

## Supporting Information

### **MgBr<sub>2</sub>-Promoted Enantioselective Aryl Addition of ArTi(OiPr)<sub>3</sub> to Ketones Catalyzed by a Titanium(IV) Catalyst of N,N'- Sulfonylated (1R,2R)-Cyclohexane-1,2-diamine**

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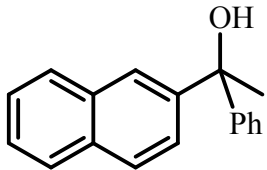
*E-mail: slzhou@mail.ahnu.edu.cn; [hmgau@dragon.nchu.edu.tw](mailto:hmgau@dragon.nchu.edu.tw)*

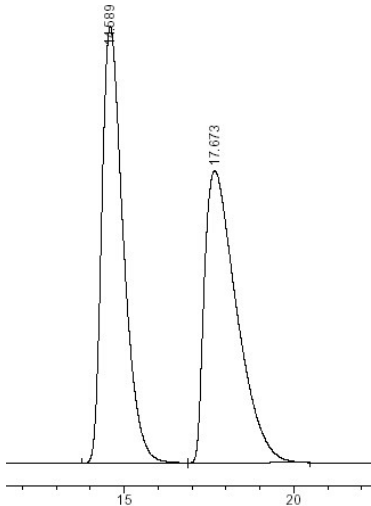
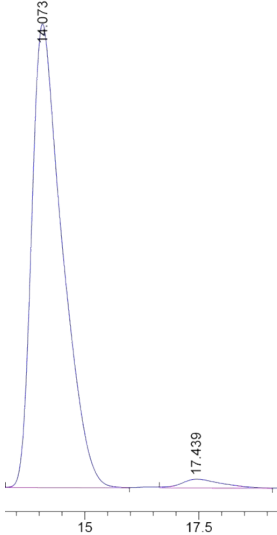
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## I. HPLC Conditions of Aryl Addition Products

1. 1-Naphthalen-2-yl-1-phenyl-ethanol (**4a**) (Table 2, entry 1, 95% ee).

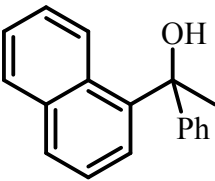
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	Eluent:	Hexane/IPA = 80/20
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	Retention time:	14.589 min, 17.673 min

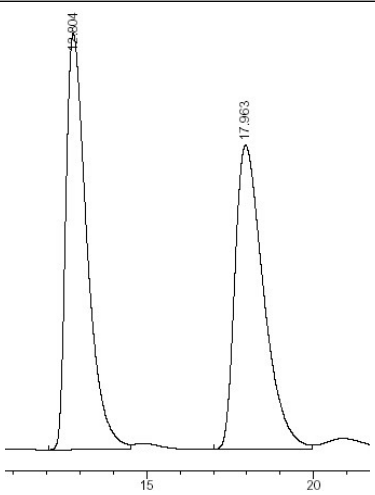
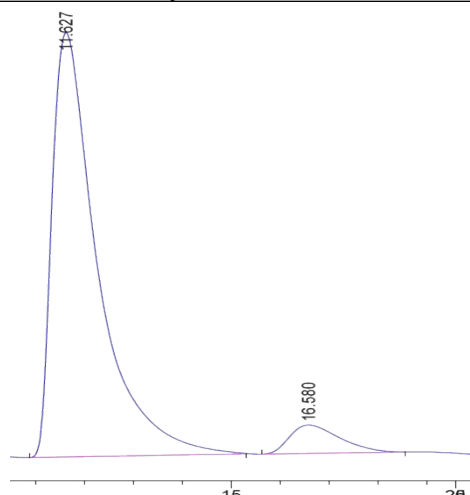
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	14.589	17.673	Time	14.073	17.439
Height (mAU)	731.907	489.963	Height (mAU)	66.324	1.270
Area (mAU-s)	$3.223 \times 10^4$	$3.226 \times 10^4$	Area (mAU-s)	3095.531	79.937
Area (%)	49.973	50.026	Area (%)	97.483	2.517

### Catalytic Reaction Conditions:

2'-acetonaphthone: 0.5 mmol, **1h**: 10 mol%, MgBr<sub>2</sub>: 20 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 16 h.

2. 1-Naphthalen-1-yl-1-phenyl-ethanol (**4b**)(Table 2, entry 2, 86% ee).

