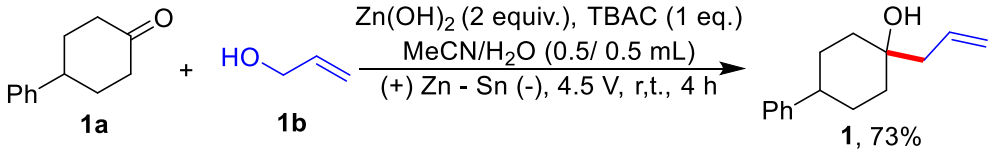
7. Mechanistic Investigations



The electrochemical allylation of **37a** and **14b** was carried out according to the general procedure A. The reaction mixture was tracked with TLC until full conversion. Then the reaction mixture was concentrated and the residue was purified on silica gel to give **37** (Colorless oil, 121 mg, 71%).



The electrochemical allylation of **37a** and **15b** was carried out according to the general procedure **C** while replacing MeCN with CD_3CN. The reaction mixture was tracked with TLC until full conversion. Then the reaction mixture was concentrated and the residue was purified on silica gel to give **38** (White solid, 228 mg, 86%).



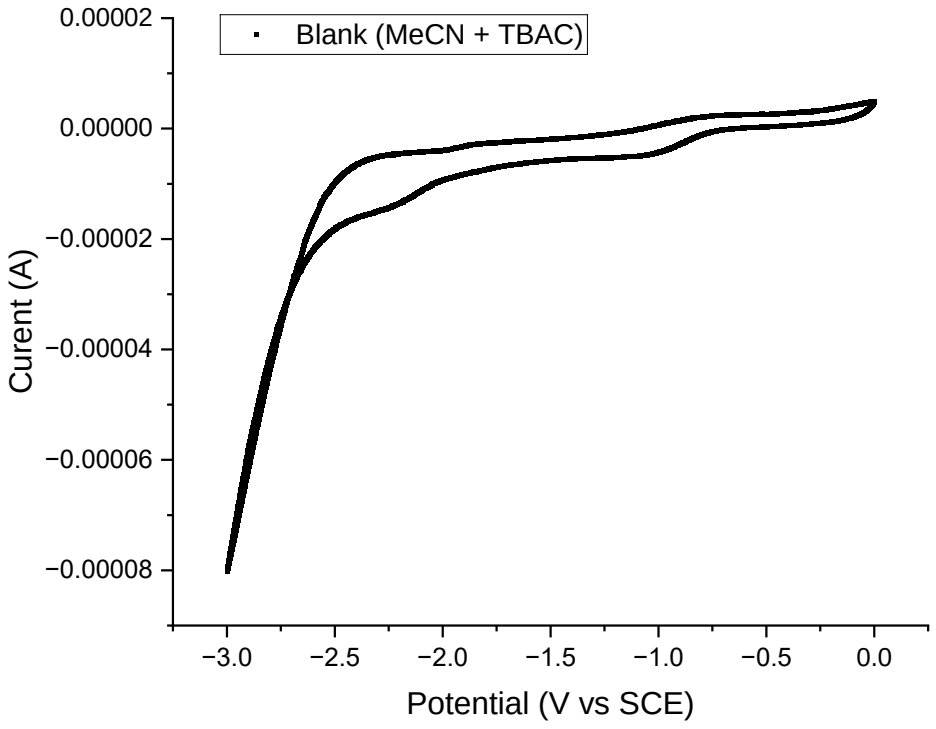
The electrochemical allylation of **1a** and **1b** was carried out according to the general procedure **A**. To verify whether $Zn(OH)_2$ could accelerate the reaction, we added 2 eq of $Zn(OH)_2$ to the reaction. The reaction mixture was tracked with TLC until full conversion (ca. 4.0 hours). Then the reaction mixture was concentrated and the residue was purified on silica gel to give **1** (White solid, 158 mg, 73%).

8. Cyclic voltammetry (CV) experiments

Cyclic voltammograms were measured using a CHI 730E bipotentiostat equipped with electrochemical analysis software. A reaction was set up using General Procedure with three electrodes: Sn as working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter as electrode, the electrodes were polished with 0.05 μm aluminum oxide, ultrasonically rinsed with ethanol and ultrapure water before measurements. The solvent deoxygenated by nitrogen bubbling for 0.5 h. The CV plotting convention was IUPAC. The starting point was 0.0 V, and the direction of the initial scan was oxidative. A saturated calomel electrode was used as a reference electrode with a salt bridge charged with a solution of TBAC (0.01 M) in MeCN (10.0

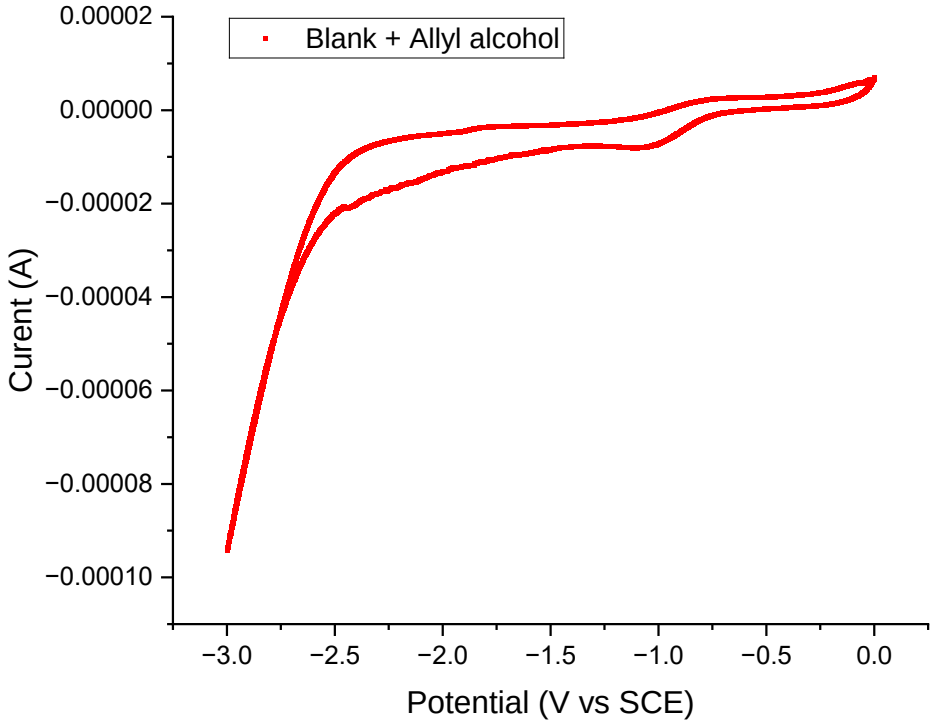
mL), acetophenone (0.01 mmol), and allyl alcohol (0.02 mmol). The scan rate was 0.1 V/s at the range of -3.0-0.0 V. Scan temperature: room temperature.

8.1. Cyclic voltammetry of Blank



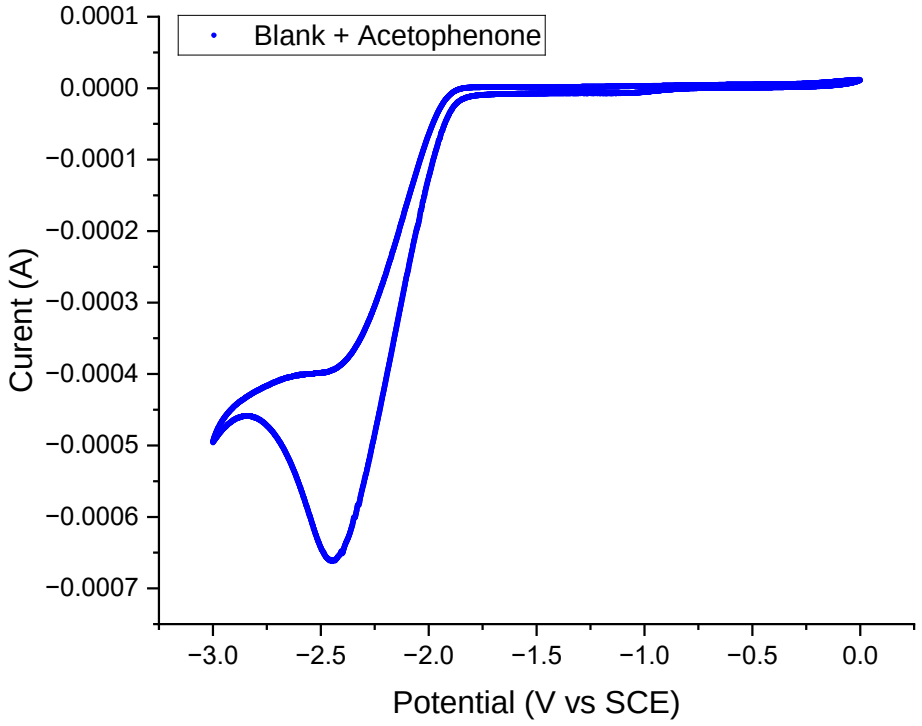
A solution of TBAC (0.01 M) in 10 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a Sn wire (1.0 mm diameter, 20.0 mm length) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of KCl (100g in 1000mL water). Potential sweep rate was 0.1 V/s.

8.2. Cyclic voltammetry of Blank + allyl alcohol



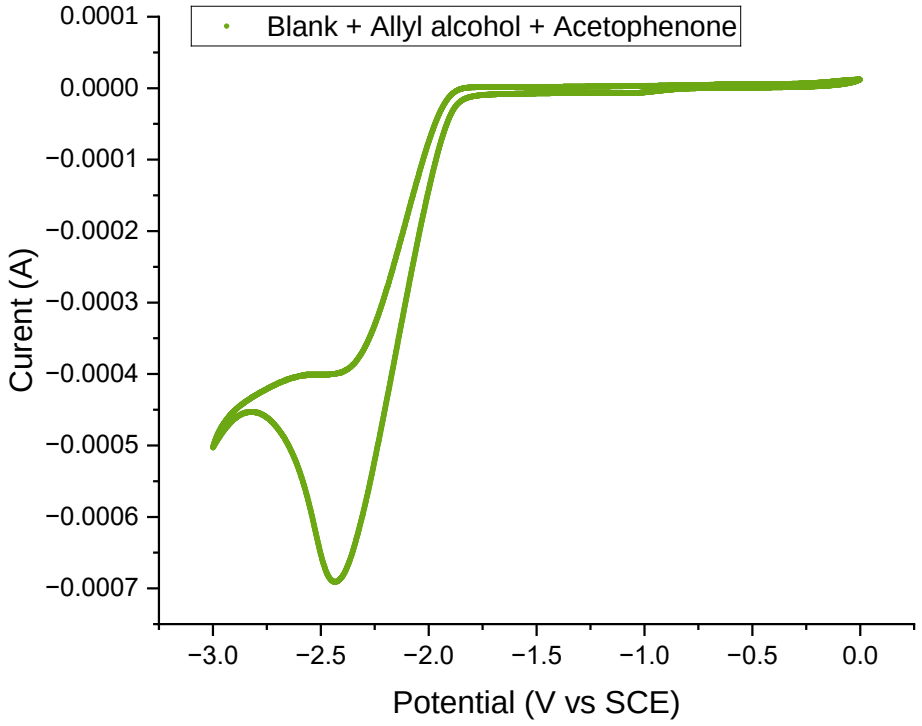
A solution of TBAC (0.01 M) and allyl alcohol (0.02 mmol) in 10 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a Sn wire (1.0 mm diameter, 20.0 mm length) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of KCl (100g in 1000mL water). Potential sweep rate was 0.1 V/s.

8.3. Cyclic voltammetry of Blank + acetophenone.



A solution of TBAC (0.01 M) and acetophenone (0.01 mmol) in 10 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a Sn wire (1.0 mm diameter, 20.0 mm length) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of KCl (100g in 1000mL water). Potential sweep rate was 0.1 V/s.

8.4. Cyclic voltammetry of Blank+ allyl alcohol+ acetophenone.



A solution of TBAC (0.01 M), allyl alcohol (0.02 mmol) and acetophenone (0.01 mmol) in 10 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a Sn wire (1.0 mm diameter, 20.0 mm length) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of KCl (100g in 1000mL water). Potential sweep rate was 0.1 V/s.

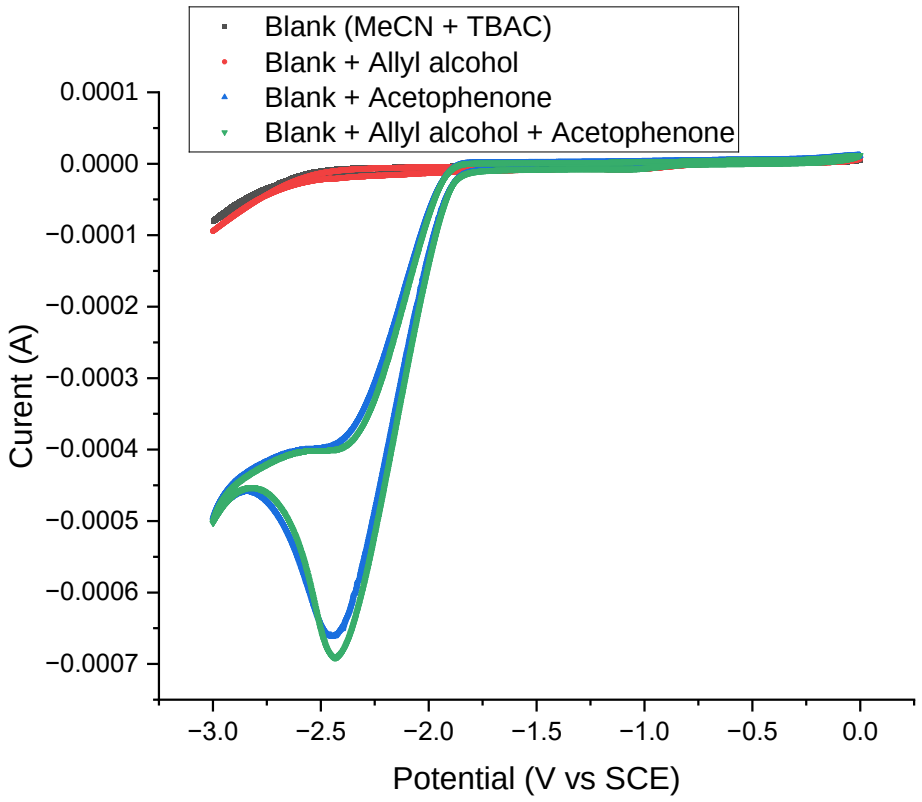
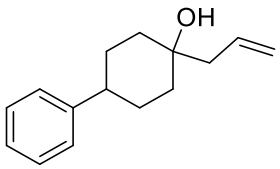


Figure S1. Cyclic voltammetry (CV) experiments

[a] Cyclic voltammograms. Conditions: A Sn wire (1.0 mm diameter, 20.0 mm length) working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE), the CV plotting convention was IUPAC. The starting point was 0.0 V, and the direction of the initial scan was oxidative. TBAC (0.01 M in 10.0 mL MeCN), 0.1 V/s scan rate with Blank (black line); Blank + allyl alcohol (0.02 mmol, red line); Blank + acetophenone (0.01 mmol, blue line); Blank + acetophenone (0.01 mmol) + allyl alcohol (0.02 mmol, green line).

9. Characterization Data of Products

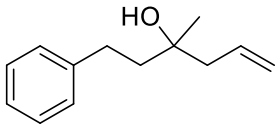


Compound 1

1-allyl-4-phenylcyclohexan-1-ol [1]

White solid, 162 mg, 75% yield, R_f=0.4 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.21 (m, 3H), 5.97 (td, *J* = 17.3, 7.4 Hz, 1H), 5.26 – 5.20 (m, 2H), 2.61 (s, 1H), 2.46 (d, *J* = 7.5 Hz, 2H), 1.90 (d, *J* = 8.9 Hz, 4H), 1.62 (d, *J* = 9.3 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.4, 133.6, 128.4, 126.8, 126.1, 119.1, 71.4, 43.4, 41.4, 38.2, 31.0.

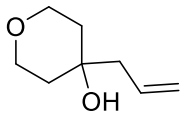


Compound 2

3-methyl-1-phenylhex-5-en-3-ol [2]

Colorless oil, 182 mg, 96% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.29 – 7.24 (m, 3H), 5.97 (ddt, *J* = 16.8, 10.4, 7.5 Hz, 1H), 5.24 (ddd, *J* = 7.0, 3.6, 1.8 Hz, 2H), 2.81 – 2.75 (m, 2H), 2.37 (d, *J* = 7.5 Hz, 2H), 1.99 – 1.88 (m, 1H), 1.87 – 1.83 (m, 2H), 1.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.6, 134.0, 128.5, 128.4, 125.8, 118.8, 72.1, 46.6, 43.8, 30.3, 26.8.

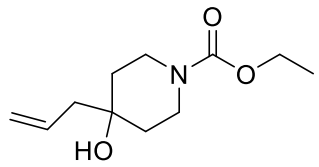


Compound 3

4-allyltetrahydro-2H-pyran-4-ol [3]

Colorless oil, 101 mg, 71% yield, R_f=0.6 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 – 5.82 (m, 1H), 5.20 – 5.11 (m, 2H), 3.79 – 3.71 (m, 4H), 2.23 (dt, *J* = 7.5, 1.2 Hz, 2H), 1.69 (ddd, *J* = 13.7, 10.8, 5.4 Hz, 2H), 1.47 (dd, *J* = 14.1, 2.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.6, 119.5, 68.2, 63.8, 47.5, 37.5.

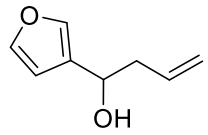


Compound 4

ethyl 4-allyl-4-hydroxypiperidine-1-carboxylate [4]

Colorless oil, 175 mg, 82% yield, R_f=0.3 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (tt, *J* = 17.0, 7.6 Hz, 1H), 5.20 (dd, *J* = 27.0, 13.6 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 3.30 – 3.17 (m, 2H), 2.25 (d, *J* = 7.5 Hz, 2H), 1.57 (d, *J* = 5.8 Hz, 2H), 1.55 (d, *J* = 4.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.6, 132.5, 119.9, 69.1, 61.2, 47.3, 39.8, 36.6, 14.7.

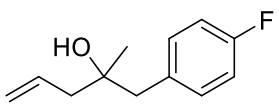


Compound 5

1-(furan-3-yl)but-3-en-1-ol [5]

Colorless oil, 63 mg, 46% yield, R_f=0.5 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 6.42 (s, 1H), 5.83 (ddt, *J* = 14.7, 10.6, 7.2 Hz, 1H), 5.17 (t, *J* = 12.4 Hz, 2H), 4.72 (dq, *J* = 11.2, 4.2 Hz, 1H), 2.51 (p, *J* = 6.9, 6.3 Hz, 2H), 2.27 – 2.09 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.3, 139.1, 134.1, 128.5, 118.5, 108.6, 66.1, 42.4.

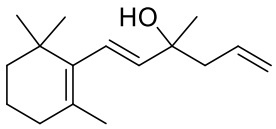


Compound 6

1-(4-fluorophenyl)-2-methylpent-4-en-2-ol [6]

Colorless oil, 153 mg, 79% yield, R_f=0.6 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.04 – 6.99 (m, 2H), 5.94 (ddt, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.24 – 5.11 (m, 2H), 2.81 – 2.71 (m, 2H), 2.28 – 2.23 (m, 2H), 1.52 (s, 1H), 1.16 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8, 160.8, 133.8, 133.2(d), 132.0(d), 119.0, 115.0(d), 72.0, 47.0, 46.3, 26.5.

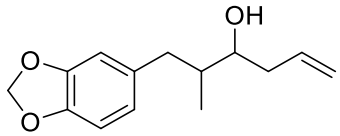


Compound 7

(E)-3-methyl-1-(2,6,6-trimethylcyclohex-1-en-1-yl)hexa-1,5-dien-3-ol [7]

Colorless oil, 140 mg, 60% yield, R_f=0.6 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (d, *J* = 16.1 Hz, 1H), 5.84 (tdd, *J* = 16.8, 8.1, 1.8 Hz, 1H), 5.49 (dd, *J* = 16.1, 1.8 Hz, 1H), 5.18 – 5.10 (m, 2H), 2.39 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.31 (dd, *J* = 13.3, 7.8 Hz, 1H), 1.97 (t, *J* = 6.6 Hz, 2H), 1.84 (s, 1H), 1.66 (s, 3H), 1.63 – 1.58 (m, 2H), 1.45 (dt, *J* = 8.0, 2.2 Hz, 2H), 1.33 (d, *J* = 2.0 Hz, 3H), 0.99 (s, 3H), 0.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.1, 137.0, 134.0, 128.0, 125.2, 118.9, 72.5, 47.4, 39.4, 34.0, 32.6, 28.7, 28.7, 28.1, 21.4, 19.3.



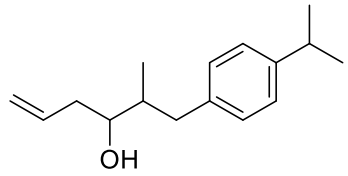
Compound 8

1-(benzo[d][1,3]dioxol-5-yl)-2-methylhex-5-en-3-ol [8]

Colorless oil, 164 mg, 70% yield, R_f=0.6 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 7.7, 4.5 Hz, 1H), 5.92 (s, 2H), 5.90 – 5.75 (m, 1H), 5.21 – 5.12 (m, 2H), 3.61 – 3.48 (m, 1H), 2.82 (ddd, *J* = 61.9, 13.6, 5.4 Hz, 1H), 2.39 (dd, *J* = 13.4, 8.4 Hz, 1H), 2.34 – 2.15 (m, 2H), 1.89 (d, *J* = 18.4 Hz, 1H), 1.85 – 1.78 (m, 1H), 0.88 (dd, *J* = 17.4, 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.5 (d), 145.6 (d), 135.4 (d), 134.9

(d), 121.9 (d), 117.8 (d), 109.5 (d), 108.0 (d), 100.7, 73.9, 72.5, 40.5, 40.0, 39.5, 38.5, 38.3,15.1, 13.2.

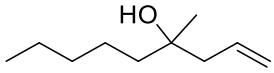


Compound 9

1-(4-isopropylphenyl)-2-methylhex-5-en-3-ol

Colorless oil, 179 mg, 77% yield, R_f=0.7 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dt, *J* = 8.2, 1.9 Hz, 2H), 7.17 (dt, *J* = 8.1, 2.0 Hz, 2H), 5.97 – 5.82 (m, 1H), 5.28 – 5.16 (m, 2H), 3.61 (ddt, *J* = 37.2, 9.4, 4.2 Hz, 1H), 3.00 – 2.84 (m, 2H), 2.53 – 2.44 (m, 1H), 2.43 – 2.22 (m, 2H), 1.97 – 1.68 (m, 2H), 1.32 (d, *J* = 1.8 Hz, 3H), 1.30 (d, *J* = 1.8 Hz, 3H), 0.94 (ddd, *J* = 15.8, 6.8, 1.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.3 (d), 138.3 (d), 135.5 (d), 129.2 (d), 126.3 (d), 118.3 (d), 74.1,72.8, 40.5 (d), 39.5, 38.6 (d), 33.7, 24.1, 15.3,13.4. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{16}H_{24}O_1$ 233.1900; Found: 233.1901.

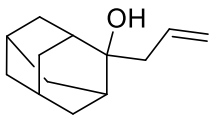


Compound 10

4-methylnon-1-en-4-ol [9]

Colorless oil, 128 mg, 82% yield, R_f=0.7 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 17.8, 10.7, 7.5 Hz, 1H), 5.18 – 5.08 (m, 2H), 2.22 (d, *J* = 7.6 Hz, 2H), 1.64 – 1.51 (m, 1H), 1.48 – 1.42 (m, 2H), 1.36 (dd, *J* = 6.7, 3.3 Hz, 2H), 1.34 – 1.31 (m, 2H), 1.31 – 1.27 (m, 2H), 1.17 (s, 3H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.1, 118.5, 72.2, 46.3, 41.8, 32.4, 26.7, 23.5, 22.6, 14.0.

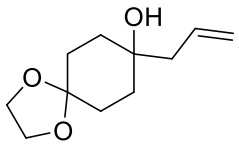


Compound 11

2-allyladamantan-2-ol [10]

White solid, 162 mg, 84% yield, R_f=0.7 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.5, 10.4, 7.5 Hz, 1H), 5.20 – 5.11 (m, 2H), 2.45 (d, *J* = 7.5 Hz, 2H), 2.21 (dd, *J* = 12.5, 3.2 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.82 (dp, *J* = 10.2, 3.2 Hz, 2H), 1.73 (d, *J* = 6.5 Hz, 2H), 1.70 (s, 2H), 1.70 – 1.69 (m, 2H), 1.57 – 1.52 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.7, 118.7, 74.5, 42.7, 38.4, 37.1, 34.4, 32.9, 27.4, 27.3.

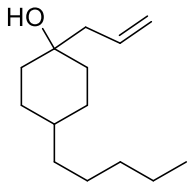


Compound 12

8-allyl-1,4-dioxaspiro[4.5]decan-8-ol [11]

Colorless oil, 158 mg, 80% yield, R_f=0.6 (PE: EA = 2: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 17.3, 9.8, 7.6 Hz, 1H), 5.16 – 5.06 (m, 2H), 3.95 – 3.88 (m, *J* = 3.4 Hz, 4H), 2.21 (d, *J* = 7.5 Hz, 2H), 1.88 (td, *J* = 12.0, 5.3 Hz, 2H), 1.69 – 1.61 (m, 4H), 1.60 – 1.54 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.5, 119.0, 108.8, 69.9, 64.2, 64.1, 46.9, 34.6, 30.4.



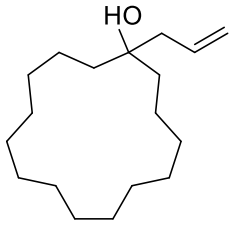
Compound 13

1-allyl-4-pentylcyclohexan-1-ol

Colorless oil, 170 mg, 81% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (ddt, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.19 – 5.11 (m, 2H), 2.30 (d, *J* = 7.5 Hz, 2H), 1.71 (dq, *J* = 7.8, 4.5, 3.6 Hz, 4H), 1.68 (s, 1H), 1.44 – 1.37 (m, 2H), 1.35 – 1.24 (m, 8H), 1.22 (t, *J* = 6.9 Hz, 2H), 1.10 – 1.01 (m, 2H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.7, 118.7, 71.9, 42.0, 37.3, 36.4,

35.9, 32.2, 29.5, 26.9, 22.7, 14.1. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{27}O$ 211.2056; Found: 211.2056.

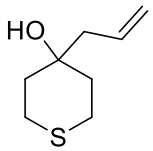


Compound 14

1-allylcyclopentadecan-1-ol [12]

Colorless oil, 200 mg, 75% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.5, 10.1, 7.4 Hz, 1H), 5.18 – 5.08 (m, 2H), 2.20 (d, *J* = 7.5 Hz, 2H), 1.51 (d, *J* = 7.1 Hz, 1H), 1.49 – 1.41 (m, 4H), 1.40 – 1.27 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.9, 118.6, 74.2, 45.4, 38.0, 27.8, 27.0, 26.7, 26.7, 26.2, 21.9.

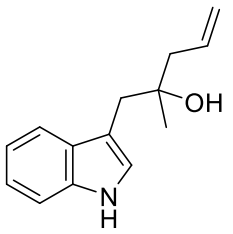


Compound 15

4-allyltetrahydro-2H-thiopyran-4-ol [27]

Colorless oil, 120 mg, 76% yield, R_f=0.6 (PE: EA = 2: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.20 (dd, *J* = 10.2, 2.1 Hz, 2H), 2.98 (ddd, *J* = 14.1, 11.4, 3.0 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.21 (dt, *J* = 7.6, 1.1 Hz, 2H), 1.88 – 1.83 (m, 2H), 1.78 – 1.72 (m, 2H), 1.65 – 1.52 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.5, 119.7, 69.4, 47.9, 38.2, 24.2.

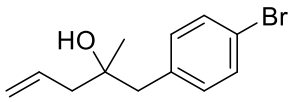


Compound 16

1-(1H-indol-3-yl)-2-methylpent-4-en-2-ol

Brown oil, 147 mg, 68% yield, R_f=0.5 (PE: EA = 2: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 12.2 Hz, 1H), 7.72 (dd, *J* = 8.0, 3.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.21 (td, *J* = 7.6, 2.9 Hz, 1H), 7.06 (d, *J* = 2.9 Hz, 1H), 6.04 (ddtd, *J* = 17.3, 10.0, 7.2, 2.8 Hz, 1H), 5.26 – 5.17 (m, 2H), 3.05 – 2.95 (m, 2H), 2.40 (dd, *J* = 7.5, 3.9 Hz, 2H), 1.95 (d, *J* = 11.8 Hz, 1H), 1.31 – 1.27 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.2, 134.5, 128.5, 123.9, 122.0, 119.6, 119.5, 118.4, 111.3, 111.2, 72.8, 46.3, 37.4, 26.7. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{18}NO$ 216.1383; Found: 216.1387.

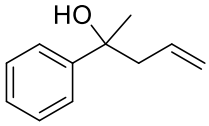


Compound 17

1-(4-bromophenyl)-2-methylpent-4-en-2-ol [28]

Yellow oil, 186 mg, 73% yield, R_f=0.6 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.97 – 5.88 (m, 1H), 5.17 (dd, *J* = 26.7, 13.6 Hz, 2H), 2.77 – 2.67 (m, 2H), 2.24 (d, *J* = 7.4 Hz, 2H), 1.65 (s, 1H), 1.14 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.6, 133.8, 132.3, 131.2, 120.5, 119.0, 72.0, 47.2, 46.3, 26.6.



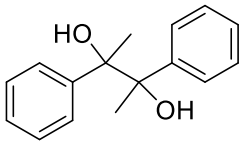
Compound 18

2-phenylpent-4-en-2-ol [29]

Colorless oil, 52 mg, 32% yield, R_f=0.6 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.38 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.30 – 7.26 (m, 1H), 5.64 (dddd, *J* = 16.7, 10.1, 8.3, 6.4 Hz, 1H), 5.20 – 5.14 (m, 2H),

2.73 (ddt, *J* = 13.7, 6.4, 1.3 Hz, 1H), 2.53 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.13 (s, 1H), 1.58 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.6, 133.7, 128.2, 126.7, 124.8, 119.6, 73.6, 48.5, 30.0.

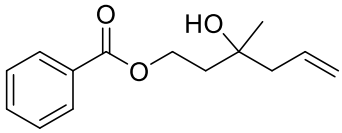


By-product of Compound 18

2,3-diphenylbutane-2,3-diol [29]

White solid, 73 mg, 60% yield, R_f=0.4 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.2, 2.1 Hz, 6H), 7.24 (p, *J* = 3.8 Hz, 4H), 2.81 (s, 2H), 1.53 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5, 127.4, 127.2, 127.1, 78.9, 24.9.

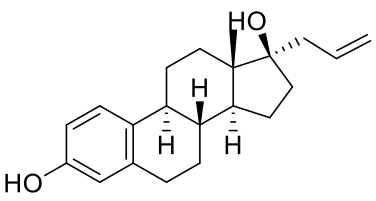


Compound 19

3-hydroxy-3-methylhex-5-en-1-yl benzoate

Colorless oil, 143 mg, 61% yield, R_f=0.6 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.96 – 5.85 (m, 1H), 5.21 – 5.13 (m, 2H), 4.52 (t, *J* = 6.9 Hz, 2H), 2.33 (d, *J* = 7.5 Hz, 2H), 2.02 (d, *J* = 5.8 Hz, 1H), 1.98 (td, *J* = 6.9, 4.0 Hz, 2H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 133.5, 133.0, 129.5, 128.4, 119.2, 71.3, 61.7, 47.0, 39.8, 27.0. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{19}O_3$ 235.1329; Found: 235.1329.

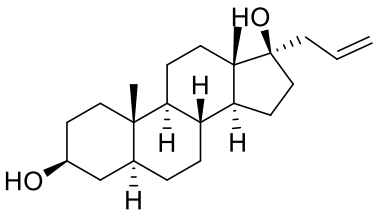


Compound 20

(8R,9S,13S,14S,17R)-17-allyl-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol [13]

White solid, 147 mg, 47% yield, R_f=0.5 (PE: EA = 2: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 6.07 – 5.97 (m, 1H), 5.46 (s, 1H), 5.25 – 5.17 (m, 2H), 2.82 (hept, *J* = 10.1, 9.1 Hz, 2H), 2.39 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.29 (tt, *J* = 13.7, 5.7 Hz, 2H), 2.15 (td, *J* = 10.6, 4.2 Hz, 1H), 2.02 (ddd, *J* = 14.6, 10.0, 5.5 Hz, 1H), 1.94 – 1.79 (m, 2H), 1.74 (s, 1H), 1.67 (dt, *J* = 7.8, 4.3 Hz, 2H), 1.53 (d, *J* = 8.6 Hz, 2H), 1.48 (t, *J* = 9.3 Hz, 1H), 1.44 – 1.36 (m, 2H), 1.35 (d, *J* = 4.9 Hz, 1H), 0.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.5, 138.2, 134.7, 132.5, 126.4, 119.3, 115.3, 112.7, 82.7, 49.5, 46.5, 43.8, 41.7, 39.5, 34.8, 31.8, 29.6, 27.4, 26.3, 23.4, 14.3.



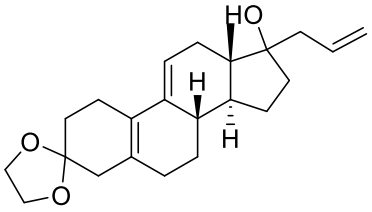
Compound 21

(3S,5S,8R,9R,10S,13S,14S,17R)-17-allyl-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,17-diol [14]

White solid, 209 mg, 65% yield, R_f=0.7 (PE: EA = 2: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.22 – 5.12 (m, 2H), 3.59 (tt, *J* = 11.0, 4.8 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.20 (dd, *J* = 13.7, 7.3 Hz, 1H), 1.94 (ddd, *J* = 14.6, 9.7, 6.5 Hz, 1H), 1.83 – 1.79 (m, 1H), 1.71 (ddd, *J* = 18.7, 11.3, 3.5 Hz, 2H), 1.64 – 1.52 (m, 6H), 1.52 – 1.44 (m, 2H), 1.43 – 1.37 (m, 1H), 1.35 – 1.24 (m, 8H), 1.23 – 1.17 (m, 1H), 1.12 (ddd, *J* = 12.7, 6.7, 3.3 Hz, 1H), 0.98 (td, *J* = 13.5, 4.0 Hz, 1H), 0.89 (s, 3H), 0.84 (s, 3H), 0.62 (td, *J* = 11.2, 4.2 Hz, 1H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 135.0, 119.0, 82.4, 71.3, 54.4, 50.6, 46.3, 45.0, 41.8, 38.2, 37.1, 36.3, 35.6, 34.9, 31.9, 31.8, 31.5, 28.6, 23.8, 20.9, 14.5, 12.4.

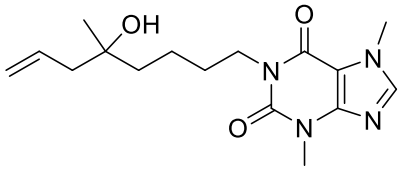


Compound 22

(8S,13S,14S,17R)-17-allyl-13-methyl-1,2,4,6,7,8,12,13,14,15,16,17-dodecahydrospiro[cyclopenta[a]phenanthrene-3,2'-[1,3]dioxolan]-17-ol [15]

White solid, 181 mg, 51% yield, R_f=0.5 (PE: EA = 2: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (tt, *J* = 17.1, 7.5 Hz, 1H), 5.66 – 5.60 (m, 1H), 5.19 (dd, *J* = 20.8, 13.6 Hz, 2H), 3.99 (s, 2H), 2.58 – 2.50 (m, 1H), 2.37 – 2.31 (m, 1H), 2.30 (d, *J* = 8.6 Hz, 3H), 2.24 (t, *J* = 7.4 Hz, 1H), 2.17 (dd, *J* = 13.7, 7.3 Hz, 2H), 2.02 (ddd, *J* = 14.5, 9.8, 5.4 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.89 – 1.82 (m, 2H), 1.82 – 1.74 (m, 2H), 1.63 (td, *J* = 13.4, 13.0, 4.2 Hz, 2H), 1.47 (td, *J* = 10.7, 7.8 Hz, 1H), 1.39 (tt, *J* = 12.6, 6.4 Hz, 1H), 1.24 (dd, *J* = 14.8, 9.7 Hz, 1H), 0.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.2, 134.9, 129.9, 126.2, 119.0, 118.3, 108.1, 82.2, 64.5, 64.3, 46.8, 44.9, 41.7, 41.3, 39.3, 34.8, 33.1, 31.3, 31.2, 27.6, 24.6, 23.9, 14.7.



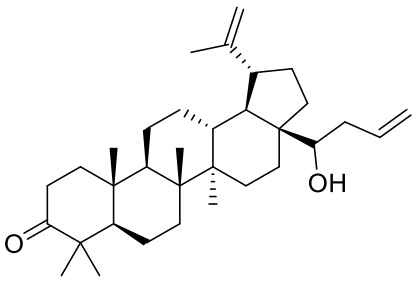
Compound 23

1-(5-hydroxy-5-methyloct-7-en-1-yl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione

White solid, 265 mg, 83% yield, R_f=0.6 (DCM: MeOH = 15: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (dq, *J* = 17.0, 7.8 Hz, 1H), 5.02 – 4.95 (m, 2H), 3.91 (d, *J* = 7.2 Hz, 2H), 3.89 (d, *J* = 1.8 Hz, 3H), 3.45 (d, *J* = 1.8 Hz, 3H), 2.27 (s, 1H), 2.12 (d, *J* = 7.5 Hz, 2H), 1.56 (p, *J* = 7.4 Hz, 2H), 1.42 (dd, *J* = 10.8, 4.4 Hz,

2H), 1.35 (h, *J* = 8.0, 6.5 Hz, 2H), 1.06 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.2, 151.4, 148.6, 141.6, 134.3, 118.1, 107.6, 71.8, 46.4, 41.0, 41.0, 33.5, 29.7, 28.2, 26.5, 20.9. **HRMS (ESI-TOF) m/z**: $[M+Na]^+$ Calcd for $C_{16}H_{24}N_4O_3Na$ 343.1741; Found: 343.1747.

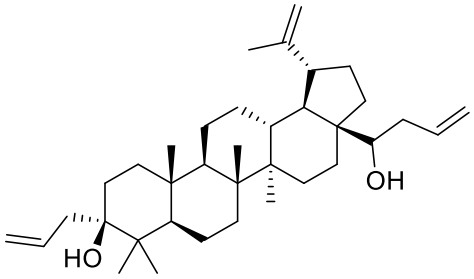


Compound 24

(1R,3aS,5aR,5bR,7aR,11aR,11bR,13aR,13bR)-3a-((S)-1-hydroxybut-3-en-1-yl)-5a,5b,8,8,11a-pentamethyl-1-(prop-1-en-2-yl)icosahydro-9H-cyclopenta[a]chrysen-9-one

White solid, 255 mg, 53% yield, R_f=0.4 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 – 5.84 (m, 1H), 5.23 – 5.17 (m, 2H), 4.73 (dd, *J* = 9.7, 2.4 Hz, 1H), 4.64 – 4.58 (m, 1H), 3.01 – 2.85 (m, 1H), 2.52 – 2.48 (m, 1H), 2.43 (dd, *J* = 7.5, 4.2 Hz, 1H), 2.38 – 2.33 (m, 1H), 2.16 – 2.08 (m, 2H), 2.04 (dtd, *J* = 19.5, 10.3, 3.9 Hz, 2H), 1.91 (ddd, *J* = 15.3, 7.7, 3.2 Hz, 2H), 1.87 – 1.83 (m, 1H), 1.74 (t, *J* = 3.3 Hz, 2H), 1.70 (s, 3H), 1.58 (dq, *J* = 6.4, 3.6 Hz, 1H), 1.55 – 1.51 (m, 1H), 1.49 – 1.47 (m, 2H), 1.46 – 1.43 (m, 2H), 1.42 (s, 1H), 1.40 – 1.37 (m, 2H), 1.34 (d, *J* = 3.6 Hz, 2H), 1.31 (d, *J* = 6.6 Hz, 1H), 1.27 (s, 1H), 1.20 (dd, *J* = 13.0, 4.5 Hz, 1H), 1.10 (s, 3H), 1.09 (s, 3H), 1.07 (s, 1H), 1.04 (s, 3H), 1.03 (s, 3H), 1.01 (s, 1H), 0.95 (d, *J* = 4.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 218.0, 151.5, 136.3, 118.5, 109.3, 70.6, 55.0, 50.5, 49.8, 49.6, 48.8, 47.3, 43.0, 42.0, 40.9, 39.6, 37.4, 36.9, 34.1, 34.1, 33.6, 33.3, 32.8, 27.8, 27.0, 26.6, 25.2, 25.0, 21.5, 21.1, 19.6, 15.9, 15.2. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{33}H_{53}O_2$ 481.4040; Found: 481.4043.

