

## Supporting information

### **Pd-Catalyzed Asymmetric Allylic Amination Using Easily Accessible Metallocenyl P,N-Ligands**

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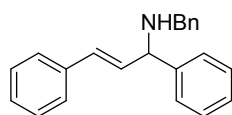
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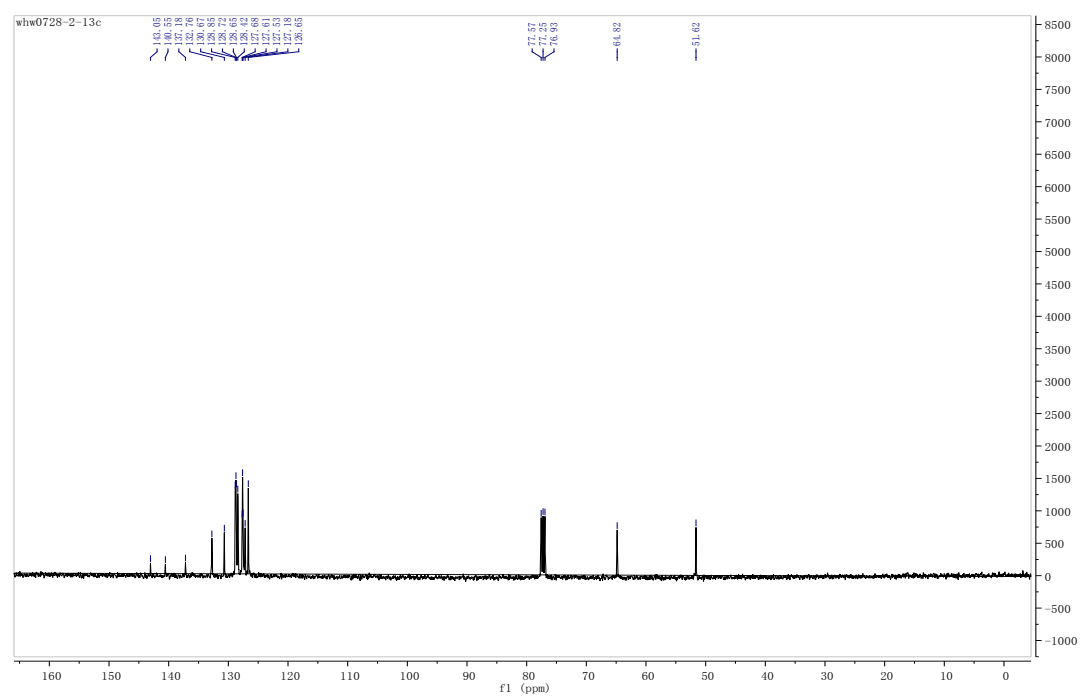
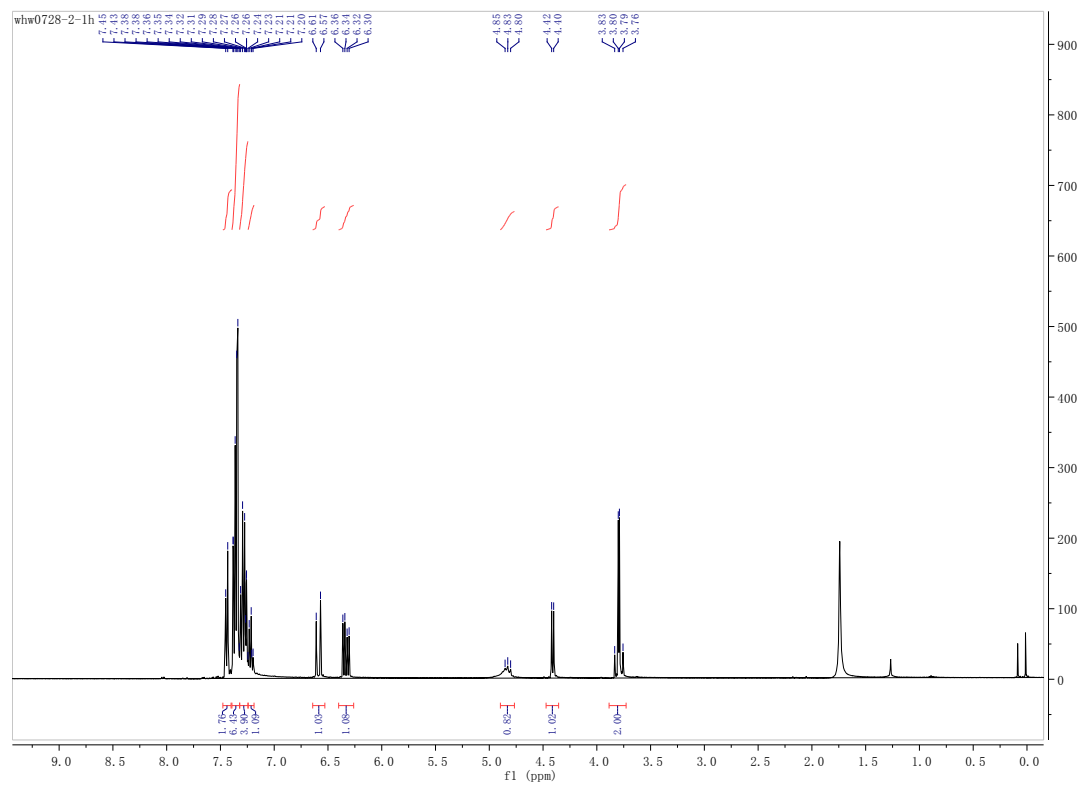
1. NMR Spectra.....	S2
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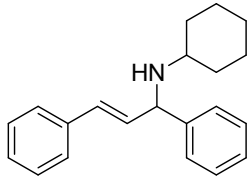
# 1. NMR spectra:



