

**CO<sub>2</sub>-Mediated Formation of Chiral Carbamates from *meso*-Epoxides via  
Polycarbonate Intermediates**

Ye Liu,\* Wei-Min Ren, Ke-Ke He, Wen-Zhen Zhang, Wen-Bing Li, Meng Wang, and  
Xiao-Bing Lu\*

**Supporting Information**

**Table of Content**

1. Determination of enantiomeric purity of carbamate derivatives .....	2
2. NMR spectrum of various carbamate derivatives .....	3
3. HPLC spectrum of various carbamate derivatives .....	17
4. Mechanistic understanding of ammonolysis reaction .....	35
5. NMR spectrum of ( <i>S,S</i> )-carbamate derivative for X-Ray analysis .....	42
6. Crystal structure determination .....	43

### 1. Determination of enantiomeric purity of carbamate derivatives

The enantiomeric excess of *trans*-carbamate derivatives **1a-1d**, **1g**, **1h**, **1i**, **2a-2c**, **3a**, **3c**, **4a**, **4b**, **5a**, **6a** and **7a** were determined by HPLC using a chiral column, the details were listed in Table S1.

**Table S1. HPLC resolution conditions and results of racemic compounds<sup>a</sup>**

Entry	substrate	Chiral column	Mobile phase ( <sup>n</sup> Hexane/ <sup>i</sup> PrOH)	$\lambda$ (nm)	Retention time (min)
1	<b>1a</b>	Chiralpak AD	95/5	210	12.2/13.6
2	<b>1b</b>	Chiralpak AD	95/5	210	10.4/11.3
3	<b>1c</b>	Chiralpak AD	90/10	210	9.3/11.5
4	<b>1d</b>	Chiralpak AD	95/5	210	19.6/48.1
5	<b>1g</b>	Chiralpak AD	90/10	254	9.2/10.4
6	<b>1h</b>	Chiralpak AD	90/10	254	8.4/9.2
7	<b>1i</b>	Chiralpak AS-H	90/10	214	5.9/10.1
8	<b>2a</b>	Chiralpak AD	90/10	210	9.7/15.5
9	<b>2b</b>	Chiralcel AD	90/10	210	8.8/12.1
10	<b>2c</b>	Chiralpak AD	90/10	210	7.4/12.9
11	<b>3a</b>	Chiralpak AS-H	95/5	210	8.6/10.2
12	<b>3c</b>	Chiralpak AD	90/10	210	13.0/15.1
13	<b>4a</b>	Chiralpak AD	90/10	210	7.3/14.2
14	<b>4b</b>	Chiralpak AD	95/5	210	22.5/30.9
15	<b>5a</b>	Chiralpak AD	90/10	210	8.5/10.2
16	<b>6a</b>	Chiralpak AD	90/10	254	12.1/15.1
17	<b>7a</b>	Chiralpak AD	90/10	210	9.1/12.1

<sup>a</sup>flow rate is 1.0 mL/min and  $\lambda$  is maximum absorption wavelength.

The determination enantiomeric excess of **1e**, **1f** and **3b** was not determined because of the low ultraviolet response in HPLC analysis

## 2. NMR spectrum of various carbamate derivatives

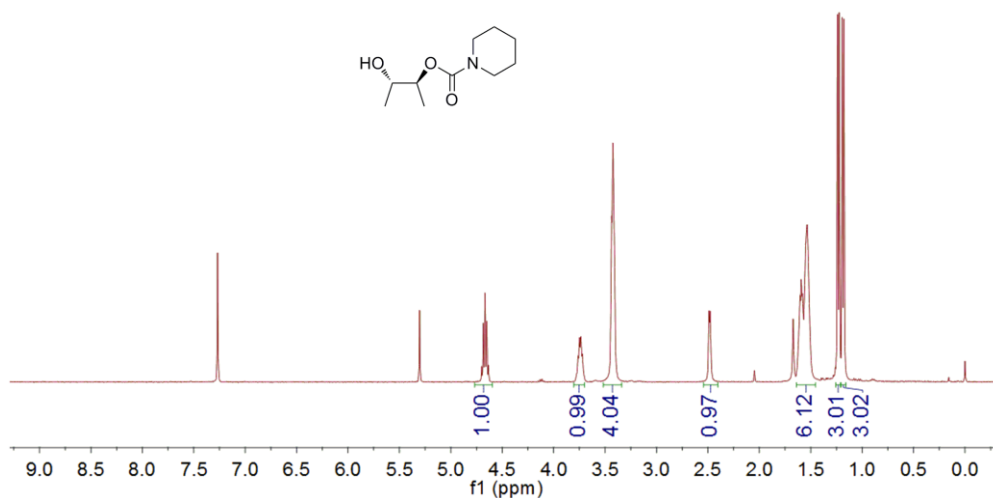


Figure S1. <sup>1</sup>H NMR spectrum of 1a

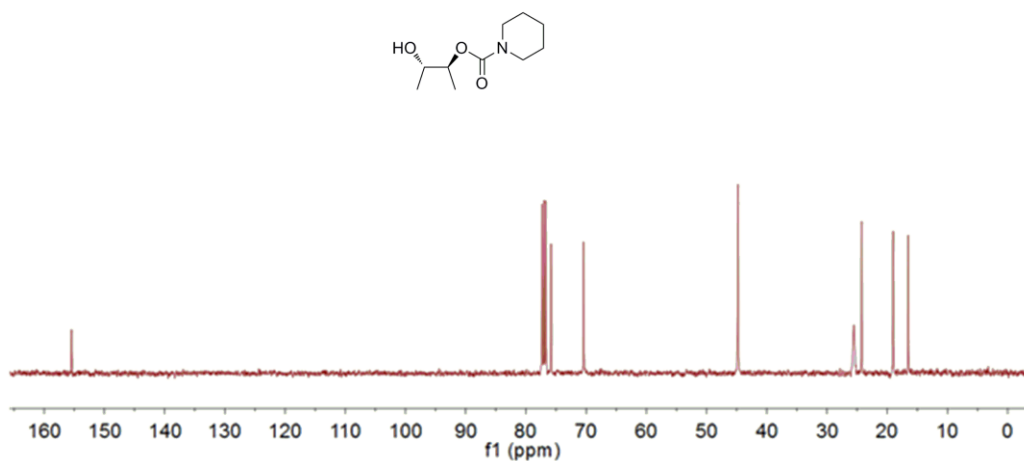


Figure S2. <sup>13</sup>C NMR spectrum of 1a

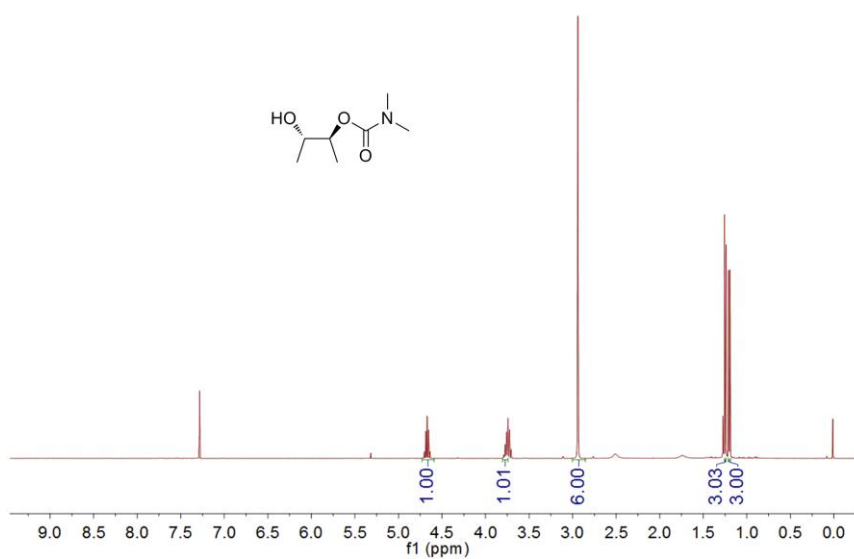
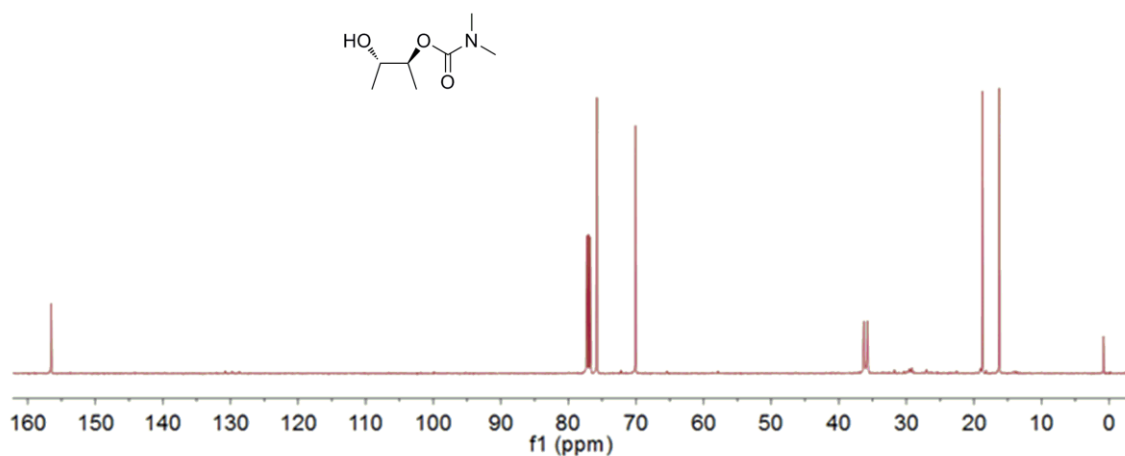
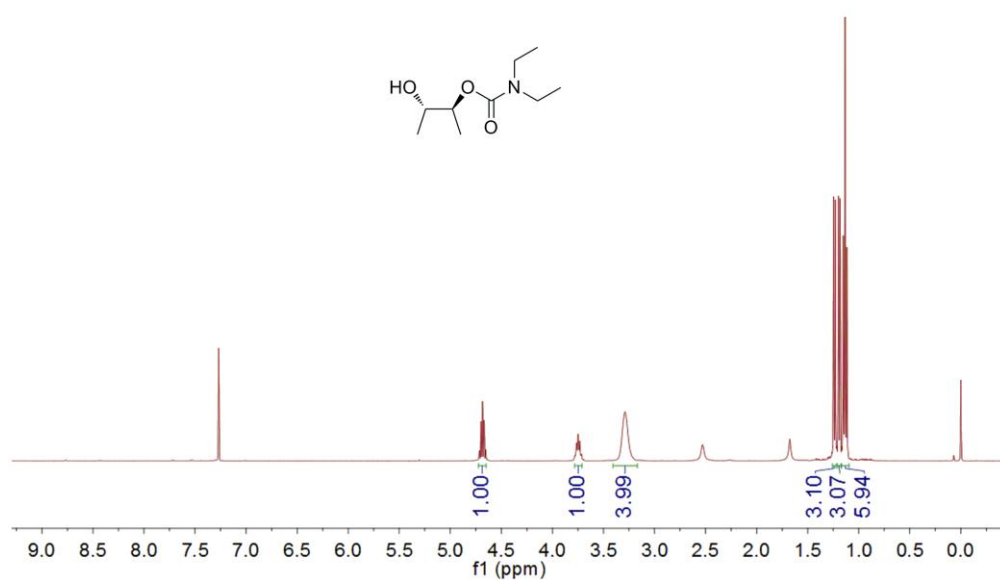


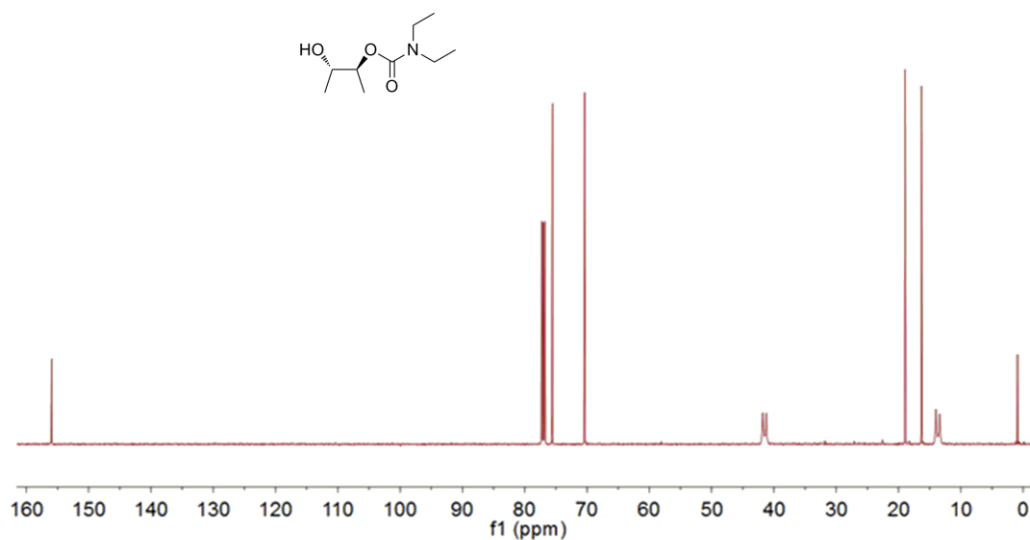
Figure S3. <sup>1</sup>H NMR spectrum of 1b



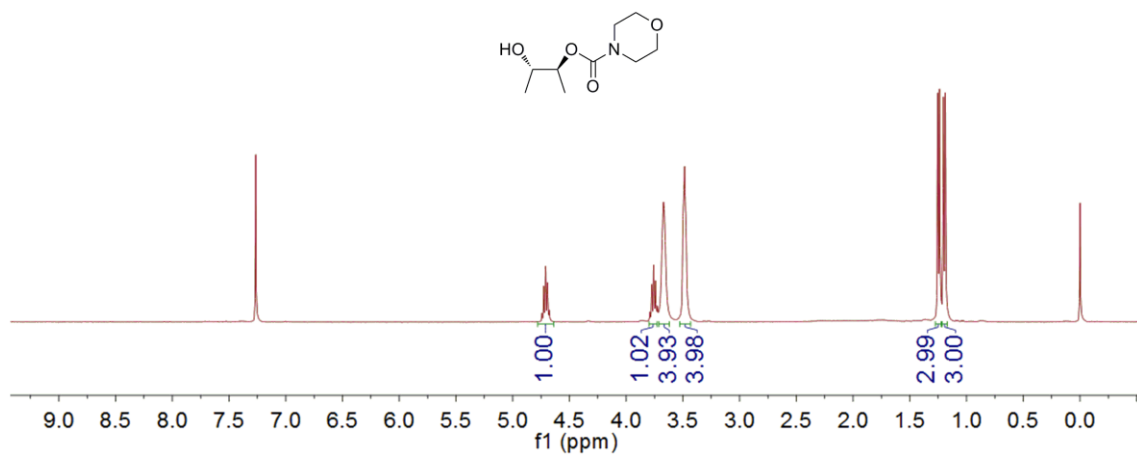
**Figure S4.** <sup>13</sup>C NMR spectrum of **1b**



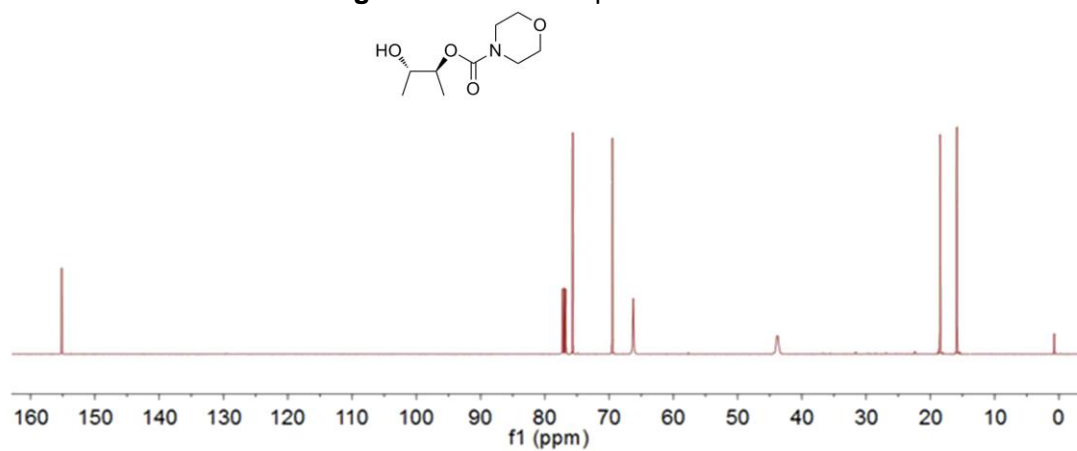
**Figure S5.** <sup>1</sup>H NMR spectrum of **1c**



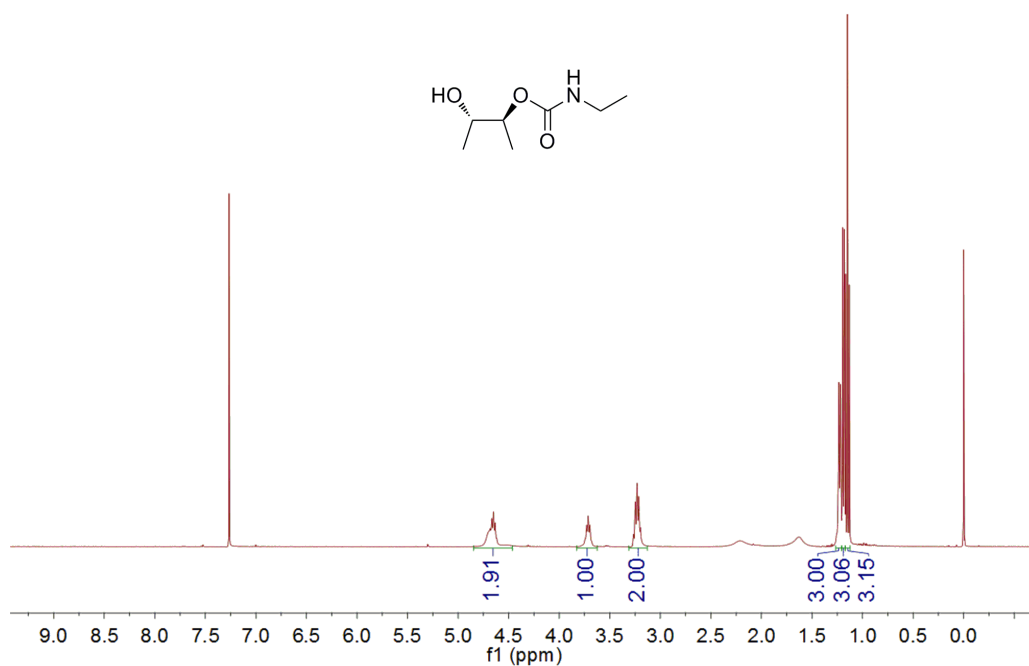
**Figure S6.** <sup>13</sup>C NMR spectrum of **1c**



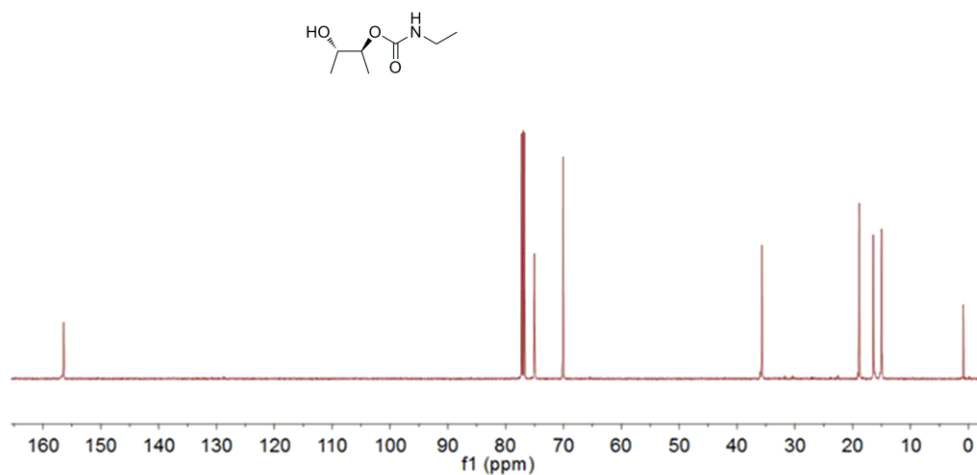
**Figure S7.** <sup>1</sup>H NMR spectrum of 1d



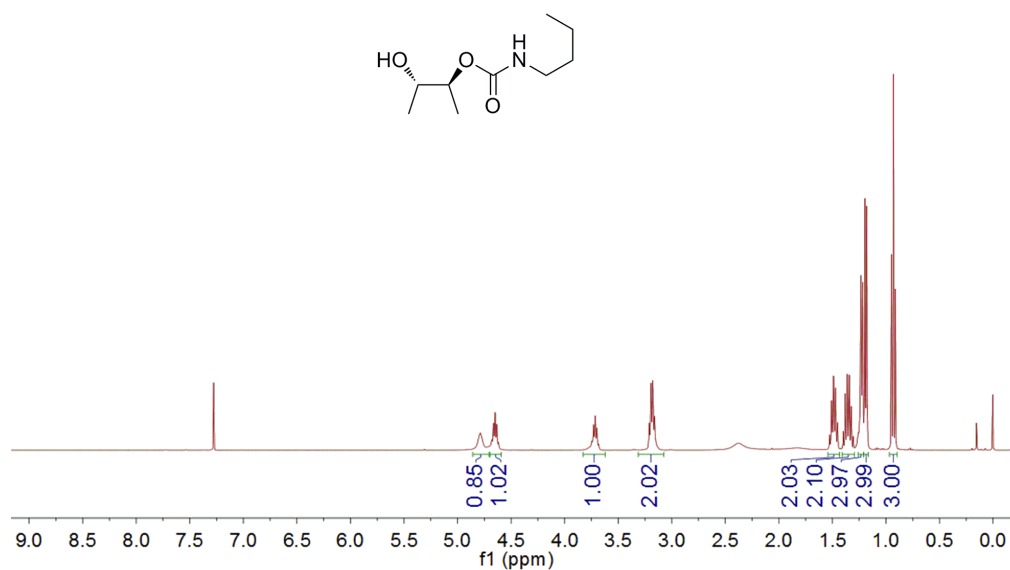
**Figure S8.** <sup>13</sup>C NMR spectrum of 1d



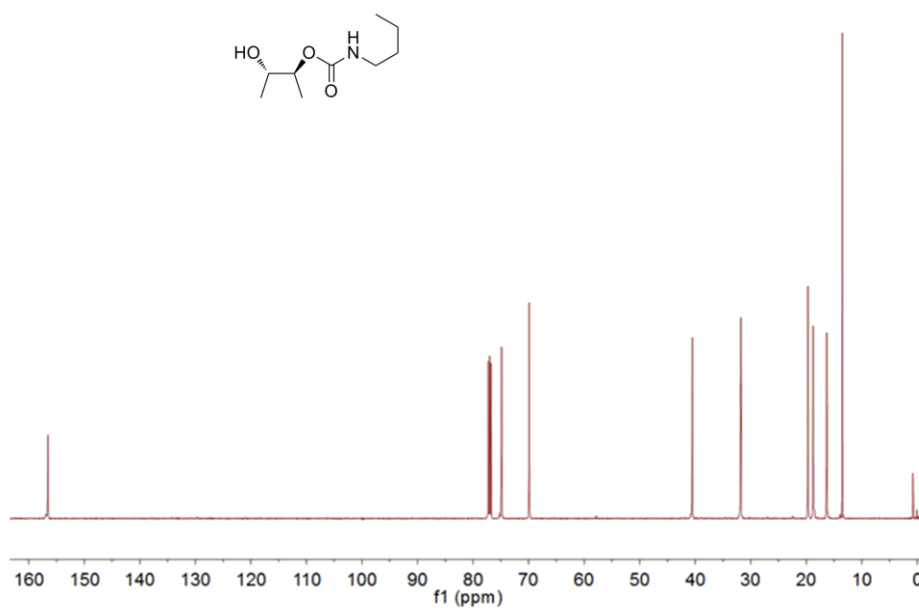
**Figure S9.** <sup>1</sup>H NMR spectrum of 1e