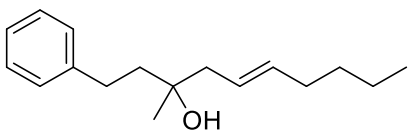


Compound 24'

(1R,3aS,5aR,5bR,7aR,9R,11aR,11bR,13aR,13bR)-9-allyl-3a-((S)-1-hydroxybut-3-en-1-yl)-5a,5b,8,8,11a-pentamethyl-1-(prop-1-en-2-yl)icosahydro-1H-cyclopenta[a]chrysen-9-ol

White solid, 303 mg, 58% yield, R_f=0.6 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 – 5.90 (m, 1H), 5.90 – 5.83 (m, 1H), 5.22 – 5.18 (m, 2H), 5.18 – 5.09 (m, 2H), 4.71 (d, *J* = 2.5 Hz, 1H), 4.58 (dd, *J* = 2.5, 1.5 Hz, 1H), 4.09 (d, *J* = 9.9 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.40 (td, *J* = 11.8, 10.0, 6.6 Hz, 2H), 2.13 – 2.08 (m, 2H), 2.08 – 1.97 (m, 2H), 1.83 (ddd, *J* = 12.9, 9.0, 1.9 Hz, 1H), 1.76 – 1.71 (m, 2H), 1.71 (s, 1H), 1.70 (s, 3H), 1.67 (d, *J* = 5.0 Hz, 1H), 1.59 – 1.53 (m, 1H), 1.51 (d, *J* = 4.1 Hz, 1H), 1.48 – 1.46 (m, 2H), 1.44 (s, 2H), 1.41 (t, *J* = 3.4 Hz, 1H), 1.39 – 1.34 (m, 2H), 1.34 (d, *J* = 4.5 Hz, 2H), 1.30 (dd, *J* = 6.1, 3.2 Hz, 2H), 1.27 (d, *J* = 2.6 Hz, 1H), 1.26 – 1.22 (m, 1H), 1.20 – 1.17 (m, 1H), 1.09 (dt, *J* = 11.9, 2.0 Hz, 1H), 1.06 (s, 3H), 1.05 (s, 3H), 1.00 – 0.97 (m, 1H), 0.93 (s, 3H), 0.91 – 0.87 (m, 1H), 0.84 (s, 3H), 0.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.6, 136.4, 134.8, 118.8, 118.5, 109.3, 75.0, 70.6, 51.0, 50.5, 50.3, 49.6, 48.9, 43.0, 41.0, 40.7, 37.4, 37.1, 36.9, 34.7, 34.3, 34.2, 33.4, 32.8, 29.0, 27.8, 26.9, 25.2, 23.6, 20.8, 20.6, 19.0, 18.7, 16.1, 15.6, 15.4. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{36}H_{59}O_2$ 523.4510; Found:523.4511.

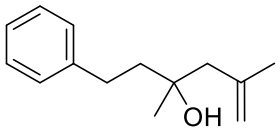


Compound 25

(E)-3-methyl-1-phenyldec-5-en-3-ol

Colorless oil, 200 mg, 81% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 3H), 5.63 (dd, *J* = 15.1, 7.0 Hz, 1H), 5.54 (q, *J* = 7.3 Hz, 1H), 2.76 (dt, *J* = 9.8, 3.8 Hz, 2H), 2.29 (d, *J* = 7.1 Hz, 2H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.82 (dd, *J* = 10.9, 6.6 Hz, 2H), 1.73 (s, 1H), 1.45 – 1.41 (m, 2H), 1.38 (d, *J* = 7.2 Hz, 2H), 1.29 (s, 3H), 0.97 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.7, 135.5, 128.4, 128.4, 125.8, 124.9, 72.1, 45.2, 43.7, 32.5, 31.7, 30.4, 26.8, 22.3, 14.0. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{17}H_{27}O$ 247.2056; Found: 247.2056.

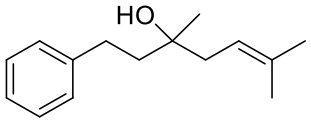


Compound 26

3,5-dimethyl-1-phenylhex-5-en-3-ol [16]

Colorless oil, 157 mg, 77% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 3H), 4.98 (dq, *J* = 2.9, 1.5 Hz, 1H), 4.82 (dd, *J* = 2.2, 1.2 Hz, 1H), 2.78 – 2.72 (m, 2H), 2.35 – 2.25 (m, 2H), 1.91 – 1.88 (m, 3H), 1.85 – 1.80 (m, 2H), 1.73 (s, 1H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.7, 142.6, 128.5, 128.4, 125.8, 115.1, 72.3, 49.6, 44.4, 30.5, 27.1, 25.2.



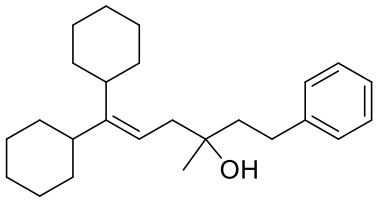
Compound 27

3,6-dimethyl-1-phenylhept-5-en-3-ol [17]

Colorless oil, 201 mg, 92% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.22 (m, 3H), 5.32 (tt, *J* = 8.0, 1.8 Hz, 1H), 2.77 (ddt, *J* = 11.3, 8.1, 4.0 Hz, 2H), 2.34 – 2.26 (m, 2H), 1.84

(dd, *J* = 10.4, 2.9 Hz, 5H), 1.73 (s, 3H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.8, 135.4, 128.4, 128.4, 125.8, 119.3, 73.0, 43.7, 40.5, 30.4, 26.8, 26.2, 18.1.

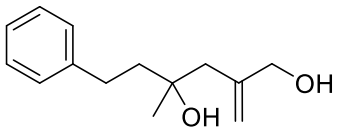


Compound 28

6,6-dicyclohexyl-3-methyl-1-phenylhex-5-en-3-ol

Colorless oil, 280 mg, 79% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 3H), 5.25 (t, *J* = 7.7 Hz, 1H), 2.78 – 2.72 (m, 2H), 2.52 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.39 – 2.32 (m, 2H), 1.97 (ddd, *J* = 11.7, 8.5, 3.3 Hz, 1H), 1.86 – 1.81 (m, 2H), 1.81 – 1.79 (m, 2H), 1.79 – 1.76 (m, 2H), 1.74 – 1.70 (m, 2H), 1.69 – 1.64 (m, 2H), 1.62 – 1.54 (m, 1H), 1.51 – 1.47 (m, 2H), 1.44 – 1.34 (m, 4H), 1.34 – 1.29 (m, 4H), 1.28 (s, 3H), 1.26 – 1.22 (m, 2H), 1.22 – 1.17 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.3, 142.8, 128.4, 128.4, 125.7, 116.3, 72.6, 43.6, 40.7, 40.3, 39.3, 35.4, 31.0, 31.0, 30.4, 27.2, 26.8, 26.6, 26.3, 26.2. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{25}H_{39}O$ 355.2995; Found: 355.2995.

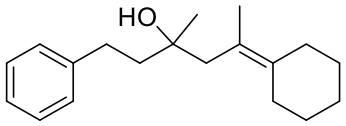


Compound 29

4-methyl-2-methylene-6-phenylhexane-1,4-diol

Colorless oil, 198 mg, 90% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 (dd, *J* = 12.4, 7.2 Hz, 3H), 5.21 (s, 1H), 4.98 (d, *J* = 1.9 Hz, 1H), 4.15 (s, 2H), 2.76 (dd, *J* = 10.3, 7.0 Hz, 2H), 2.49 – 2.35 (m, 2H), 1.86 (dt, *J* = 9.3, 6.9 Hz, 2H), 1.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.8, 142.6, 128.5, 128.4, 125.8, 117.3, 72.0, 67.1, 47.4, 44.6, 30.6, 26.8. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{14}H_{21}O_2$ 221.1536; Found: 221.1536.

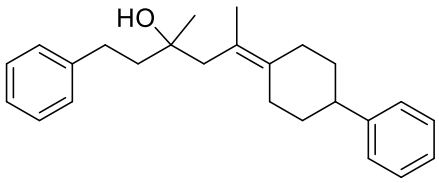


Compound 30

5-cyclohexylidene-3-methyl-1-phenylhexan-3-ol

Colorless oil, 210 mg, 77% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.18 (m, 3H), 2.79 – 2.75 (m, 1H), 2.43 (d, *J* = 13.7 Hz, 1H), 2.34 (d, *J* = 13.7 Hz, 1H), 2.23 (t, *J* = 5.9 Hz, 3H), 1.84 (d, *J* = 5.4 Hz, 1H), 1.81 (s, 3H), 1.58 (s, 2H), 1.56 (d, *J* = 6.8 Hz, 2H), 1.52 (dd, *J* = 11.5, 5.6 Hz, 2H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0, 142.8, 136.6, 128.4, 128.4, 126.9, 125.7, 121.7, 73.5, 46.0, 45.0, 44.7, 35.4, 31.1, 30.6, 30.5, 27.2, 21.3. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{19}H_{29}O$ 273.2213; Found: 273.2210.

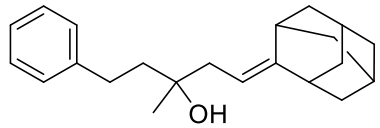


Compound 31

3-methyl-1-phenyl-5-(4-phenylcyclohexylidene)hexan-3-ol

White solid, 261 mg, 75% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 4H), 7.28 – 7.19 (m, 6H), 2.89 (d, *J* = 13.6 Hz, 2H), 2.79 (ddt, *J* = 10.4, 7.5, 4.0 Hz, 2H), 2.76 – 2.68 (m, 1H), 2.45 (s, 1H), 2.03 (dt, *J* = 17.1, 6.2 Hz, 2H), 1.99 – 1.92 (m, 2H), 1.88 (s, 3H), 1.86 (d, *J* = 5.9 Hz, 1H), 1.65 – 1.55 (m, 1H), 1.50 (tdd, *J* = 12.6, 9.4, 3.4 Hz, 2H), 1.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0, 142.8, 136.6, 128.4, 128.4, 128.3, 126.9, 126.0, 125.7, 121.7, 73.5, 46.0, 45.0, 44.7, 35.4, 31.1, 30.6, 30.5, 27.2, 21.3. $[M+H]^+$ Calcd for $C_{25}H_{33}O$ 349.2526; Found: 349.2526.

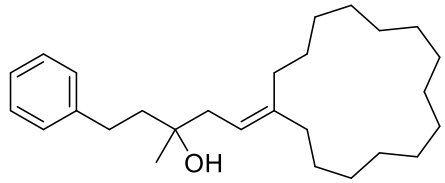


Compound 32

1-(adamantan-2-ylidene)-3-methyl-5-phenylpentan-3-ol

White solid, 271 mg, 87% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.20 (m, 3H), 5.20 (t, *J* = 7.9 Hz, 1H), 2.92 (s, 1H), 2.76 (dd, *J* = 12.1, 5.8 Hz, 2H), 2.46 (s, 1H), 2.29 (dd, *J* = 7.7, 2.6 Hz, 2H), 2.02 (s, 2H), 1.95 (s, 2H), 1.93 (s, 2H), 1.88 (s, 2H), 1.85 (s, 2H), 1.82 (d, *J* = 8.0 Hz, 2H), 1.75 (d, *J* = 12.2 Hz, 2H), 1.69 (s, 1H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.9, 142.8, 128.4, 128.4, 125.7, 110.7, 72.7, 43.6, 41.1, 40.0, 39.1, 38.9, 37.2, 32.3, 30.4, 28.6, 26.7. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{22}H_{31}O$ 311.2369; Found: 311.2369.

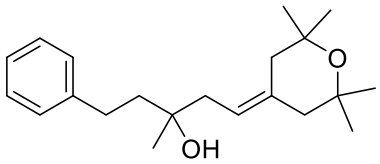


Compound 33

1-cyclopentadecylidene-3-methyl-5-phenylpentan-3-ol

Colorless oil, 289 mg, 75% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.21 (dd, *J* = 16.1, 7.6 Hz, 3H), 5.27 (t, *J* = 7.6 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.28 (p, *J* = 7.3 Hz, 2H), 2.09 (d, *J* = 7.7 Hz, 2H), 2.06 (d, *J* = 8.2 Hz, 2H), 1.81 (dd, *J* = 11.9, 5.7 Hz, 2H), 1.56 (s, 1H), 1.48 (d, *J* = 7.5 Hz, 2H), 1.44 (d, *J* = 9.7 Hz, 2H), 1.39 (s, 2H), 1.37 (s, 2H), 1.36 (s, 2H), 1.36 (s, 2H), 1.34 (s, 2H), 1.27 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 142.7, 128.4, 128.4, 125.7, 119.1, 72.7, 43.7, 40.1, 37.7, 30.4, 30.1, 27.9, 27.6, 27.5, 27.1, 26.8, 26.7, 26.7, 26.6, 26.5, 26.4. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{27}H_{45}O$ 385.3465; Found: 385.3468.

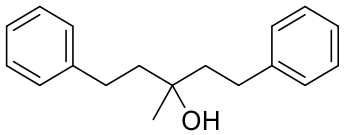


Compound 34

3-methyl-1-phenyl-5-(2,2,6,6-tetramethyltetrahydro-4H-pyran-4-ylidene)pentan-3-ol

Colorless oil, 222 mg, 70% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 3H), 5.44 (t, *J* = 7.6 Hz, 1H), 2.77 – 2.69 (m, 2H), 2.32 (d, *J* = 7.6 Hz, 2H), 2.23 (s, 1H), 2.19 (s, 2H), 2.15 (s, 2H), 1.83 (td, *J* = 7.3, 3.2 Hz, 2H), 1.63 (s, 1H), 1.44 (d, *J* = 9.1 Hz, 2H), 1.29 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.5, 135.9, 128.5, 128.4, 128.4, 128.3, 125.8, 120.1, 73.6, 73.5, 73.0, 47.8, 43.7, 40.4, 39.8, 30.6, 30.5, 30.4, 30.3, 30.2, 26.8. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{21}H_{33}O_2$ 317.2475; Found: 317.2477.

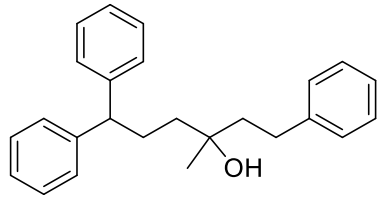


Compound 35

3-methyl-1,5-diphenylpentan-3-ol [18]

Colorless oil, 180 mg, 71% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 3.9 Hz, 2H), 7.24 (s, 3H), 7.22 (d, *J* = 8.0 Hz, 3H), 2.69 (d, *J* = 4.4 Hz, 2H), 2.67 (d, *J* = 7.1 Hz, 2H), 1.83 – 1.78 (m, 2H), 1.74 (q, *J* = 7.9 Hz, 2H), 1.61 (d, *J* = 6.5 Hz, 1H), 1.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.6, 142.4, 128.5, 128.4, 128.4, 125.8, 125.8, 72.7, 43.7, 41.6, 36.4, 30.3, 27.0, 26.0.

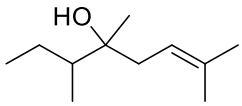


Compound 36

3-methyl-1,6,6-triphenylhexan-3-ol

Colorless oil, 293 mg, 85% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.38 (s, 2H), 7.37 (s, 1H), 7.36 (s, 2H), 7.29 (s, 2H), 7.27 (s, 2H), 7.26 (s, 1H), 3.95 (t, *J* = 7.8 Hz, 1H), 2.80 – 2.65 (m, 2H), 2.24 (q, *J* = 8.1 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.63 – 1.55 (m, 2H), 1.38 (s, 1H), 1.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.1, 145.0, 142.6, 128.6, 128.5, 128.5, 128.4, 127.9, 126.3, 125.9, 72.7, 51.9, 43.6, 40.6, 30.4, 30.2, 27.0. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{25}H_{29}O$ 345.2213; Found: 345.2219.

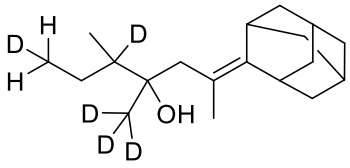


Compound 37

3,4,7-trimethyloct-6-en-4-ol

Colorless oil, 120 mg, 71% yield, R_f=0.5 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (tdp, *J* = 7.6, 3.0, 1.4 Hz, 1H), 2.23 (ddd, *J* = 14.6, 7.6, 2.9 Hz, 1H), 2.20 – 2.14 (m, 1H), 1.79 – 1.77 (m, 3H), 1.67 (d, *J* = 1.8 Hz, 3H), 1.43 – 1.34 (m, 2H), 1.09 (d, *J* = 5.7 Hz, 3H), 1.04 – 0.96 (m, 1H), 0.96 – 0.94 (m, 3H), 0.93 – 0.88 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.5 (d), 119.3 (d), 75.4 (d), 44.4 (d), 38.3, 37.7, 26.2, 24.3, 23.5 (d), 22.9, 18.0 (d), 13.9, 13.1, 12.9, 12.8. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{11}H_{23}O$ 171.1743; Found: 171.1743.

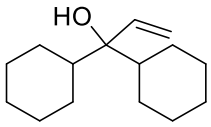


Compound 38

2-(adamantan-2-ylidene)-5-methyl-4-(methyl-d3)heptan-5,7-d2-4-ol

White solid, 242 mg, 86% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92 (d, *J* = 3.6 Hz, 1H), 2.88 (s, 1H), 2.32 (dd, *J* = 13.6, 2.8 Hz, 1H), 2.18 (dd, *J* = 13.6, 3.9 Hz, 1H), 1.93 (q, *J* = 3.7 Hz, 2H), 1.89 (p, *J* = 2.6 Hz, 2H), 1.87 (s, 2H), 1.83 (d, *J* = 3.1 Hz, 2H), 1.82 – 1.76 (m, 1H), 1.74 (d, *J* = 2.1 Hz, 3H), 1.70 (dd, *J* = 8.9, 3.5 Hz, 2H), 1.69 – 1.64 (m, 2H), 1.63 (s, 1H), 1.36 – 1.25 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 2H), 0.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.7, 116.9, 75.0 (t), 46.0 (m), 42.3, 41.5, 39.4, 39.2, 39.1, 38.8, 38.8, 37.1, 33.2, 28.0, 24.2 (m), 20.7, 14.0, 13.4, 12.8 (m). **HRMS (ESI-TOF) m/z**: $[M+Na]^+$ Calcd for $C_{19}H_{27}D_5ONa$ 304.2659; Found: 304.2667.

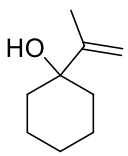


Compound 5b

1,1-dicyclohexylprop-2-en-1-ol [19]

Colorless oil, 1.70 g, 80% yield, R_f=0.6 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (dt, *J* = 16.2, 7.3 Hz, 1H), 5.22 – 5.09 (m, 2H), 1.77 (s, 2H), 1.75 (s, 2H), 1.67 (s, 2H), 1.64 (s, 2H), 1.53 (d, *J* = 12.0 Hz, 2H), 1.41 – 1.25 (m, 2H), 1.25 – 1.21 (m, 2H), 1.21 – 1.15 (m, 2H), 1.15 – 1.08 (m, 2H), 1.04 (d, *J* = 11.6 Hz, 2H), 1.01 – 0.93 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.5, 113.1, 79.2, 42.8, 42.7, 27.3, 26.9, 26.7, 26.7, 26.6, 26.1.

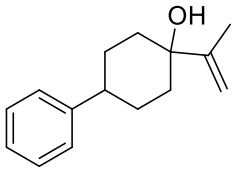


Compound 7b

1-(prop-1-en-2-yl)cyclohexan-1-ol [20]

Colorless oil, 1.3 g, 93% yield, R_f=0.7 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (s, 1H), 4.83 (s, 1H), 1.82 (s, 3H), 1.68 (d, *J* = 3.1 Hz, 2H), 1.66 (s, 2H), 1.64 (s, 1H), 1.59 (d, *J* = 6.0 Hz, 2H), 1.56 (dd, *J* = 8.2, 4.8 Hz, 2H), 1.28 (s, 1H), 1.23 (q, *J* = 4.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.0, 109.2, 73.6, 35.9, 25.6, 22.0, 19.0.

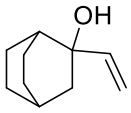


Compound 8b

4-phenyl-1-(prop-1-en-2-yl)cyclohexan-1-ol [21]

White solid, 1.7 g, 84% yield, R_f=0.6 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 5.11 (s, 1H), 4.88 (s, 1H), 2.54 (tt, *J* = 12.4, 3.4 Hz, 1H), 1.97 (td, *J* = 13.1, 4.7 Hz, 2H), 1.89 (s, 3H), 1.83 (d, *J* = 4.2 Hz, 2H), 1.80 (s, 2H), 1.78 (d, *J* = 8.7 Hz, 2H), 1.32 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.4, 147.2, 128.4, 126.9, 126.0, 109.0, 73.0, 43.8, 36.1, 29.3, 19.1.

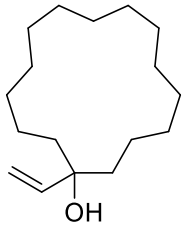


Compound 9b

2-vinylbicyclo[2.2.2]octan-2-ol [22]

White solid, 1.45 g, 95% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.28 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.37 (d, *J* = 17.5 Hz, 1H), 5.17 (d, *J* = 10.9 Hz, 1H), 2.28 (d, *J* = 12.6 Hz, 2H), 1.89 (d, *J* = 13.1 Hz, 2H), 1.83 (s, 2H), 1.75 (s, 1H), 1.73 (s, 1H), 1.71 (s, 2H), 1.59 (d, *J* = 12.5 Hz, 2H), 1.47 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.8, 113.5, 74.7, 38.0, 37.8, 34.7, 32.8, 27.4, 27.1.

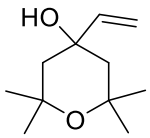


Compound 10b

1-vinylcyclopentadecan-1-ol [23]

Colorless oil, 2.40 g, 95% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.22 (d, *J* = 17.4 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 1.55 (q, *J* = 4.3 Hz, 2H), 1.52 (d, *J* = 6.2 Hz, 2H), 1.43 (s, 2H), 1.39 – 1.38 (m, 2H), 1.37 (s, 2H), 1.34 (s, 2H), 1.33 (s, 4H), 1.29 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.4, 111.5, 75.1, 38.2, 27.8, 27.0, 26.7, 26.7, 26.3, 21.9.

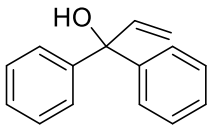


Compound 11b

2,2,6,6-tetramethyl-4-vinyltetrahydro-2H-pyran-4-ol [24]

Colorless oil, 1.77 g, 96% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (ddd, *J* = 17.3, 10.6, 1.8 Hz, 1H), 5.26 (d, *J* = 17.3 Hz, 1H), 5.07 (d, *J* = 10.6 Hz, 1H), 1.66 – 1.62 (m, 2H), 1.55 (s, 2H), 1.41 – 1.34 (m, 2H), 1.30 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 111.2, 71.8, 71.2, 45.6, 34.4, 29.7. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{11}H_{21}O_2$ 185.1536; Found: 185.1536.

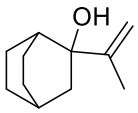


Compound 13b

1,1-diphenylprop-2-en-1-ol [25]

White solid, 2.31 g, 99% yield, R_f=0.7 (PE: EA = 10: 1, V:V)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.45 (s, 2H), 7.41 (s, 2H), 7.38 (s, 2H), 7.35 (s, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 6.57 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.42 – 5.36 (m, 2H), 2.45 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.8, 143.6, 128.2, 127.4, 127.0, 114.1, 79.5.



Compound 15b

2-(prop-1-en-2-yl)bicyclo[2.2.2]octan-2-ol [26]

White solid, 1.73 g, 90% yield, R_f=0.5 (PE: EA = 5: 1, V:V)

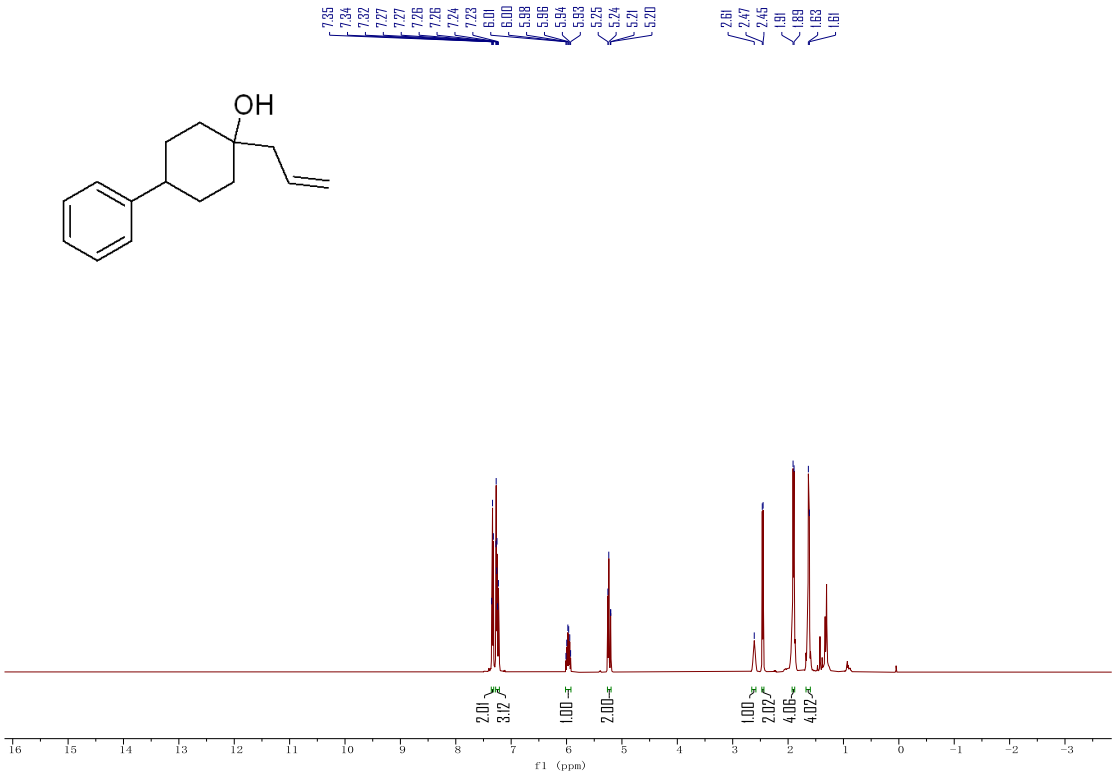
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (s, 1H), 4.97 (q, *J* = 1.5 Hz, 1H), 2.26 (dd, *J* = 12.7, 3.1 Hz, 2H), 2.11 (t, *J* = 3.2 Hz, 2H), 1.79 (d, *J* = 1.6 Hz, 3H), 1.78 (s, 1H), 1.76 (s, 2H), 1.72 – 1.66 (m, 4H), 1.60 (dq, *J* = 12.7, 2.4 Hz, 2H), 1.40 – 1.27 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.5, 111.9, 76.0, 37.7, 34.9, 34.5, 32.8, 27.2, 26.9, 18.5.

10. Reference

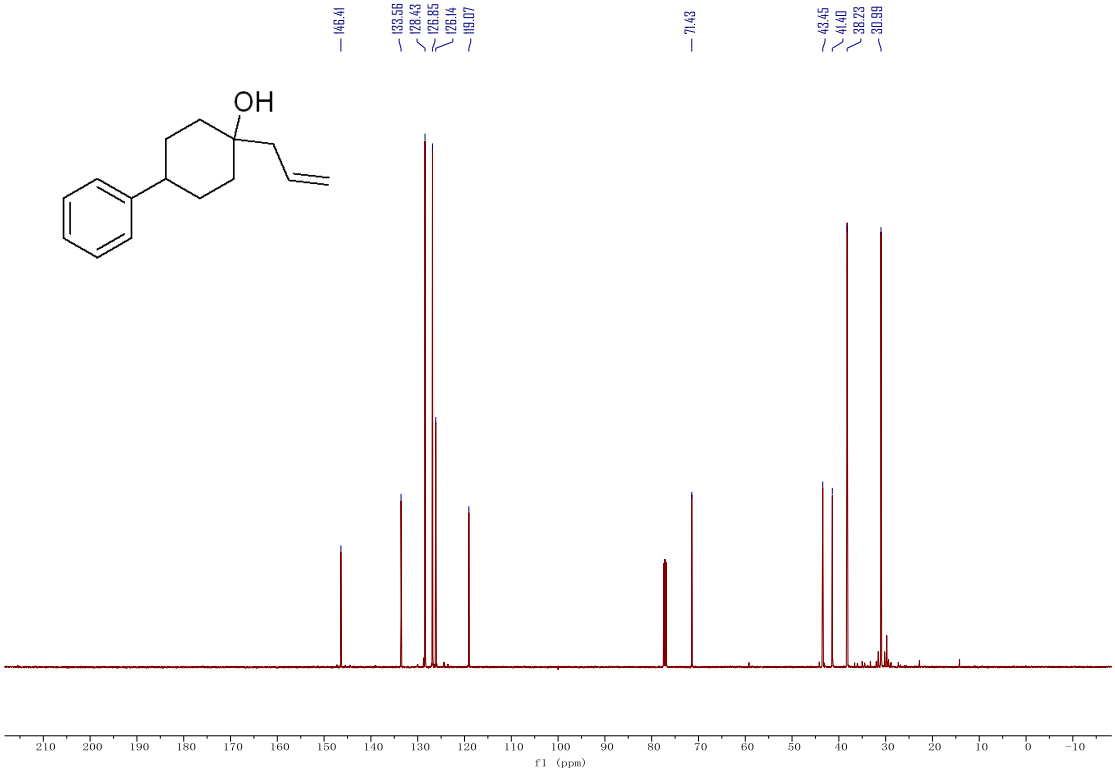
[1] A. Bokka, Y. Hua, A. S. Berlin, J. Jeon, *ACS Catal*. 2015, **5**, 3189-3195.
[2] M. Wadamoto, H. Yamamoto, *J. Am. Chem. Soc.* 2005, **127**, 14556-14557.
[3] C. Sun, Y. Li, G. Yin, *Angew. Chem., Int. Ed*. 2022, **61**, No. e20220907.
[4] S. J. Thompson, D. Q. Thach, G. Dong, *J. Am. Chem. Soc.* 2015, **137**, 11586-11589.
[5] C. Held, R. Fröhlich, P. Metz, *Angew. Chem., Int. Ed*. 2001, **40**, 1058-1060.
[6] L.-X. Ruan, B. Sun, J.-M. Liu, S.-L. Shi, *Science.* 2023, **379**, 662-670.
[7] W. Oroshnik, G. Karmas, R. A. Mallory, *J. Am. Chem. Soc*. 1954, **76**, 2325-2329.
[8] I. Triandafillidi, A. Savvidou, C. G. Kokotos, *Org. Lett*. 2019, **21**, 5533-5537.
[9] M. C. Law, K.-Y. Wong, T. H. Chan, *Green Chem*. 2002, **4**, 161-164.
[10] K.-H. Shen, C.-F. Yao, *J. Org. Chem*. 2006, **71**, 3980-3983.
[11] M. M. Kayser, C. M. Clouthier, *J. Org. Chem*. 2006, **71**, 8424-8430.
[12] D. Genevieve, F. Marcel, T. Maria C, *C. R. Seances Acad. Sci., Ser. C*. 1967, **265**, 1489-1491.

[13] R. P. Boivin, V. Luu-The, R. Lachance, F. Labrie, D. Poirier, *J. Med. Chem*. 2000, **43**, 4465-4478.
[14] Z. Paryzek, K. Blaszczyk, *Can. J. Chem*. 1987, **65**, 229-233.
[15] W. Jiang, J. J. Fiordeliso, G. Allan, O. Linton, P. Tannenbaum, J. Xu, P. Zhu, J. Gunnet, K. Demarest, S. Lundeen, Z. Sui, *Bioorg. Med. Chem. Lett*. 2007, **17**, 1471-1474.
[16] Y. Xie, P.-W. Sun, Y. Li, S. Wang, M. Ye, Z. Li, *Angew. Chem. Int. Ed*. 2019, **58**, 7097-7101.
[17] K.-T. Wong, T.-M. Yuan, M. C. Wang, H.-H. Tung, T.-Y. Luh, *J. Am. Chem. Soc*. 1994, **116**, 8920-8929.
[18] P. C. Too, Y. L. Tnay, S. Chiba, *Beilstein J. Org. Chem*. 2013, **9**, 1217-1225.
[19] M. Berger, D. Carboni, P. Melchiorre, *Angew. Chem. Int. Ed*. 2021, **60**, 26373-26377.
[20] Y. Liu, Y.-Y. Yeung, *Org. Lett*. 2017, **19**, 1422-1425.
[21] D. C. Magri, M. S. Workentin, *Chem. Eur. J*. 2008, **14,** 1698-1709.
[22] S. R. Wilson, G. M. Georgiadis, *J. Org. Chem*. 1983, **48**, 4143-4144.
[23] M. Nagel, G. Fráter, H.-J. Hansen, *Chimia*, 2003, **57**, 196-199.
[24] P. Magnus, T. E. Mansley, *Tetrahedron Lett*. 1999, **40**, 6909-6912.
[25] Y. Yu, U. K. Tambar, *Chem. Sci*. 2015, **6**, 2777-2781.
[26] A. Masuyama, T. Sugawara, M. Nojima, K. J. McCullough, *Tetrahedron*, 2003, **59**, 353-366.
[27] F.-S. Li, Y.-Q. Chen, S.-J. Lin, C.-Z. Shi, X.-Y. Li, Y.-C. Sun, Z.-W. Guo, L. Shi, *Org. Chem. Front,* 2020, **7**, 3434-3438.
[28] A. Clerici, N. Pastori, O. Porta, *J. Org. Chem*, 2005, **10**, 4174–4176.
[29] M. Nakajima, E. Fava, S. Loescher, Z. Jiang, M. Rueping, *Angew. Chem. Int. Ed.* 2015, **54**, 8828 –8832.

^{1}H-NMR and ^{13}C-NMR spectra



^{1}H NMR of compound **1** (500 MHz, $CDCl_3$)



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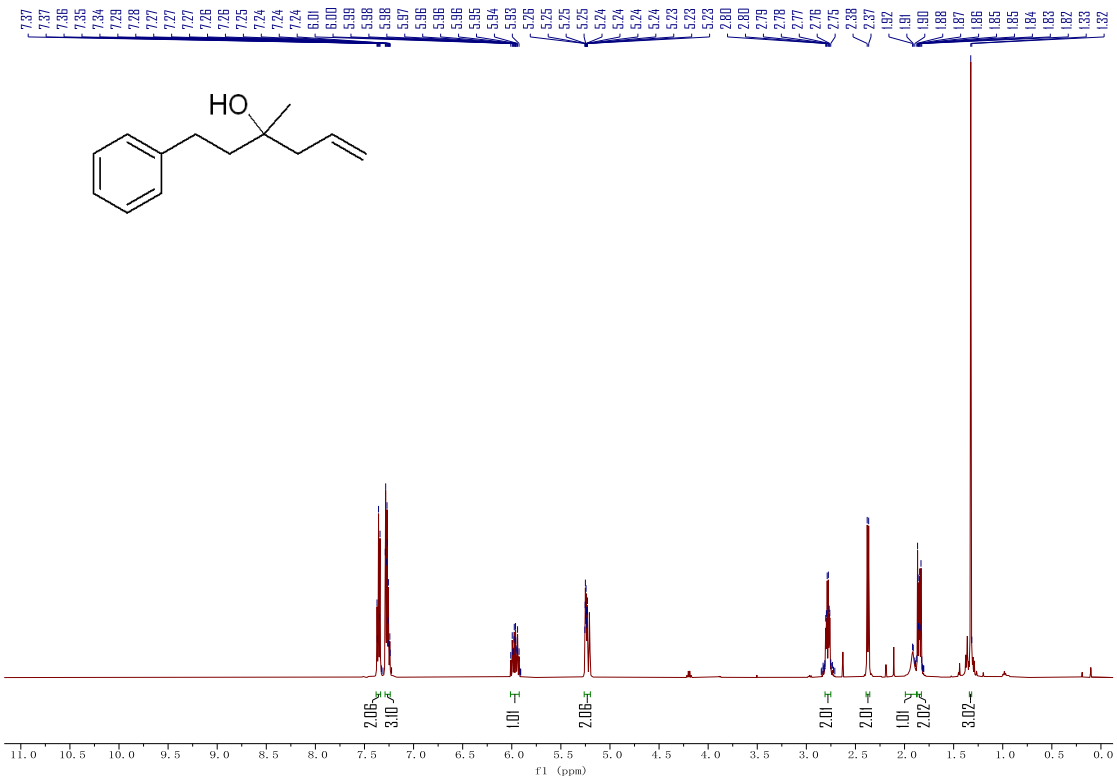

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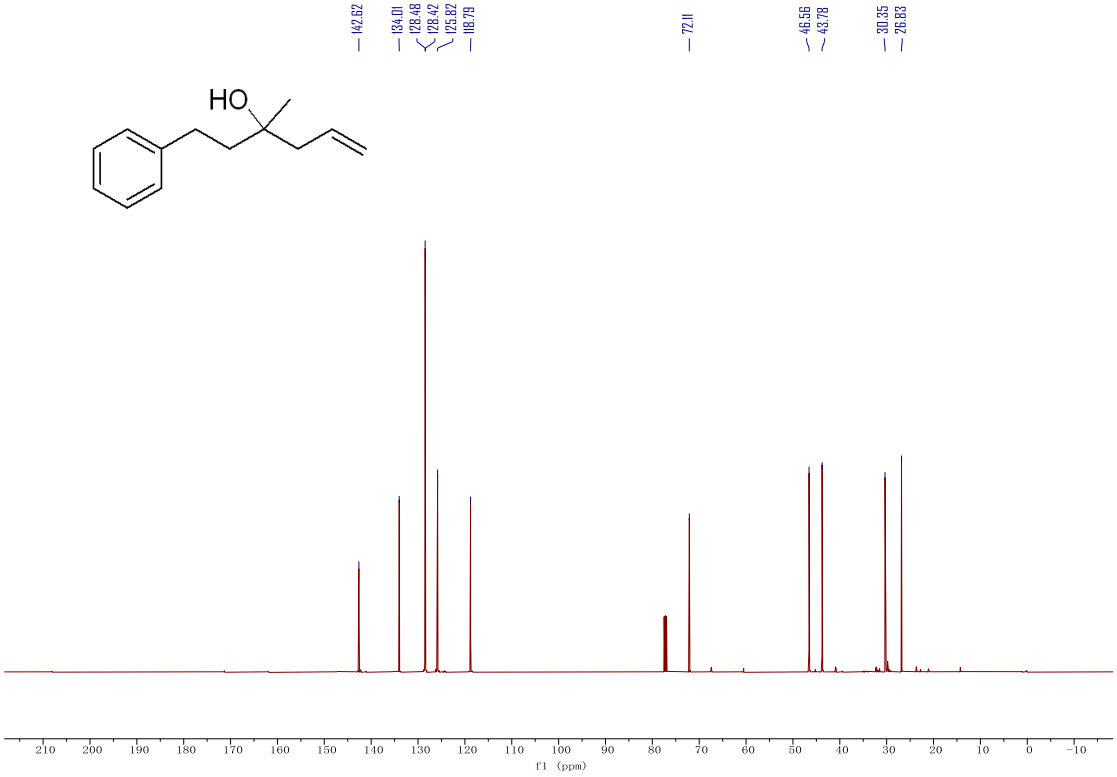

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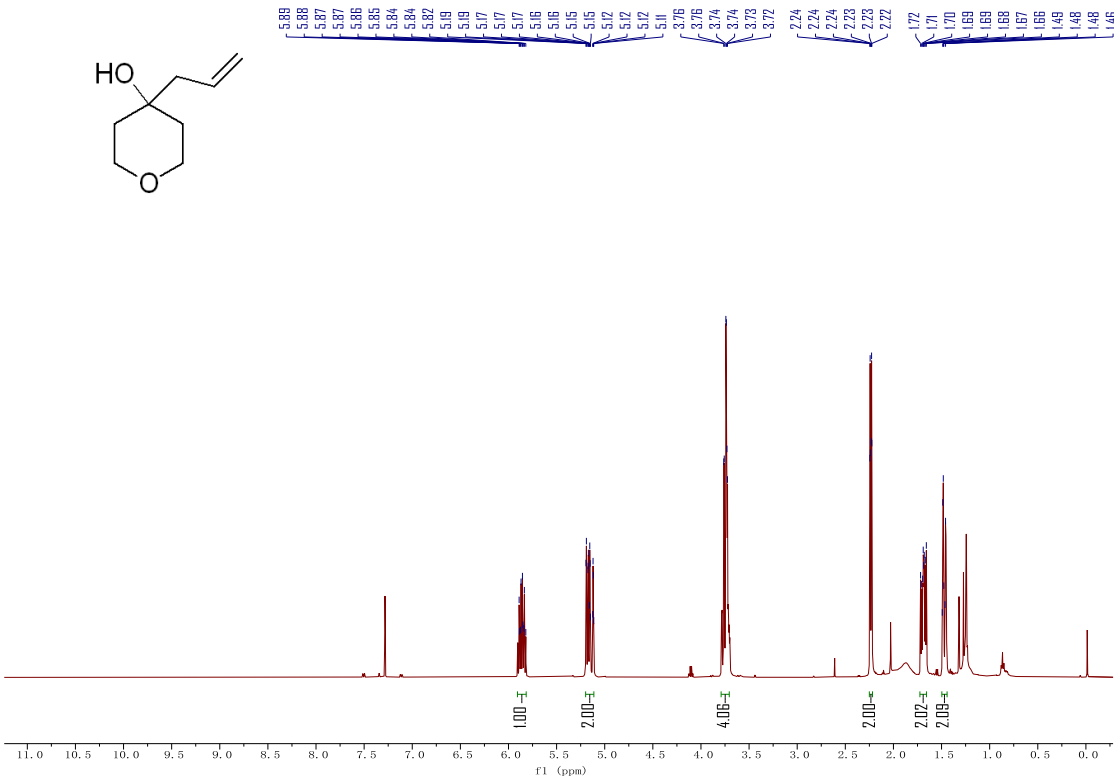