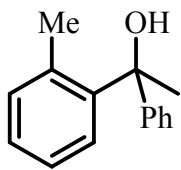
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	12.804 min, 17.963 min

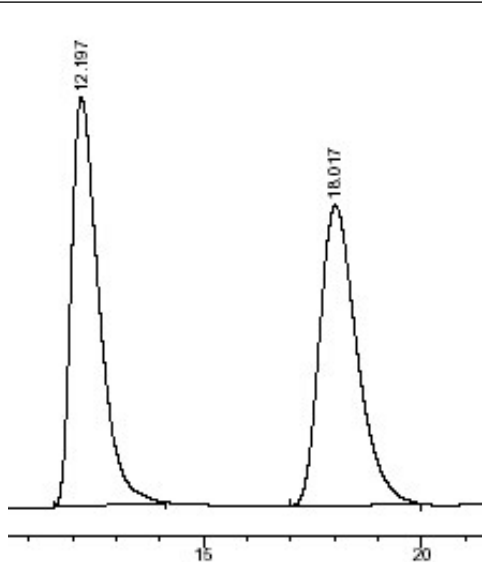
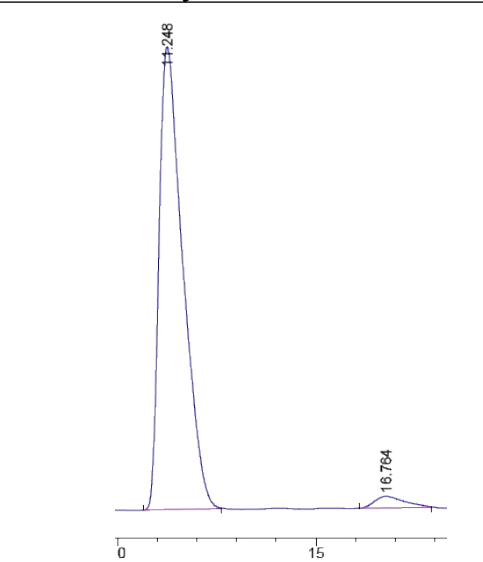
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	12.804	17.963	Time	11.627	16.580
Height (mAU)	186.591	136.297	Height (mAU)	108.484	7.280
Area (mAU-s)	8162.958	8114.976	Area (mAU-s)	7011.706	516.543
Area (%)	50.147	49.852	Area (%)	93.139	6.861

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 10 mol%, MgBr<sub>2</sub>: 20 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 72 h.

3. 1-phenyl-1-*o*-tolyl-ethanol (**4c**) (Table 2, entry 3, 94% ee)

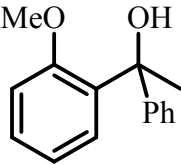
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	12.197 min, 18.017 min

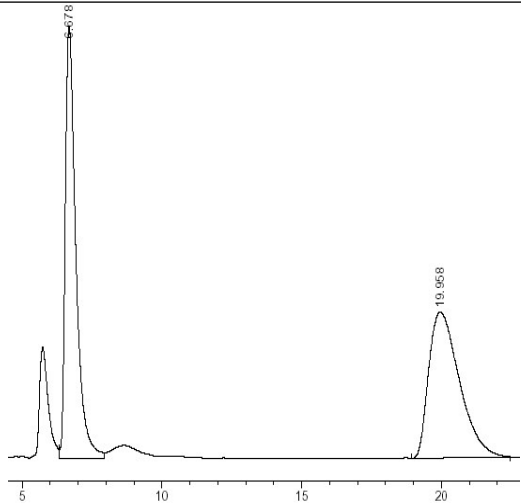
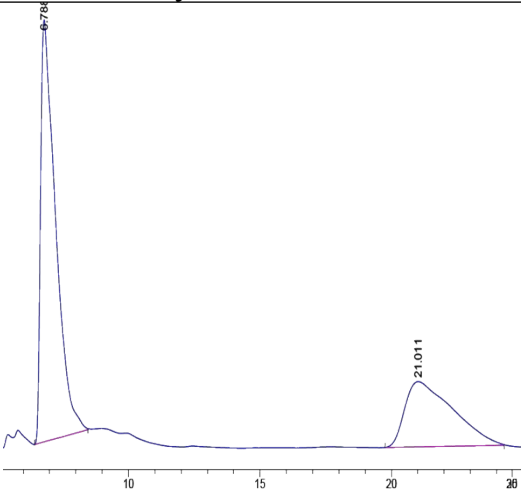
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	12.197	18.017	Time	11.248	16.754
Height (mAU)	56.667	41.683	Height (mAU)	50.971	1.284
Area (mAU-s)	2499.153	2468.502	Area (mAU-s)	2107.530	68.349
Area (%)	50.308	49.691	Area (%)	96.859	3.141

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

4. 1-(2-Methoxyphenyl)-1-phenyl-ethanol (**4d**) (Table 2, entry 4, 34% ee)

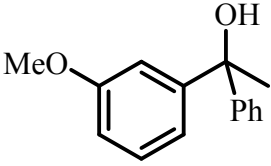
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 80/20
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	6.678 min, 19.958 min

