



Supporting Information

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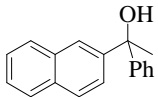
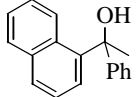
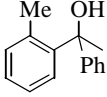
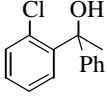
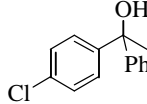
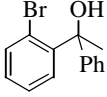
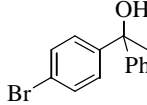
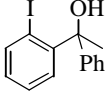
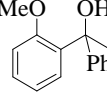
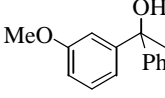
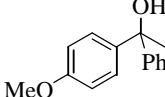
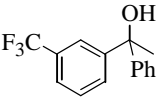
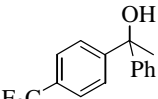
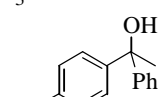
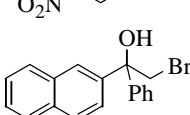
69451 Weinheim, Germany

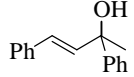
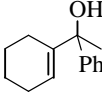
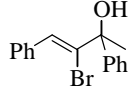
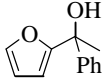
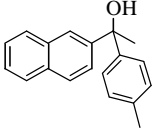
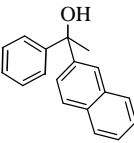
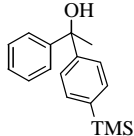
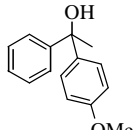
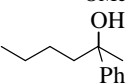

**Highly Enantioselective Aryl Additions of  $\text{AlAr}_3(\text{THF})$  to Ketones Catalyzed by the  
Titanium(IV) Catalyst of (S)-BINOL**

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Department of Chemistry, National Chung-Hsing University  
Taichung 402, Taiwan

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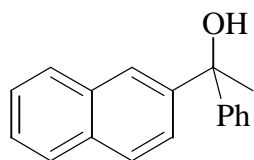
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## I. Reagents and Instruments

$\text{AlAr}_3(\text{THF})$  was synthesized according to literature procedures<sup>1</sup> and kept in a dry box.  $\text{Ti}(\text{O}-i\text{-Pr})_4$  was freshly distilled prior to use. (*S*)-(-)-1,1'-bi(2-naphthol) ((*S*)-BINOL) was obtained from Lancaster. All ketones were purchased from Acros and Lancaster. Solvents were dried by heating under refluxing for at least 24 h over  $\text{P}_2\text{O}_5$  (dichloromethane) or sodium/benzophenone (toluene, THF or diethyl ether). All catalytic reactions were carried out under a dry nitrogen atmosphere.  $^1\text{H}$  NMR spectra were obtained with a Varian Mercury-400 (400 MHz) and  $^{13}\text{C}$  NMR spectra were recorded with the Varian Mercury-400 (100 MHz) spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were measured relative to tetramethylsilane as the internal reference. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. High resolution molecular masses were determined by Finnigan MAT 95XL spectrometer. Enantiomeric excesses of tertiary alcohols were performed on a Rainin Dynamax<sup>®</sup> or an Agilent 1100 HPLC using appropriate chiral columns from Daicel.

## II. HPLC, <sup>1</sup>H and <sup>13</sup>C NMR, HRMS Data, and <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Tertiary Alcohols

### 1-Naphthalen-2-yl-1-phenyl-ethanol (Table 2, entry 1; 93% ee)<sup>2,3</sup>



Column: Chiralcel OJ  
 Eluent: Hexane/IPA = 80/20  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 14.589 min, 17.673 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	14.589	17.673	Time	14.513	17.460
Height (mAU)	731.907	489.963	Height (mAU)	4.039	84.610
Area (mAU-s)	3.223×10 <sup>4</sup>	3.226×10 <sup>4</sup>	Area (mAU-s)	156.546	4255.514
Area (%)	49.973	50.026	Area (%)	3.548	96.451

#### Catalytic Reaction Conditions:

2'-acetonaphthone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

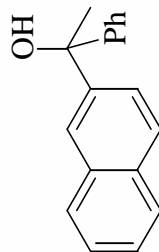
#### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* = 1.2 Hz, 1H), 7.84-7.75 (m, 3H), 7.49-7.25 (m, 8H), 2.27 (br, 1H), 2.06 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.70, 145.22, 132.96, 132.35, 128.22, 128.18, 127.91, 127.45, 127.00, 126.08, 125.92, 124.91, 123.70, 76.31, 30.66 ppm.

2-acetonaphthone

Pulse Sequence: s2pu1

7.981  
7.978  
7.835  
7.814  
7.797  
7.791  
7.774  
7.753  
7.489  
7.484  
7.481  
7.473  
7.464  
7.458  
7.446  
7.425  
7.421  
7.404  
7.399  
7.345  
7.343  
7.326  
7.325  
7.321  
7.307  
7.270  
7.257  
7.253



0.001  
0.000

2.056

6.05 29.88  
18.61 23.93

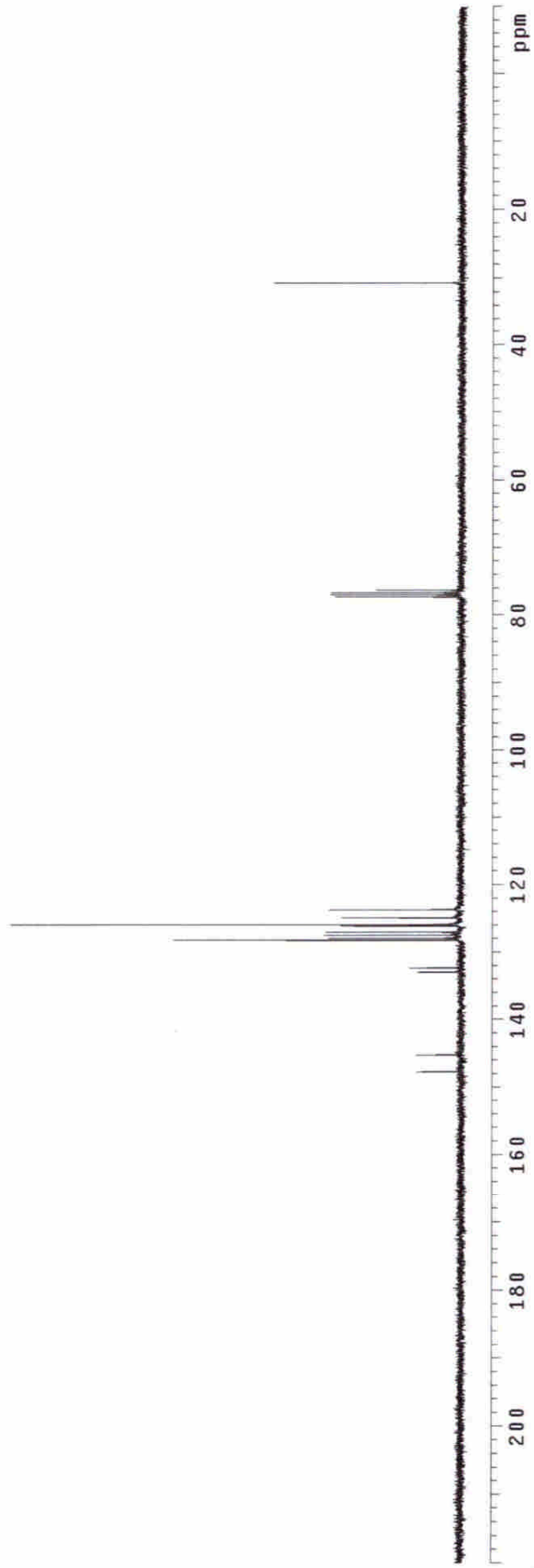
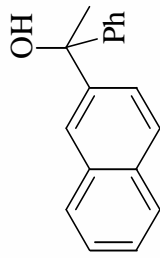
21.42

2-acetonaphthone  
Pulse Sequence: s2pu1

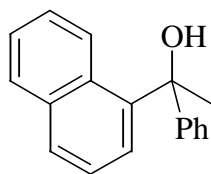
147.698  
145.218  
132.957  
132.345  
128.219  
128.181  
127.913  
127.454  
127.002  
126.084  
125.915  
124.905  
123.696

77.314  
77.000  
76.679  
76.311

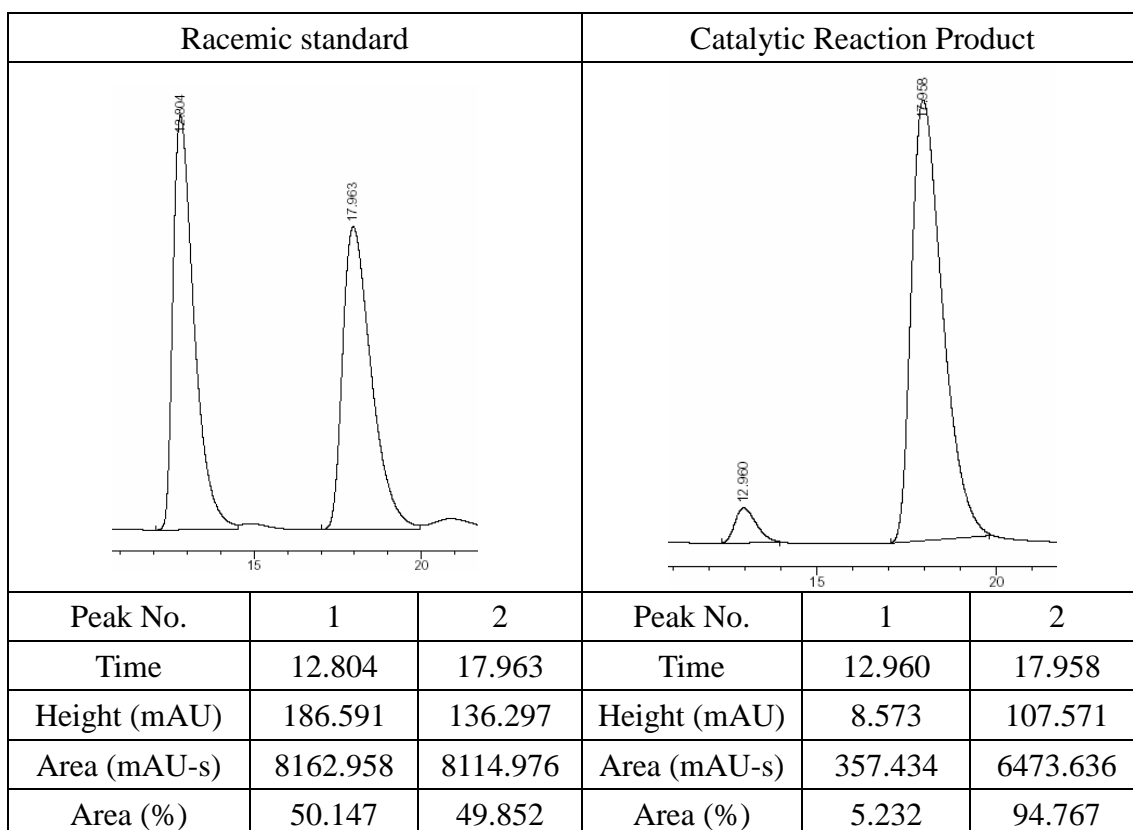
30.664



## 1-Naphthalen-1-yl-1-phenyl-ethanol (Table 2, entry 2; 90% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 90/10  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 12.804 min, 17.963 min



### Catalytic Reaction Conditions:

1'-acetonaphthone: 0.5 mmol, (*S*)-BINOL: 10 mol%,  $\text{AlPh}_3(\text{THF})$ : 1.25 mmol,  $\text{Ti}(\text{O-}i\text{-Pr})_4$ : 2.5 mmol, 0 °C, toluene: 6 mL, 36 h.

### Spectroscopic Data:

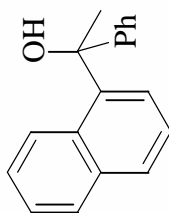
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90-7.80 (m, 4H), 7.49 (dd,  $J = 7.2, 8.0$  Hz, 1H), 7.38-7.32 (m, 3H), 7.27-7.18 (m, 4H), 2.45 (br, 1H), 2.06 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.53, 142.03, 134.88, 130.66, 129.03, 128.73, 128.27, 127.27, 126.71, 125.36, 125.20, 125.13, 124.62, 124.04, 77.09, 32.77 ppm.

HRMS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{16}\text{O}$ , 248.1202 [ $\text{M}^+$ ]; Found 248.1193.

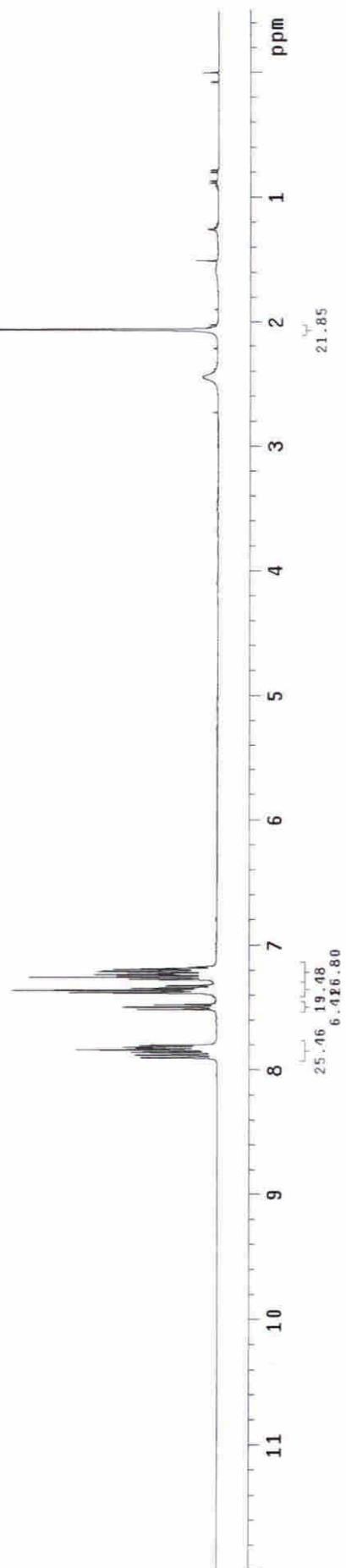
1-acetonaphthone

Pulse Sequence: s2p1

7.184  
7.190  
7.201  
7.205  
7.208  
7.223  
7.227  
7.232  
7.233  
7.234  
7.238  
7.250  
7.254  
7.271  
7.274  
7.322  
7.325  
7.340  
7.342  
7.345  
7.357  
7.359  
7.360  
7.363  
7.373  
7.378  
7.381  
7.473  
7.492  
7.494  
7.512  
7.801  
7.802  
7.813  
7.819  
7.821  
7.823  
7.836  
7.855  
7.857  
7.878  
7.900

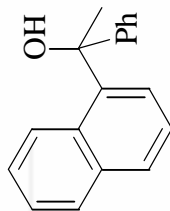


2.058



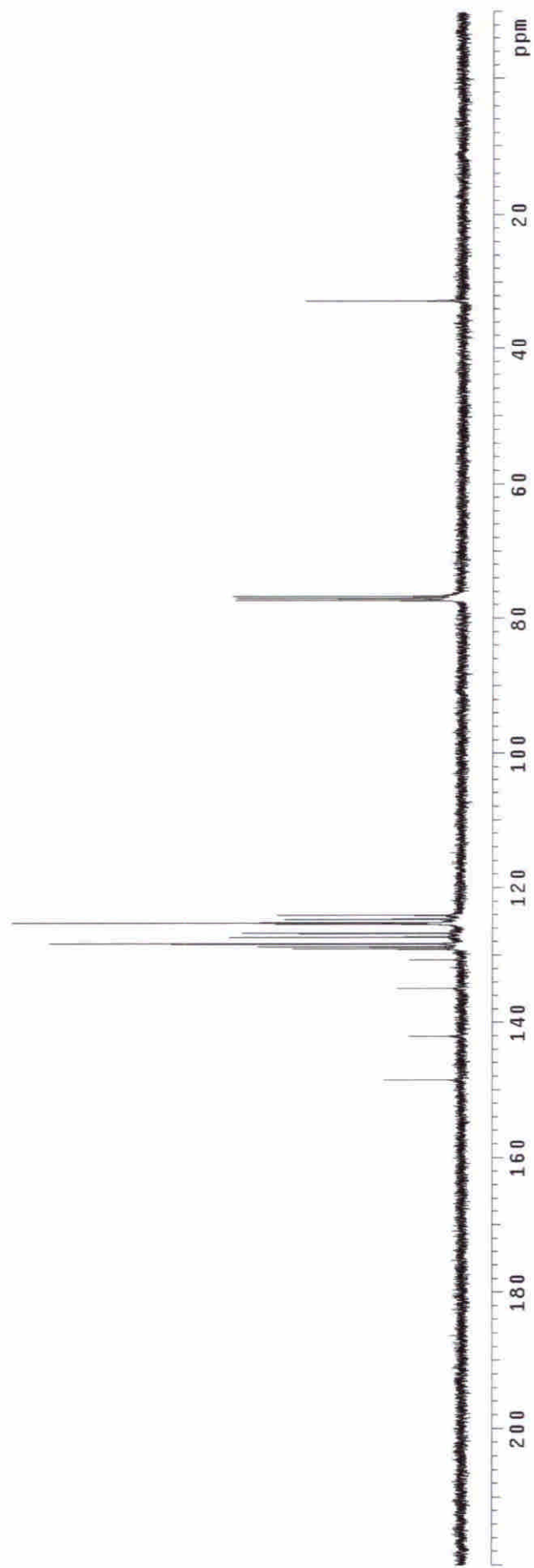
1-acetonaphthone  
Pulse Sequence: s2pul

148.525  
142.027  
134.878  
130.661  
129.031  
128.732  
128.273  
127.270  
126.711  
125.357  
125.204  
125.127  
124.622  
124.040

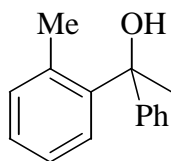


77.314  
77.092  
77.000  
76.679

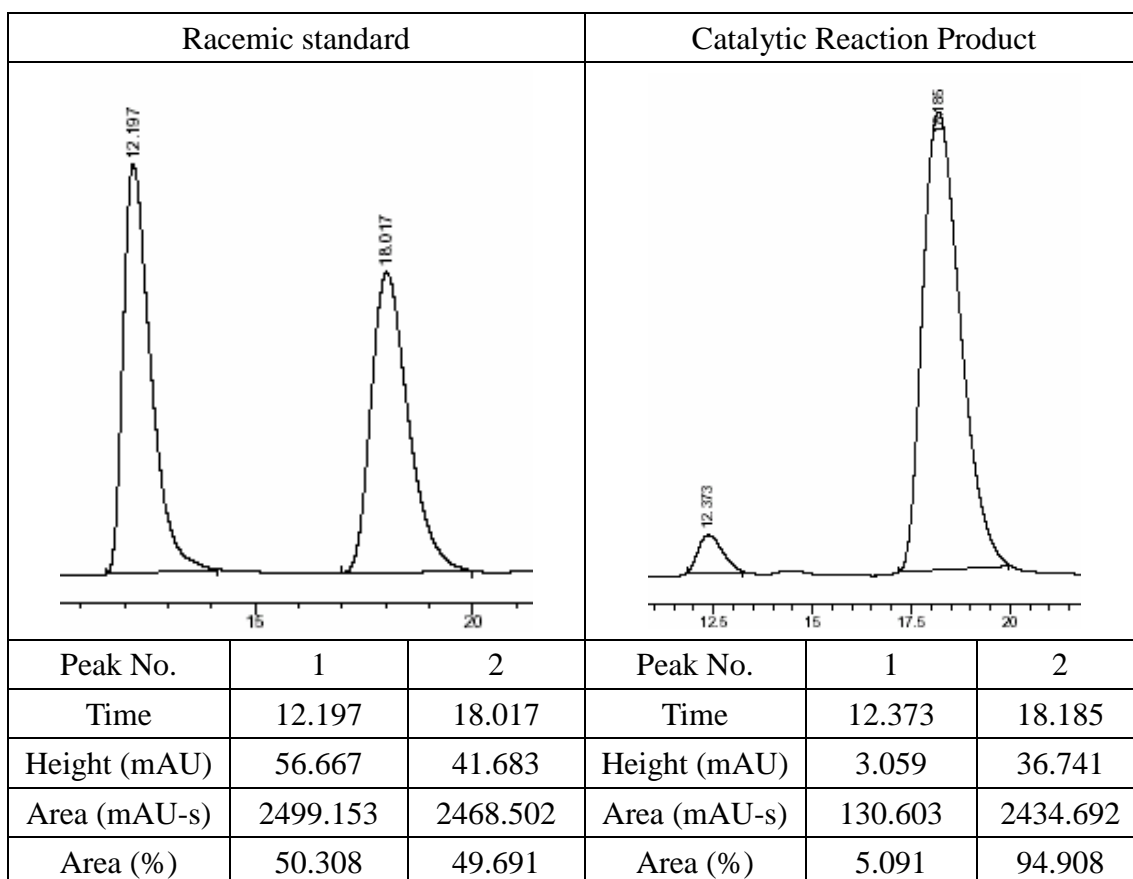
32.769



## 1-Phenyl-1-*o*-tolyl-ethanol (Table 2, entry 3; 90% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 95/5  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 12.197 min, 18.017 min



### Catalytic Reaction Conditions:

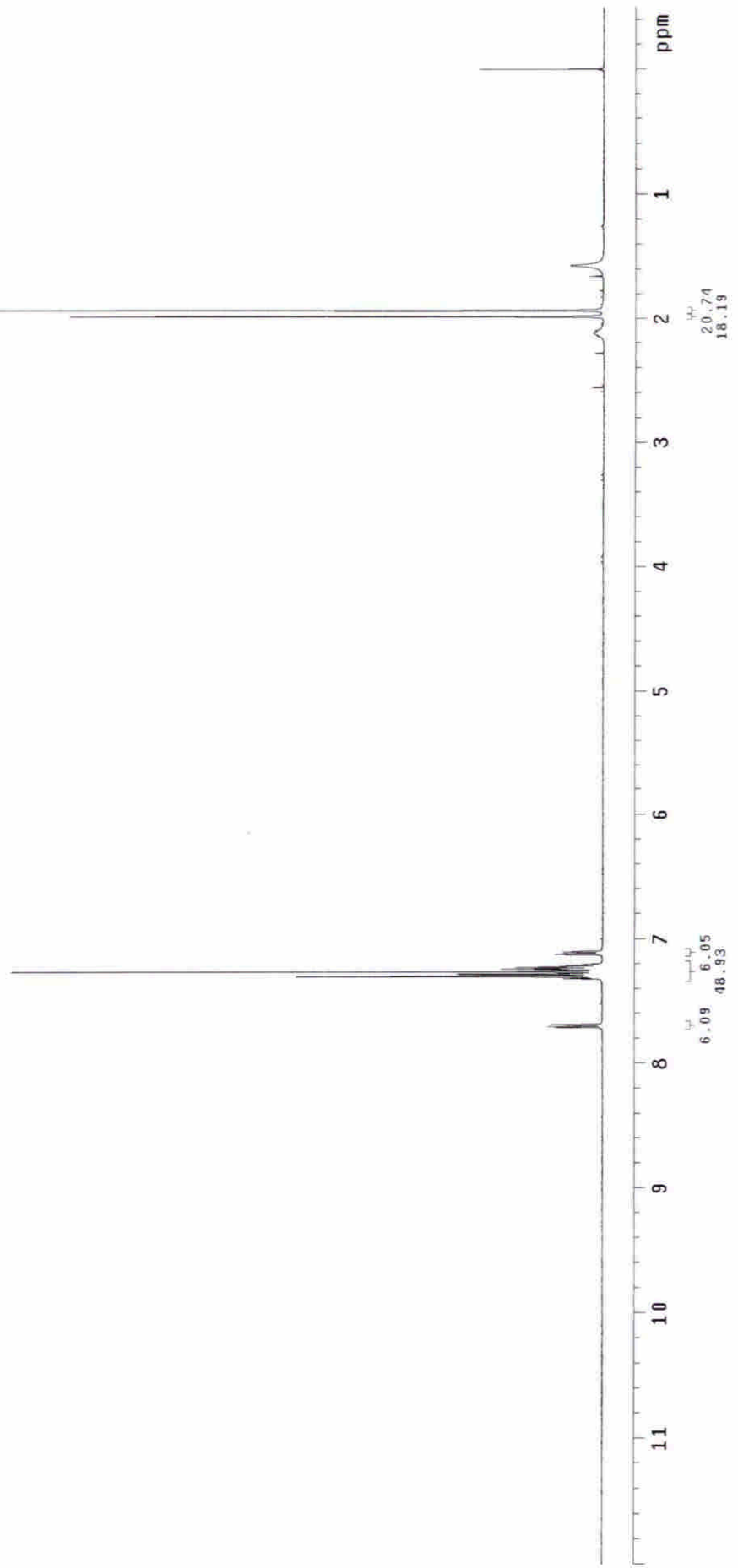
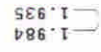
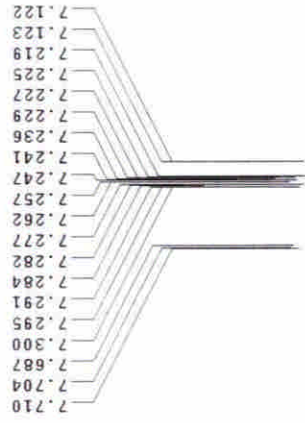
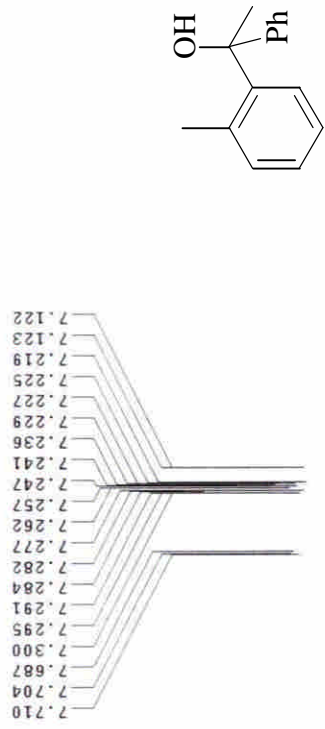
2'-methylacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%,  $\text{AlPh}_3(\text{THF})$ : 1.25 mmol,  $\text{Ti}(\text{O-}i\text{-Pr})_4$ : 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

### Spectroscopic Data:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71-7.69 (m, 1H), 7.30-7.22 (m, 7H), 7.12-7.10 (m, 1H), 2.12 (br, 1H), 1.98 (s, 3H), 1.94 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.94, 144.57, 137.10, 132.39, 128.06, 127.61, 126.54, 125.93, 125.32, 125.26, 76.73, 32.05, 21.30 ppm.

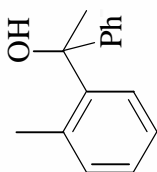
HRMS:  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{16}\text{O}$ , 212.1201 [ $\text{M}^+$ ]; Found 212.1207.