7a

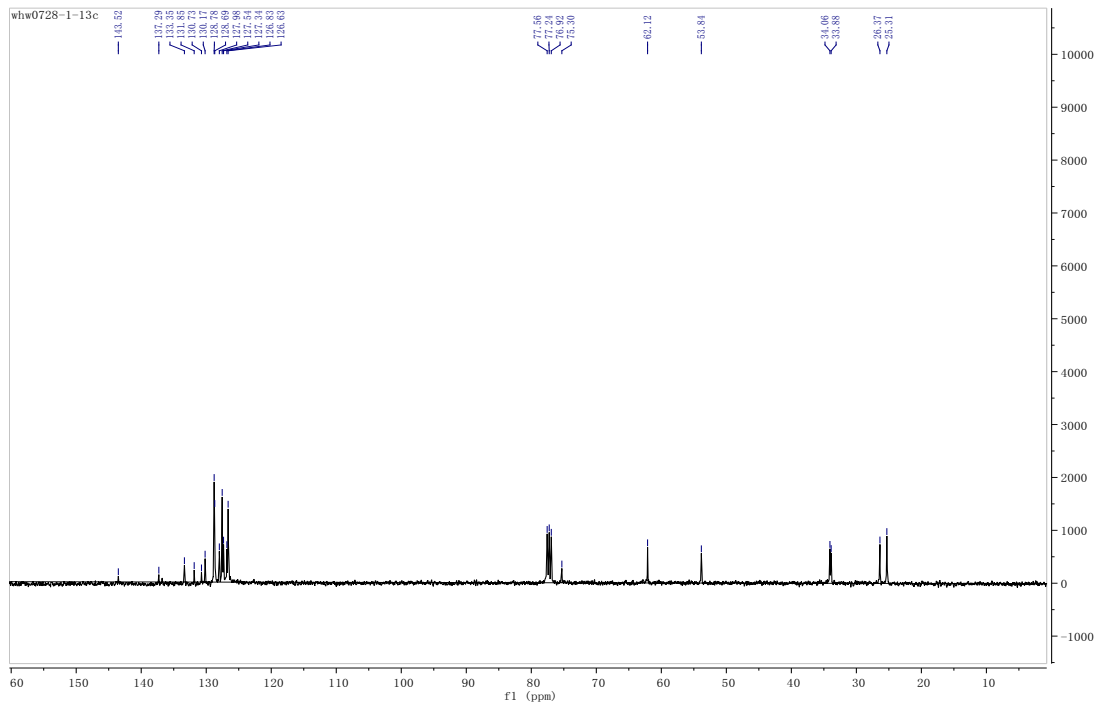
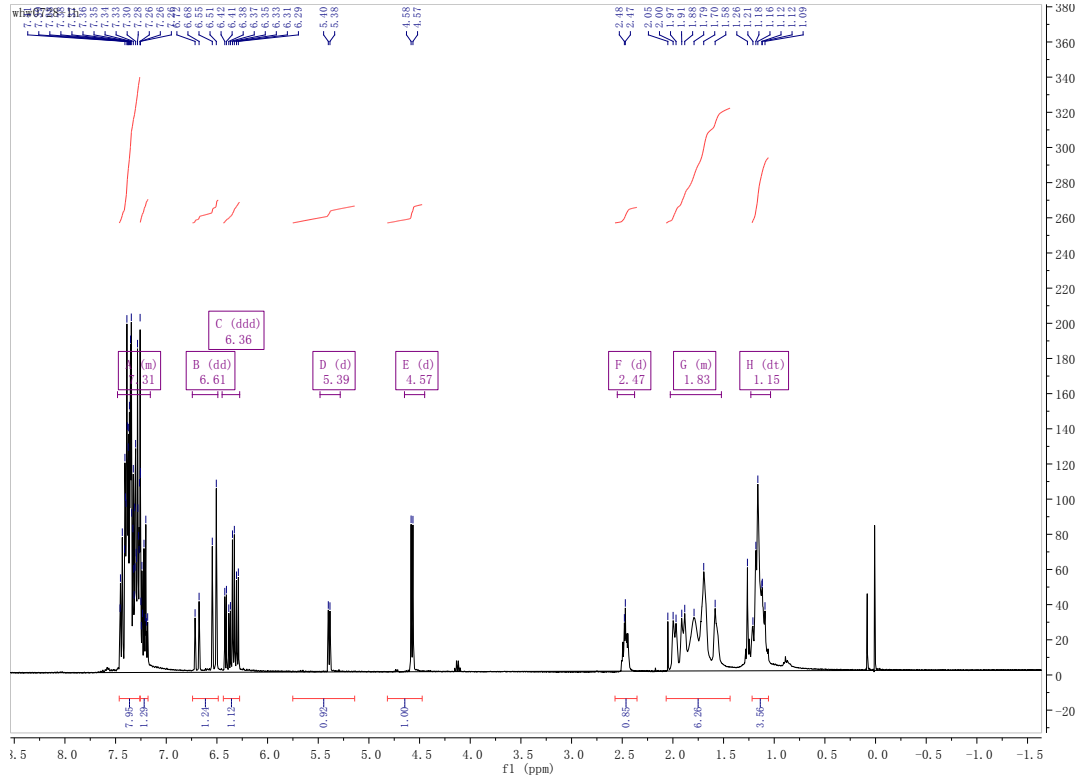
## (E)-N-Benzyl-1,3-diphenylprop-2-en-1-amine(7a):



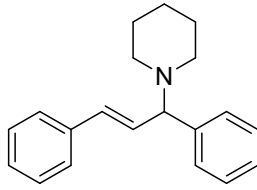


7b

(*E*)-N-(1,3-Diphenylallyl)cyclohexanamine(7b):

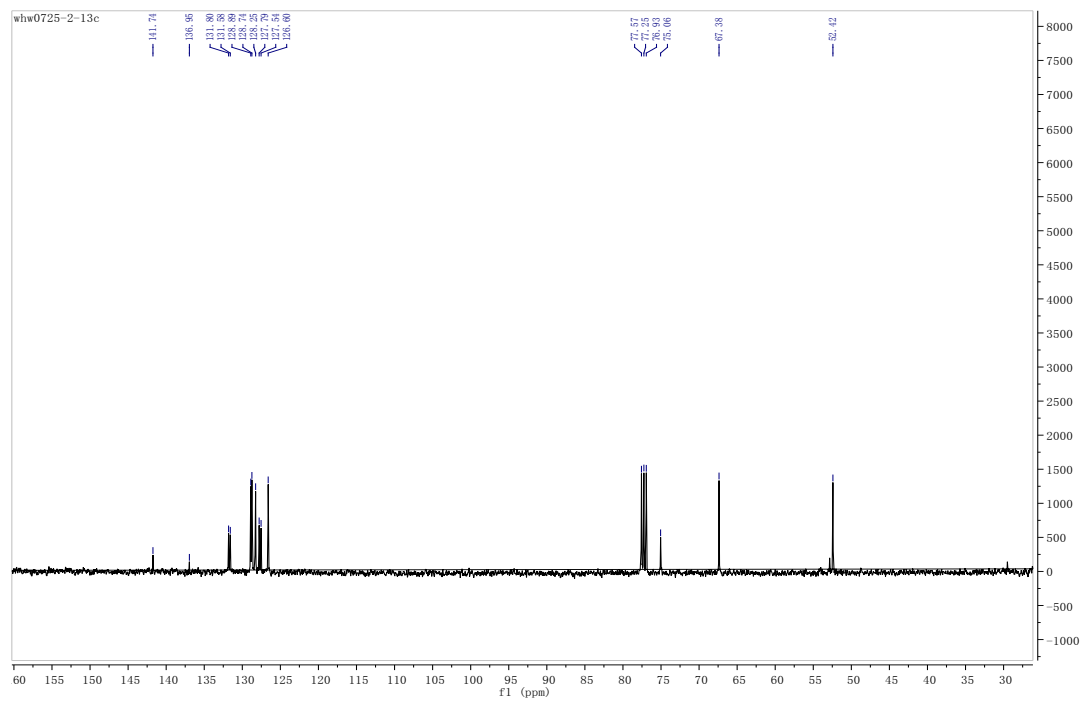
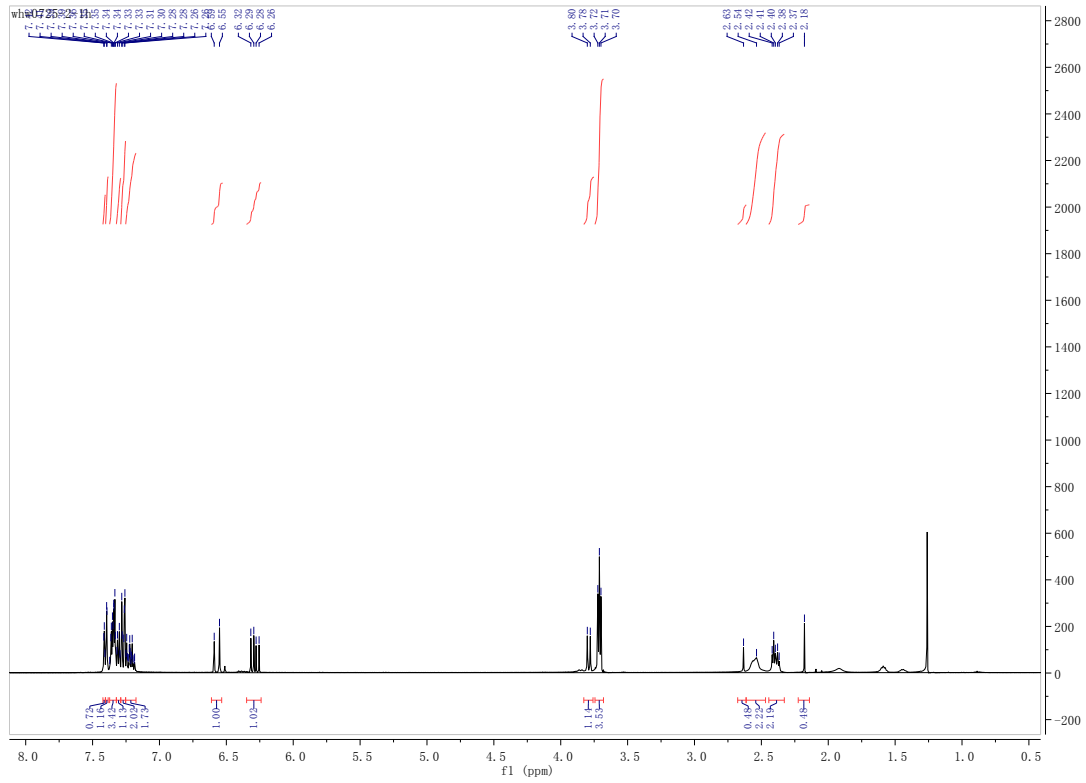