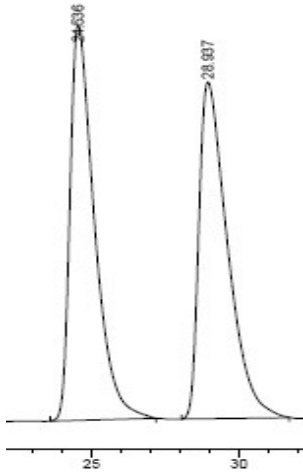
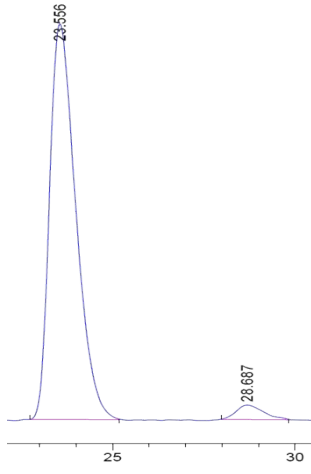
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	6.678	19.958	Time	6.788	21.011
Height (mAU)	120.649	40.907	Height (mAU)	43.710	6.766
Area (mAU-s)	3173.506	3124.634	Area (mAU-s)	1730.966	855.851
Area (%)	50.388	49.612	Area (%)	66.915	33.085

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 36 h.

5. 1-(3-Methoxyphenyl)-1-phenylethanol (**4e**)(Table 2, entry 5, 93% ee)

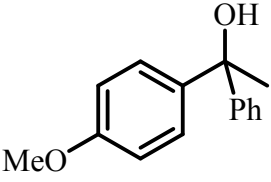
	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 98/2
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	25.536 min, 28.937 min

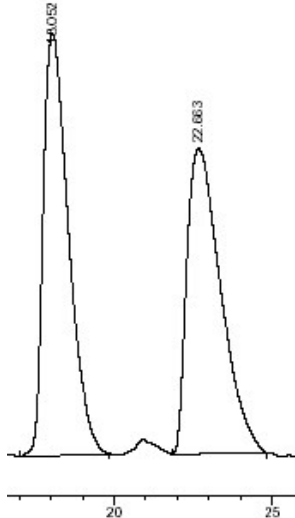
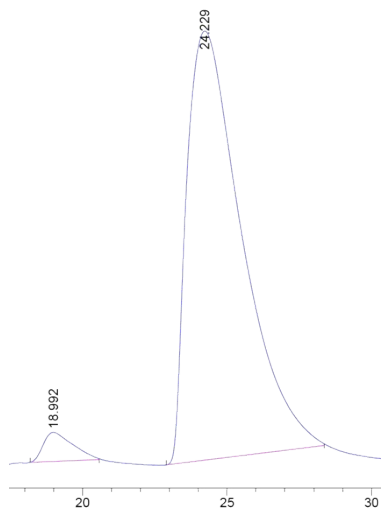
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	25.536	28.937	Time	23.556	28.687
Height (mAU)	74.2554	63.1799	Height (mAU)	34.786	1.285
Area (mAU-s)	4273.9565	4255.1719	Area (mAU-s)	1738.220	66.923
Area (%)	50.1101	49.8899	Area (%)	96.293	3.707

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 16 h.

6. 1-(4-Methoxyphenyl)-1-phenyl-ethanol (**4f**) (Table 2, entry 6, 93% ee).

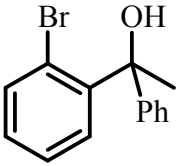
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 80/20
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	18.052 min, 22.663 min

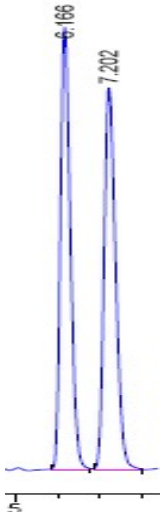
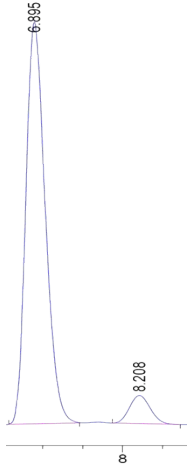
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	18.052	22.663	Time	18.992	24.229
Height (mAU)	55.824	40.397	Height (mAU)	1.773	26.087
Area (mAU-s)	3088.596	3007.313	Area (mAU-s)	125.512	3449.815
Area (%)	50.666	49.333	Area (%)	3.511	96.490

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 10 mol%, MgBr<sub>2</sub>: 20 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

7. 1-(2-Bromophenyl)-1-phenyl-ethanol (**4g**)(Table 2, entry 7, 85% ee).