2-methylacetophenone  
Pulse Sequence: s2pu1



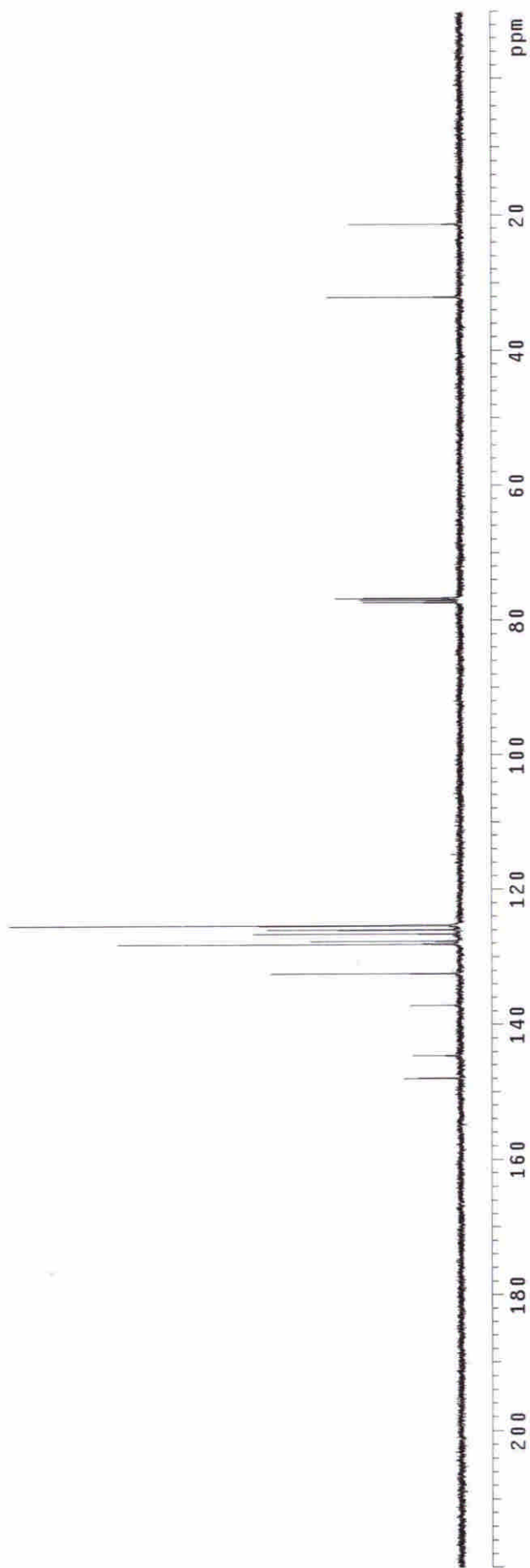
2-methylacetophenone  
Pulse Sequence: s2pu1

147.935  
144.568  
137.098  
132.381  
128.059  
127.607  
126.535  
125.931  
125.318  
125.257

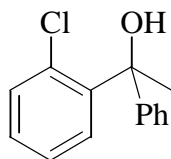


77.314  
77.000  
76.732  
76.686

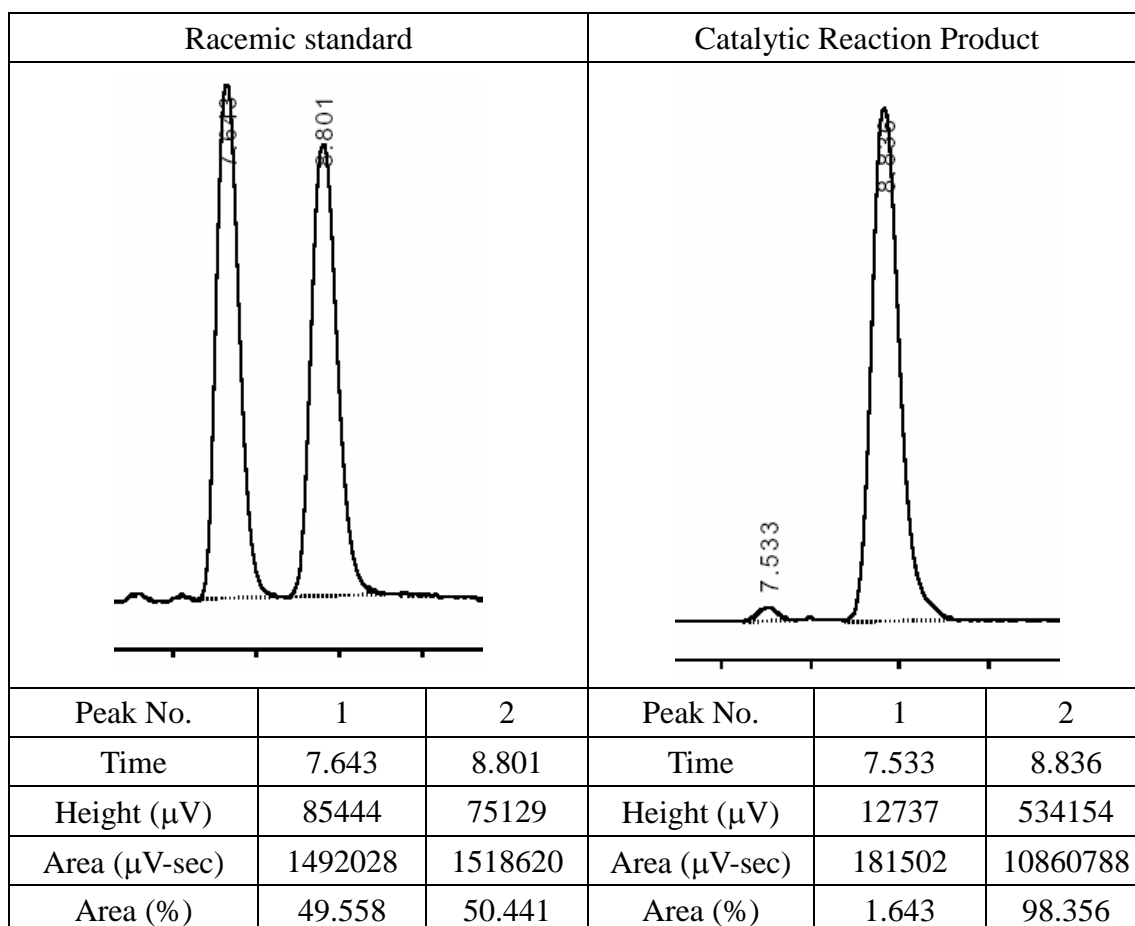
32.049  
21.303



## 1-(2-Chloro-phenyl)-1-phenyl-ethanol (Table 2, entry 4; 97% ee)



Column: Chiralcel OD-H  
Eluent: Hexane/IPA = 99/1  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 7.643 min, 8.801 min



### Catalytic Reaction Conditions:

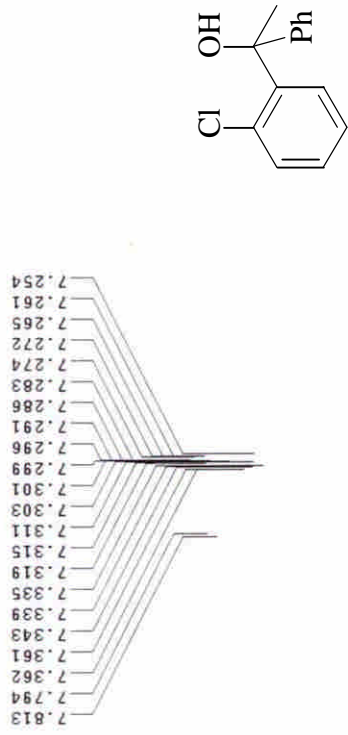
2'-chloroacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (d, J = 7.6 Hz, 1H), 7.36-7.25 (m, 8H), 3.40 (br, 1H), 1.96 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.55, 143.63, 132.56, 131.30, 128.86, 128.12, 128.01, 126.88, 126.73, 125.24, 76.69, 29.86 ppm.

HRMS: m/z calcd. for C<sub>14</sub>H<sub>13</sub>ClO, 232.0655 [M<sup>+</sup>]; Found 232.0651.

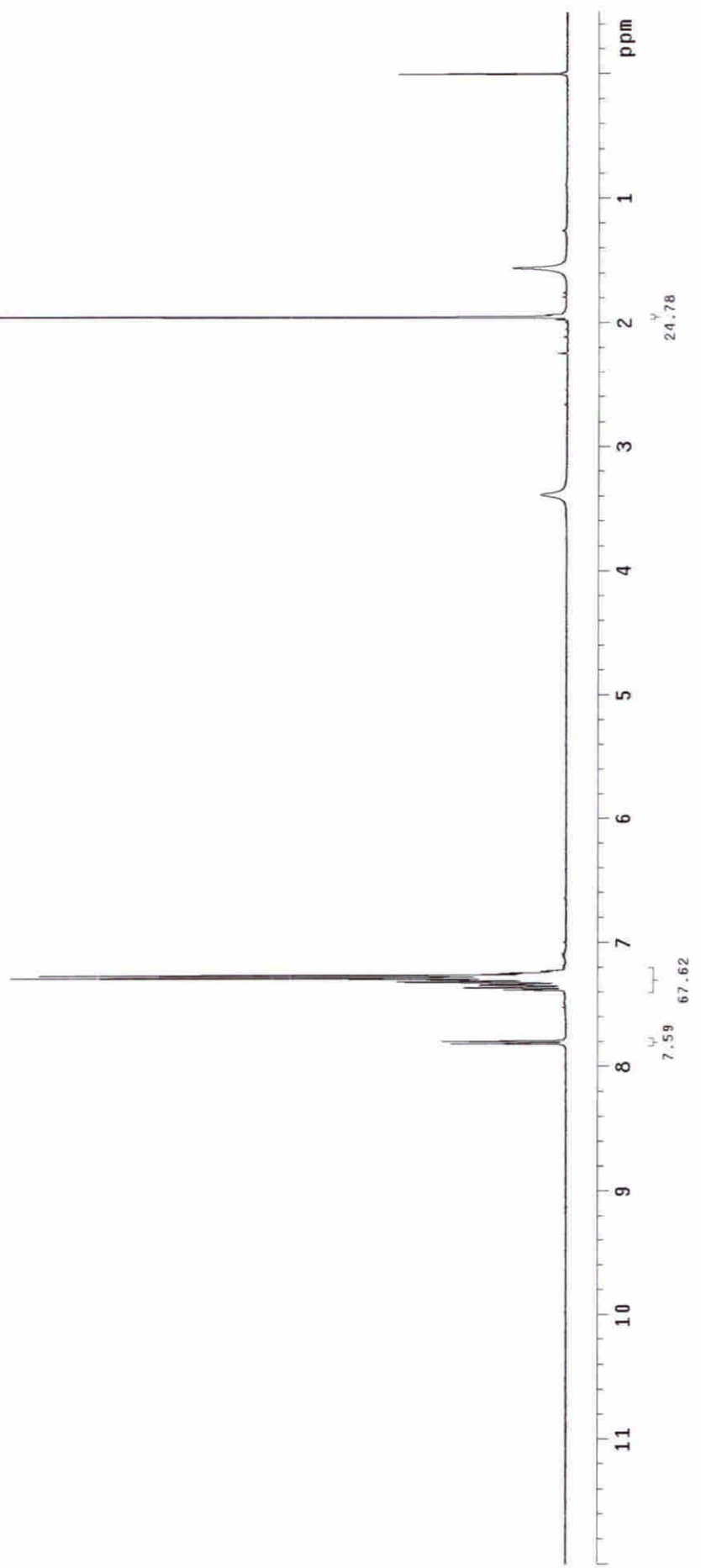
2-chloroacetophenone  
Pulse Sequence: s2pu1



7.813  
7.794  
7.362  
7.361  
7.343  
7.339  
7.335  
7.319  
7.315  
7.311  
7.303  
7.301  
7.299  
7.296  
7.291  
7.286  
7.283  
7.274  
7.272  
7.265  
7.261  
7.254

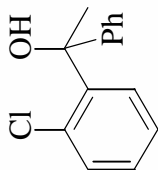
1.957  
1.953

0.005  
-0.000



2-chloroacetophenone

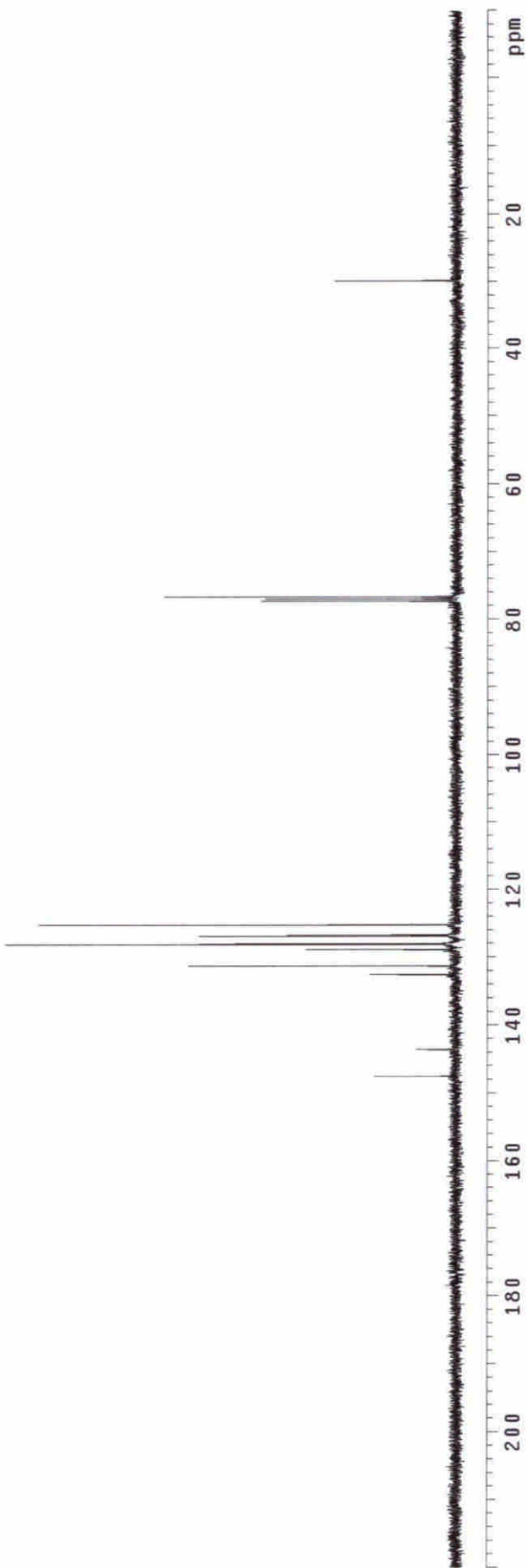
Pulse Sequence: s2pu1



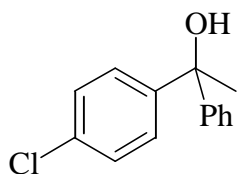
29.860

77.321  
77.000  
76.694

147.553  
143.626  
132.559  
131.296  
128.862  
128.120  
128.013  
126.880  
126.727  
125.242



**1-(4-Chloro-phenyl)-1-phenyl-ethanol (Table 2, entry 5; 93% ee)<sup>5</sup>**



Column: Chiralcel OD-H  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 13.431 min 16.476 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	13.431	16.476	Time	13.060	16.210
Height (μV)	6634	5381	Height (μV)	451	7517
Area (μV-sec)	240913	240544	Area (μV-sec)	12775	335659
Area (%)	50.038	49.961	Area (%)	3.666	96.333

**Catalytic Reaction Conditions:**

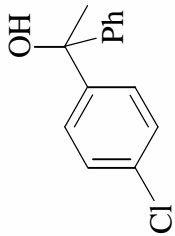
4'-chloroacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C; toluene: 6 mL, 12 h.

**Spectroscopic Data:**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41-7.26 (m, 9H), 2.14 (br, 1H), 1.94 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.37, 146.50, 132.64, 128.23, 128.15, 127.28, 127.14, 125.72, 75.80, 30.68 ppm.

HRMS: m/z calcd. for C<sub>14</sub>H<sub>13</sub>ClO, 232.0655 [M<sup>+</sup>]; Found 232.0656.

4-chloroacetophenone  
Pulse Sequence: s2pu1



7.405  
7.387  
7.385  
7.360  
7.345  
7.338  
7.327  
7.286  
7.280  
7.274  
7.264  
7.261  
7.258

-0.000

1.936



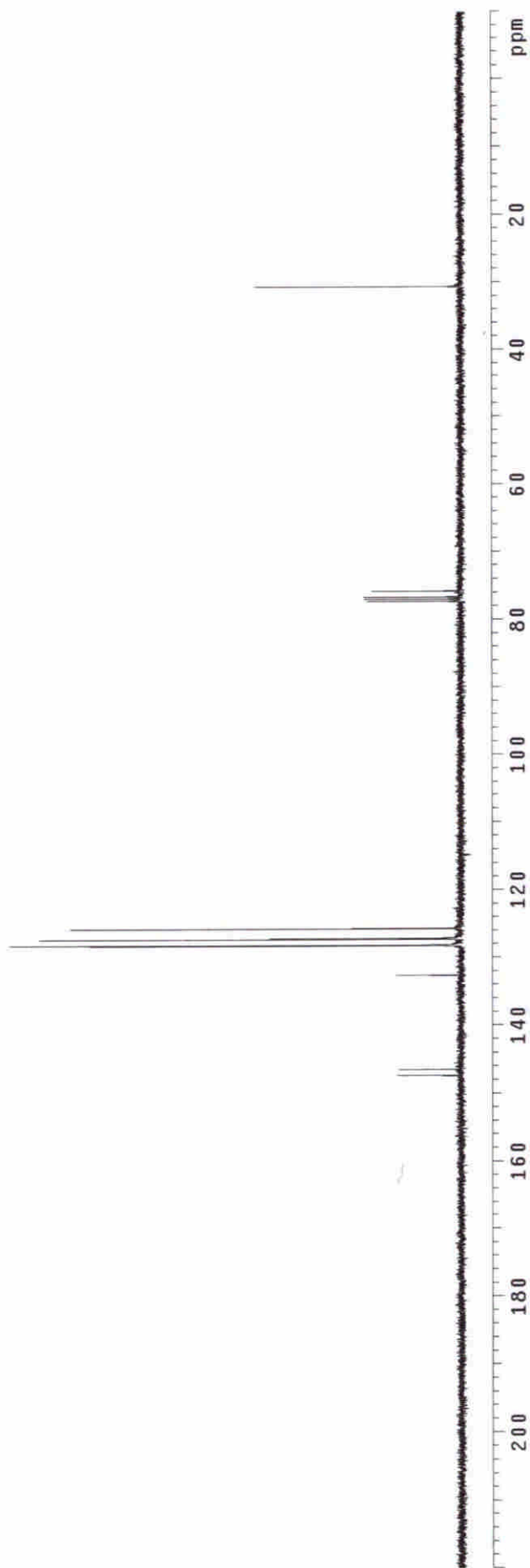
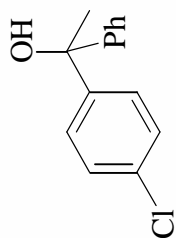
4-chloroacetophenone  
Pulse Sequence: s2pu1

30.679

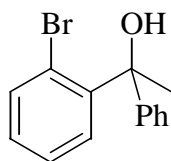
77.314  
77.000  
76.679  
75.798

132.636  
128.227  
128.150  
127.278  
127.140  
125.716

147.369  
146.497



**1-(2-Bromo-phenyl)-1-phenyl-ethanol (Table 2, entry 6; 97% ee)<sup>3</sup>**



Column: Chiralcel OD-H  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 7.780 min, 9.186 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	7.780	9.186	Time	7.948	9.666
Height (μV)	101692	82950	Height (μV)	9306	379542
Area (μV-sec)	1876583	1844405	Area (μV-sec)	128082	8425232
Area (%)	50.432	49.567	Area (%)	1.497	98.502

**Catalytic Reaction Conditions:**

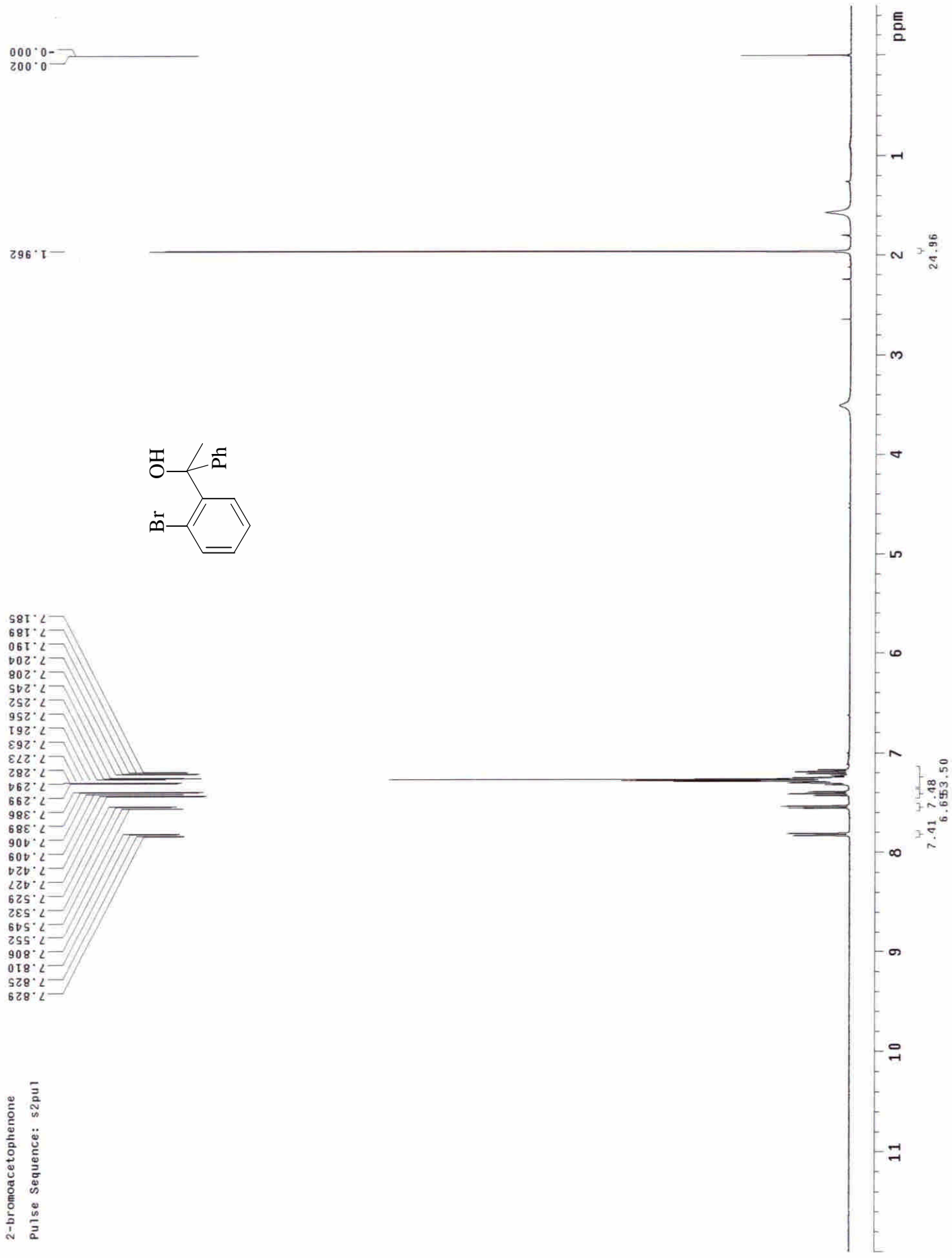
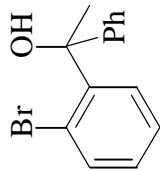
2'-bromacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol,  
 Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 36 h.

**Spectroscopic Data:**

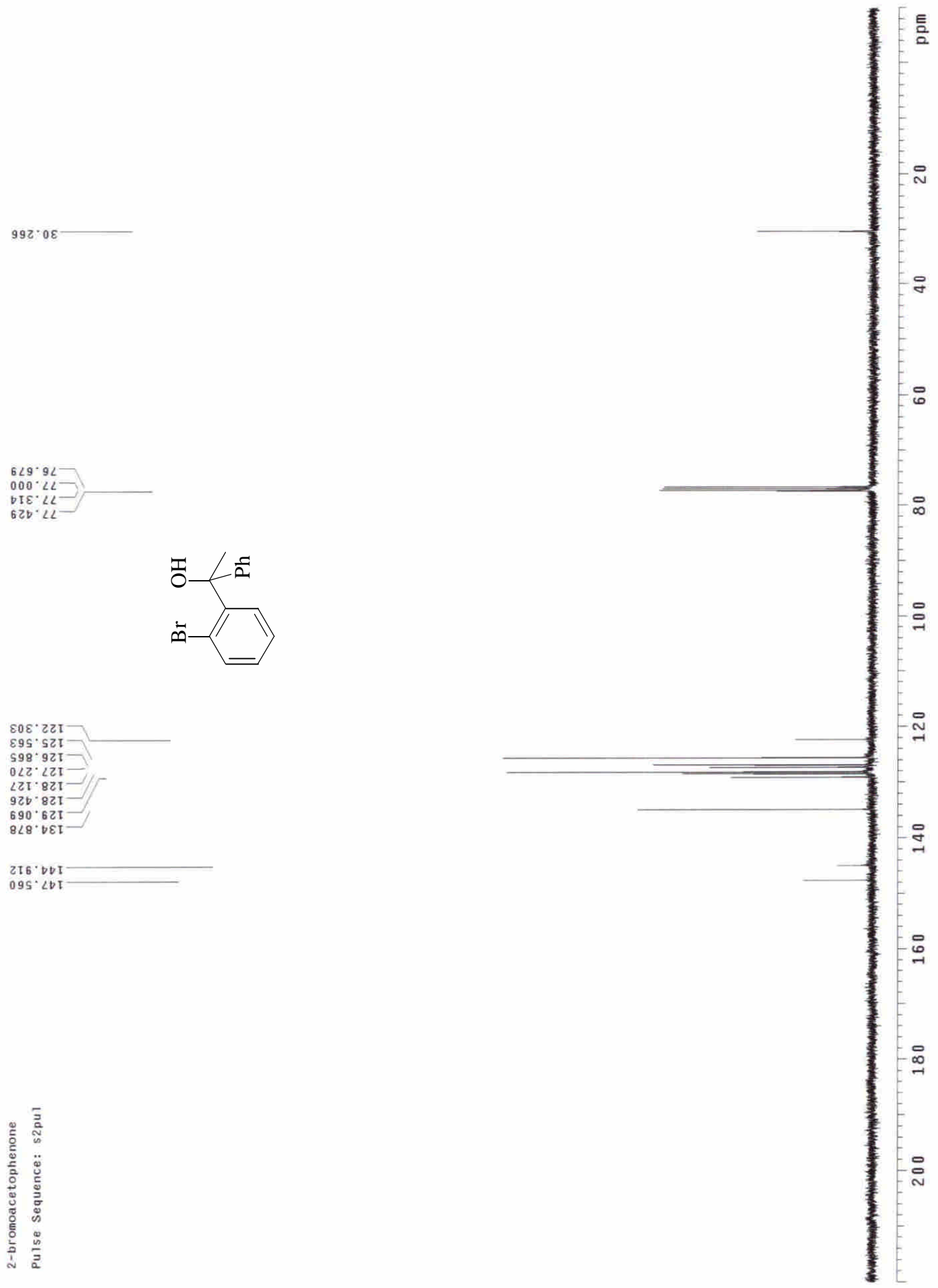
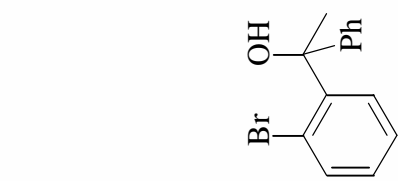
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.82 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.54 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.43-7.39 (m, 1H), 7.30-7.19 (m, 6H), 3.51 (br, 1H), 1.96 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.56, 144.91, 134.88, 129.07, 128.43, 128.13, 127.27, 126.87, 125.56, 122.30, 77.43, 30.27 ppm.