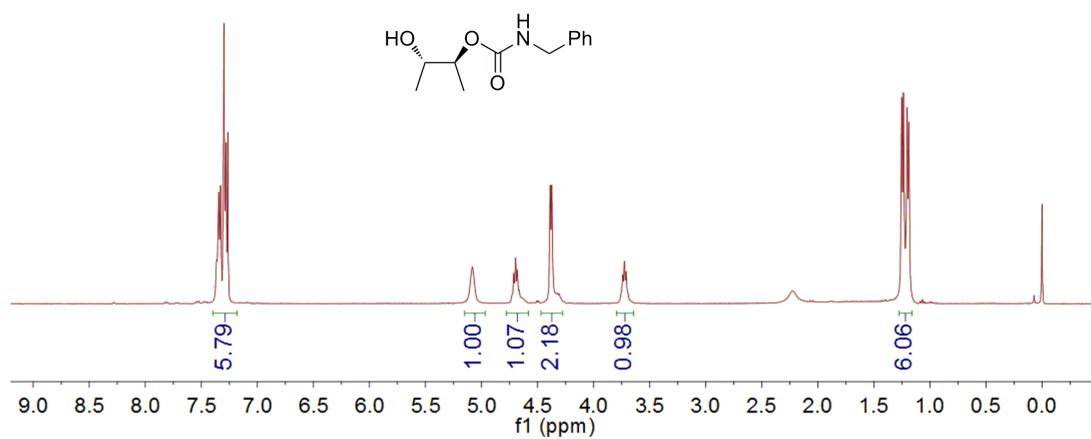
**Figure S10.** <sup>13</sup>C NMR spectrum of 1e



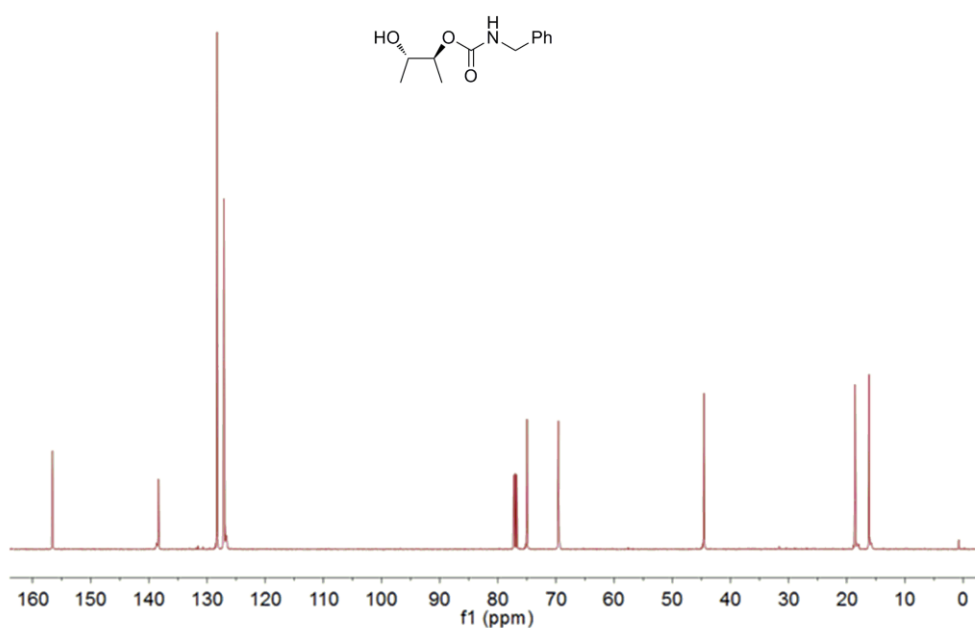
**Figure S11.** <sup>1</sup>H NMR spectrum of 1f



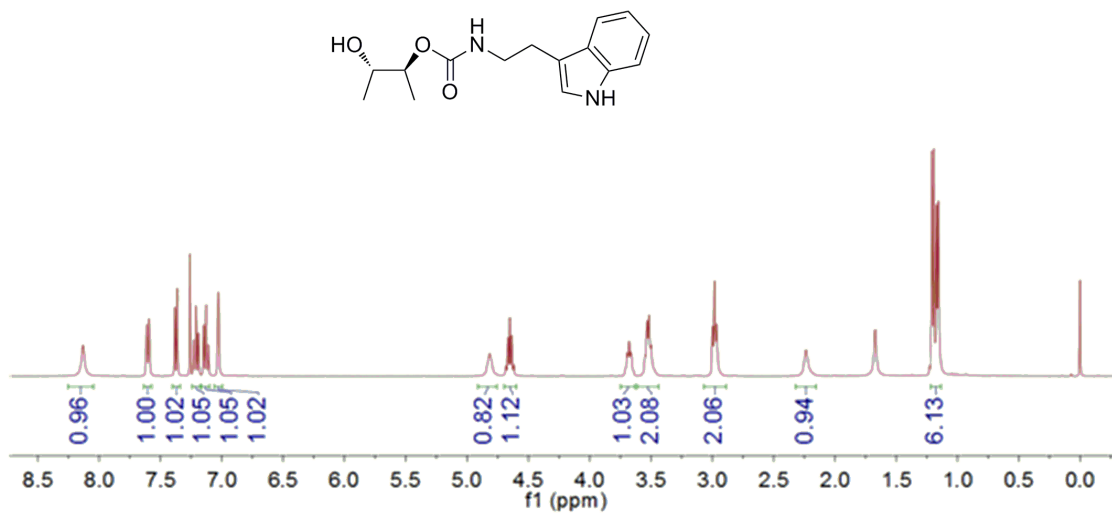
**Figure S12.** <sup>13</sup>C NMR spectrum of 1f



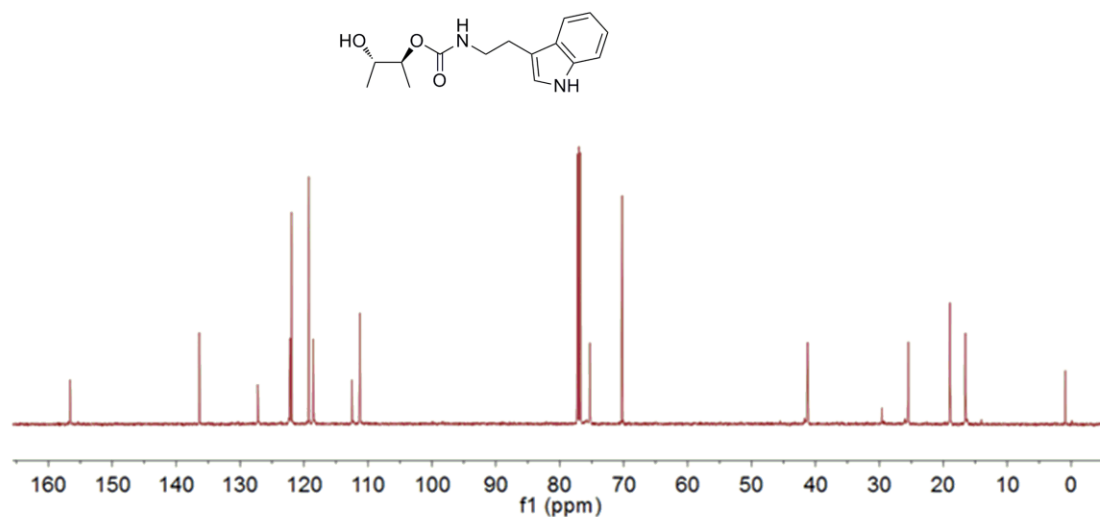
**Figure S13.** <sup>1</sup>H NMR spectrum of **1g**



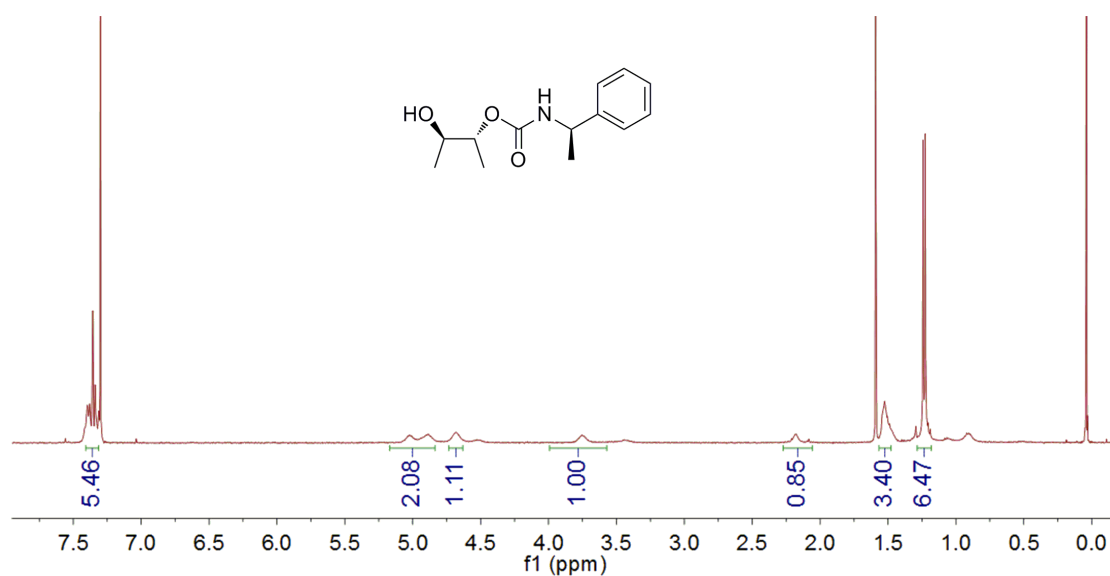
**Figure S14.** <sup>13</sup>C NMR spectrum of **1g**



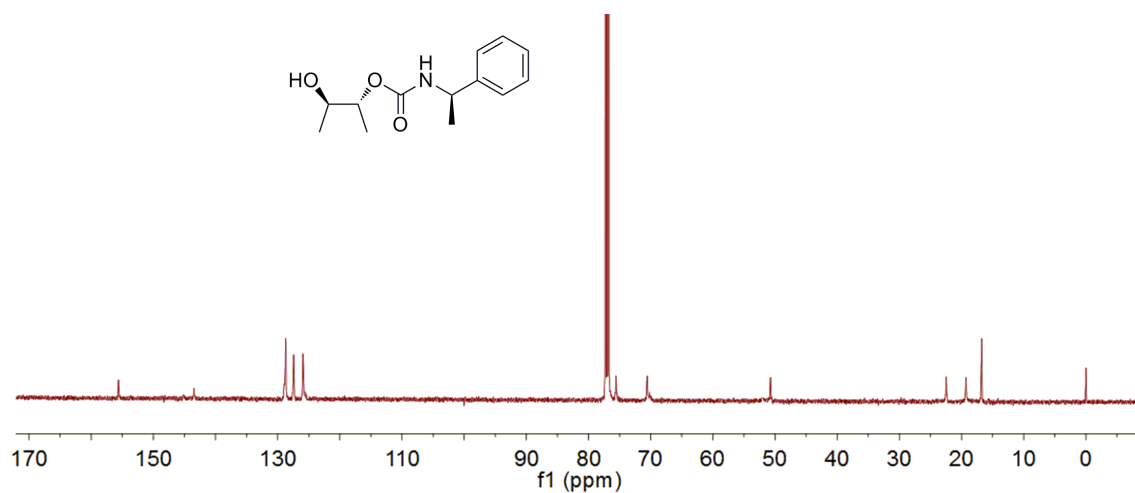
**Figure S15.** <sup>1</sup>H NMR spectrum of **1h**



**Figure S16.** <sup>13</sup>C NMR spectrum of 1h



**Figure S17.** <sup>1</sup>H NMR spectrum of (R,R,R)-1i



**Figure S18.** <sup>13</sup>C NMR spectrum of (R,R,R)-1i



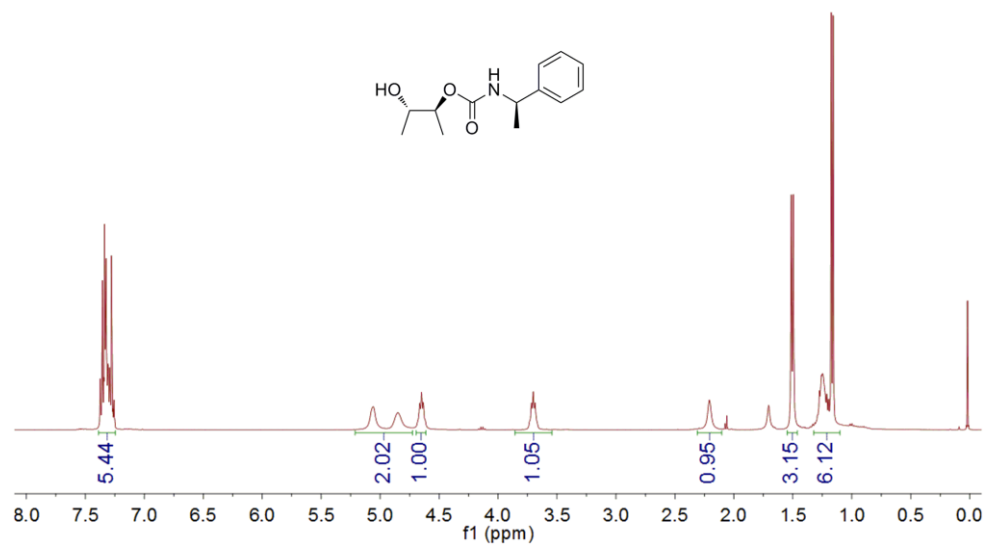


Figure S19. <sup>1</sup>H NMR spectrum of (*R,S,S*)-1i

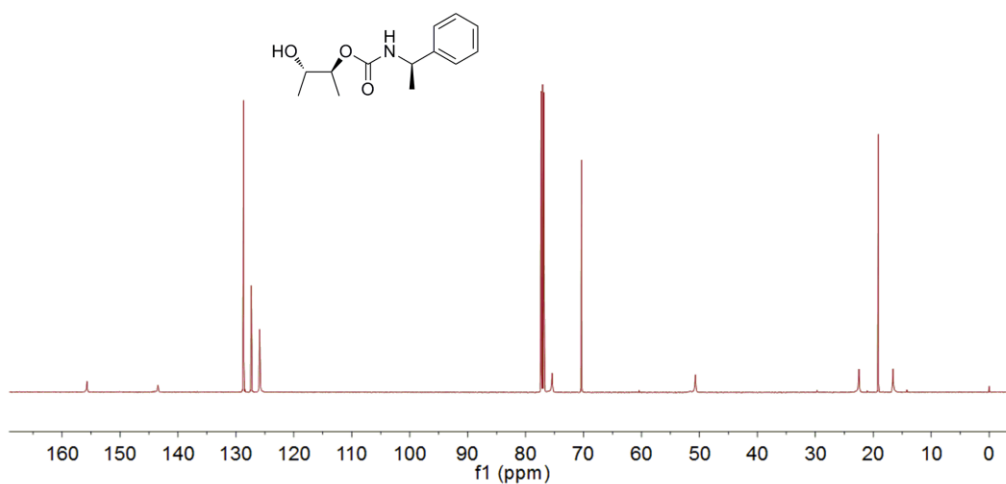


Figure S20. <sup>13</sup>C NMR spectrum of (*R,S,S*)-1i

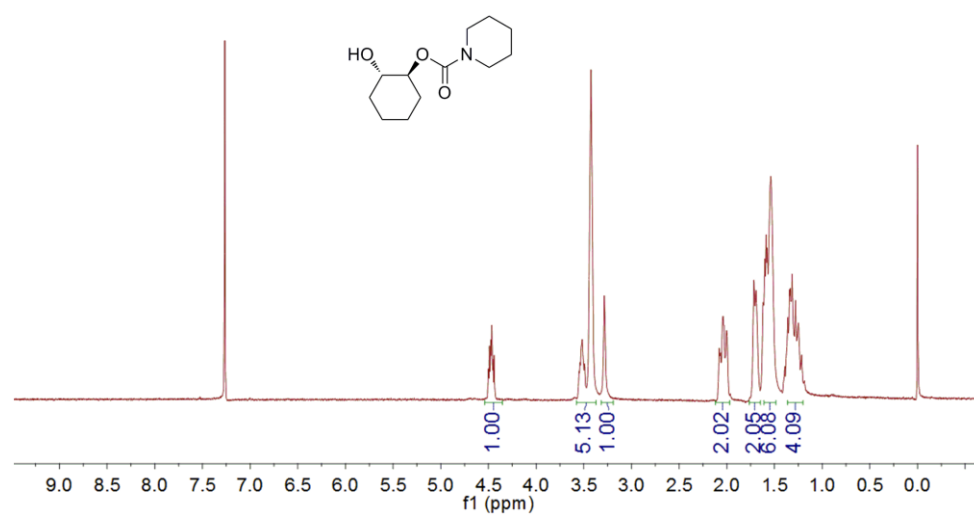
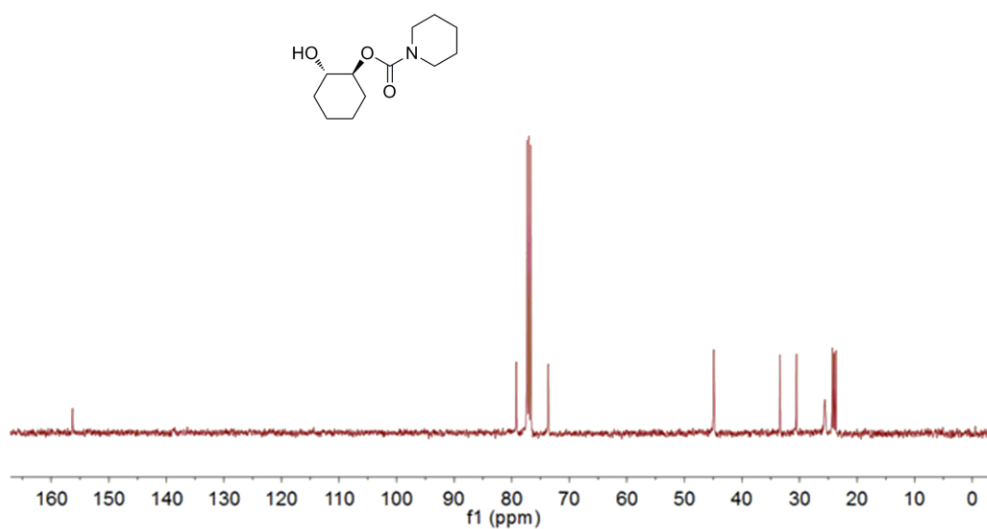
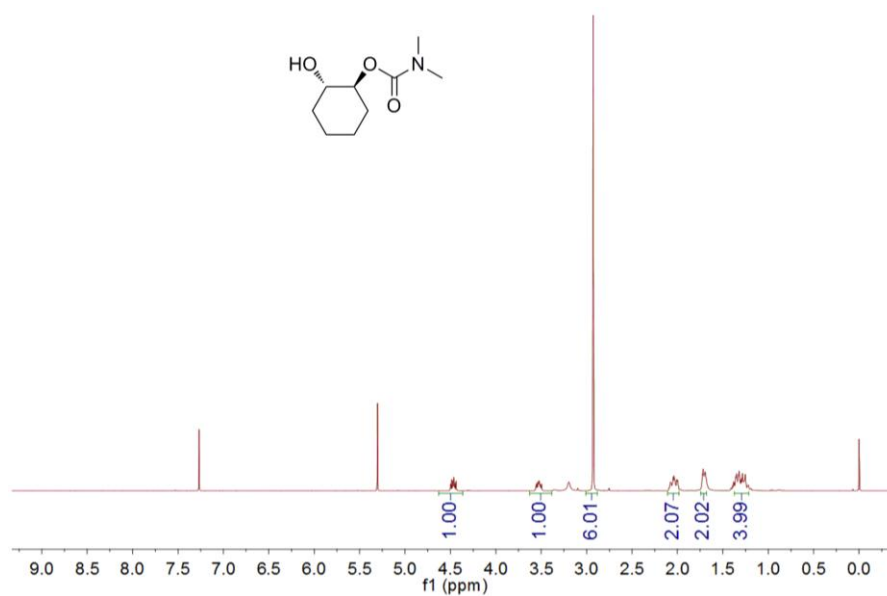


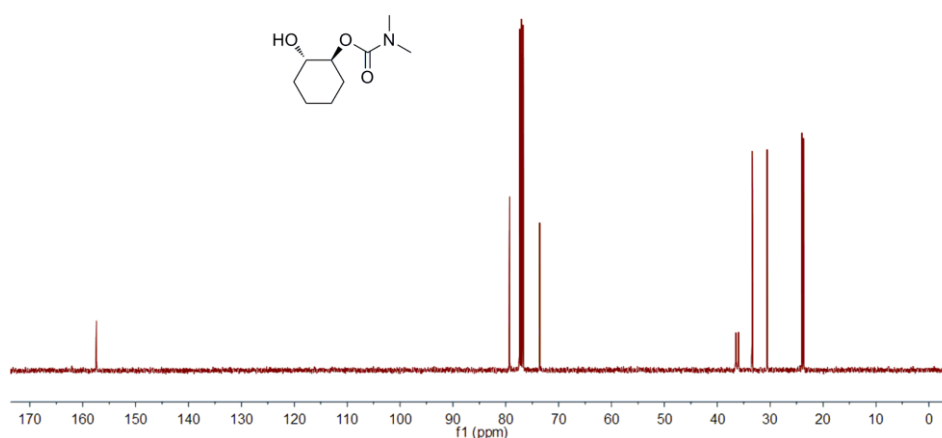
Figure S21. <sup>1</sup>H NMR spectrum of 2a