	Column:	Chiralcel OD-H
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	6.166 min, 7.202 min

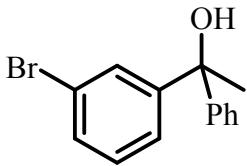
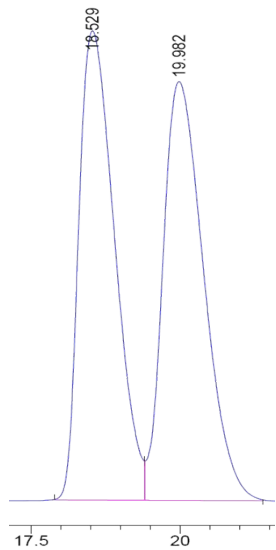
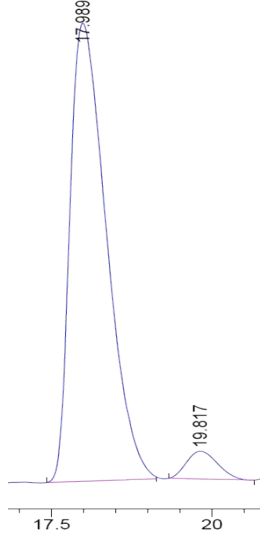
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	6.166	7.202	Time	6.895	8.208
Height (mAU)	236.7261	204.1879	Height (mAU)	99.140	6.939
Area (mAU-s)	3790.7075	3803.9639	Area (mAU-s)	1665.955	124.514
Area (%)	49.9127	50.0873	Area (%)	93.046	6.954

**Catalytic Reaction Conditions:**

2'-Bromoacetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 72 h.



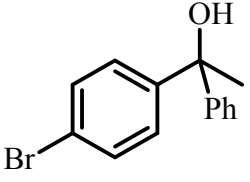
8. 1-(3-Bromophenyl)-1-phenyl-ethanol (**4h**) (Table 2, entry 8, 90% ee).

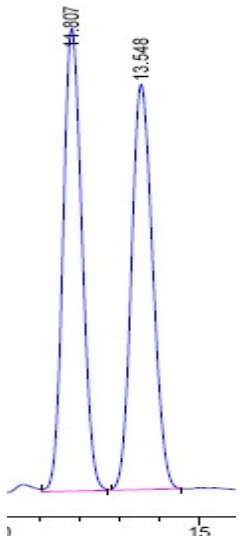
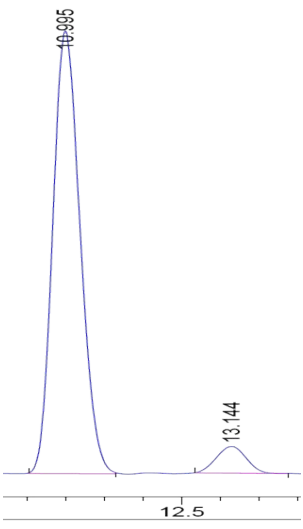
	Column:		Chiralcel OD		
	Eluent:		Hexane/IPA = 99/1		
	Flow rate:		1 mL/min		
	Detector:		UV, 254 nm		
	Retention time:		18.529 min, 19.982 min		
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	18.529	19.982	Time	17.989	19.817
Height (mAU)	53.103	47.398	Height (mAU)	49.034	2.964
Area (mAU-s)	2211.78	2246.756	Area (mAU-s)	1928.094	100.131
Area (%)	49.608	50.392	Area (%)	95.063	4.937

**Catalytic Reaction Conditions:**

3'-Bromoacetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

9. 1-(4-Bromophenyl)-1-phenyl-ethanol (**4i**) (Table 2, entry 9, 88% ee).

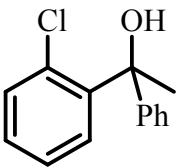
	Column:	Chiralcel OD-H
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	11.907 min, 13.548 min



Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	11.807	13.548	Time	10.995	13.144
Height (mAU)	31.051	27.209	Height (mAU)	58.57137	3.538
Area (mAU-s)	1019.858	1004.815	Area (mAU-s)	1439.485	95.546
Area (%)	50.372	49.628	Area (%)	93.776	6.224

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 10 mol%, MgBr<sub>2</sub>: 20 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 16 h.