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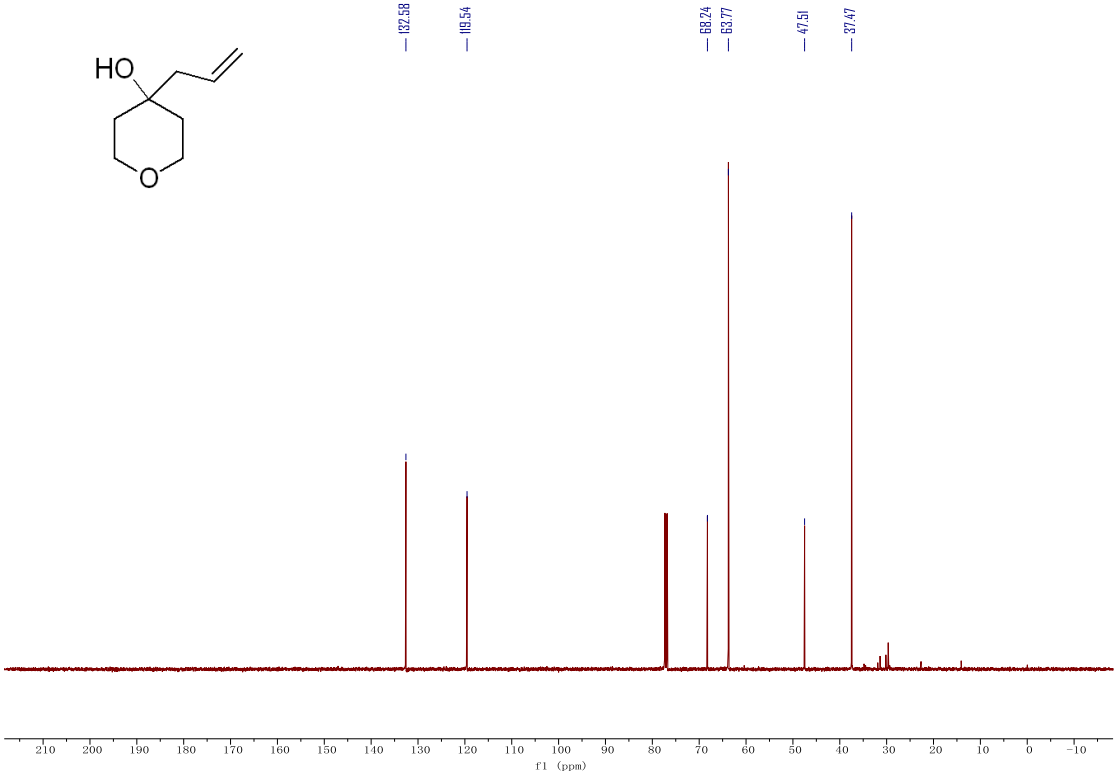

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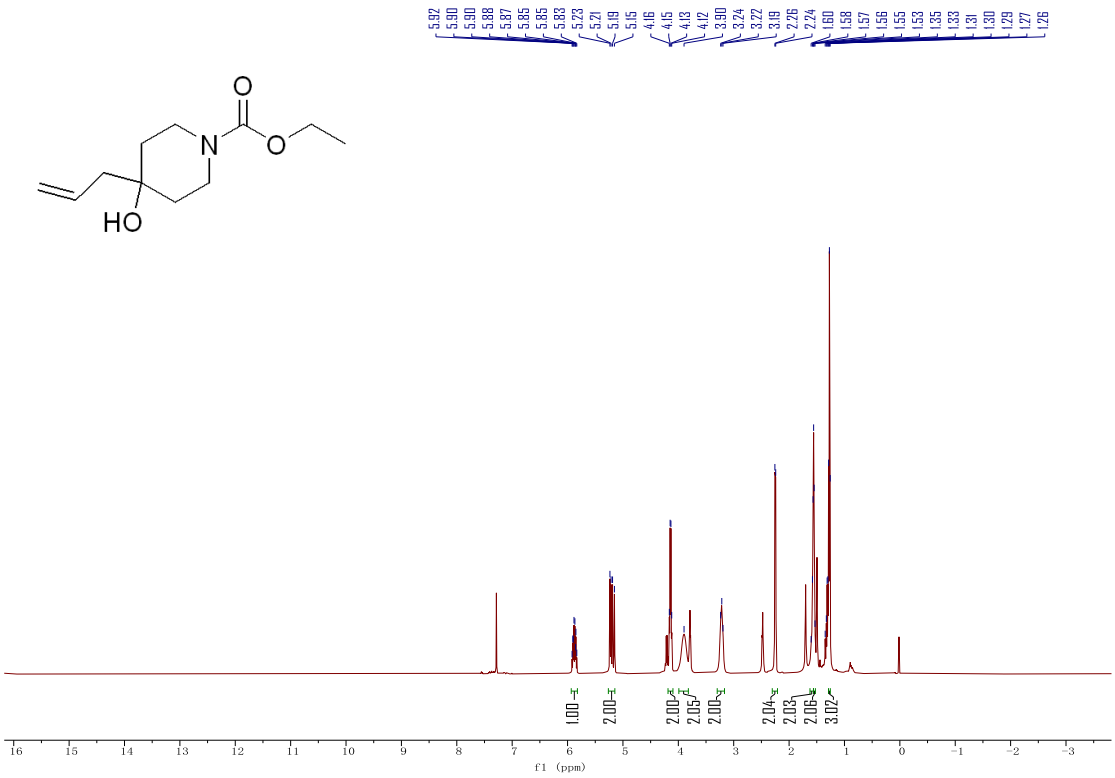
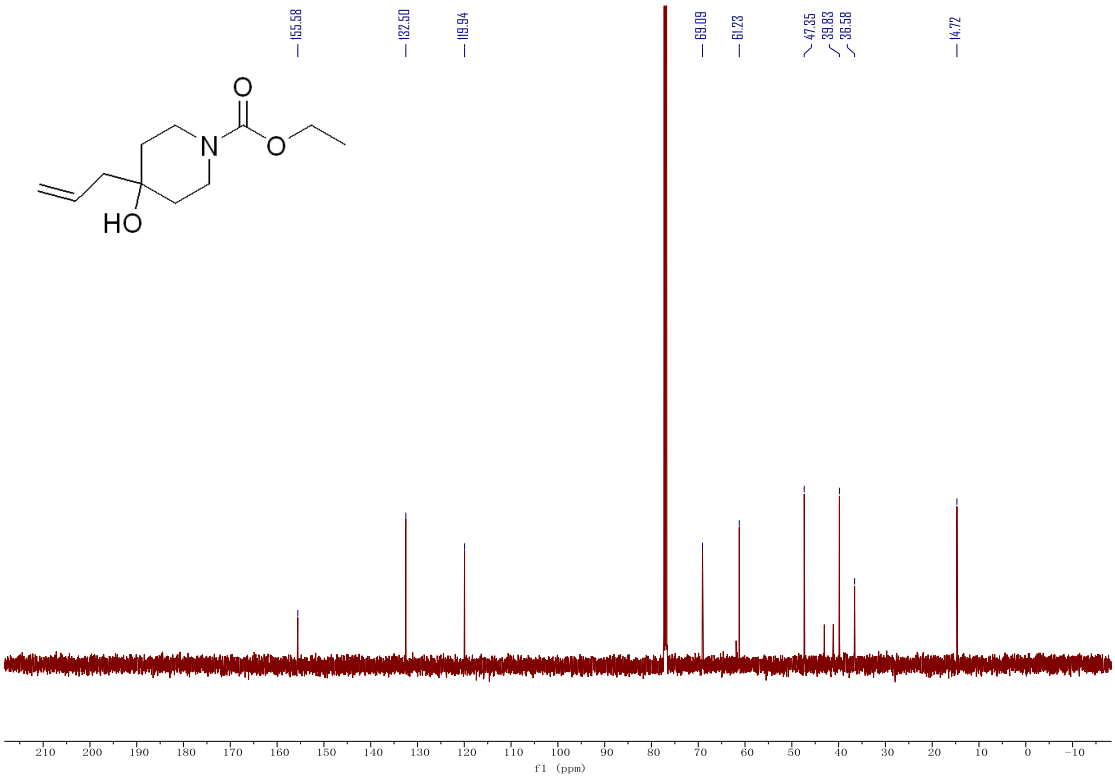
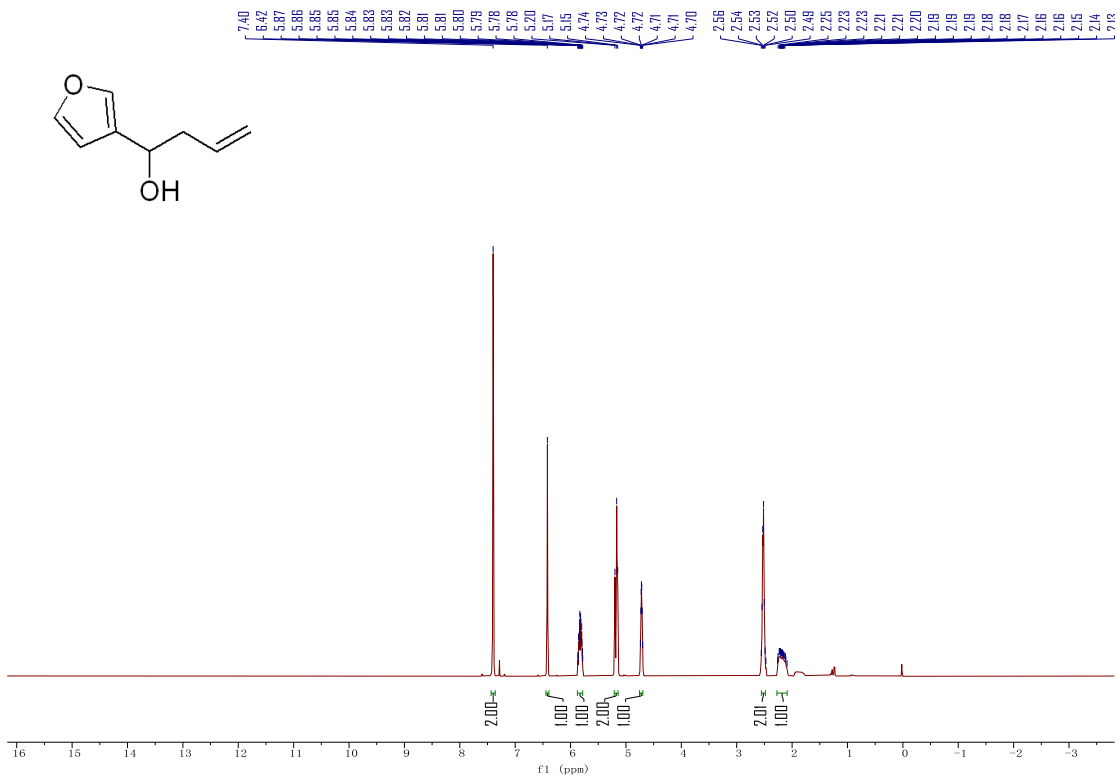


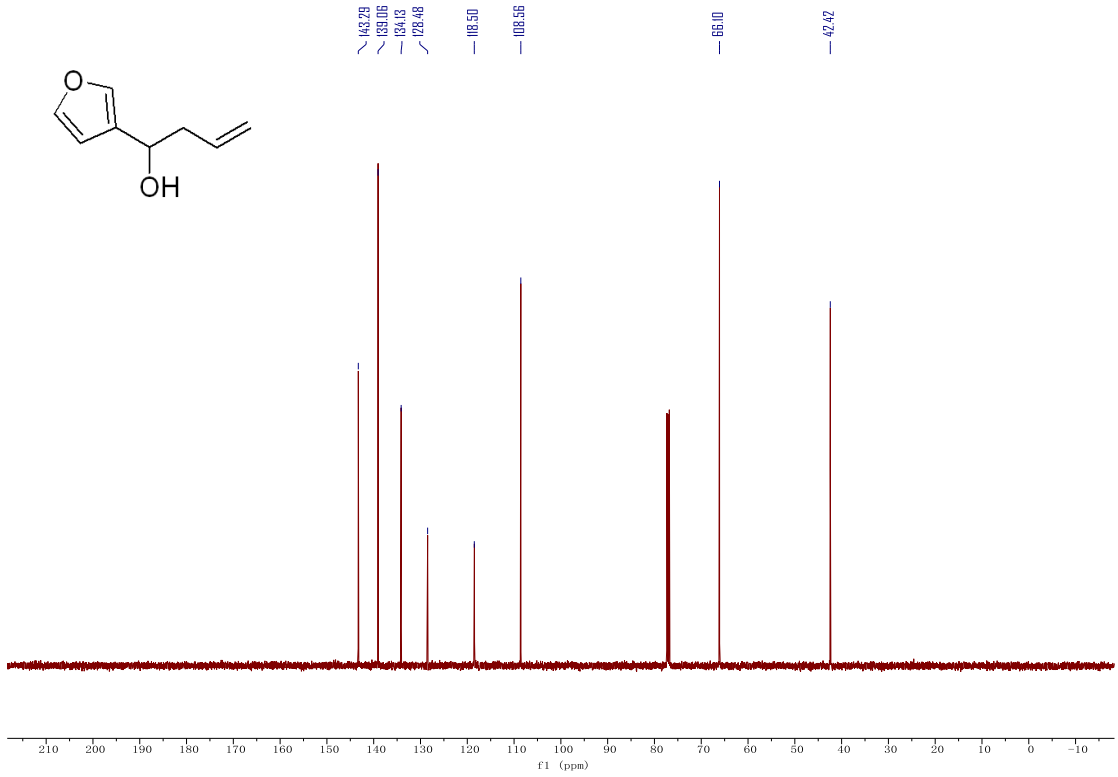
^{1}H NMR of compound **4** (500 MHz, $CDCl_3$)



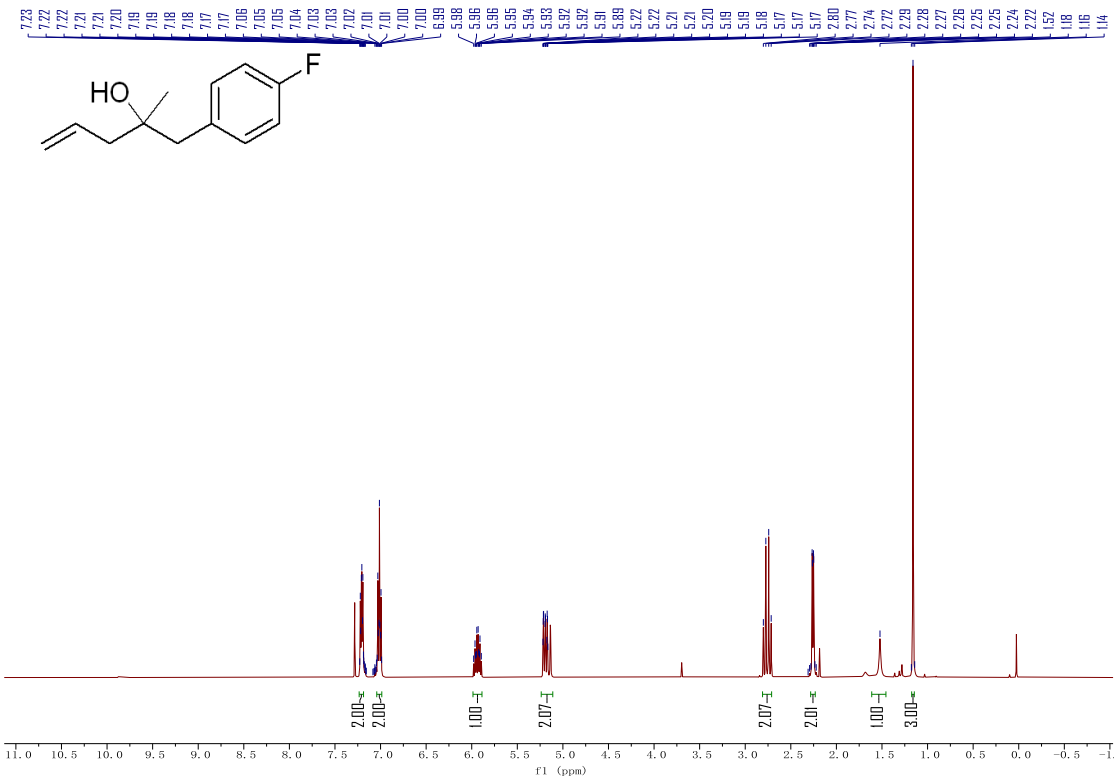
^{13}C NMR of compound **4** (126 MHz, $CDCl_3$)



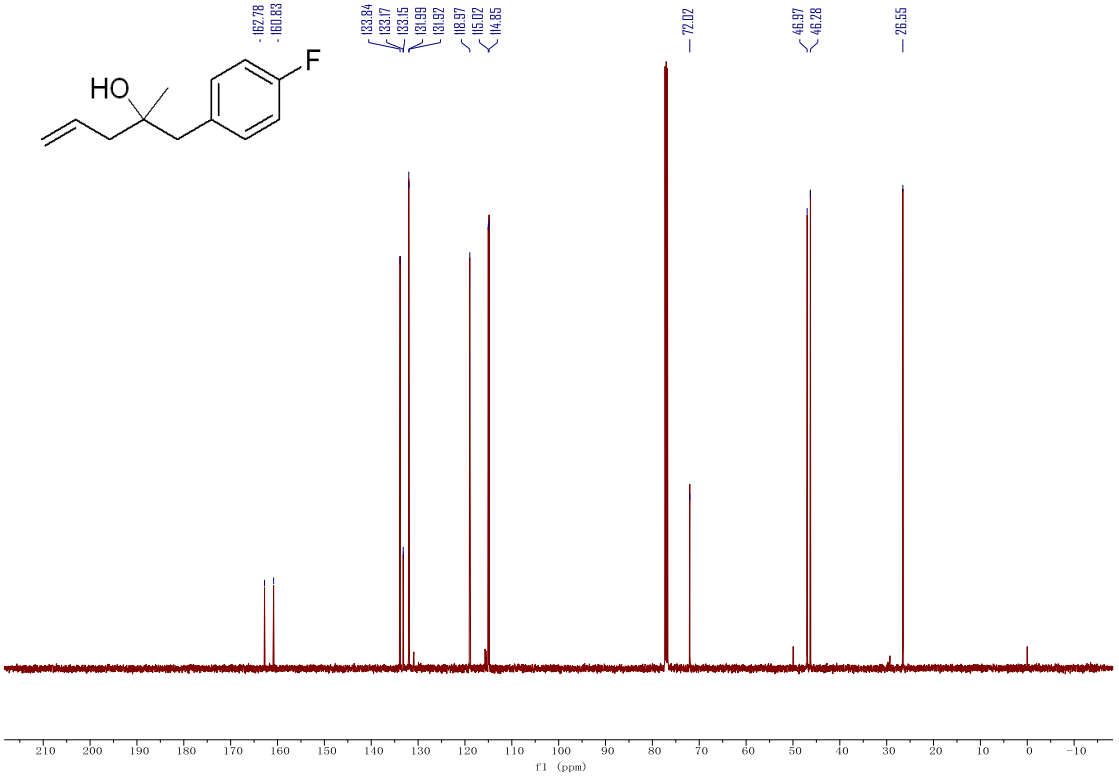
^{1}H NMR of compound **5** (500 MHz, $CDCl_3$)



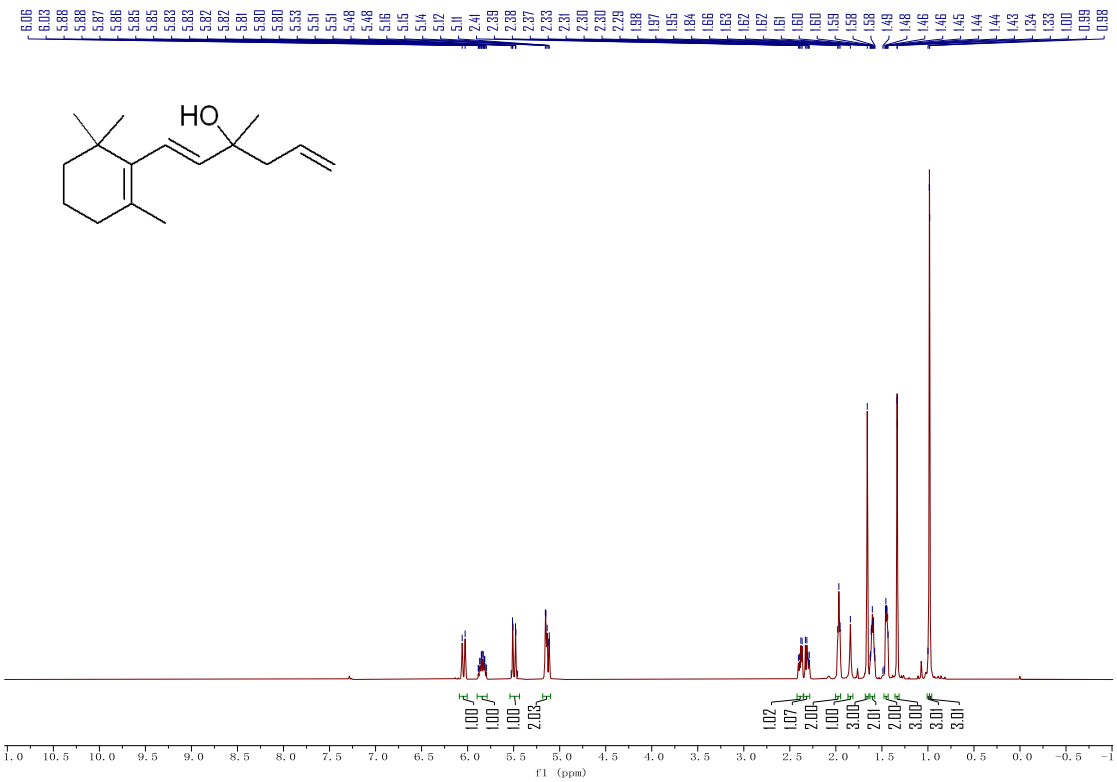
^{13}C NMR of compound **5** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **6** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **6** (126 MHz, $CDCl_3$)



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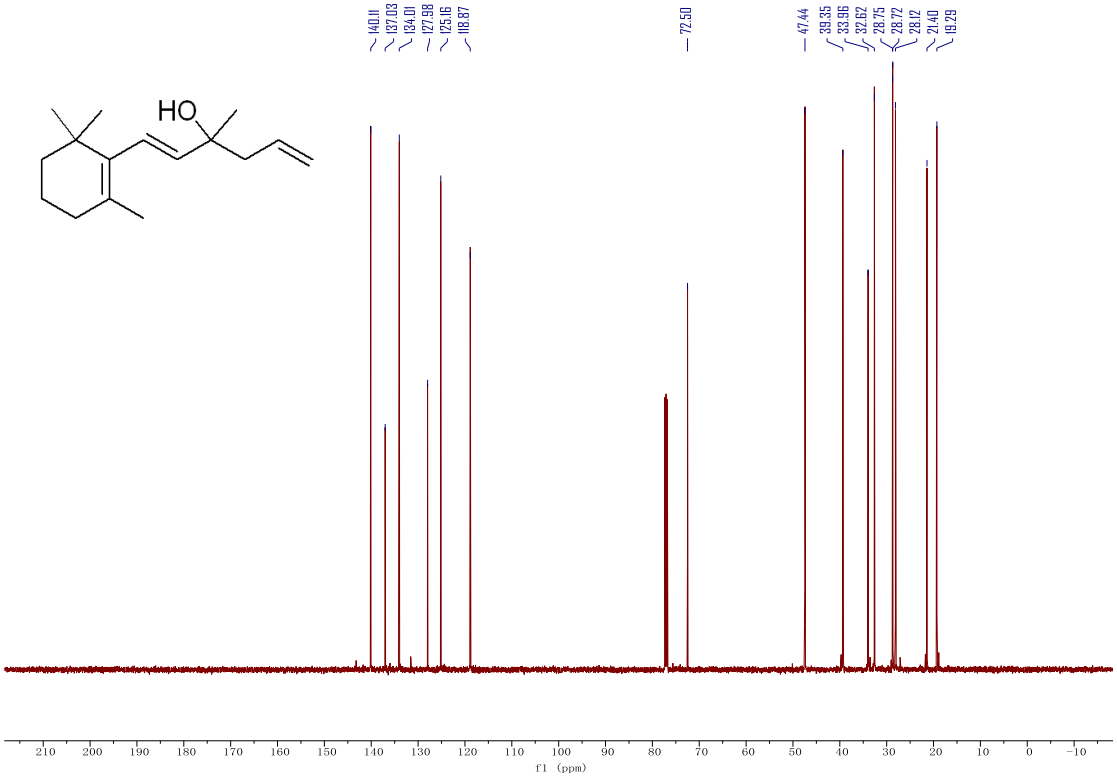

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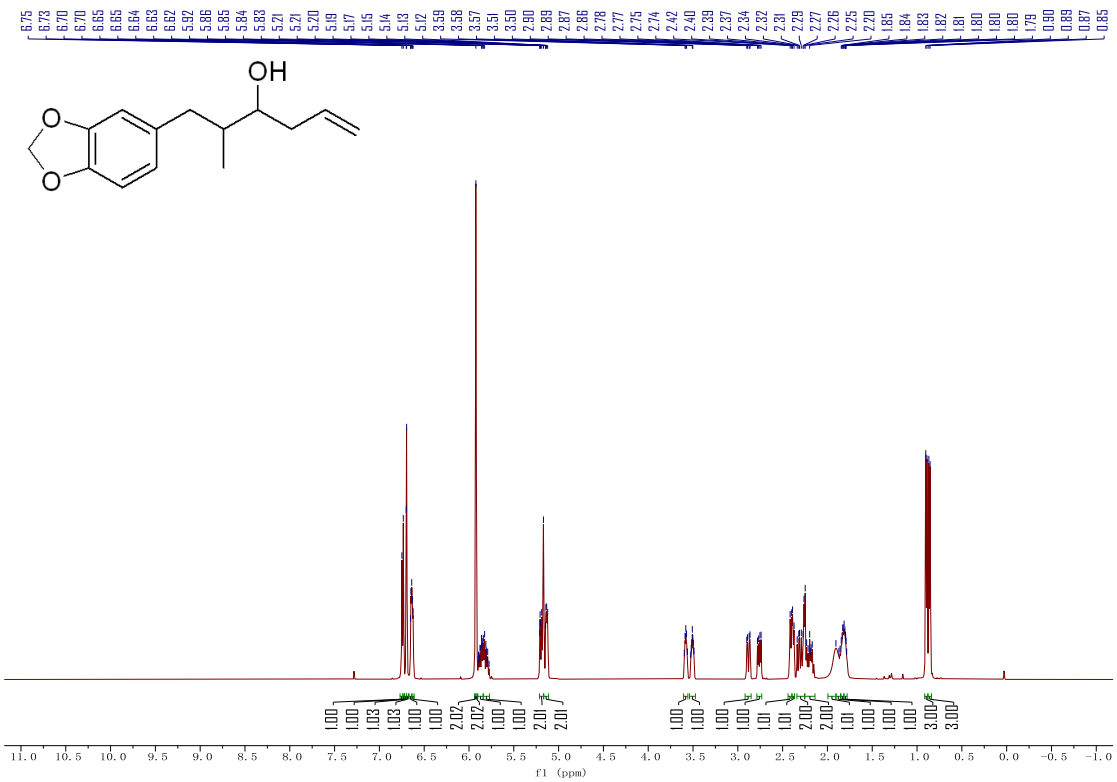
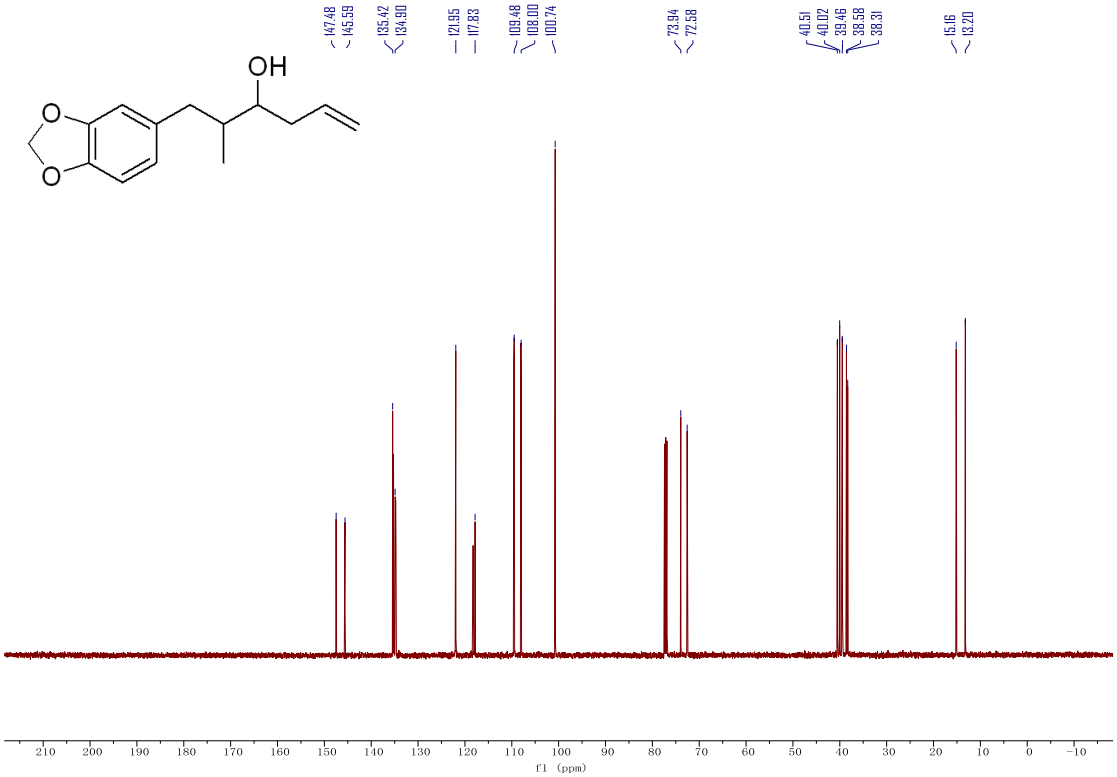


^{1}H NMR of compound **8** (500 MHz, $CDCl_3$)



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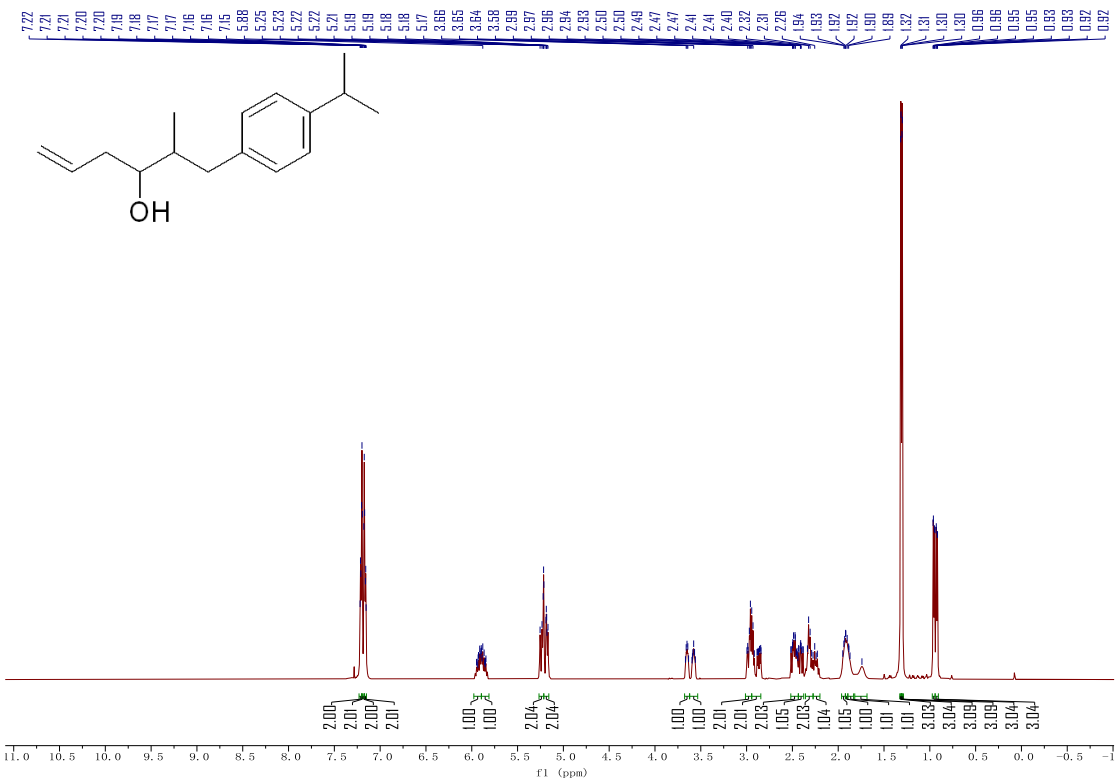
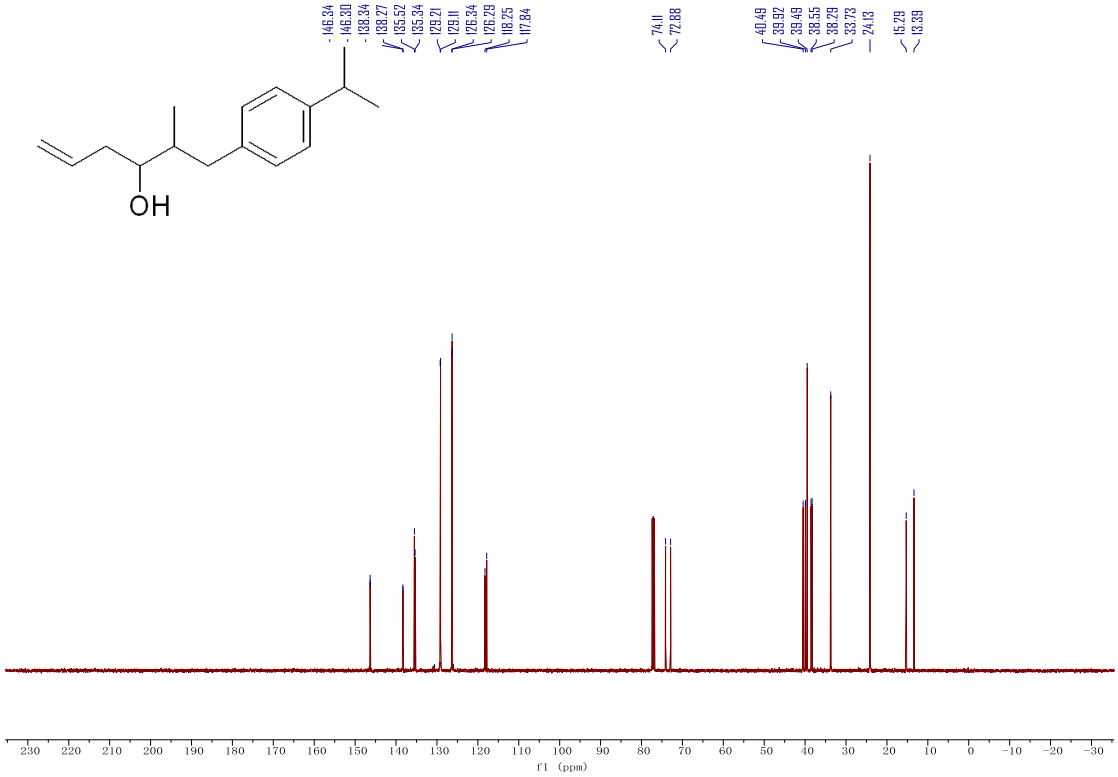


^{1}H NMR of compound **9** (500 MHz, $CDCl_3$)



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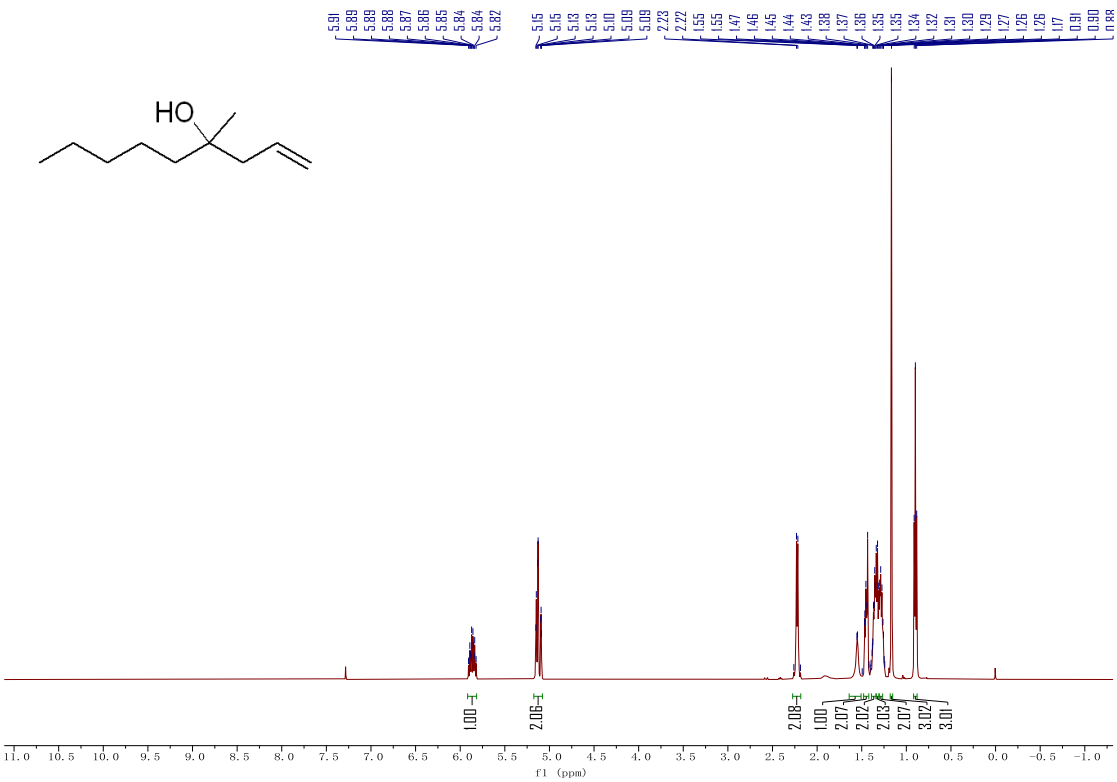

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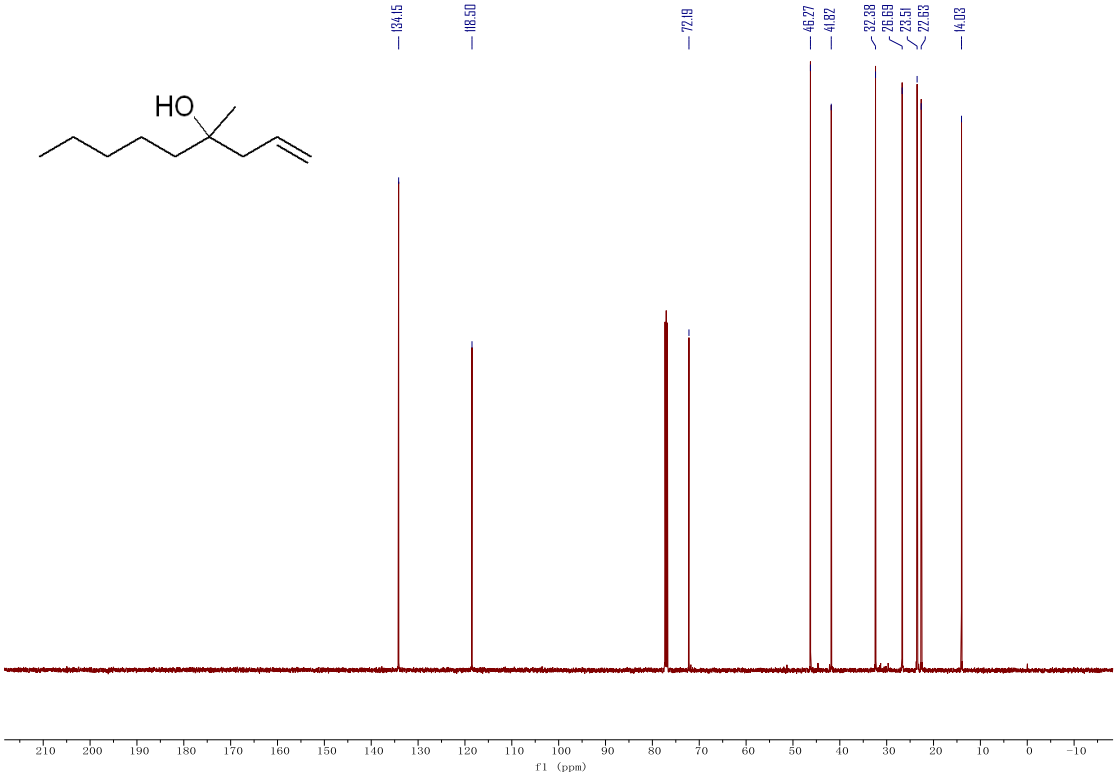