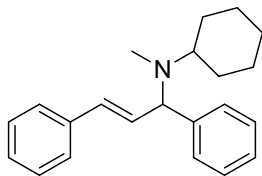


**7d**

**(E)-1-(1,3-Diphenylallyl)piperidine (7d):**

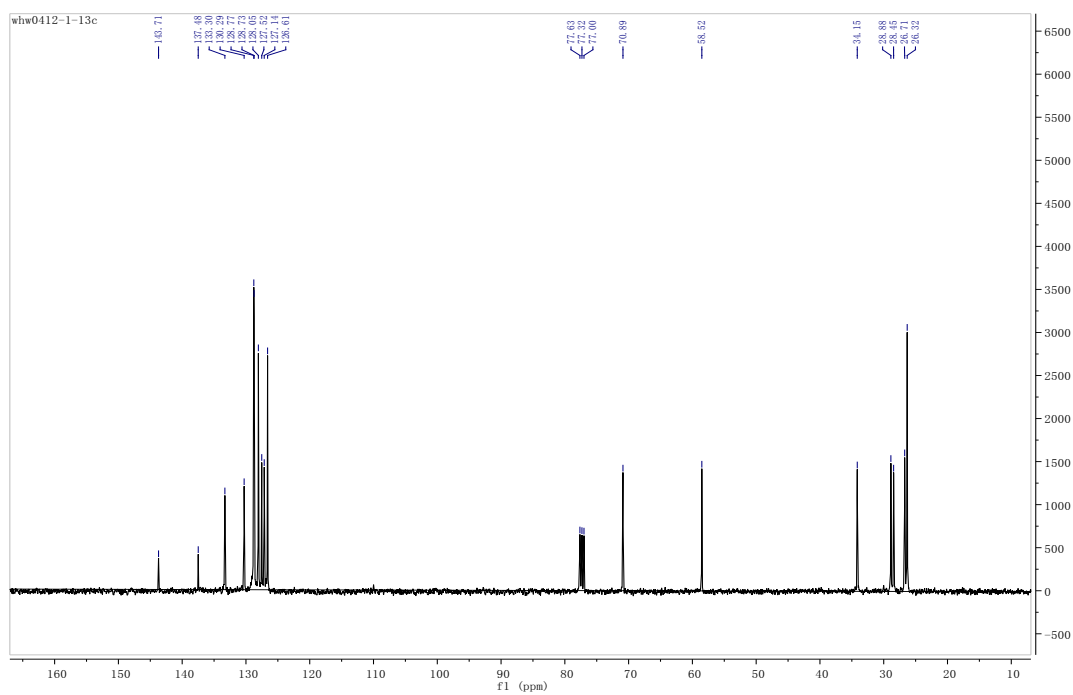
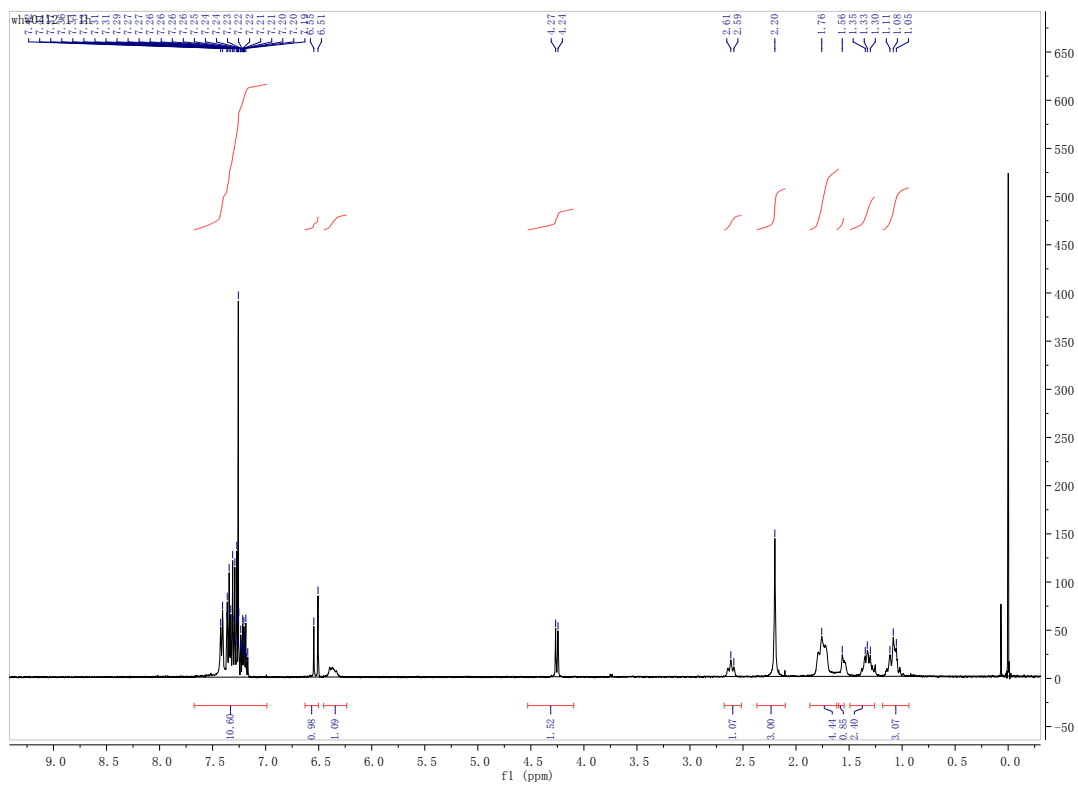