2-bromoacetophenone  
Pulse Sequence: s2pu1

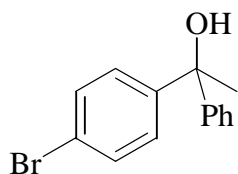
7.829  
7.825  
7.810  
7.806  
7.552  
7.549  
7.532  
7.529  
7.427  
7.424  
7.409  
7.406  
7.389  
7.386  
7.299  
7.294  
7.282  
7.273  
7.263  
7.261  
7.256  
7.252  
7.245  
7.208  
7.204  
7.190  
7.189  
7.185



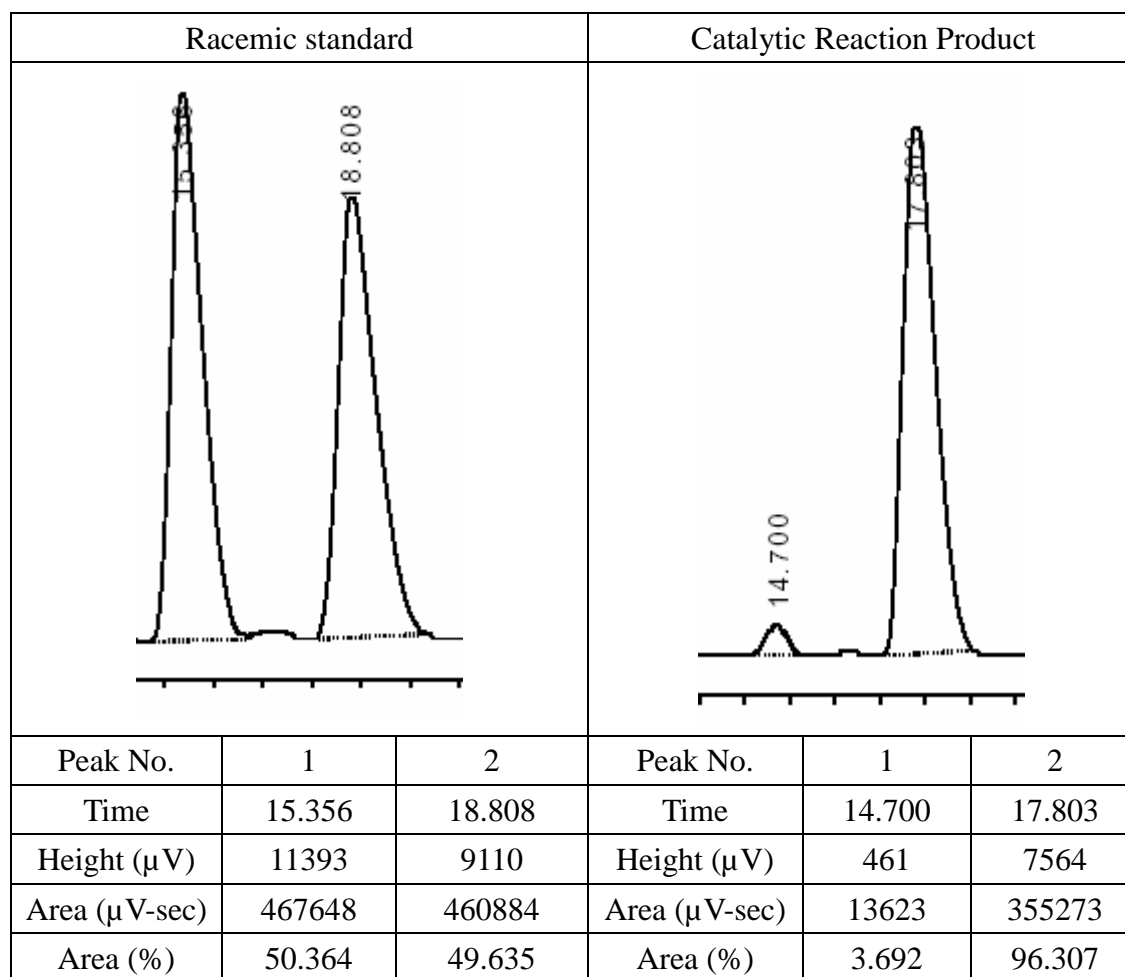
2-bromoacetophenone  
Pulse Sequence: s2pu1



**1-(4-Bromo-phenyl)-1-phenyl-ethanol (Table 2, entry 7; 93% ee)<sup>4</sup>**



Column: Chiralcel OD-H  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 15.356 min, 18.808 min



**Catalytic Reaction Conditions:**

4'-bromacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

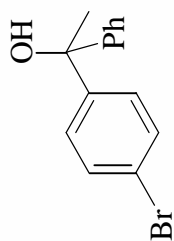
**Spectroscopic Data:**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.44-7.26 (m, 9H), 2.16 (br, 1H), 1.93 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.30, 147.05, 131.13, 128.26, 127.65, 127.18, 125.72, 120.84, 75.86, 30.66 ppm.

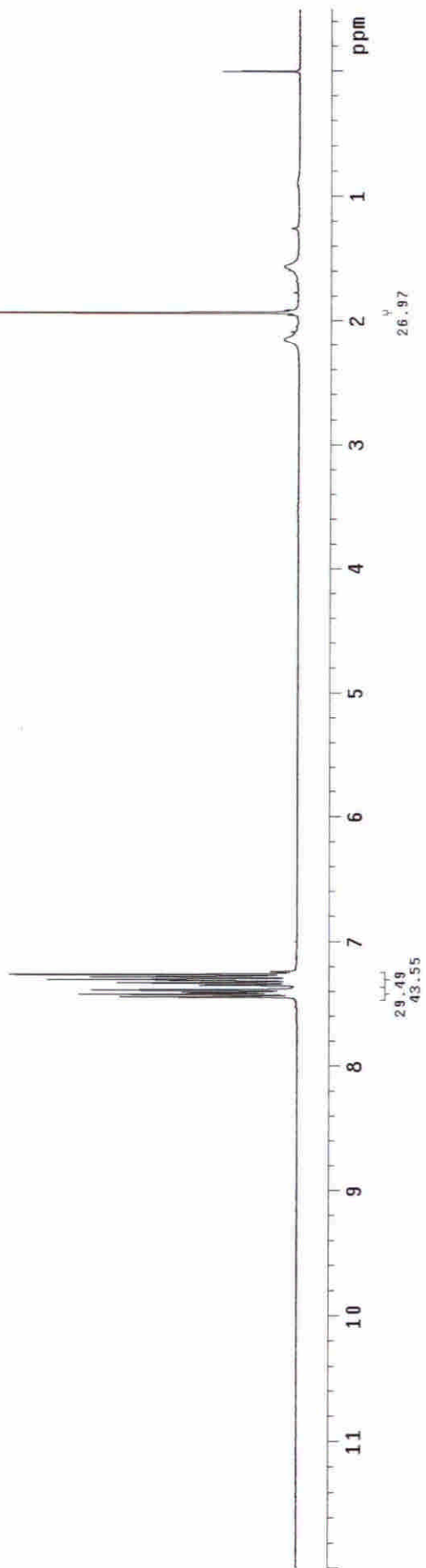
HRMS: *m/z* calcd. for C<sub>14</sub>H<sub>13</sub>BrO, 276.0150 [M<sup>+</sup>]; Found 276.0144.

4-bromoacetophenone  
Pulse Sequence: s2pu1

7.440  
7.420  
7.403  
7.385  
7.328  
7.306  
7.300  
7.279  
7.261  
7.259



1.933  
1.932



4-bromoacetophenone

Pulse Sequence: s2pu1

147.300

147.048

131.128

128.258

127.645

127.178

125.724

120.841

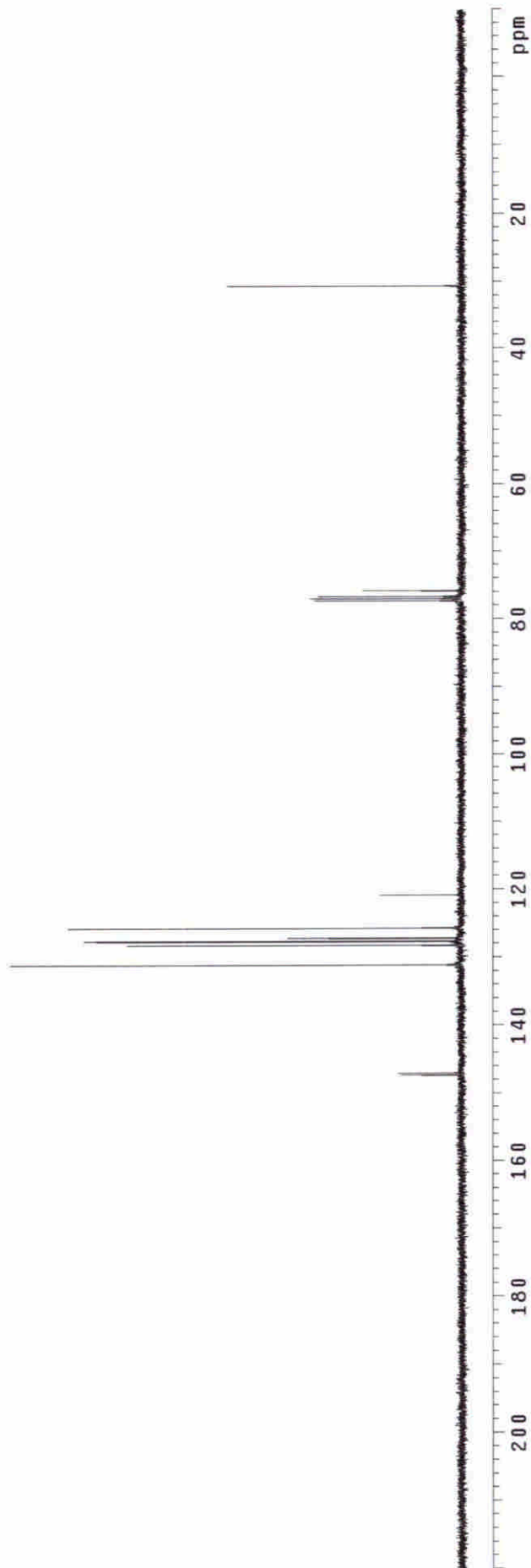
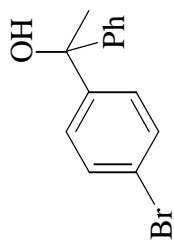
77.314

77.000

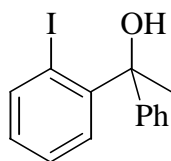
76.679

75.860

30.656



## 1-(2-Iodo-phenyl)-1-phenyl-ethanol (Table 2, entry 8; 96% ee)



Column: Chiralcel OD-H  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 7.786 min, 9.523 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	7.786	9.523	Time	7.951	9.858
Height (μV)	218575	193554	Height (μV)	8741	313662
Area (μV-sec)	4989956	4979404	Area (μV-sec)	180266	8310323
Area(%)	50.052	49.947	Area(%)	2.123	97.876

### Catalytic Reaction Conditions:

2'-iodoacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 168 h.

### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.83 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.46-7.42 (m, 1H), 7.32-7.26 (m, 5H), 7.01-6.96 (m, 1H), 3.26 (s, 1H), 1.98 (s, 3H) ppm.

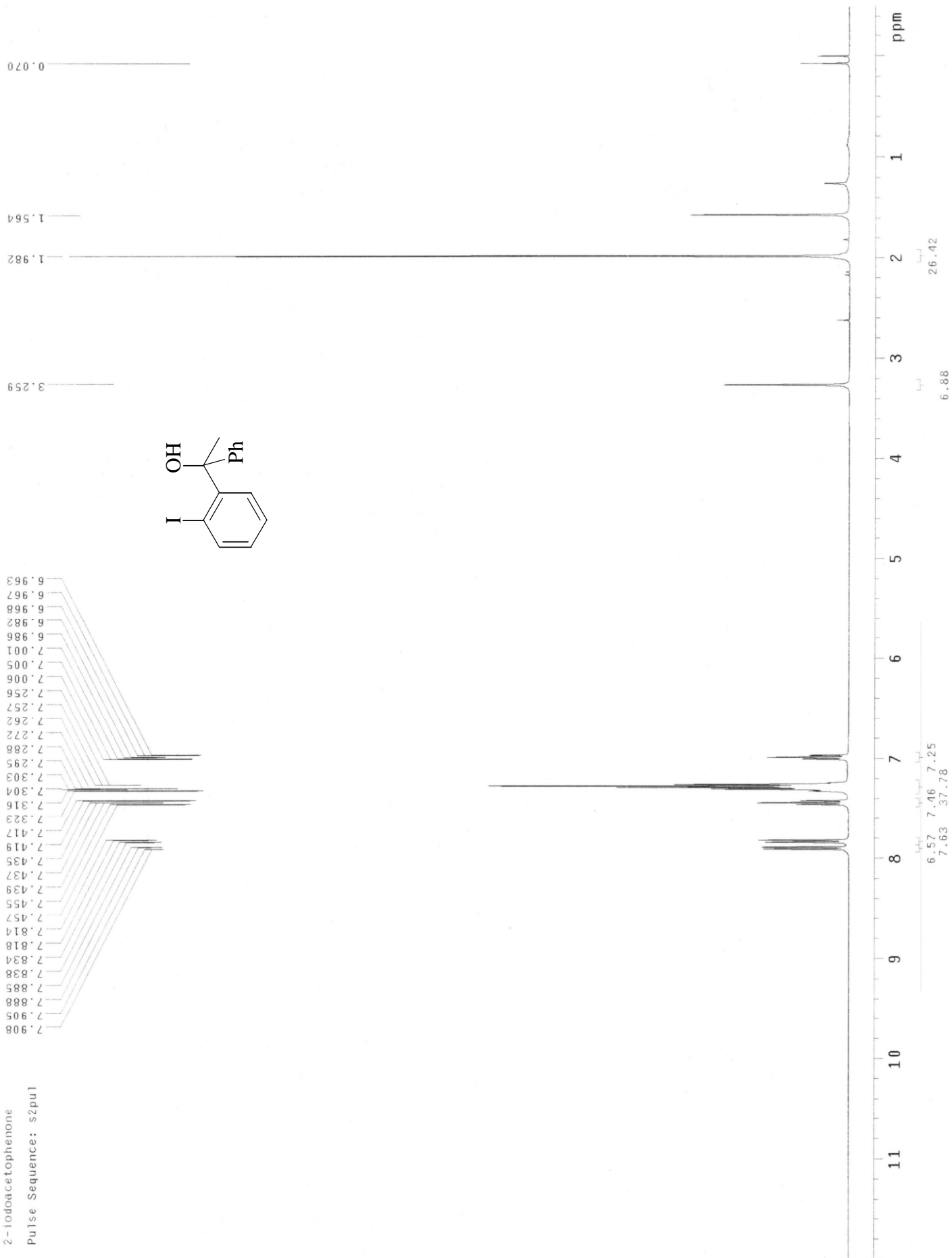
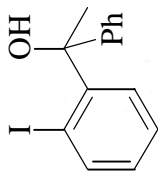
<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.48, 147.14, 142.34, 129.09, 128.19, 128.17, 127.94, 126.99, 126.43, 96.32, 78.12, 30.65 ppm.

HRMS: *m/z* calcd. for C<sub>14</sub>H<sub>13</sub>IO, 324.0012 [M<sup>+</sup>]; Found 324.0013.

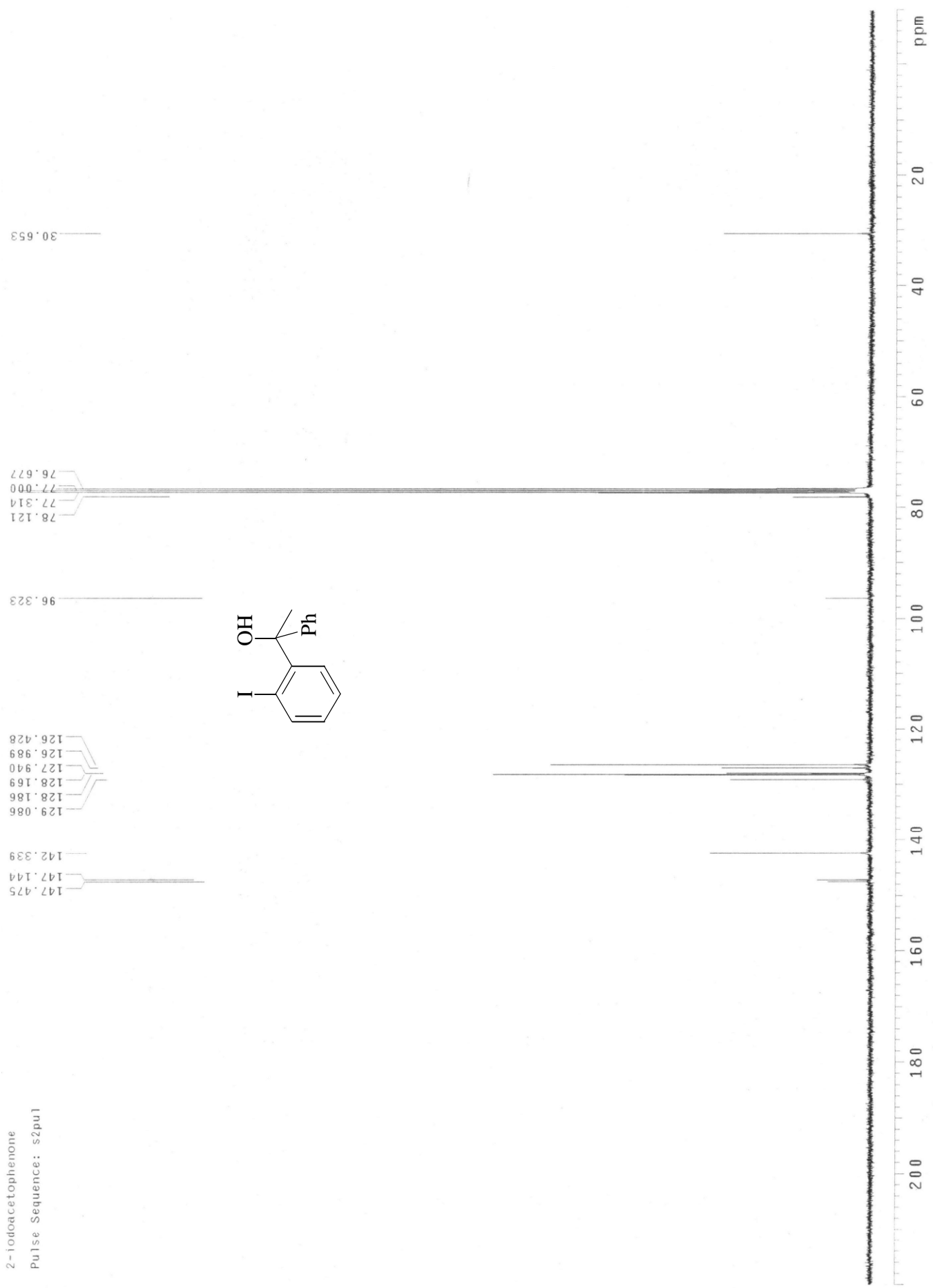
[α]<sub>D</sub><sup>25</sup> = + 35.4 (CH<sub>2</sub>Cl<sub>2</sub>).

2-iodoacetophenone

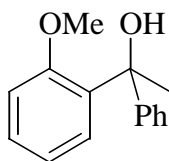
Pulse Sequence: s2pul



2-iodoacetophenone  
Pulse Sequence: s2pu1



## 1-(2-Methoxy-phenyl)-1-phenyl-ethanol (Table 2, entry 9; 30% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 80/20  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 6.678 min, 19.958 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	6.678	19.958	Time	6.633	19.549
Height (mAU)	120.649	40.907	Height (mAU)	109.450	66.460
Area (mAU-s)	3173.506	3124.634	Area (mAU-s)	2897.398	5353.871
Area (%)	50.388	49.612	Area (%)	35.114	64.885

### Catalytic Reaction Conditions:

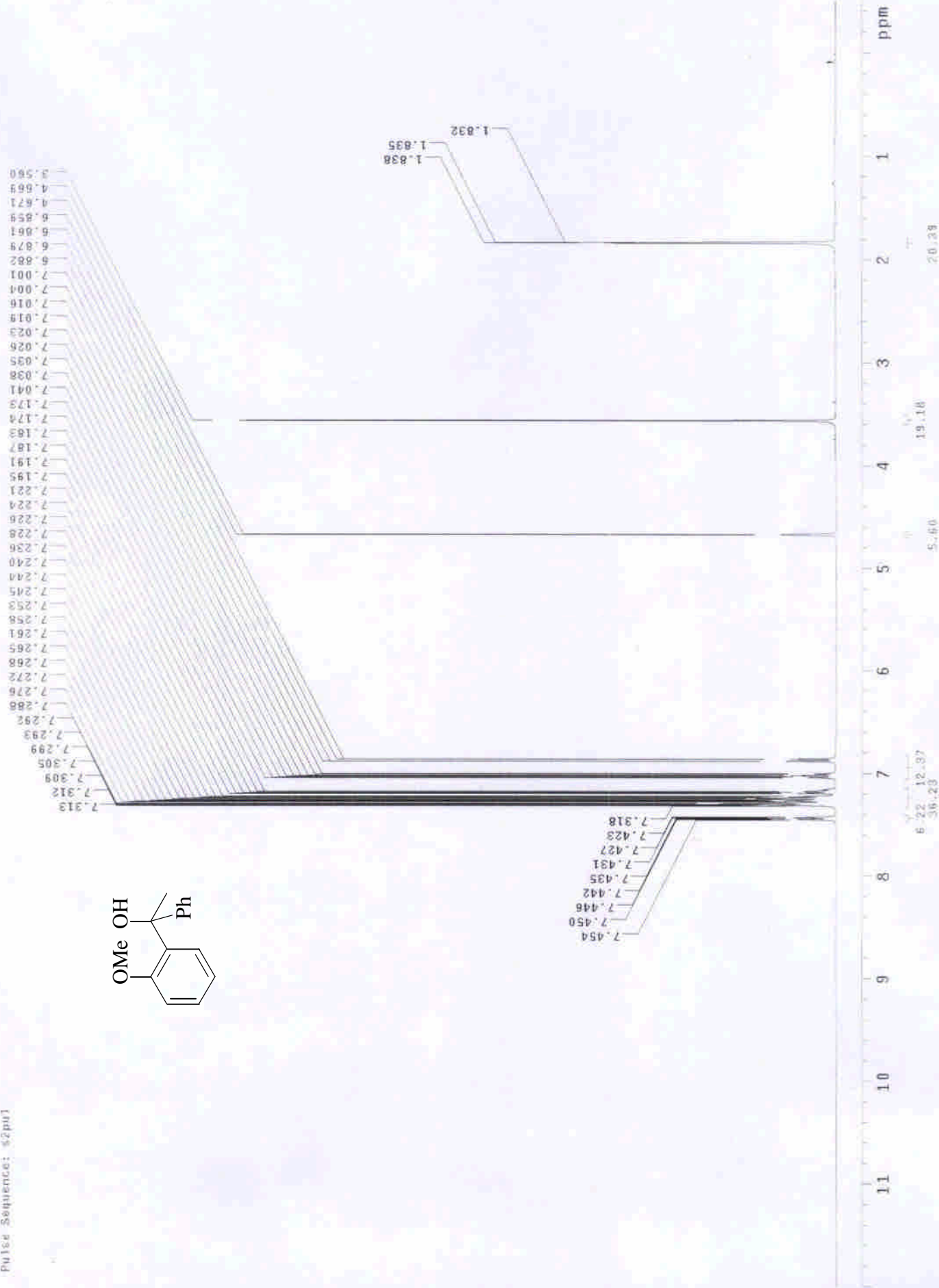
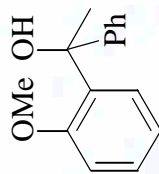
2'-methoxyacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene : 6 mL, 12 h.

### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45-7.42 (m, 1H), 7.32-7.17 (m, 6H), 7.04-7.00 (m, 1H), 6.87 (dd, *J* = 1.2, 8.4 Hz, 1H), 4.67 (s, 1H), 3.56 (s, 3H), 1.84 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 157.02, 149.59, 135.25, 128.73, 127.66, 126.98, 126.20, 124.80, 120.85, 112.22, 76.20, 55.52, 30.08 ppm.

HRMS: *m/z* calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>, 228.1150 [M<sup>+</sup>]; Found 228.1158.

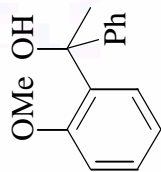
2-OMe  
Pulse Sequence: zgpg30



2-DMF

Pulse Sequence: s2pu1

127.661  
126.979  
126.199  
124.798



120.849

128.732

112.223

55.523

30.075

77.314  
77.000  
76.679  
76.198

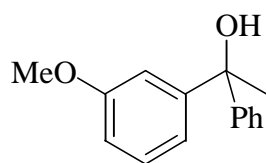
149.589

157.021

135.253

180 160 140 120 100 80 60 40 20 0 ppm

## 1-(3-Methoxy-phenyl)-1-phenyl-ethanol (Table 2, entry 10; 77% ee)



Column: Chiralcel OD  
 Eluent: Hexane/IPA = 98/2  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 24.536 min, 28.937 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	24.536	28.937	Time	24.836	28.375
Height (mAU)	74.255	63.179	Height (mAU)	10.120	60.481
Area (mAU-s)	4273.956	4255.171	Area (mAU-s)	515.186	4027.693
Area (%)	50.110	49.889	Area (%)	11.340	88.659

### Catalytic Reaction Conditions:

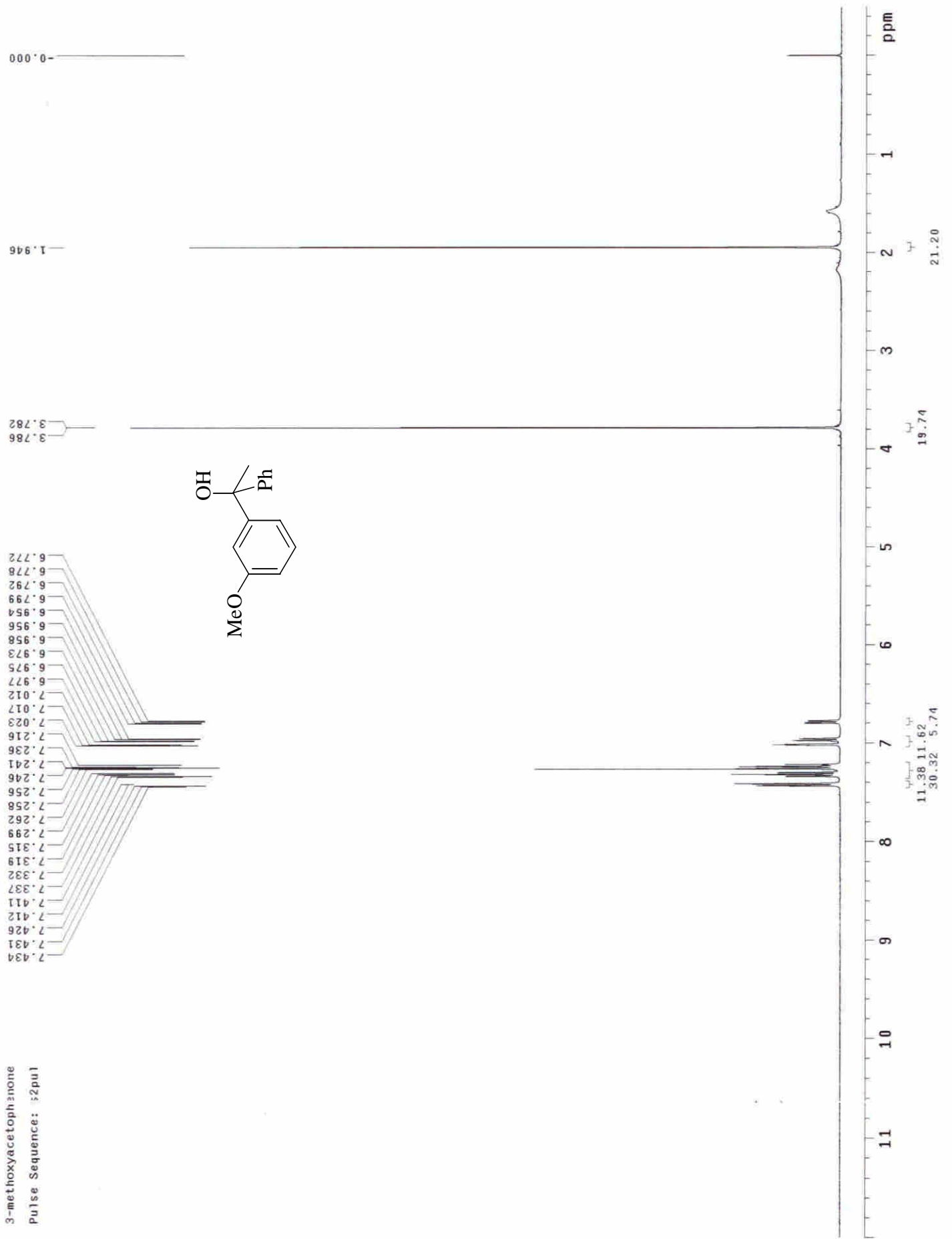
3'-methoxyacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0°C, toluene: 6 mL, 36 h.