10. 1-(2-Chlorophenyl)-1-phenyl-ethanol (**4j**) (Table 2, entry 10, 80% ee)

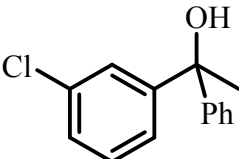
	Column:	Chiralcel OD-H
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	6.203 min, 7.244 min

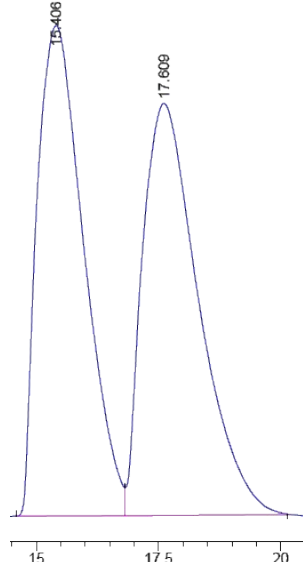
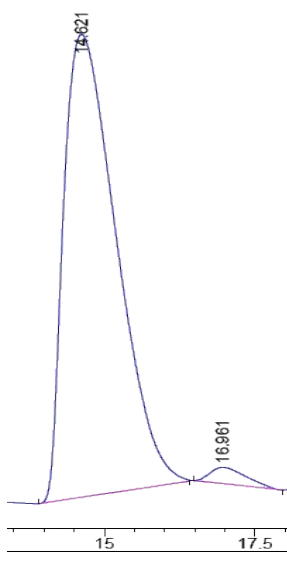
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	6.203	7.244	Time	6.220	7.066
Height (mAU)	286.004	250.572	Height (mAU)	26.053	2.653
Area (mAU-s)	5065.582	48.657	Area (mAU-s)	350.191	39.911
Area (%)	5345.219	51.343	Area (%)	89.769	10.231

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 36 h.

11. 1-(3-Chlorophenyl)-1-phenyl-ethanol (**4k**) (Table 2, entry 11, 90% ee)

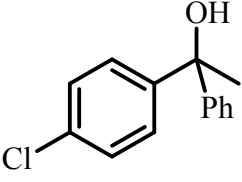
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 97/3
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	15.406min, 17.609 min

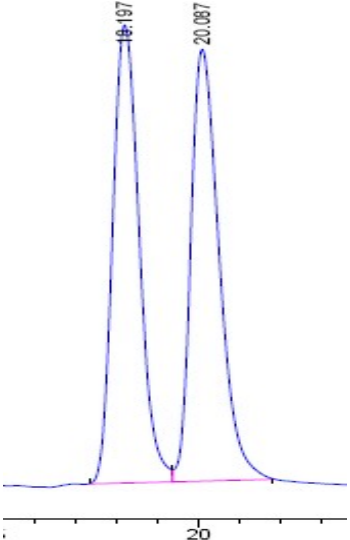
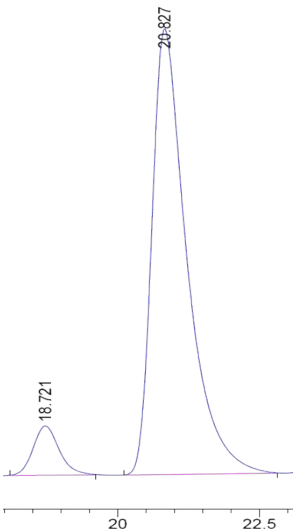
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	15.406	17.609	Time	14.621	16.961
Height (mAU)	66.665	55.981	Height (mAU)	26.596	9.474
Area (mAU-s)	4414.11	4464.991	Area (mAU-s)	1611.219	39.527
Area (%)	49.714	50.286	Area (%)	97.606	2.394

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

12. 1-(4-Chlorophenyl)-1-phenyl-ethanol (**4I**) (Table 2, entry 12, 85% ee).

	Column:	Chiralcel AD
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	18.197 min, 20.087 min

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	18.197	20.087	Time	18.721	20.827
Height (mAU)	66.275	62.460	Height (mAU)	10.303	93.109
Area (mAU-s)	2972.738	2991.497	Area (mAU-s)	330.591	4002.524
Area (%)	49.843	50.157	Area (%)	7.629	92.371

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

13. 1-(4-trifluoromethylphenyl)-1-phenyl-ethanol (**4m**) (Table 2, entry 13, 87% ee)

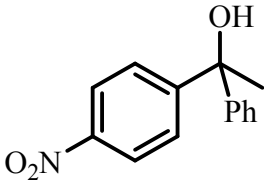
	Column:	Chiralcel AD
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	13.744 min, 15.408 min

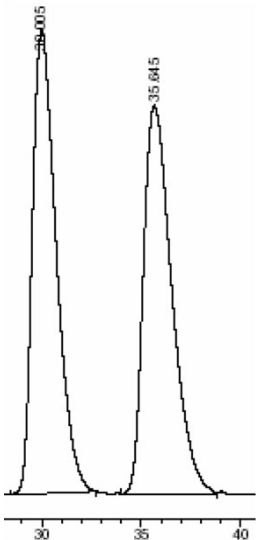
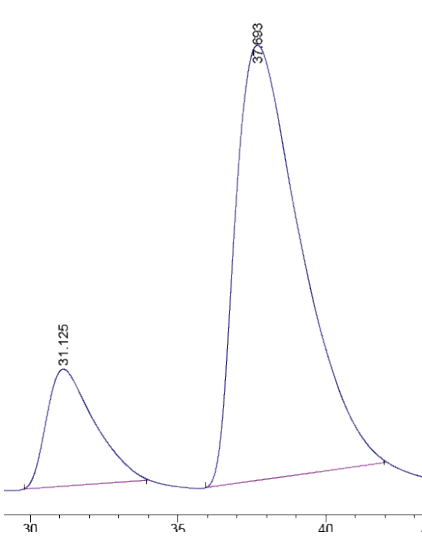
Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	13.744	15.408	Time	13.240	14.387
Height (mAU)	8.2054	7.6166	Height (mAU)	112.193	963.729
Area (mAU-s)	376.8533	360.0422	Area (mAU-s)	2521.834	3.494
Area (%)	51.1407	48.8593	Area (%)	6.731	93.269