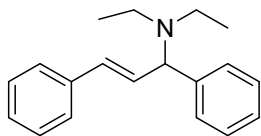




7f

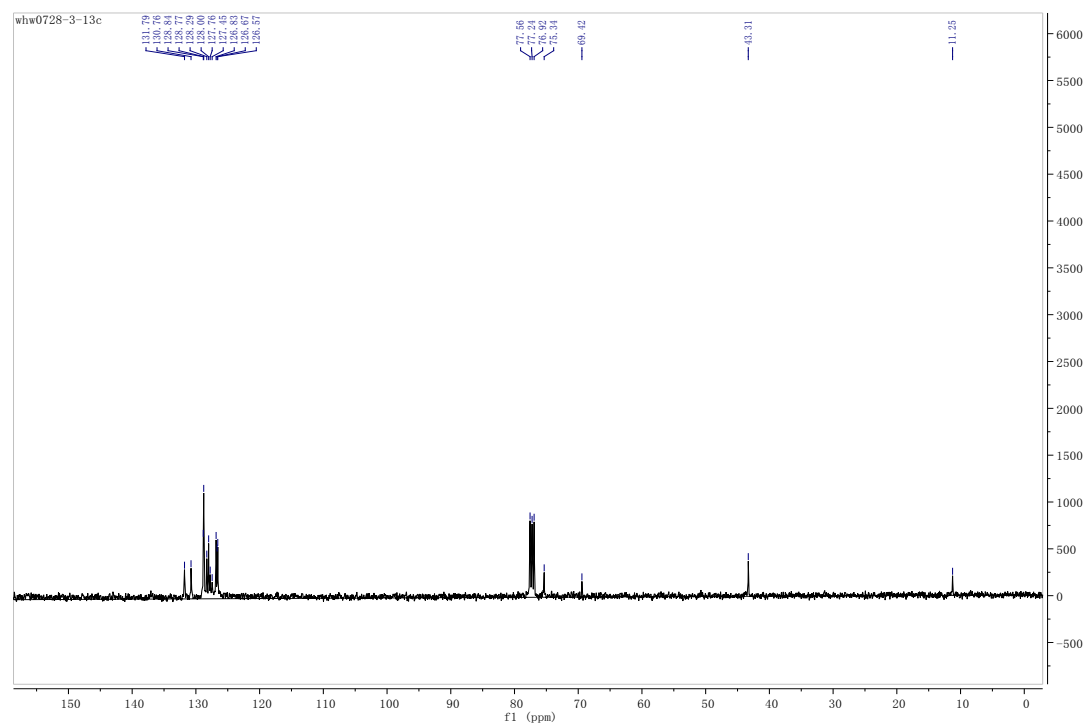
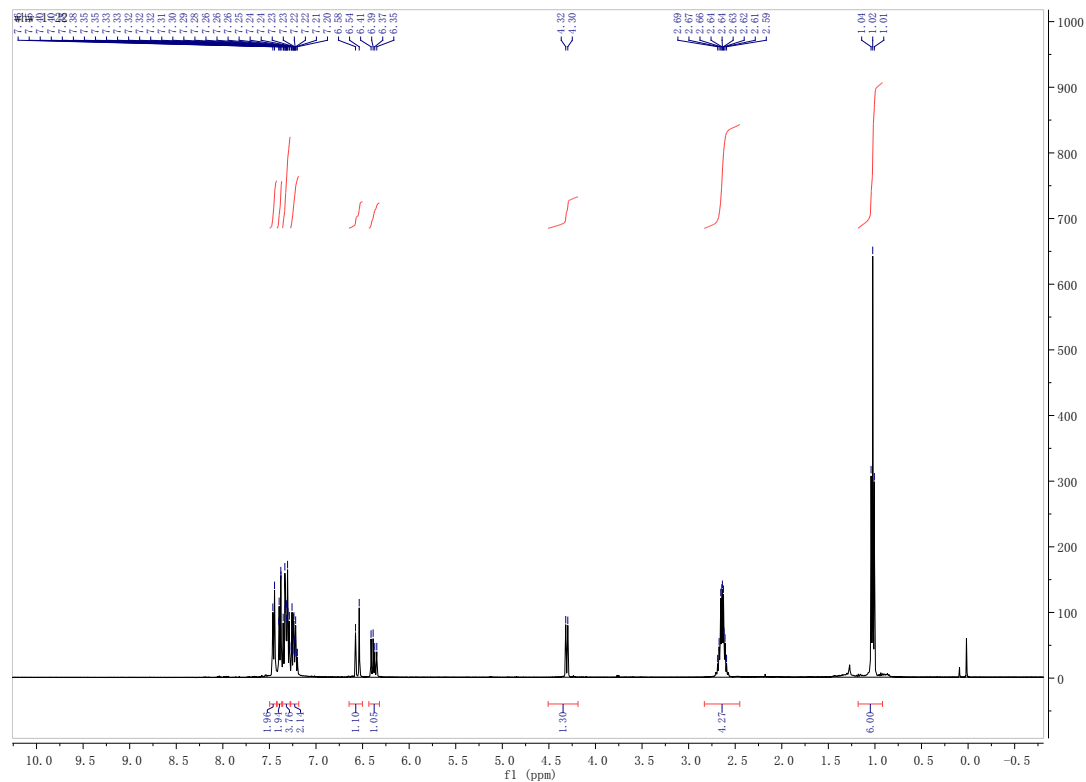
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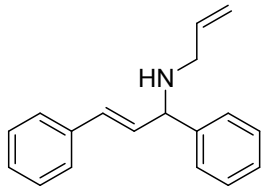


7g

(*E*)-*N,N*-Diethyl-1,3-diphenylprop-2-en-1-amine (7g):

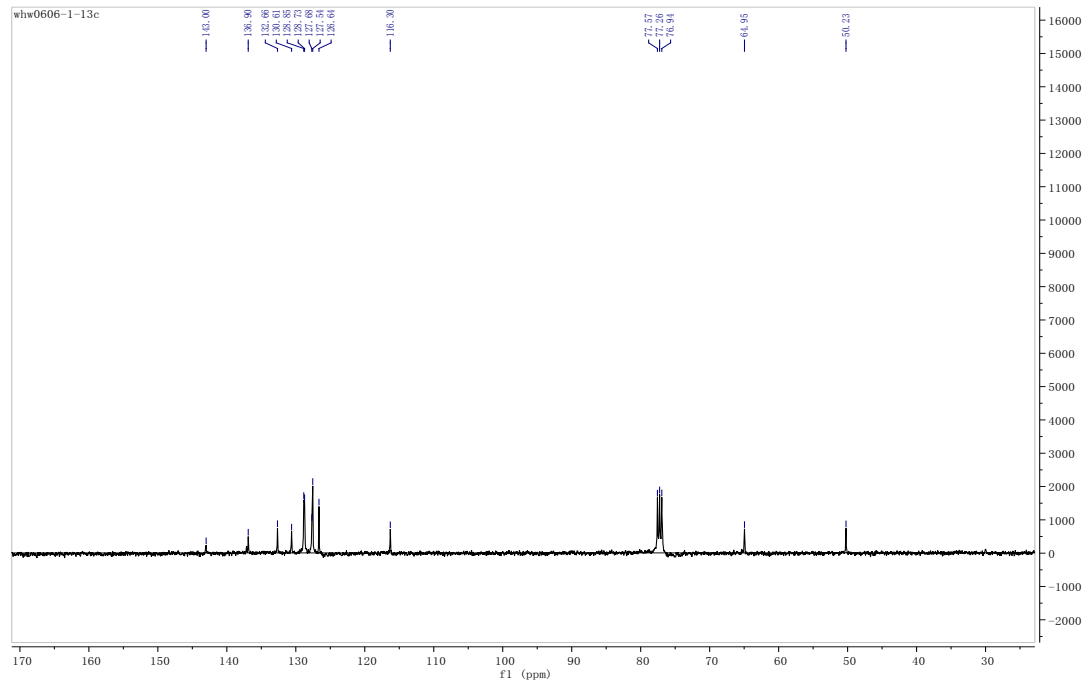
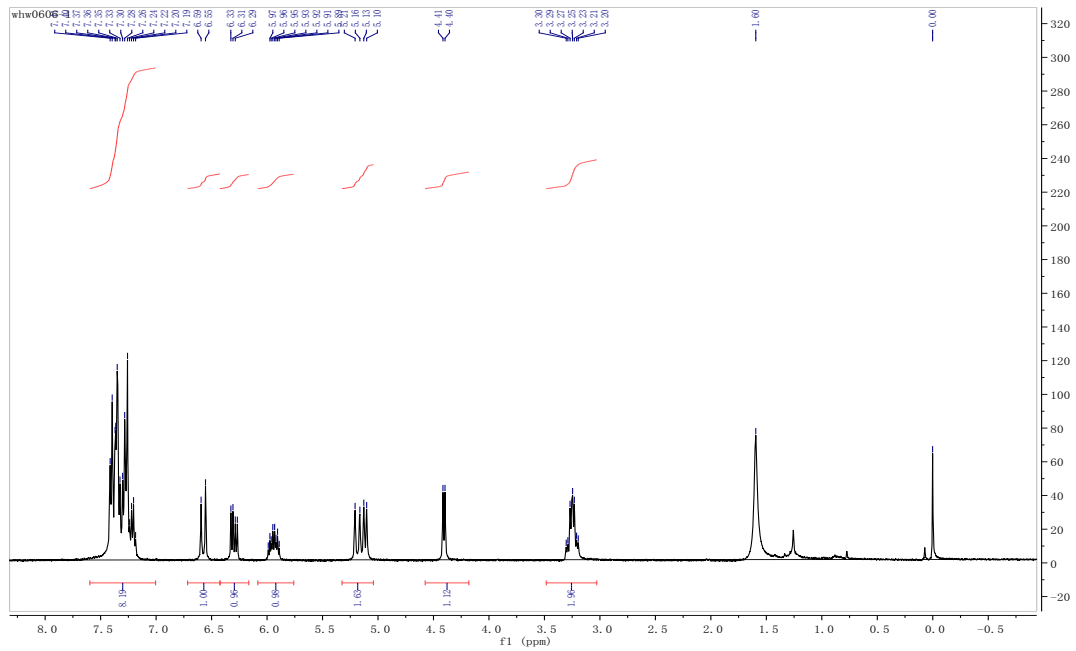