### Spectroscopic Data:

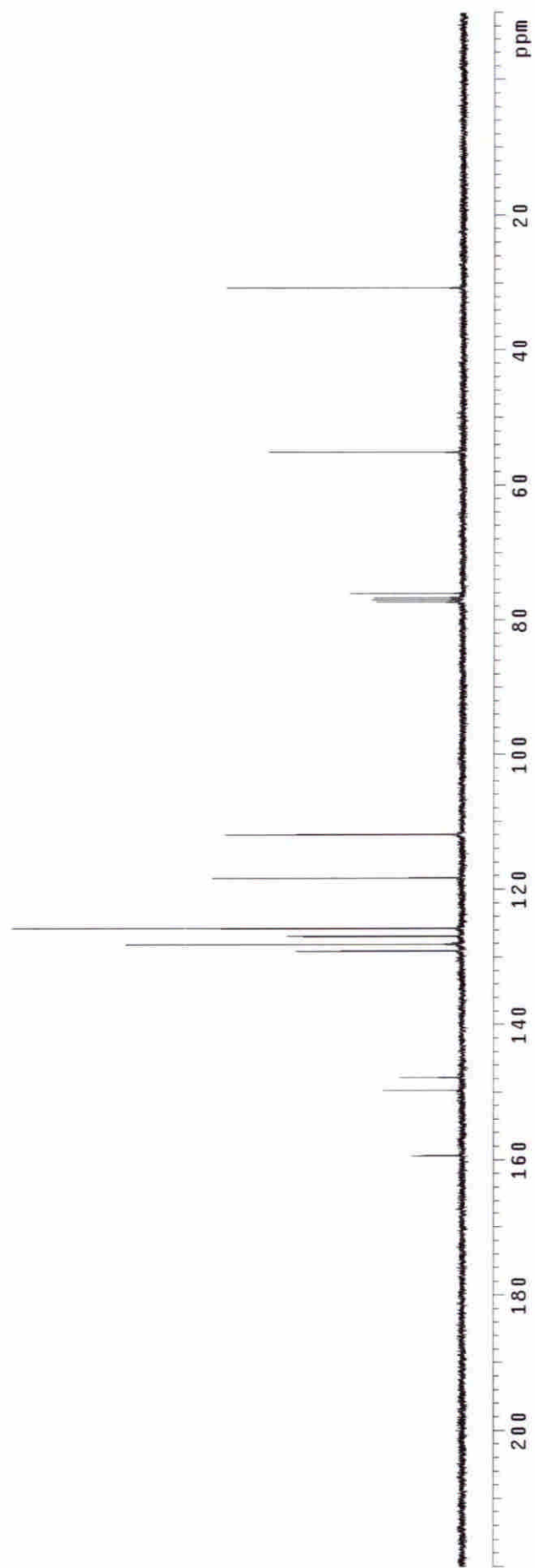
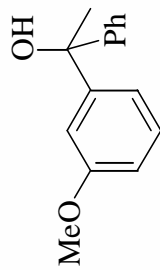
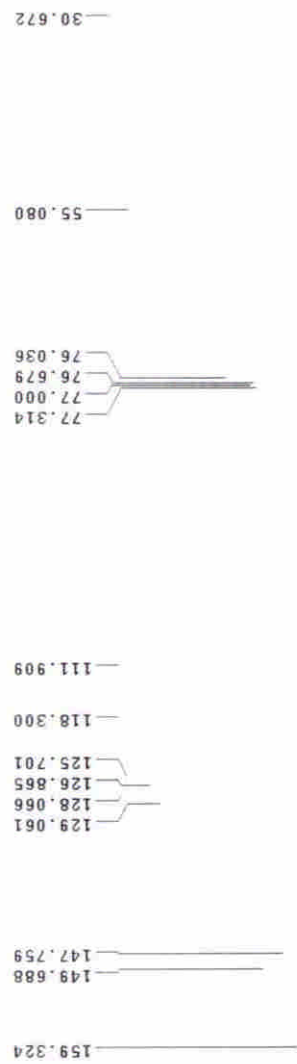
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43-7.41 (m, 2H), 7.34-7.22 (m, 4H), 7.02-6.95 (m, 2H), 6.79 (dd, *J* = 2.8, 8.4 Hz, 1H), 3.78 (s, 3H), 2.18 (br, 1H), 1.95 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 159.32, 149.69, 147.76, 129.06, 128.07, 126.87, 125.70, 118.30, 111.91, 76.04, 55.08, 30.67 ppm.

HRMS: *m/z* calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>, 228.1151 [M<sup>+</sup>]; Found 228.1154.

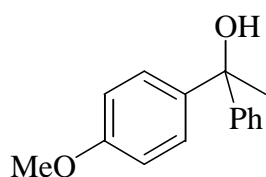
3-methoxyacetophenone  
Pulse Sequence: s2pu1



3-methoxyacetophenone  
Pulse Sequence: s2pu1



## 1-(4-Methoxy-phenyl)-1-phenyl-ethanol (Table 2, entry 11; 93% ee)



Column: Chiralcel OJ  
 Eluent: Hexane/IPA = 80/20  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 18.052 min, 22.663 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	18.052	22.663	Time	17.936	22.470
Height (mAU)	55.824	40.397	Height (mAU)	31.269	1.140
Area (mAU-s)	3088.596	3007.313	Area (mAU-s)	1562.419	58.108
Area (%)	50.666	49.333	Area (%)	96.414	3.585

### Catalytic Reaction Conditions:

4'-methoxyacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0°C, toluene: 6 mL, 36 h.

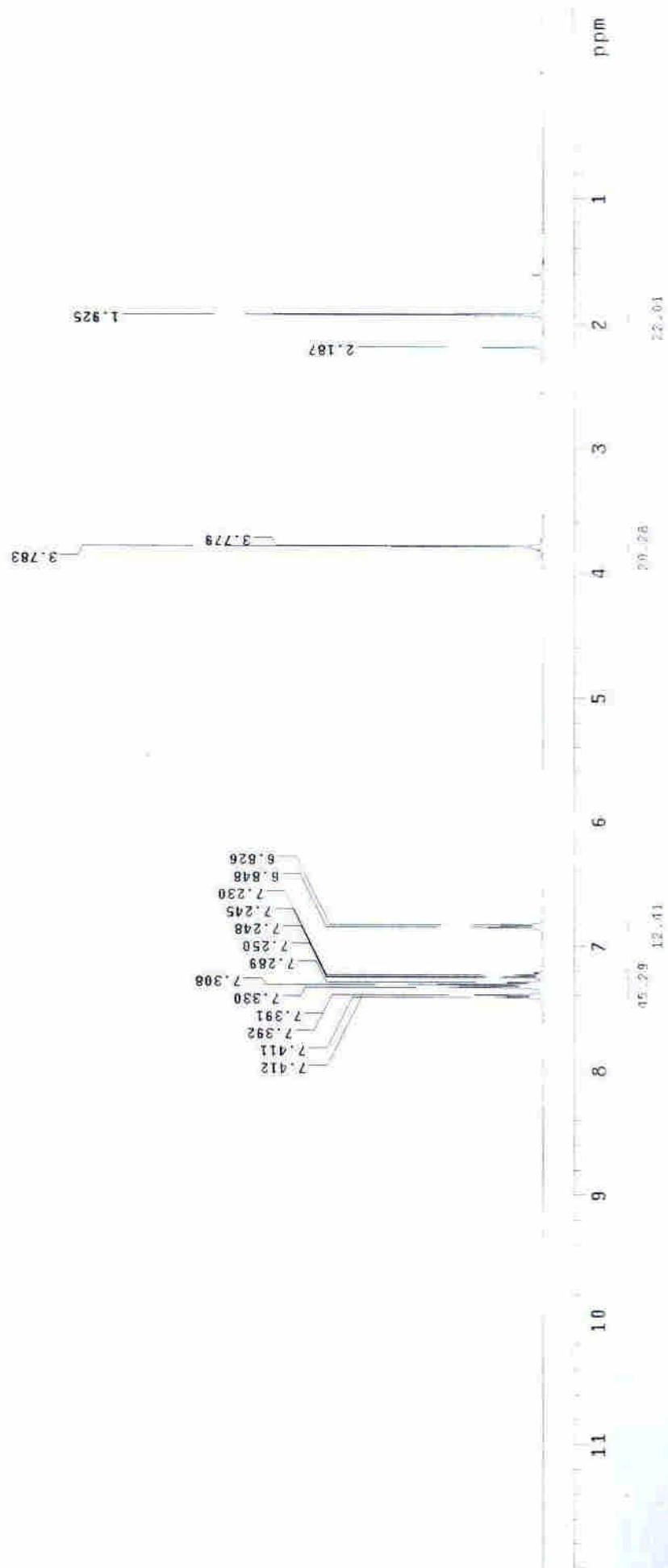
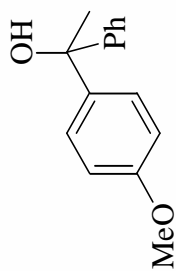
### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41-7.23 (m, 7H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.19 (s, 1H), 1.93 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 158.36, 148.23, 140.27, 128.01, 127.09, 126.73, 125.70, 113.36, 75.82, 55.14, 30.88 ppm.

HRMS: *m/z* calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>, 228.1151 [M<sup>+</sup>]; Found 228.1150.

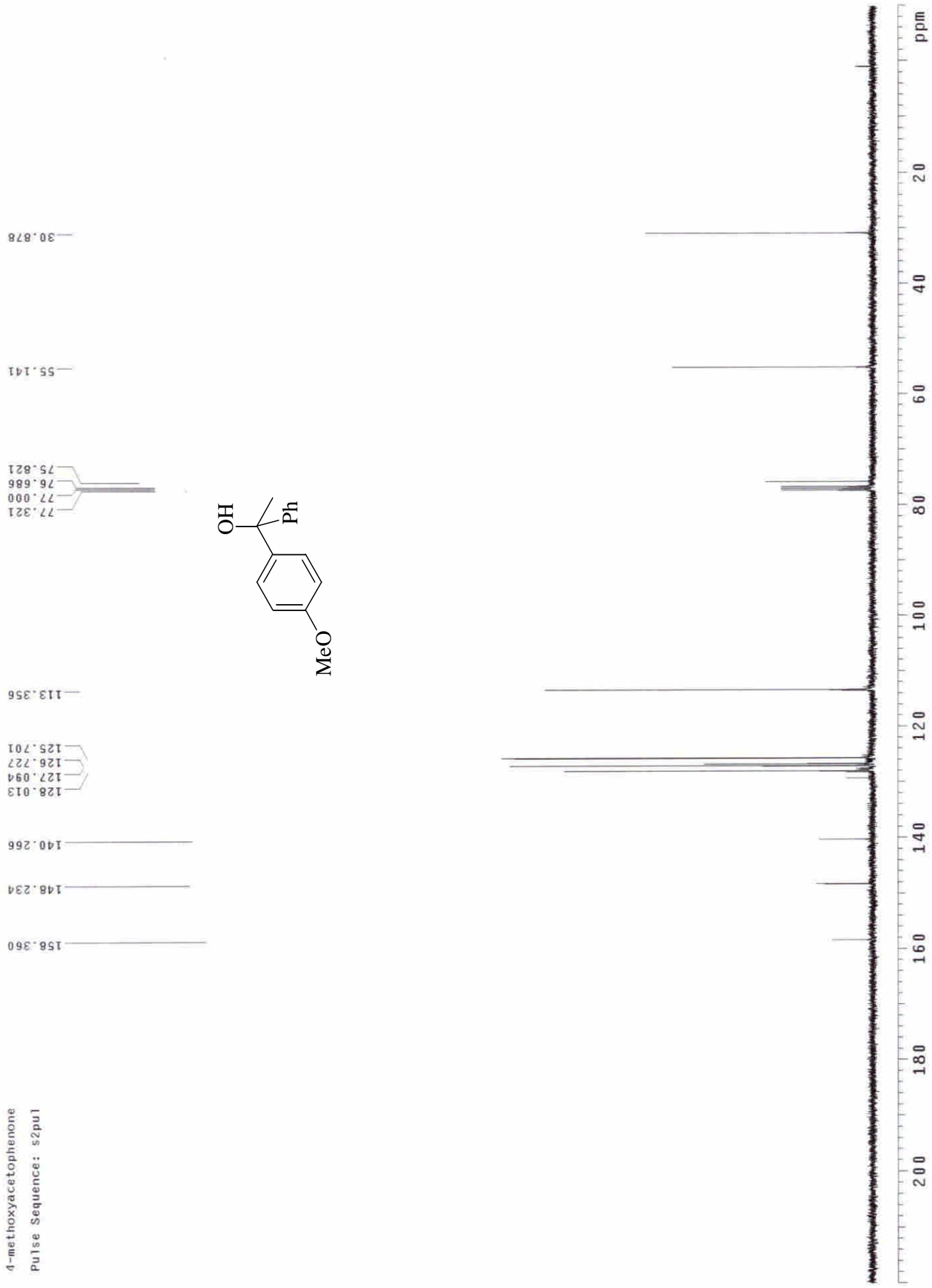
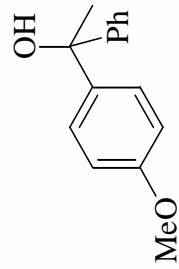
4-DME

Pulse Sequence: h2nut

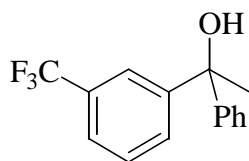


4-methoxyacetophenone

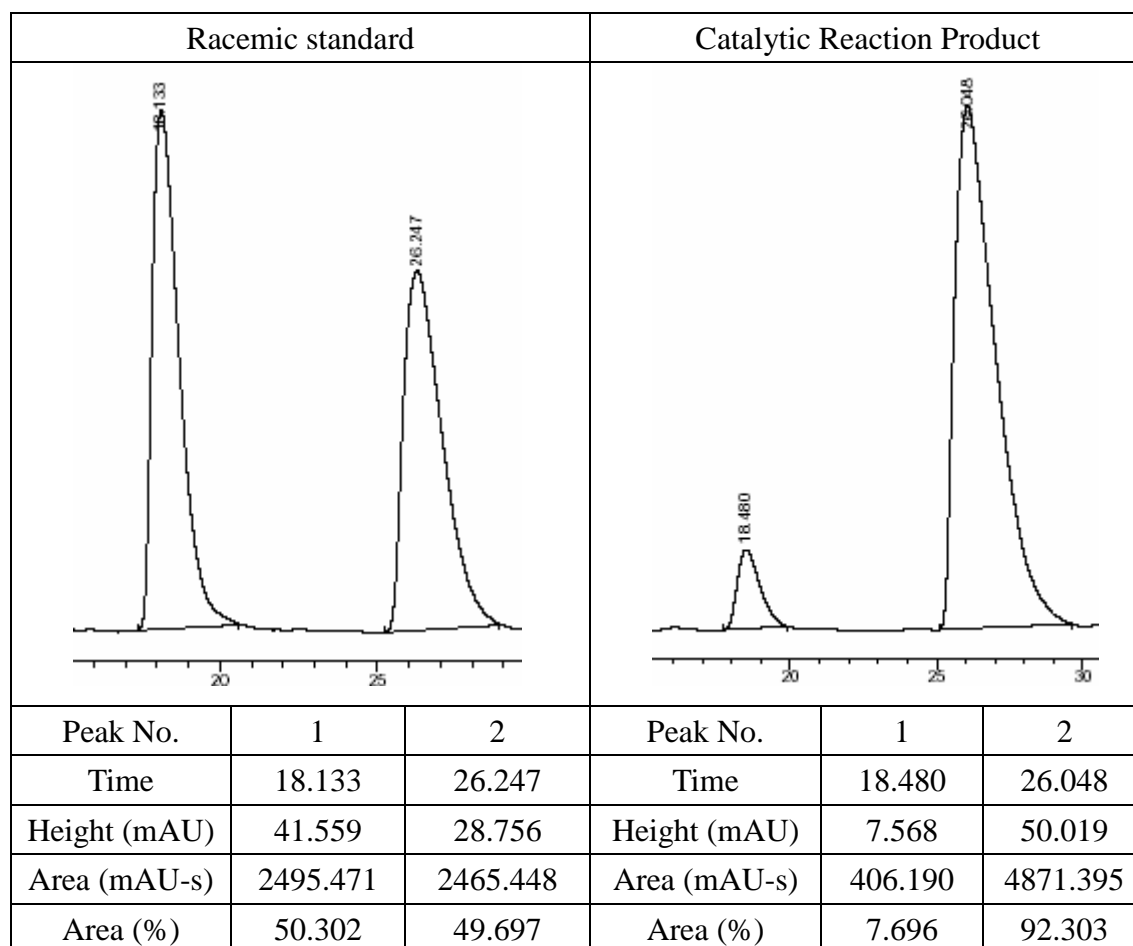
Pulse Sequence: szpu1



## 1-Phenyl-1-(3-trifluoromethyl-phenyl)-ethanol (Table 2, entry 12; 85% ee)<sup>3</sup>



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 99/1  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 18.133 min, 26.247 min



### Catalytic Reaction Conditions:

3'-trifluoromethylacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0°C, toluene: 6 mL, 12 h.

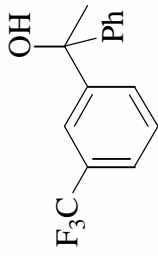
### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.76 (s, 1H), 7.53-7.26 (m, 8H), 2.22 (br, 1H), 1.98 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 149.05, 147.04, 129.42, 128.56, 128.40, 127.39, 125.79, 123.74, 123.70, 122.36, 122.33, 75.94, 30.73 ppm.

3-trifluoromethylacetophenone

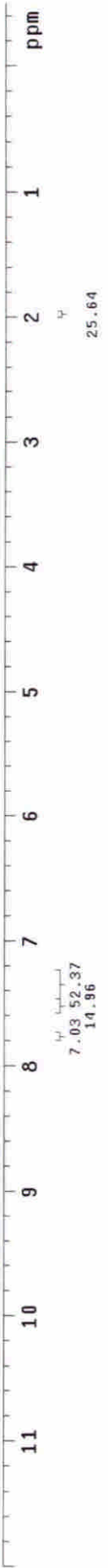
Pulse Sequence: s2pu1

7.764  
7.534  
7.492  
7.434  
7.422  
7.420  
7.414  
7.401  
7.363  
7.361  
7.343  
7.340  
7.325  
7.293  
7.291  
7.274  
7.262  
7.261



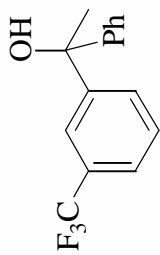
0.002  
-0.000

1.977



3-trifluoromethylacetophenone

Pulse Sequence: s2pul

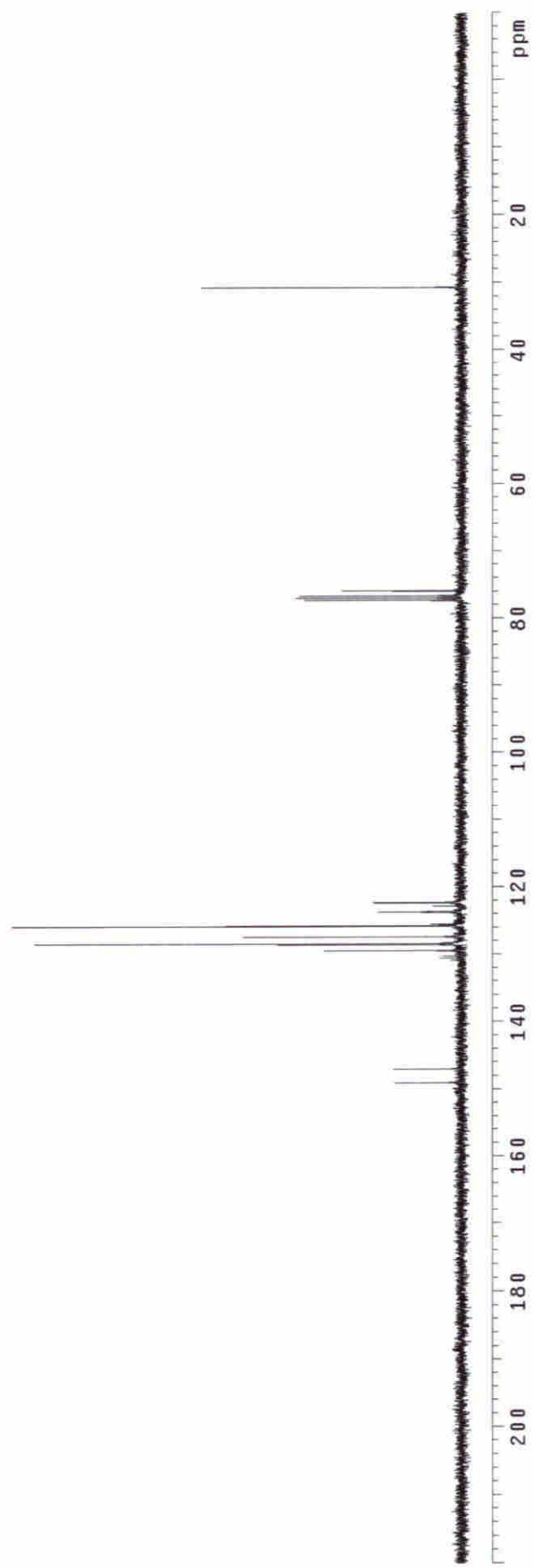


30.733

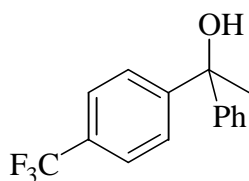
77.314  
77.000  
76.679  
75.936

129.421  
128.564  
128.395  
127.385  
125.785  
123.742  
123.704  
122.364  
122.326

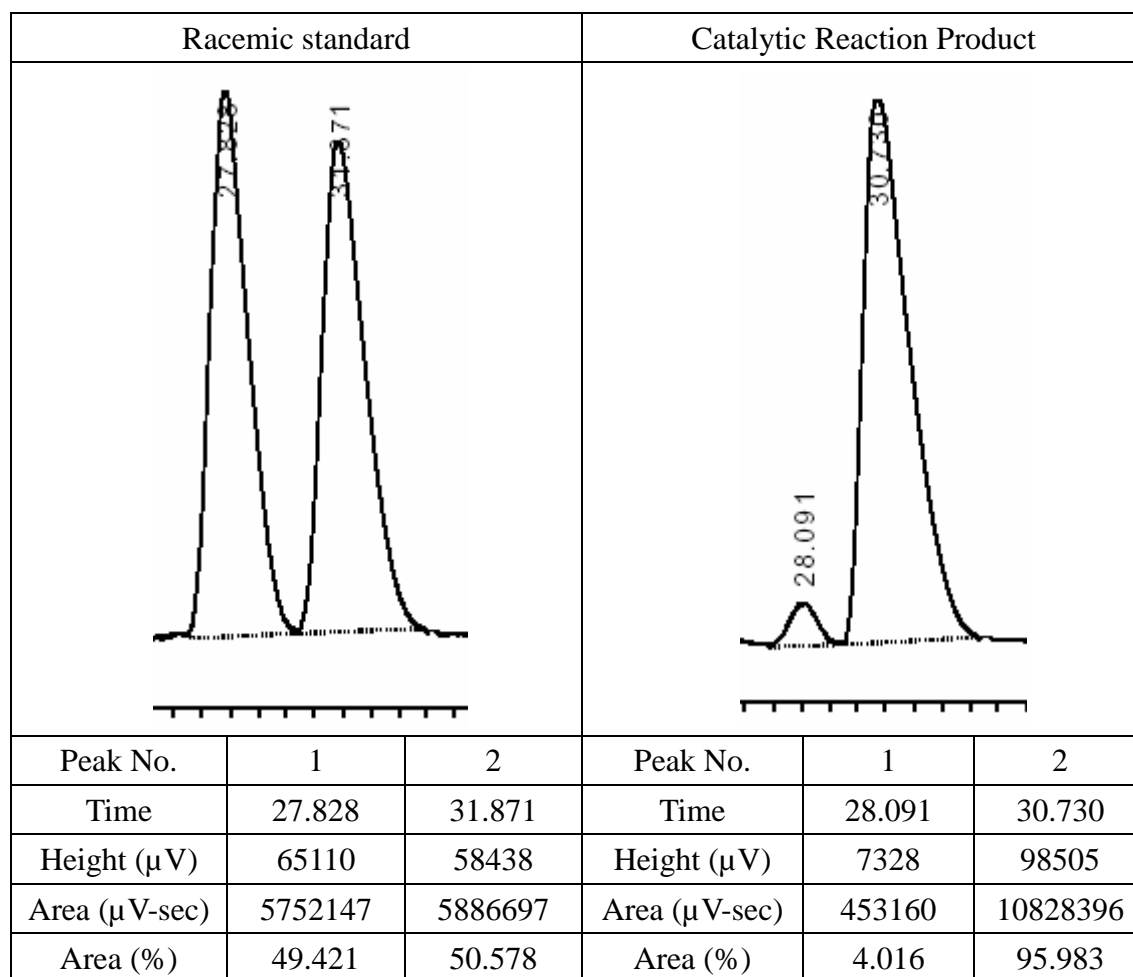
149.053  
147.040



**1-Phenyl-1-(4-trifluoromethyl-phenyl)-ethanol (Table 2, entry 13; 92% ee)<sup>4</sup>**



Column: Chiralcel OD-H  
 Eluent: Hexane/IPA = 99.5/0.5  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention Time: 27.828 min, 31.871 min



**Catalytic Reaction Conditions:**

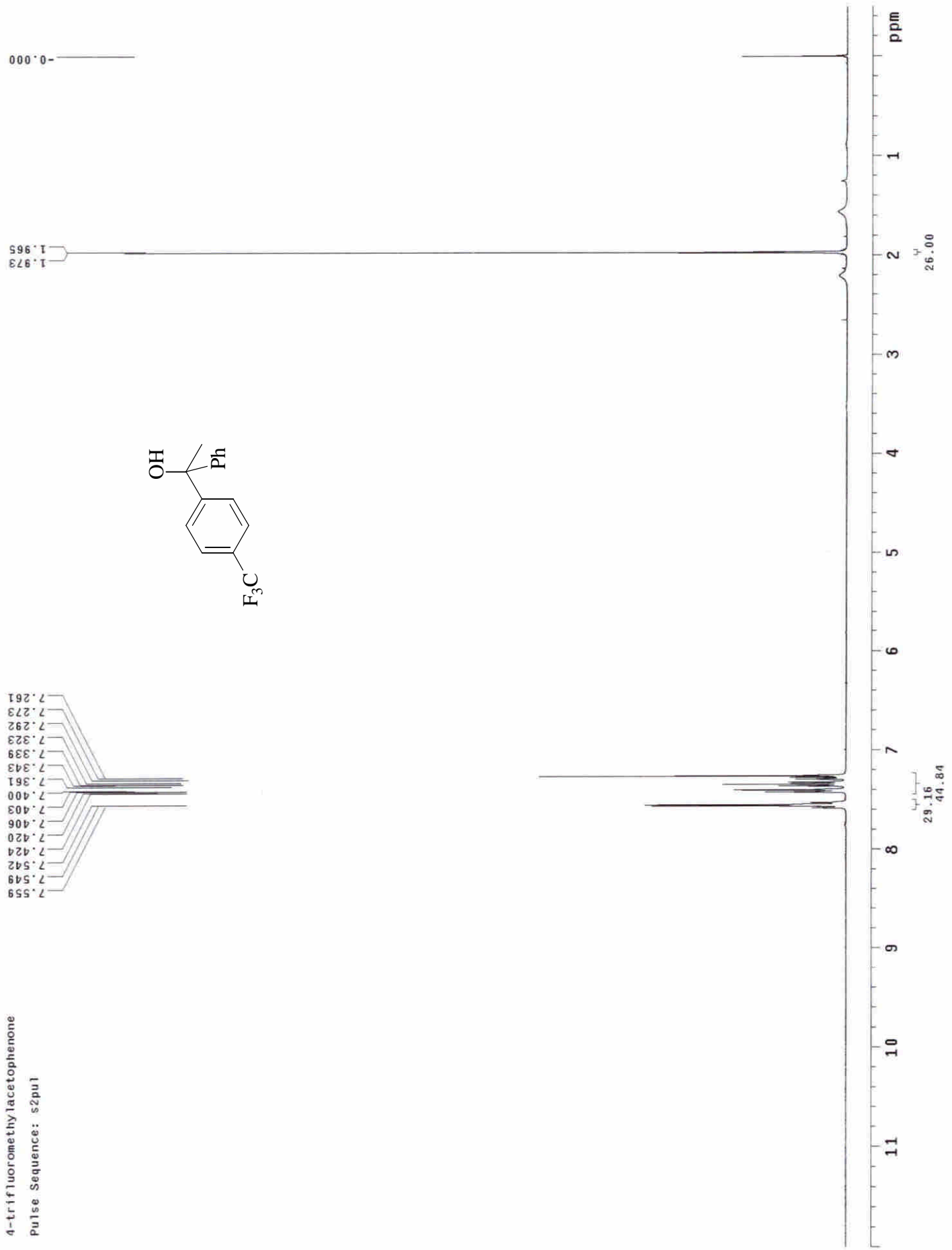
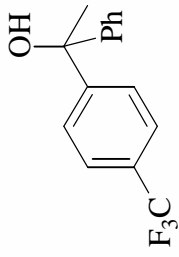
4'-trifluoromethylacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0°C, toluene: 6 mL, 12 h.