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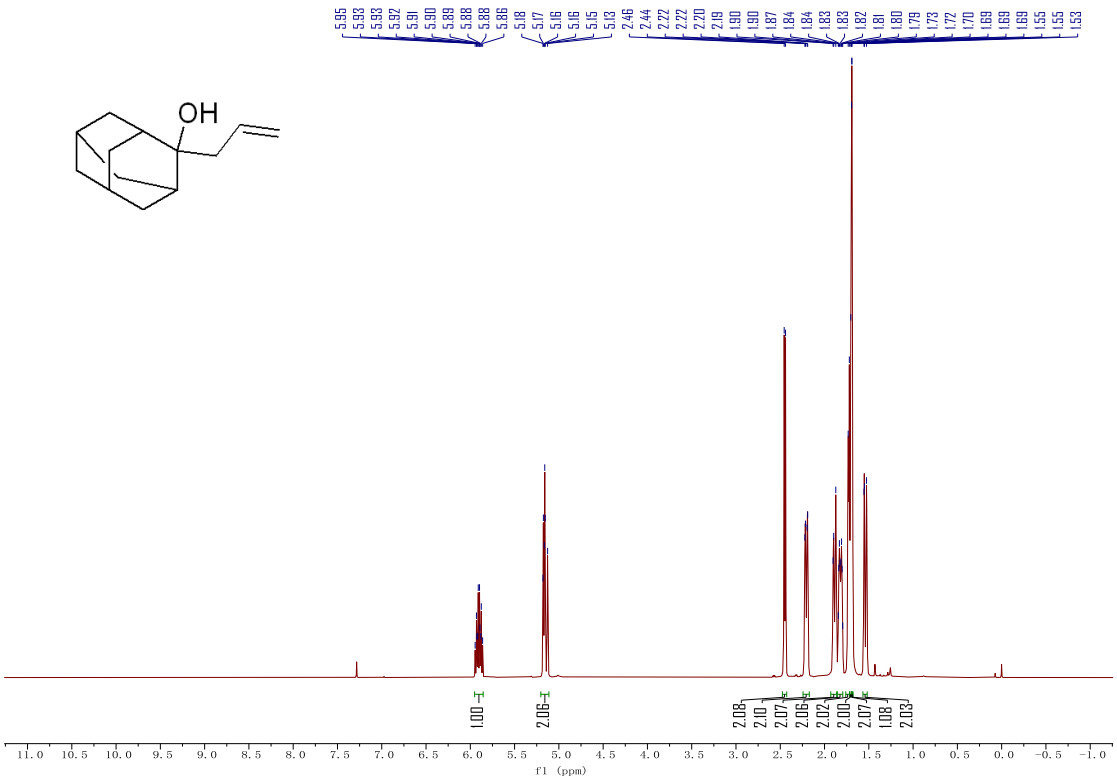
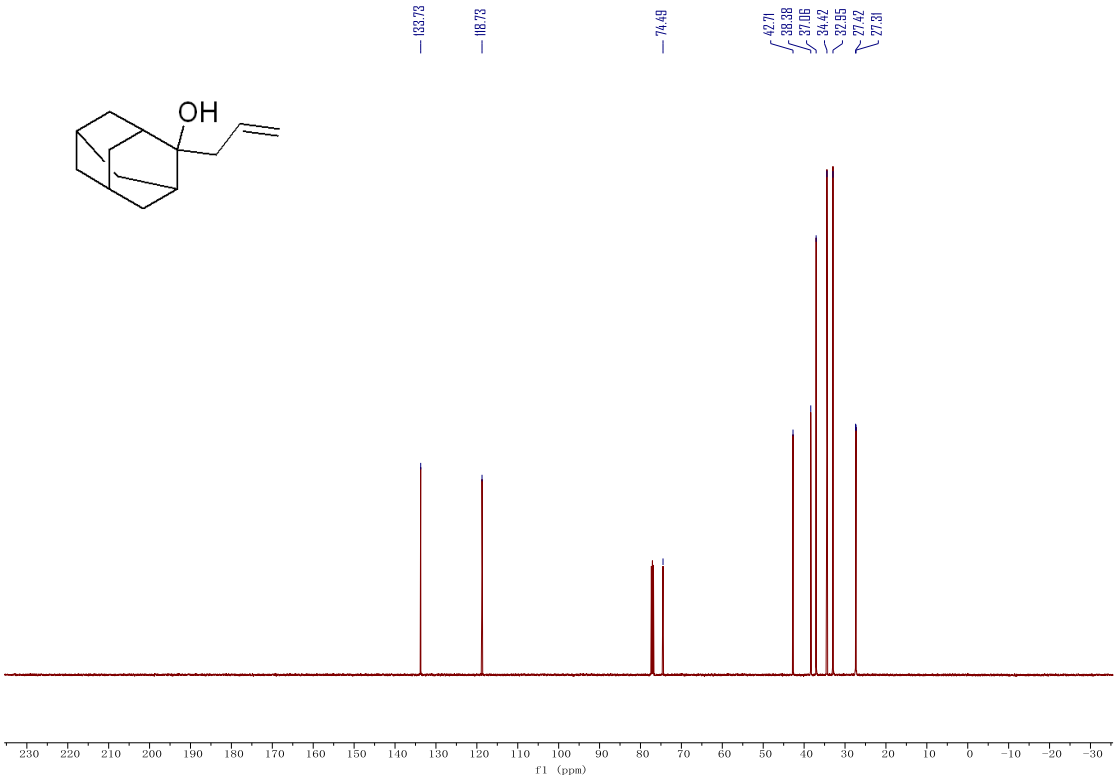
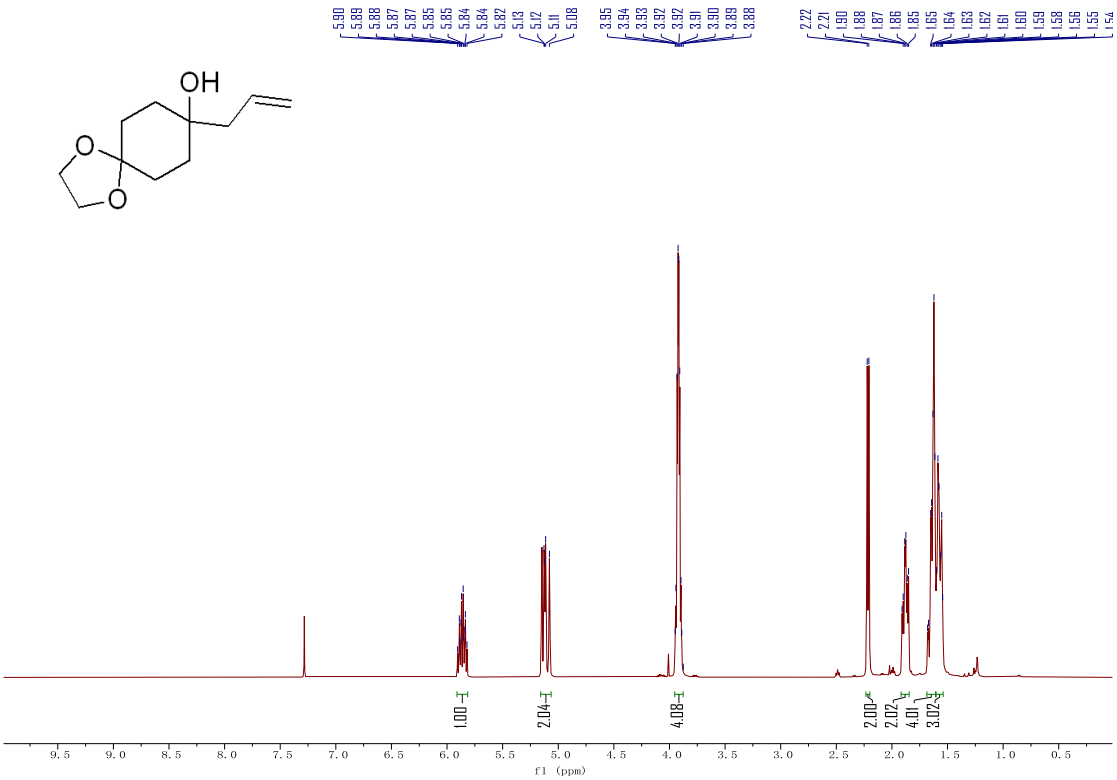


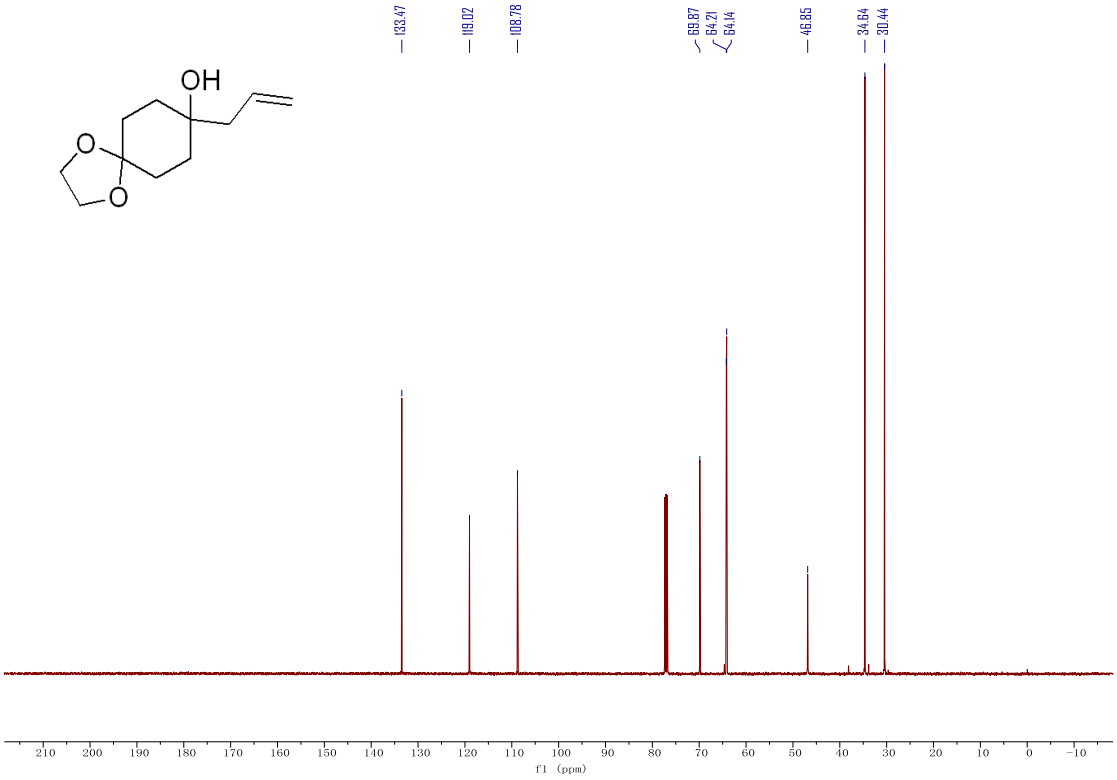
^{1}H NMR of compound **11** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **11** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **12** (500 MHz, $CDCl_3$)



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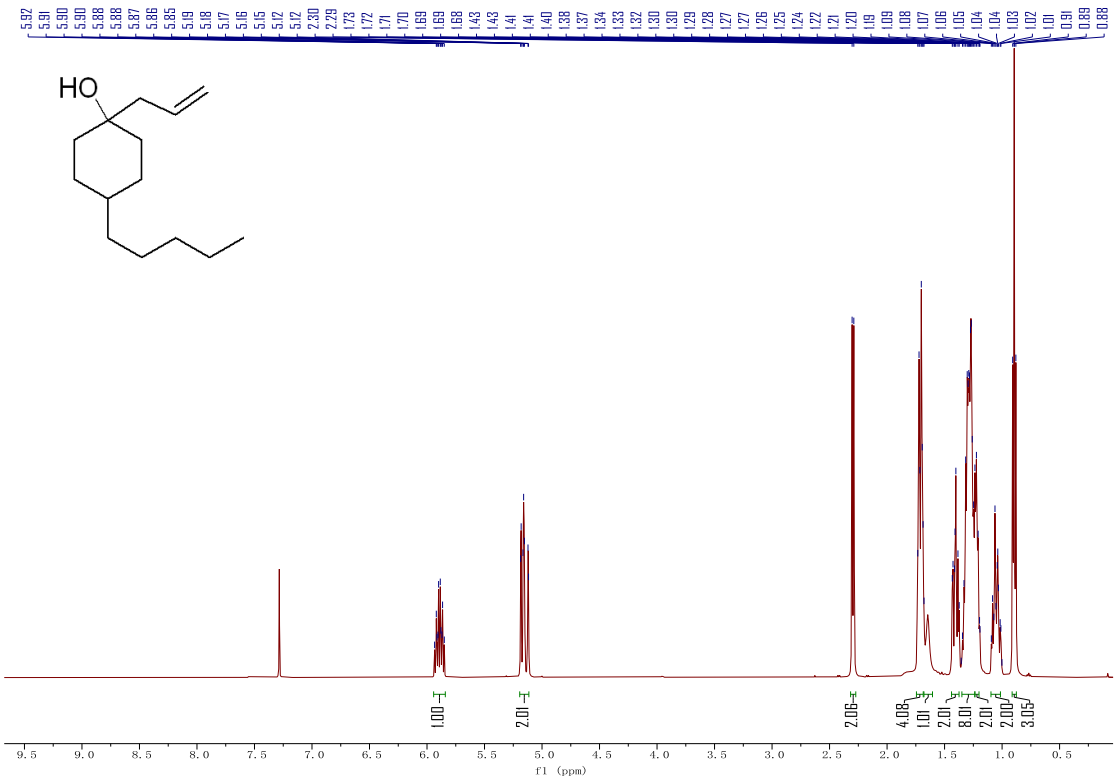

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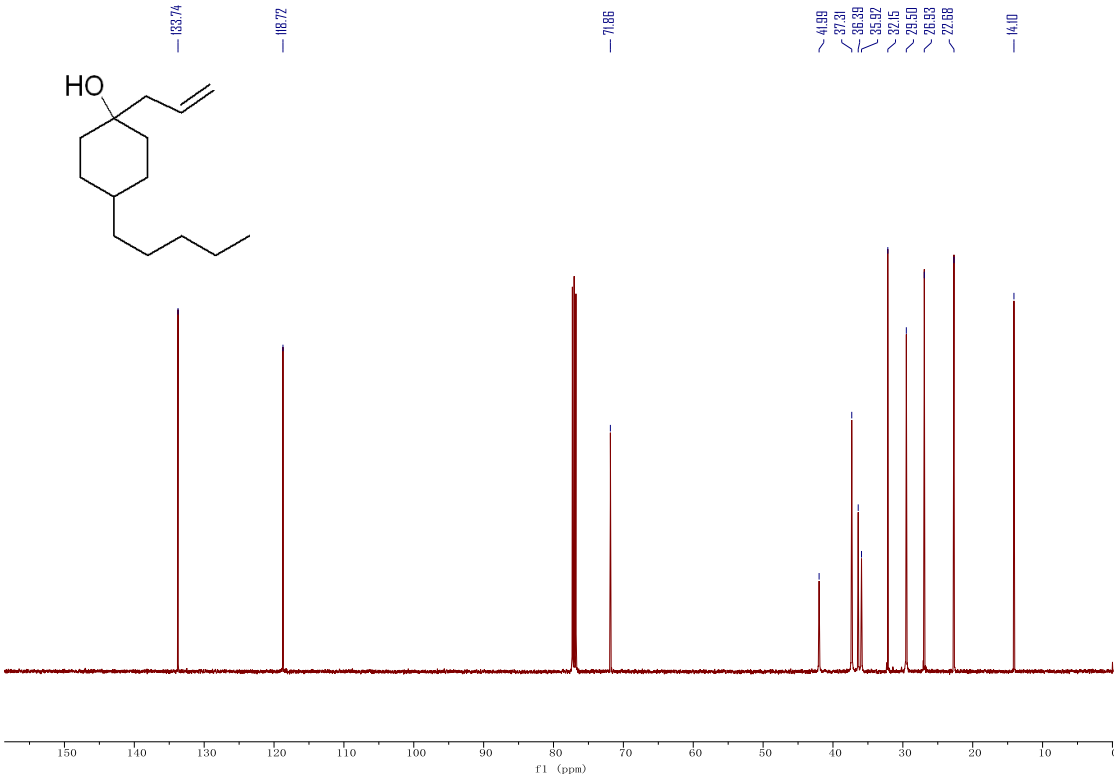

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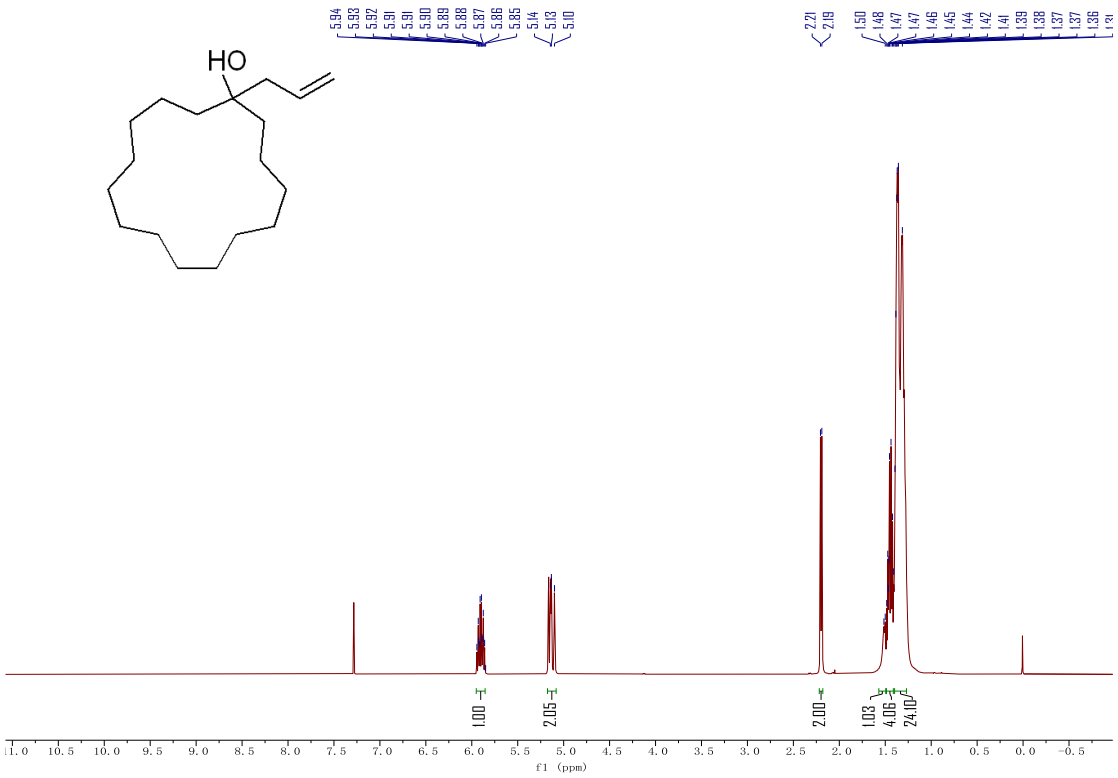
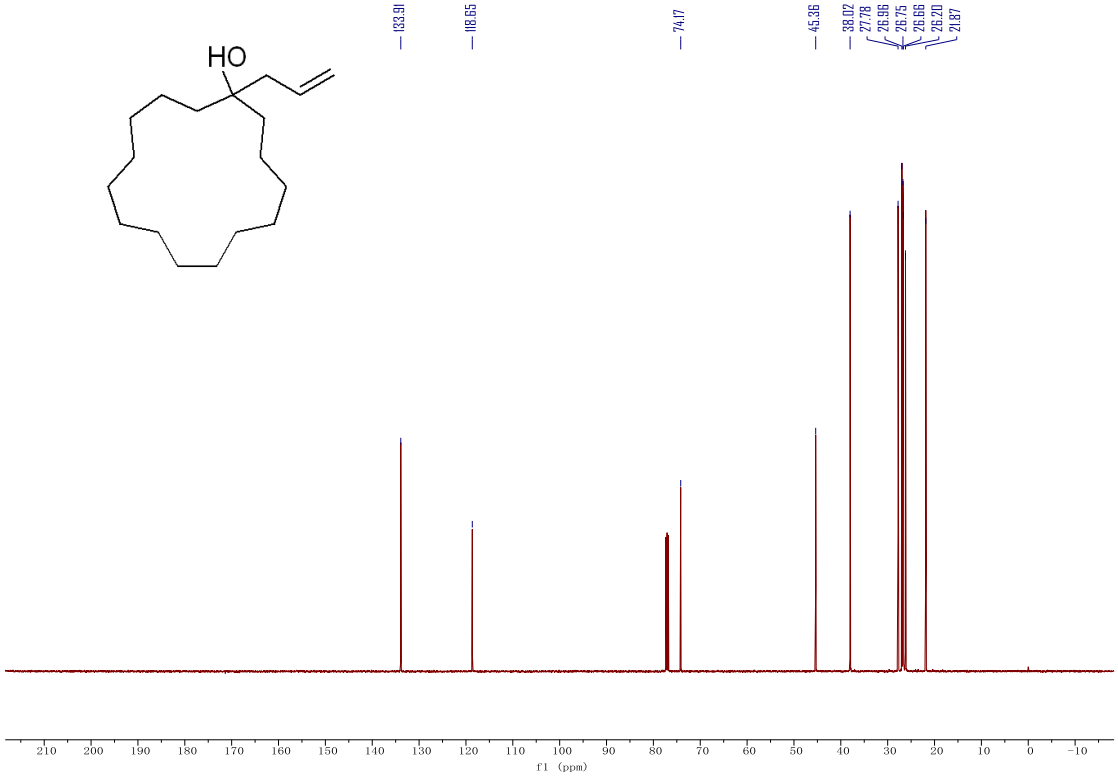


^{1}H NMR of compound **14** (500 MHz, $CDCl_3$)



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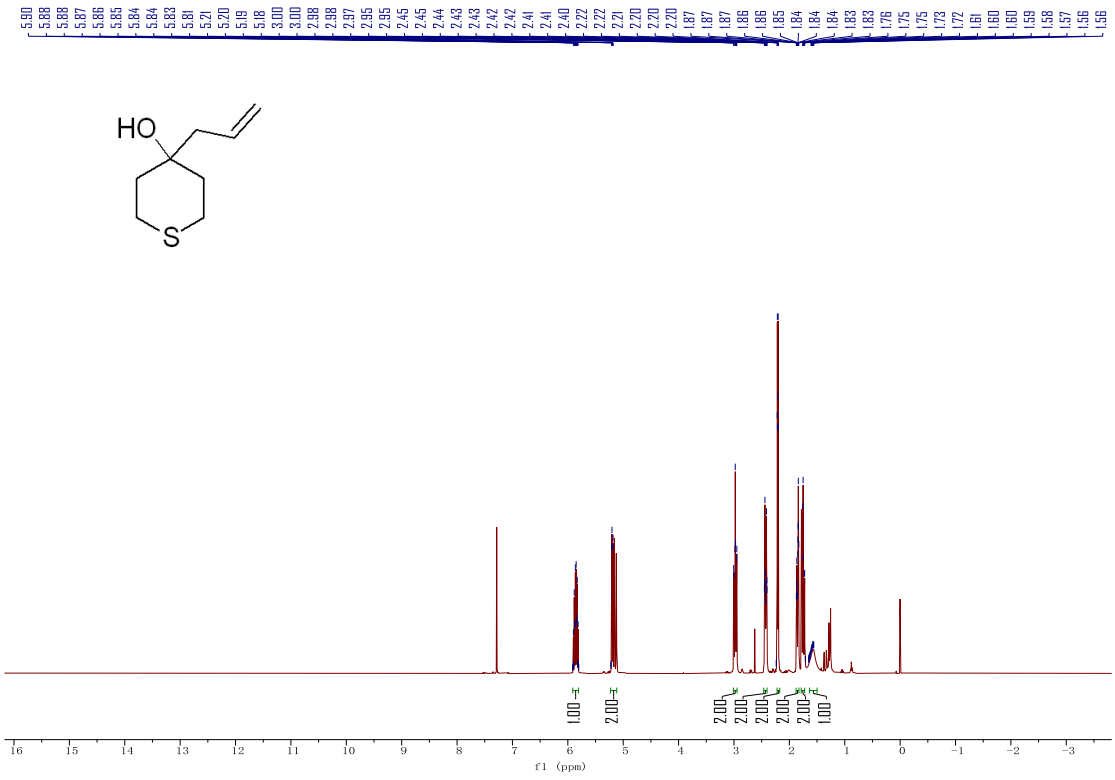
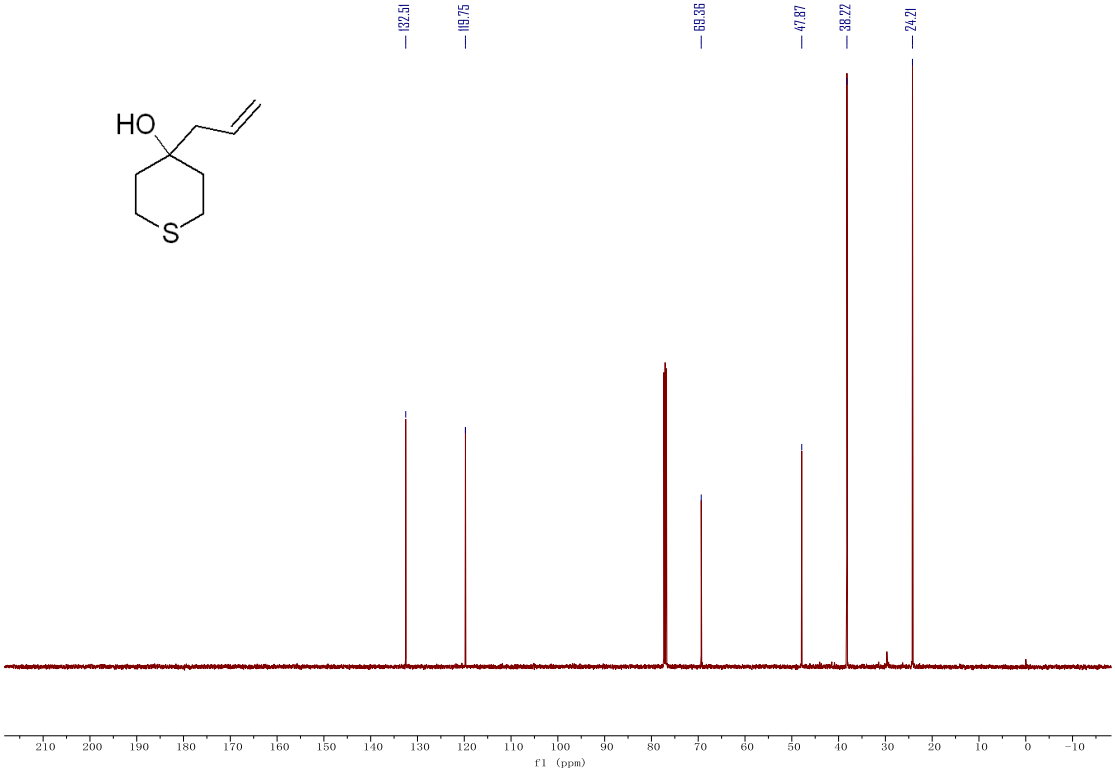
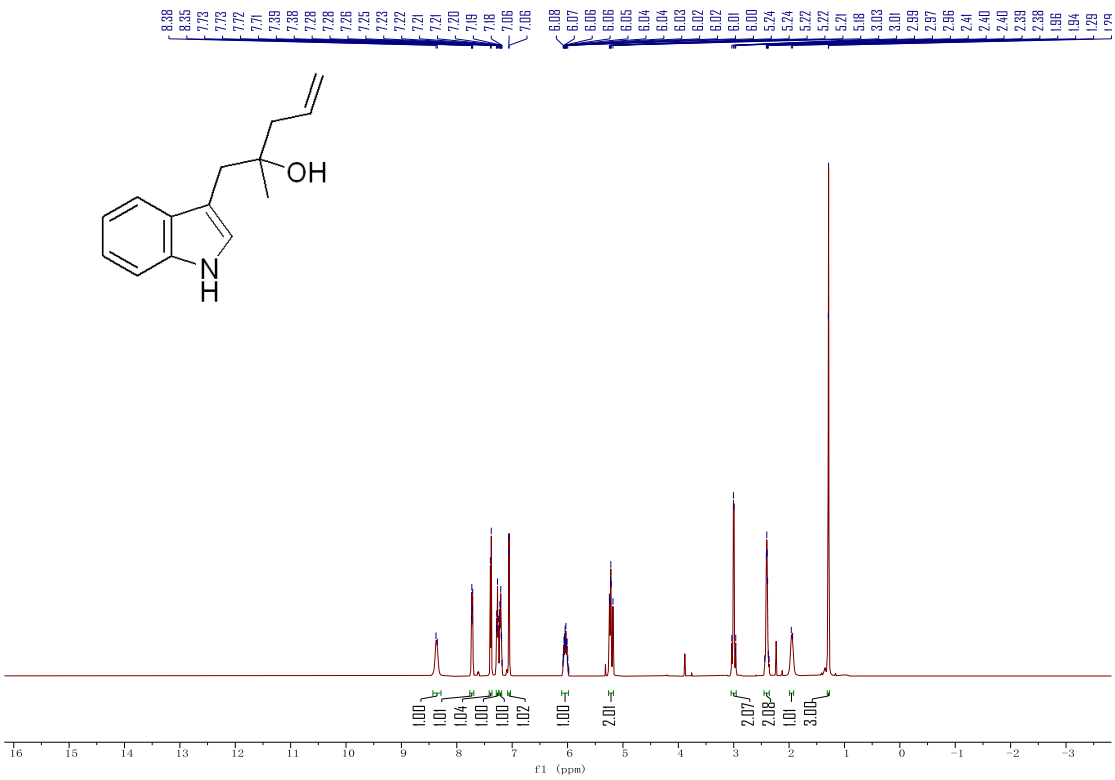


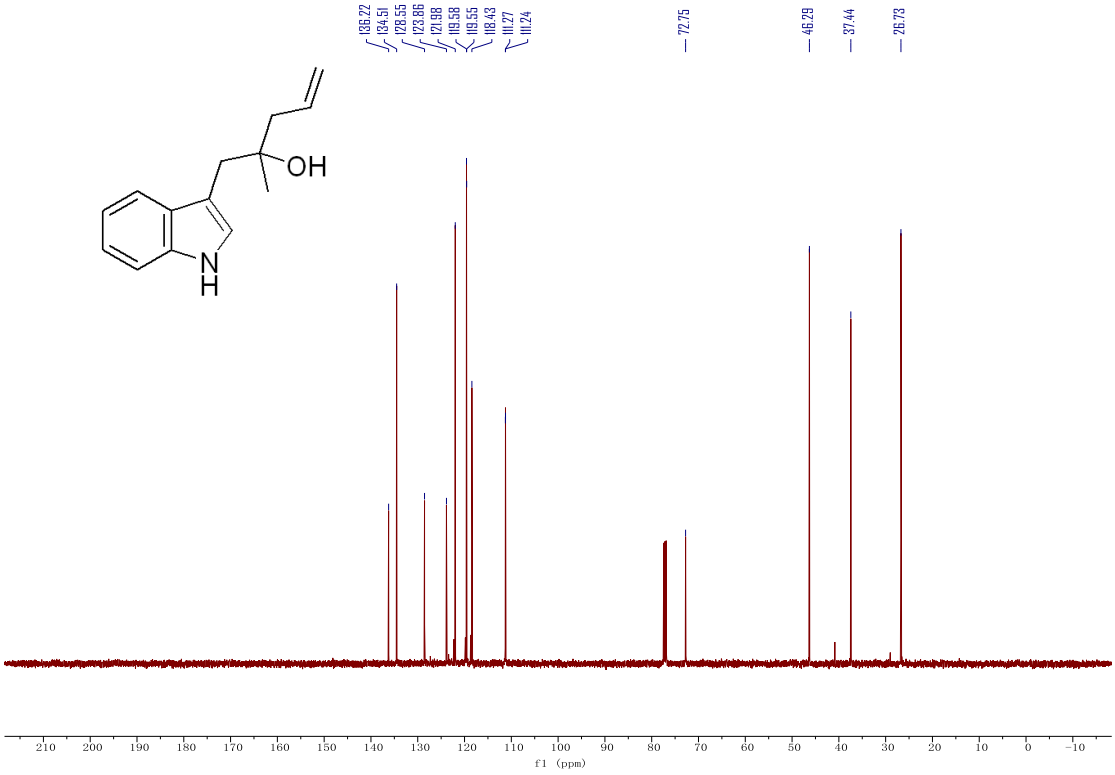
^{1}H NMR of compound **15** (500 MHz, $CDCl_3$)



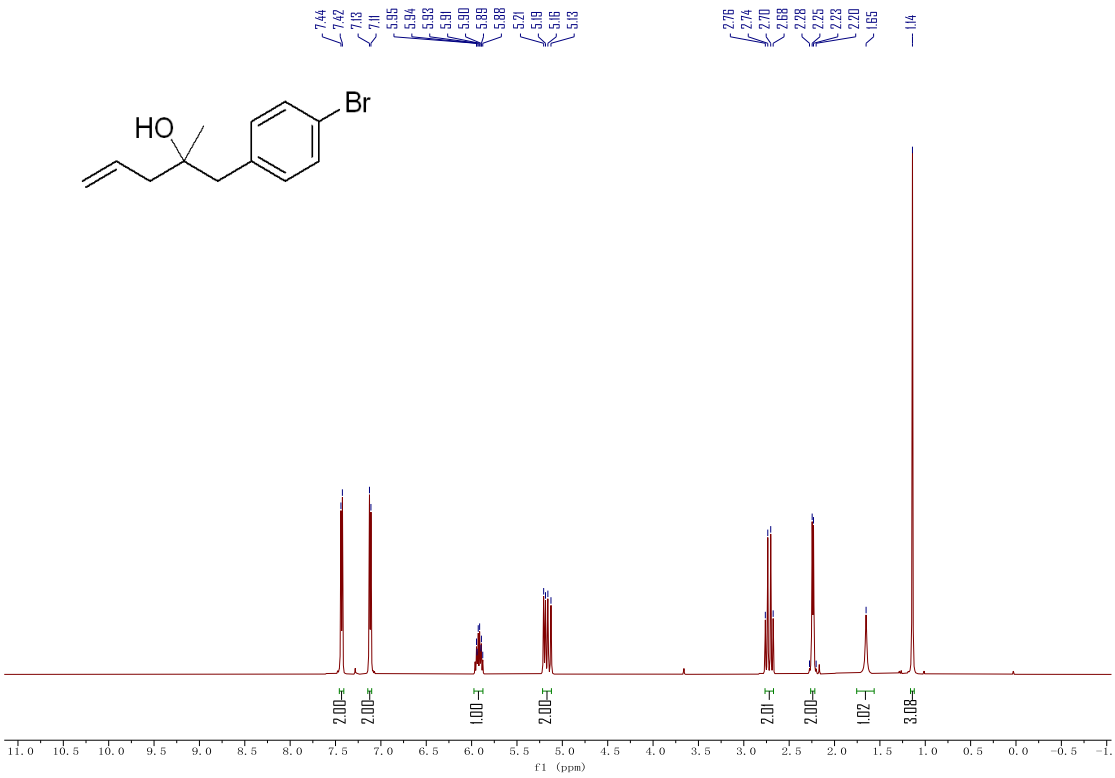
^{13}C NMR of compound **15** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **16** (500 MHz, $CDCl_3$)

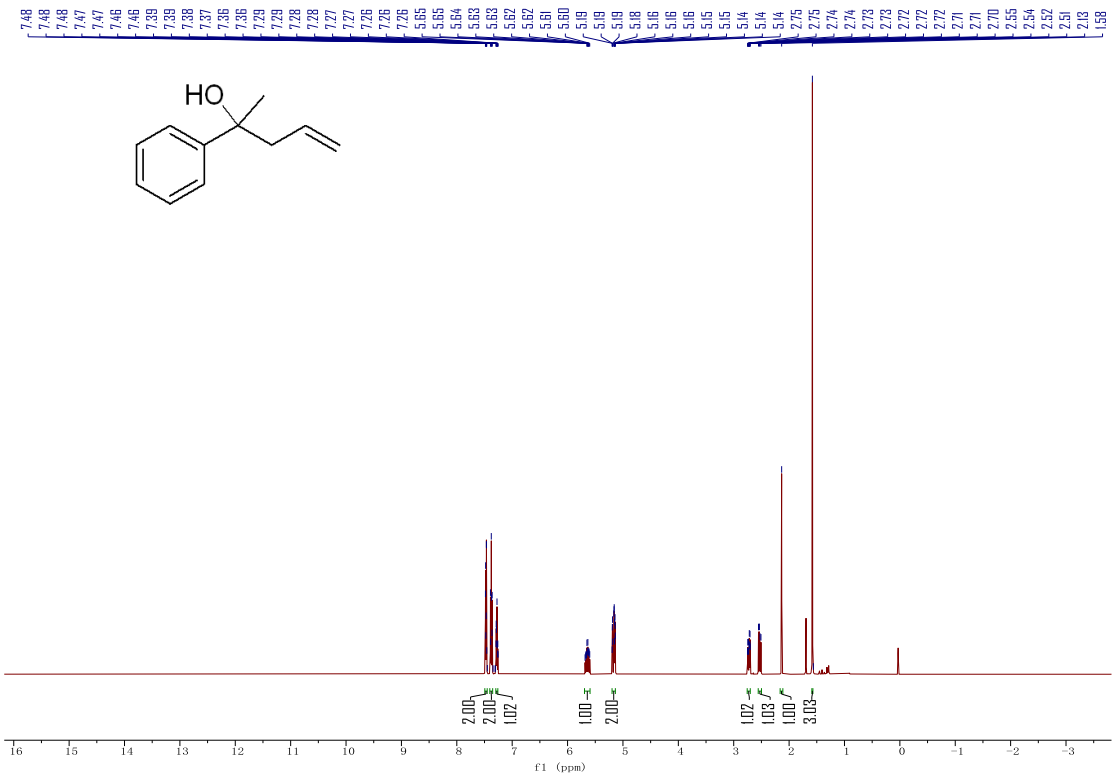


^{13}C NMR of compound **16** (126 MHz, $CDCl_3$)

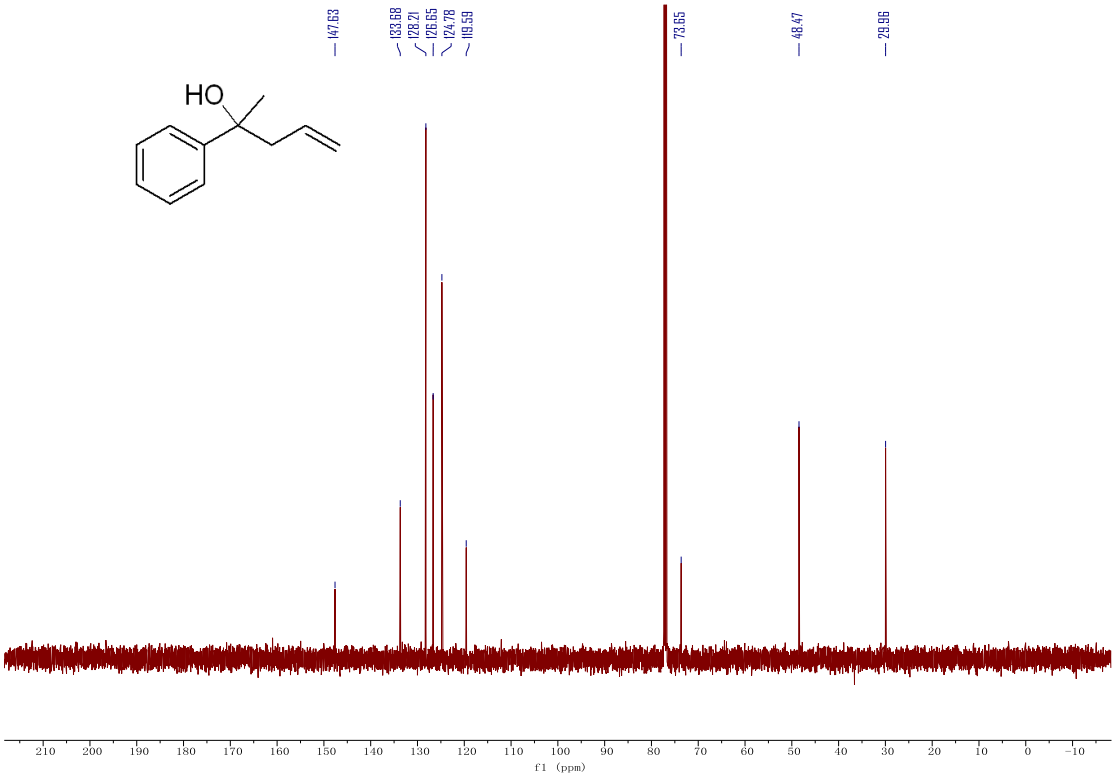


^{1}H NMR of compound **17** (500 MHz, $CDCl_3$)

^{13}C NMR of compound **17** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **18** (500 MHz, $CDCl_3$)