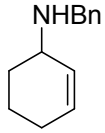




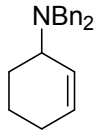
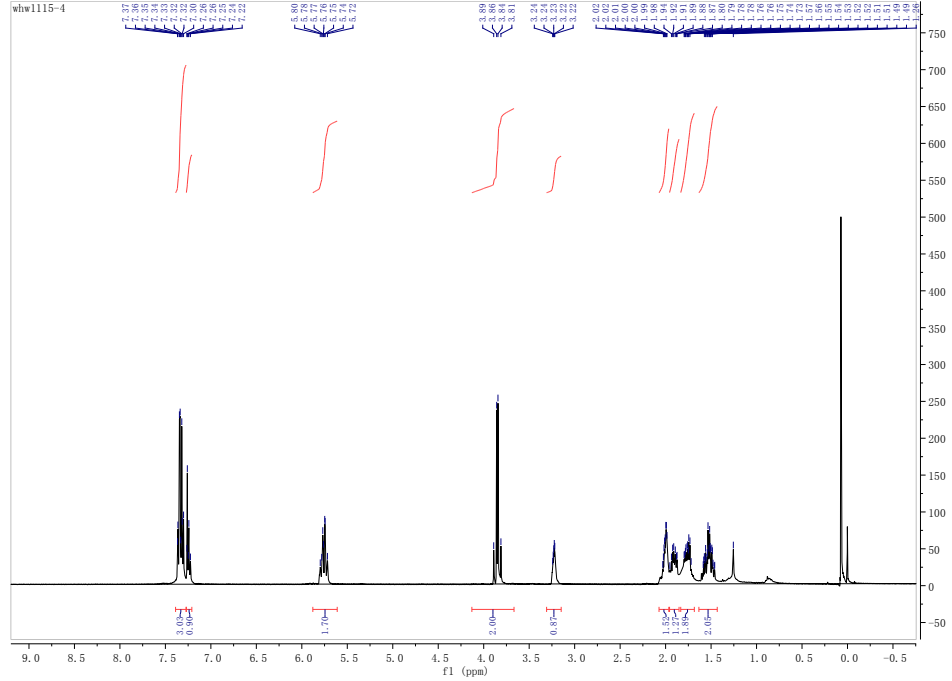
7h

(*E*)-N-Allyl-1,3-diphenylprop-2-en-1-amine (7h):