**Spectroscopic Data:**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56-7.54 (m, 4H), 7.42-7.26 (m, 5H), 2.21 (br, 1H), 1.97 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 151.92, 147.03, 129.16, 128.84, 128.37, 127.39, 126.12, 125.81, 125.53, 125.11, 125.07, 125.04, 125.00, 122.82, 75.97, 30.56 ppm. HRMS: *m/z* calcd. for C<sub>15</sub>H<sub>13</sub>OF<sub>3</sub>, 266.0919 [M<sup>+</sup>]; Found 266.0925.

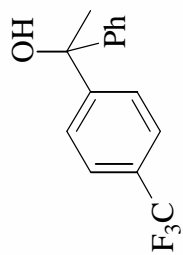
4-trifluoromethylacetophenone  
Pulse Sequence: s2pu1

7.559  
7.549  
7.542  
7.424  
7.420  
7.406  
7.403  
7.400  
7.361  
7.343  
7.339  
7.323  
7.292  
7.273  
7.261



4-trifluoromethylacetophenone

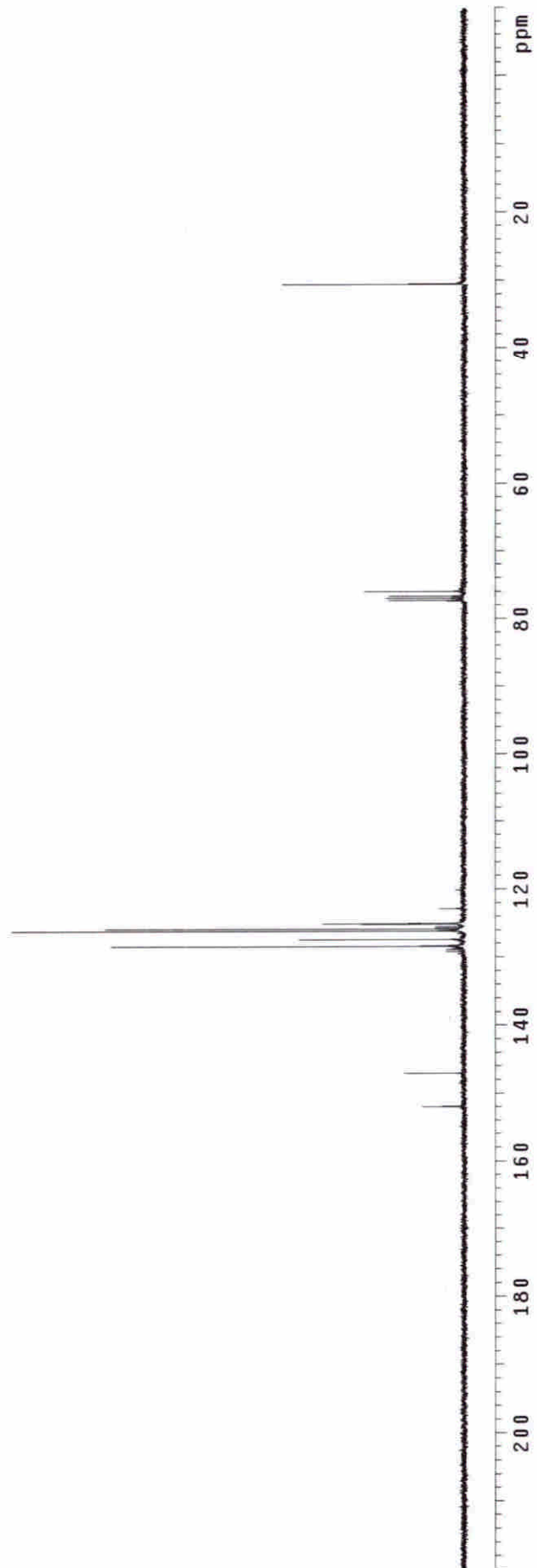
Pulse Sequence: s2pu1

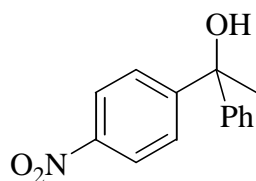


30.557

77.321  
77.000  
76.686  
75.974

151.923  
147.025  
129.161  
128.839  
128.572  
127.385  
126.122  
125.808  
125.525  
125.112  
125.074  
125.035  
124.997  
122.823



**1-(4-Nitro-phenyl)-1-phenyl-ethanol (Table 2, entry 14; 93% ee)**

Column: Chiralcel OJ  
 Eluent: Hexane/IPA = 90/10  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 30.005 min, 35.645 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	30.005	35.645	Time	29.768	35.851
Height (mAU)	84.264	70.742	Height (mAU)	176.037	6.260
Area (mAU-s)	6985.151	7011.107	Area (mAU-s)	$1.572 \times 10^4$	577.305
Area (%)	49.907	50.092	Area (%)	96.459	3.541

**Catalytic Reaction Conditions:**

4'-nitroacetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%,  $\text{AlPh}_3(\text{THF})$ : 1.25 mmol,  $\text{Ti}(\text{O-}i\text{-Pr})_4$ : 2.5 mmol, 0°C, toluene: 6 mL, 12 h.

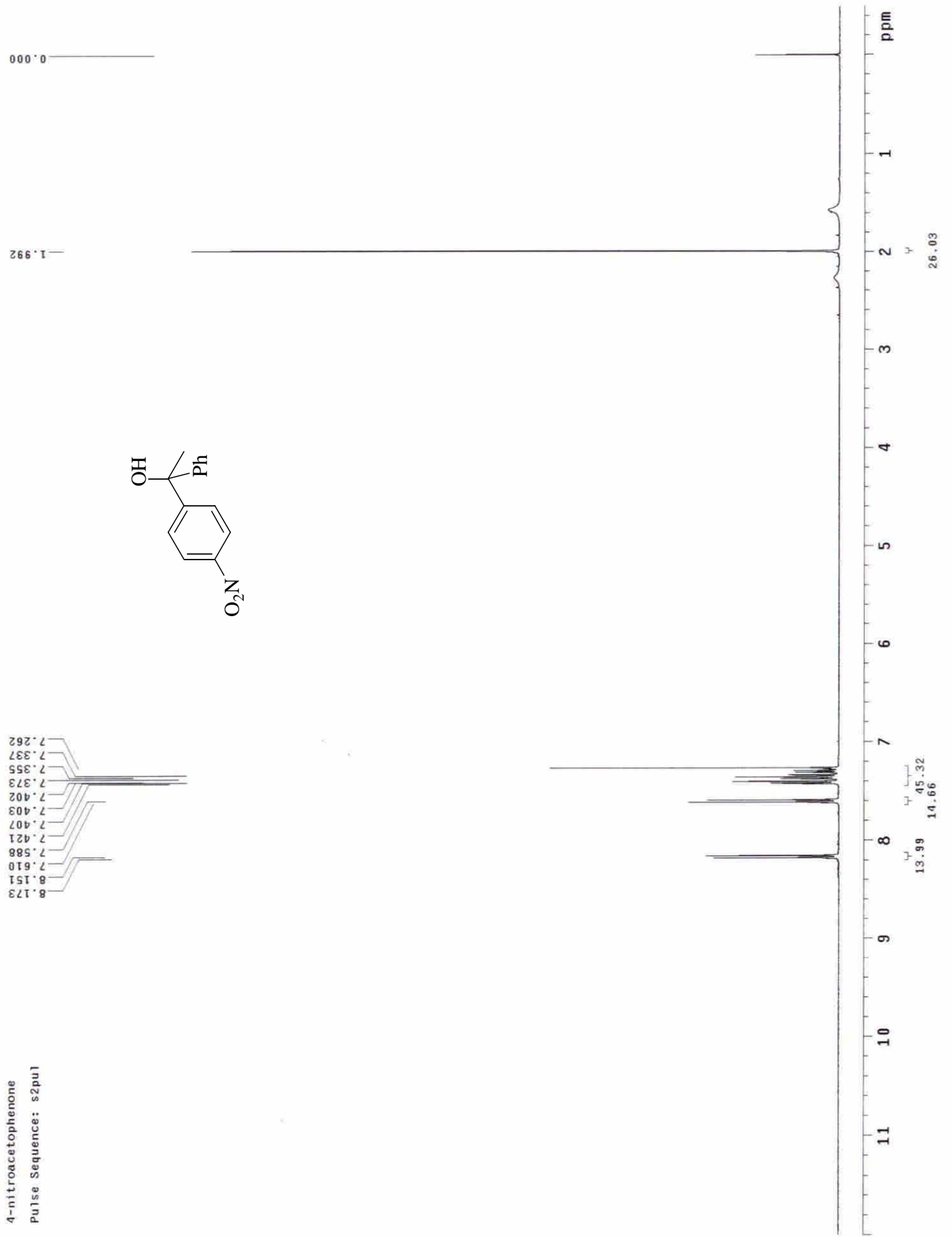
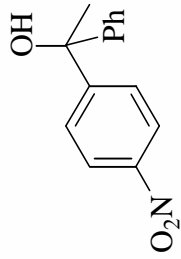
**Spectroscopic Data:**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (d,  $J = 8.8$  Hz, 2H), 7.60 (d,  $J = 8.8$  Hz, 2H), 7.42-7.26 (m, 5H), 2.27 (br, 1H), 1.99 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.29, 146.59, 146.41, 128.49, 127.62, 126.61, 125.72, 123.29, 75.88, 30.43 ppm.

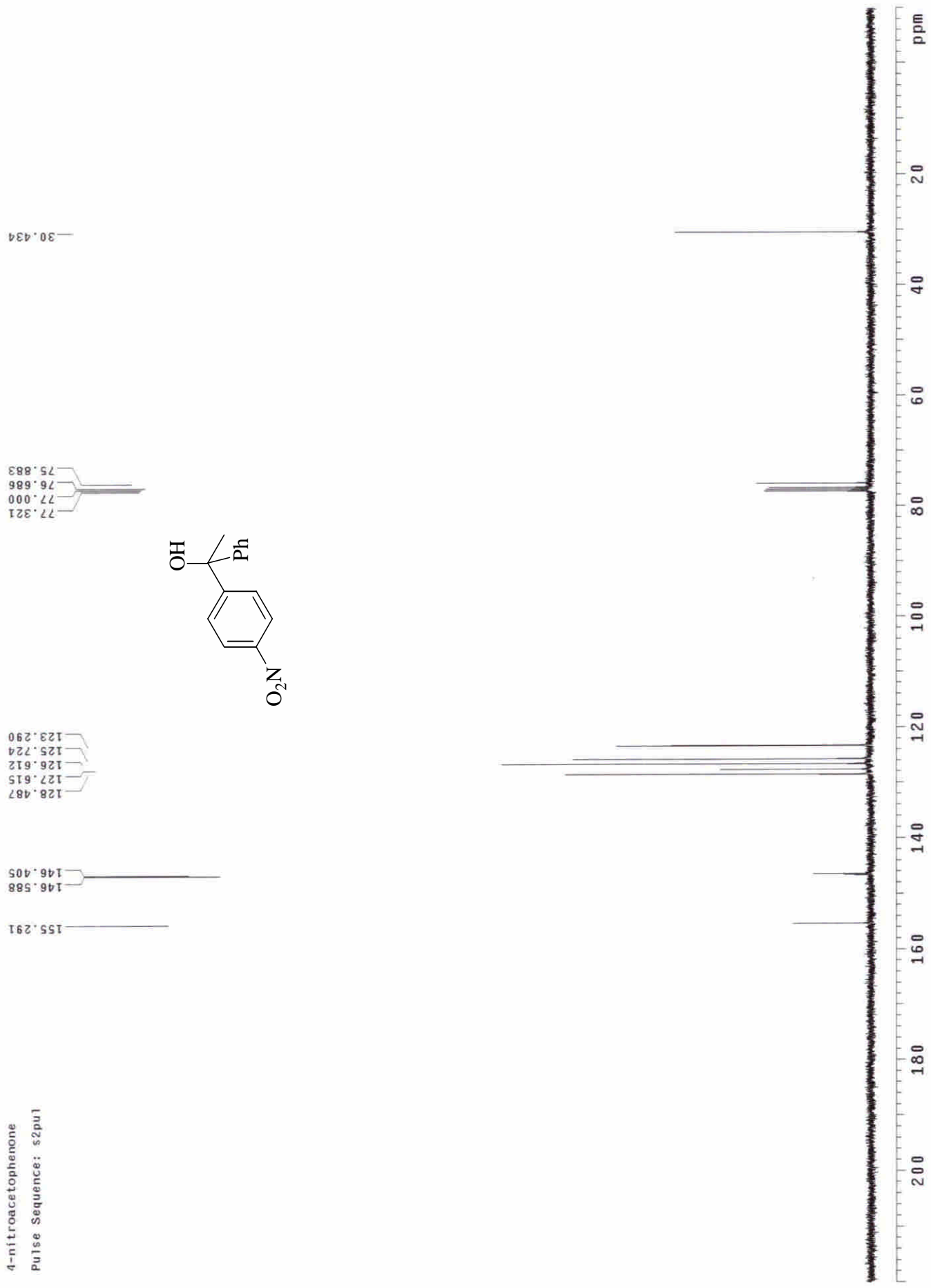
HRMS:  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{13}\text{NO}_3$ , 243.0895 [ $\text{M}^+$ ]; Found 243.0886.

4-nitroacetophenone  
Pulse Sequence: s2pu1

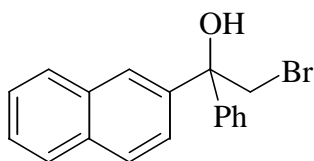
8.173  
8.151  
7.610  
7.588  
7.421  
7.407  
7.403  
7.402  
7.373  
7.355  
7.337  
7.262



4-nitroacetophenone  
Pulse Sequence: s2pu1



## 2-Bromo-1-naphthalen-2-yl-1-phenyl-ethanol (Table 2, entry 15; 80% ee)



Column: Chiralcel OD  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 40.787 min, 44.344 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	40.787	44.344	Time	40.523	43.580
Height (mAU)	96.001	84.773	Height (mAU)	1.344	11.068
Area (mAU-s)	8102.891	8100.793	Area (mAU-s)	98.061	965.377
Area (%)	50.006	49.993	Area (%)	9.221	90.778

### Catalytic Reaction Conditions:

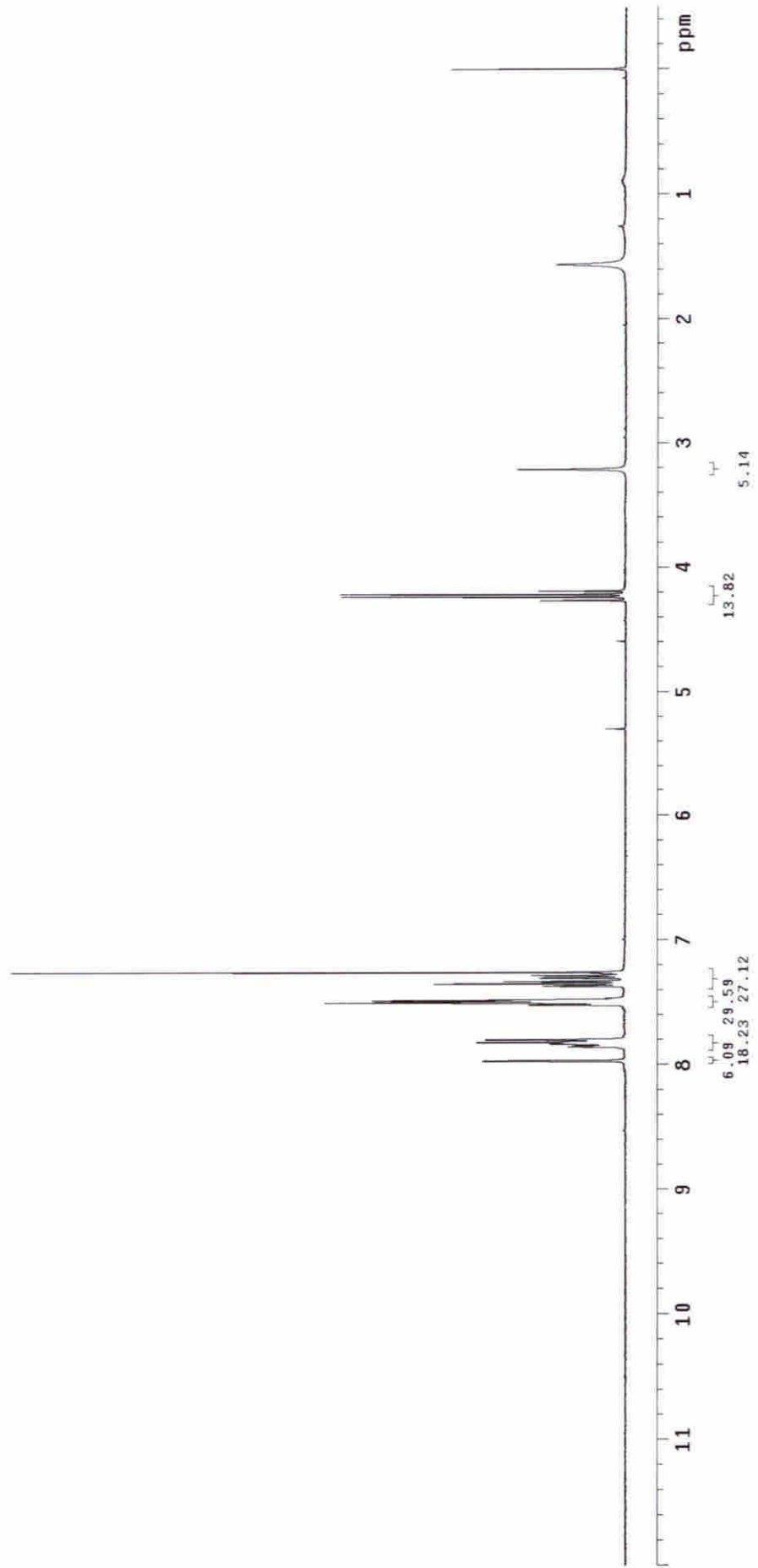
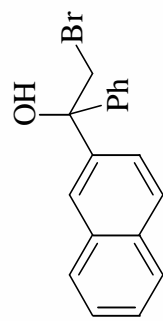
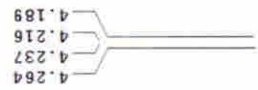
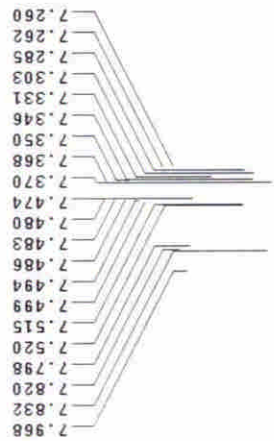
$\alpha$ -bromo-2'-acetonaphthone: 0.5 mmol, (*S*)-BINOL: 10 mol%,  $\text{AlPh}_3(\text{THF})$ : 1.25 mmol,  $\text{Ti}(\text{O-}i\text{-Pr})_4$ : 2.5 mmol, 0°C, toluene: 6 mL, 12 h.

### Spectroscopic Data:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (s, 1H), 7.83-7.80 (m, 3H), 7.52-7.47 (m, 5H), 7.37-7.26 (m, 3H), 4.23 (dd,  $J = 10.8, 19.2$  Hz, 2H), 3.21 (s, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.17, 140.63, 132.90, 132.62, 128.37, 128.33, 128.17, 127.77, 127.49, 126.37, 126.31, 126.26, 125.12, 124.45, 77.26, 43.80 ppm.

HRMS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{15}\text{BrO}$ , 326.0306 [ $\text{M}^+$ ]; Found 326.0304.

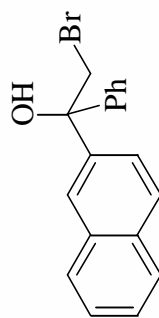
alpha-bromo-2-acetonaphthone  
Pulse Sequence: s2pu1



alpha-bromo-2-acetonaphthone

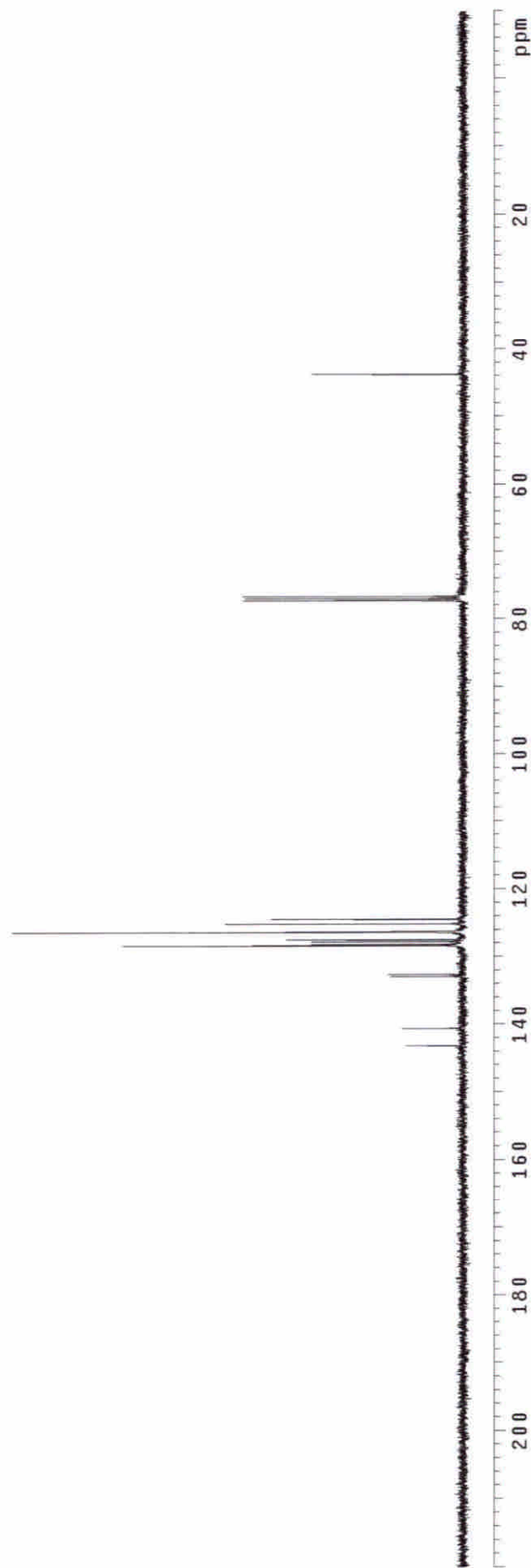
Pulse Sequence: szpu1

143.167  
140.634  
132.903  
132.620  
128.372  
128.326  
128.166  
127.768  
127.492  
126.367  
126.313  
126.260  
125.119  
124.446

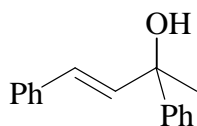


77.314  
77.260  
77.000  
76.679

43.798



**2,4-Diphenyl-but-3-en-2-ol (Table 2, entry 16; 87% ee)<sup>3</sup>**



Column: Chiralcel OD  
 Eluent: Hexane/IPA = 95/5  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 13.067 min, 16.734 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	13.067	16.734	Time	12.306	15.104
Height (mAU)	165.473	135.582	Height (mAU)	172.342	1800.710
Area (mAU-s)	4742.026	4721.952	Area (mAU-s)	3490.712	4.836×10 <sup>4</sup>
Area (%)	50.106	49.893	Area (%)	6.731	93.268

**Catalytic Reaction Conditions:**

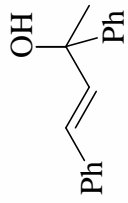
benzylideneacetone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(*O-i-Pr*)<sub>4</sub>: 2.5 mmol, 0°C, toluene: 6 mL, 12 h.