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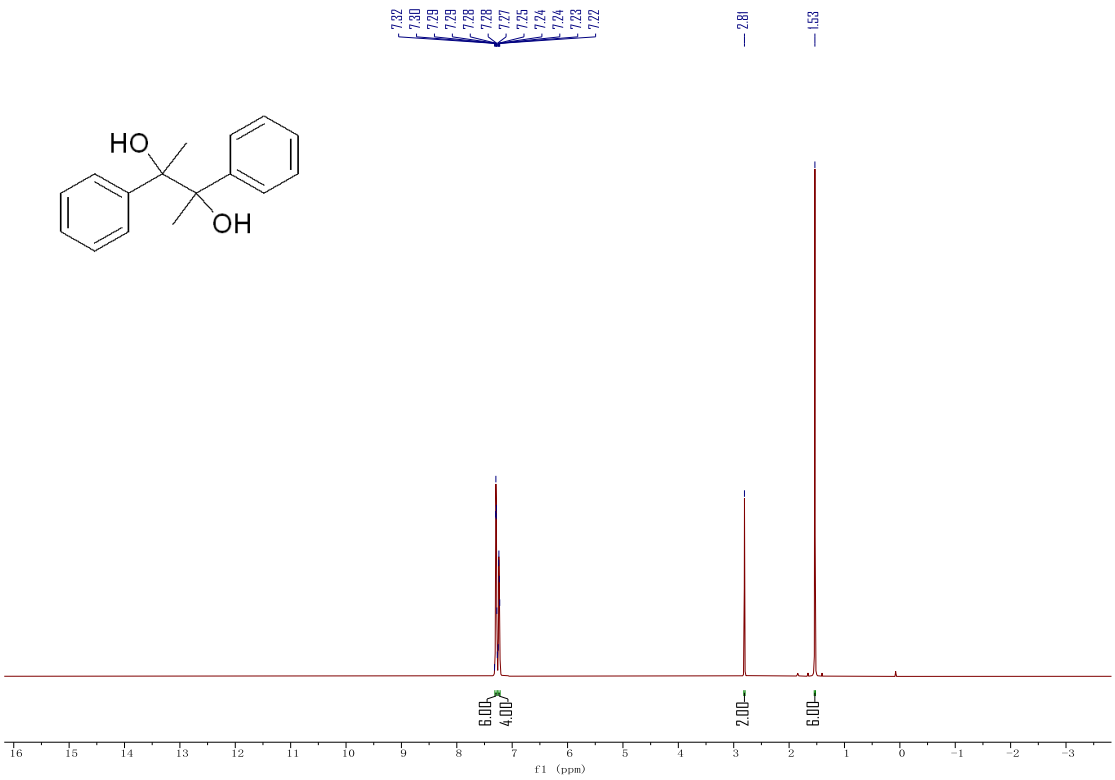
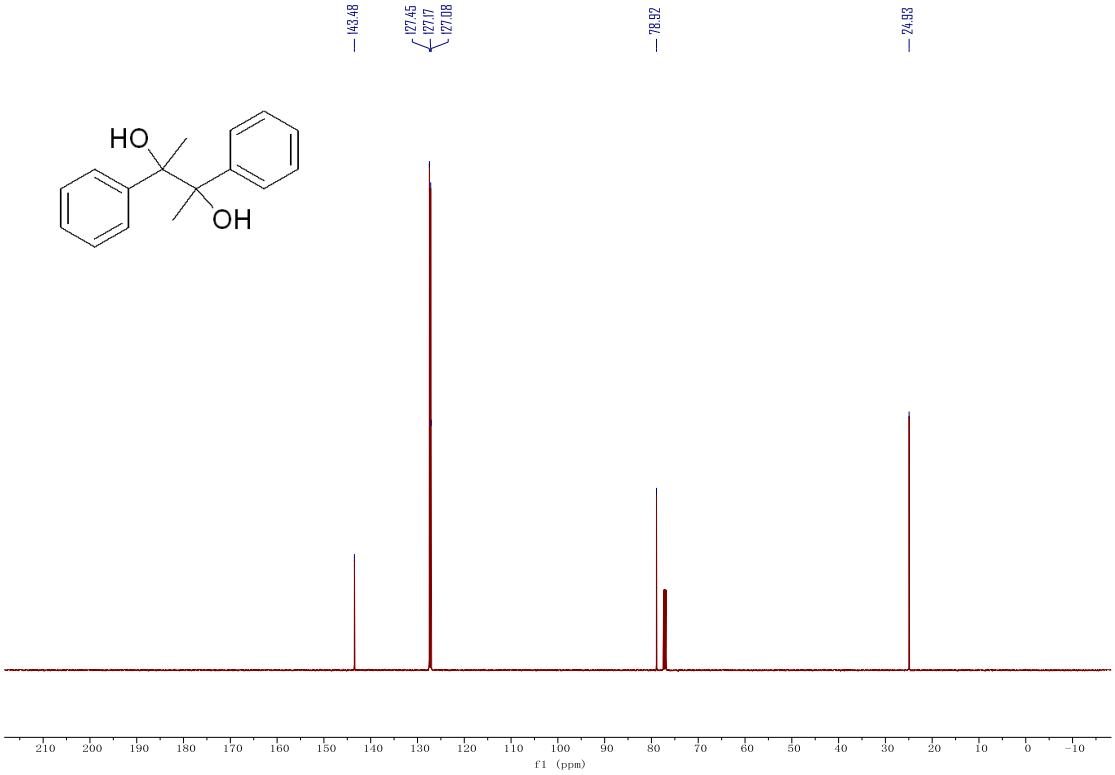
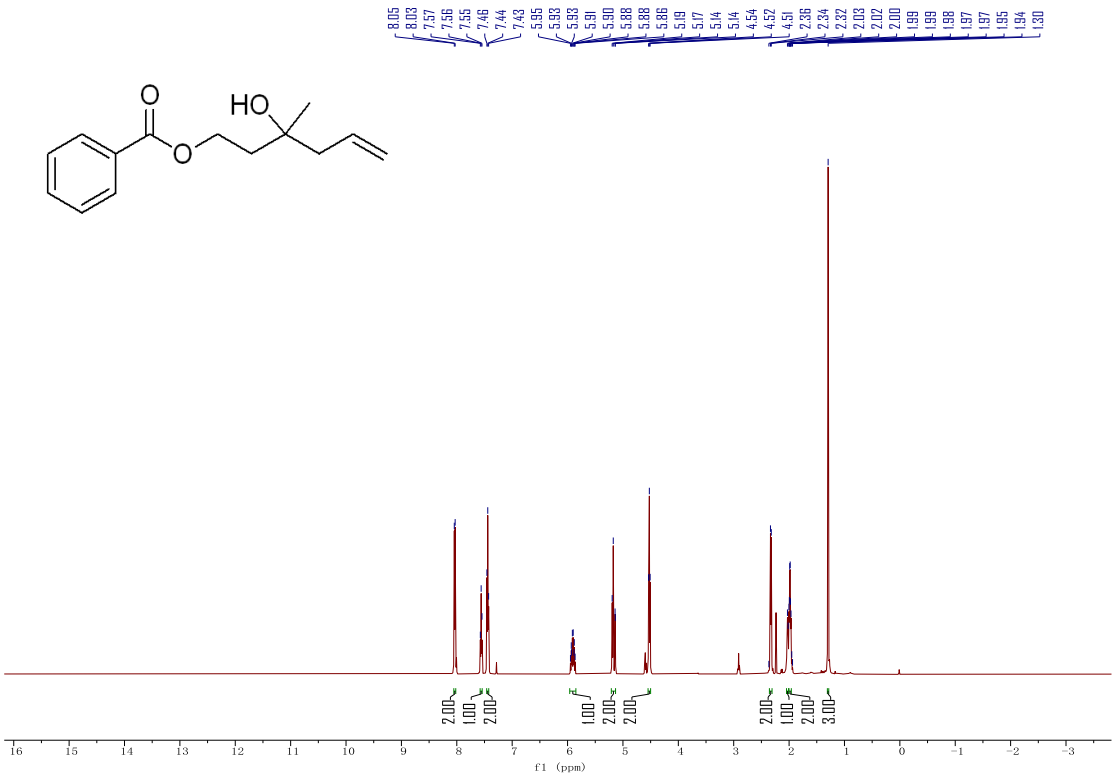


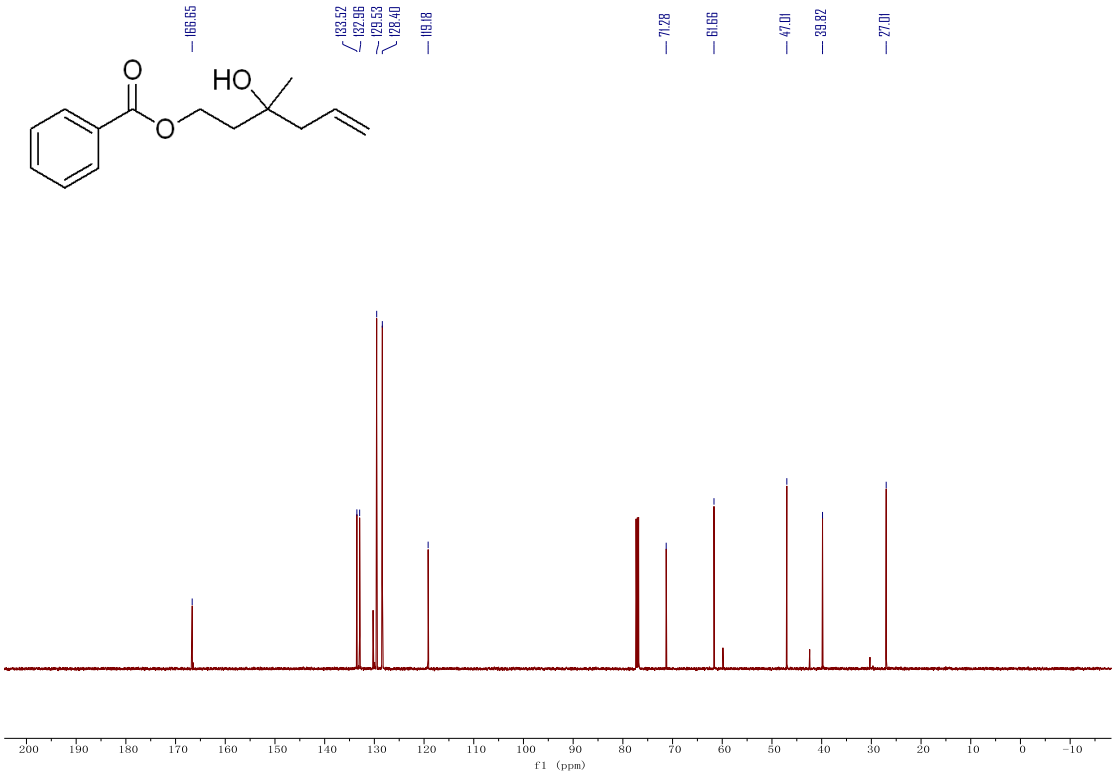
^{1}H NMR of compound **18-byproduct** (500 MHz, $CDCl_3$)



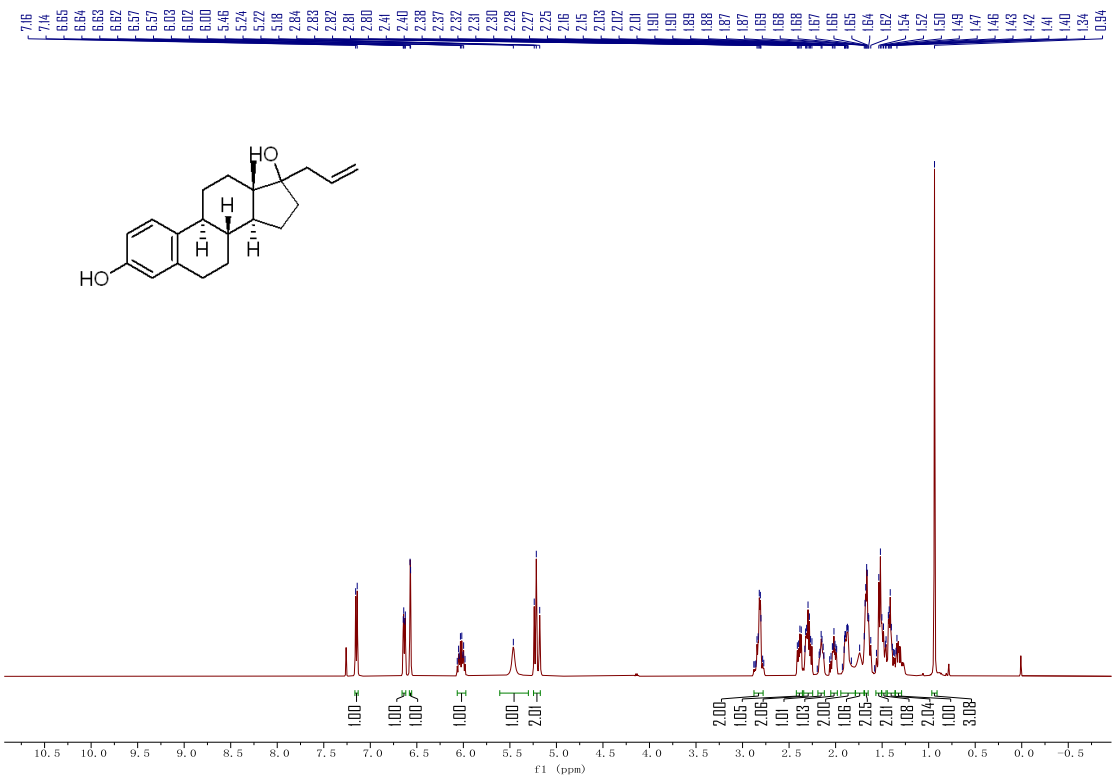
^{13}C NMR of compound **18-byproduct** (126 MHz, $CDCl_3$)



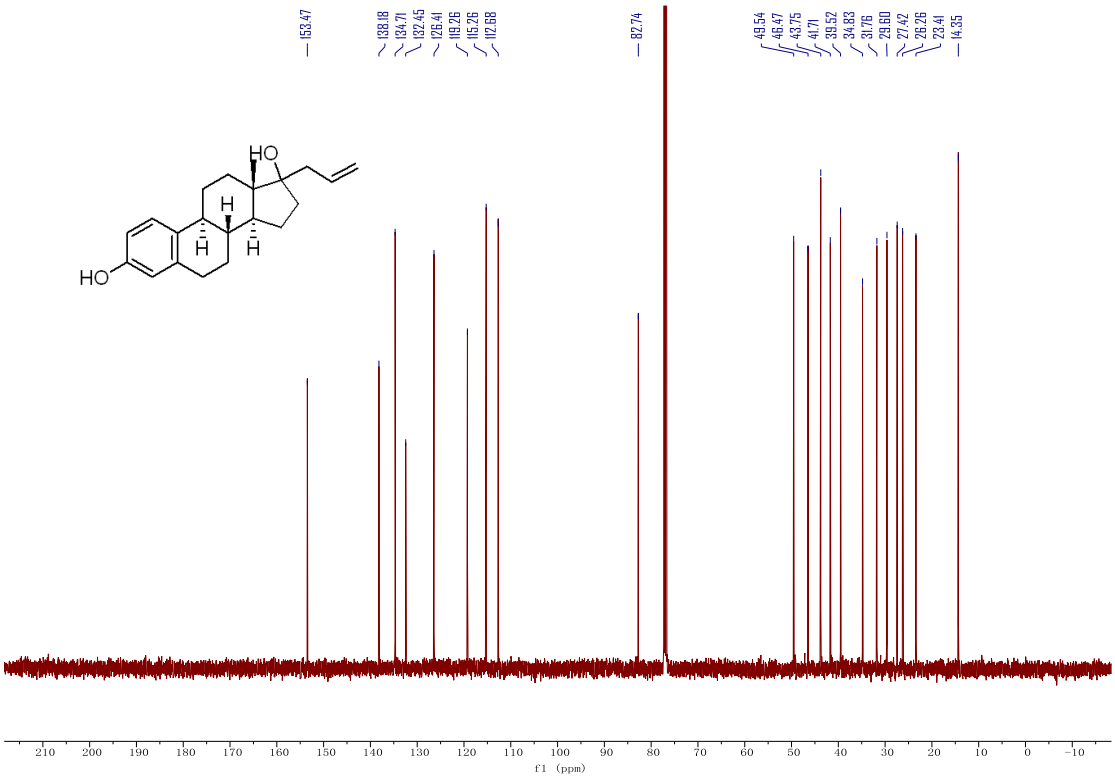
^{1}H NMR of compound **19** (500 MHz, $CDCl_3$)



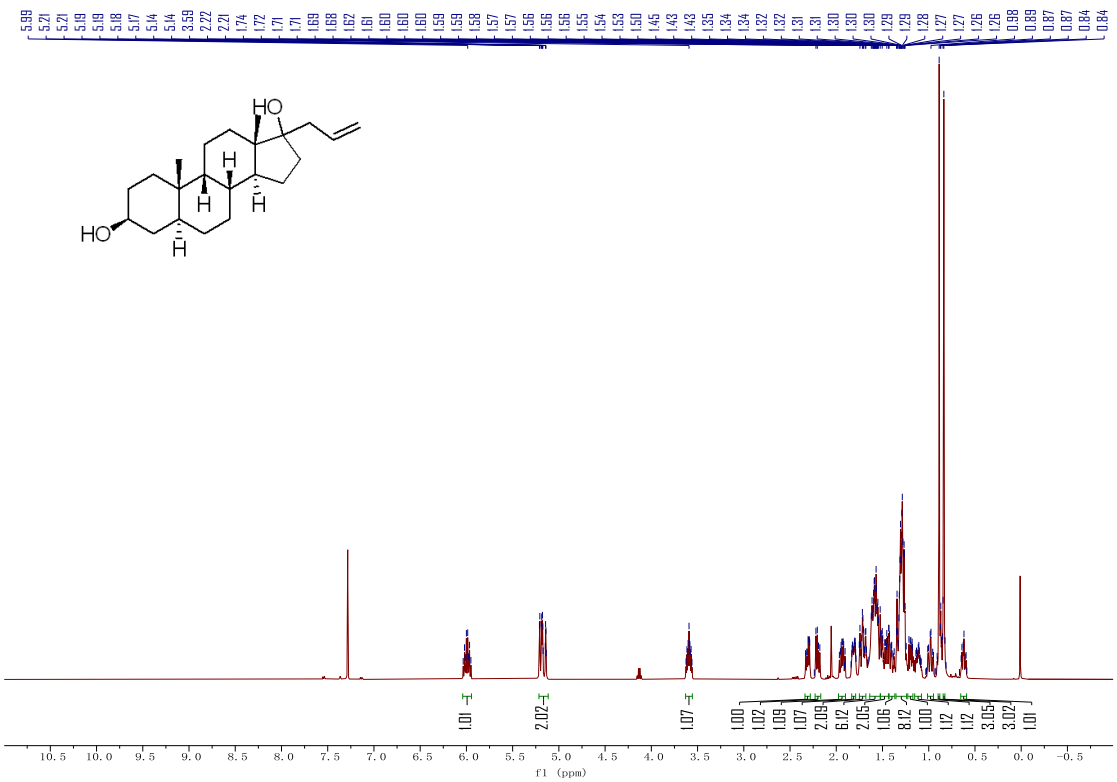
^{13}C NMR of compound **19** (126 MHz, $CDCl_3$)



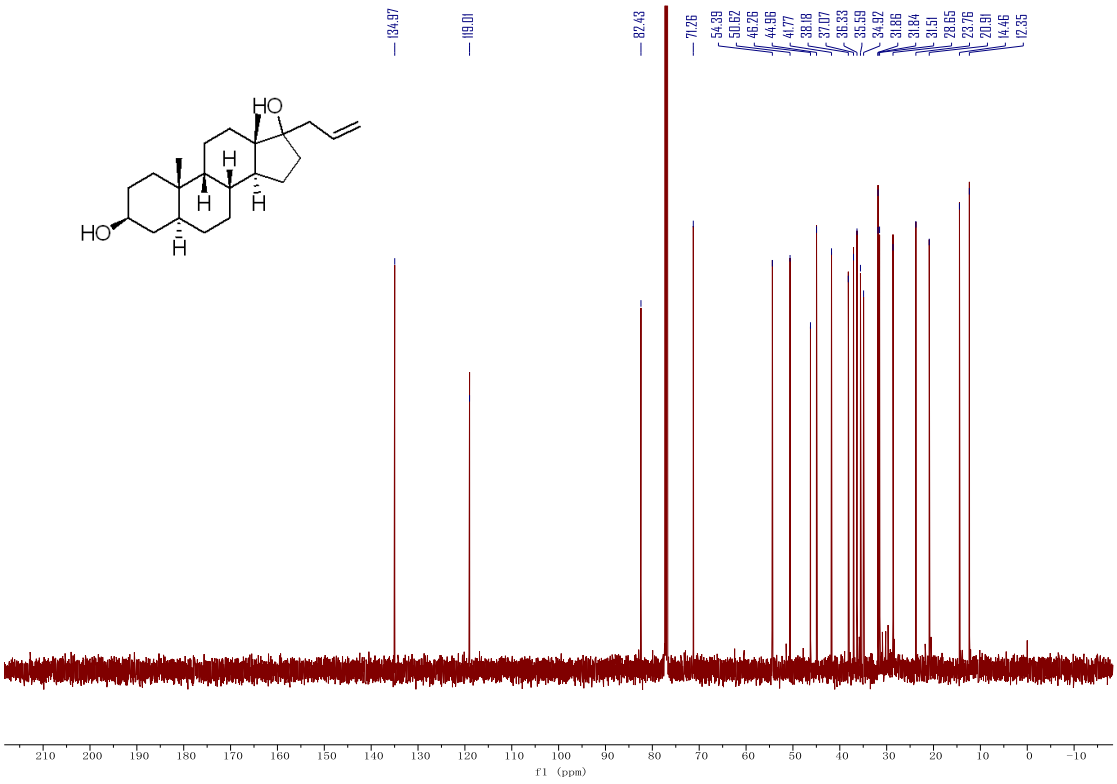
^{1}H NMR of compound **20** (500 MHz, $CDCl_3$)



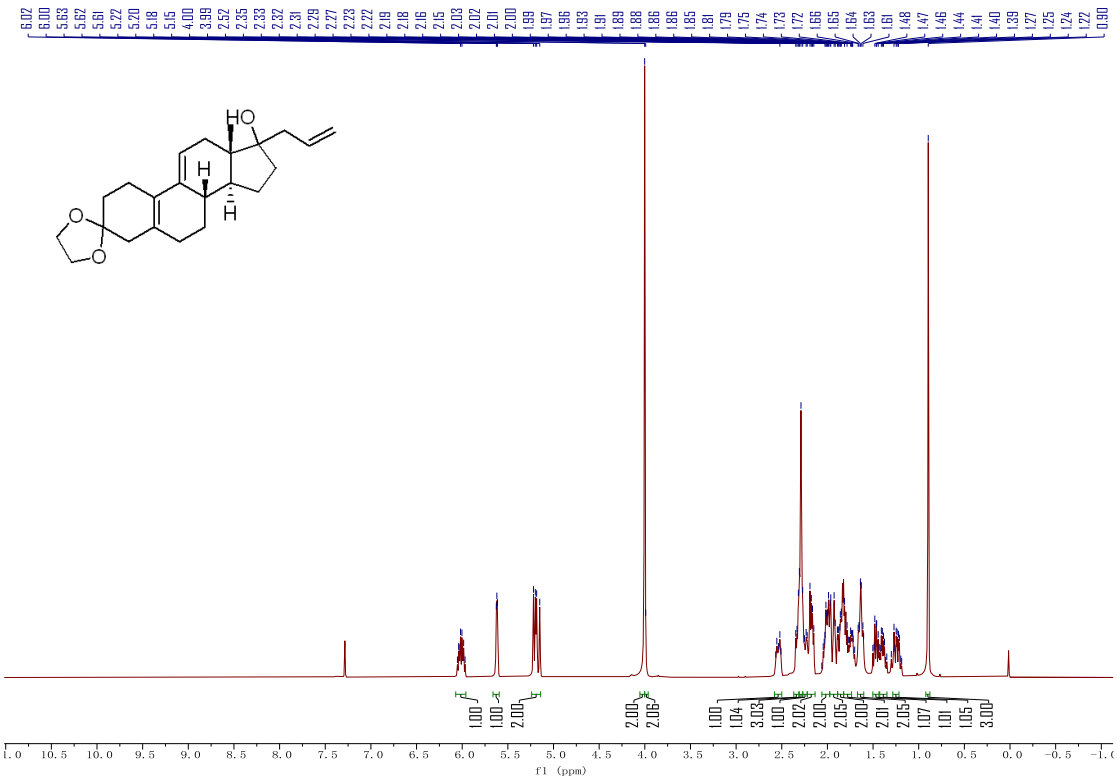
^{13}C NMR of compound **20** (126 MHz, $CDCl_3$)



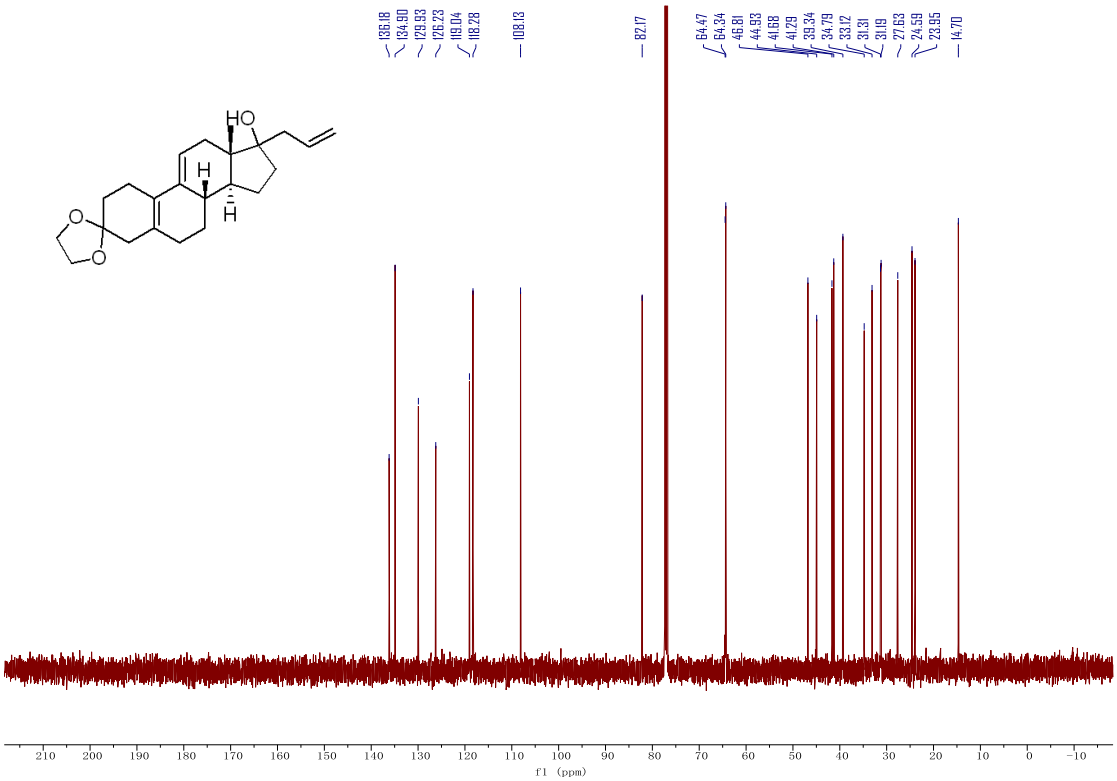
^{1}H NMR of compound **21** (500 MHz, $CDCl_3$)



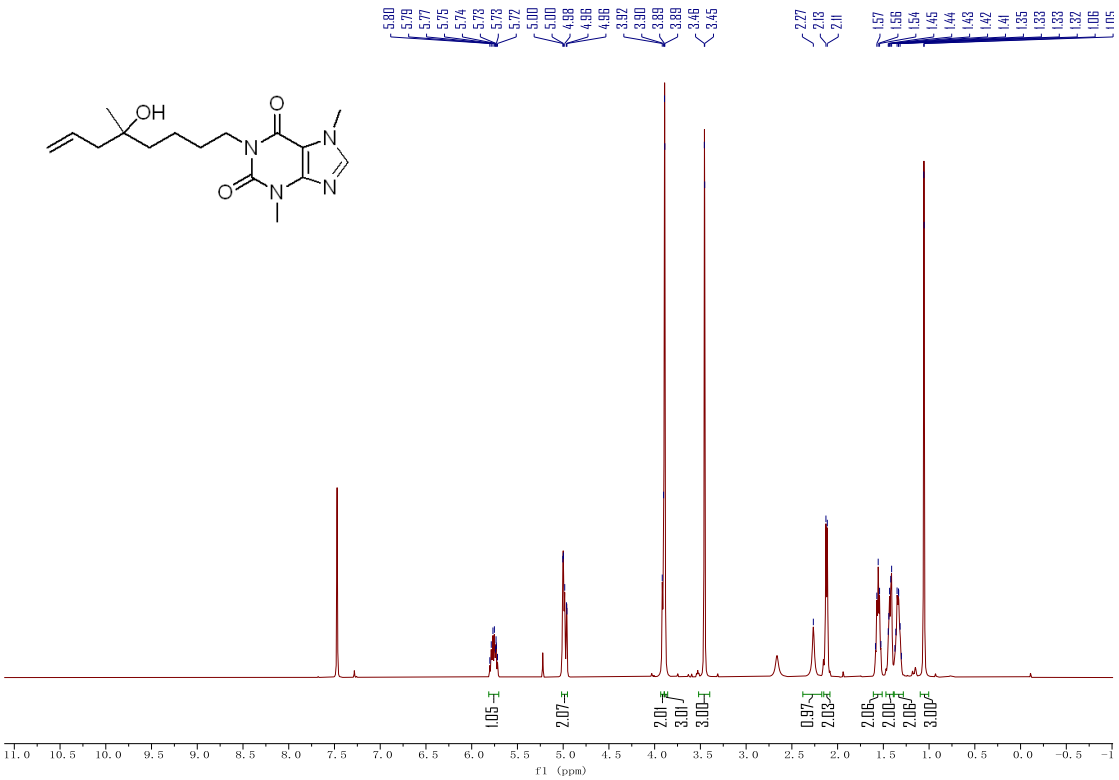
^{13}C NMR of compound **21** (126 MHz, $CDCl_3$)



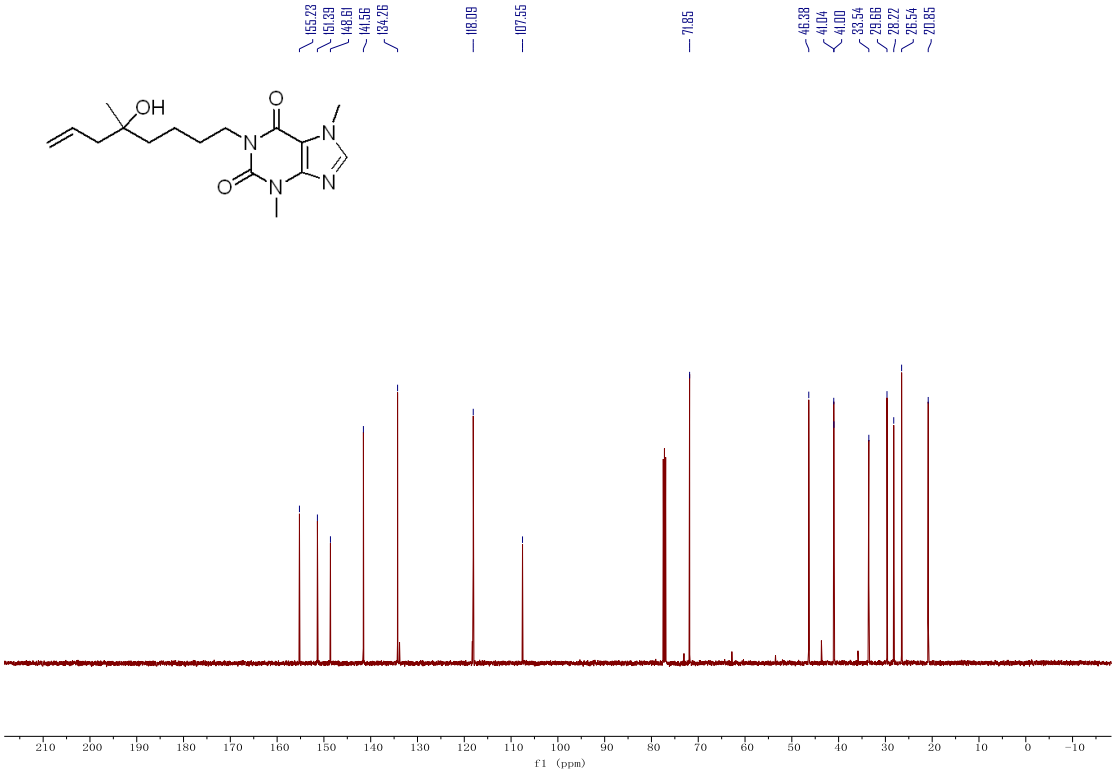
^{1}H NMR of compound **22** (500 MHz, $CDCl_3$)



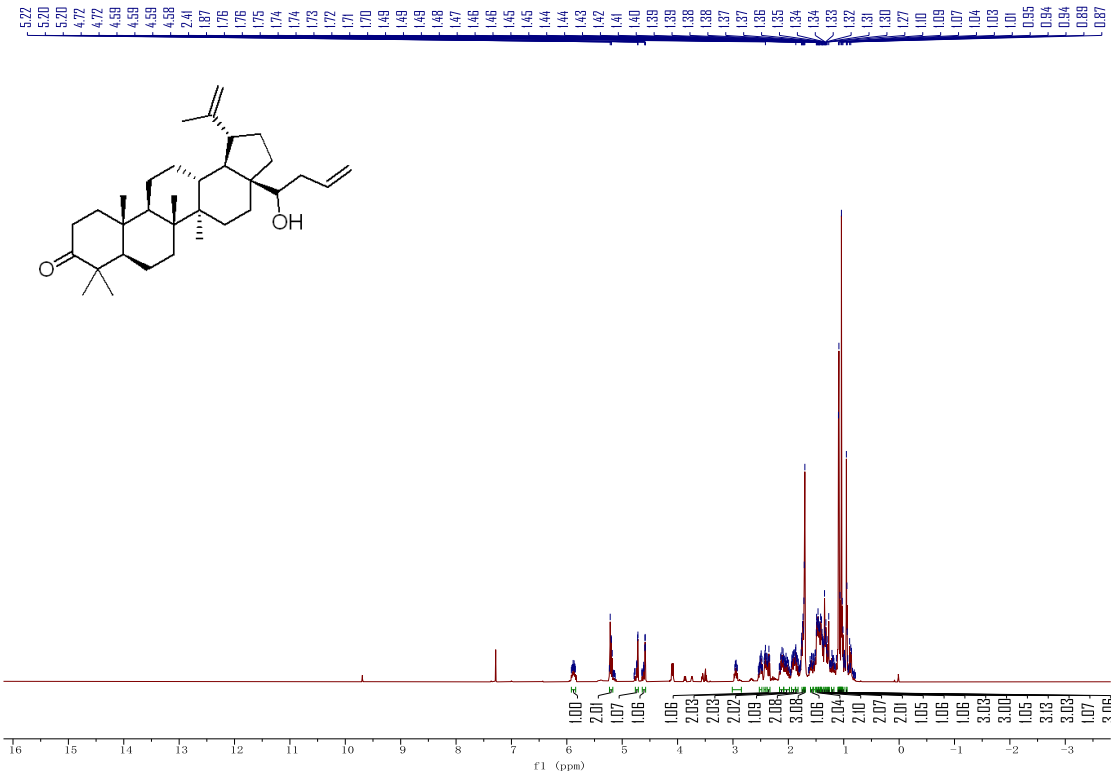
^{13}C NMR of compound **22** (126 MHz, $CDCl_3$)



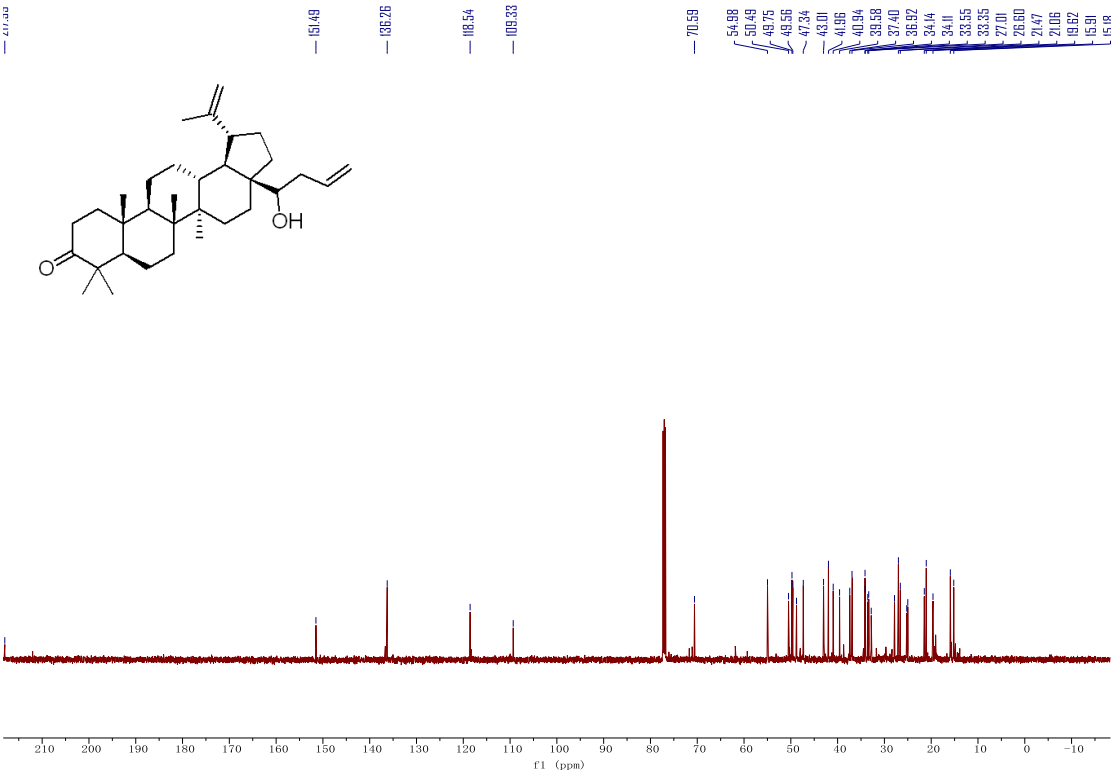
^{1}H NMR of compound **23** (500 MHz, $CDCl_3$)



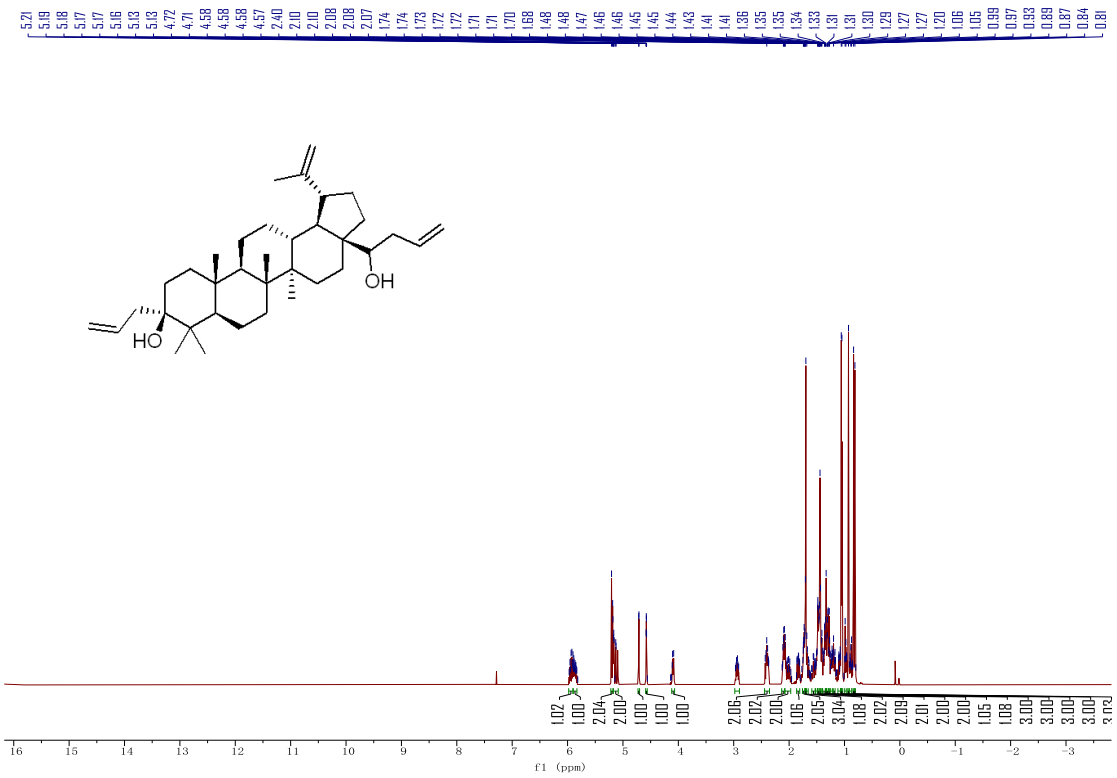
^{13}C NMR of compound **23** (126 MHz, $CDCl_3$)