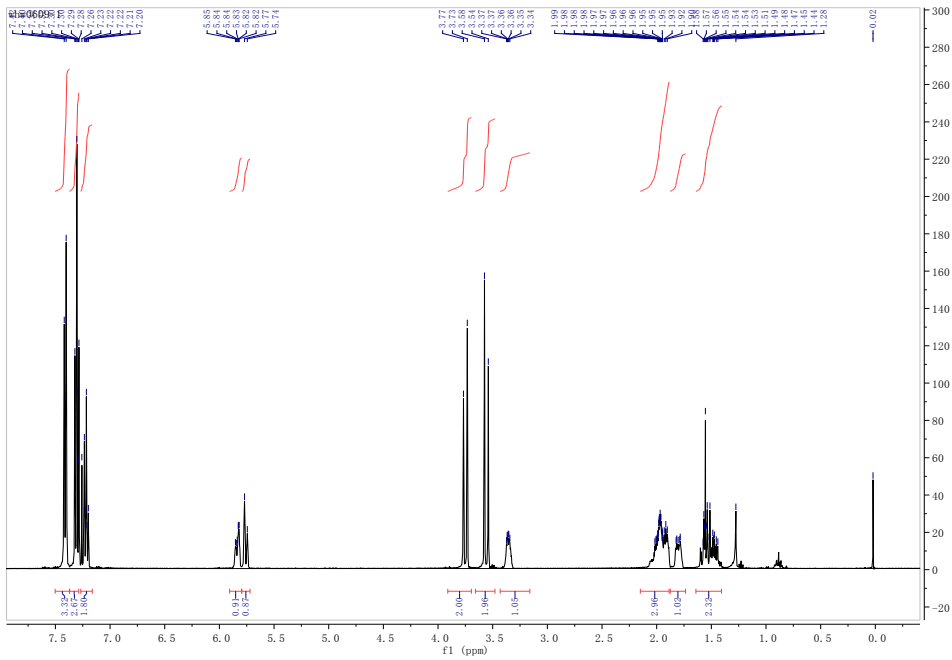


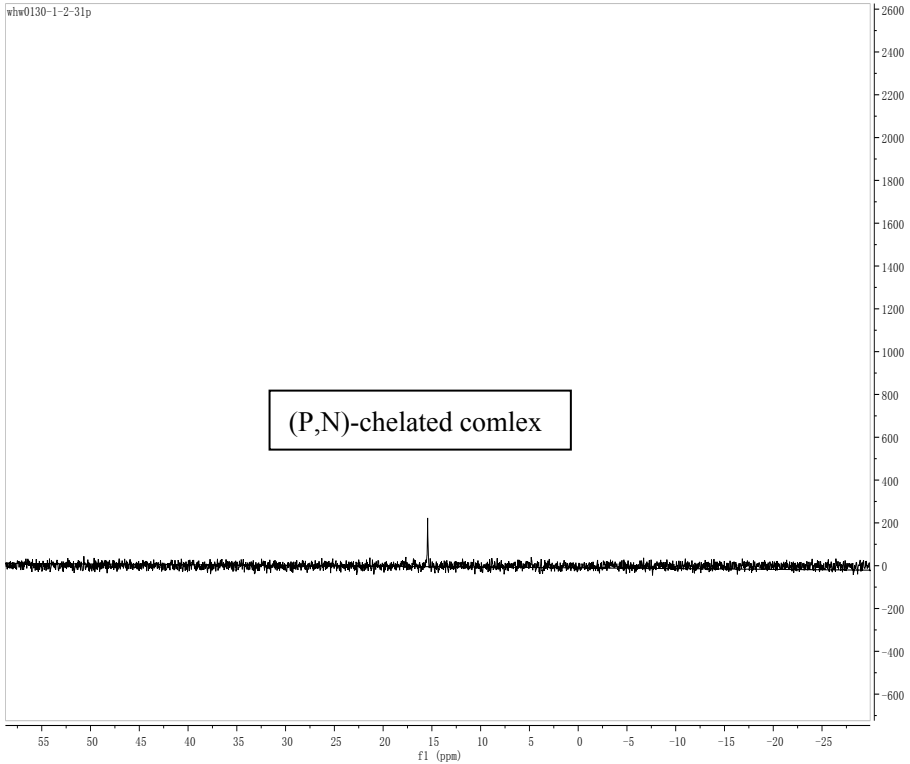
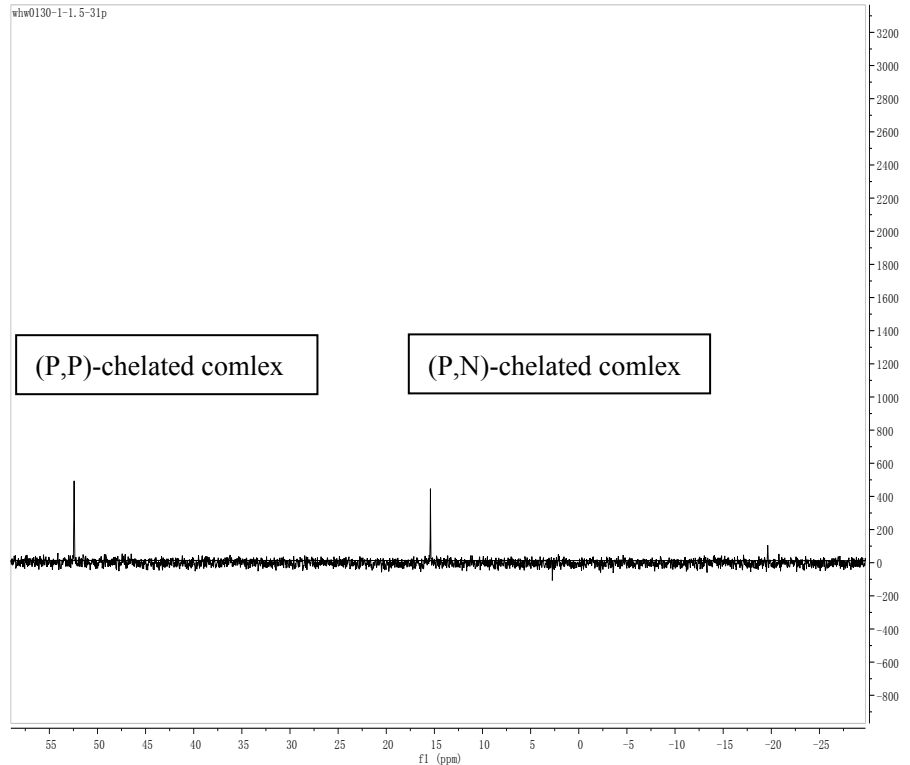


***N*-benzylcyclohex-2-enamine (7i):**



***N,N*-dibenzylcyclohex-2-enamine (7j):**



<b>1b / Pd salt</b>	<b><math>^{31}\text{P}</math> NMR</b>
1 / 2	 <p>whw0130-1-2-31p</p> <p>(P,N)-chelated complex</p> <p>The spectrum shows a single sharp peak at approximately 15 ppm. The x-axis is labeled 'f1 (ppm)' and ranges from 55 to -25. The y-axis ranges from -600 to 2600.</p>
1.5 / 2	 <p>whw0130-1-1.5-31p</p> <p>(P,P)-chelated complex      (P,N)-chelated complex</p> <p>The spectrum shows two sharp peaks: one at approximately 55 ppm (labeled (P,P)-chelated complex) and one at approximately 15 ppm (labeled (P,N)-chelated complex). The x-axis is labeled 'f1 (ppm)' and ranges from 55 to -25. The y-axis ranges from -800 to 3200.</p>

## 2. HPLC spectra:

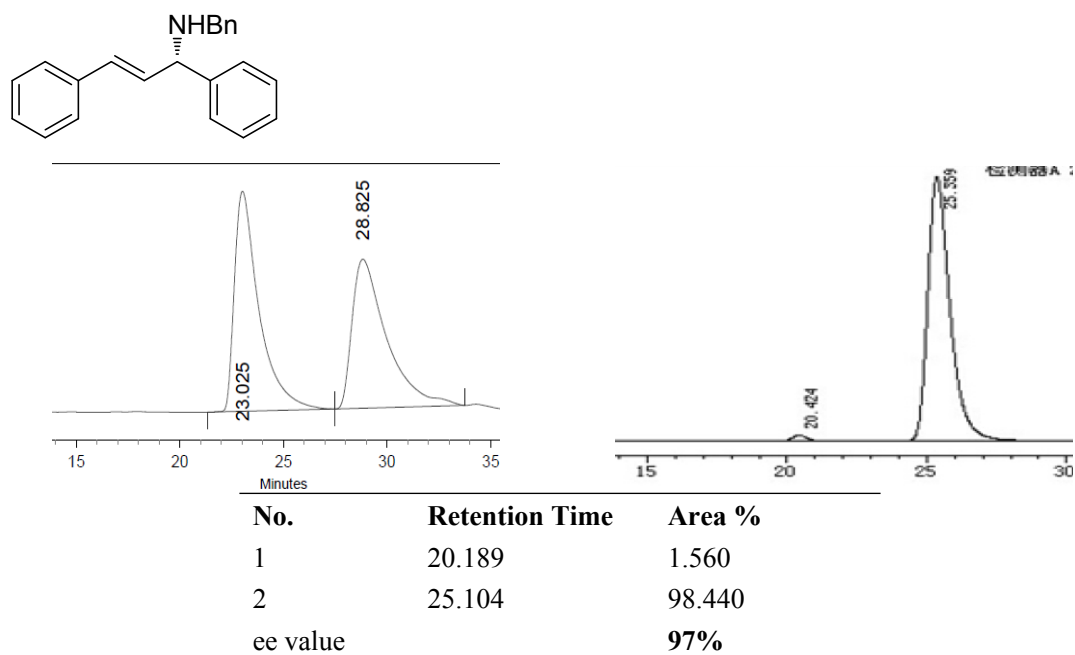


Figure 1. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with benzylamine using **8b** as chiral ligand in Et<sub>2</sub>O at 25 °C (Table 5, entry 6).