**Spectroscopic Data:**

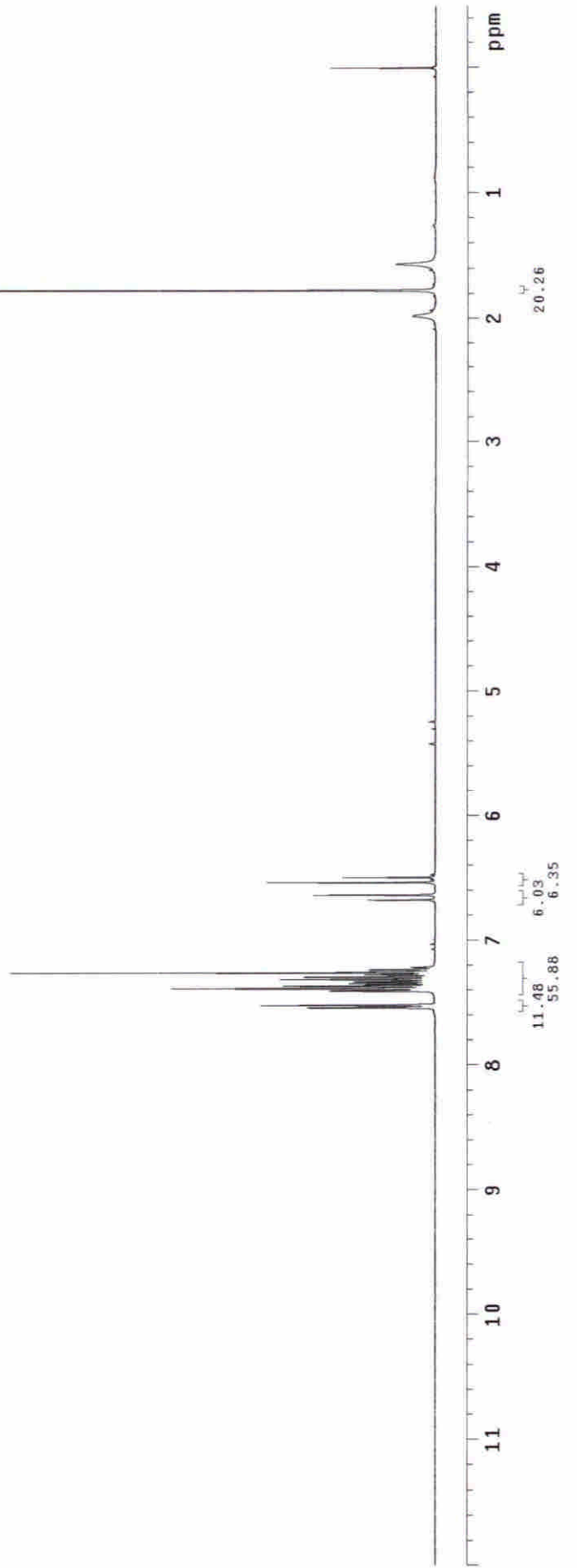
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.54-7.52 (m, 2H), 7.41-7.24 (m, 8H), 6.65 (d, J = 16.0 Hz, 1H), 6.52 (dd, J = 1.2, 16.0 Hz, 1H), 1.98 (br, 1H), 1.78 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 146.56, 136.65, 136.29, 128.50, 128.24, 127.60, 127.54, 127.00, 126.51, 125.22, 74.60, 29.69 ppm.

benzylidenacetone  
Pulse Sequence: s2pu1

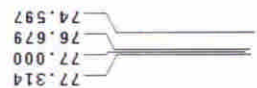
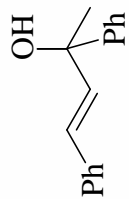
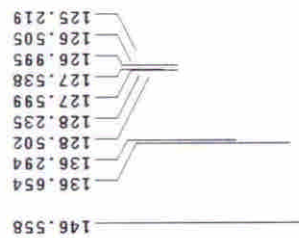
7.543  
7.540  
7.537  
7.522  
7.519  
7.516  
7.407  
7.405  
7.386  
7.367  
7.366  
7.362  
7.349  
7.347  
7.346  
7.333  
7.331  
7.312  
7.295  
7.292  
7.275  
7.262  
7.259  
7.258  
7.255  
7.252  
7.235  
6.674  
6.634  
6.537  
6.534  
6.497  
6.494



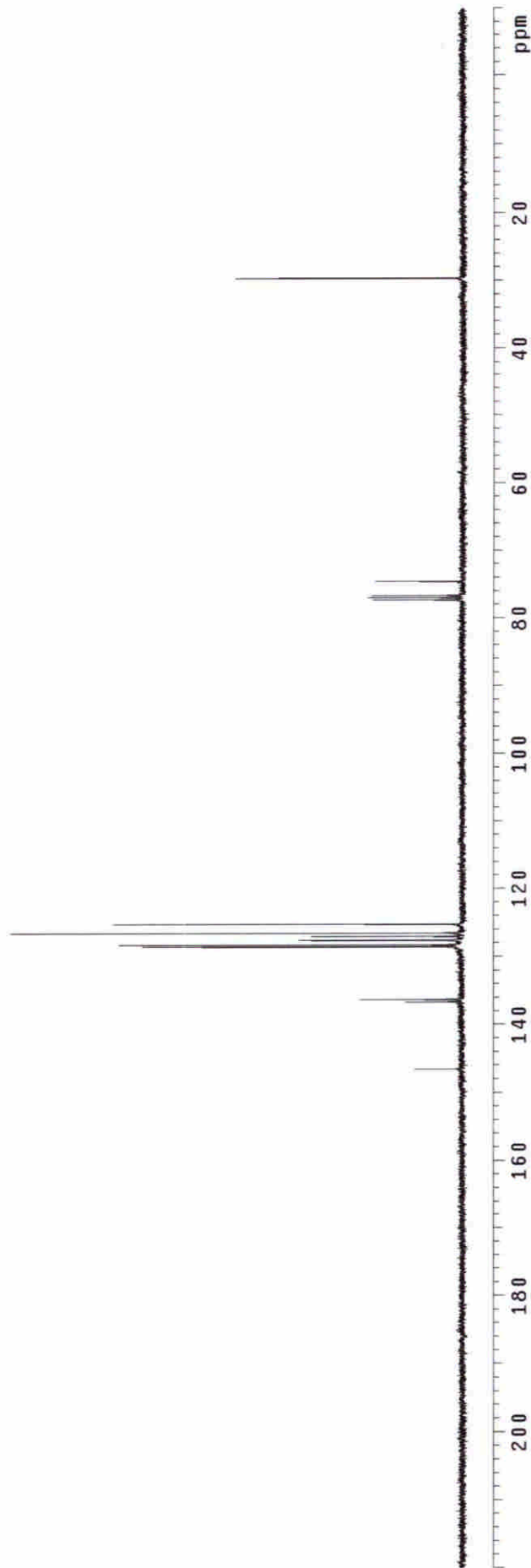
1.777  
1.774  
0.004  
0.000



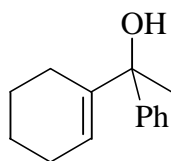
benzylideneacetone  
Pulse Sequence: s2pu1



29.692



**1-Cyclohex-1-enyl-1-phenyl-ethanol (Table 2, entry 17; 91% ee; 20 mol%)<sup>3</sup>**



Column: Chiralcel OD-H  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 6.823 min, 7.982 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	6.823	7.982	Time	6.245	7.554
Height (mAU)	7.466	6.364	Height (mAU)	2.599	41.076
Area (mAU-s)	100.555	101.523	Area (mAU-s)	29.499	597.487
Area (%)	49.760	50.239	Area (%)	4.705	95.295

**Catalytic Reaction Conditions:**

1-acetyl-1-cyclohexene: 0.5 mmol, (*S*)-BINOL: 20 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol,  
 Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

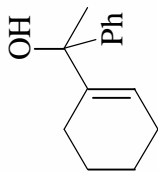
**Spectroscopic Data:**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43-7.41 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 1H),  
 5.92-5.90 (m, 1H), 2.13-2.12 (m, 2H), 1.94-1.68 (m, 3H), 1.64 (s, 3H), 1.58-1.52 (m, 4H)  
 ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 146.80, 142.38, 127.93, 126.51, 125.25, 121.49,  
 76.97, 28.69, 25.15, 24.48, 22.81, 22.21 ppm.

1-acety1-1-cyclohexene

Pulse Sequence: s2pu1

2.129  
2.122  
1.941  
1.938  
1.897  
1.810  
1.745  
1.734  
1.701  
1.694  
1.683  
1.643  
1.581  
1.572  
1.556  
1.547  
1.532  
1.516



5.918  
5.912  
5.908  
5.899

7.431  
7.428  
7.410  
7.408  
7.391  
7.322  
7.303  
7.263  
7.250  
7.233  
7.214

10.53  
16.74  
17.055, 48

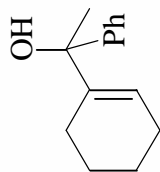
4.88

9.68, 78  
9.91

ppm

1-acetyl-1-cyclohexene

Pulse Sequence: szpu1

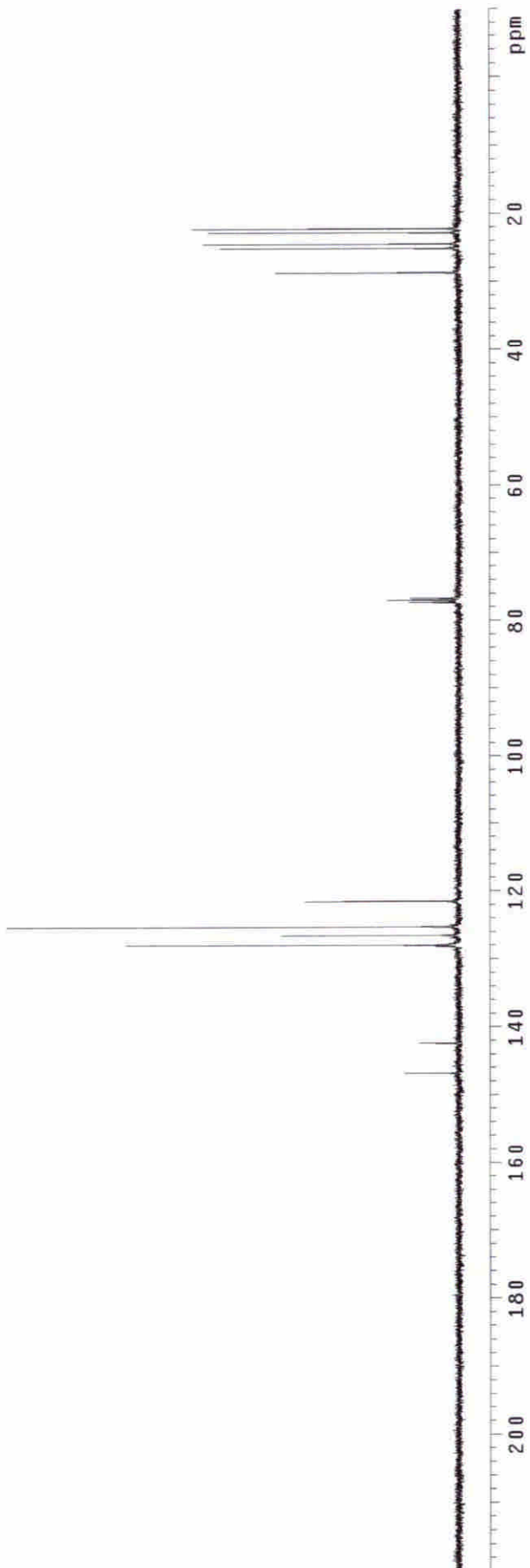


28.689  
25.145  
24.480  
22.811  
22.206

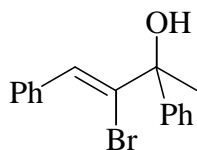
77.329  
76.969  
76.686

127.928  
126.512  
125.250  
121.492

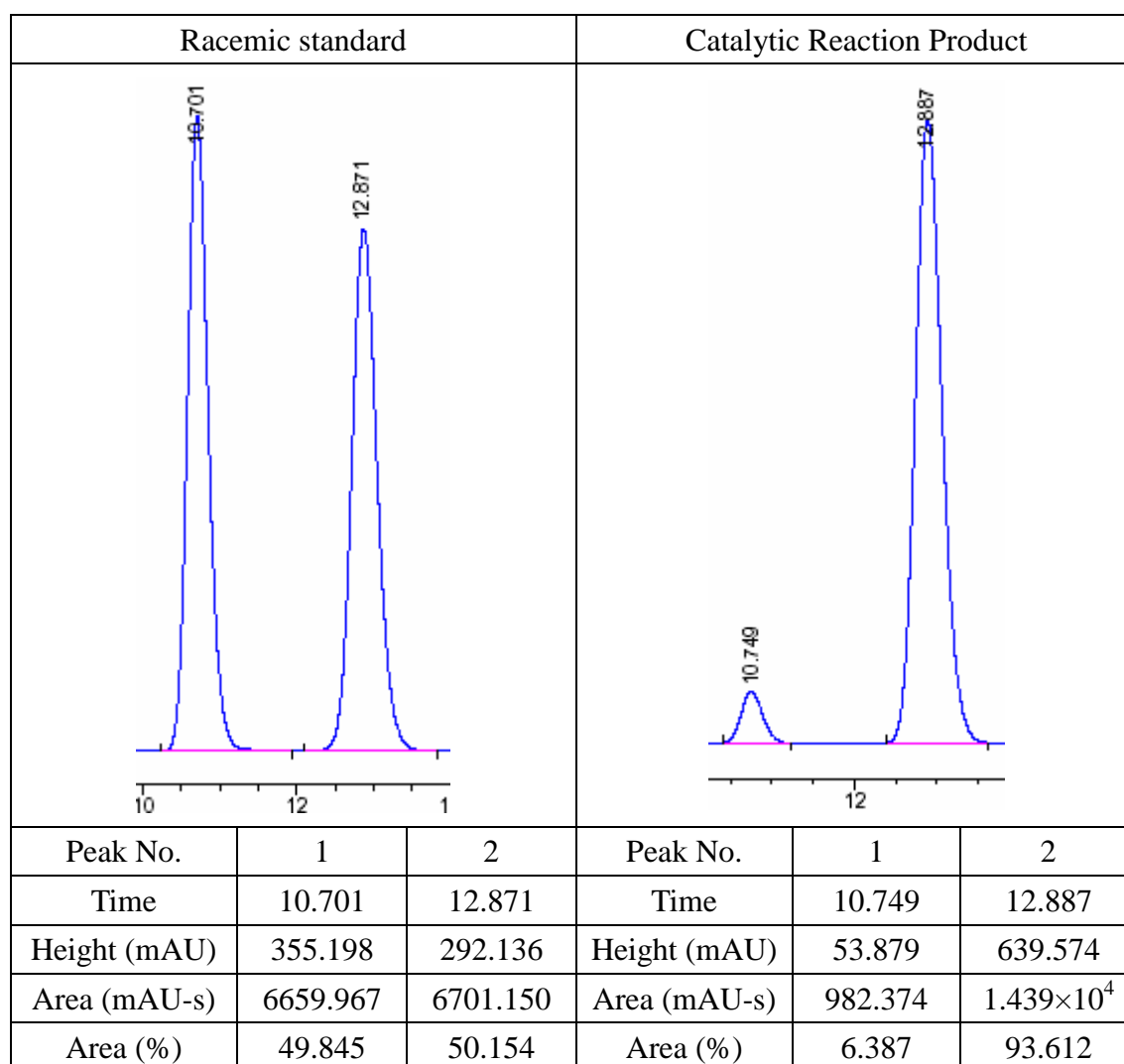
146.803  
142.379



### 3-Bromo-2,4-diphenyl-but-3-en-2-ol (Table 2, entry 18; 87% ee; 20 mol%)



Column: Chiralcel OD  
 Eluent: Hexane/IPA = 95/5  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 10.701 min, 12.871 min



#### Catalytic Reaction Conditions:

3-bromo-4-phenyl-but-3-en-2-one: 0.5 mmol, (*S*)-BINOL: 20 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 24 h.

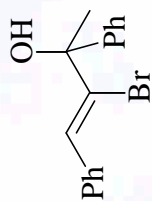
#### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.61-7.52 (m, 4H), 7.40-7.31 (m, 7H), 2.76 (br, 1H), 1.92 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 145.20, 135.58, 134.56, 129.12, 128.36, 128.14, 128.09, 127.81, 127.57, 125.46, 78.67, 28.95 ppm.

HRMS: m/z calcd. for C<sub>16</sub>H<sub>15</sub>OBr, 302.0306 [M<sup>+</sup>]; Found 302.0299.



bezny 11densaceton-Br  
Pulse Sequence: szpu1



77.306  
76.985  
76.671

28.949

78.669

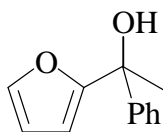
129.115  
128.357  
128.135  
128.089  
127.814  
127.569  
125.484

134.564  
135.582

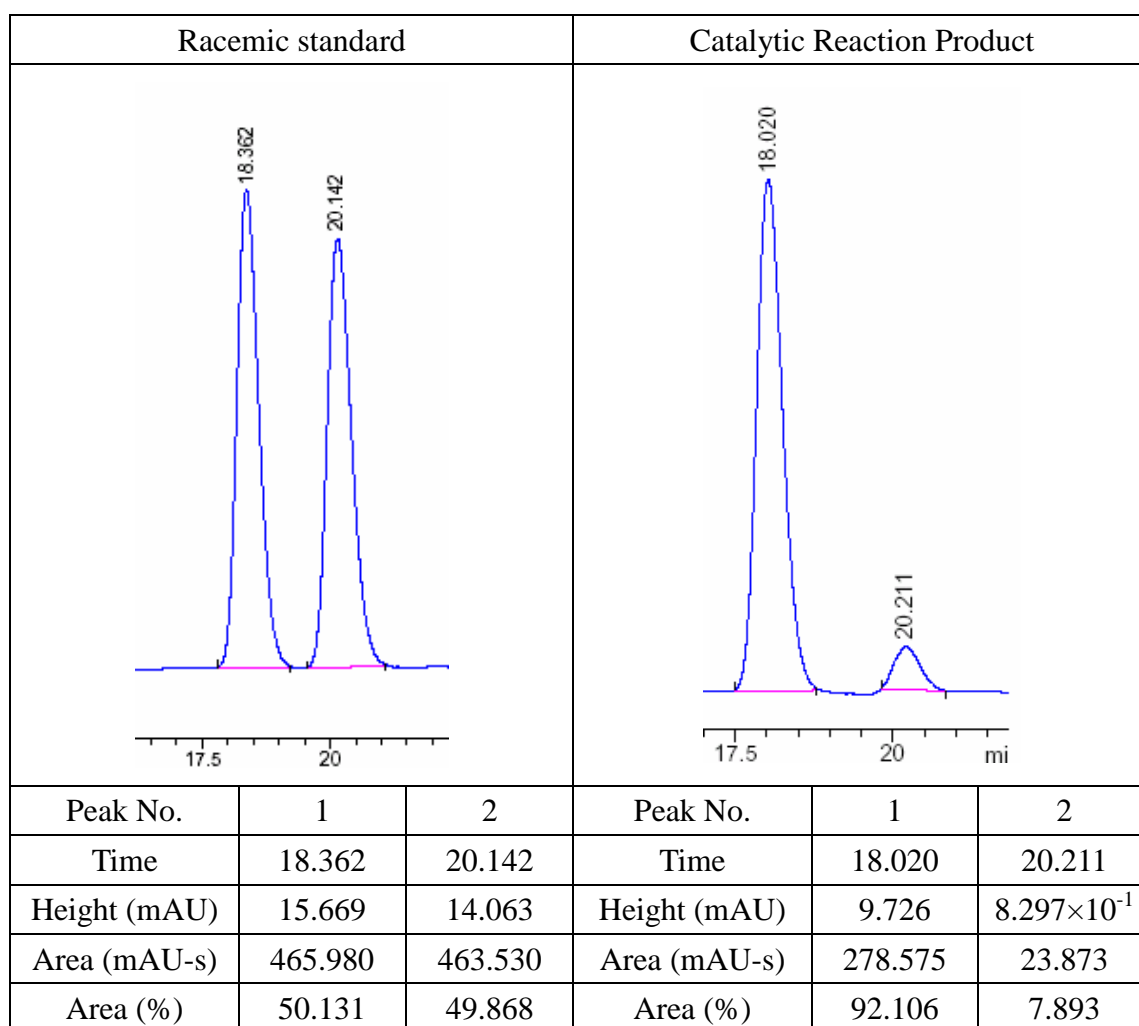
145.195

180 160 140 120 100 80 60 40 20 0 ppm

## 1-Furan-2-yl-1-phenyl-ethanol (Table 2, entry 19; 84% ee; 20 mol%)



Column: Chiralcel OD  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 18.362 min, 20.142 min



### Catalytic Reaction Conditions:

2-acetylfuran: 0.5 mmol, (*S*)-BINOL: 20 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 16 h.

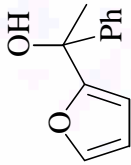
### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41-7.25 (m, 6H), 6.34-6.33 (m, 1H), 6.25-6.24 (m, 1H), 2.56 (br, 1H), 1.87 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 158.90, 145.78, 142.10, 128.13, 127.27, 125.19, 110.01, 106.19, 72.94, 29.19 ppm.

HRMS: *m/z* calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>, 188.0837 [M<sup>+</sup>]; Found 188.0834.

2-acetyl(1000)

Pulse Sequence: zgpg30



1.870  
1.866

1.679

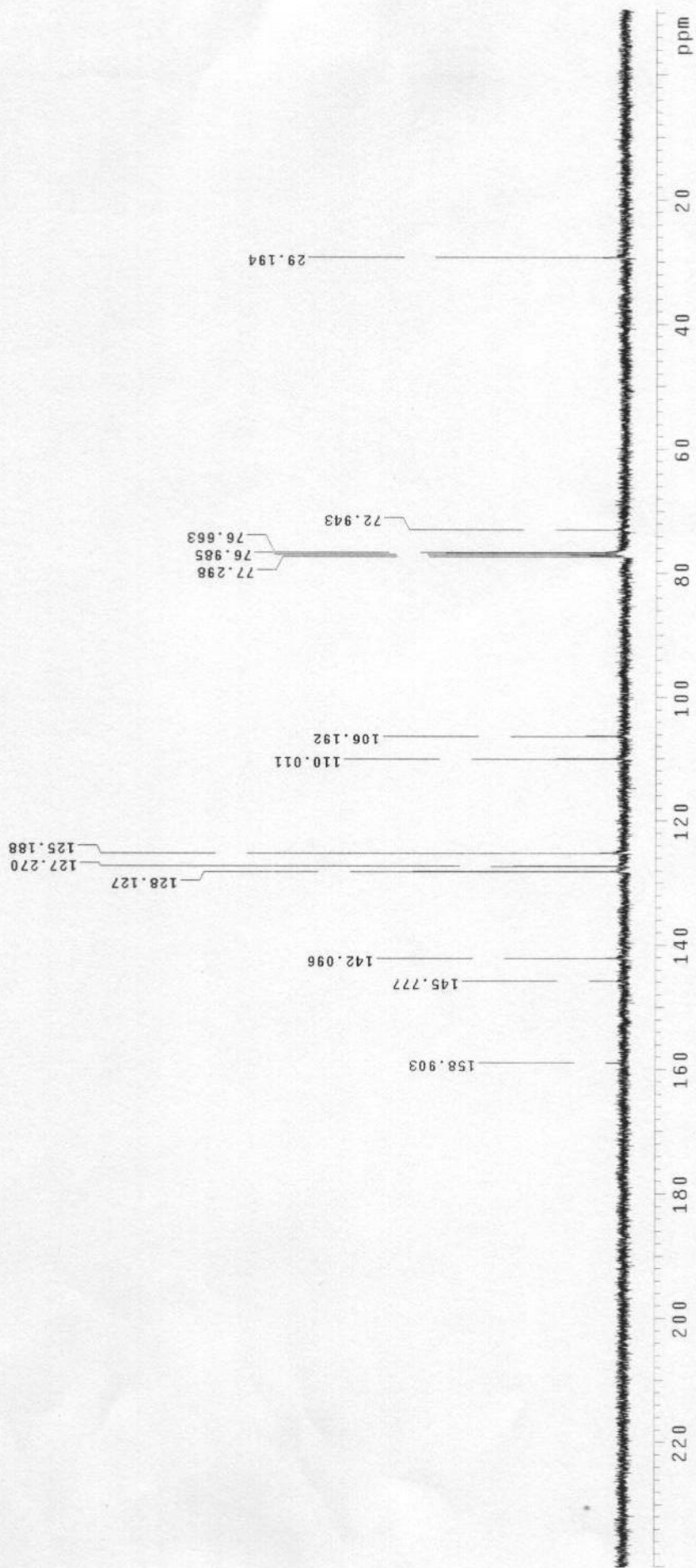
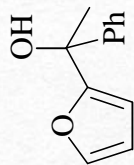
2.561

7.407  
7.405  
7.403  
7.401  
7.396  
7.385  
7.383  
7.375  
7.369  
7.361  
7.358  
7.354  
7.352  
7.348  
7.345  
7.343  
7.332  
7.331  
7.326  
7.312  
7.286  
7.284  
7.282  
7.278  
7.272  
7.266  
7.249  
7.247  
7.245  
6.340  
6.338  
6.335  
6.333  
6.332  
6.330  
6.327  
6.325  
6.248  
6.246  
6.244  
6.240  
6.238

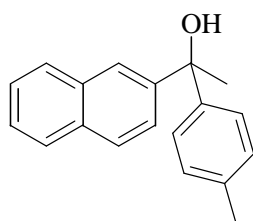
ppm

30.55

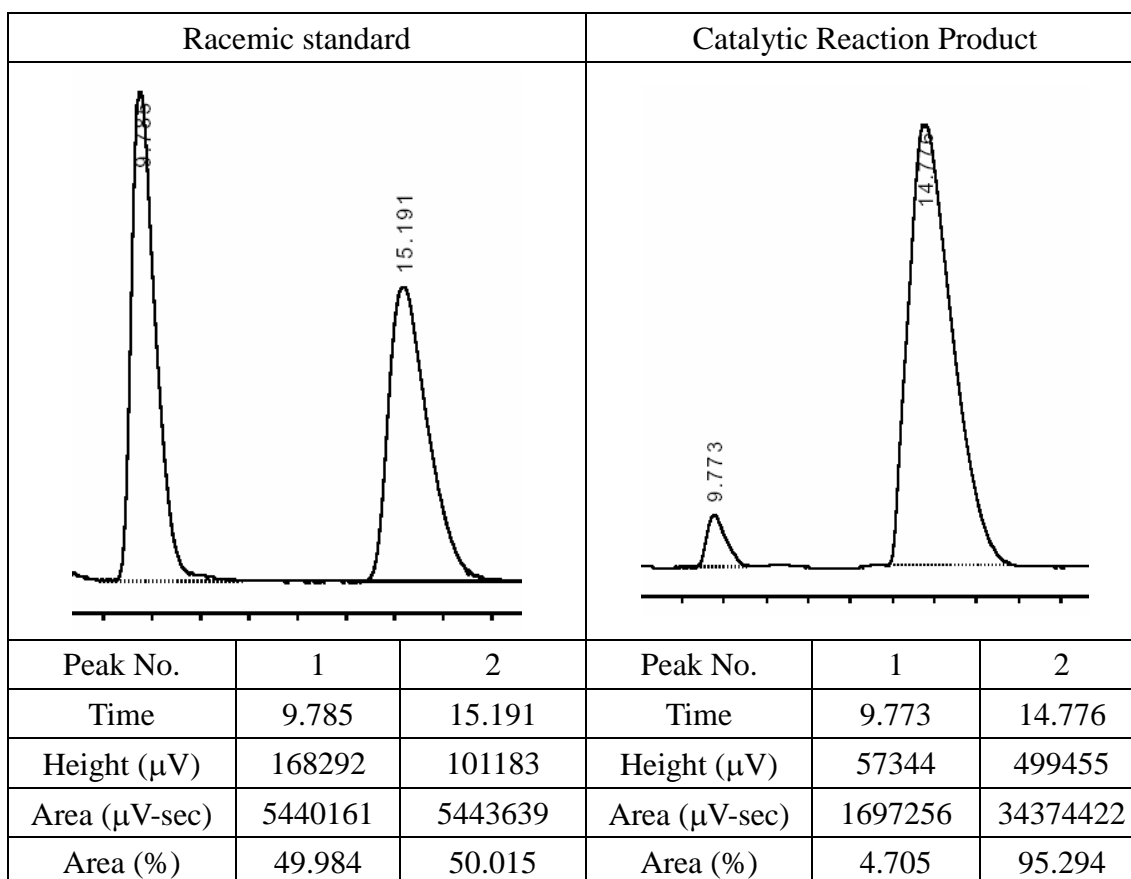
55.79  
7.94  
7.94



## 1-Naphthalen-2-yl-1-*p*-tolyl-ethanol (Table 2, entry 20; 91% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 70/30  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 9.785 min, 15.191 min



### Catalytic Reaction Conditions:

2'-acetonaphthone: 0.5 mmol, (*S*)-BINOL: 10 mol%, Al(4-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

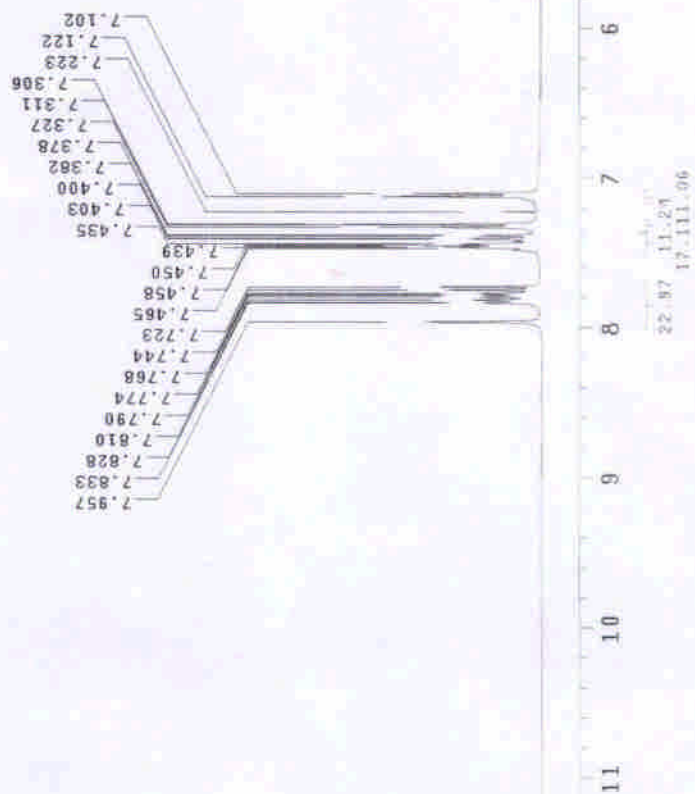
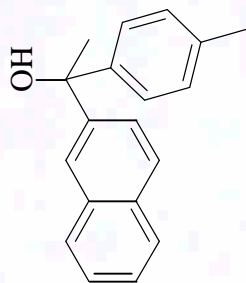
### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96 (s, 1H), 7.83-7.72 (m, 3H), 7.47-7.38 (m, 3H), 7.33-7.31 (m, 2H), 7.12-7.10 (m, 2H), 2.32 (s, 3H), 2.28 (br, 1H), 2.01 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 145.46, 144.88, 136.68, 133.01, 132.36, 128.89, 128.24, 127.88, 127.47, 126.06, 125.89, 125.85, 124.93, 123.64, 76.22, 30.73, 20.97 ppm.