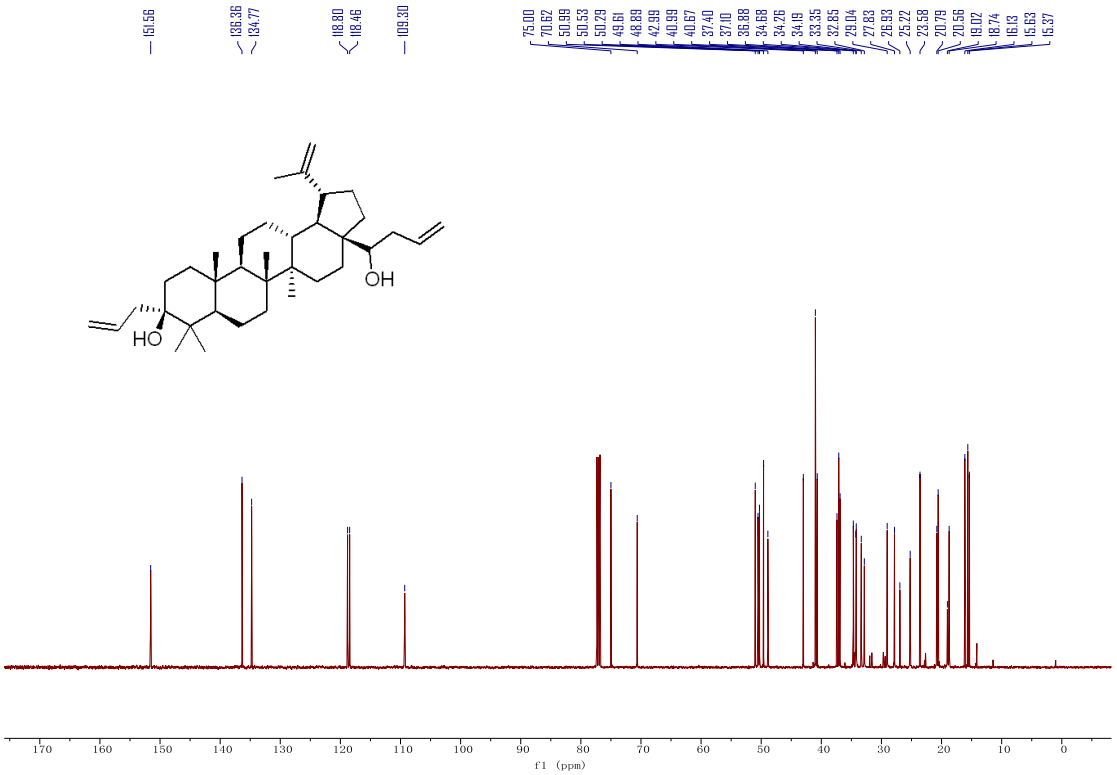
^{1}H NMR of compound **24** (500 MHz, $CDCl_3$)



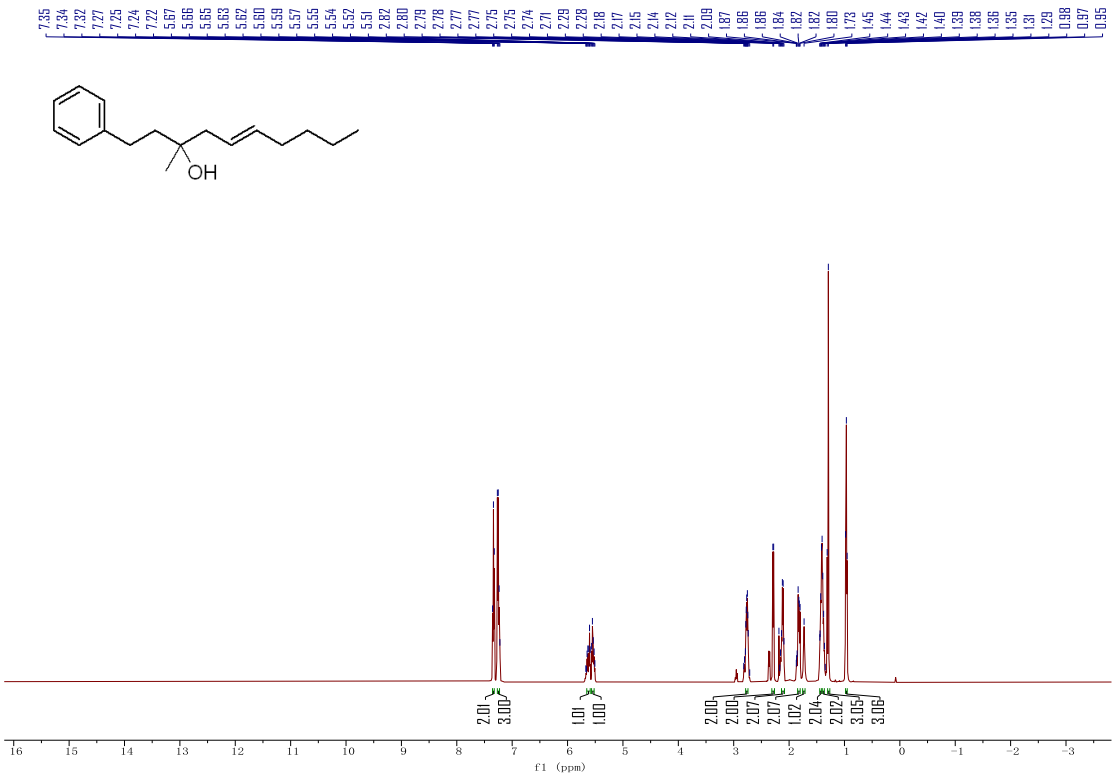
^{13}C NMR of compound **24** (126 MHz, $CDCl_3$)



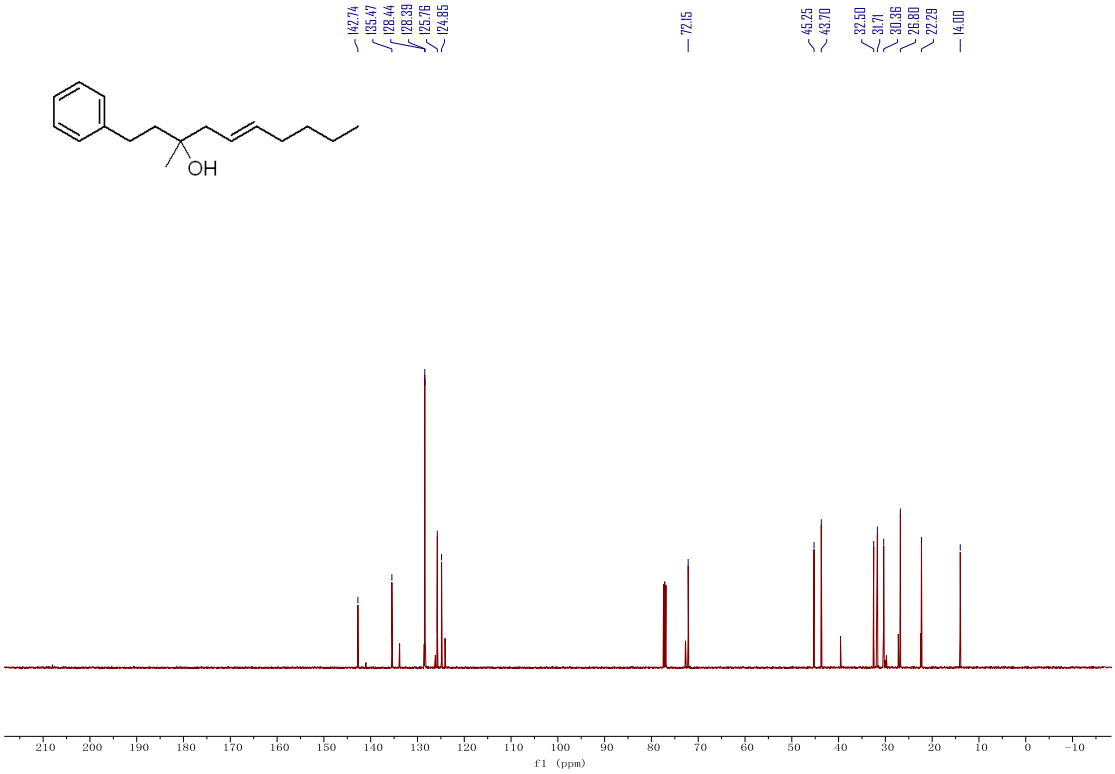
^{1}H NMR of compound **24'** (500 MHz, $CDCl_3$)



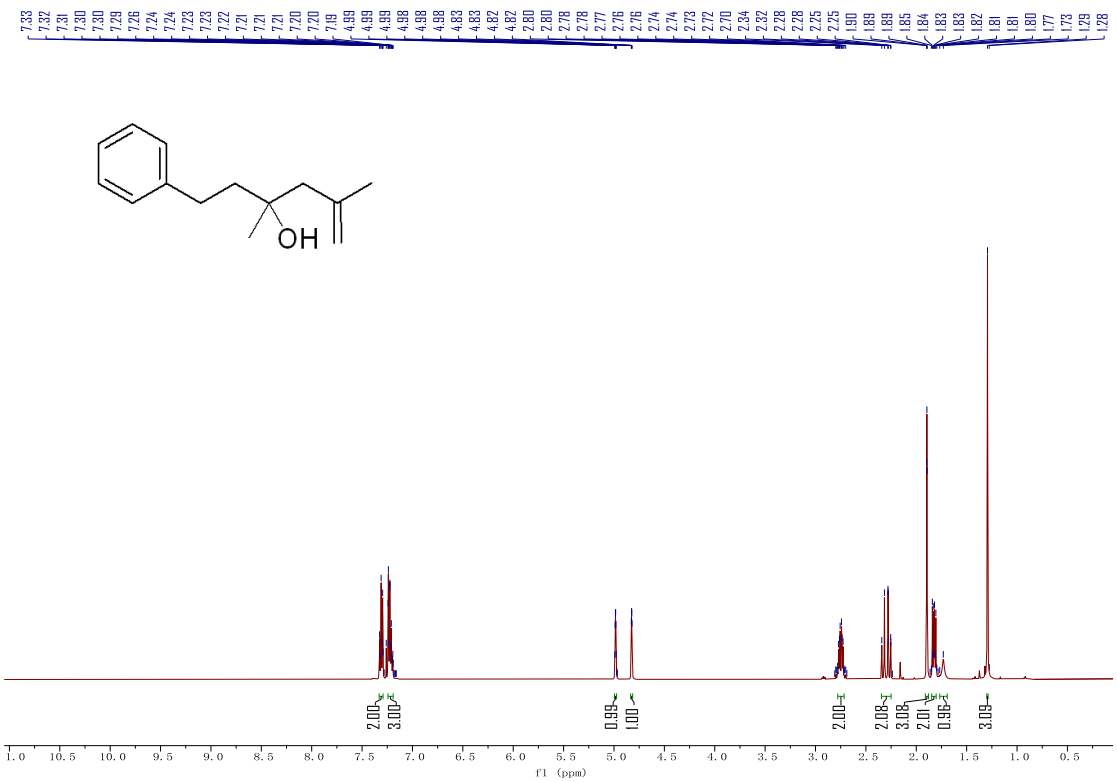
^{13}C NMR of compound **24'** (126 MHz, $CDCl_3$)



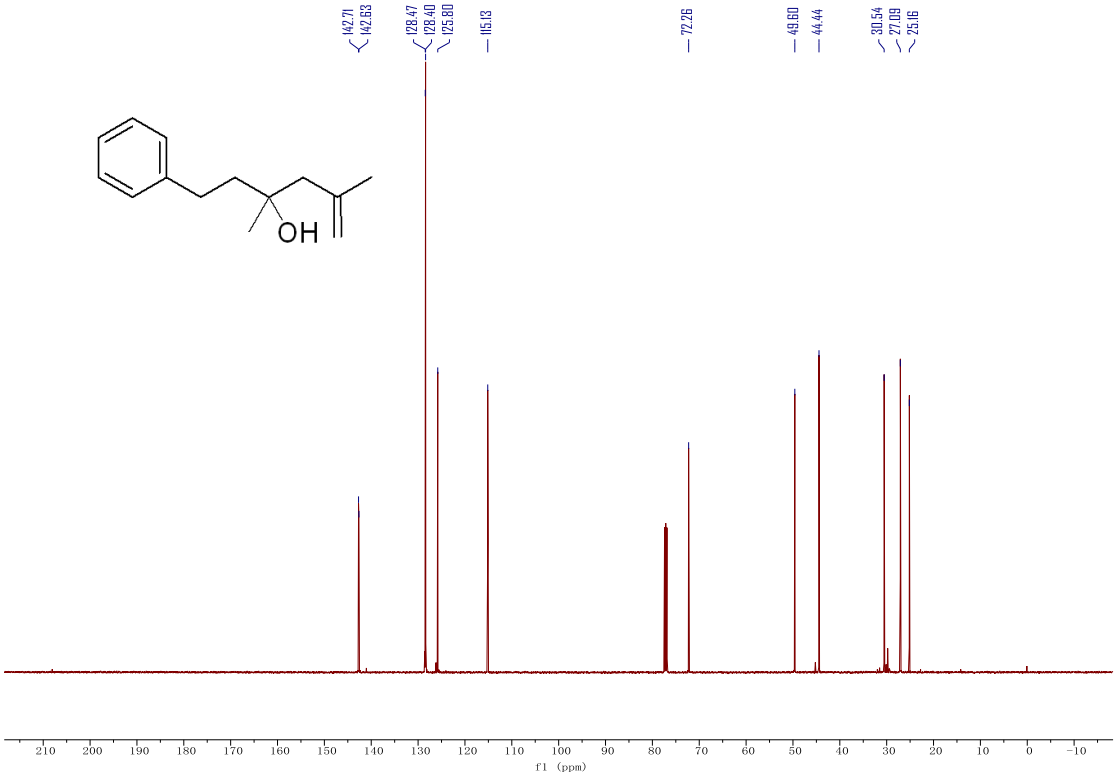
^{1}H NMR of compound **25** (500 MHz, $CDCl_3$)



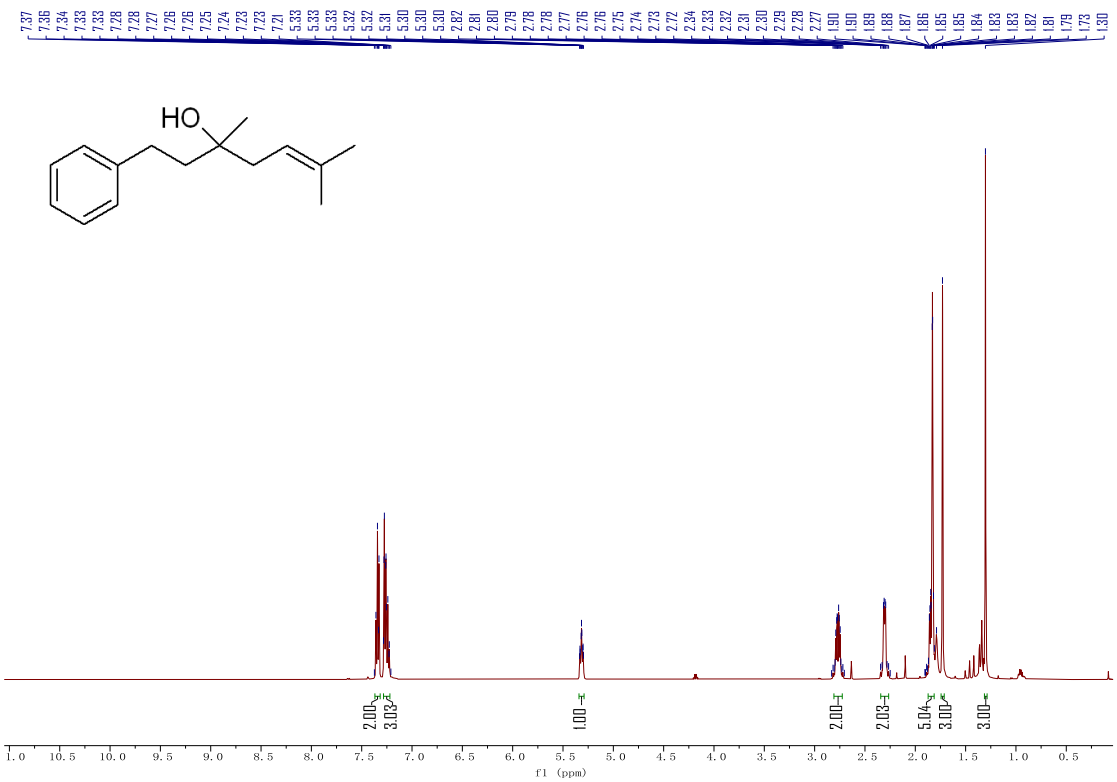
^{13}C NMR of compound **25** (126 MHz, $CDCl_3$)



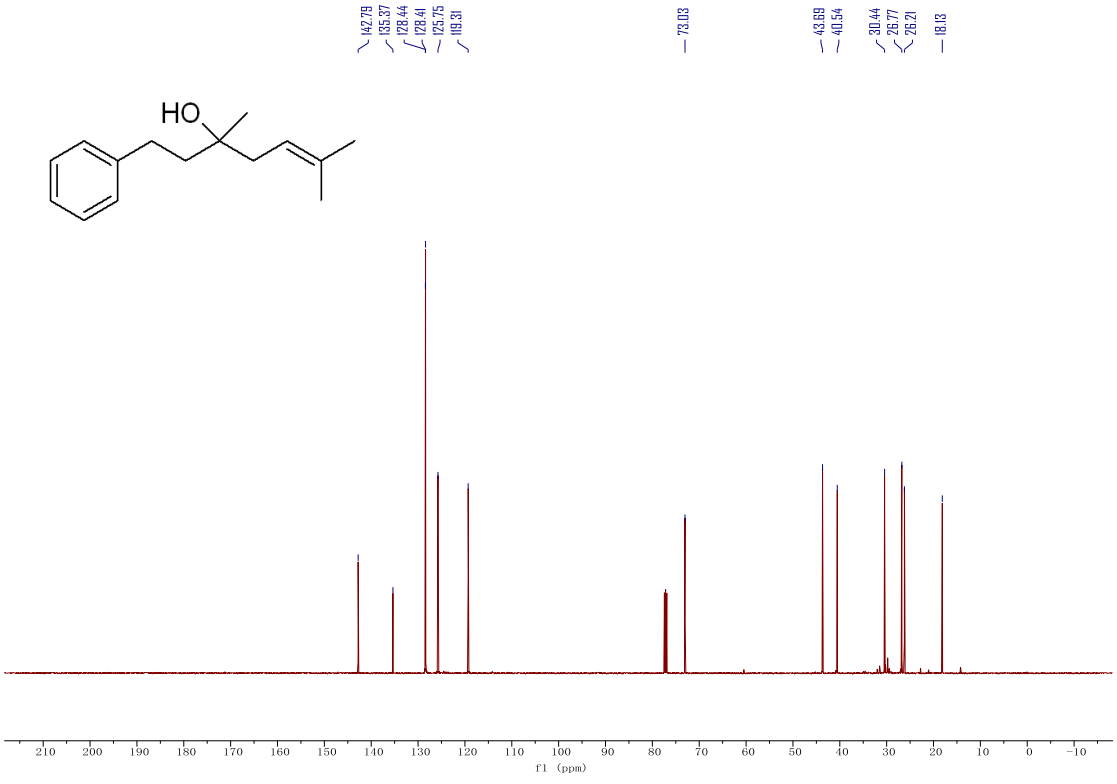
^{1}H NMR of compound **26** (500 MHz, $CDCl_3$)



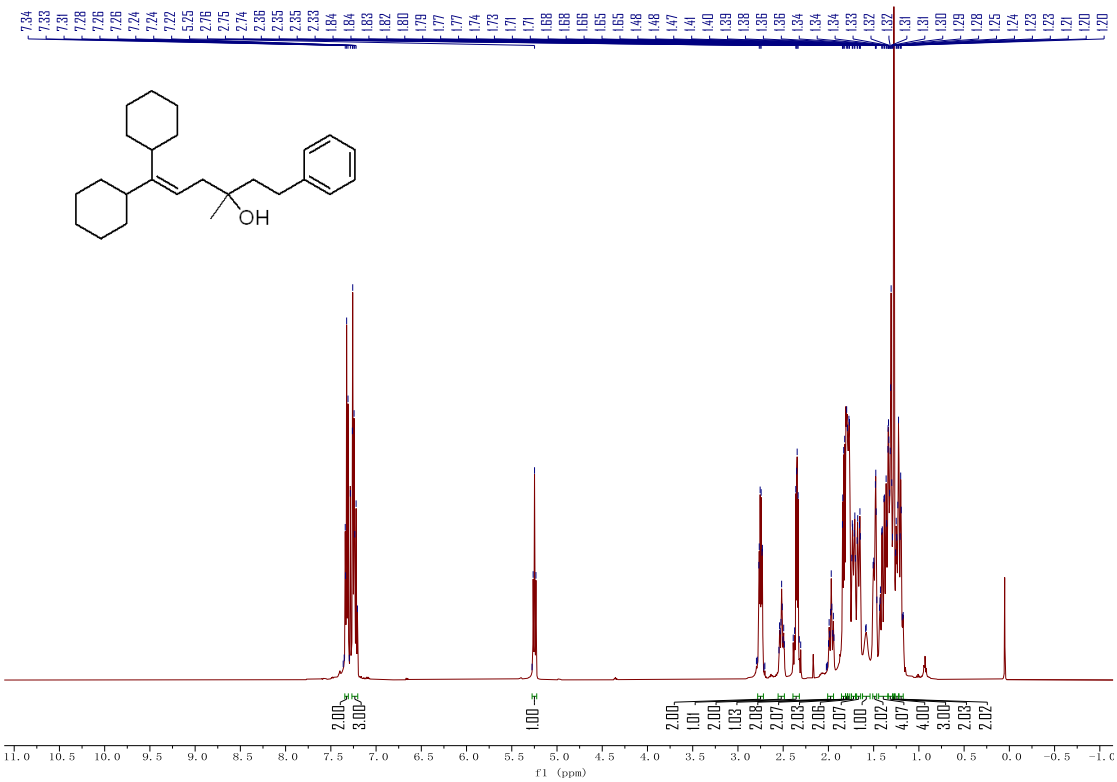
^{13}C NMR of compound **26** (126 MHz, $CDCl_3$)



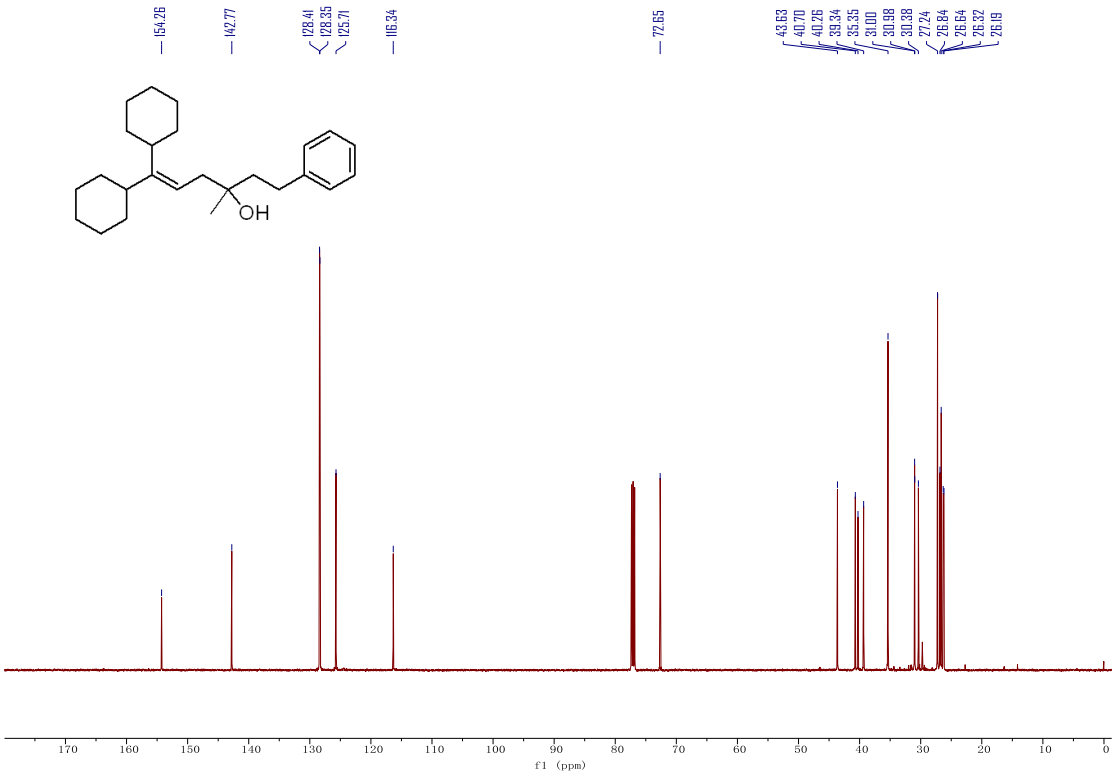
^{1}H NMR of compound **27** (500 MHz, $CDCl_3$)



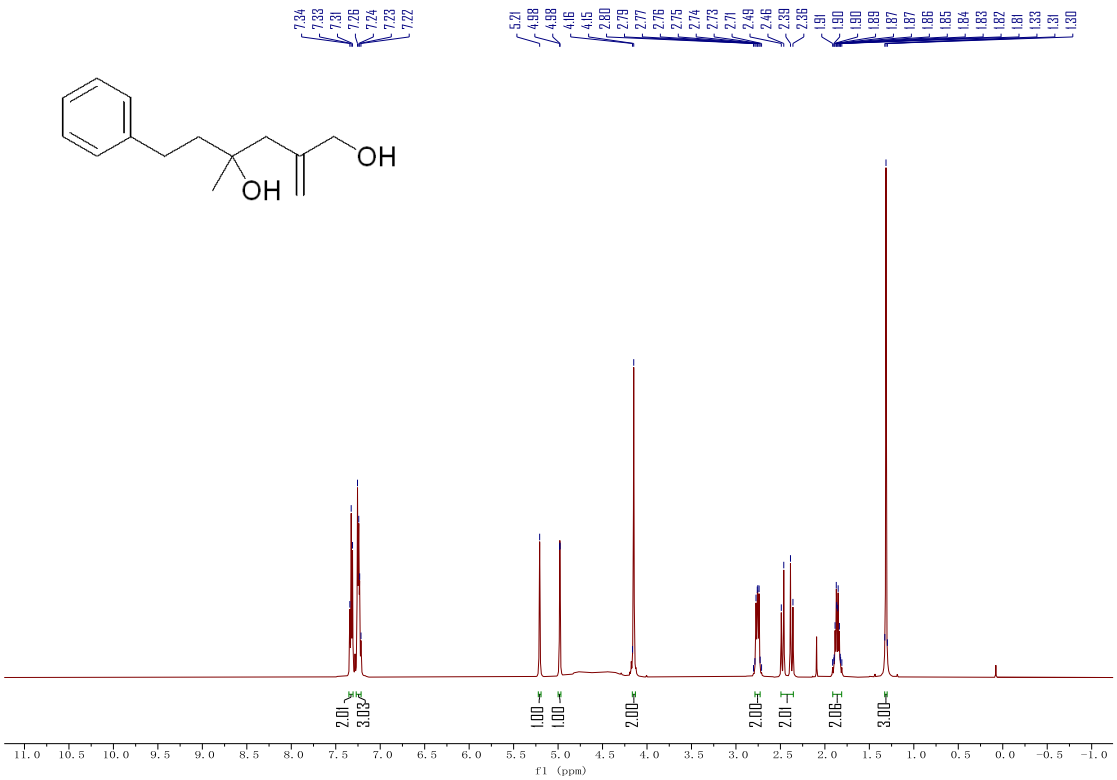
^{13}C NMR of compound **27** (126 MHz, $CDCl_3$)



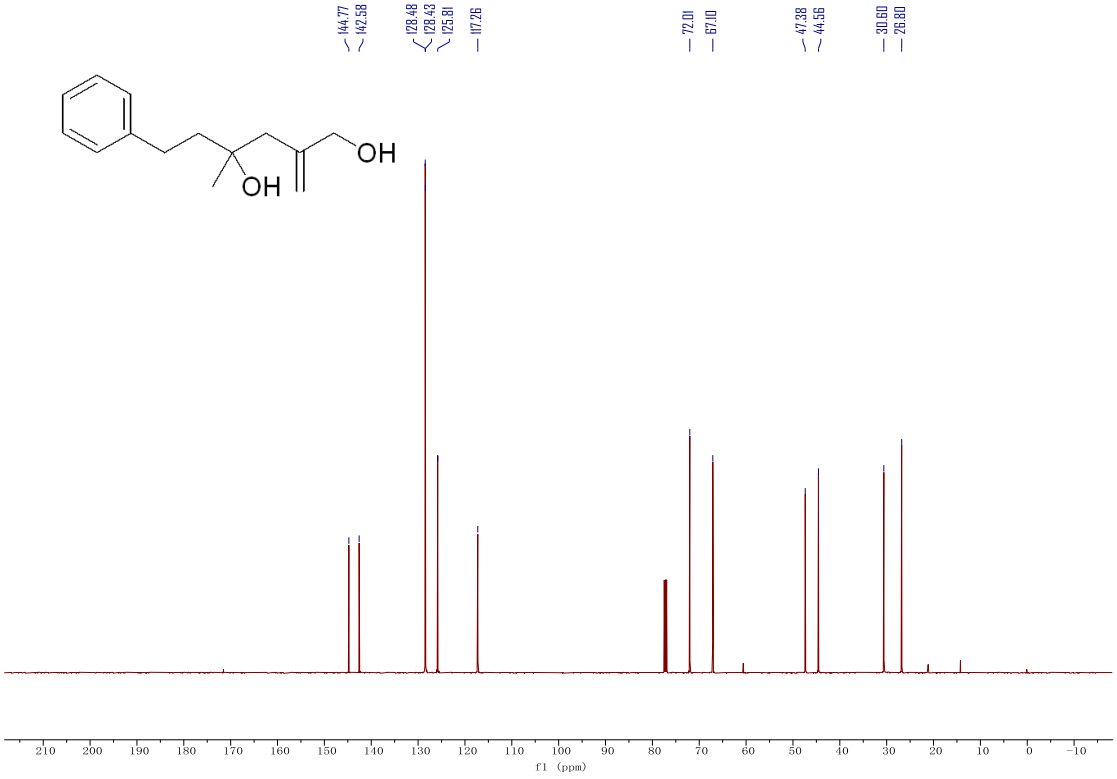
^{1}H NMR of compound **28** (500 MHz, $CDCl_3$)



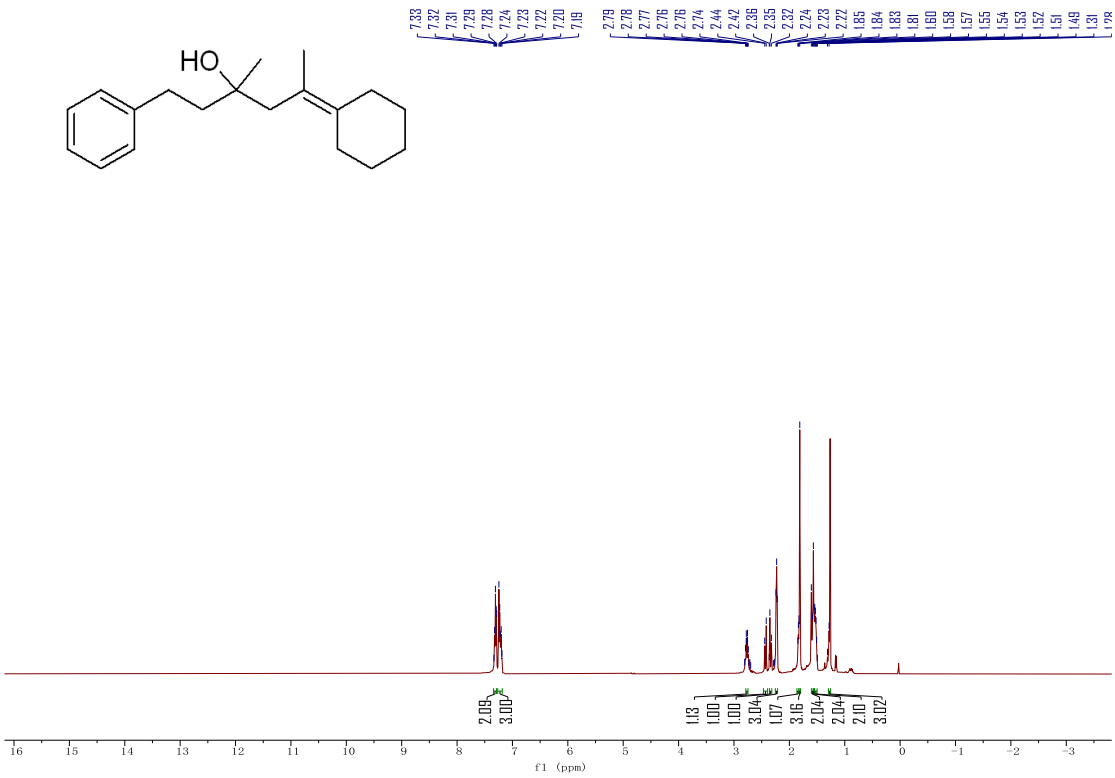
^{13}C NMR of compound **28** (126 MHz, $CDCl_3$)



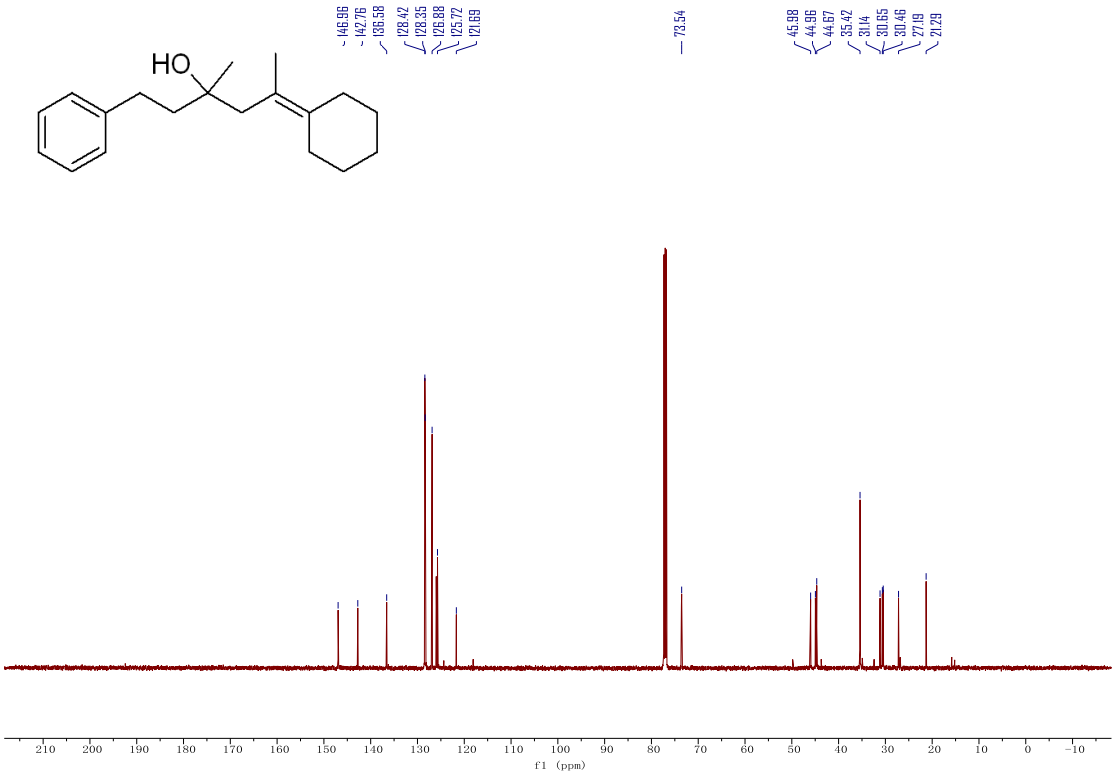
^{1}H NMR of compound **29** (500 MHz, $CDCl_3$)



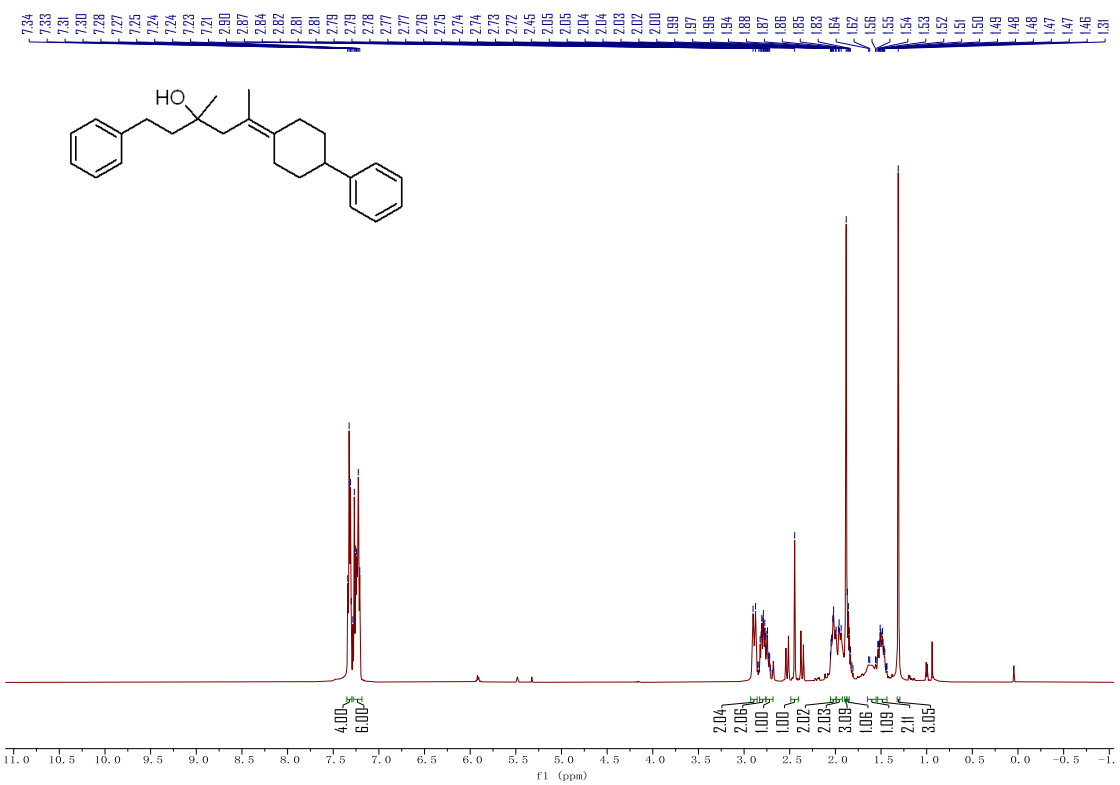
^{13}C NMR of compound **29** (126 MHz, $CDCl_3$)



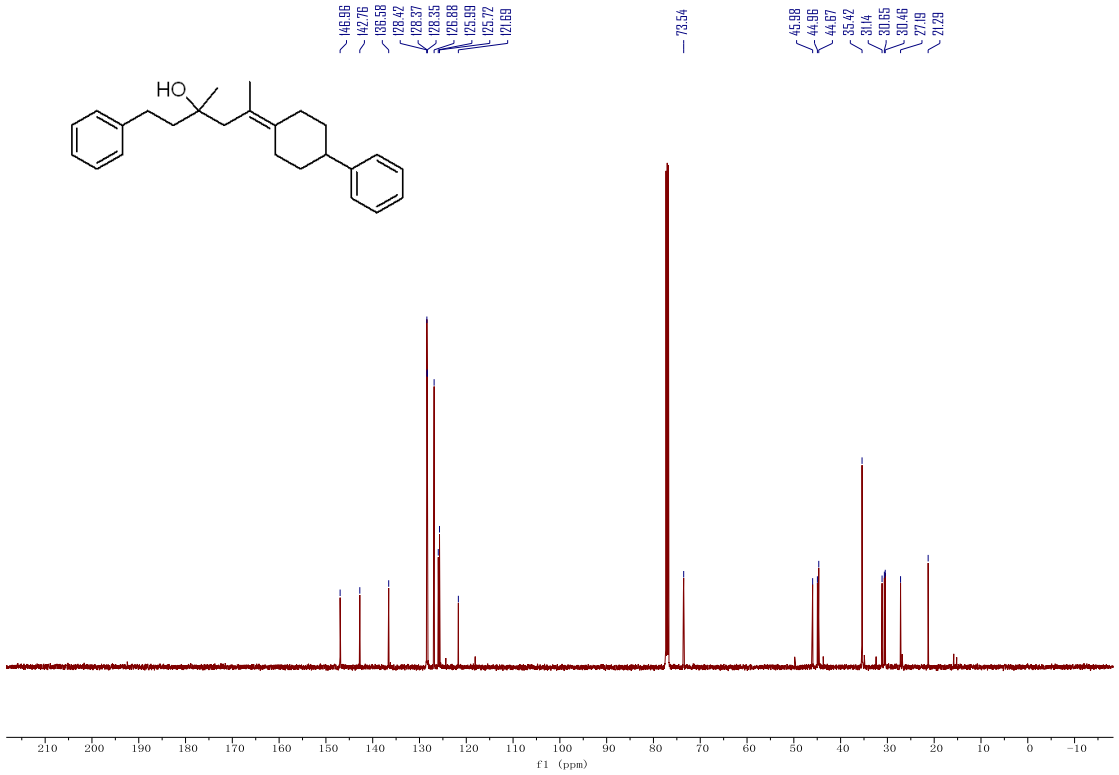
^{1}H NMR of compound **30** (500 MHz, $CDCl_3$)