**Figure S22.**  $^{13}\text{C}$  NMR spectrum of **2a**



**Figure S23.**  $^1\text{H}$  NMR spectrum of **2b**



**Figure S24.**  $^{13}\text{C}$  NMR spectrum of **2b**

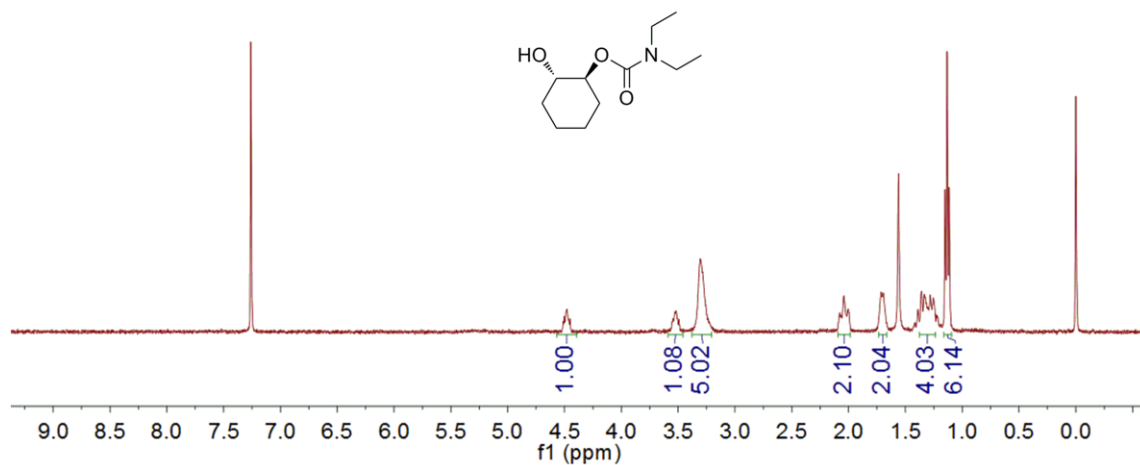


Figure S25. <sup>1</sup>H NMR spectrum of 2c

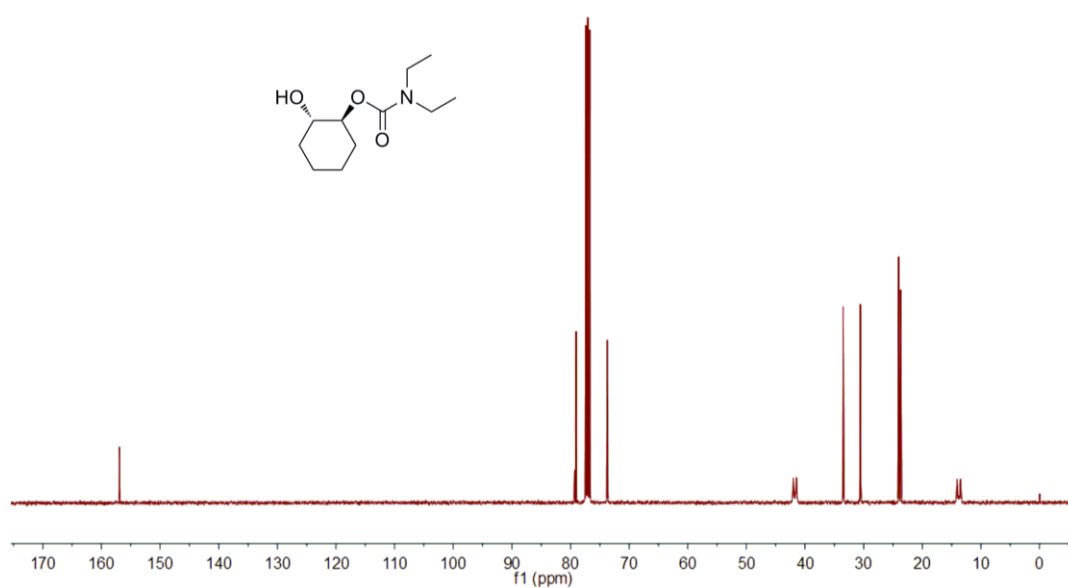


Figure S26. <sup>13</sup>C NMR spectrum of 2c

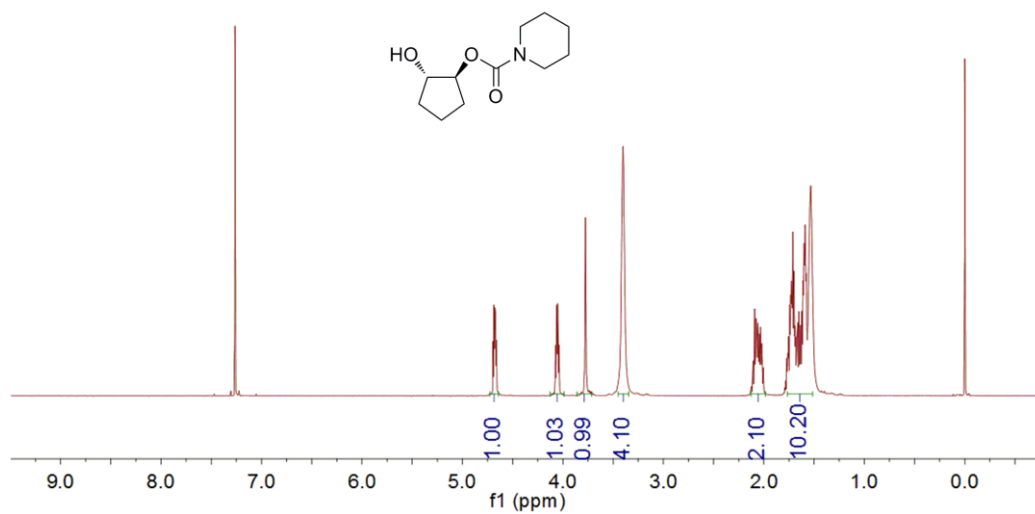


Figure S27. <sup>1</sup>H NMR spectrum of 3a

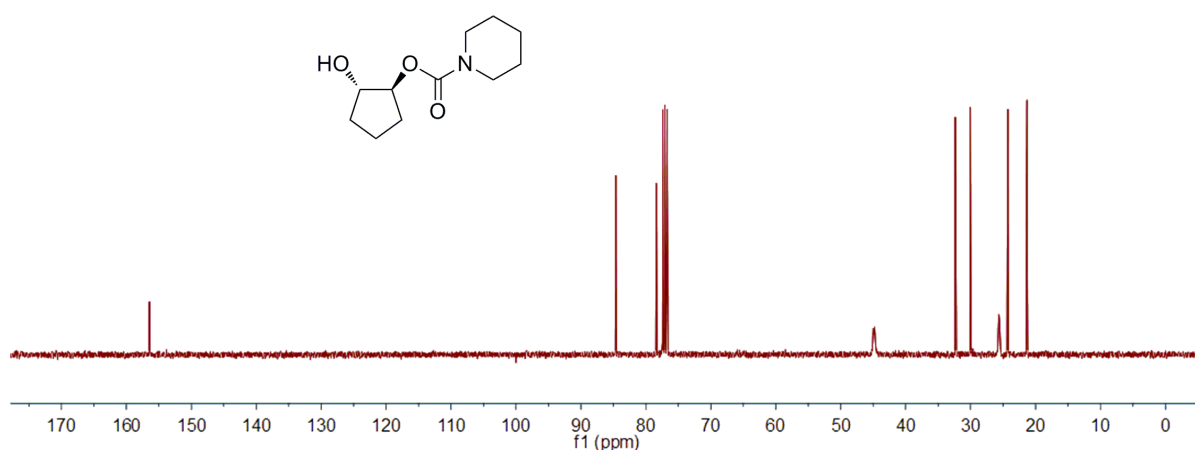


Figure S28. <sup>13</sup>C NMR spectrum of 3a

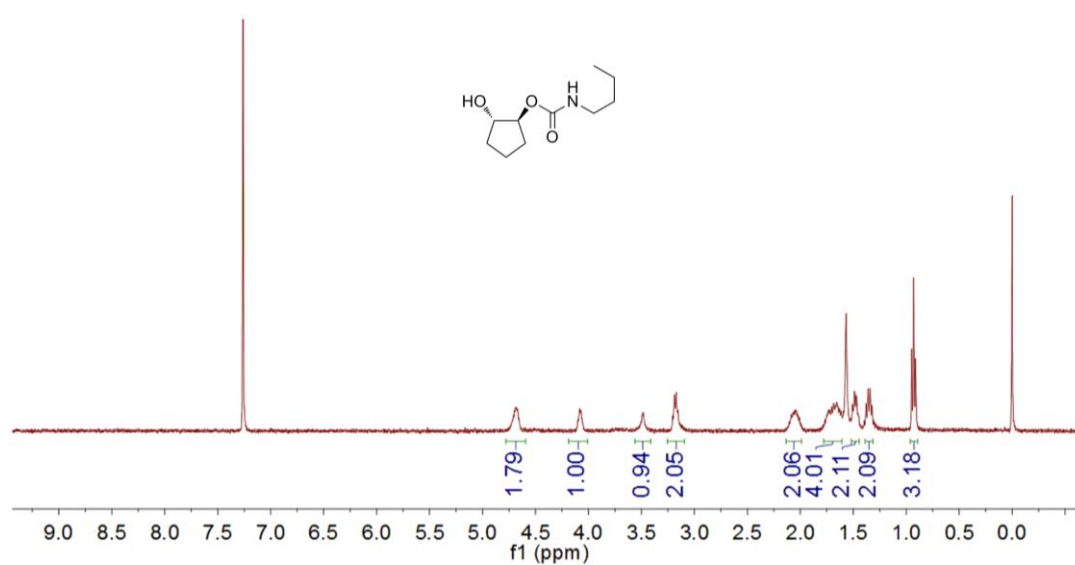


Figure S29. <sup>1</sup>H NMR spectrum of 3b

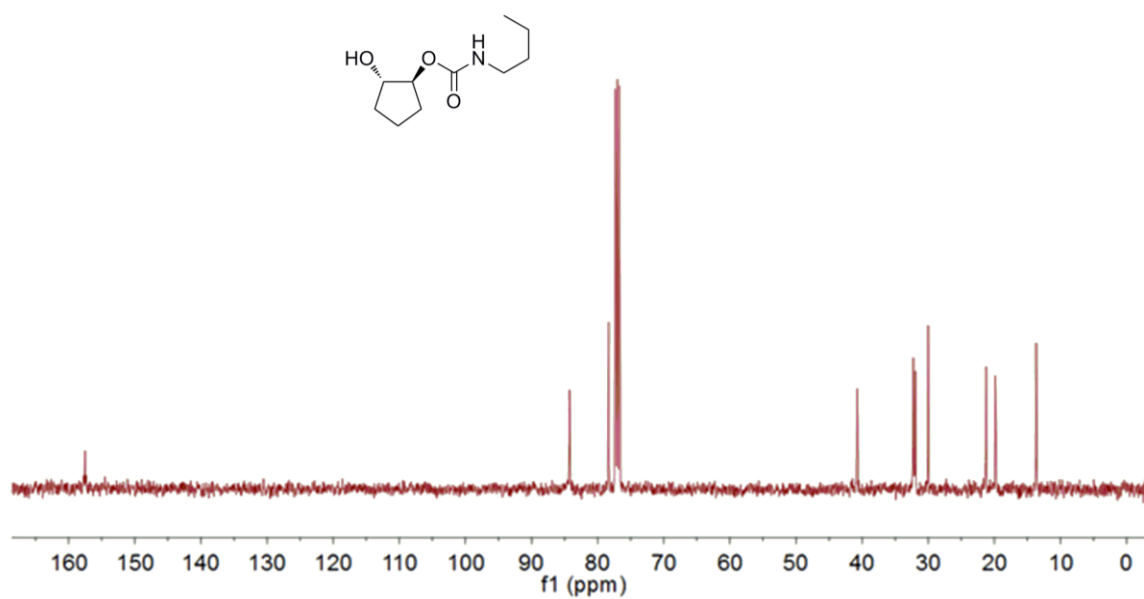


Figure S30. <sup>13</sup>C NMR spectrum of 3b

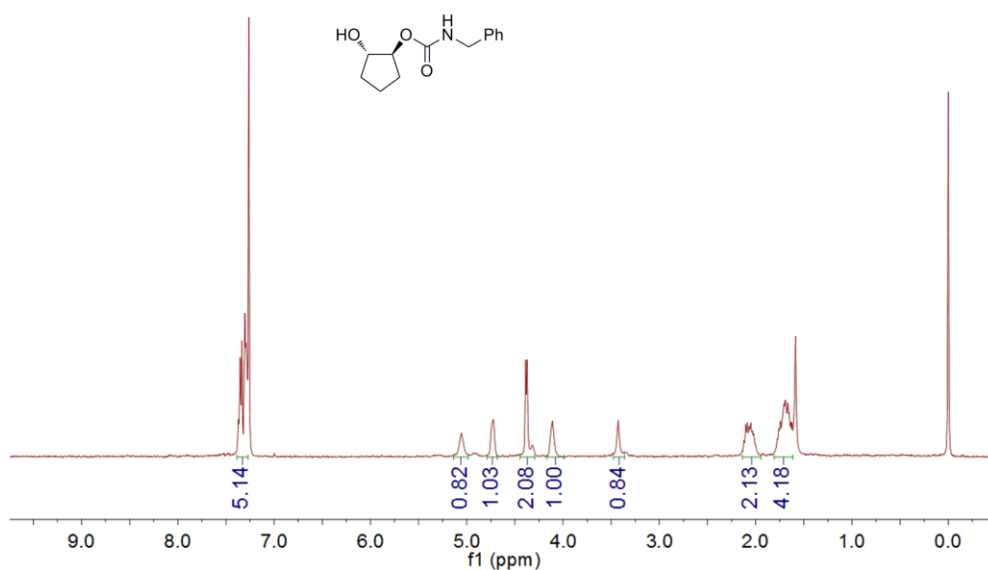


Figure S31. <sup>1</sup>H NMR spectrum of 3c

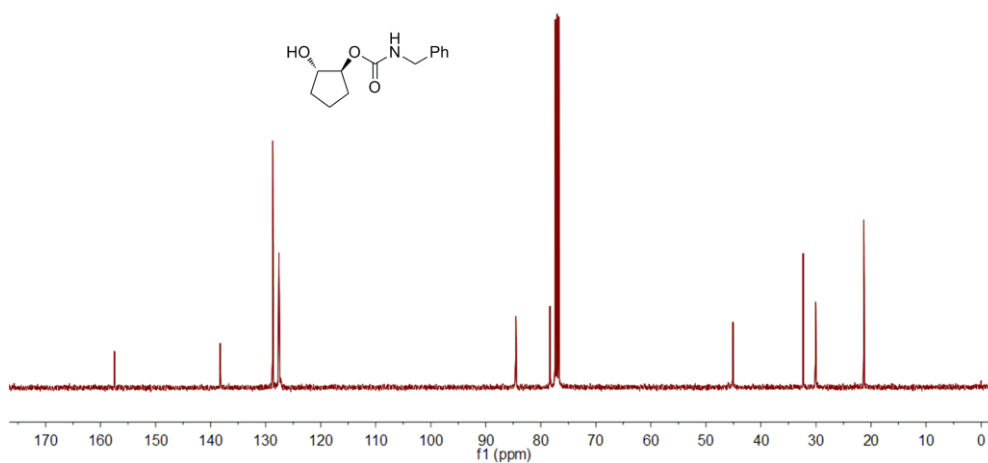


Figure S32. <sup>13</sup>C NMR spectrum of 3c

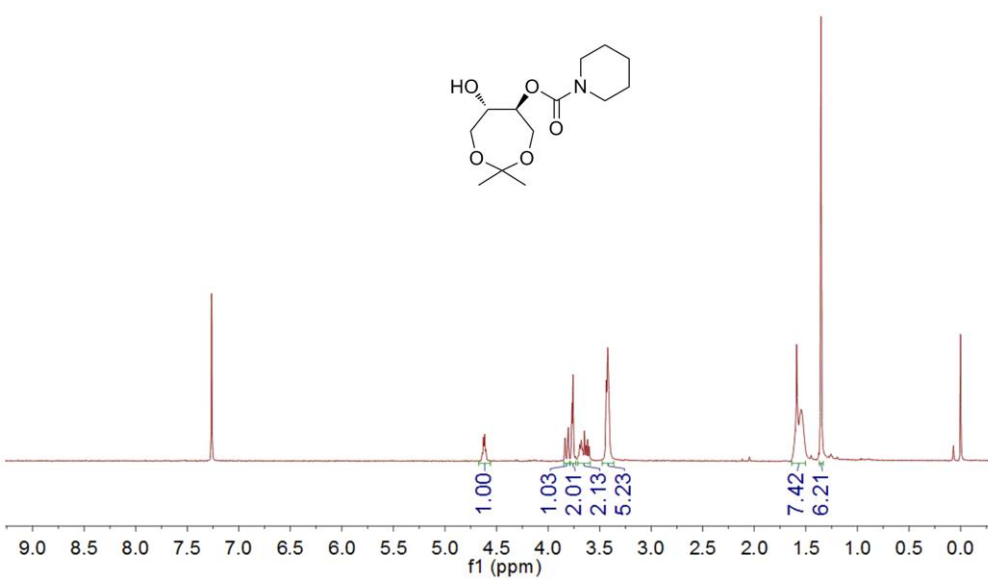
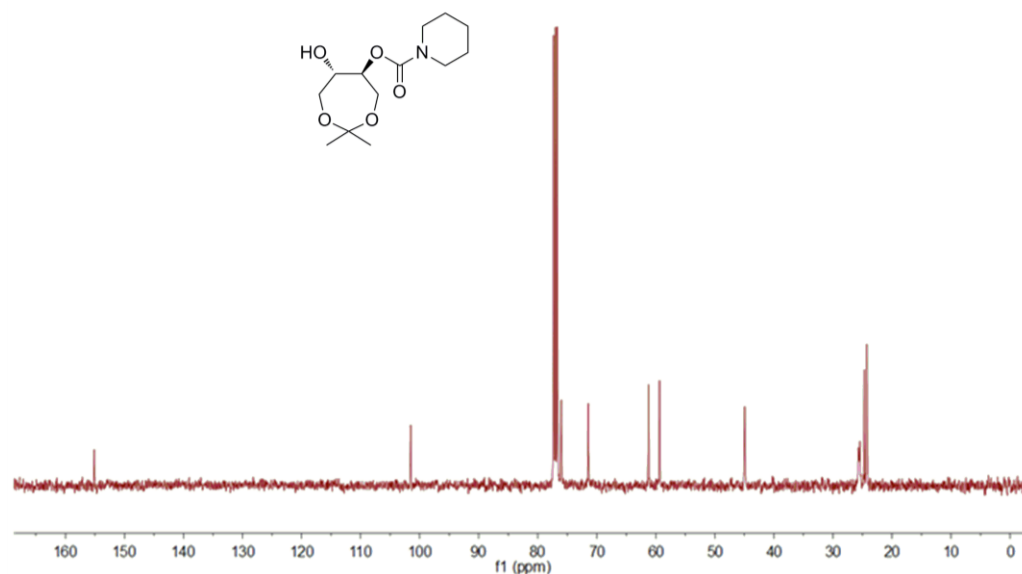
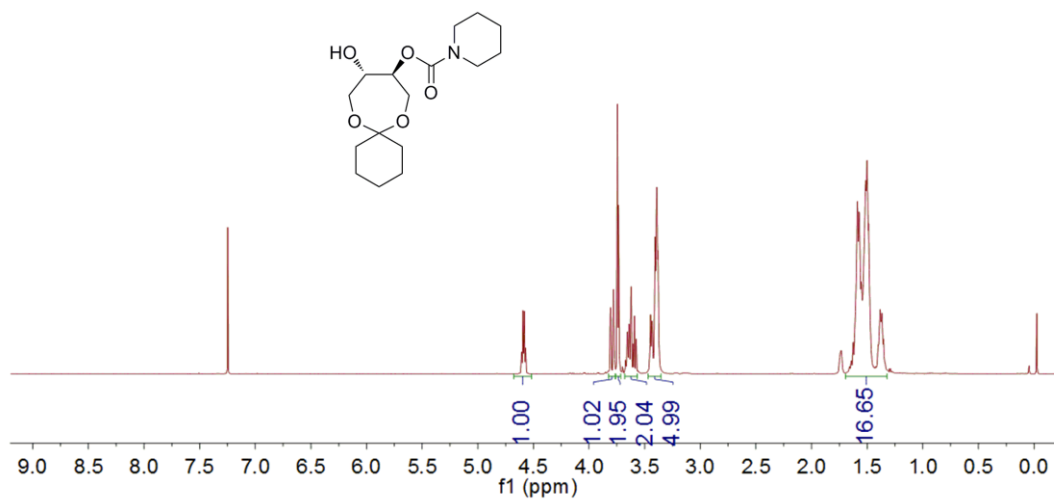


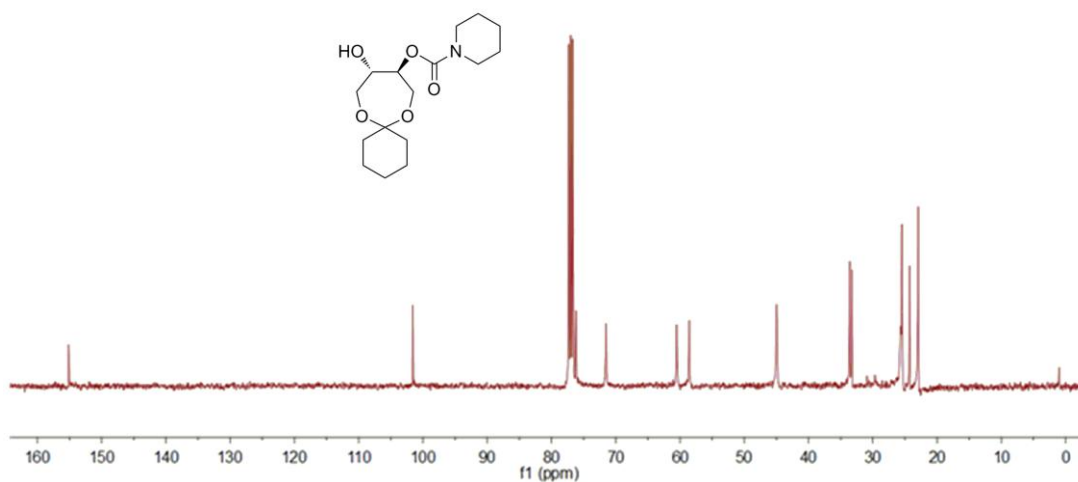
Figure S33. <sup>1</sup>H NMR spectrum of 4a