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

14. 1-(4-Nitrophenyl)-1-phenyl-ethanol (**4n**) (Table 2, entry 14, 67% ee)

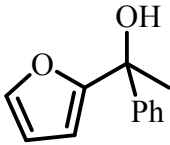
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	30.005 min, 35.645 min

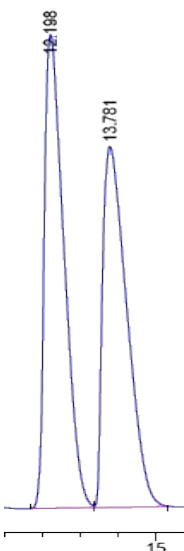
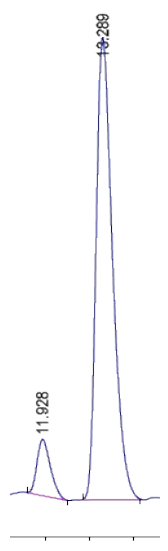
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	30.005	35.645	Time	31.125	37.693
Height (mAU)	84.264	70.742	Height (mAU)	22.037	81.856
Area (mAU-s)	6985.151	7011.107	Area (mAU-s)	2476.117	1.264
Area (%)	49.907	50.092	Area (%)	16.383	83.617

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>*i*</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

15. 1-(Furan-2-yl)-1-phenyl-ethanol (**4o**) (Table 2, entry 15, 82% ee)

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	12.198 min, 13.781 min

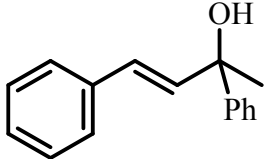
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	12.198	13.781	Time	11.928	13.289
Height (mAU)	307.4265	234.2073	Height (mAU)	2.159	17.708
Area (mAU-s)	11142.6	10469.8	Area (mAU-s)	45.468	457.269
Area (%)	51.5566	48.4434	Area (%)	9.044	90.956

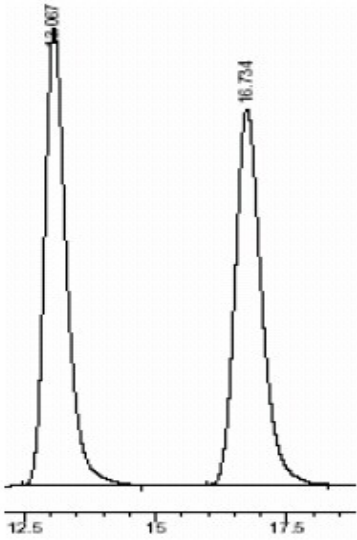
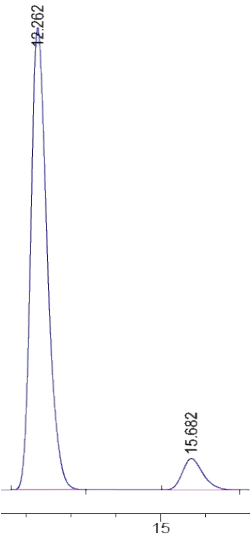
**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.



16. 2,4-Diphenyl-but-3-en-2-ol (**4p**) (Table 2, entry 16, 84% ee)

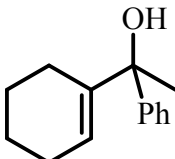
	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	13.067 min, 16.734 min

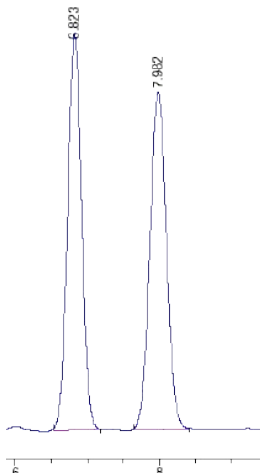
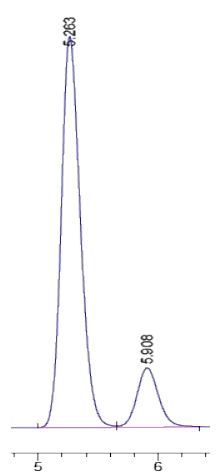
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	13.067	16.734	Time	12.262	15.682
Height (mAU)	165.473	135.582	Height (mAU)	1811.658	122.743
Area (mAU-s)	4742.026	4721.952	Area (mAU-s)	4.590×10 <sup>4</sup>	3909.238
Area (%)	50.106	49.893	Area (%)	92.151	7.849

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 18 h.