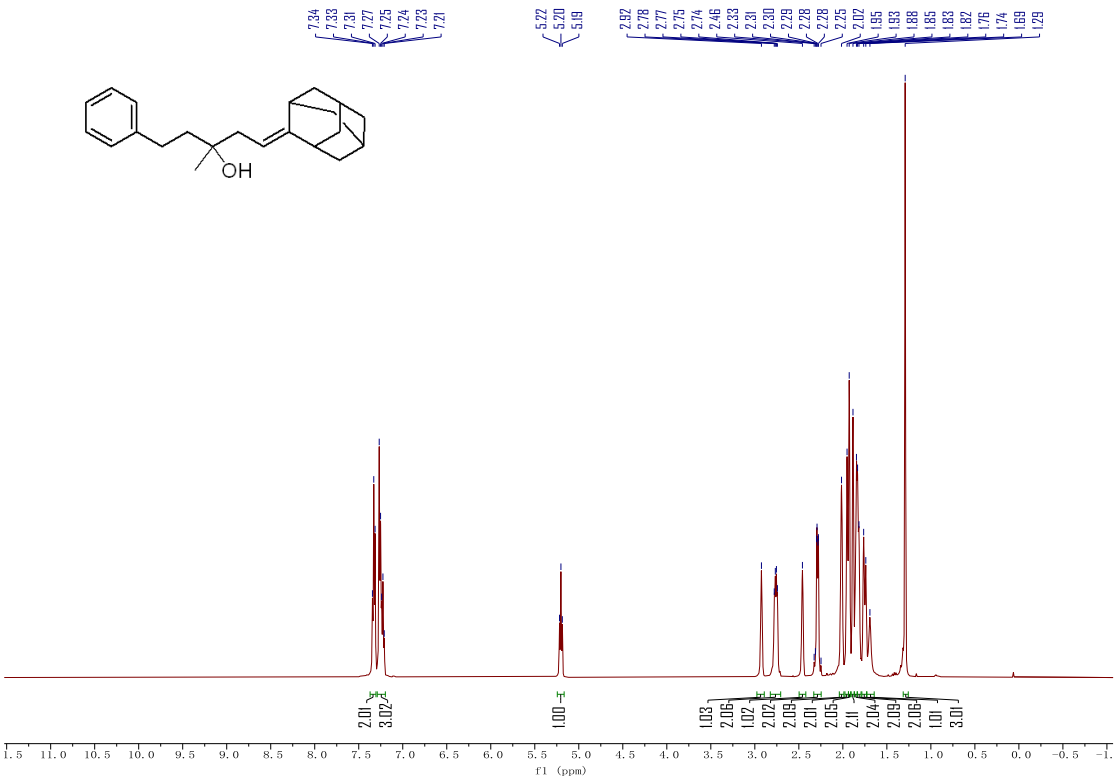
^{13}C NMR of compound **30** (126 MHz, $CDCl_3$)



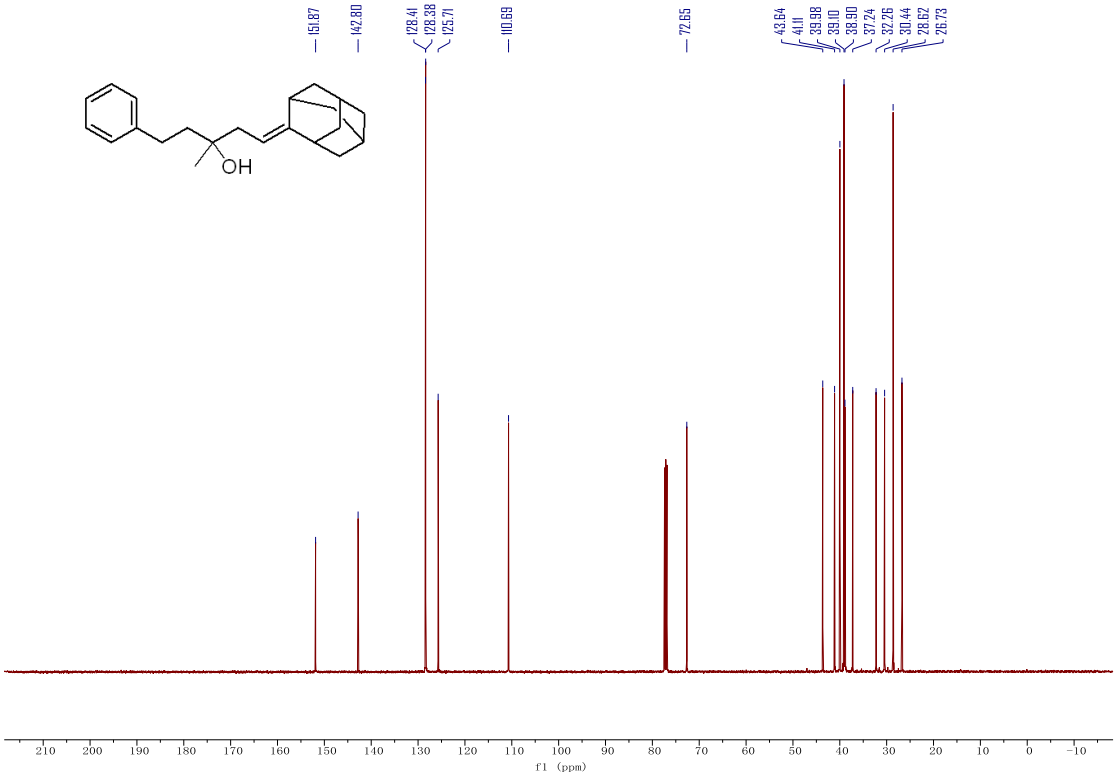
^{1}H NMR of compound **31** (500 MHz, $CDCl_3$)



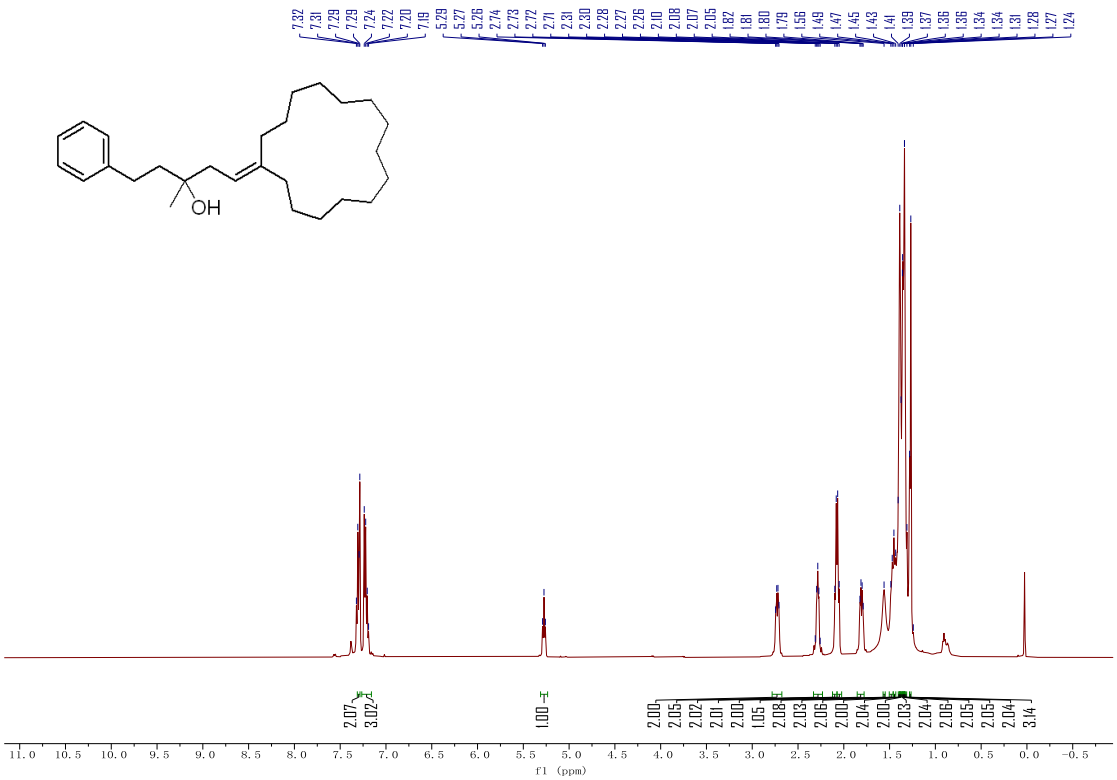
^{13}C NMR of compound **31** (126 MHz, $CDCl_3$)



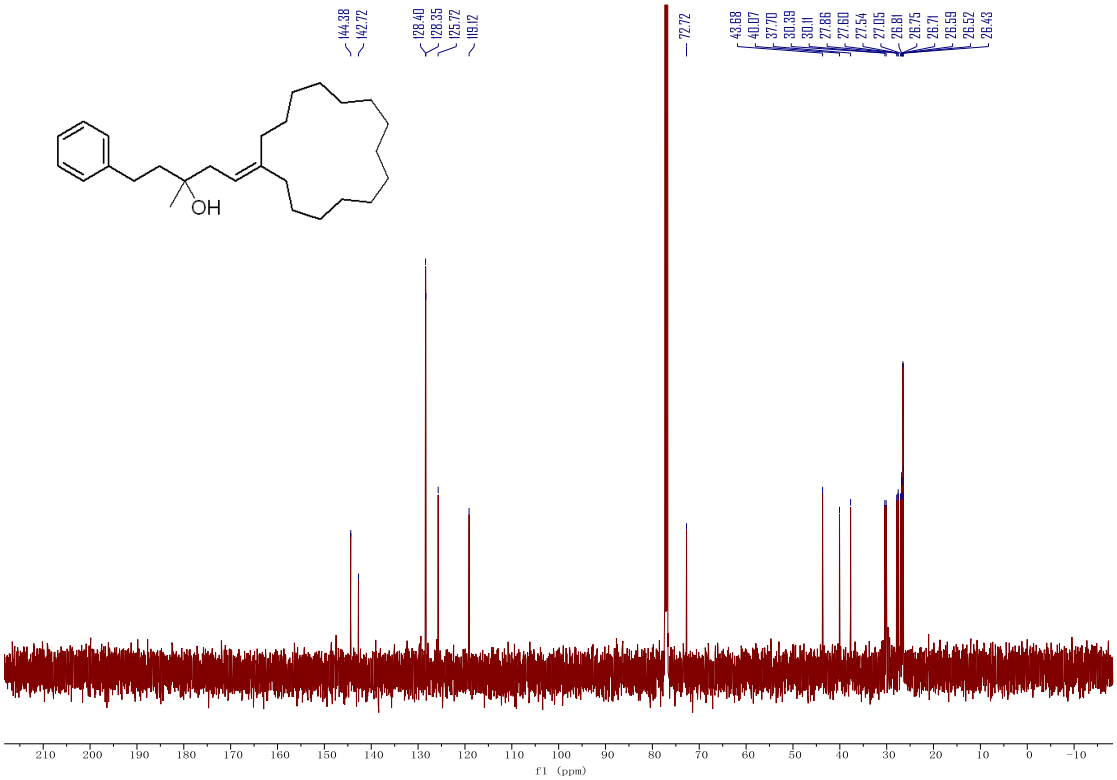
^{1}H NMR of compound **32** (500 MHz, $CDCl_3$)



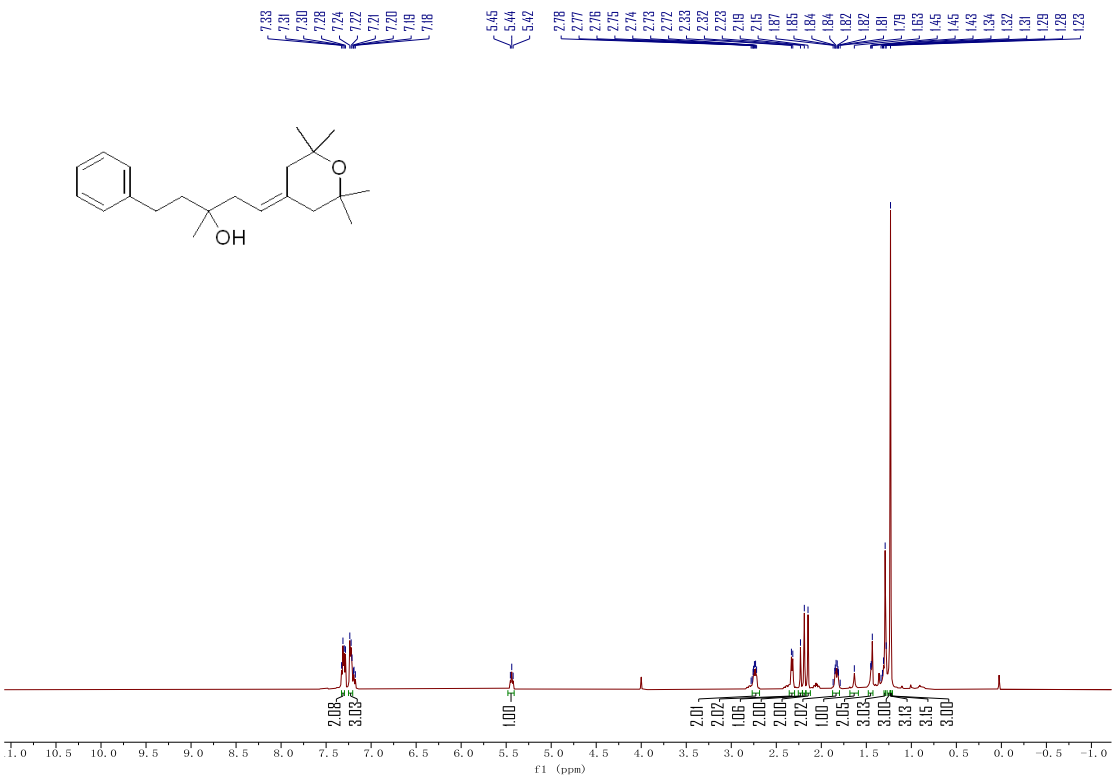
^{13}C NMR of compound **32** (126 MHz, $CDCl_3$)



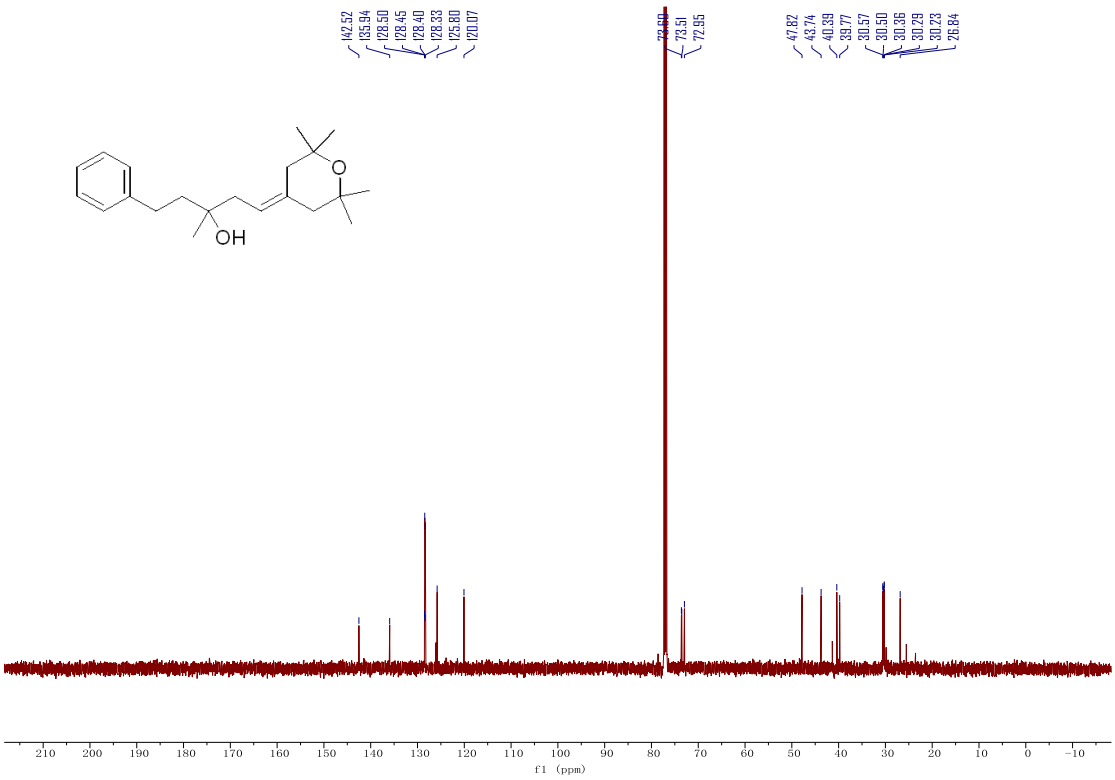
^{1}H NMR of compound **33** (500 MHz, $CDCl_3$)



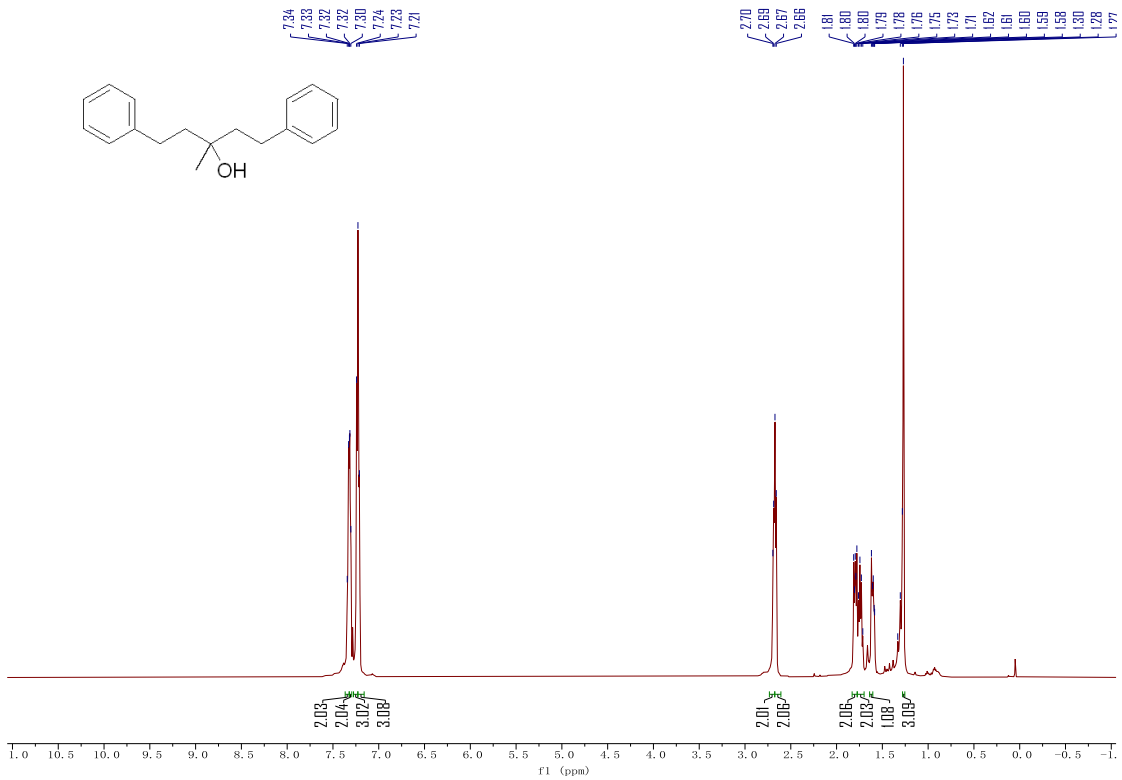
^{13}C NMR of compound **33** (126 MHz, $CDCl_3$)



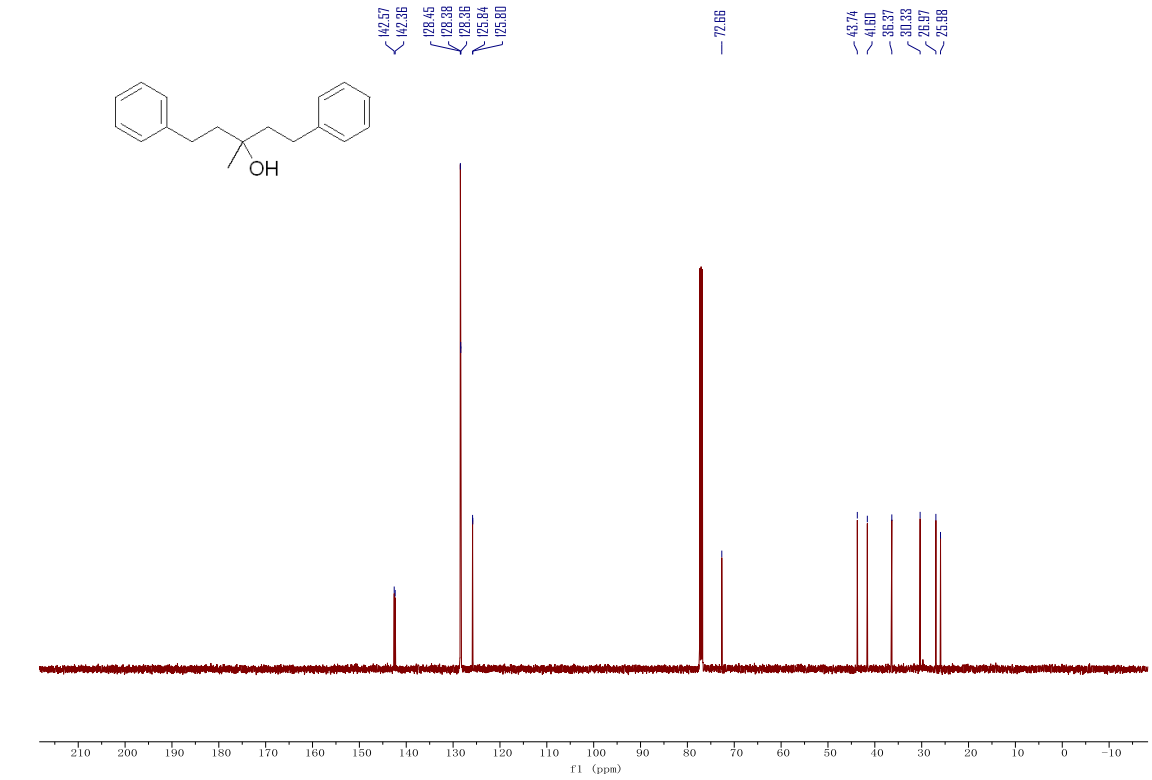
^{1}H NMR of compound **34** (500 MHz, $CDCl_3$)



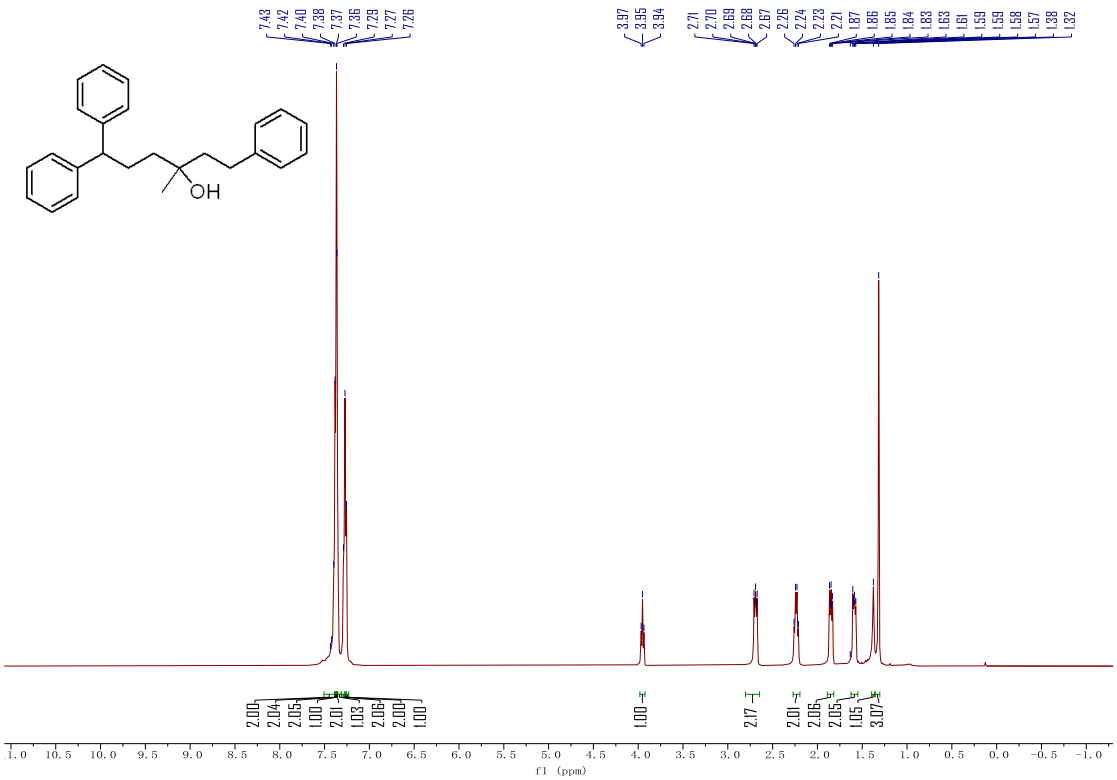
^{13}C NMR of compound **34** (126 MHz, $CDCl_3$)



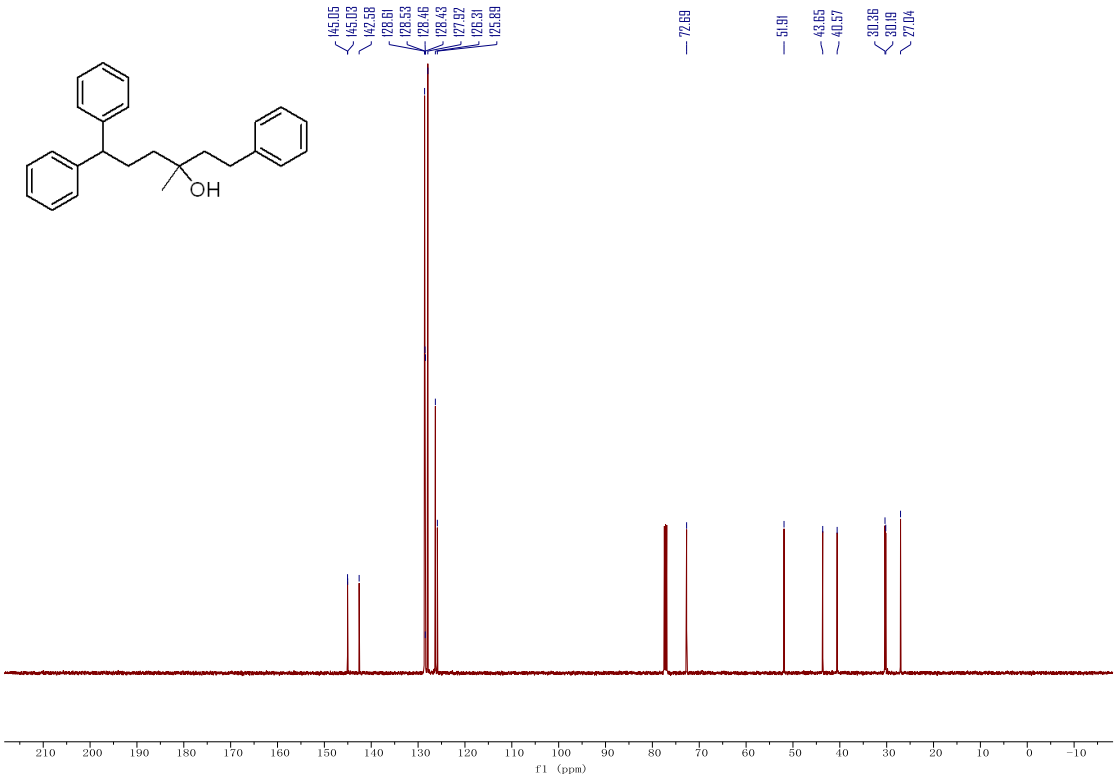
^{1}H NMR of compound **35** (500 MHz, $CDCl_3$)



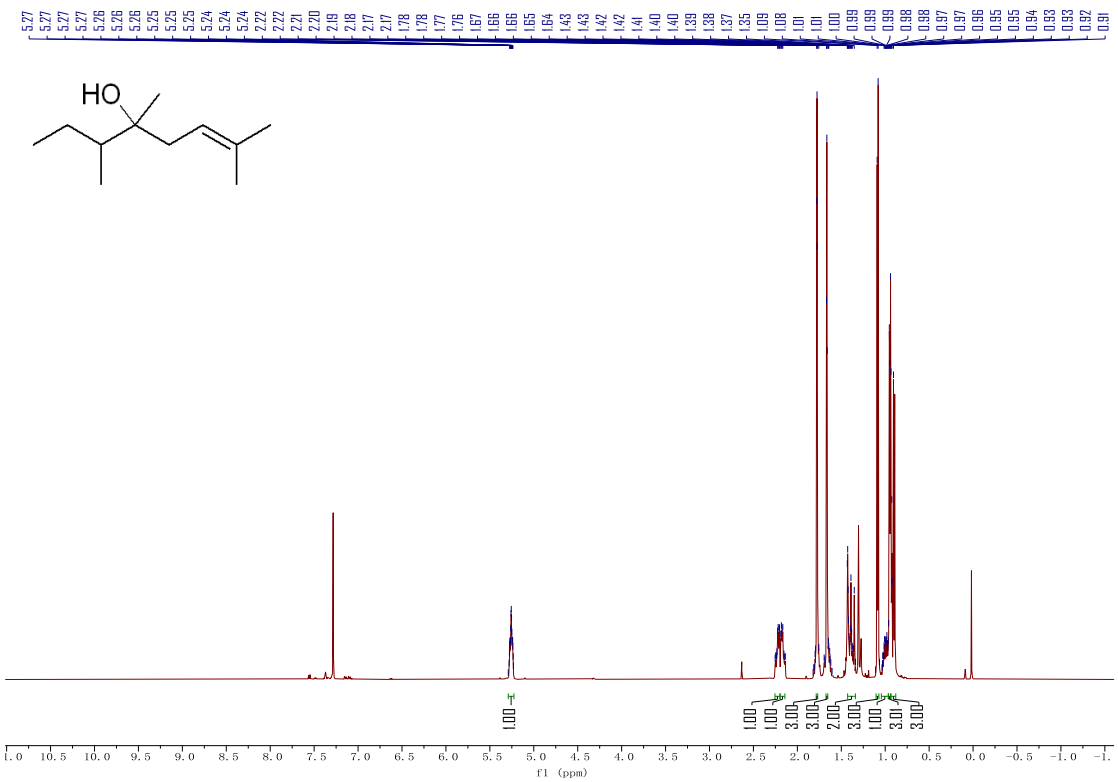
^{13}C NMR of compound **35** (126 MHz, $CDCl_3$)



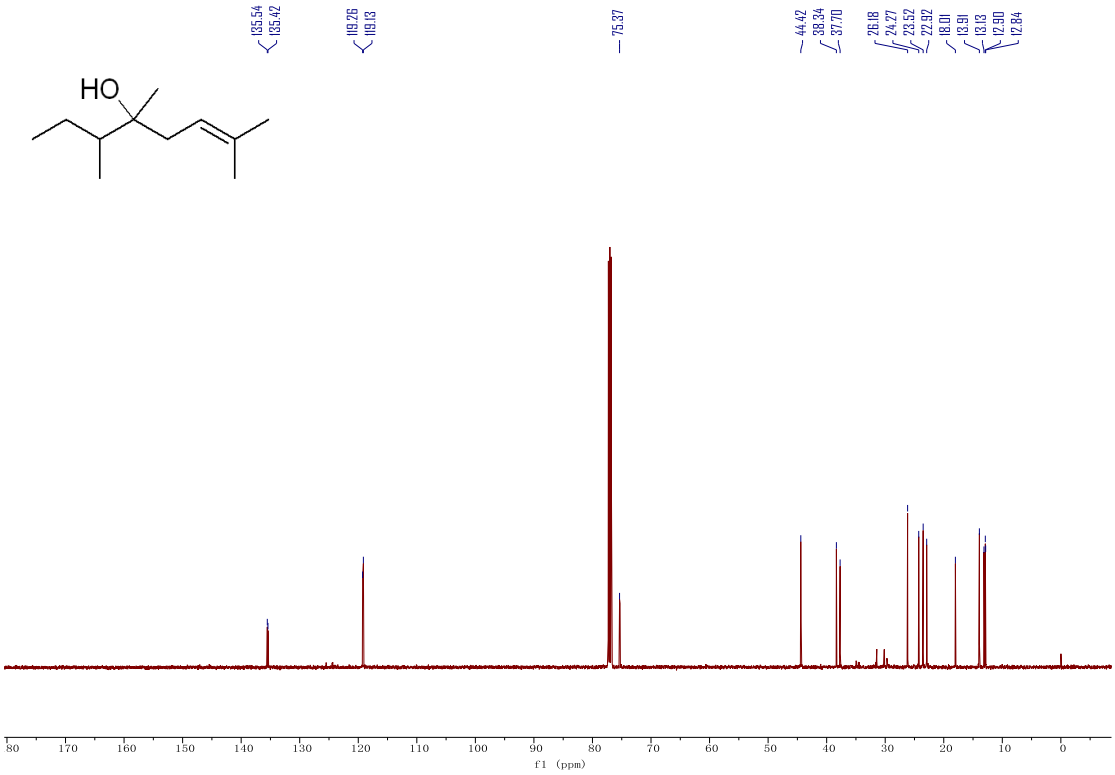
^{1}H NMR of compound **36** (500 MHz, $CDCl_3$)



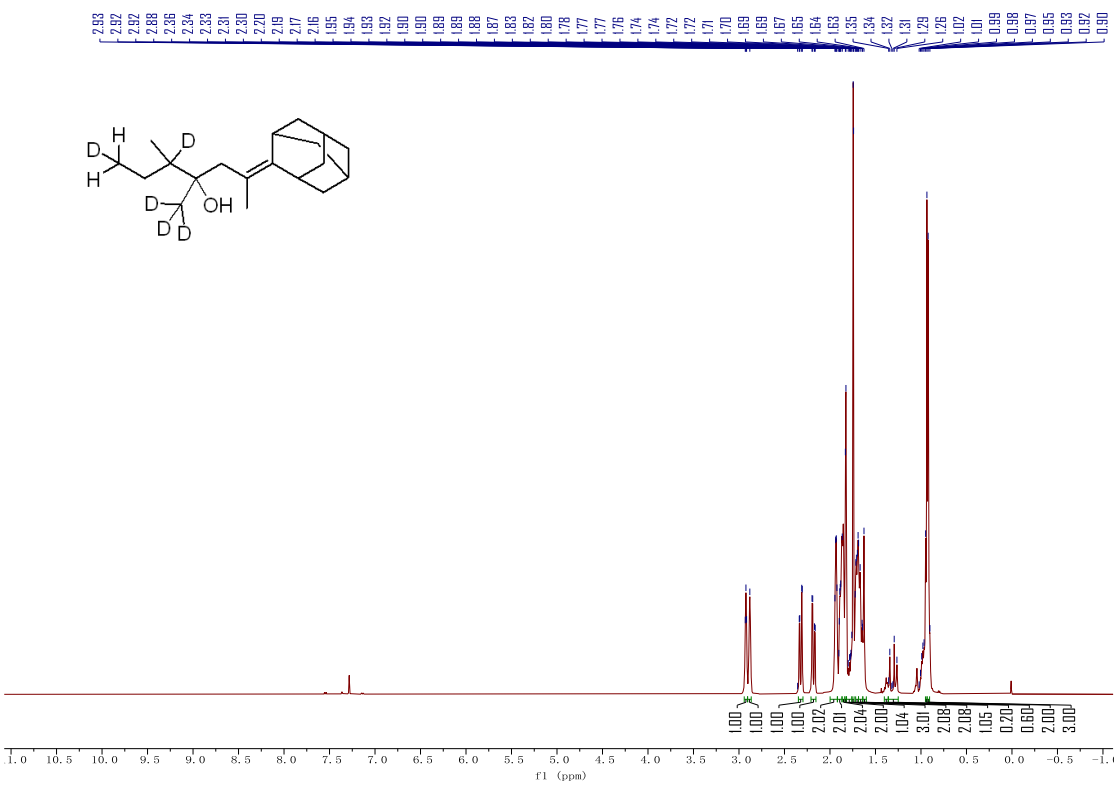
^{13}C NMR of compound **36** (126 MHz, $CDCl_3$)



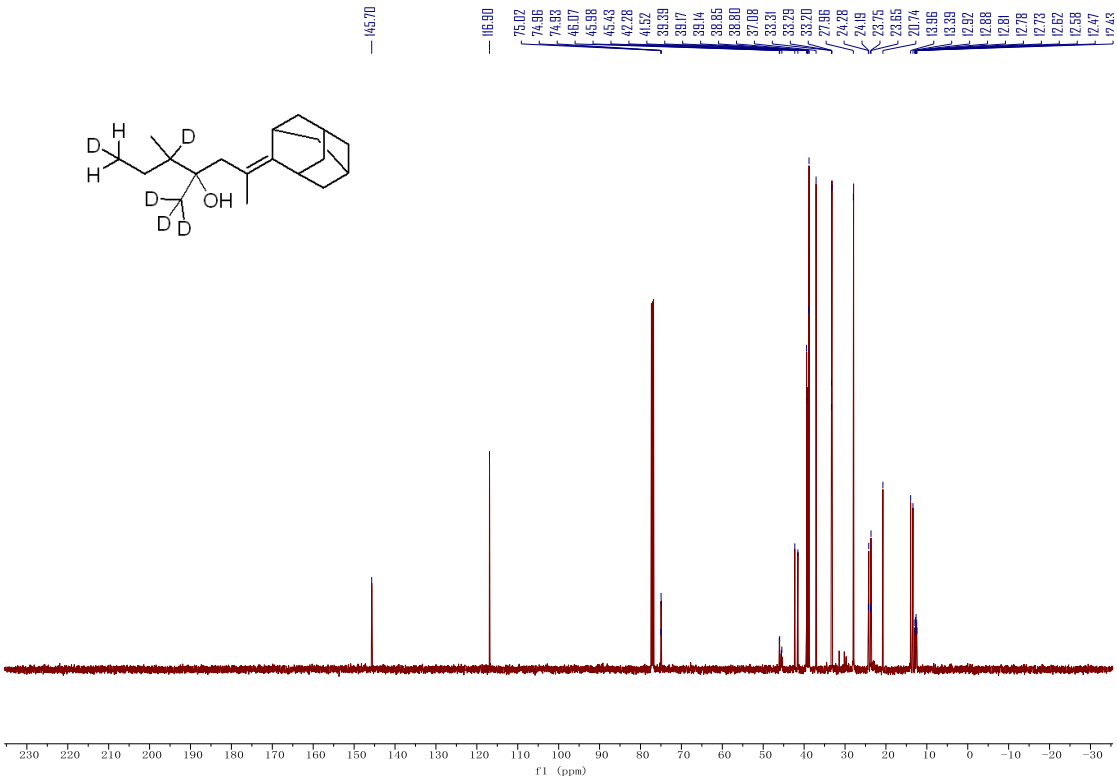
^{1}H NMR of compound **37** (500 MHz, $CDCl_3$)



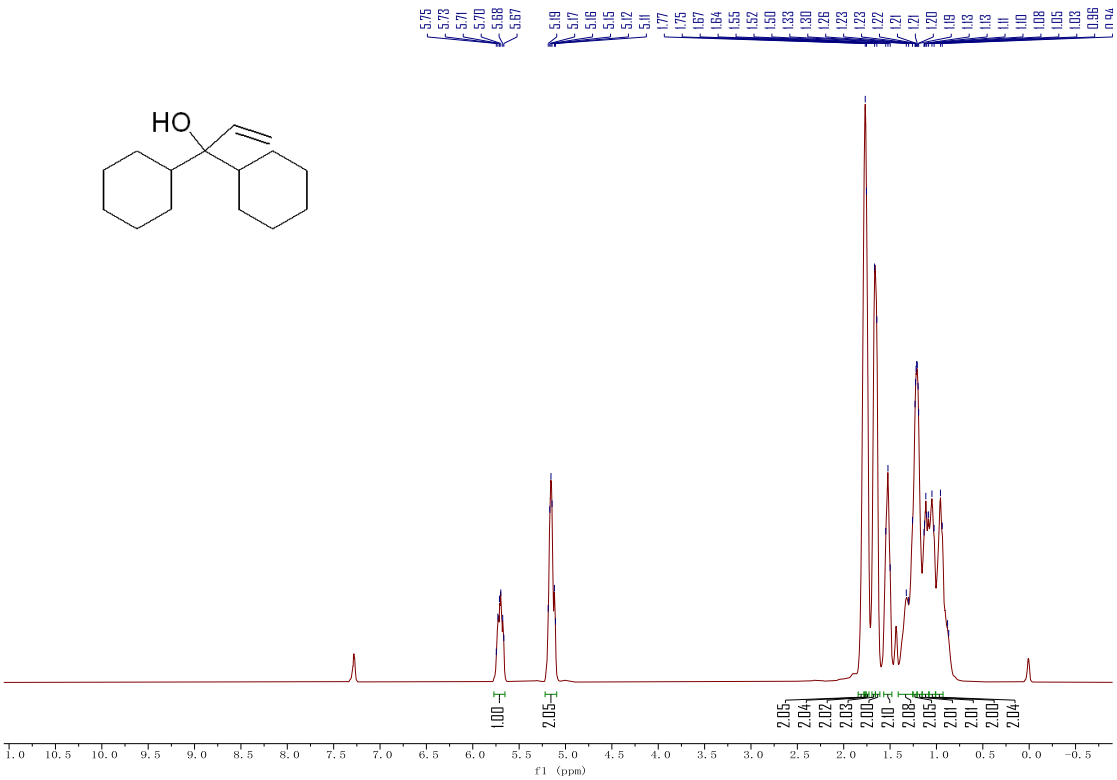
^{13}C NMR of compound **37** (126 MHz, $CDCl_3$)