**Figure S34.** <sup>13</sup>C NMR spectrum of 4a



**Figure S35.** <sup>1</sup>H NMR spectrum of 4b



**Figure S36.** <sup>13</sup>C NMR spectrum of 4b

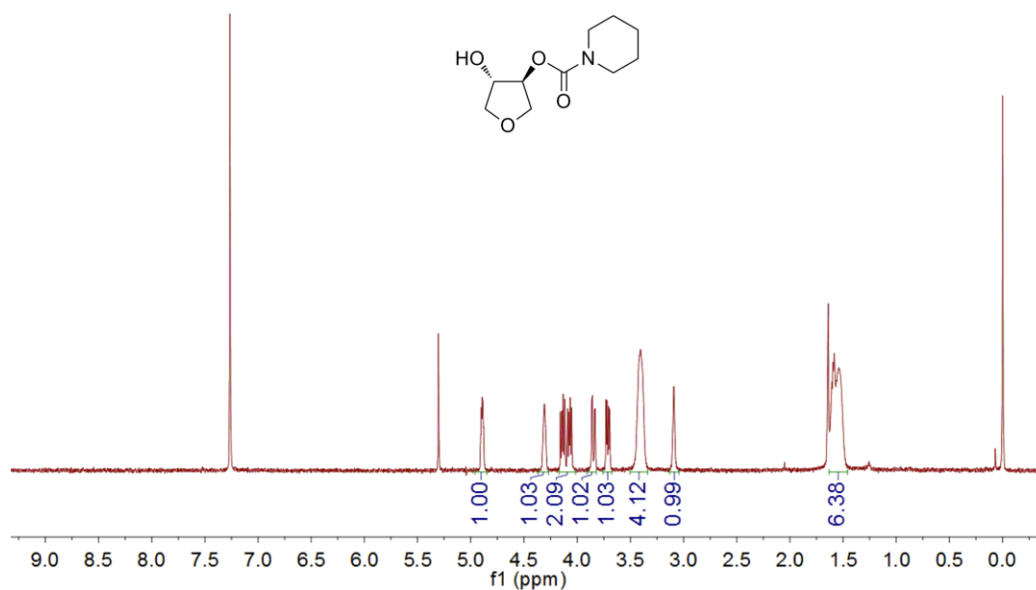


Figure S37. <sup>1</sup>H NMR spectrum of 5a

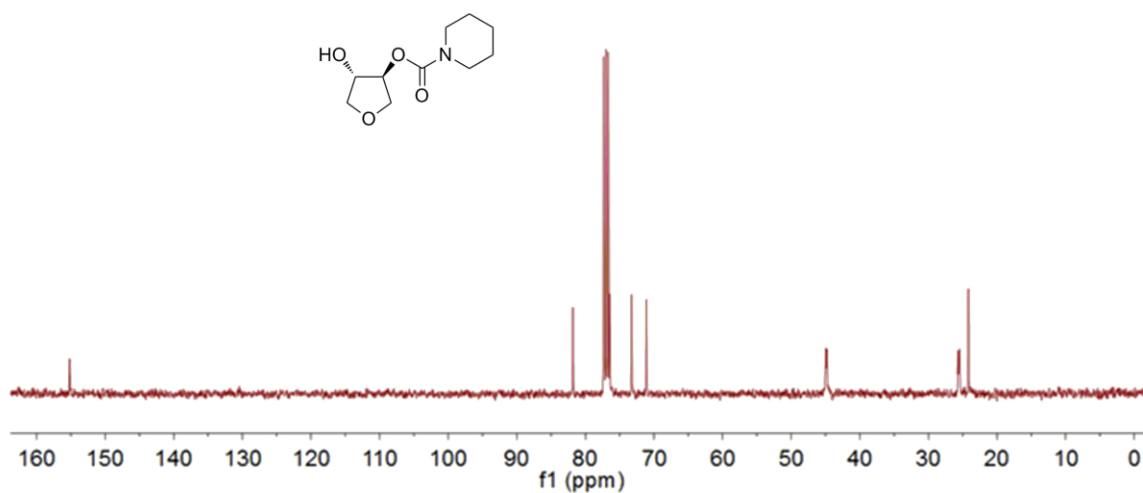


Figure S38. <sup>13</sup>C NMR spectrum of 5a

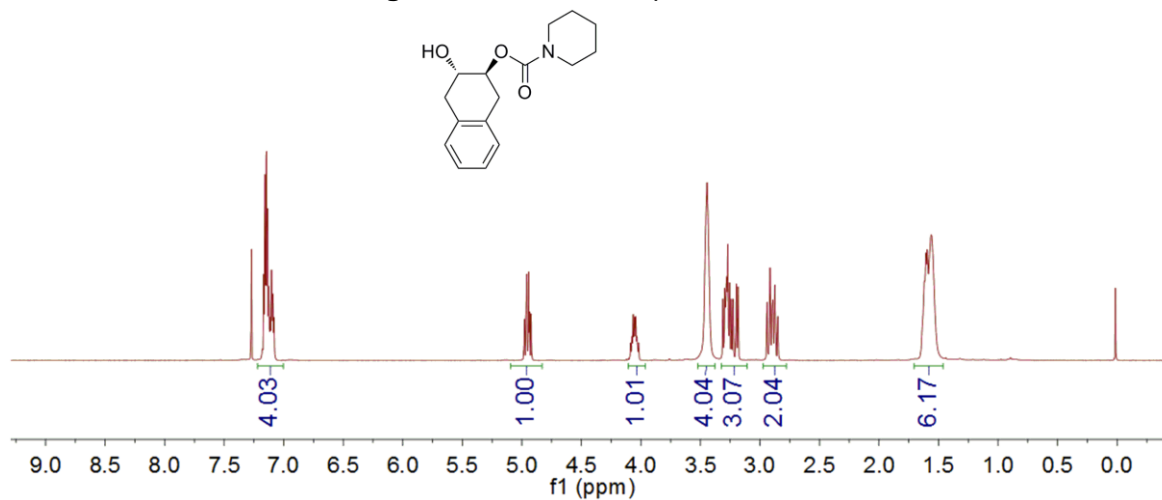
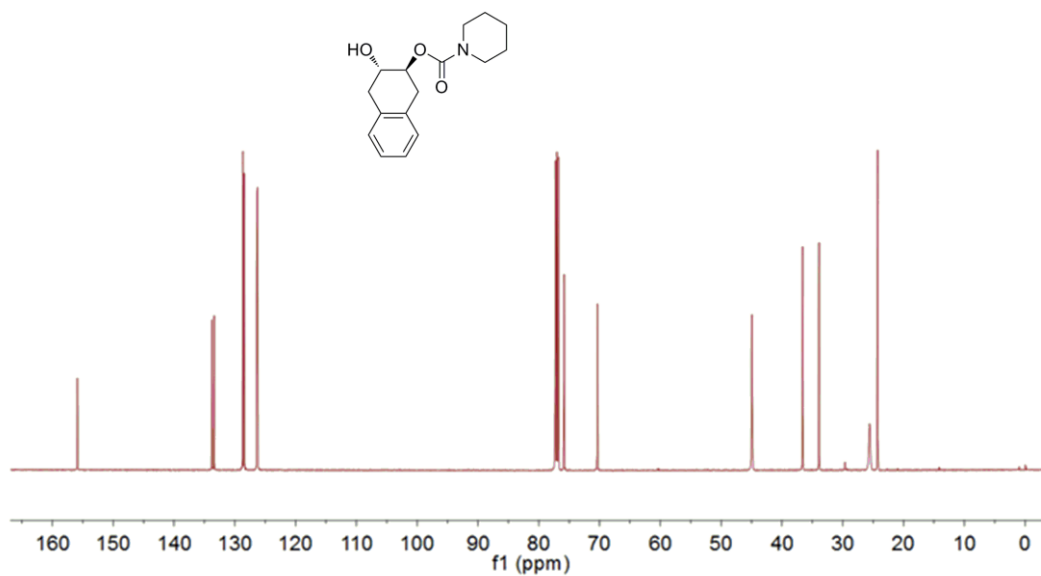
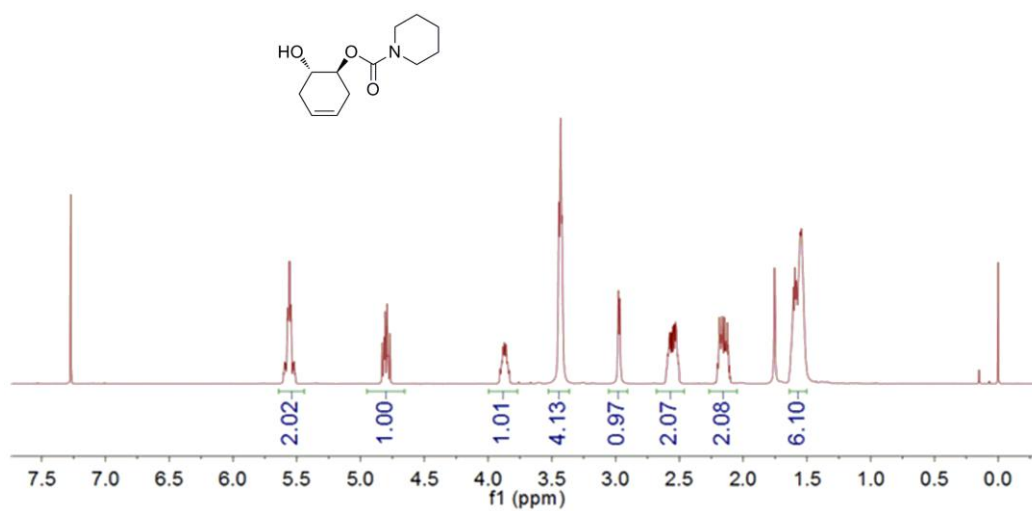


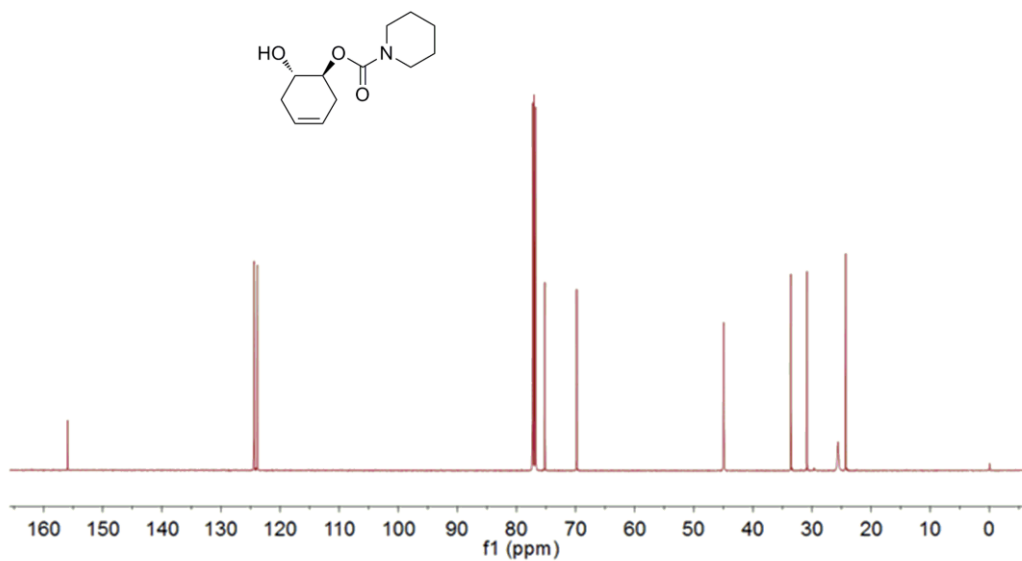
Figure S39. <sup>1</sup>H NMR spectrum of 6a



**Figure S40.** <sup>13</sup>C NMR spectrum of 6a



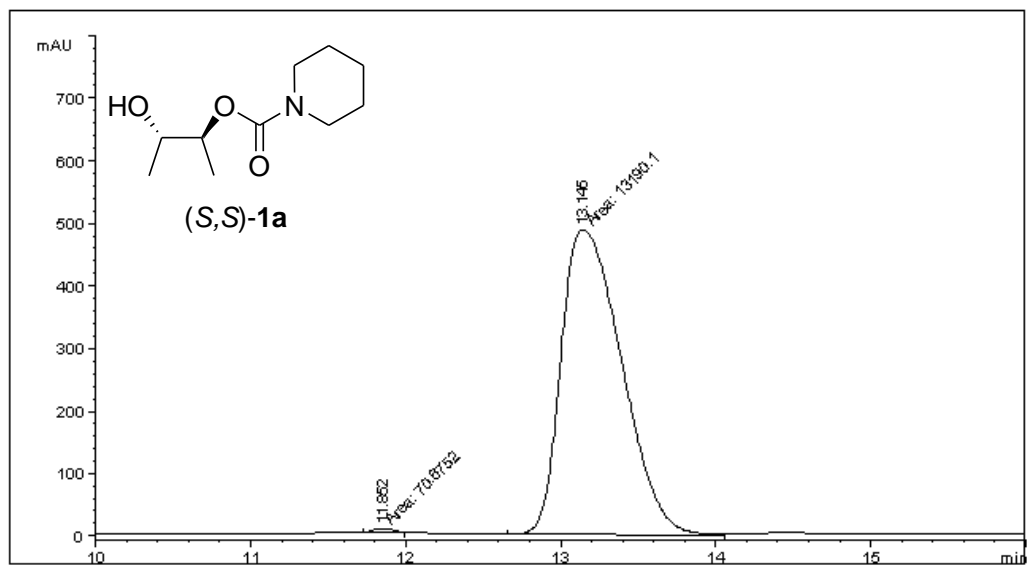
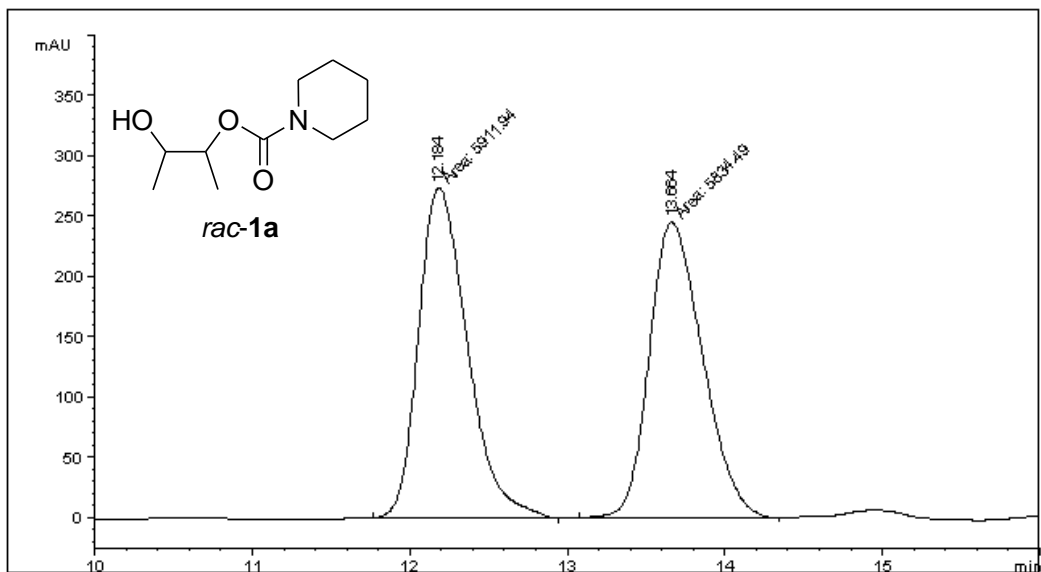
**Figure S41.** <sup>1</sup>H NMR spectrum of 7a



**Figure S42.** <sup>13</sup>C NMR spectrum of 7a



### 3. HPLC spectrum of various carbamate derivatives



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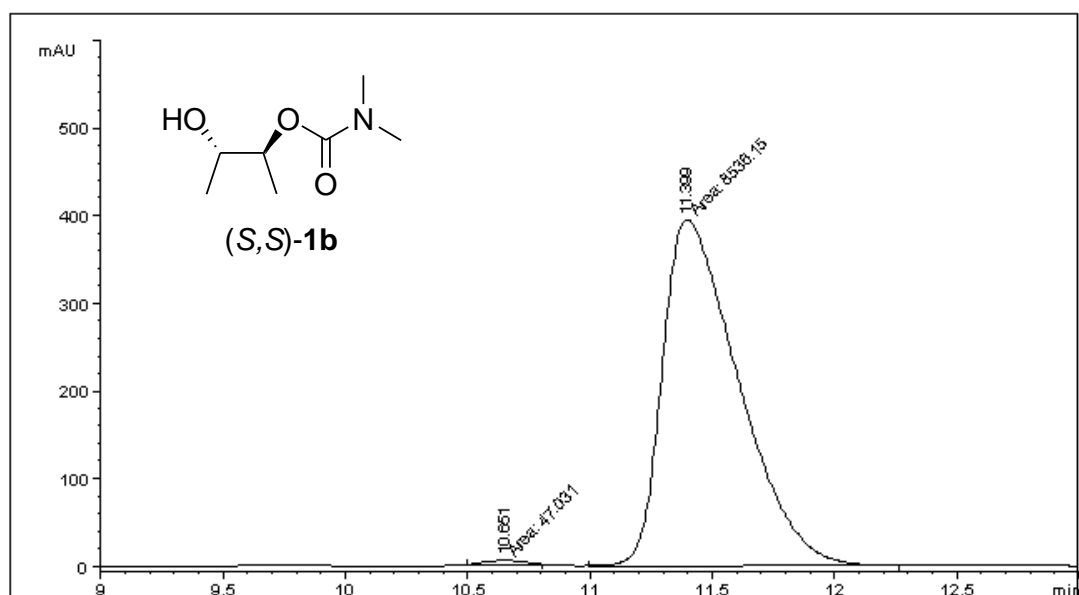
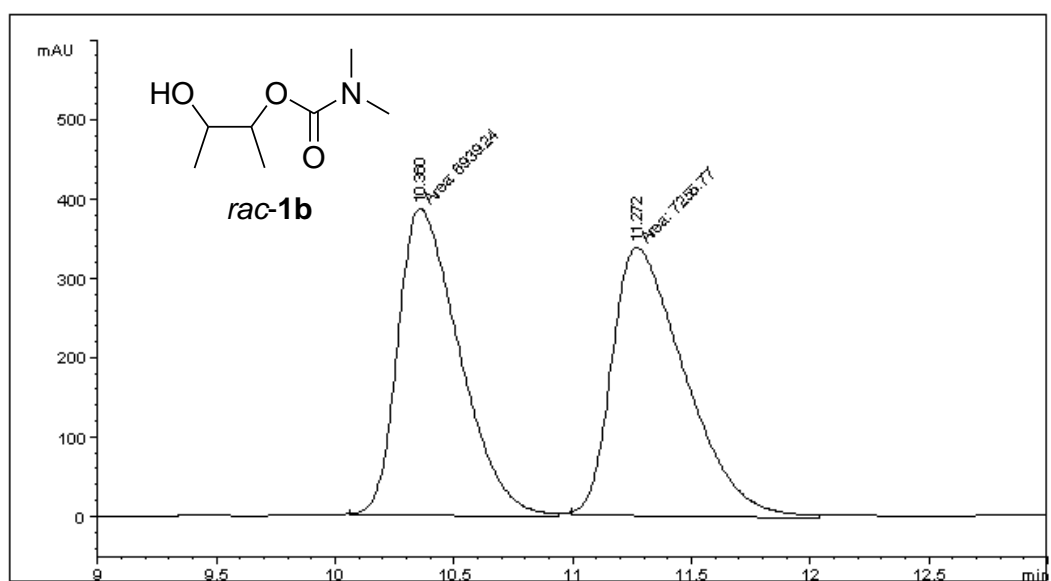
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Use Multiplier & Dilution Factor with ISTDs
  
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1	11.852	MM	0.1714	70.67524	6.87367	0.5330	
2	13.145	MM	0.4519	1.31901e4	486.52310	99.4670	

Totals : 1.32608e4 493.39677

**Figure S43.** HPLC spectrum of **1a**



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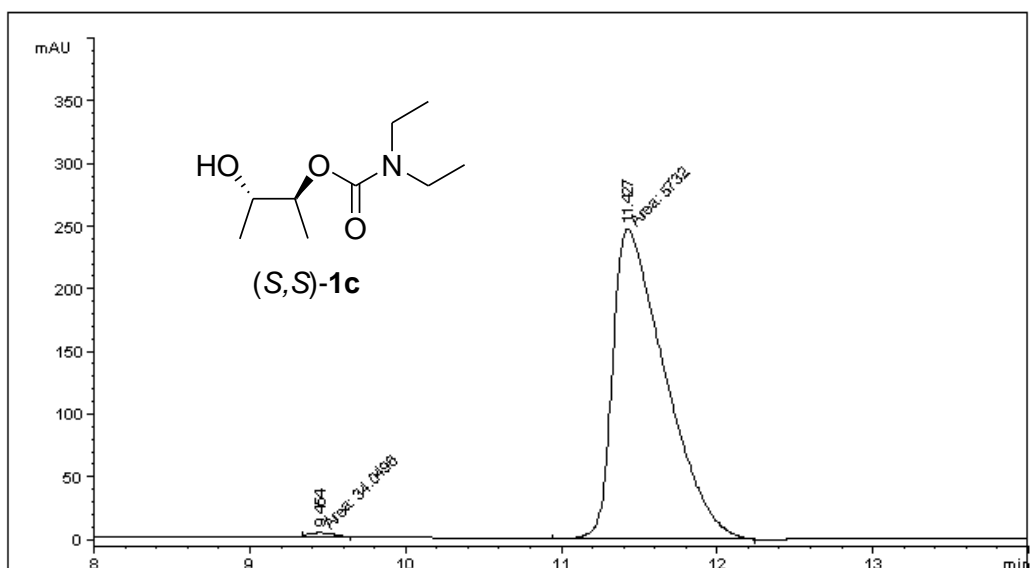
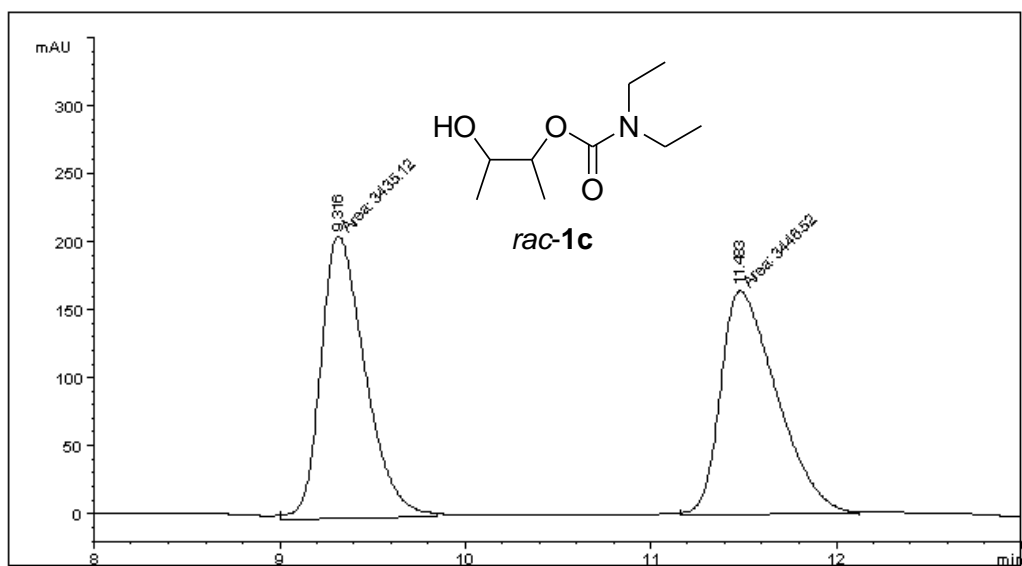
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Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	10.651	MM	0.1882	47.03099	4.16606	0.5479
2	11.399	MM	0.3601	8536.14941	395.13409	99.4521

Totals : 8583.18041 399.30016

**Figure S44.** HPLC spectrum of 1b



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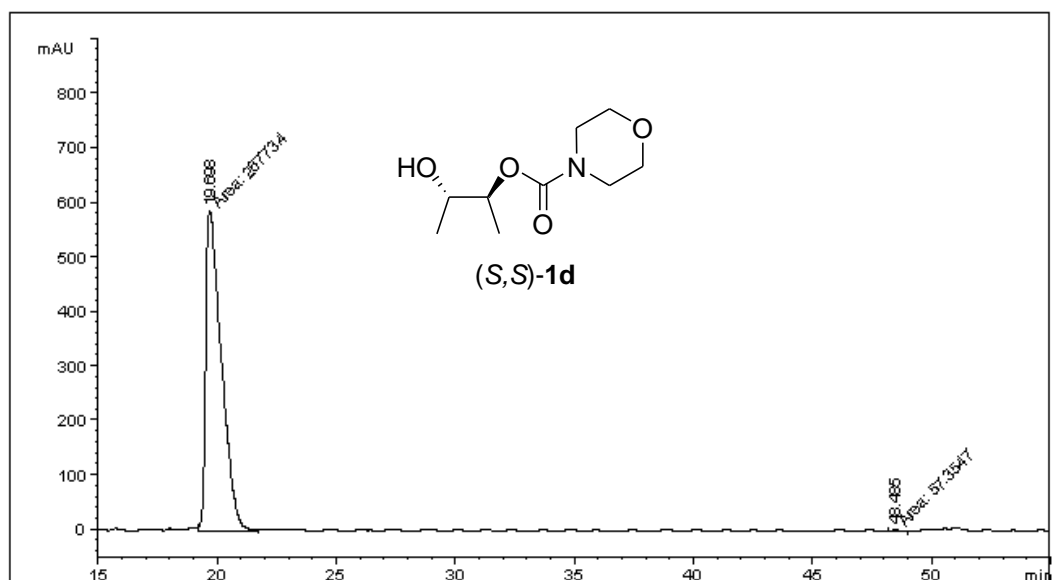
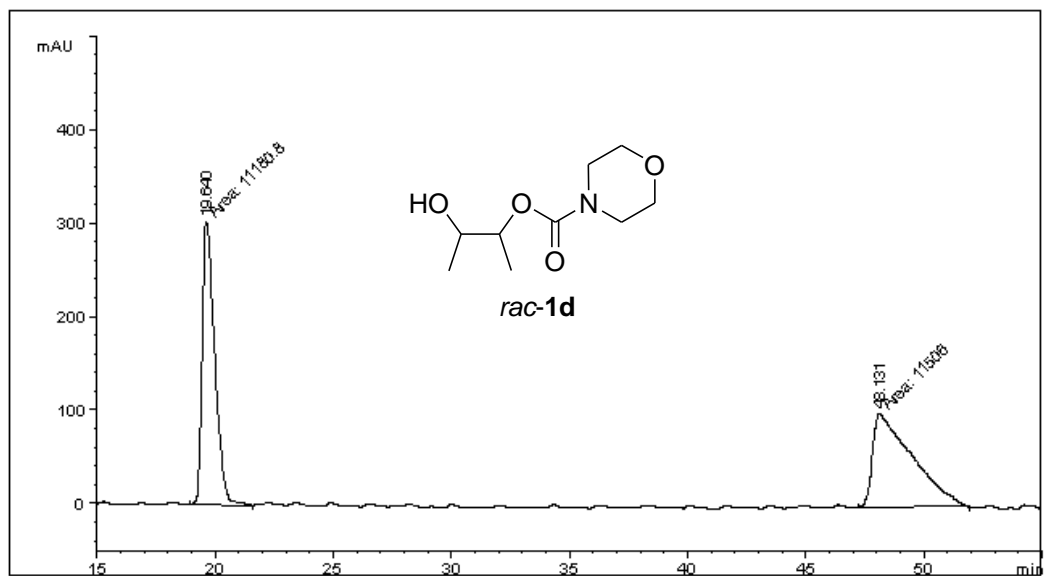
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Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	9.454	MM	0.1767	34.04962		3.21191	0.5905
2	11.427	MM	0.3878	5731.99854		246.32578	99.4095