17. 1-(Cyclohexen-1-yl)-1-phenyl-ethanol(**4q**) (Table 2, entry 17, 71% ee)

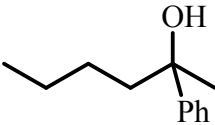
	Column:	Chiralcel OD-H
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	6.823 min, 7.982 min

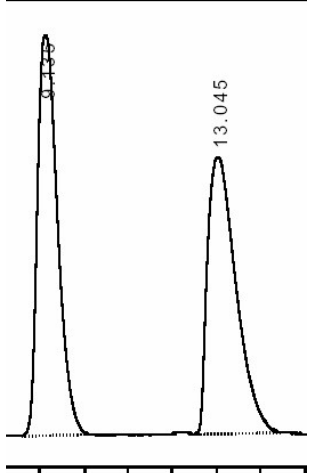
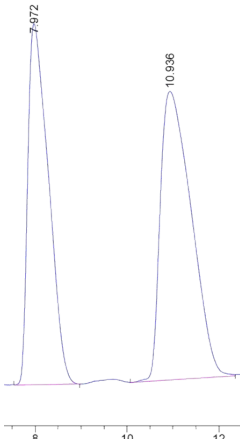
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	6.823	7.982	Time	5.263	5.908
Height (mAU)	7.466	6.364	Height (mAU)	87.871	13.342
Area (mAU-s)	100.555	101.523	Area (mAU-s)	972.832	167.848
Area (%)	49.760	50.239	Area (%)	85.285	14.714

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 48 h.

18. 2-Phenyl-hexan-2-ol (**4r**) (Table 2, entry 18, 13% ee)

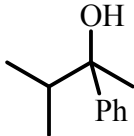
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	9.135 min, 13.045 min

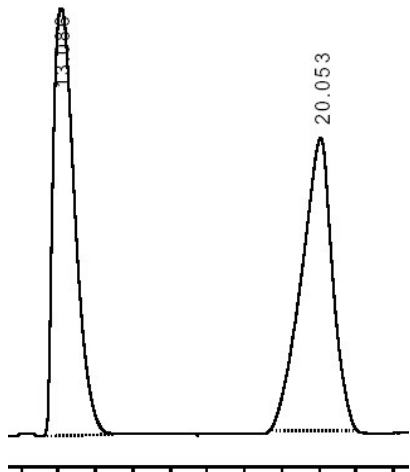
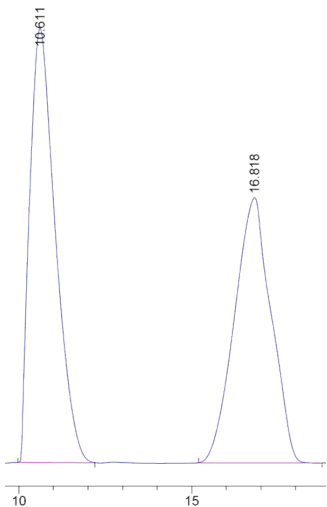
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	9.135	13.045	Time	7.972	10.936
Height (mAU)	68200	46998	Height (mAU)	8.118	6.484
Area (mAU-s)	1984825	1983039	Area (mAU-s)	252.862	301.0
Area (%)	50.022	49.977	Area (%)	45.490	54.510

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

19. 3-Methyl-2-Phenyl-butan-2-ol (**4s**) (Table 2, entry 19, 7% ee)

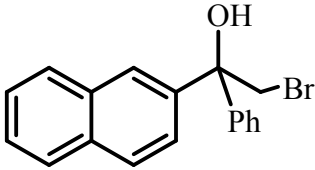
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	13.086 min, 20.053 min