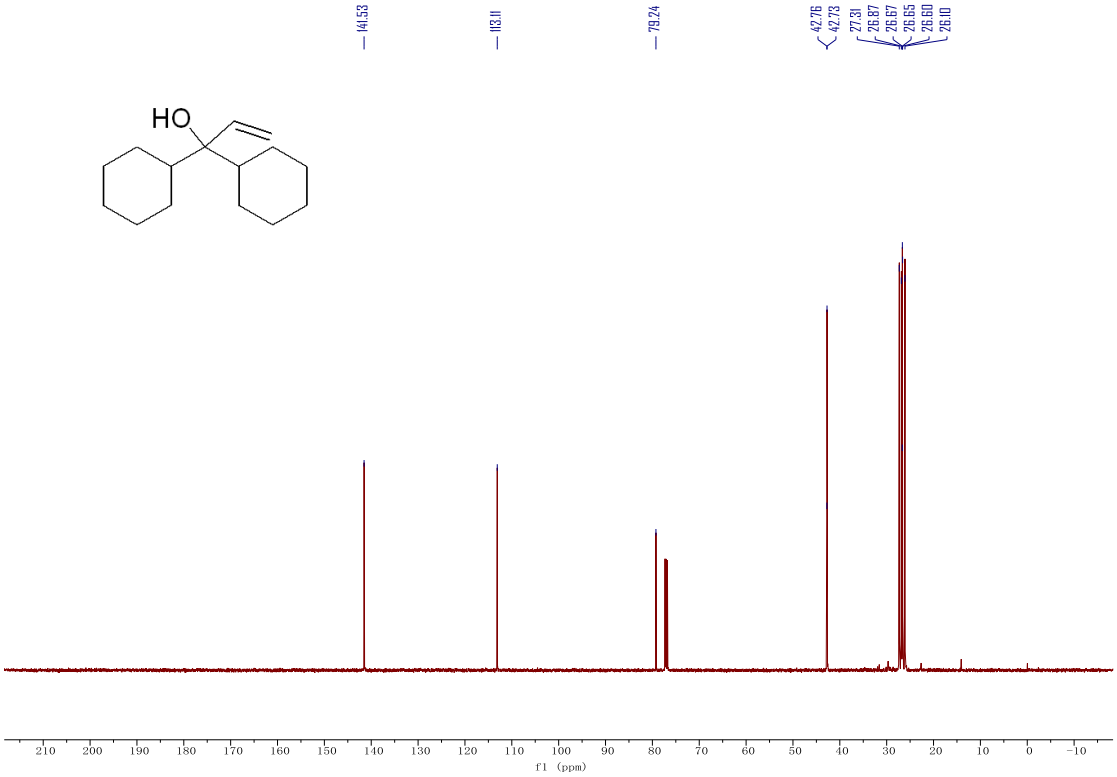
^{1}H NMR of compound **38** (500 MHz, $CDCl_3$)



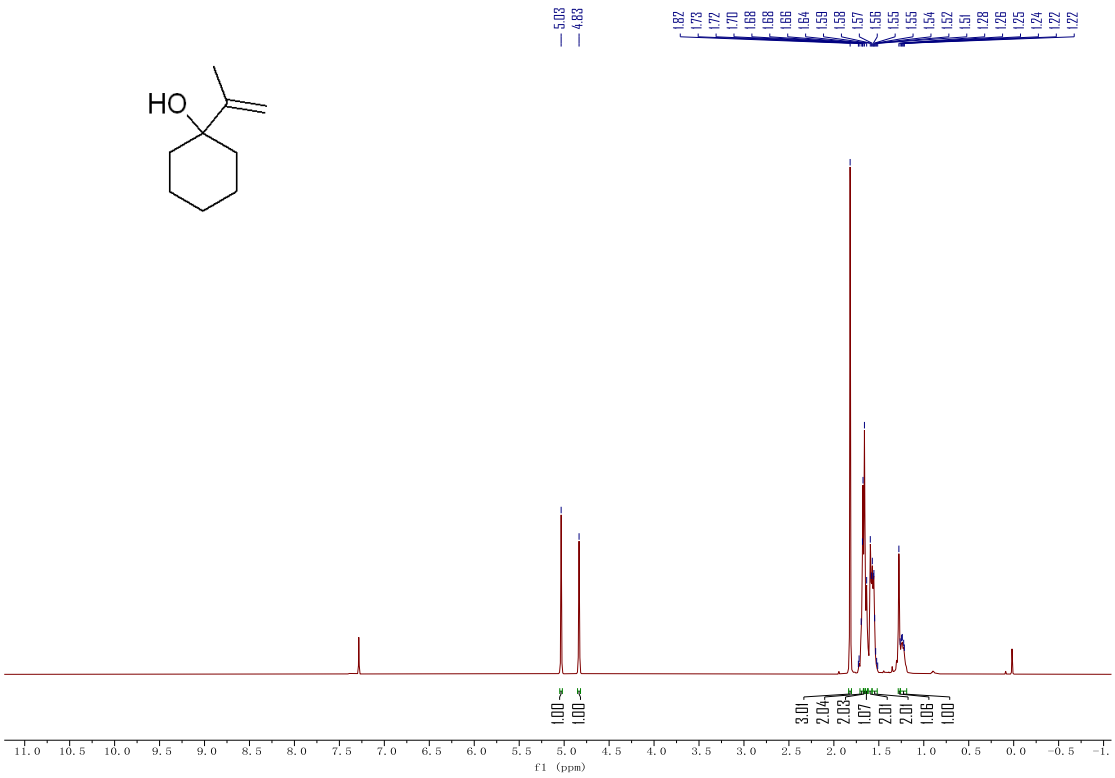
^{13}C NMR of compound **38** (126 MHz, $CDCl_3$)



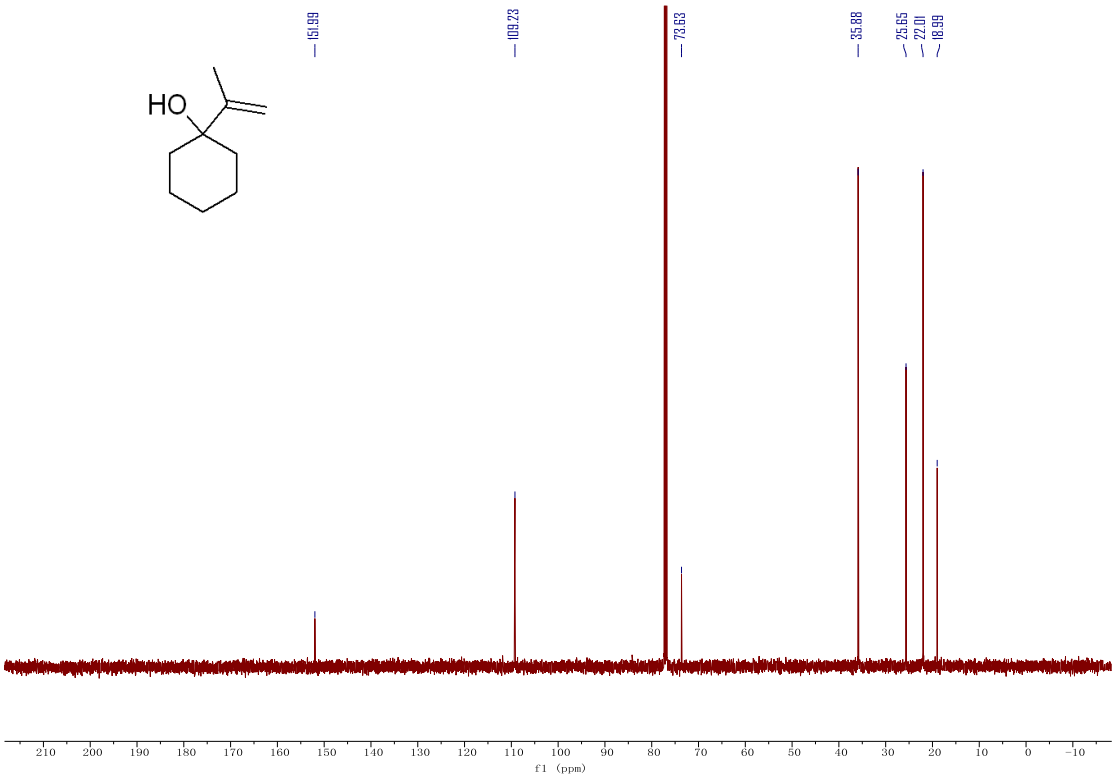
^{1}H NMR of compound **5b** (500 MHz, $CDCl_3$)



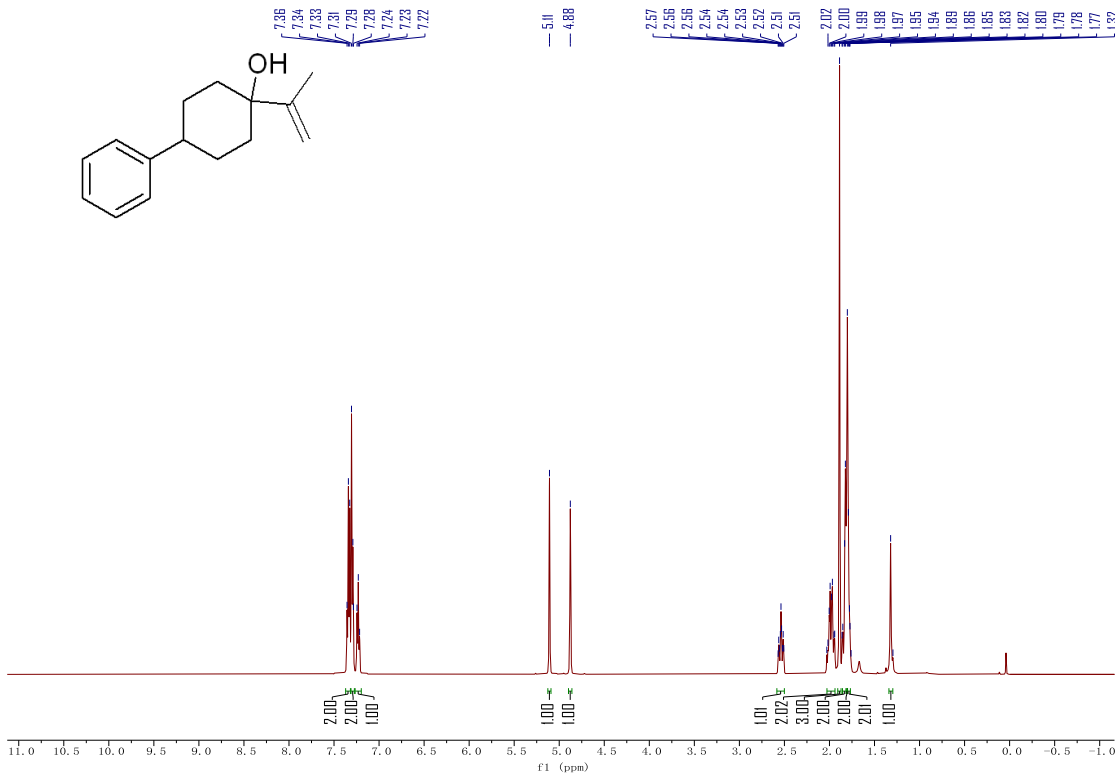
^{13}C NMR of compound **5b** (126 MHz, $CDCl_3$)



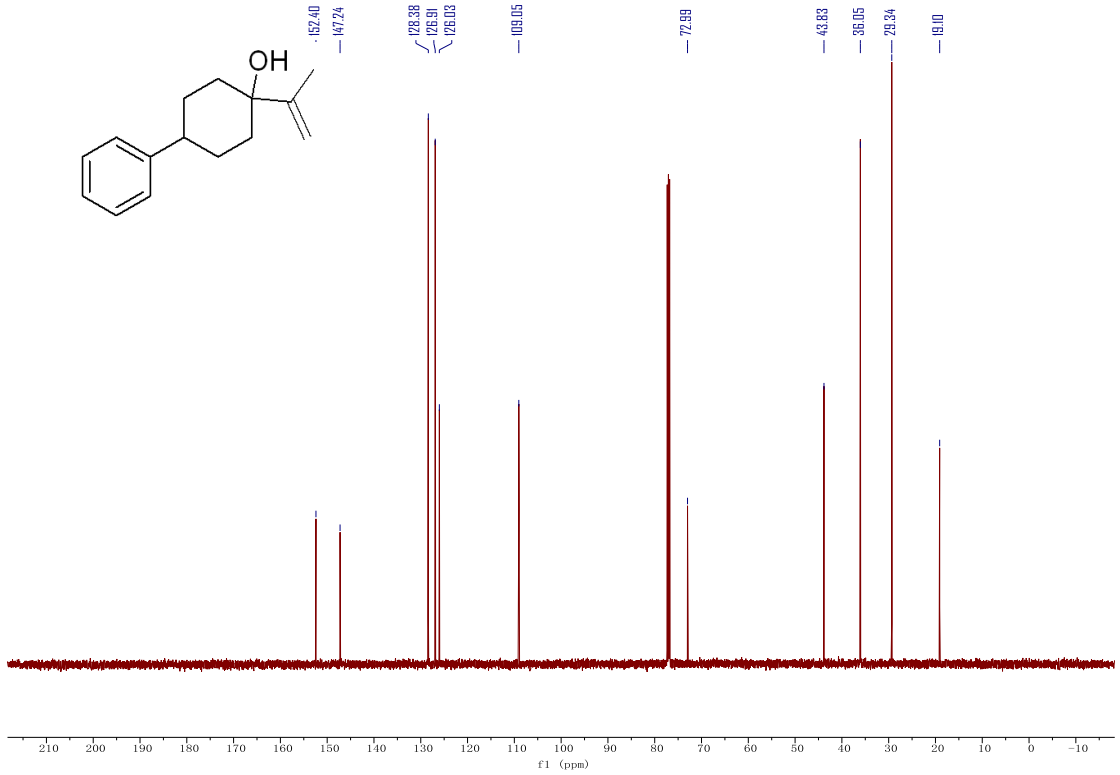
^{1}H NMR of compound **7b** (500 MHz, $CDCl_3$)



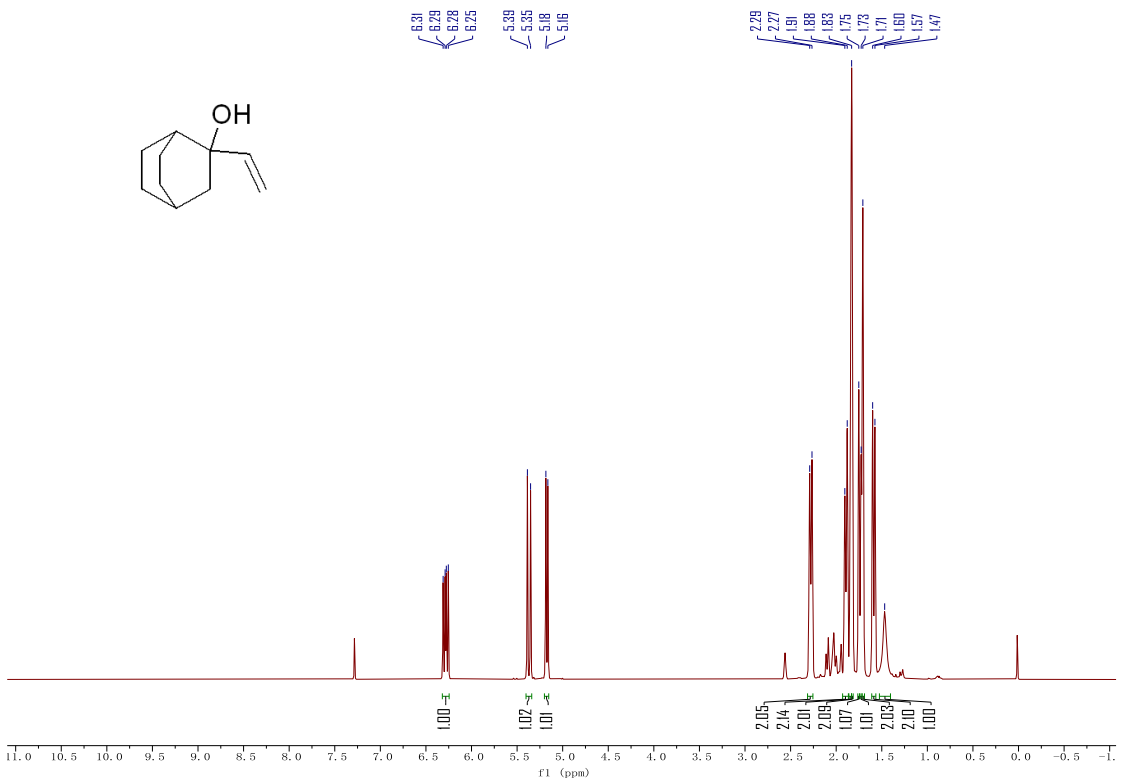
^{13}C NMR of compound **7b** (126 MHz, $CDCl_3$)



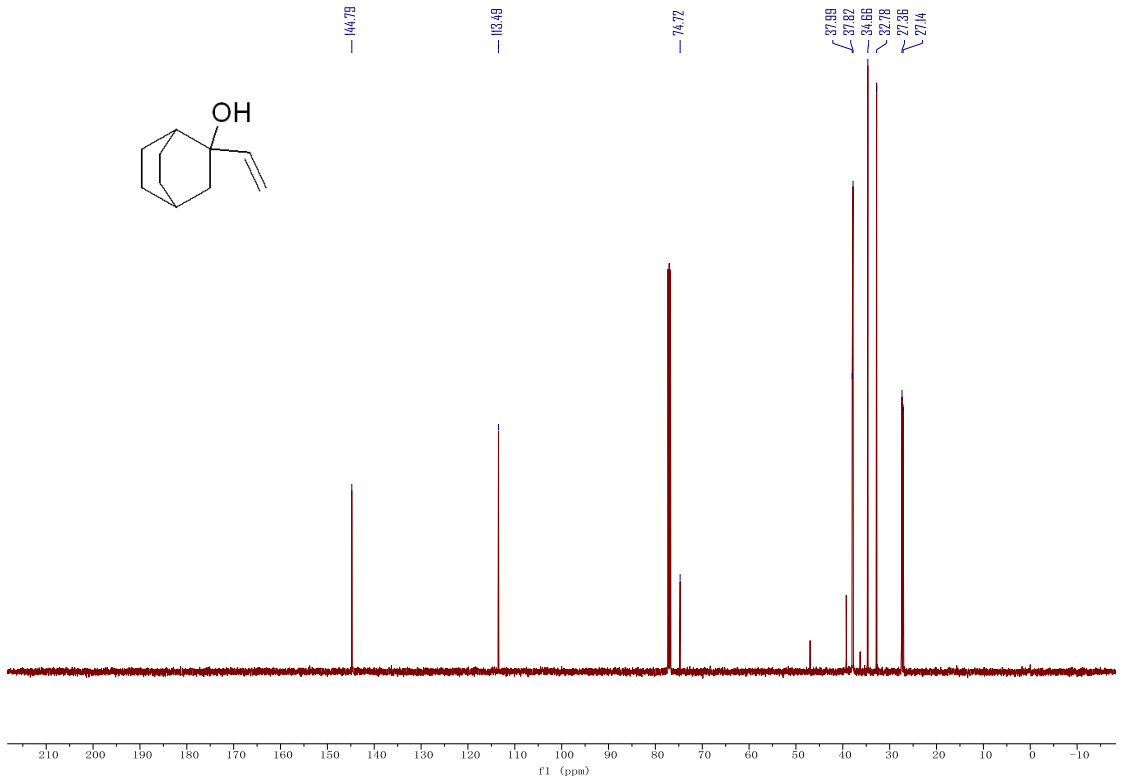
^{1}H NMR of compound **8b** (500 MHz, $CDCl_3$)



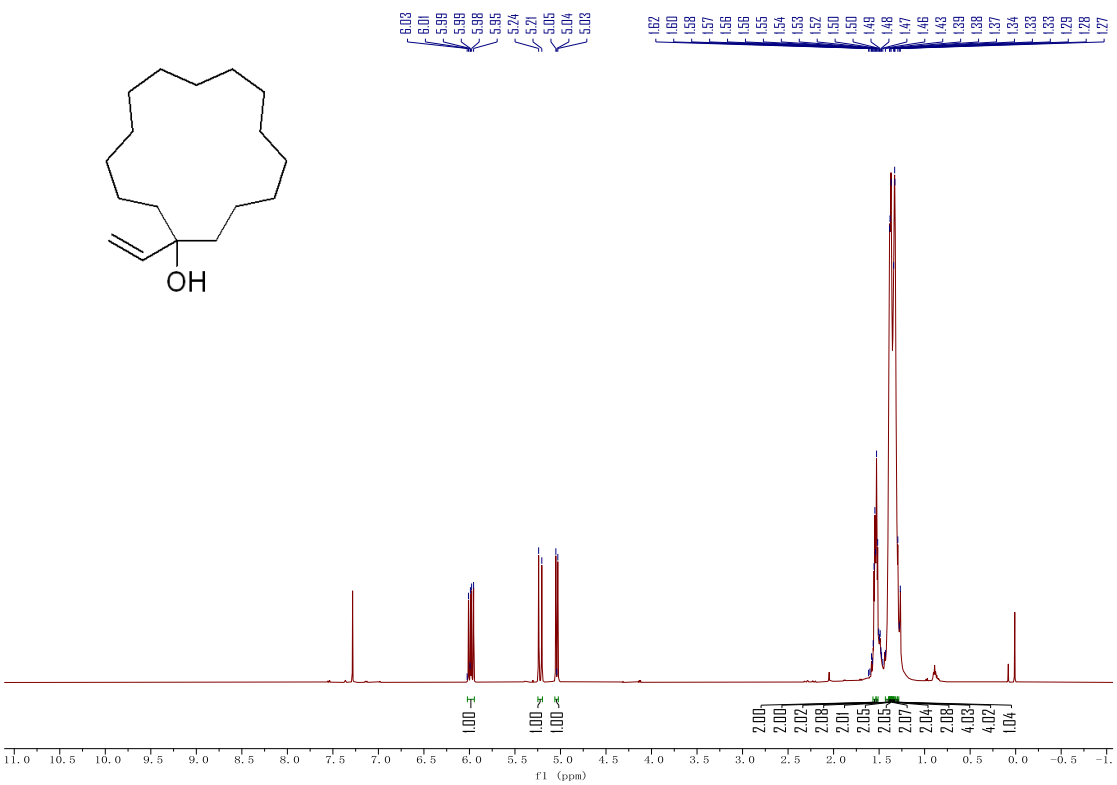
^{13}C NMR of compound **8b** (126 MHz, $CDCl_3$)



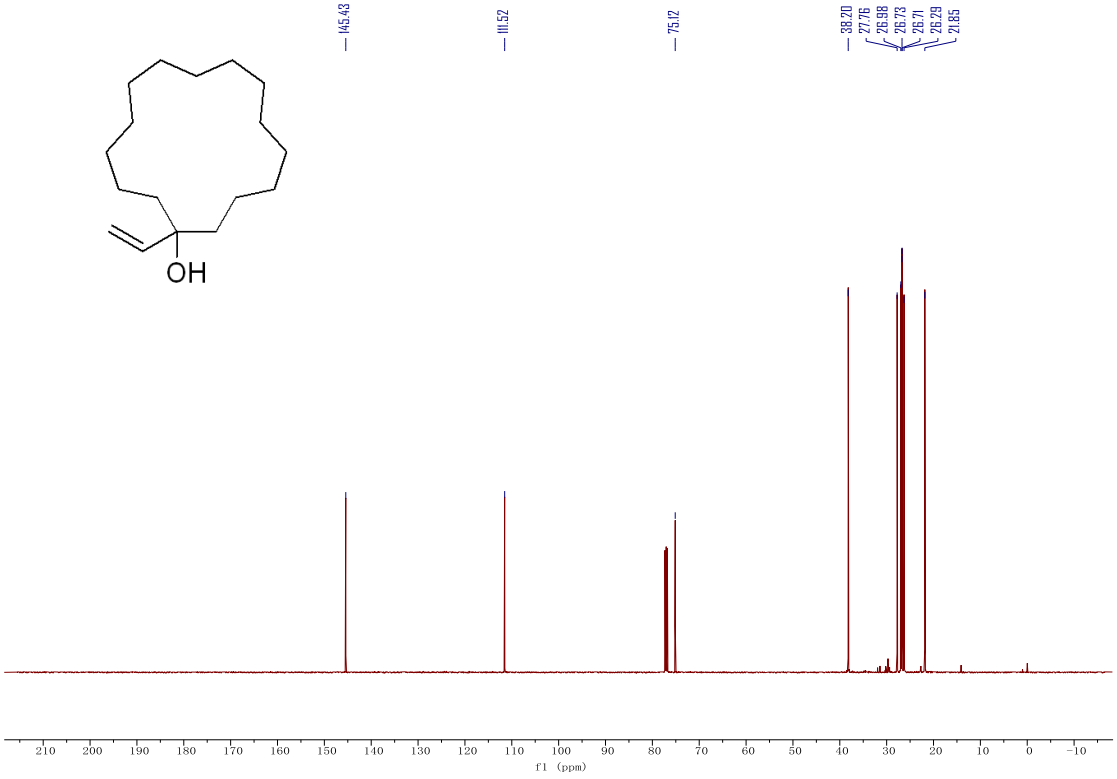
^{1}H NMR of compound **9b** (500 MHz, $CDCl_3$)



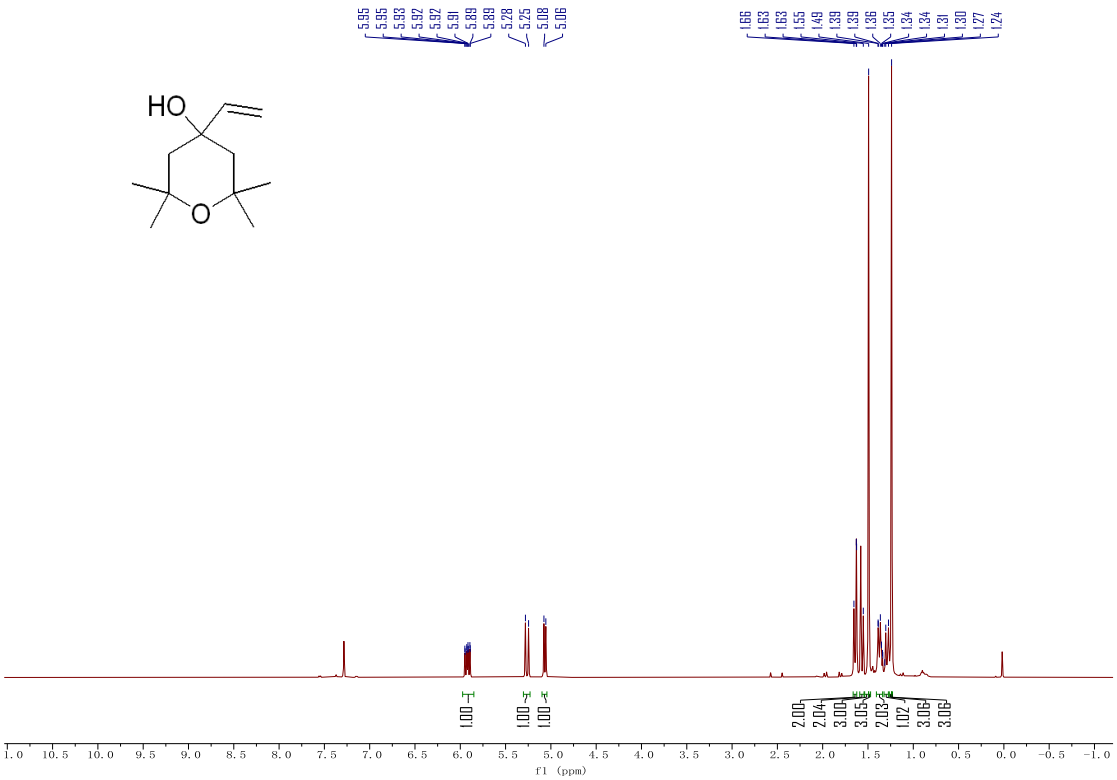
^{13}C NMR of compound **9b** (126 MHz, $CDCl_3$)



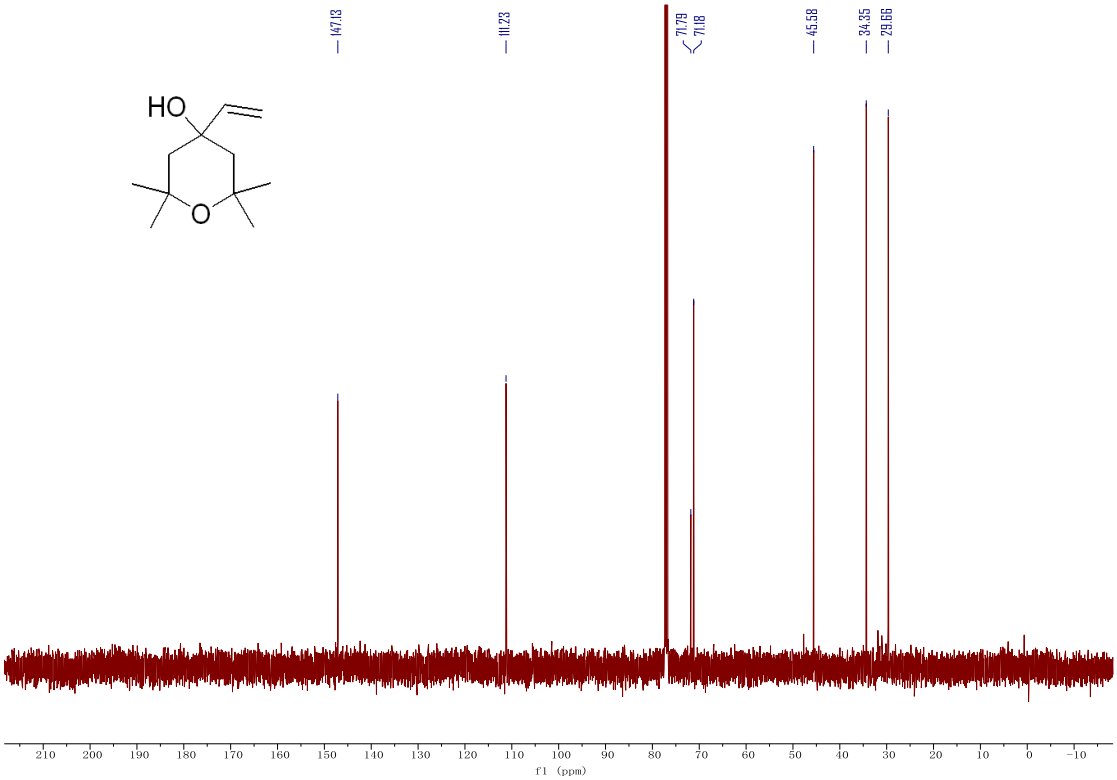
^{1}H NMR of compound **10b** (500 MHz, $CDCl_3$)



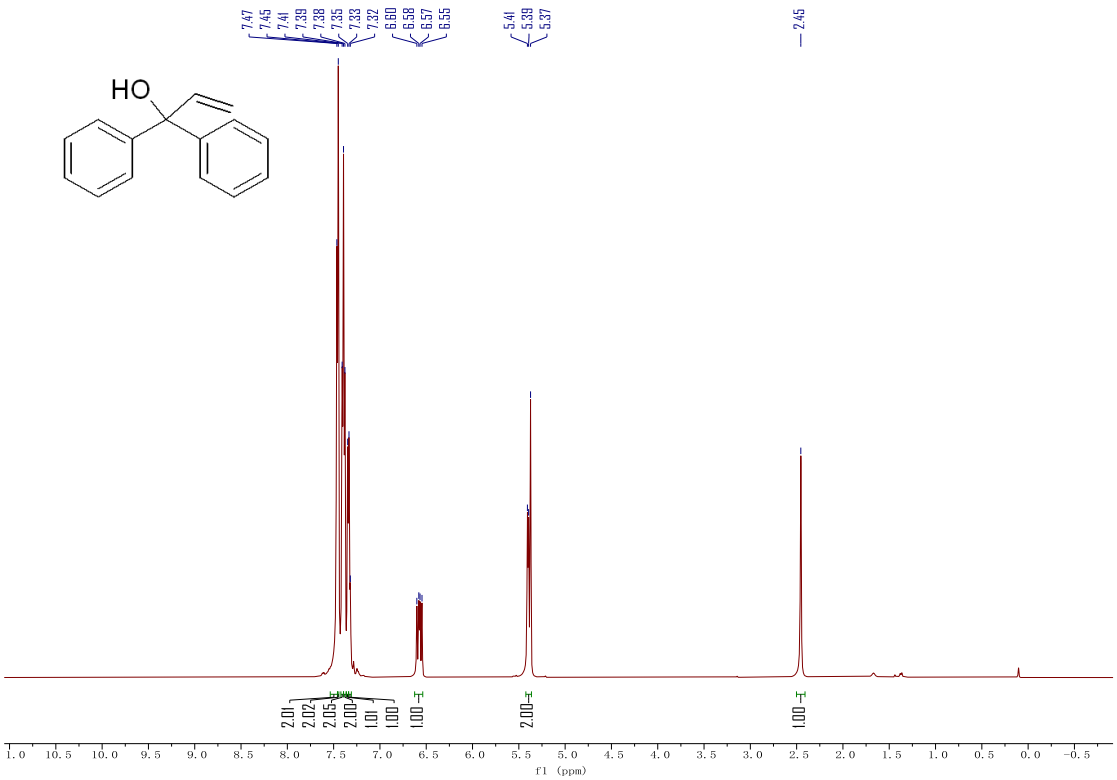
^{13}C NMR of compound **10b** (126 MHz, $CDCl_3$)



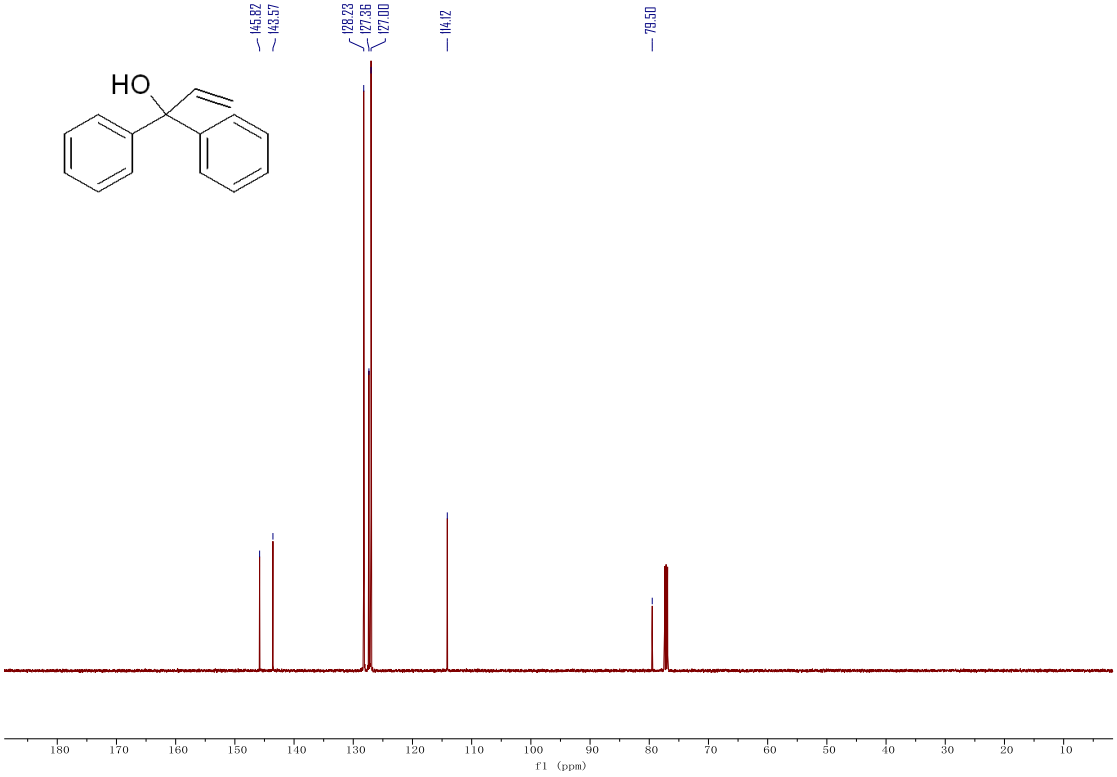
^{1}H NMR of compound **11b** (500 MHz, $CDCl_3$)



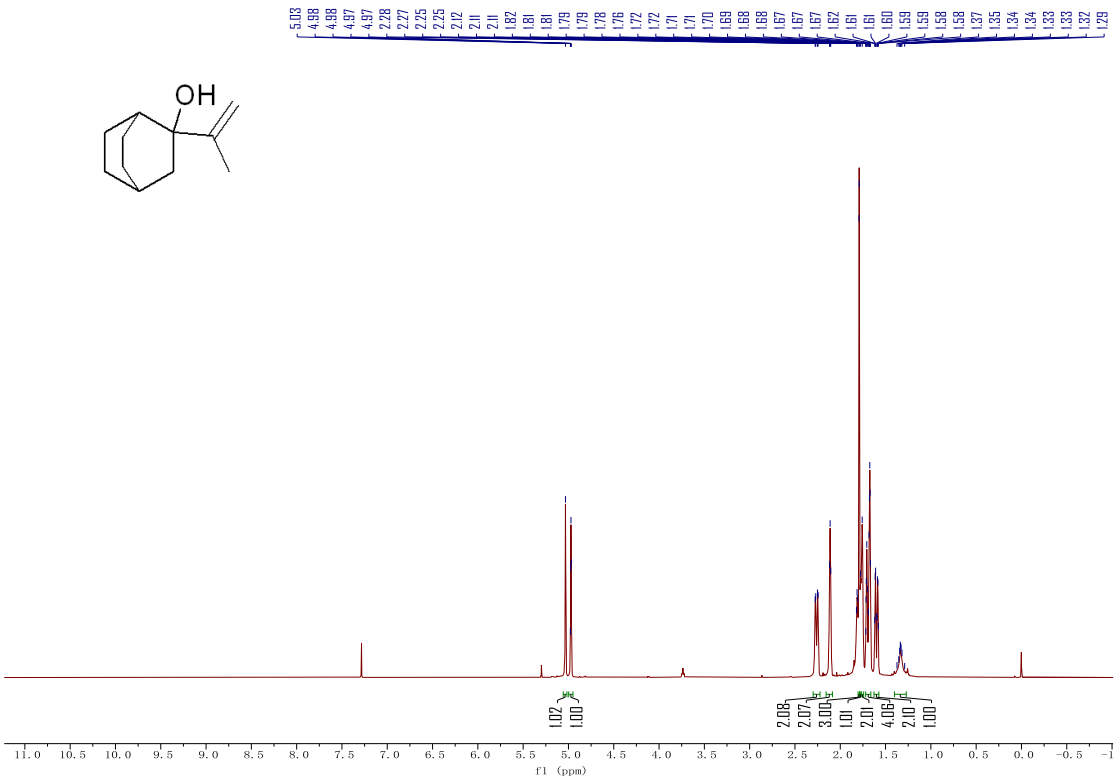
^{13}C NMR of compound **11b** (126 MHz, $CDCl_3$)



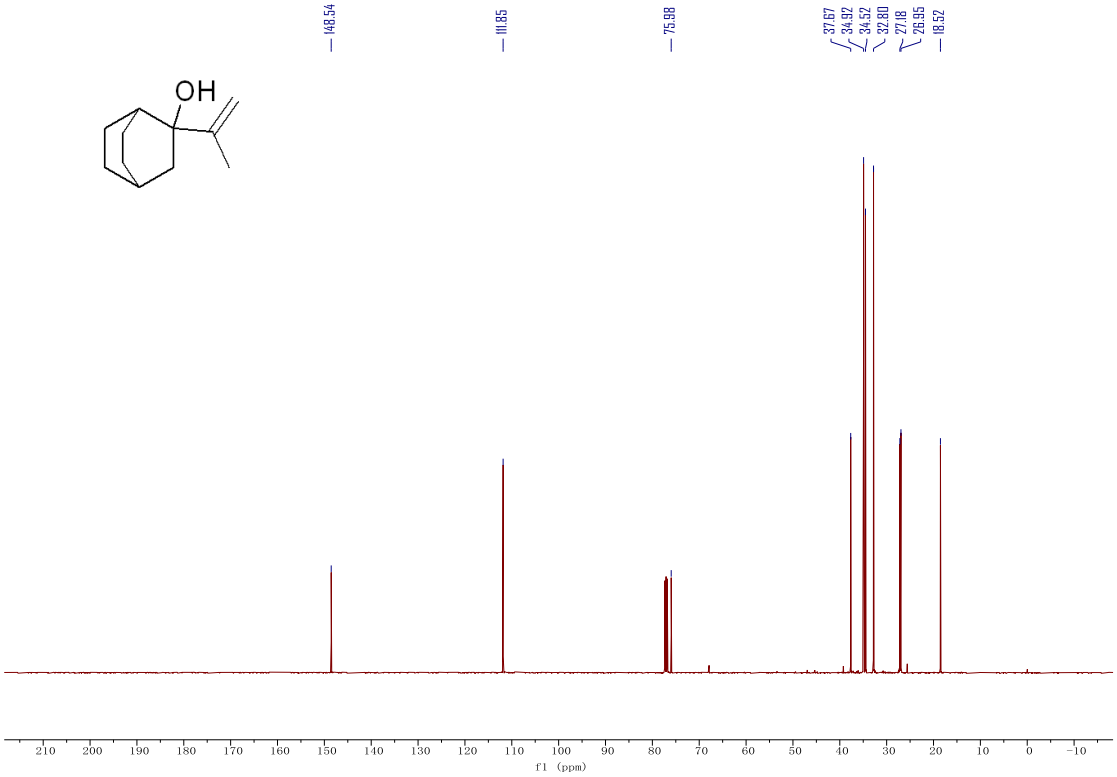
^{1}H NMR of compound **13b** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **13b** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **15b** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **15b** (126 MHz, $CDCl_3$)