Totals : 5766.04816 249.53768

**Figure S45.** HPLC spectrum of 1c



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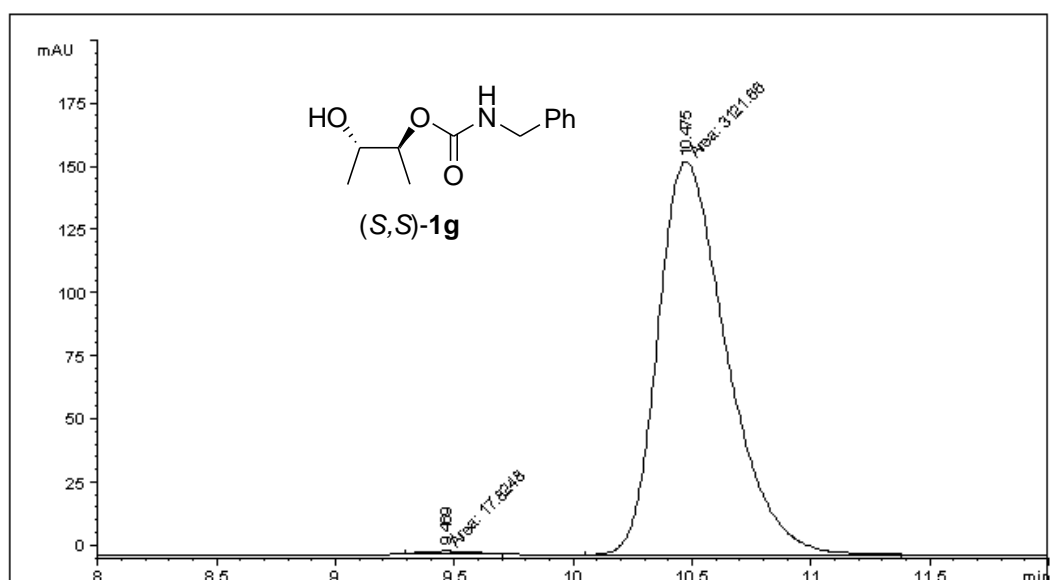
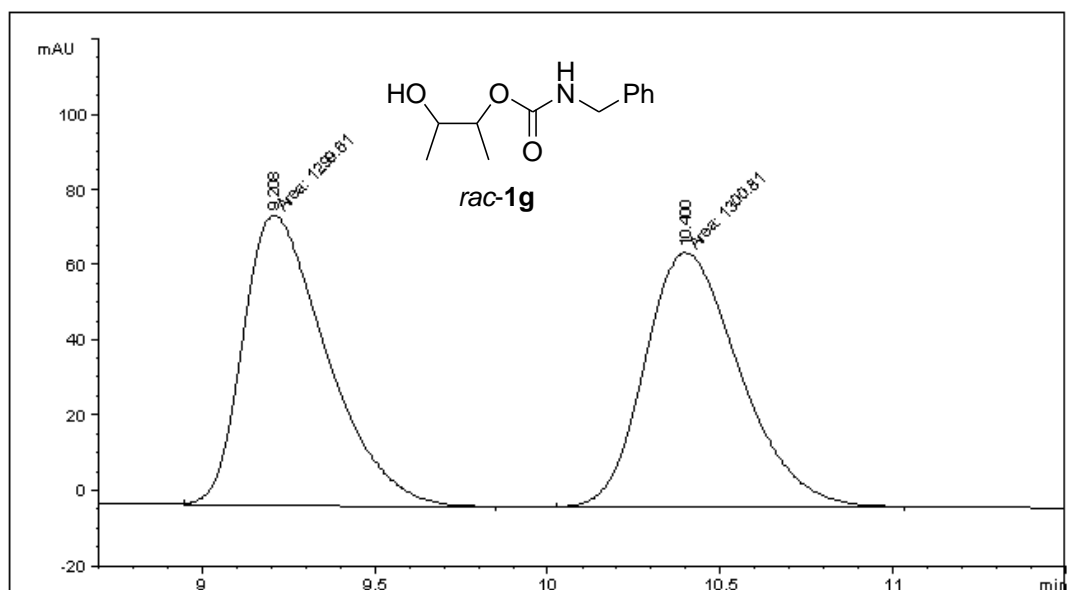
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Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	19.698	MM	0.7617	2.67734e4	585.84711	99.7862
2	48.485	MM	0.3967	57.35474	2.40937	0.2138

Totals : 2.68308e4 588.25648

**Figure S46.** HPLC spectrum of 1d



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 Area Percent Report  
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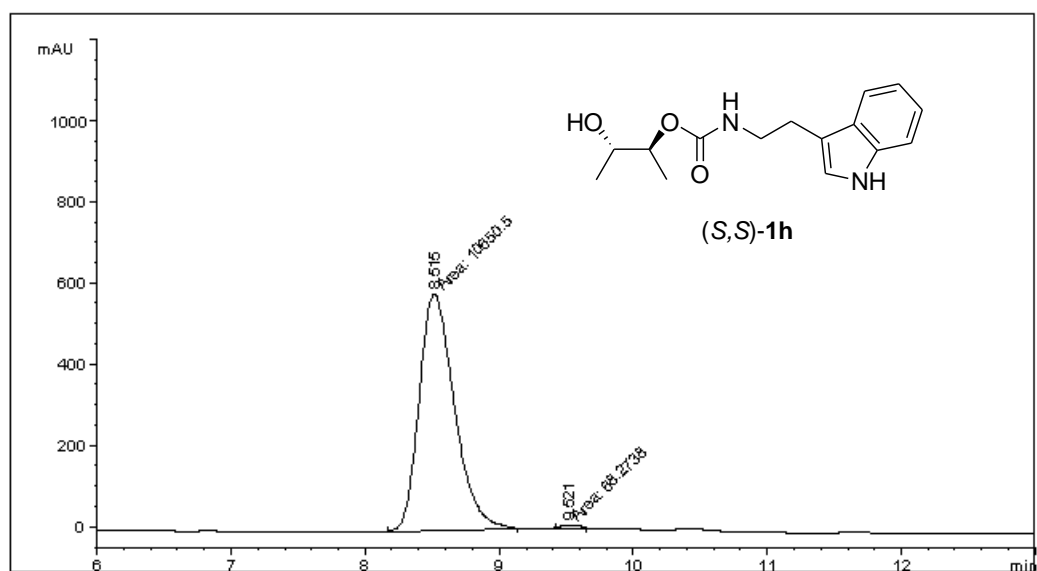
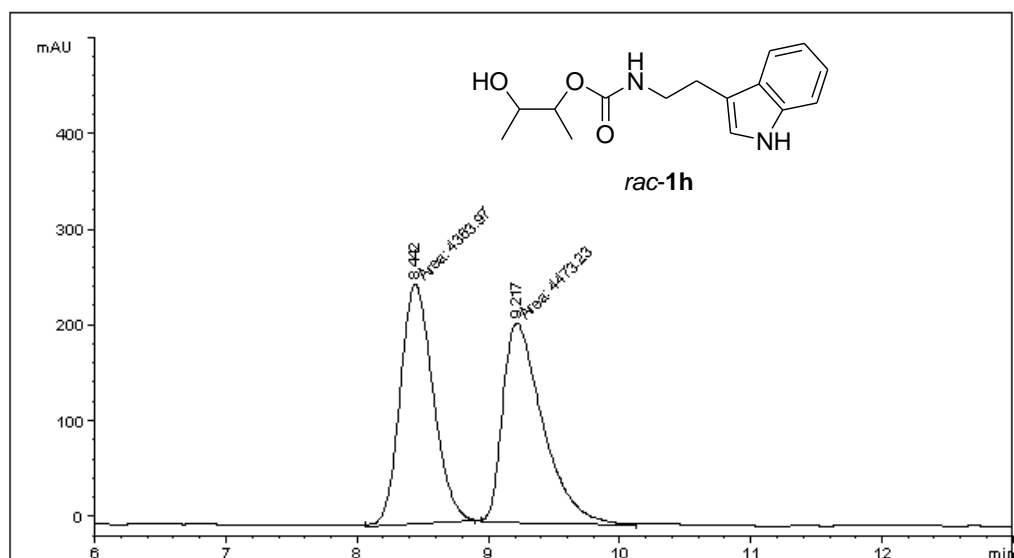
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1	9.469	MM	0.2316	17.82478		1.28300	0.5678
2	10.475	MM	0.3342	3121.66064		155.68118	99.4322

Totals : 3139.48543 156.96419

**Figure S47.** HPLC spectrum of **1g**



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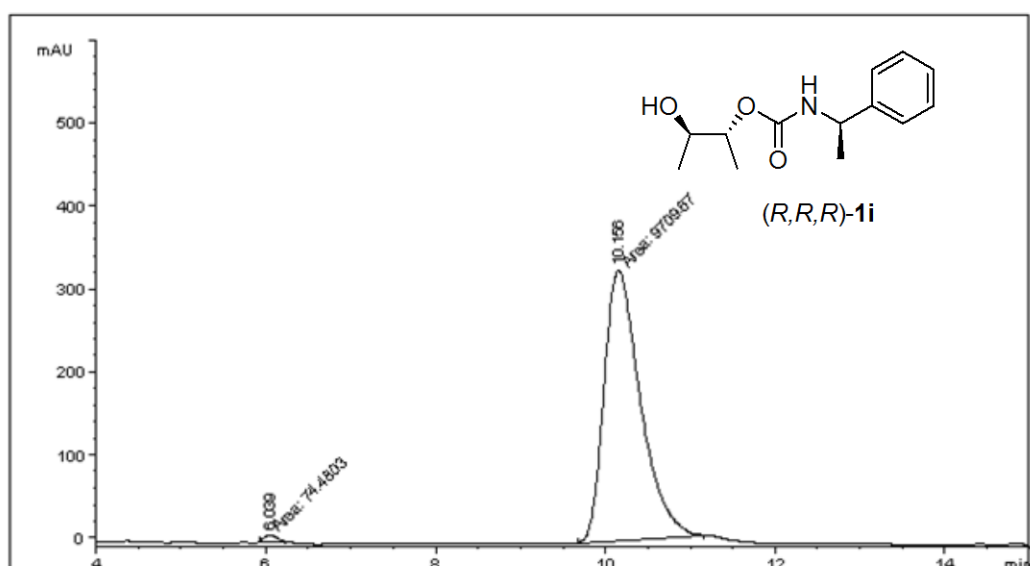
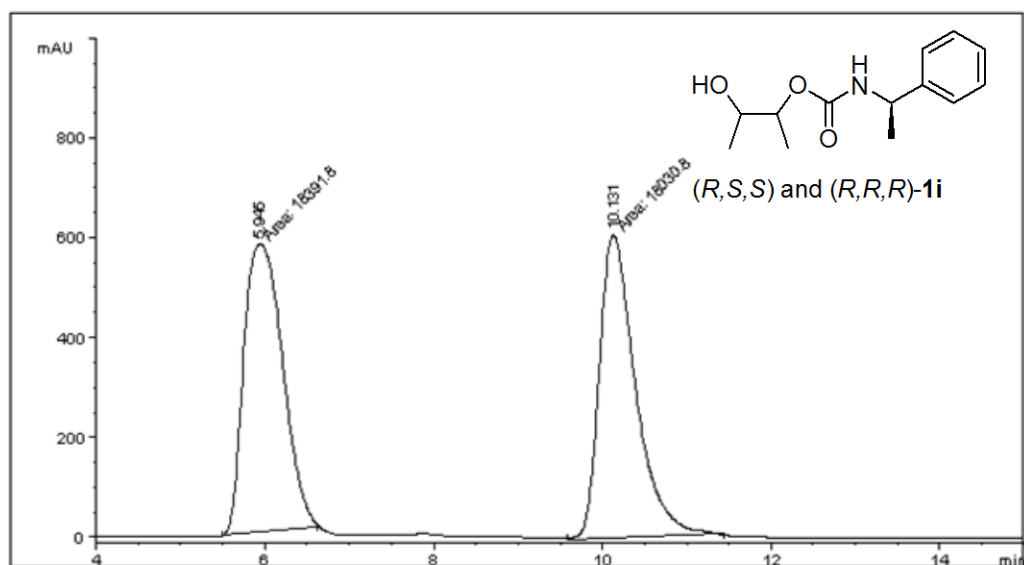
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Signal 1: VWD1 A, Wavelength=254 nm

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2	9.521	MM	0.1444	68.27383	0.6370	7.87924

Totals : 1.07187e4 589.27939

**Figure S48.** HPLC spectrum of 1h



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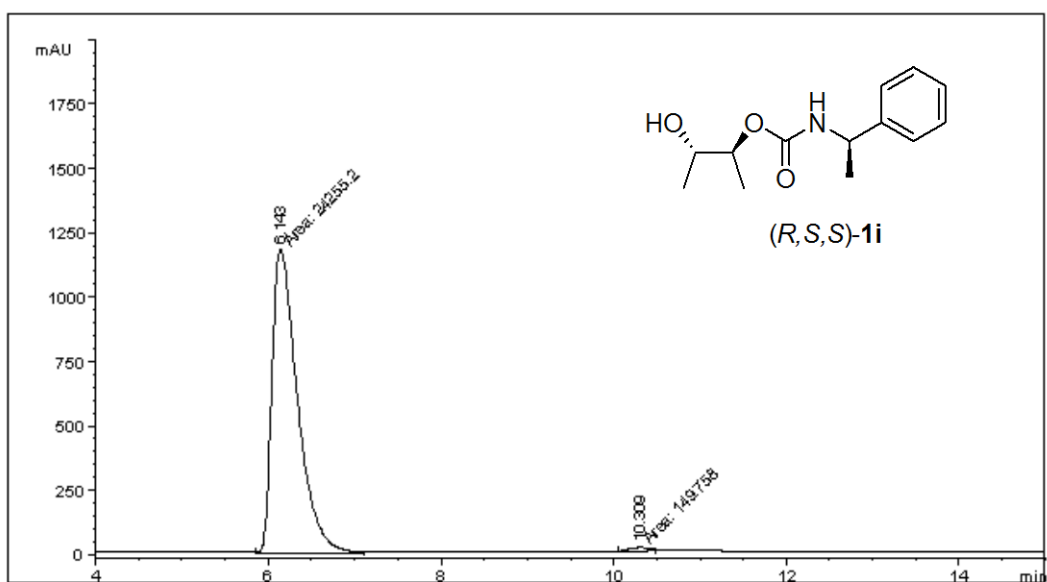
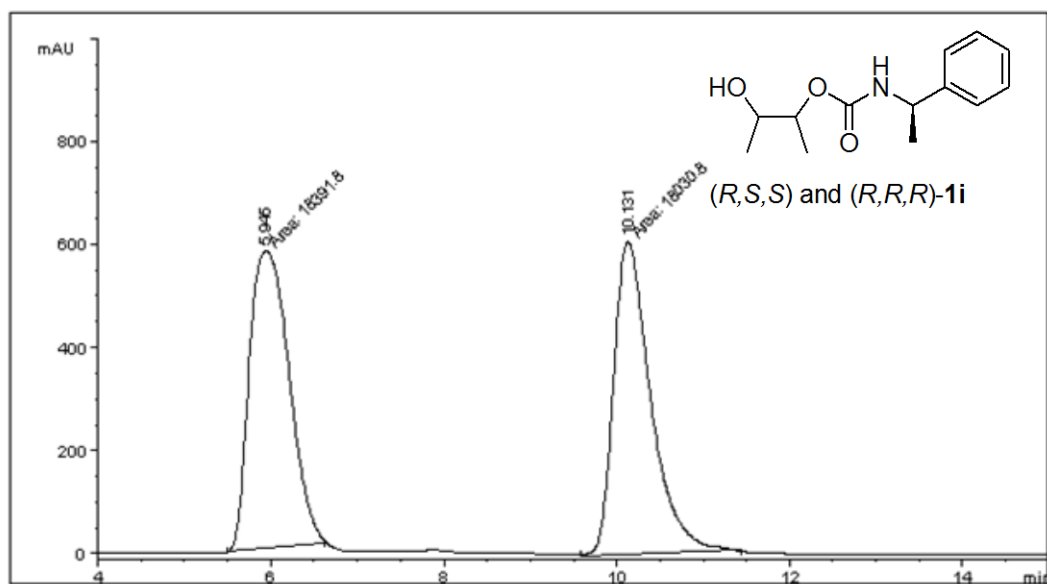
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Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	6.039	MM	0.1731	74.48032	0.7612	7.17204
2	10.156	MM	0.4974	9709.66895	99.2388	325.32822

Totals : 9784.14927 332.50025

**Figure S49.** HPLC spectrum of (R,R,R)-1i



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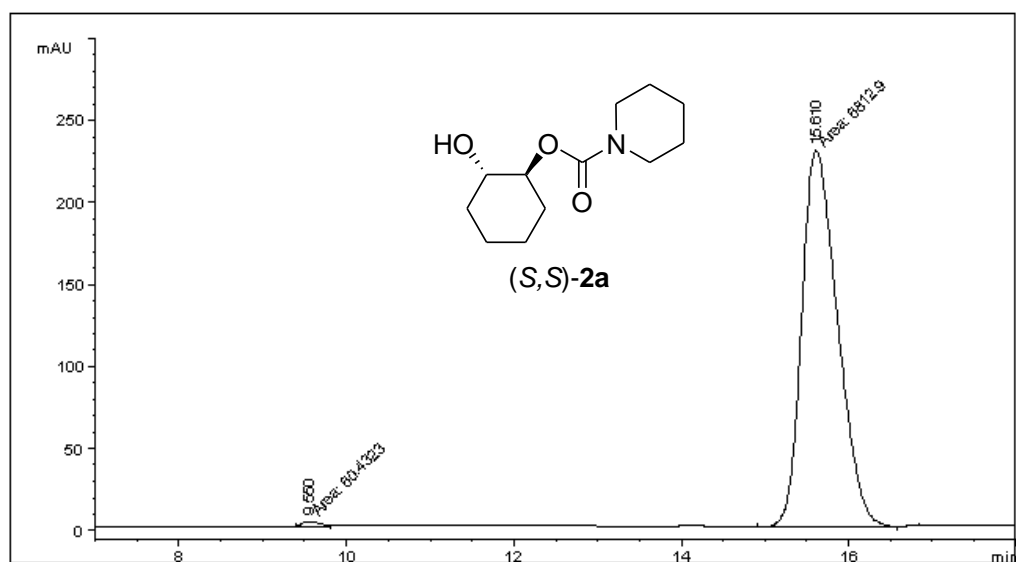
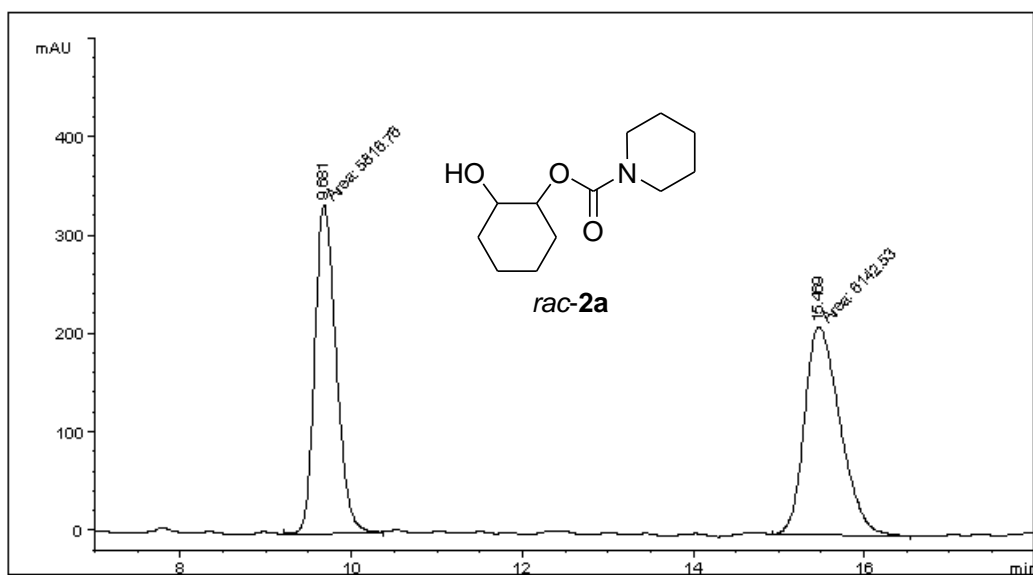
Signal 1: VWD1 A, Wavelength=214 nm

Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU] %
-----|-----|-----|-----|-----|
1 6.143 MM 0.3425 2.42552e4 1180.28345 99.3864
2 10.309 MM 0.2689 149.75768 9.28065 0.6136
Totals : 2.44050e4 1189.56410

```

**Figure S50.** HPLC spectrum of (R,S,S)-1i





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 Area Percent Report  
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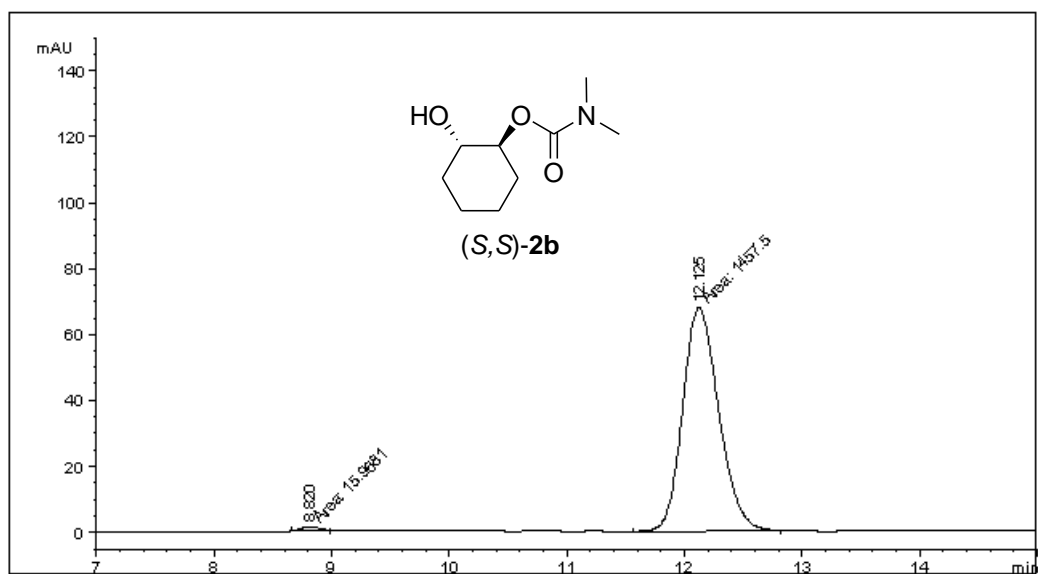
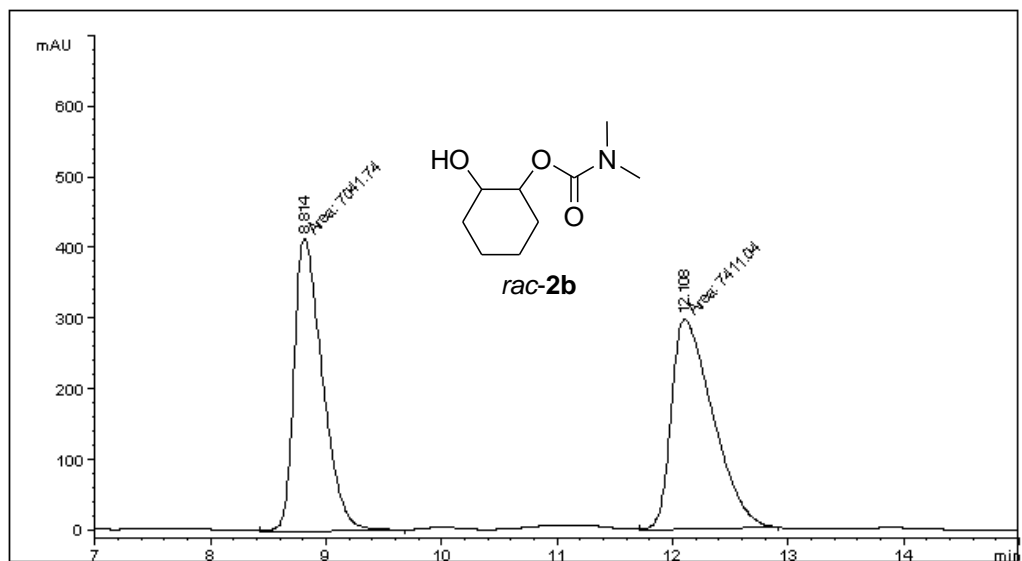
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.550	MM	0.2592	60.43233	3.88596	0.8792
2	15.610	MM	0.4948	6812.89600	229.48106	99.1208

Totals : 6873.32833 233.36702

**Figure S51.** HPLC spectrum of **2a**



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 Area Percent Report  
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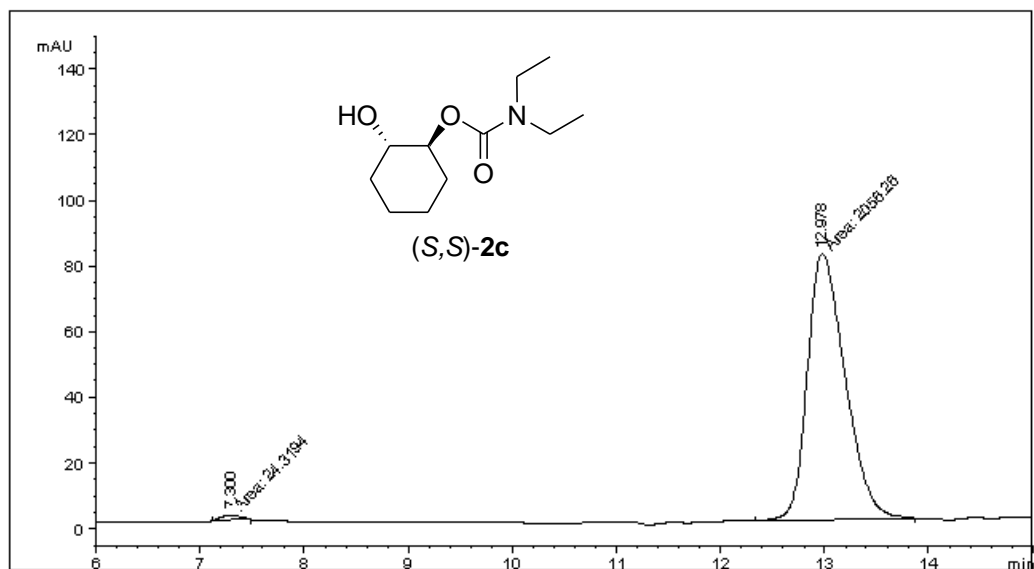
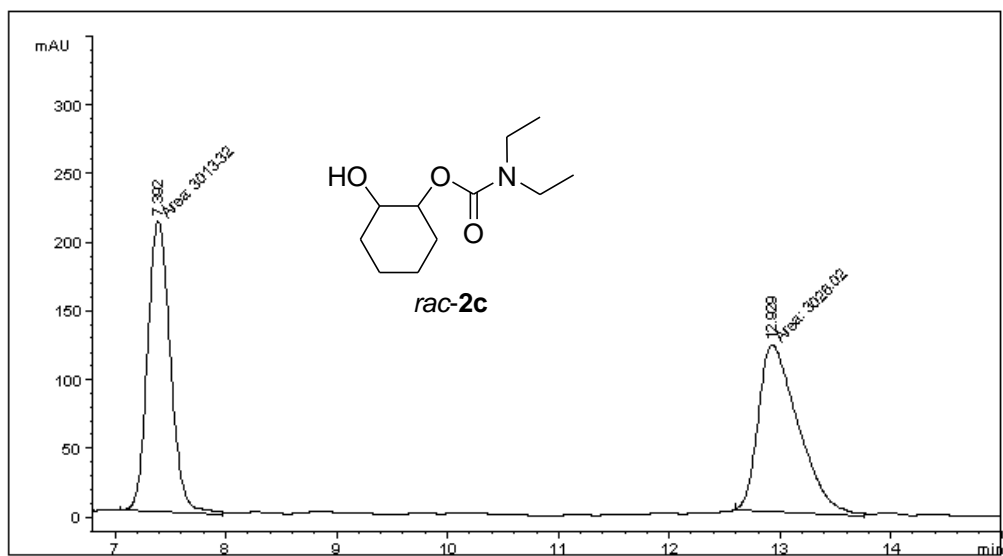
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.820	MM	0.1878	15.96810	1.41725	1.0837
2	12.125	MM	0.3570	1457.50232	68.04016	98.9163

Totals : 1473.47042 69.45741

**Figure S52.** HPLC spectrum of **2b**



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 Area Percent Report  
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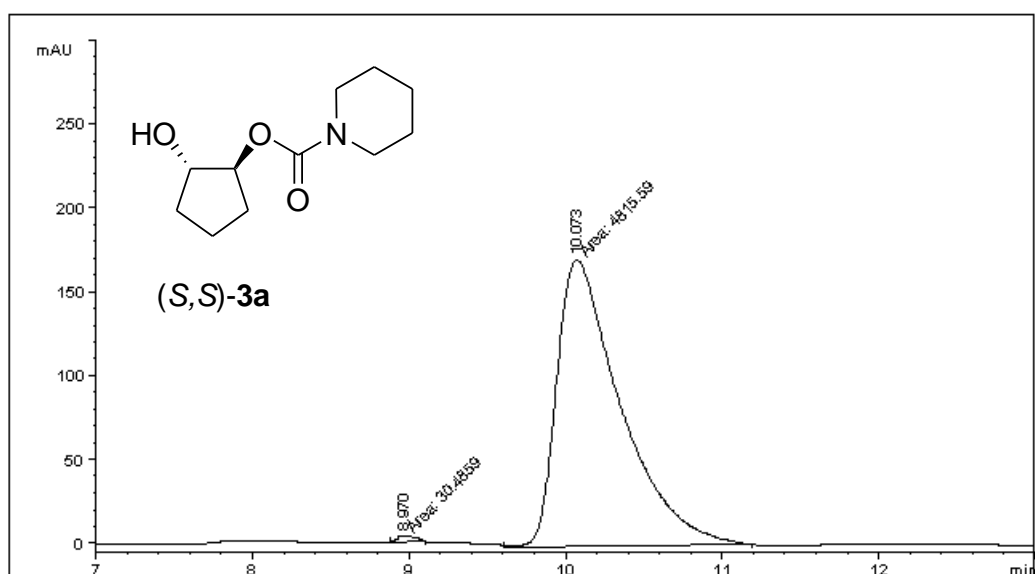
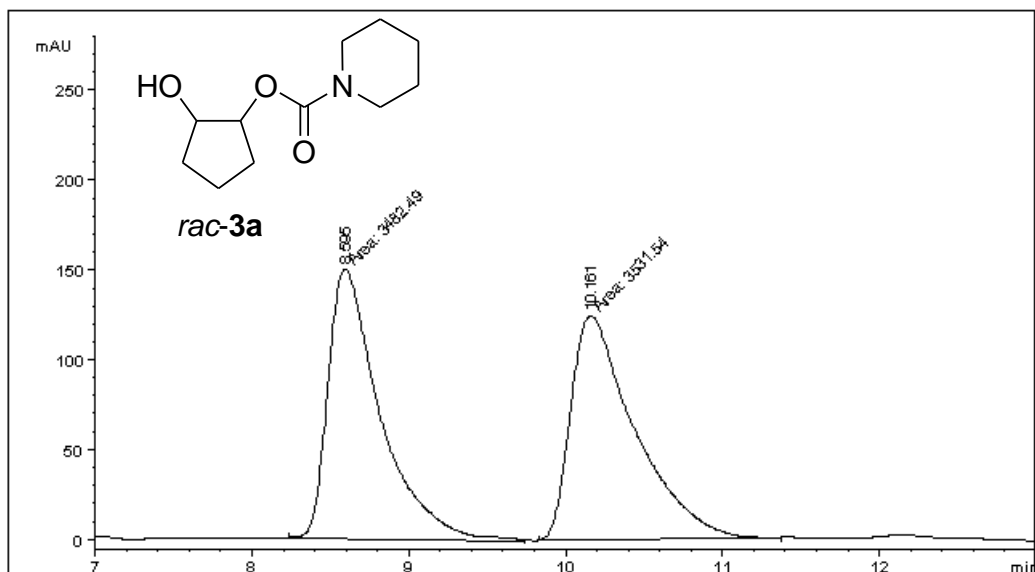
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %s	Height [mAU]	Area %
1	7.300	MM	0.1184	24.31938		3.42200	1.1689
2	12.978	MM	0.4222	2056.25537		81.18111	98.8311

Totals : 2080.57475 84.60311

**Figure S53.** HPLC spectrum of **2c**



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 Area Percent Report  
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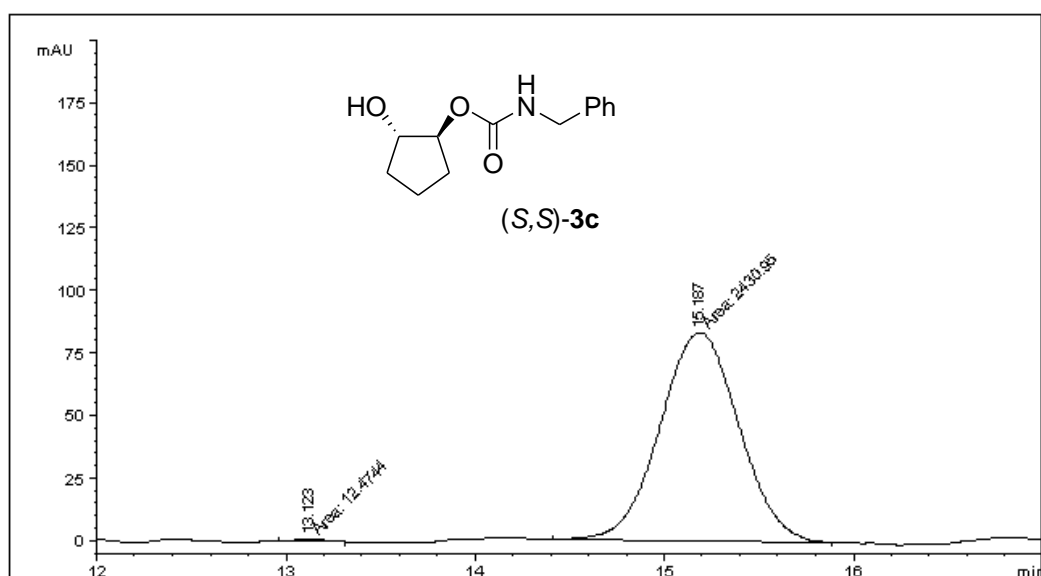
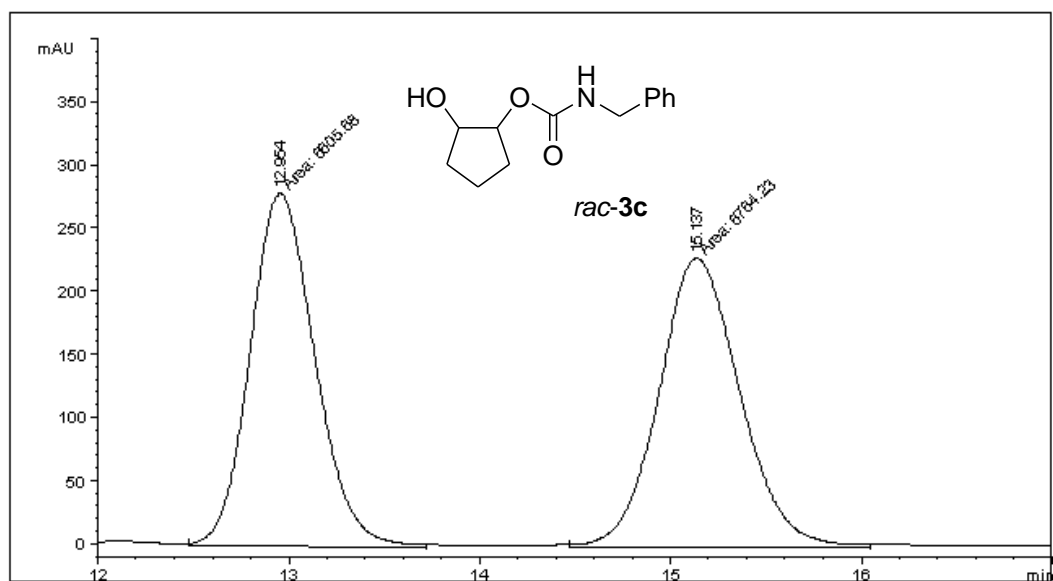
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	8.970	MM	0.1476	30.48592	3.44282	0.6291	
2	10.073	MM	0.4702	4815.59180	170.69839	99.3709	

Totals : 4846.07771 174.14121

**Figure S54.** HPLC spectrum of **3a**



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 Area Percent Report  
 =====

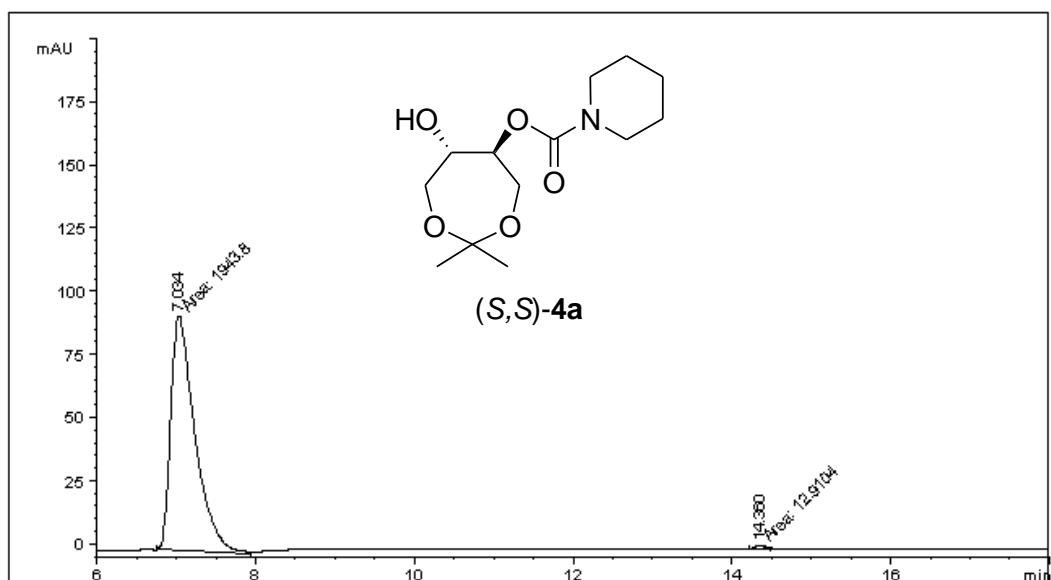
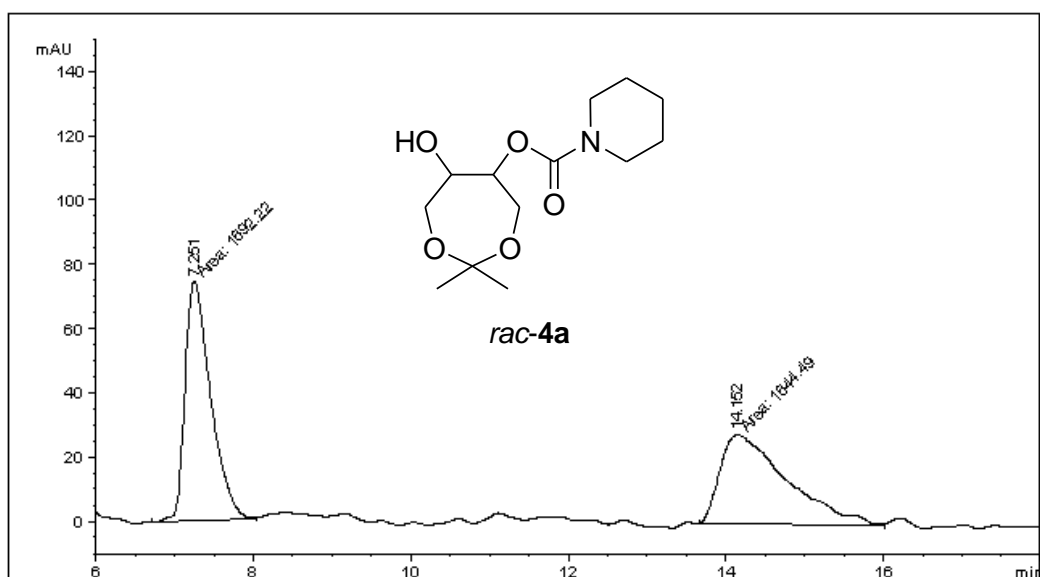
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	13.123	MM	0.1860	12.47439		1.11766	0.5105
2	15.187	MM	0.4855	2430.95068		83.44405	99.4895

Totals : 2443.42507 84.56171

**Figure S55.** HPLC spectrum of 3c



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 Area Percent Report  
 =====

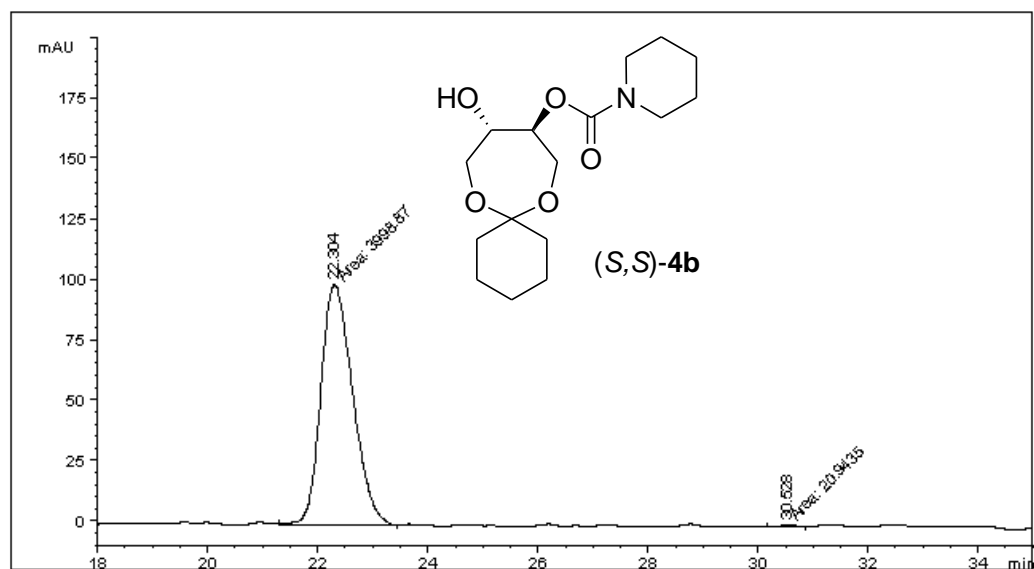
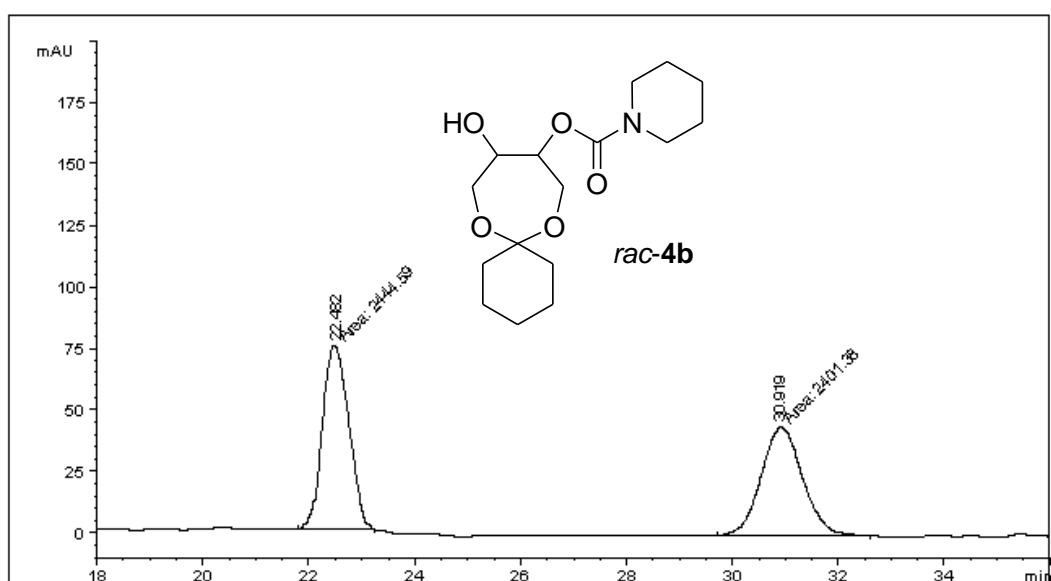
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.034	MM	0.3502	1943.80432	92.51027	99.3402
2	14.360	MM	0.1739	12.91043	1.23733	0.6598

Totals : 1956.71475 93.74760

**Figure S56.** HPLC spectrum of 4a



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 Area Percent Report  
 =====

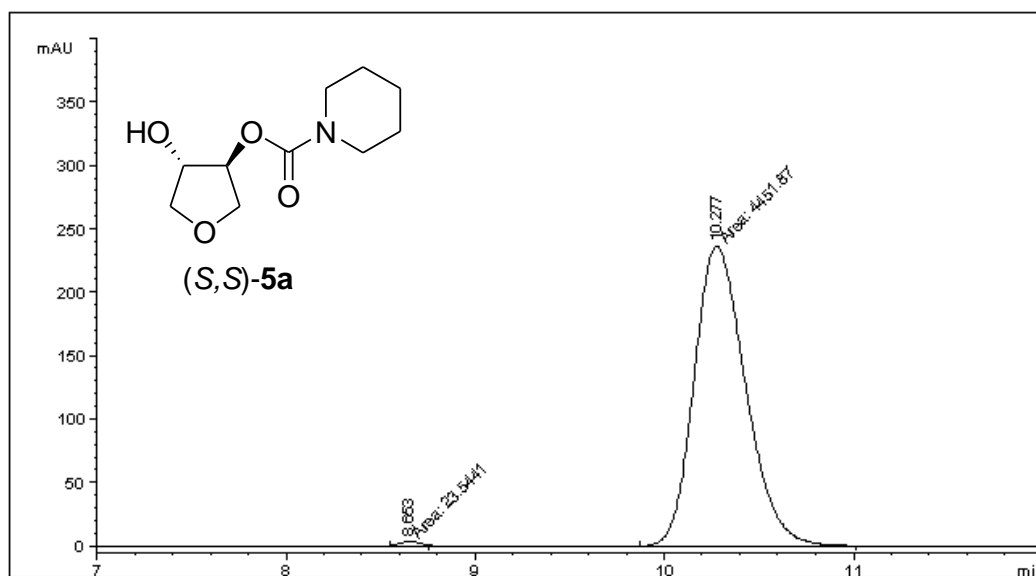
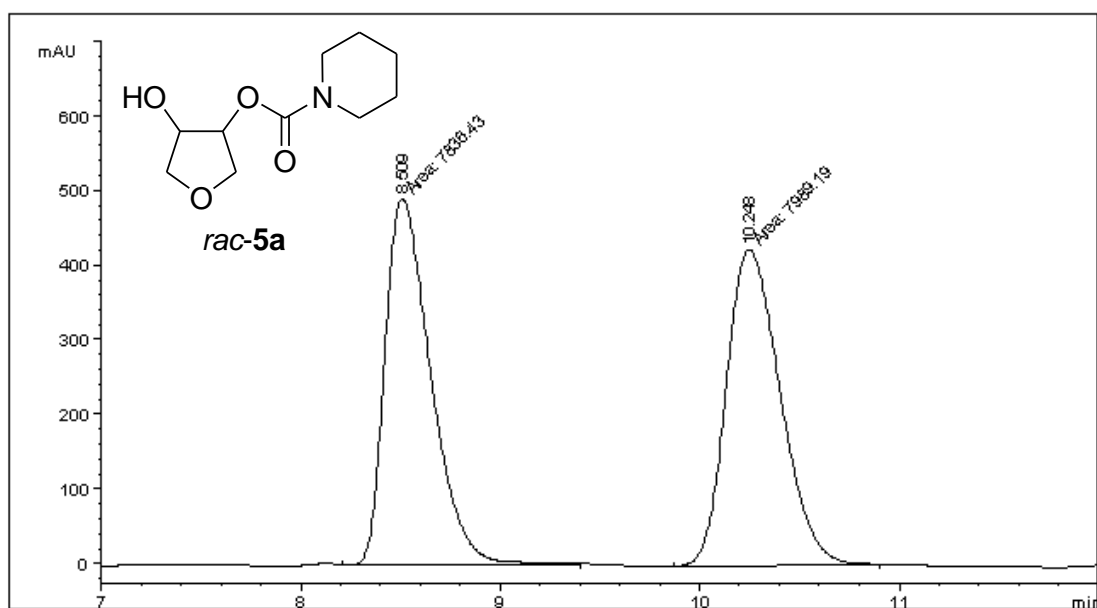
Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	22.304	MM	0.6699	3998.87476	99.4790	99.48444
2	30.528	MM	0.3338	20.94353	0.5210	1.04560

Totals : 4019.81828 100.53004

**Figure S57. HPLC spectrum of 4b**



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 Area Percent Report  
 =====

Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

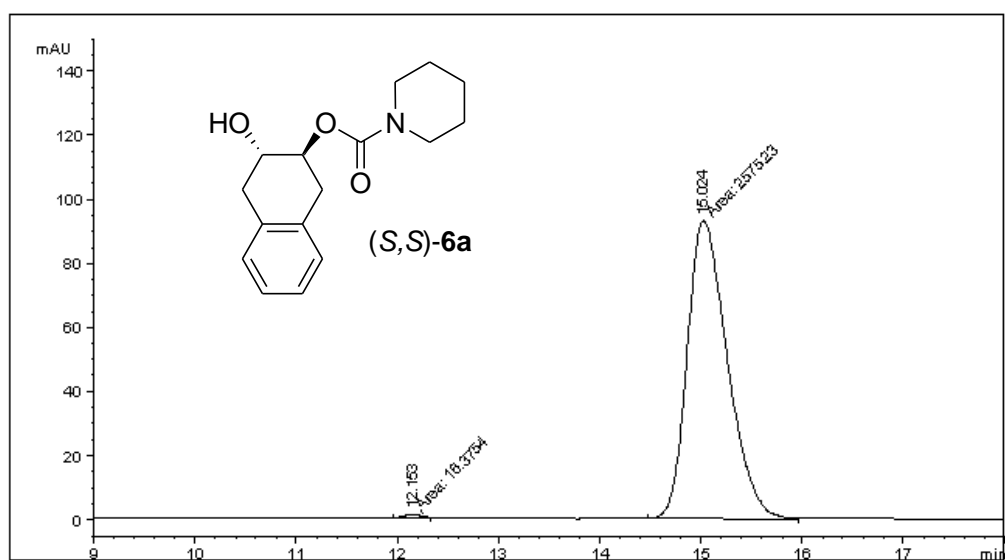
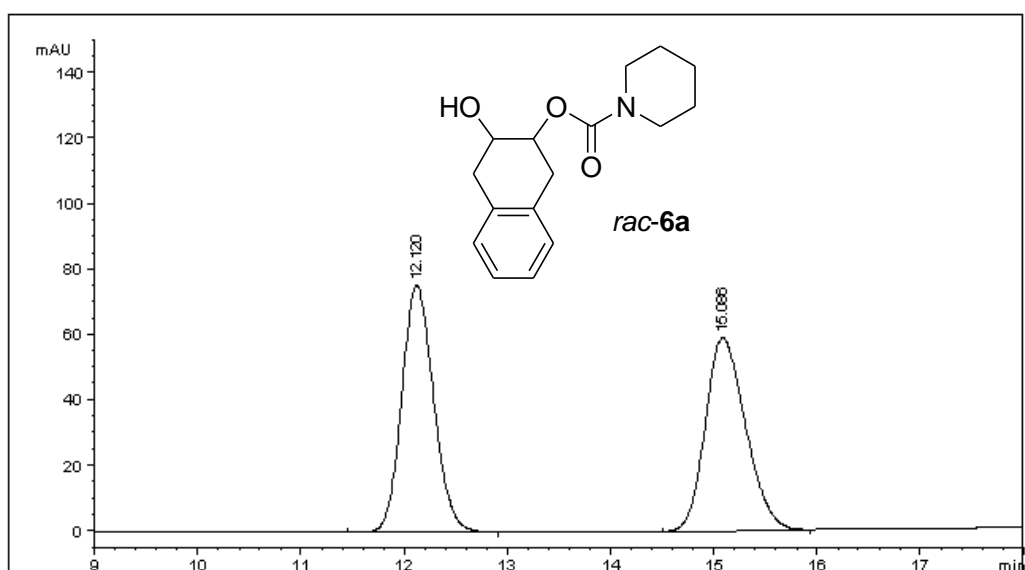
Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	8.653	MM	0.1294	23.54413	0.5261	3.03139
2	10.277	MM	0.3147	4451.87256	99.4739	235.73959

Totals : 4475.41669 238.77099