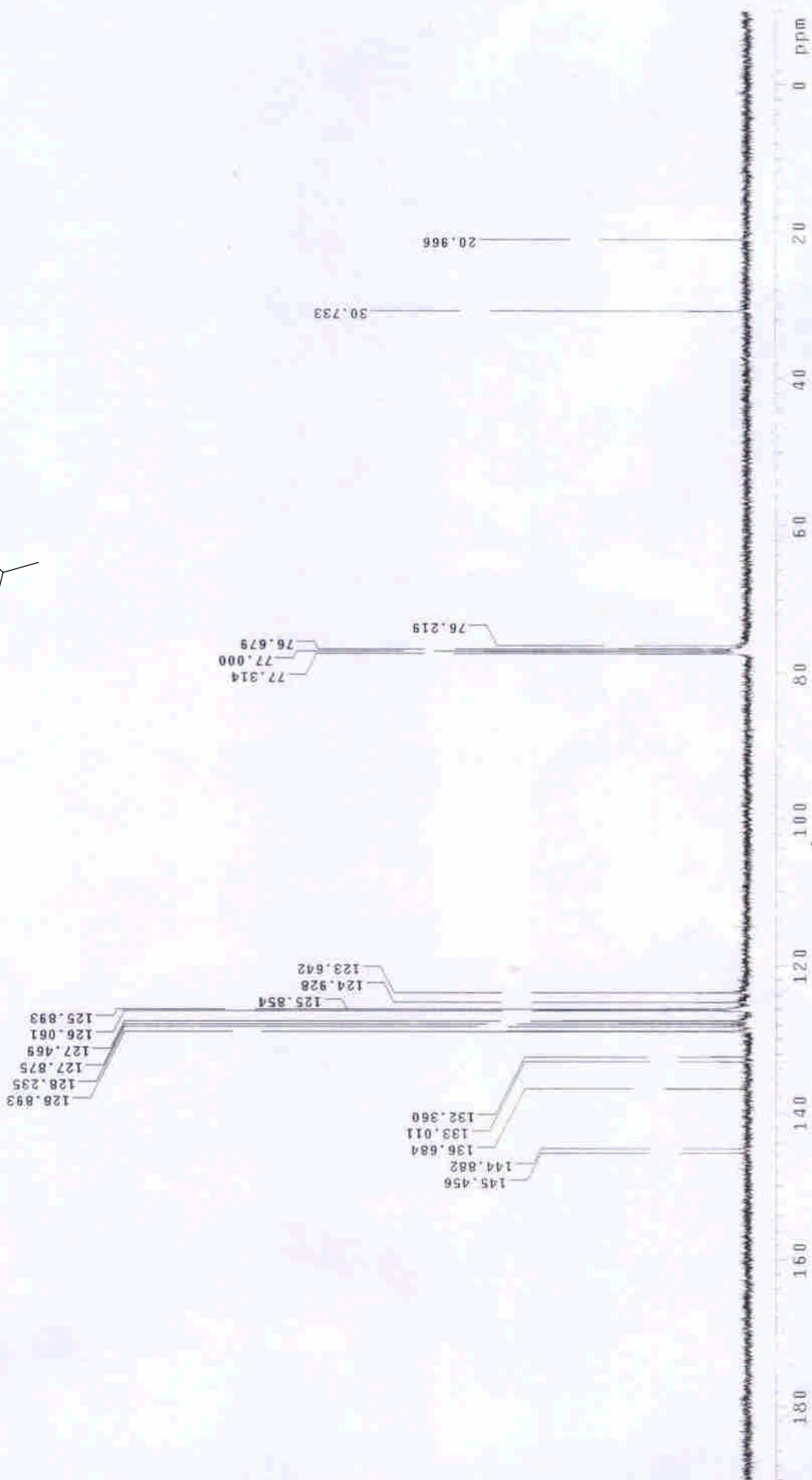
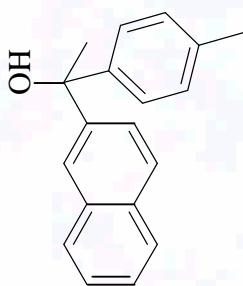
HRMS: *m/z* calcd. for C<sub>19</sub>H<sub>18</sub>O, 262.1358 [M<sup>+</sup>]; Found 262.1364.

Acetophenone, 4-Me-PhA (THF)

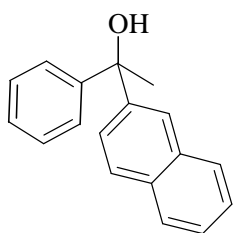
Pulse Sequence: szpu1



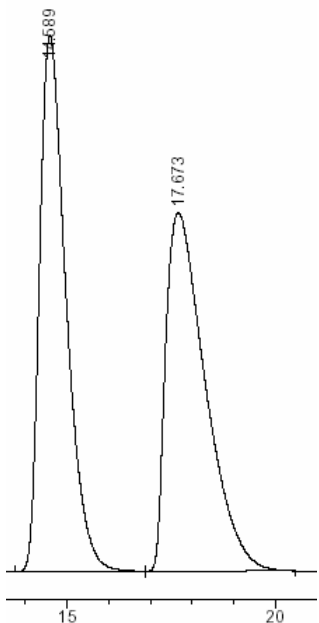
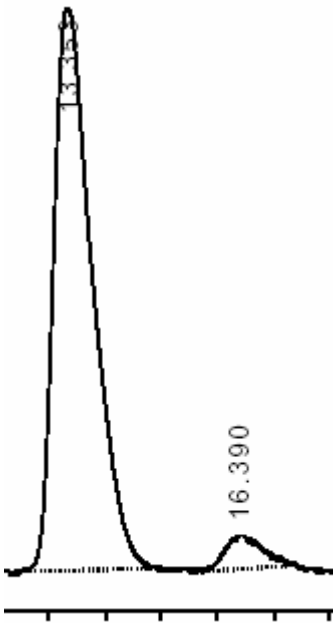
acetophenone, 4-(4-methylphenyl)-  
Pulse Sequence: s2pr1



## 1-Naphthalen-2-yl-1-phenyl-ethanol (Table 2, entry 21; 90% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 80/20  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 14.589 min, 17.673 min

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	14.589	17.673	Time	13.353	16.390
Height (mAU)	731.907	489.963	Height ( $\mu$ V)	73367	4242
Area (mAU-s)	$3.223 \times 10^4$	$3.226 \times 10^4$	Area ( $\mu$ V-sec)	3295433	174300
Area (%)	49.973	50.026	Area (%)	94.976	5.023

### Catalytic Reaction Conditions:

acetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, Al(2-naphthyl)<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

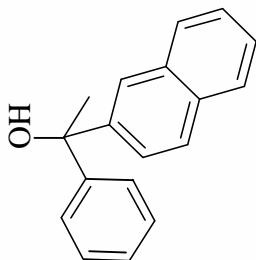
### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.98 (d, *J* = 1.2 Hz, 1H), 7.84-7.75 (m, 3H), 7.49-7.25 (m, 8H), 2.27 (br, 1H), 2.06 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.70, 145.22, 132.96, 132.35, 128.22, 128.18, 127.91, 127.45, 127.00, 126.08, 125.92, 124.91, 123.70, 76.31, 30.66 ppm.

2-acetonaphthone

Pulse Sequence: s2pu1

7.981  
7.978  
7.835  
7.814  
7.797  
7.791  
7.774  
7.753  
7.489  
7.484  
7.481  
7.473  
7.464  
7.458  
7.446  
7.425  
7.421  
7.404  
7.399  
7.345  
7.343  
7.326  
7.325  
7.321  
7.307  
7.270  
7.257  
7.253



0.001  
0.000

2.056

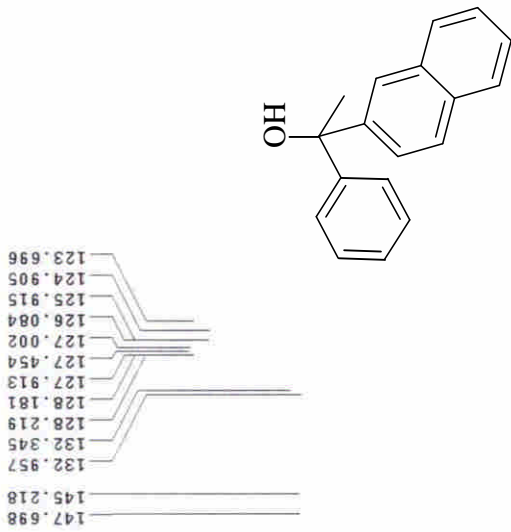
11 10 9 8 7 6 5 4 3 2 1 ppm

6.05 29.98  
18.61 23.93

21.42

2-acetonaphthone

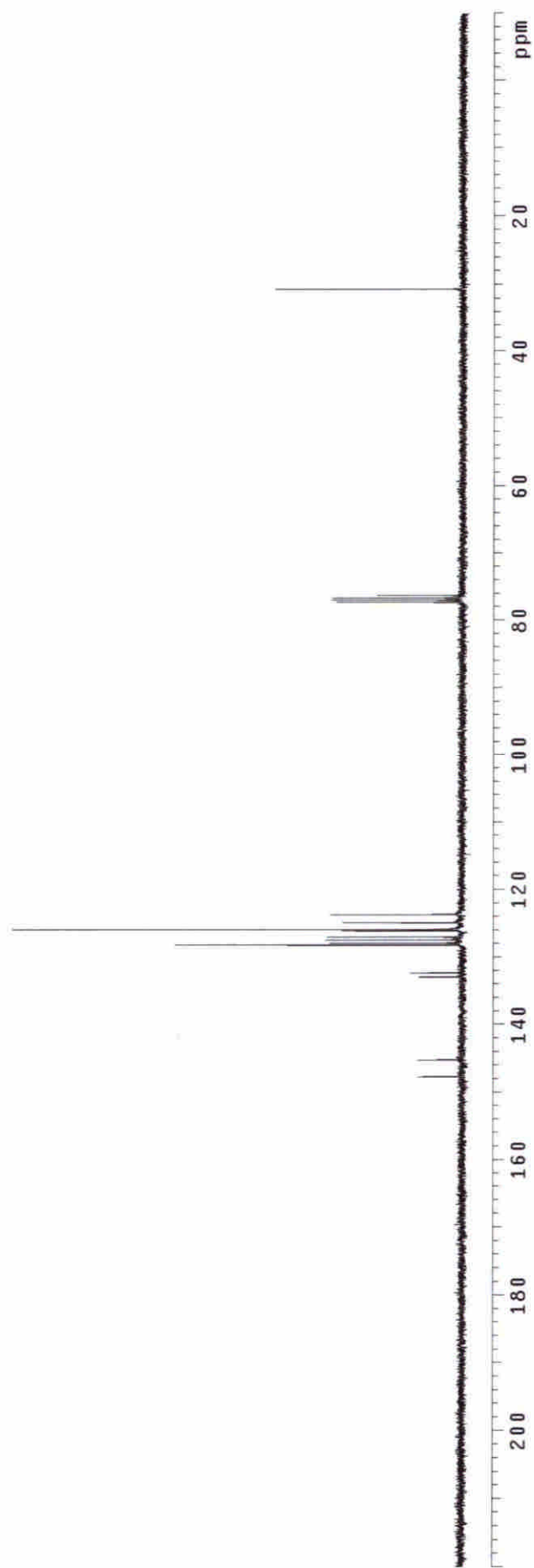
Pulse Sequence: s2pu1



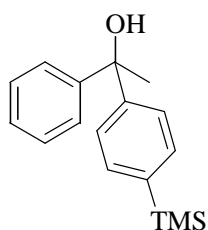
147.698
145.218
132.957
132.345
128.219
128.181
127.913
127.454
127.002
126.084
125.915
124.905
123.696

77.314
77.000
76.679
76.311

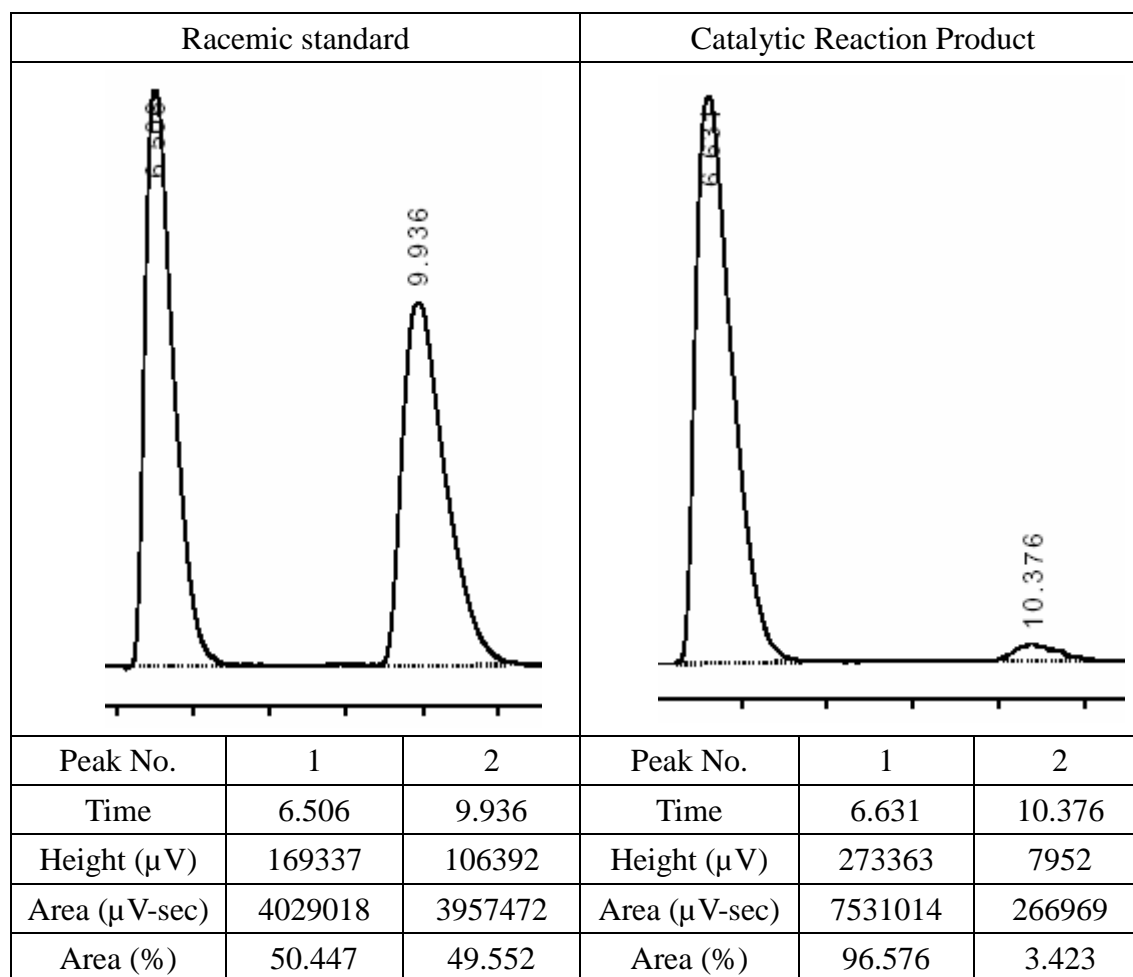
30.664
--------



## 1-Phenyl-1-(4-trimethylsilyl-phenyl)-ethanol (Table 2, entry 22; 93% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 95/5  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 6.506 min, 9.936 min



### Catalytic Reaction Conditions:

acetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, Al(4-TMSC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

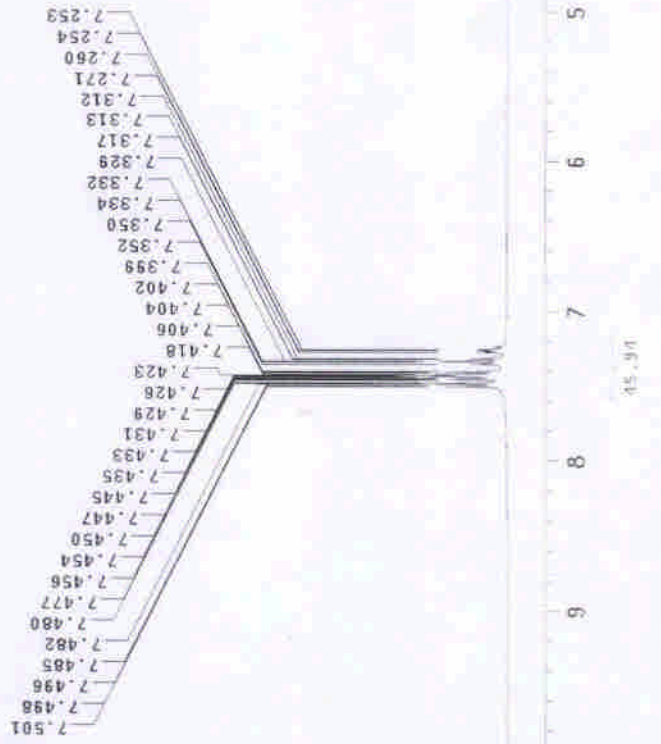
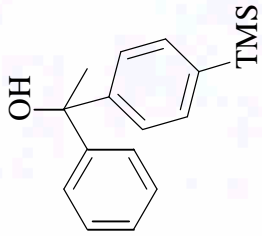
### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50-7.25 (m, 9H), 2.22 (br, 1H), 1.96 (s, 3H), 0.27 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 148.48, 147.93, 138.93, 133.26, 128.15, 126.92, 125.81, 125.10, 76.17, 30.75, -1.14 ppm.

HRMS: *m/z* calcd. for C<sub>17</sub>H<sub>22</sub>SiO, 270.1440 [M<sup>+</sup>]; Found 270.1433.

acetone-d6, 4-TMS-PhA1 (THF)

Pulse Sequence: zgpg30



ppm

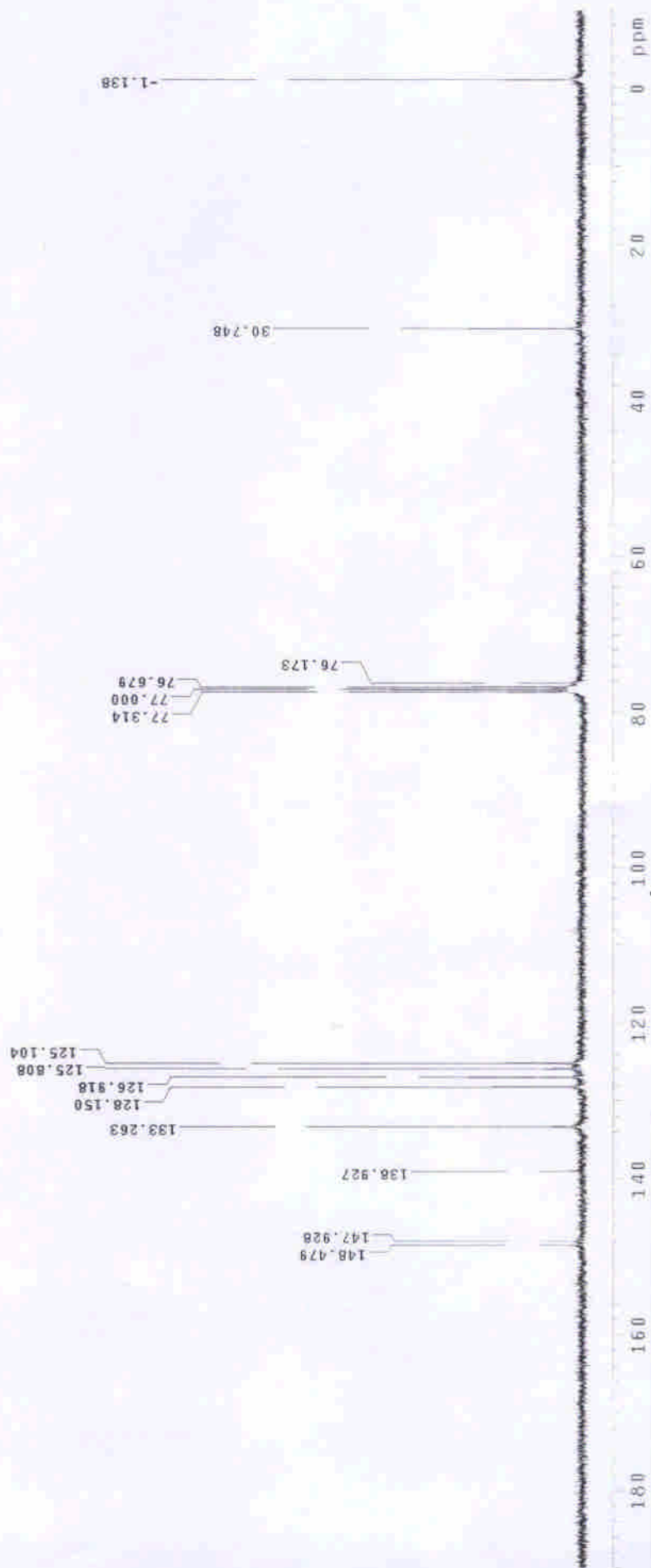
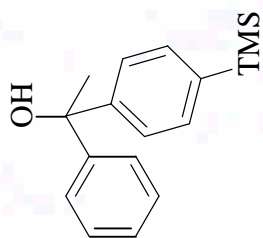
37.90

16.46

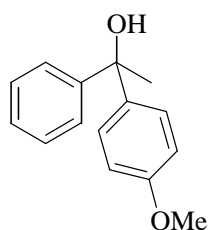
45.94

acetophenone/4-TMS-Ph5 (TMS)

Pulse Sequence: s2pu1



## 1-(4-Methoxy-phenyl)-1-phenyl-ethanol (Table 2, entry 23; 78% ee)



Column: Chiralcel OJ  
 Eluent: Hexane/IPA = 80/20  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 14.265 min, 17.500 min

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	14.265	17.500	Time	14.813	18.218
Height(uV)	317485	236568	Height(uV)	11380	60188
Area(uV-sec)	18102188	17776126	Area(uV-sec)	493939	3900009
Area(%)	50.454	49.545	Area(%)	11.241	88.758

### Catalytic Reaction Conditions:

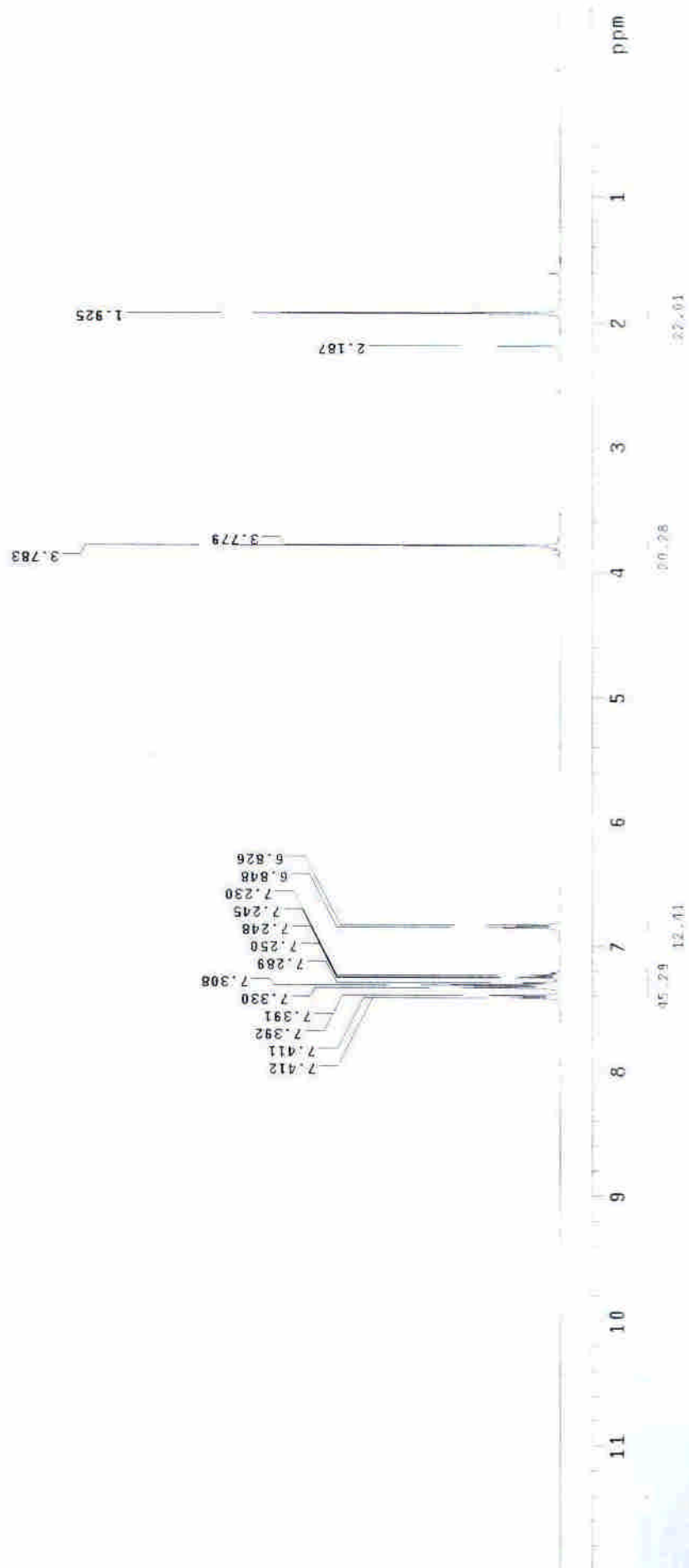
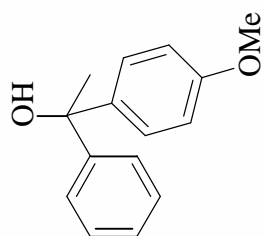
acetophenone: 0.5 mmol, (*S*)-BINOL: 10 mol%, Al(4-OMeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41-7.23 (m, 7H), 6.84 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.19 (s, 1H), 1.93 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 158.36, 148.23, 140.27, 128.01, 127.09, 126.73, 125.70, 113.36, 75.82, 55.14, 30.88 ppm.