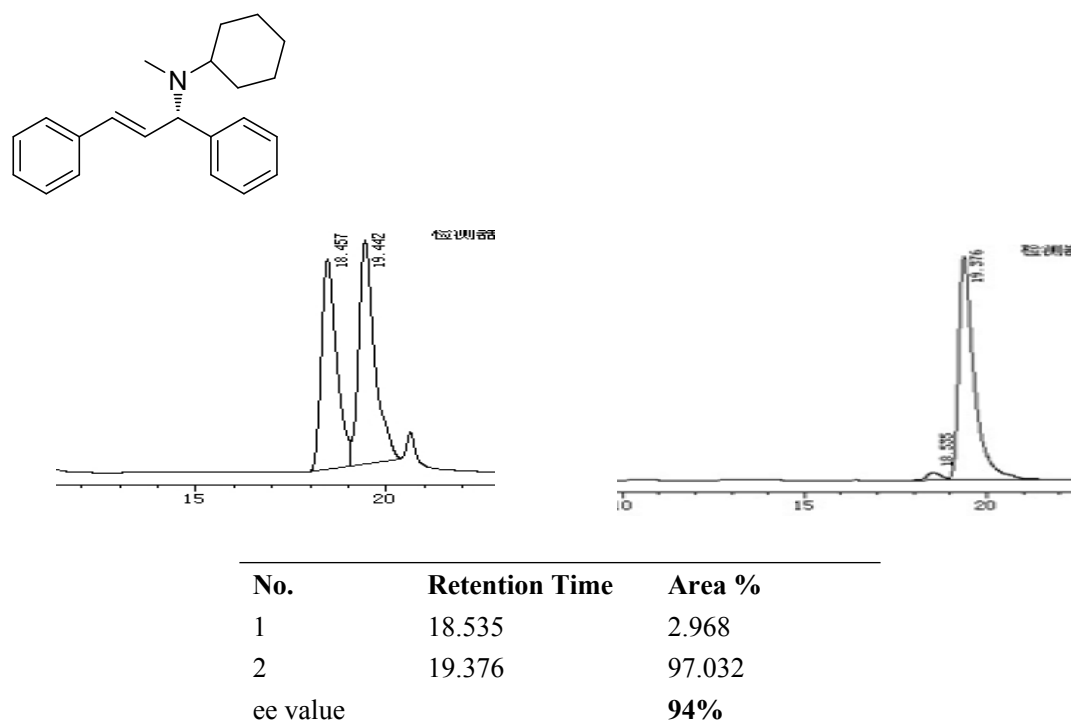
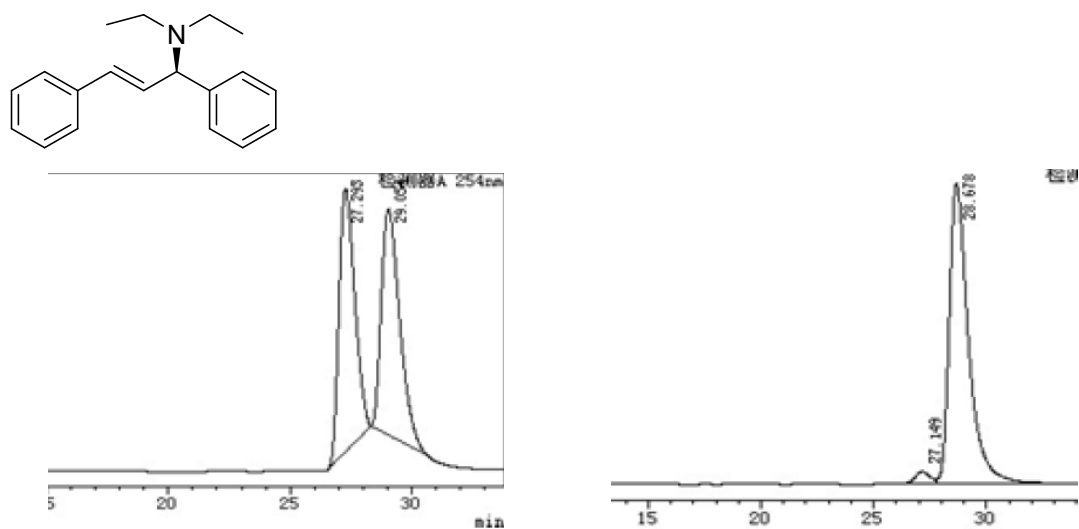
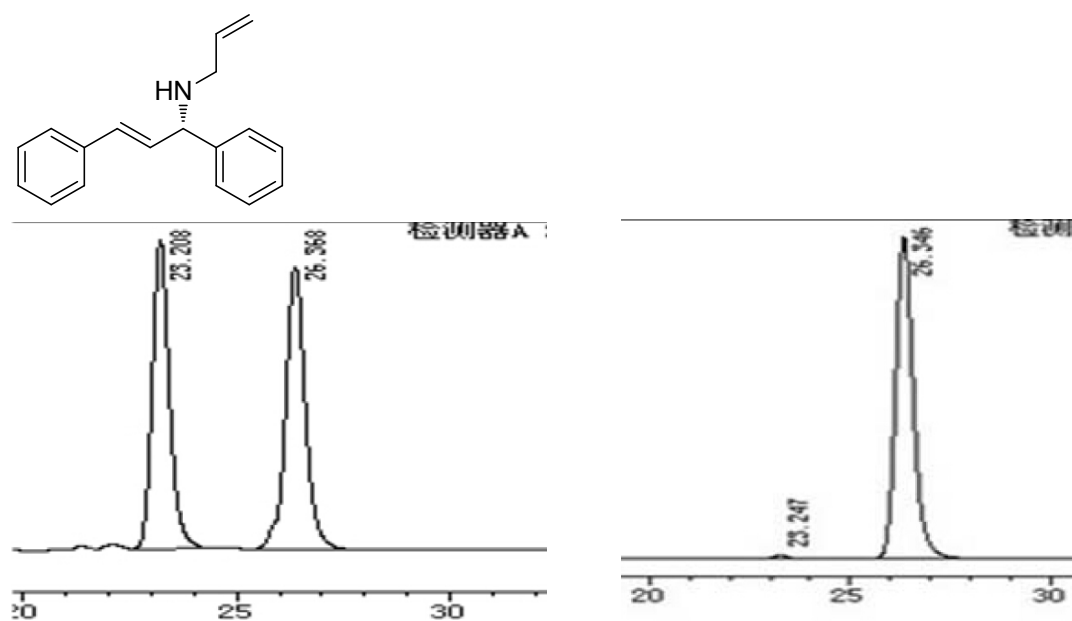


Figure 2. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with N-methylcyclohexanamine using **8b** as chiral ligand in Et<sub>2</sub>O at 25 °C (Table 6, entry 6).



No.	Retention Time	Area %
1	27.149	2.857
2	28.678	97.143
ee value		<b>94%</b>

Figure 3. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with diethylamine using **8b** as chiral ligand in Et<sub>2</sub>O at 25 °C (Table 6, entry 7).



No.	Retention Time	Area %
1	23.247	0.941
2	26.346	99.059
ee value		<b>98%</b>

Figure 4. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with prop-2-en-1-amine using **8b** as chiral ligand in Et<sub>2</sub>O at 25 °C (Table 6, entry 3).

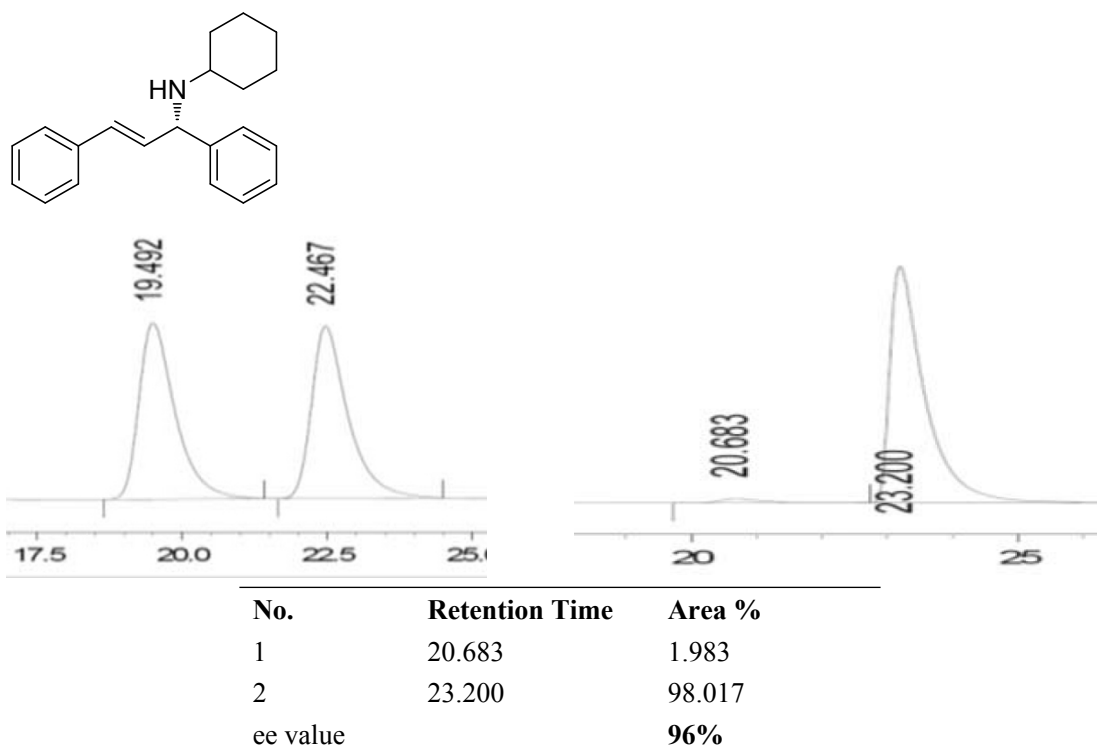


Figure 5. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with cyclohexanamine using **3b** as chiral ligand in PhCH<sub>3</sub> at 25 °C (Table 3, entry 1).