**Figure S58.** HPLC spectrum of **5a**





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Area Percent Report  
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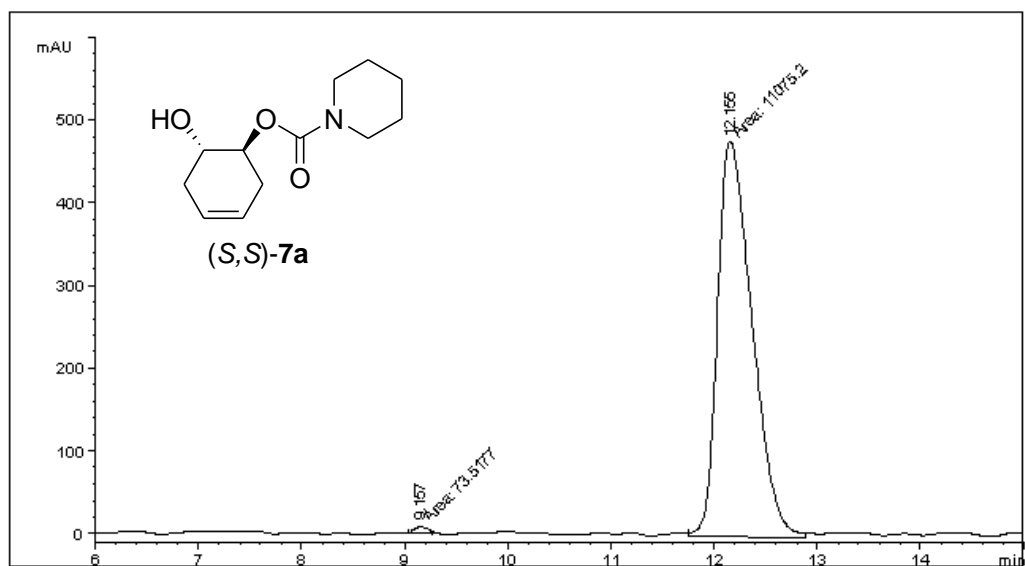
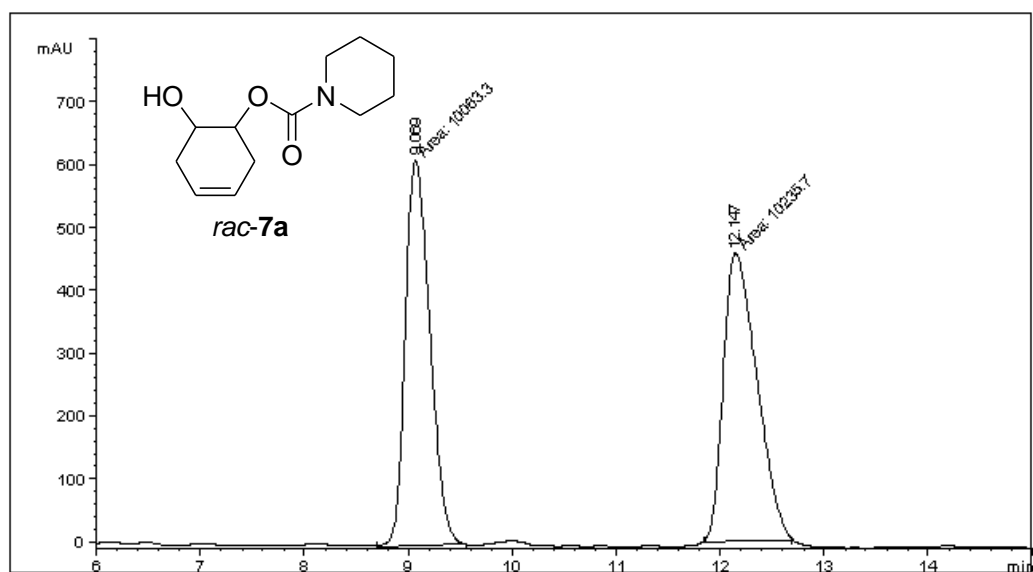
Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	12.153	MM	0.2192	16.37545		1.24499	0.6319
2	15.024	MM	0.4614	2575.22681		93.03033	99.3681

Totals : 2591.60225 94.27532

**Figure S59.** HPLC spectrum of **6a**



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 Area Percent Report  
 =====

Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

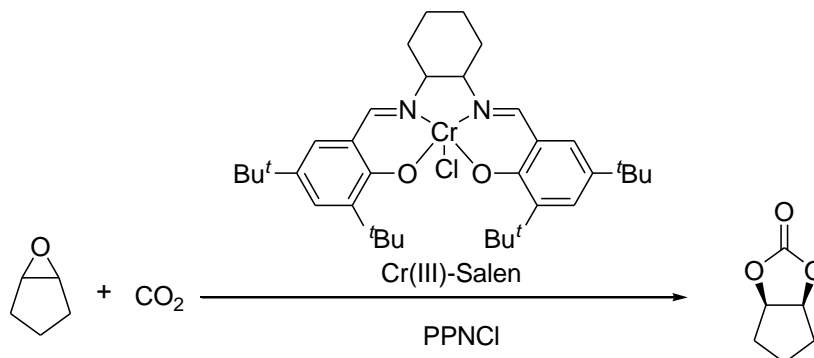
Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.157	MM	0.1357	73.51771	9.02688	0.6594
2	12.155	MM	0.3866	1.10752e4	477.42279	99.3406

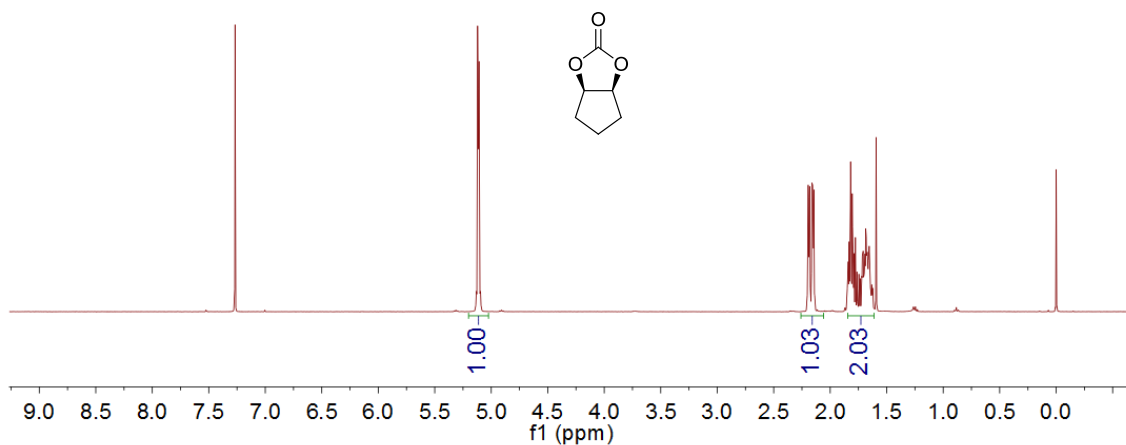
Totals : 1.11487e4 486.44967

**Figure S60.** HPLC spectrum of **7a**

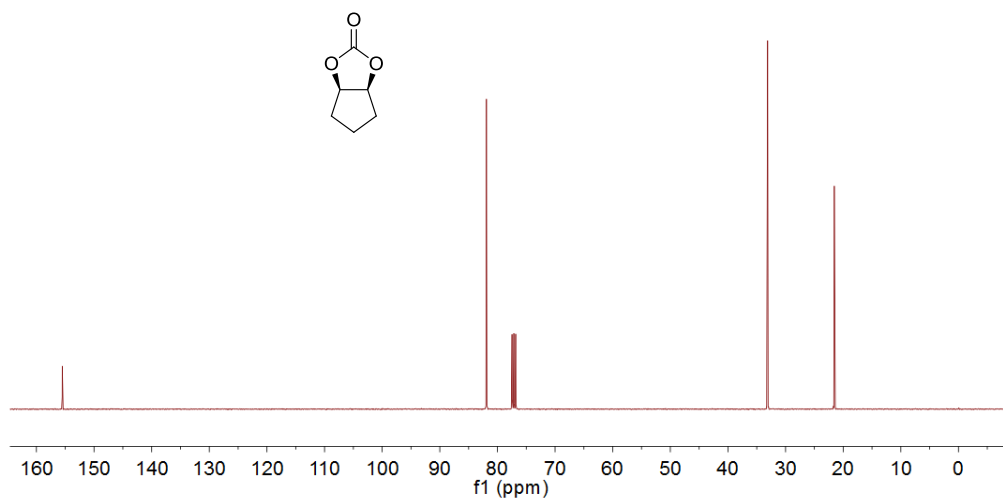
#### 4. Mechanistic understanding of ammonolysis reaction



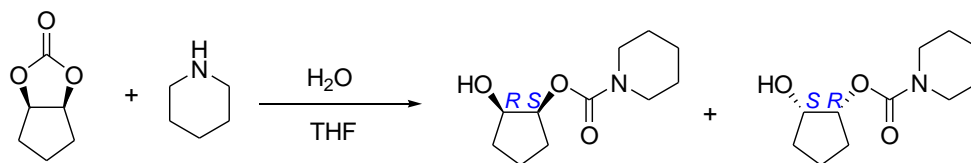
**Scheme S1.** Synthesis of *cis*-carbamates from CO<sub>2</sub>/cyclopentene oxide



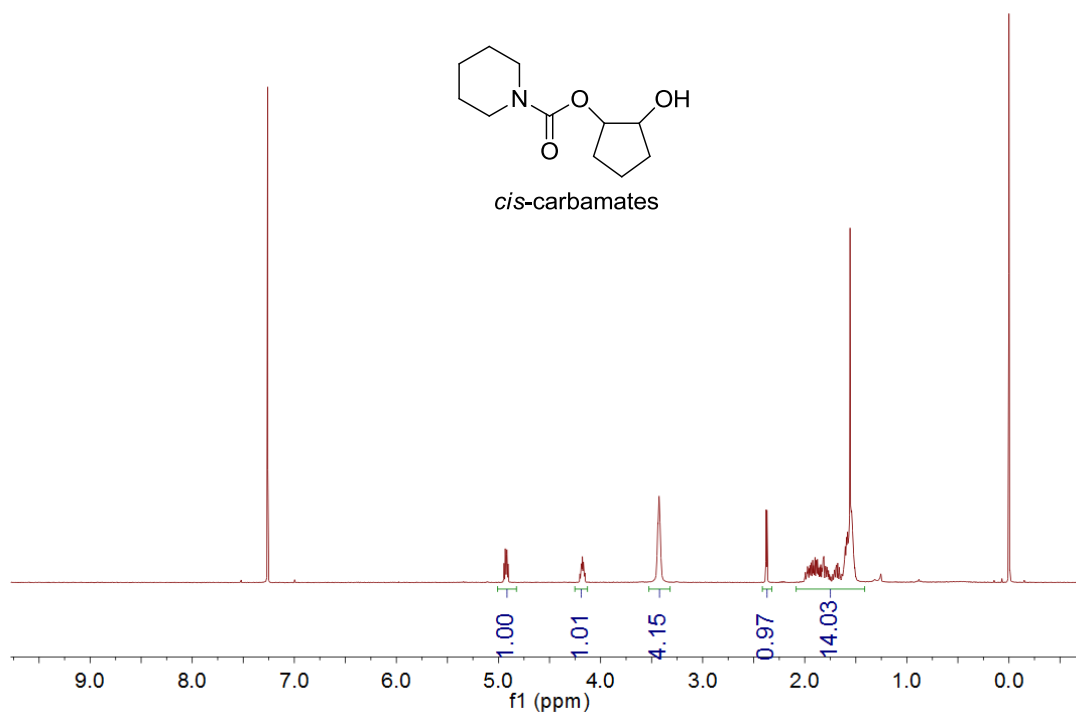
**Figure S61.** <sup>1</sup>H NMR spectrum of *cis*-cyclopentene carbonate



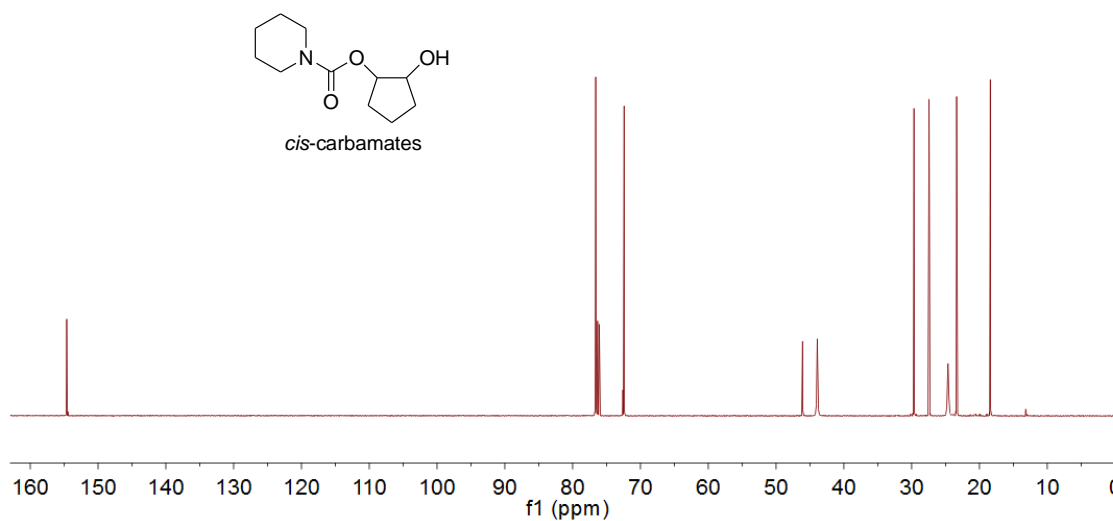
**Figure S62.** <sup>13</sup>C NMR spectrum of *cis*-cyclopentene carbonate



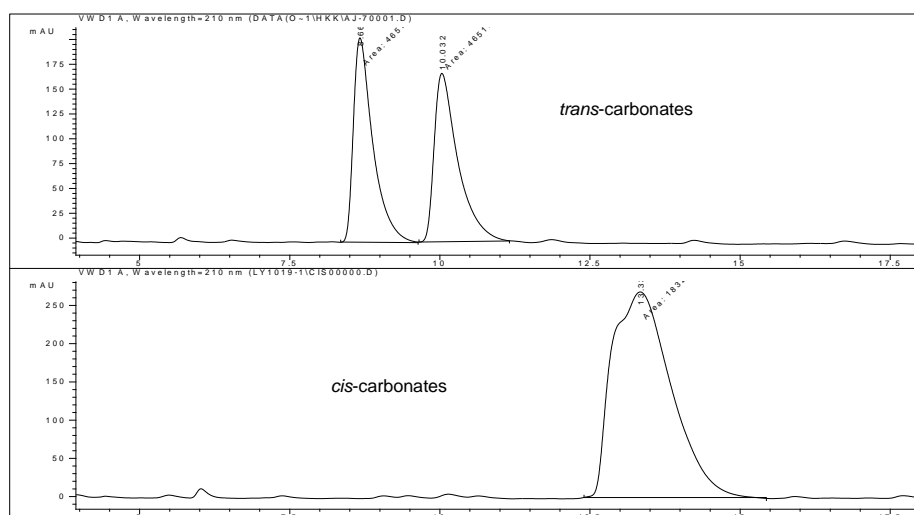
**Scheme S2.** Synthesis of *cis*-carbamates from aminolysis of carbonates



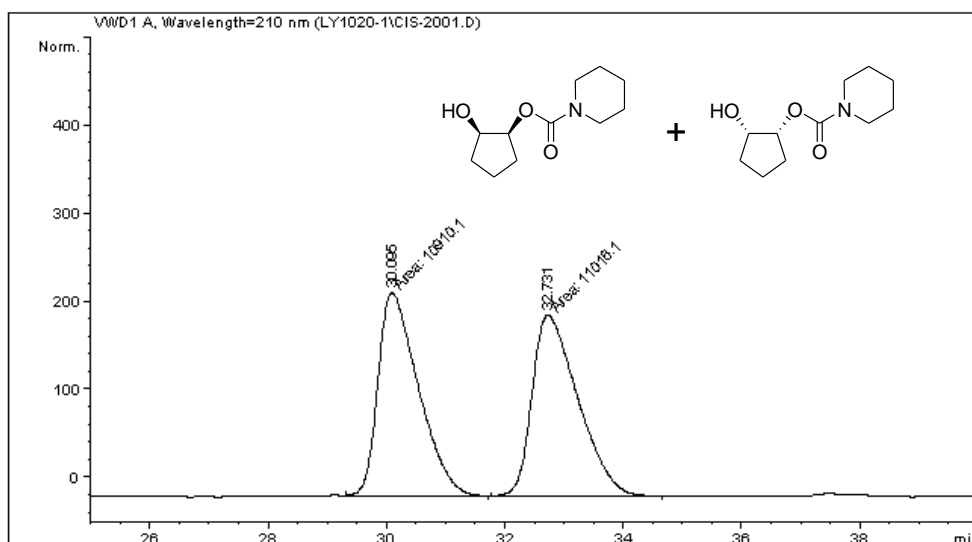
**Figure S63.**  $^1\text{H}$  NMR spectrum of *cis*-carbamates.



**Figure S64.**  $^{13}\text{C}$  NMR spectrum of *cis*-carbamates.



**Figure S65.** HPLC spectrum of *cis*-carbamate and *trans*-carbamate (HPLC conditons: Chiralpak AS-H, hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, maximum absorption wavelength  $\lambda$  = 210 nm).



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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

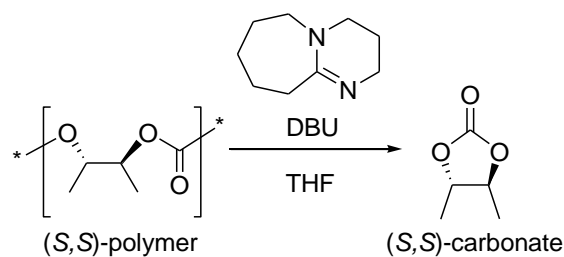
Peak RetTime Type Width Area Height Area
# [min] [min] [min] mAU *s [mAU ] %
-----|-----|-----|-----|-----|
1 30.095 MM 0.7886 1.09101e4 230.58556 49.7583
2 32.731 MM 0.8968 1.10161e4 204.73941 50.2417

Totals :                      2.19261e4 435.32497

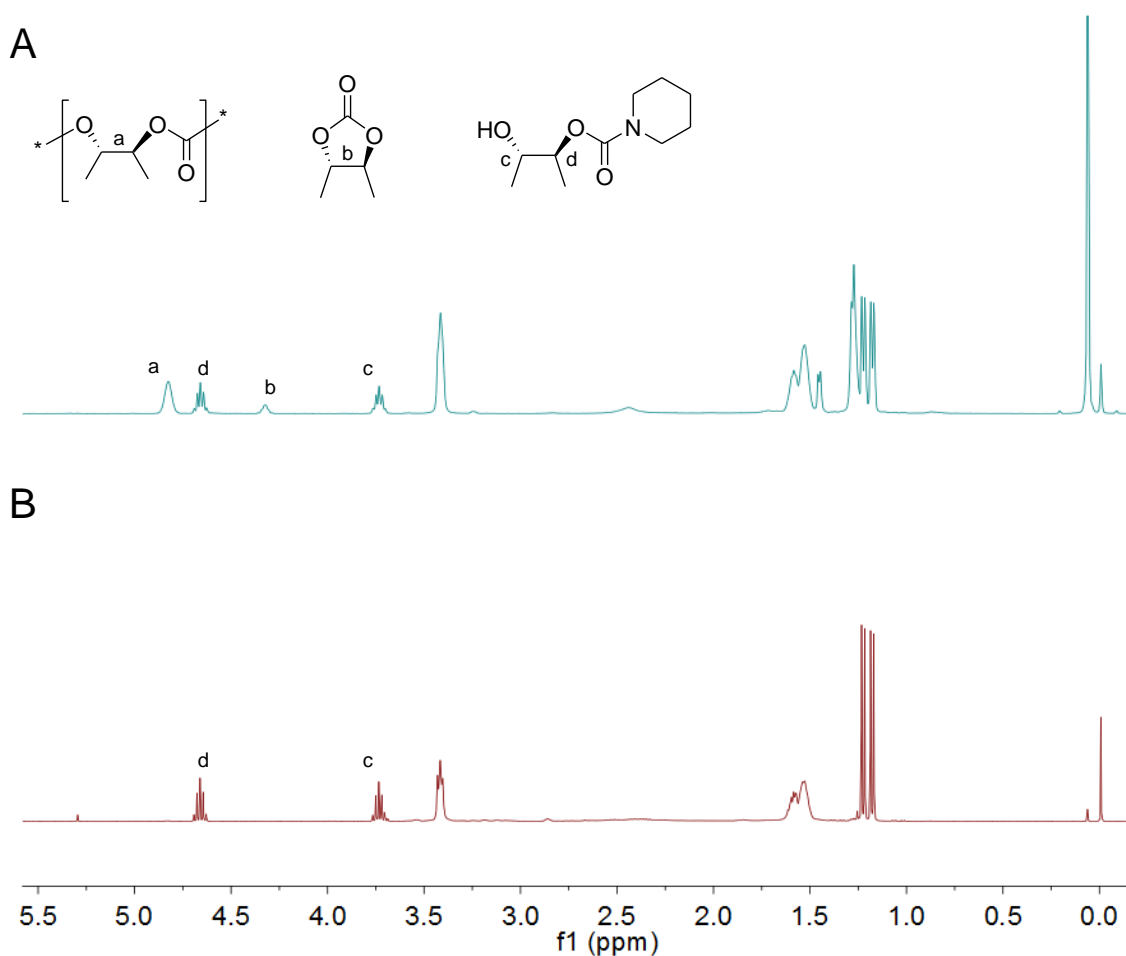
Results obtained with enhanced integrator!
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*** End of Report ***

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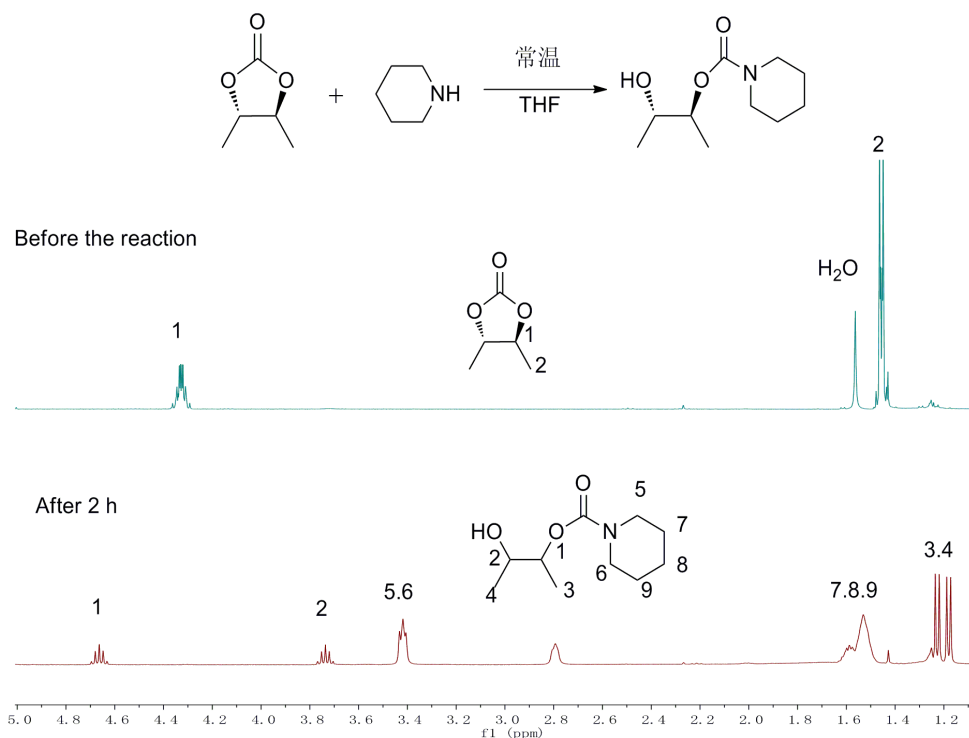
**Figure S66.** HPLC spectrum of *cis*-carbamate. HPLC conditons: Chiralpak AD-H, hexane/*i*PrOH = 98/2, flow rate = 0.8 mL/min, maximum absorption wavelength  $\lambda$  = 210 nm.



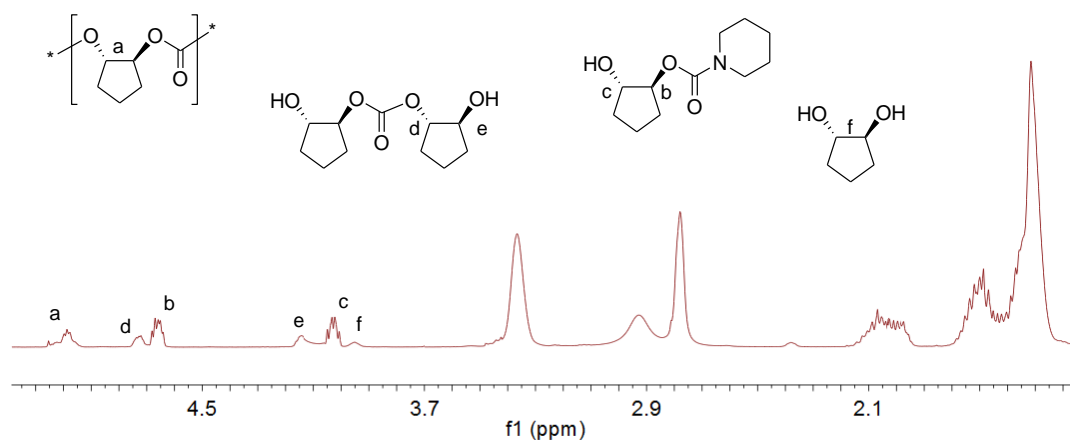
**Scheme S3.** Synthesis of *trans*-2-butene carbonate



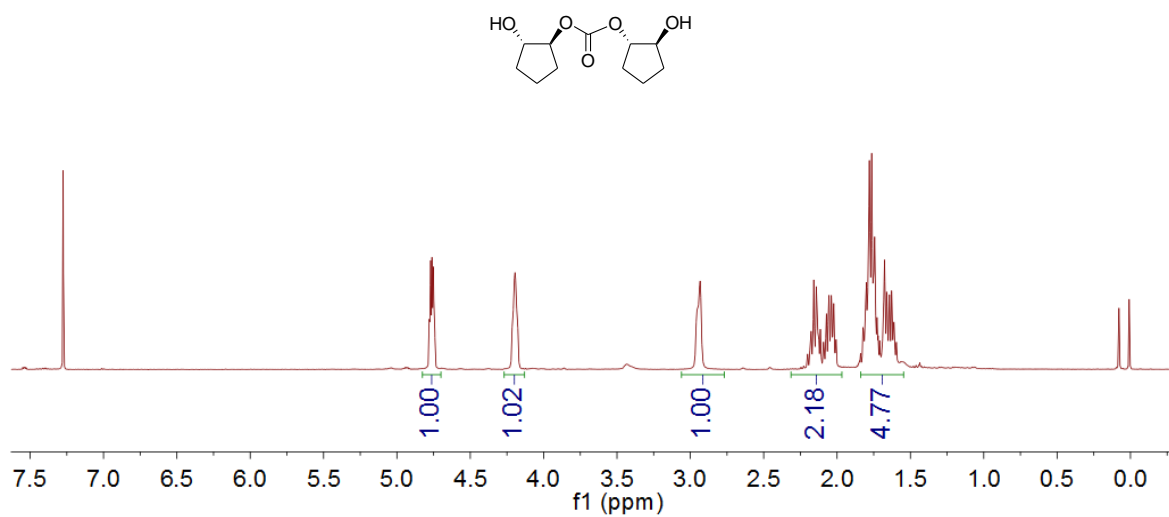
**Figure S67.**  $^1\text{H}$  NMR spectrum of the reaction mixture of poly(*trans*-2-butene carbonate) with piperidine in  $\text{CDCl}_3$ . A) the reaction was carried out in absence of water; B) the reaction was carried out in presence of water. (Reaction condition:  $\text{CO}_2$  polymers (464 mg, 4 mmol), amine (4 mmol, 1 equiv to per carbonate unit), water (4 mmol, 1 equiv to per carbonate unit) were dissolved in 10 mL THF at room temperature. The reaction mixture was stirred at 60  $^\circ\text{C}$  for 1 h. A small amount of mixture was removed for  $^1\text{H}$  NMR analysis after the removal of the solvent under reduced pressure



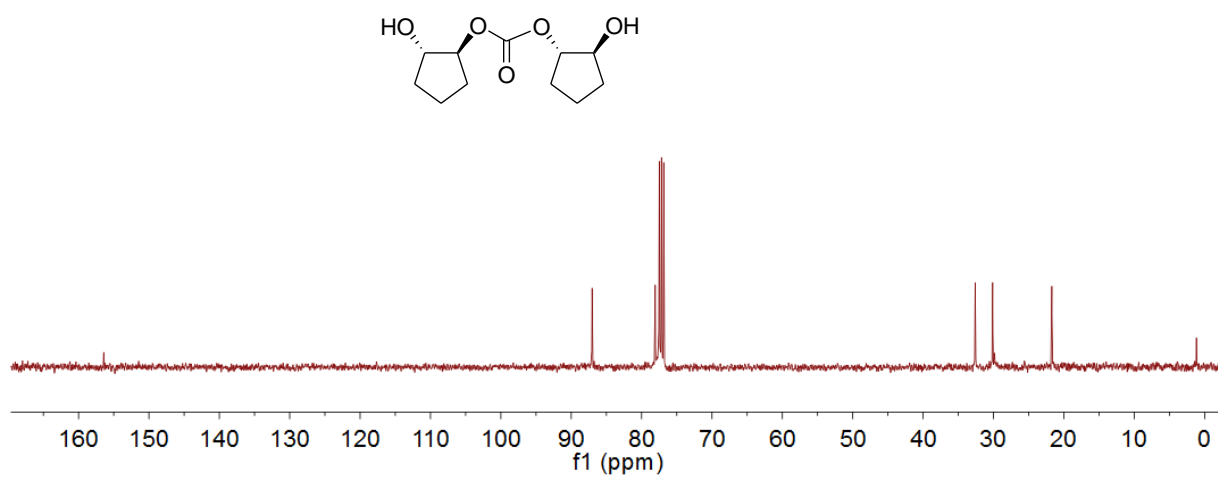