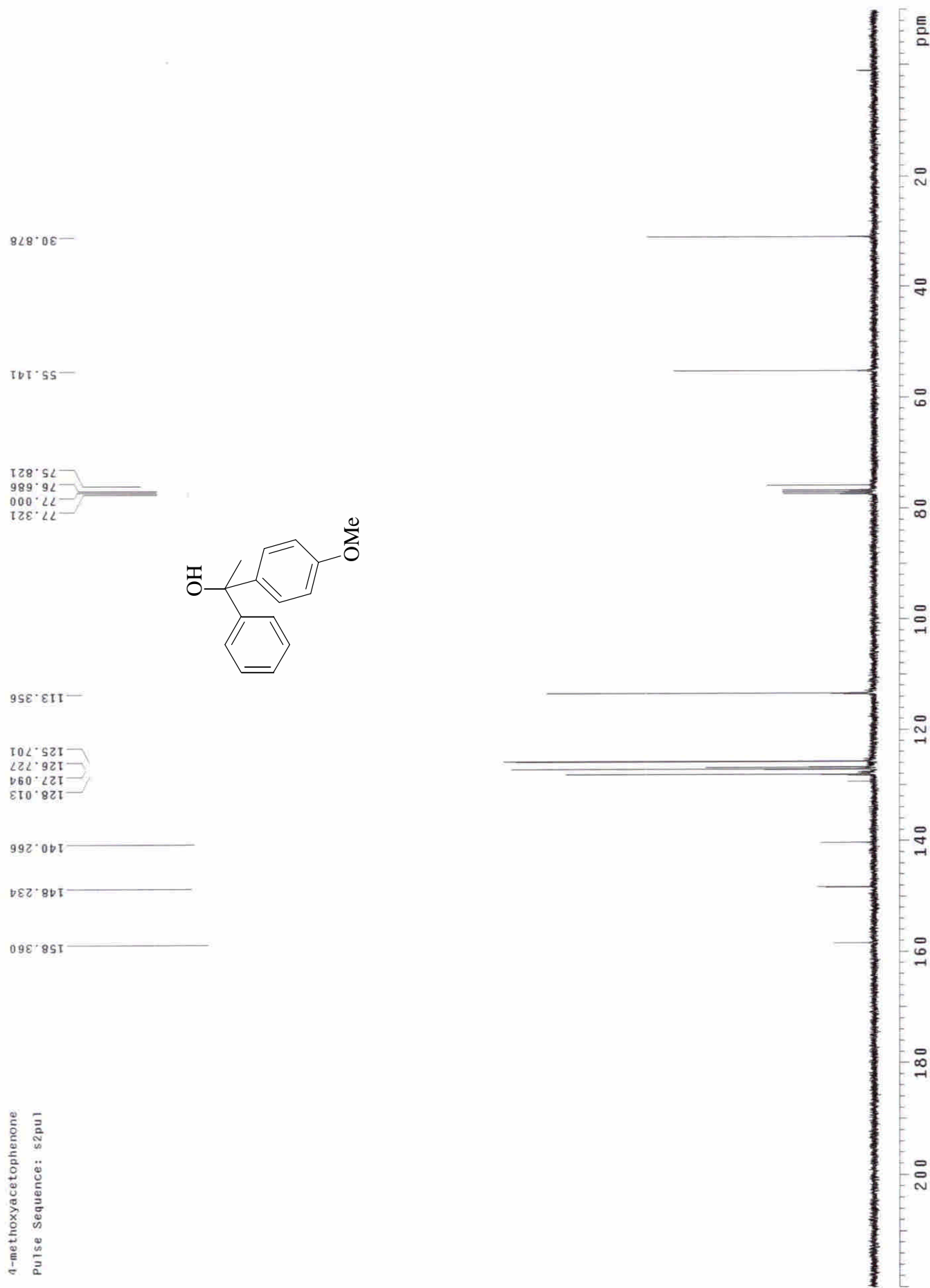
4-OMe

Pulse Sequence: h2pu1

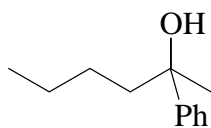


4-methoxyacetophenone

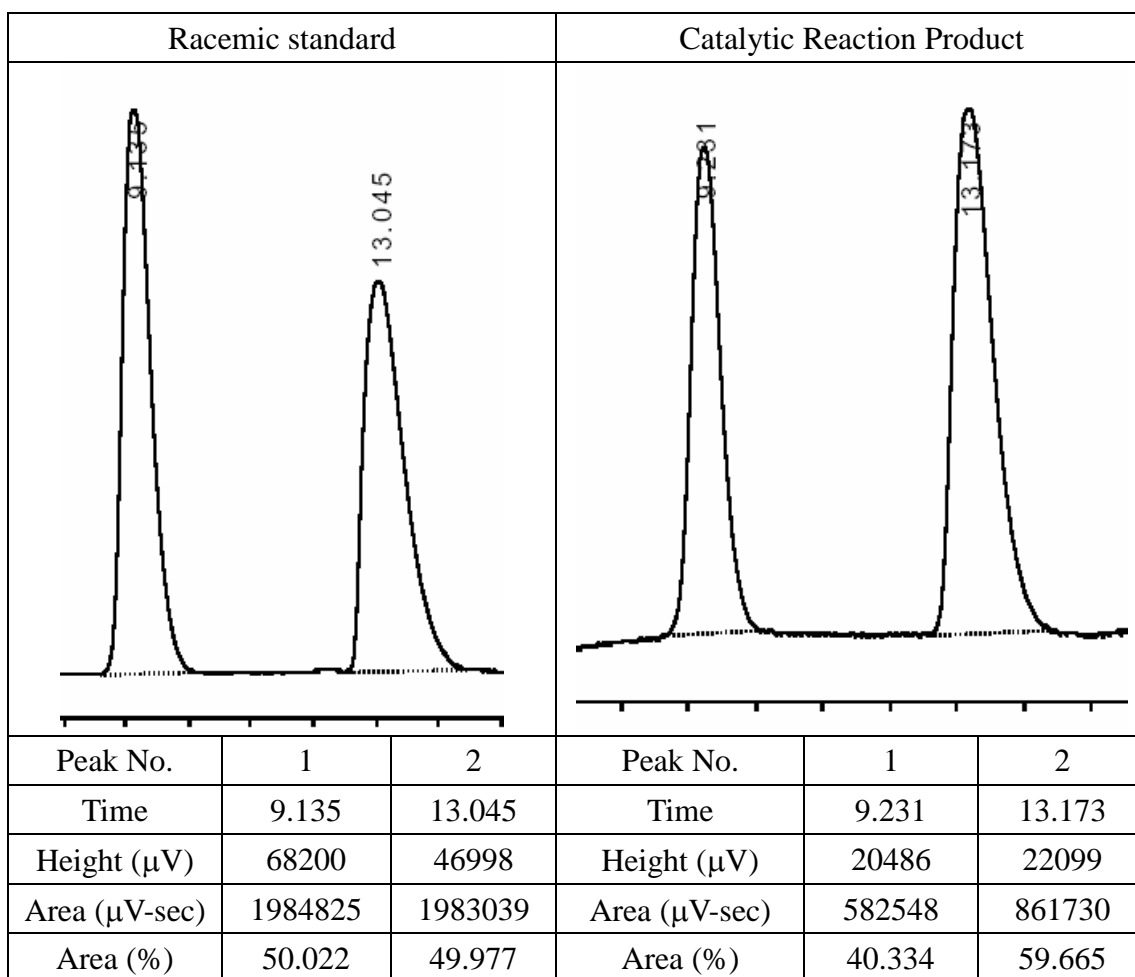
Pulse Sequence: s2pul



## 2-Phenyl-hexan-2-ol (Table 2, entry 24; 19% ee)



Column: Chiralcel OJ  
Eluent: Hexane/IPA = 99/1  
Flow rate: 1 mL/min  
Detector: UV, 254 nm  
Retention time: 9.135 min, 13.045 min



### Catalytic Reaction Conditions:

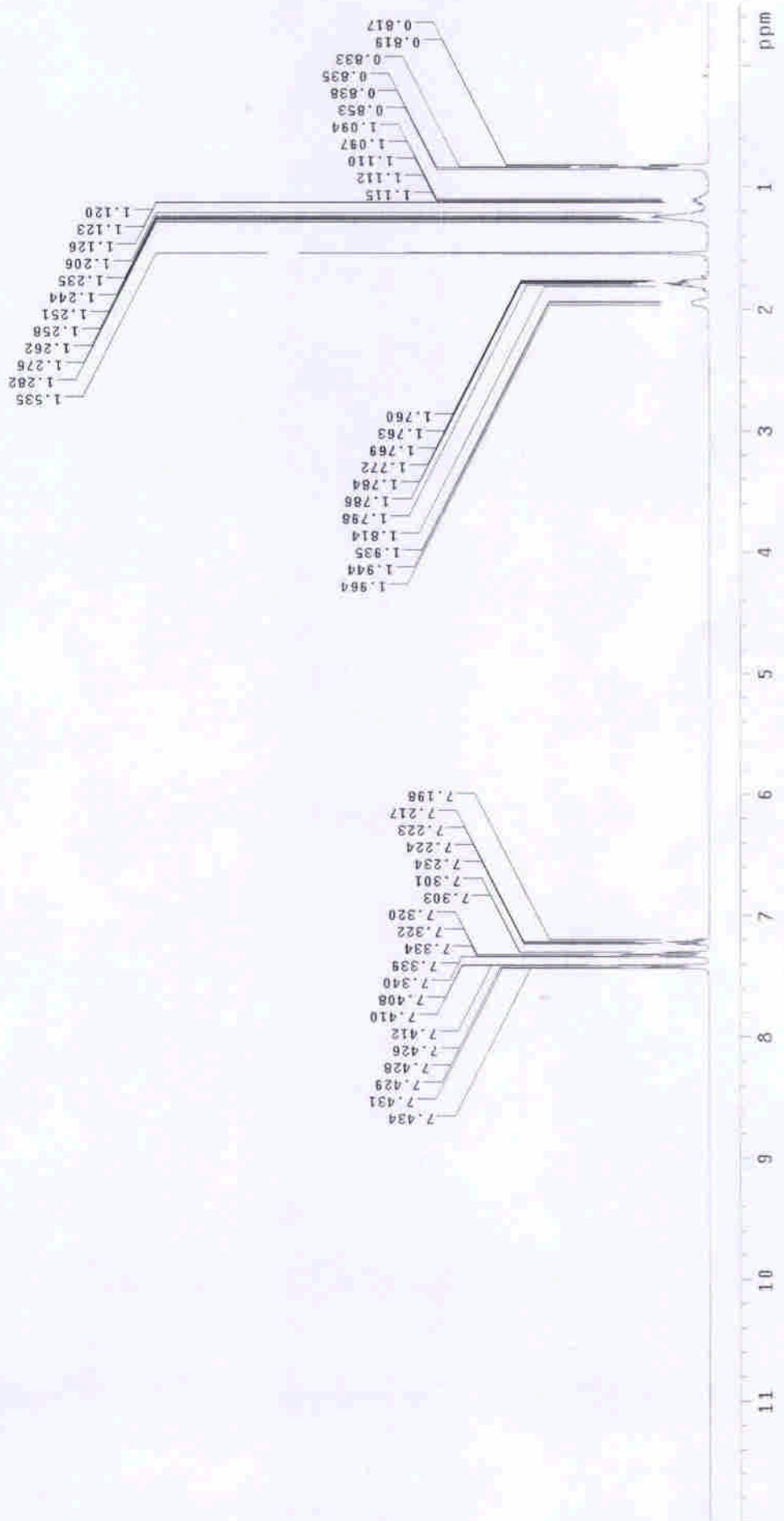
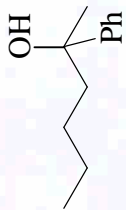
2-hexanone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(*O-i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 12 h.

### Spectroscopic Data:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43-7.41 (m, 2H), 7.34-7.30 (m, 2H), 7.23-7.20 (m, 1H), 1.95 (br, 1H), 1.81-1.76 (m, 2H), 1.54 (s, 3H), 1.28-1.21 (m, 3H), 1.13-1.09 (m, 1H), 0.85-0.82 (m, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 148.09, 128.02, 126.38, 124.74, 74.63, 43.91, 30.03, 26.10, 22.96, 13.93 ppm.

n-butyl/

Pulse Sequence: zgpg01

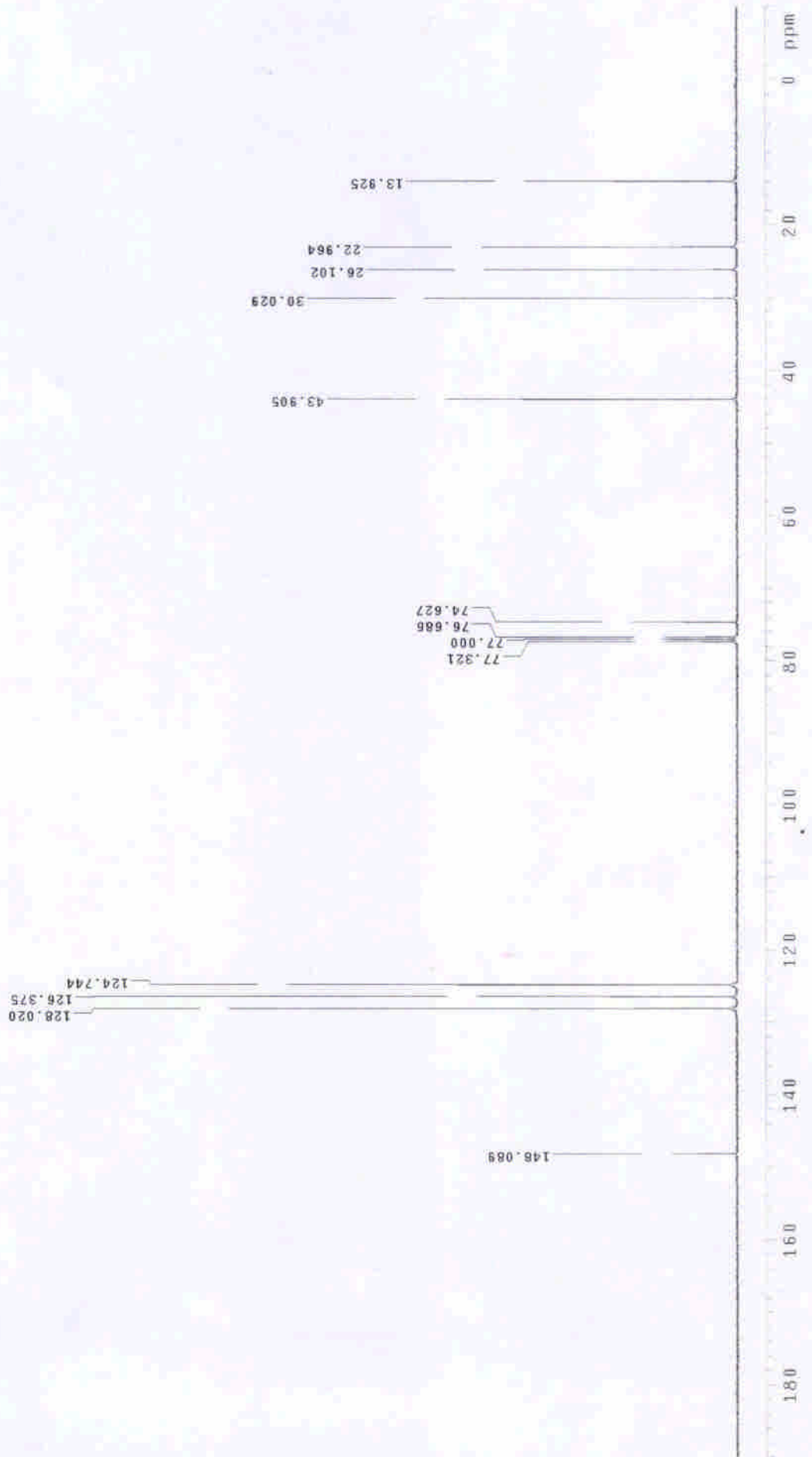
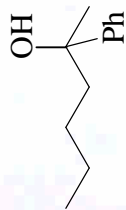


11.16 17.6216.10  
9.37 17.52 5.60

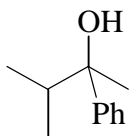
26.01

n-butyl

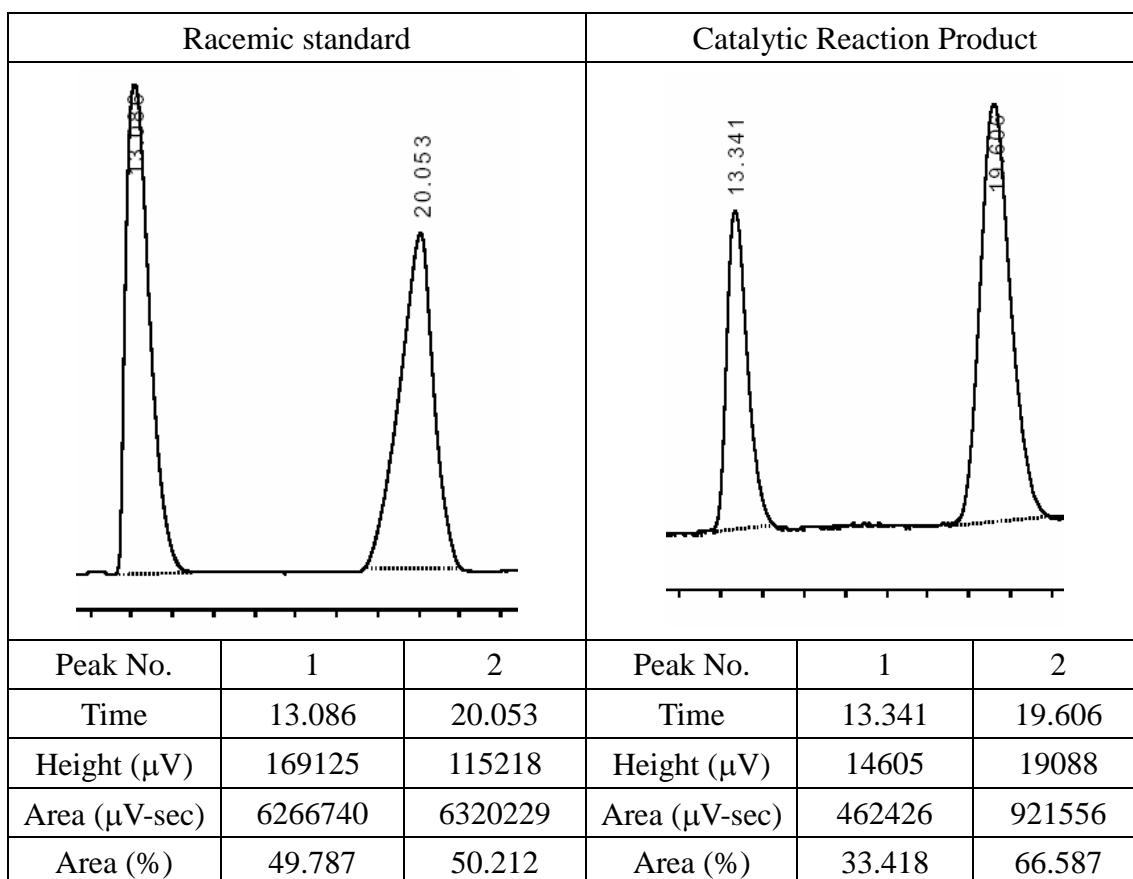
Pulse Sequence: s2pu1



### 3-Methyl-2-phenyl-butan-2-ol (Table 2, entry 25; 33% ee)<sup>2,3</sup>



Column: Chiralcel OJ  
 Eluent: Hexane/IPA = 99/1  
 Flow rate: 1 mL/min  
 Detector: UV, 254 nm  
 Retention time: 13.086 min, 20.053 min



#### Catalytic Reaction Conditions:

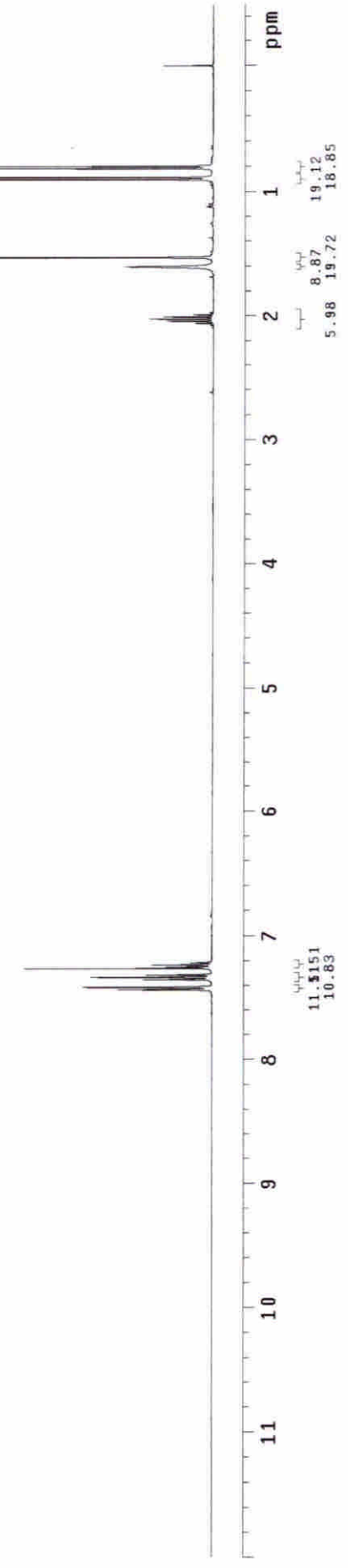
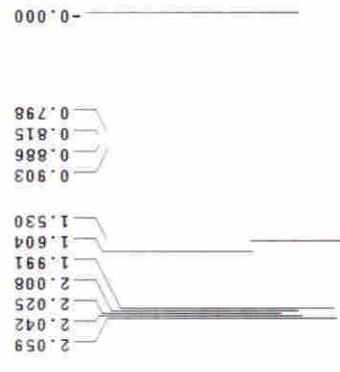
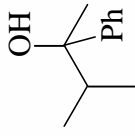
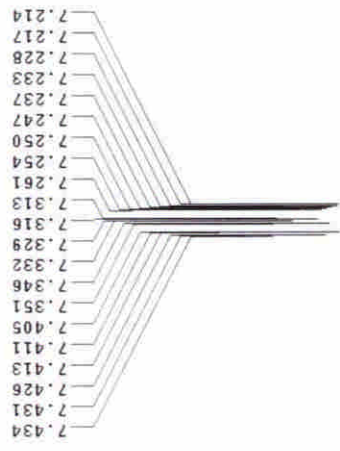
3-methyl-2-butanone: 0.5 mmol, (*S*)-BINOL: 10 mol%, AlPh<sub>3</sub>(THF): 1.25 mmol, Ti(O-*i*-Pr)<sub>4</sub>: 2.5 mmol, 0 °C, toluene: 6 mL, 36 h.

#### Spectroscopic Data:

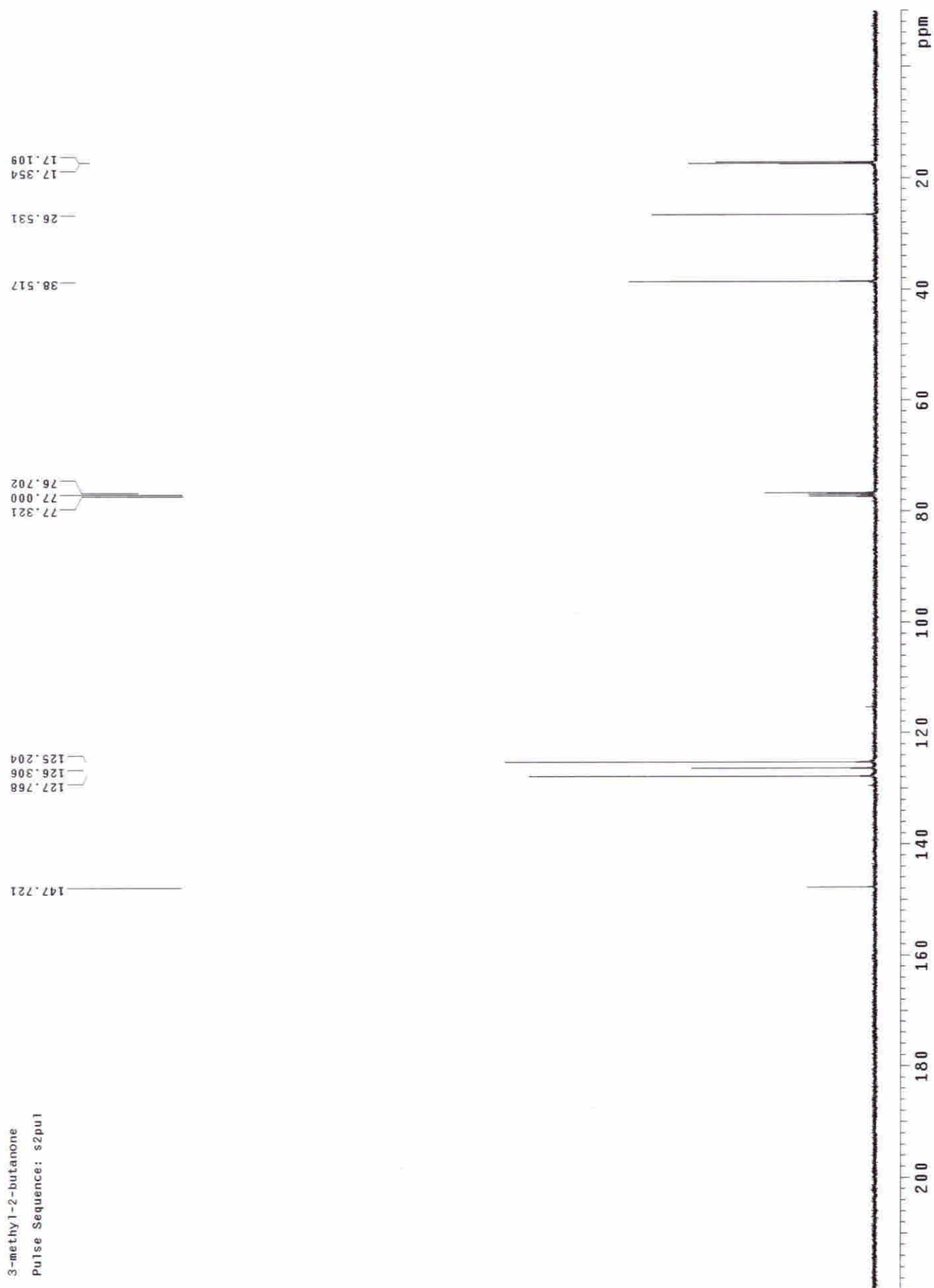
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.25-7.21 (m, 1H), 2.06-1.99 (m, 1H), 1.53 (s, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 147.72, 127.77, 126.31, 125.20, 76.70, 38.52, 26.53, 17.35, 17.11 ppm.

3-methyl-2-butanone  
Pulse Sequence: s2pu1



3-methyl-2-butanone  
Pulse Sequence: szpul



### III. References

1. a) V. Srimi, J. De Mel and J. P. Oliver, *Organometallic*, **1989**, 8, 827; b) K.-H. Wu and H.-M. Gau, *J. Am. Chem. Soc.* **2006**, 128, 14808.
2. P. I. Dosa, G. C. Fu, *J. Am. Chem. Soc.* **1998**, 120, 445.
3. C. Garcia, P. J. Walsh, *Org. Lett.* **2003**, 5, 3641.
4. O. Prieto, D. J. Ramon, M. Yus, *Tetrahedron: Asymmetry* **2003**, 14, 1955.
5. V. J. Forrat, O. Prieto, D. J. Ramon, M. Yus, *Eur. J. Chem.* **2006**, 12, 4431 & 6727.