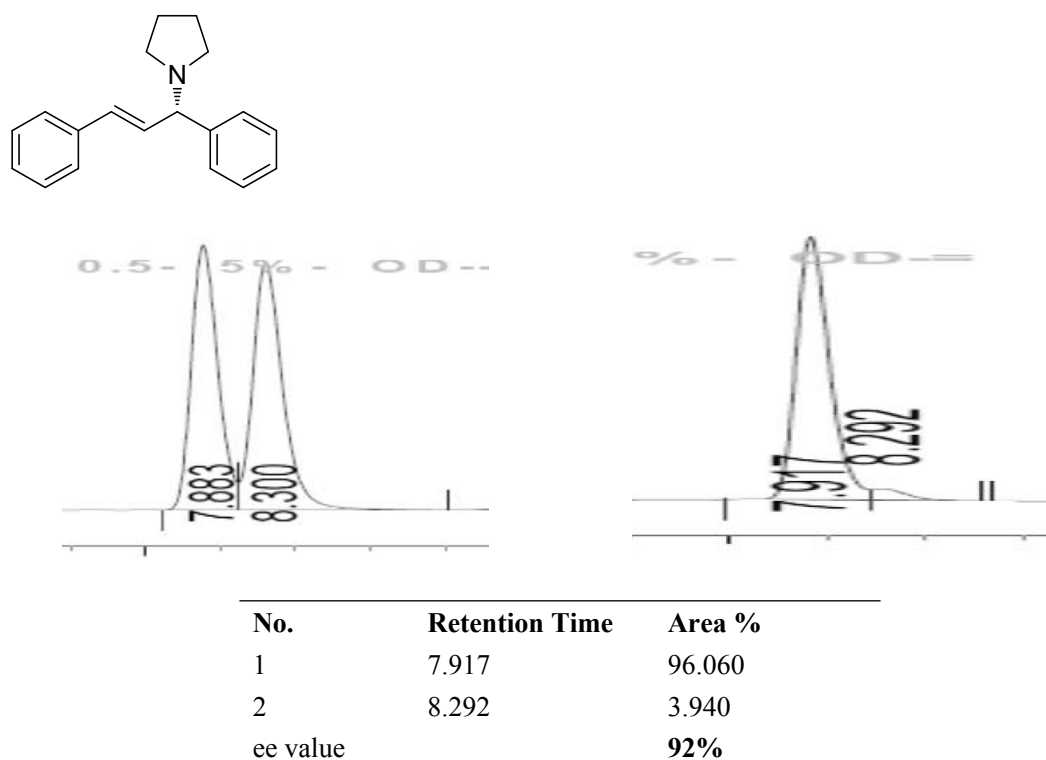
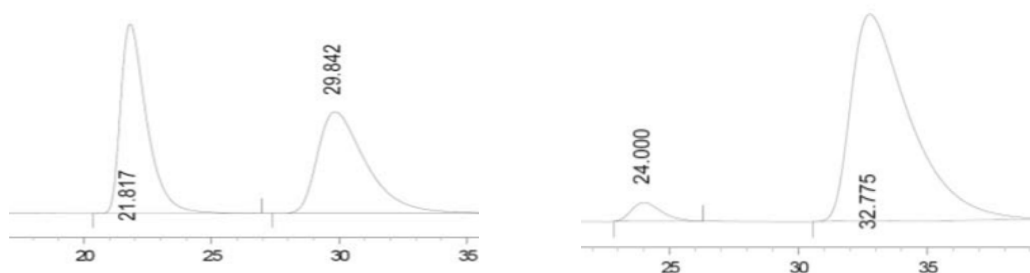
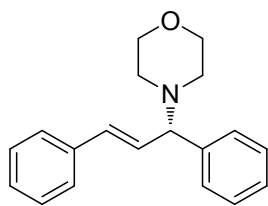
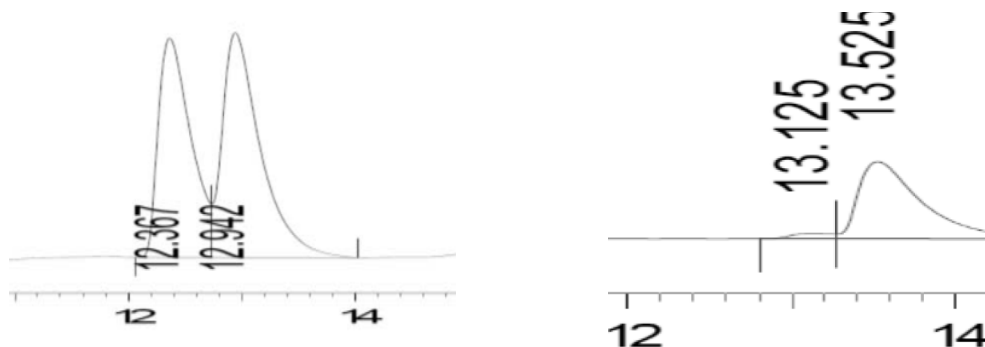
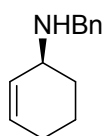


Figure 6. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with pyrrolidine using **3b** as chiral ligand in PhCH<sub>3</sub> at 25 °C (Table 3, entry 3).



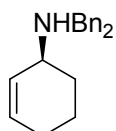
No.	Retention Time	Area %
1	24.000	4.390
2	32.775	95.610
ee value		<b>91%</b>

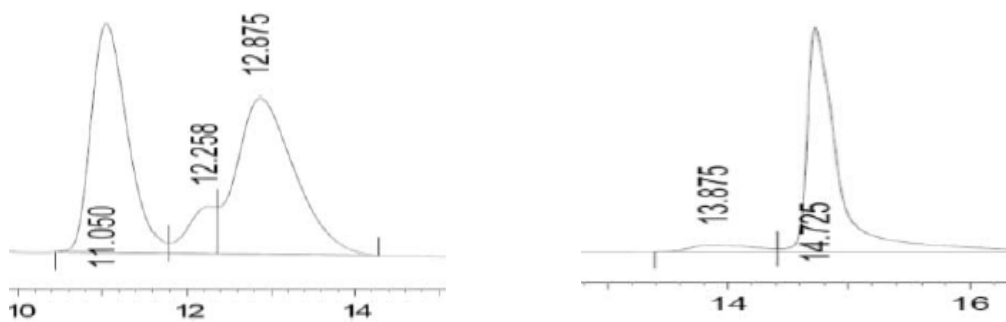
Figure 7. Enantioselective product of 1,3-diphenyl-2-propenyl acetate with morpholine using **3b** as chiral ligand in PhCH<sub>3</sub> at 25 °C (Table 3, entry 5).



No.	Retention Time	Area %
1	13.125	4.068
2	13.525	95.932
ee value		<b>92%</b>

Figure 8. Enantioselective product of cyclohexen-1-yl acetate with benzylamine using **3b** as chiral ligand in PhCH<sub>3</sub> at 25 °C (Table 4, entry 1).





No.	Retention Time	Area %
1	13.875	5.189
2	14.725	94.811
ee value		<b>90%</b>

Figure 9. Enantioselective product of cyclohexen-1-yl acetate with dibenzylamine using **3b** as chiral ligand in PhCH<sub>3</sub> at 25 °C (Table 4, entry 3).