**Figure S68.**  $^1\text{H}$  NMR spectrum of the reaction of *trans*-2-butene carbonate with piperidine in  $\text{CDCl}_3$ . Reaction condition: *trans*-2-butene carbonate (0.2 mmol), piperidine (0.2 mmol, 1 equiv to per carbonate unit) and water (0.2 mmol, 1 equiv to per carbonate unit) were dissolved in 5 mL THF. The reaction mixture was stirred for 2 h at room temperature. A small amount of mixture was removed for  $^1\text{H}$  NMR analysis after the removal of the solvent under reduced pressure



**Figure S69.**  $^1\text{H}$  NMR spectrum of the reaction mixture of poly(cyclopentene carbonate) with piperidine in  $\text{CDCl}_3$ . Reaction condition:  $\text{CO}_2$  polymers (512 mg, 4.0 mmol), amine (20 mmol, 5 equiv to per carbonate unit), water (20 mmol, 5 equiv to per carbonate unit) were dissolved in 10 mL THF at room temperature. The reaction mixture was stirred at  $60^\circ\text{C}$  for 24 h. A small amount of mixture was removed for  $^1\text{H}$  NMR analysis after the removal of the solvent under reduced pressure

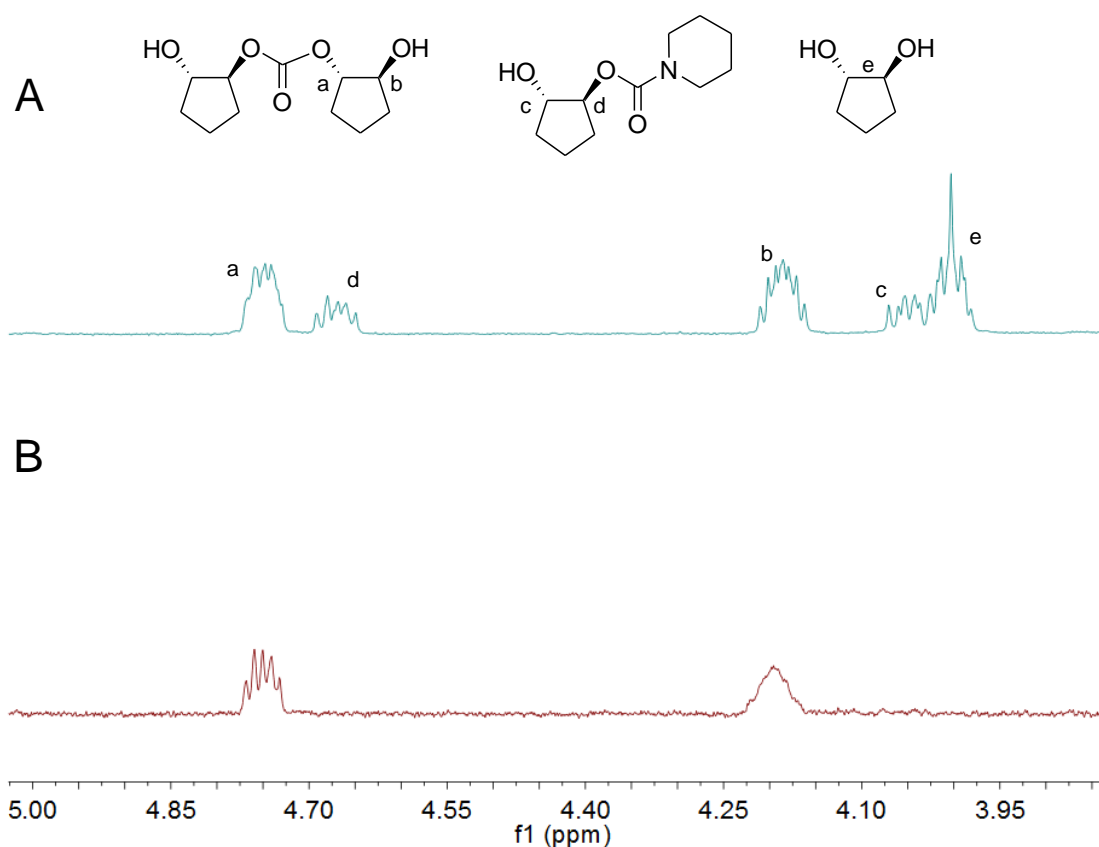


**Figure S70.** <sup>1</sup>H NMR spectrum of 2,2'-carbonyldioxydicyclopentanol.



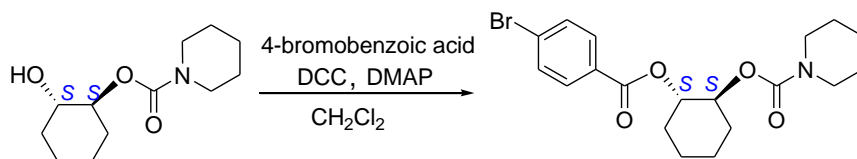
**Figure S71.** <sup>13</sup>C NMR spectrum of 2,2'-carbonyldioxydicyclopentanol.



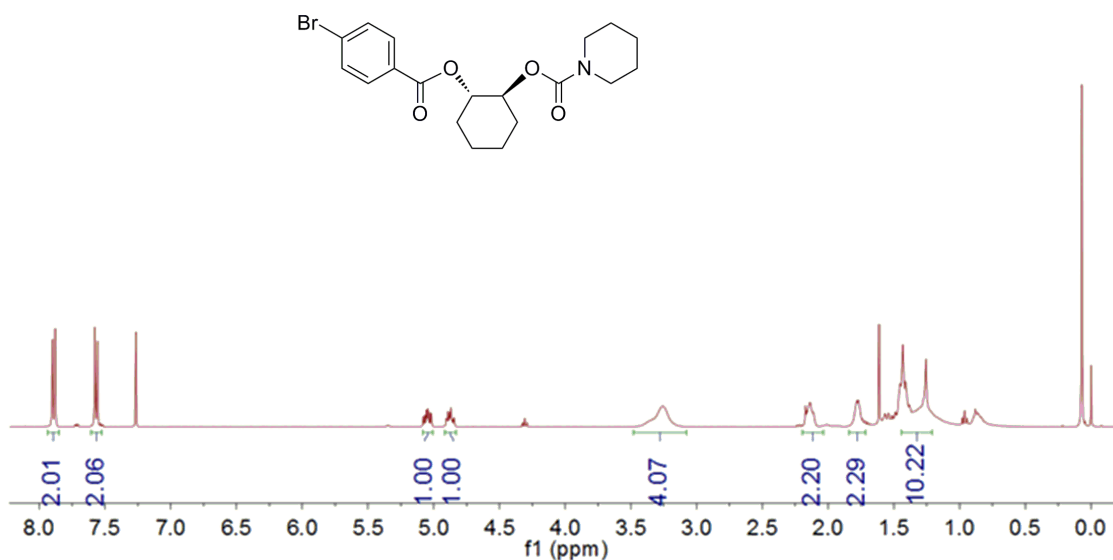


**Figure S72.** The aminolysis reaction of 2,2'-carbonyldioxydicyclopentanol with piperidine in presence (top, plot-A) and absence (bottom, plot-B) of water. Reaction condition: 2,2'-carbonyldioxydicyclohexanol (0.2 mmol), piperidine (0.2 mmol) and water (0.2 mmol) were dissolved in 5 mL THF at room temperature. The reaction mixture was stirred at room temperature for 24 h. A small amount of mixture was removed for  $^1\text{H}$  NMR analysis after the removal of the solvent under reduced pressure

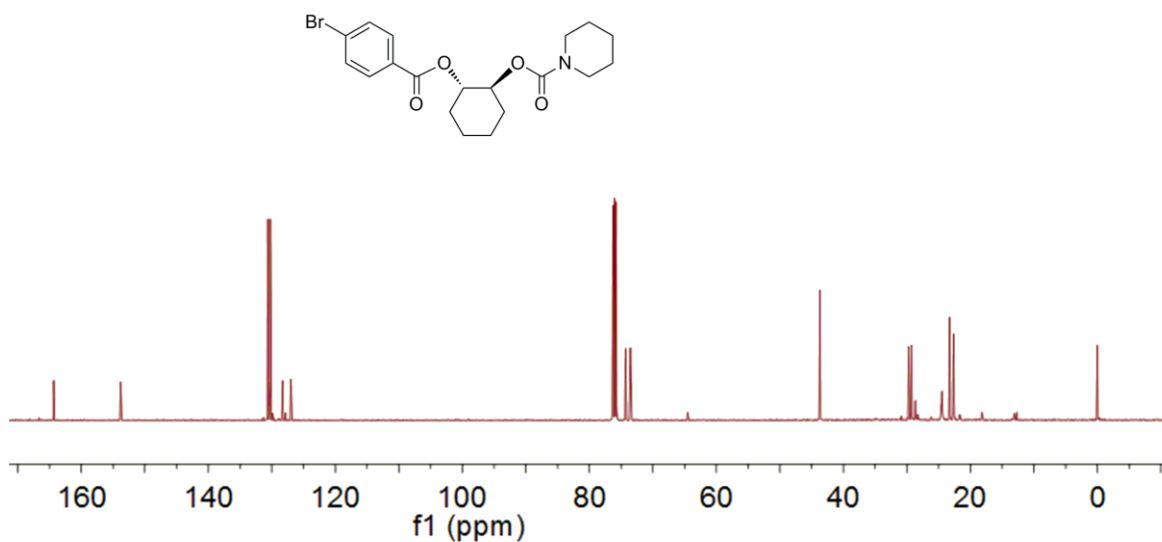
## 5. NMR spectrum of (S,S)-carbamate derivative for X-Ray analysis



**Scheme S4.** Synthesis of (S,S)-carbamate derivative for X-Ray analysis



**Figure S73.** <sup>1</sup>H NMR spectrum of (S,S)-carbamate derivative for X-Ray analysis

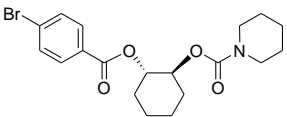


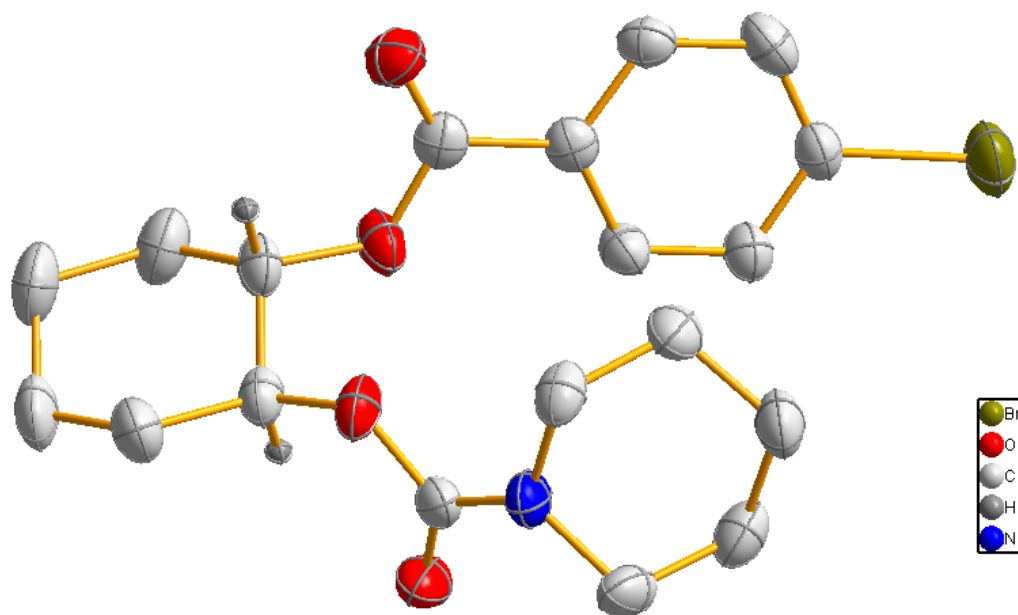
**Figure S74.** <sup>13</sup>C NMR spectrum of (S,S)-carbamate derivative for X-Ray analysis

## 6. Crystal structure determination

**Crystal structure determination.** The single crystal of (*S,S*)-carbamate derivative (CCDC: 1491321) suitable for X-ray structural analysis was obtained from a hexane at -7 °C. Diffraction data were collected at 200 K on a CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software packages. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S2.** Summary of crystal data and structural refinement details of carbamate derivative

	( <i>S,S</i> )-carbamate derivative
structure	
mol formula	C <sub>19</sub> H <sub>24</sub> Br N O <sub>4</sub>
mol wt	410.30
cryst syst	Orthorhombic
space group	P2(1)2(1)2(1)
<i>a</i> /Å	9.586(4)
<i>b</i> /Å	10.266(4)
<i>c</i> /Å	19.842(8)
$\alpha$ /deg	90.00
$\beta$ /deg	90.00
$\gamma$ /deg	90.00
<i>V</i> /Å <sup>3</sup>	1952.8(14)
<i>Z</i>	4
abs coeff/mm <sup>-1</sup>	2.127
<i>R</i> <sub>int</sub>	0.0496
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ )	0.0438 (2616)
w <i>R</i> 2 ( <i>I</i> > 2 $\sigma$ )	0.982
GOF	1.007



**Figure S75.** X-Ray molecular structures of (S,S)-carbamate derivative. Hydrogen atoms and uncoordinated solvent omitted for clarity, and thermal ellipsoids are at the 30% probability level.