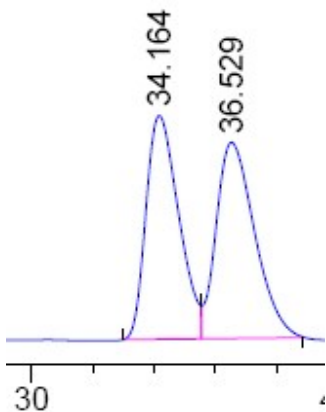
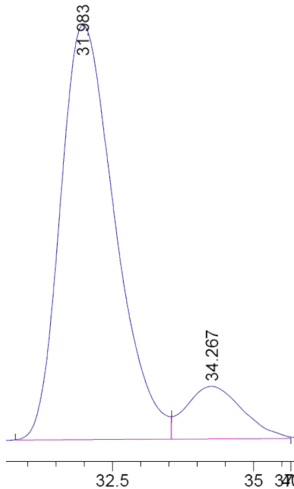
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	13.086	20.053	Time	10.611	16.818
Height (mAU)	169125	115218	Height (mAU)	153.143	93.587
Area (mAU-s)	6266740	6320229	Area (mAU-s)	7869.380	6905.077
Area (%)	49.787	50.212	Area (%)	53.263	46.737

**Catalytic Reaction Conditions:**

1'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

20. 2-Bromo-1-(naphthalen-2-yl)-1-phenyl-ethanol (**4t**) (Table 2, entry 20, 78% ee)

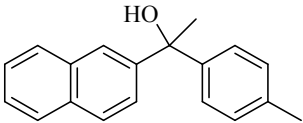
	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	34.164 min, 36.529 min

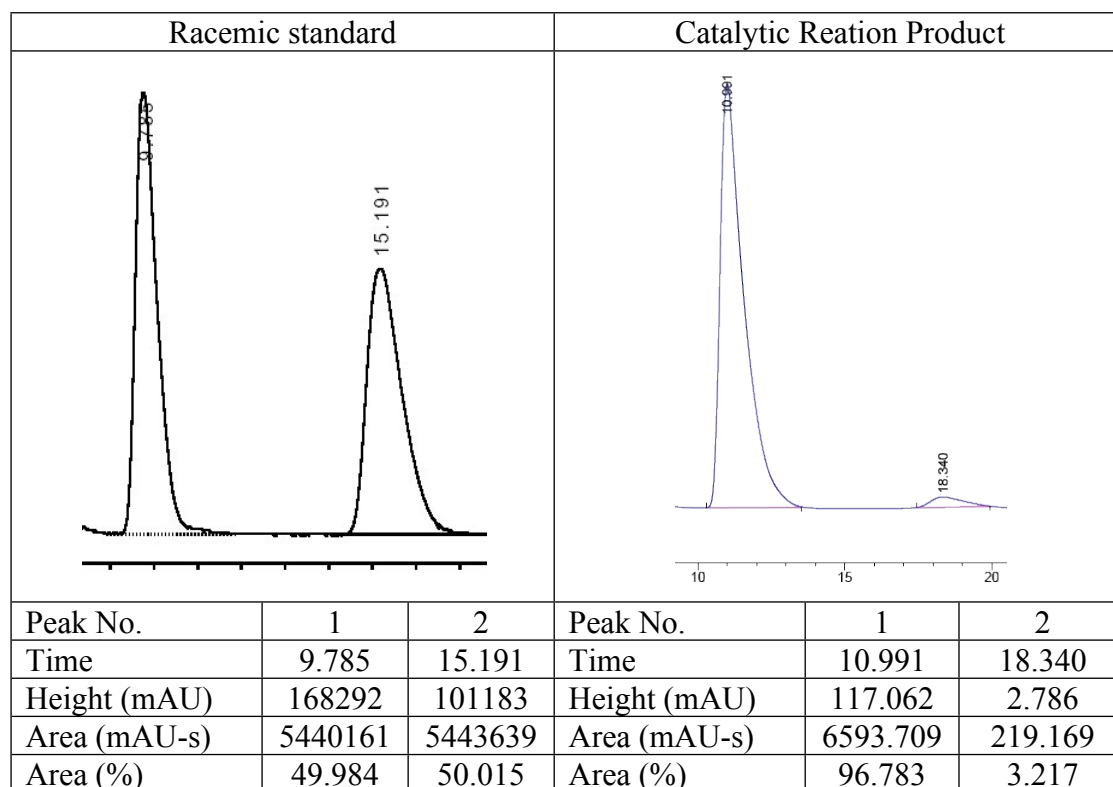
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	34.164	36.529	Time	31.983	34.267
Height (mAU)	98.1797	86.0638	Height (mAU)	41.870	5.309
Area (mAU-s)	7341.985	7555.035	Area (mAU-s)	2804.885	371.020
Area (%)	49.2849	50.7151	Area (%)	88.318	11.682

**Catalytic Reaction Conditions:**

$\alpha$ -bromo-2'-acetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

21 1-(Naphthalen-2-yl)-1-(*p*-tolyl)ethanol (**4u**) (Table 2, entry 21, 93% ee)

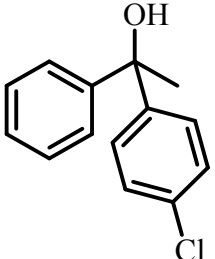
	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 70/30
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	9.785 min, 15.191 min

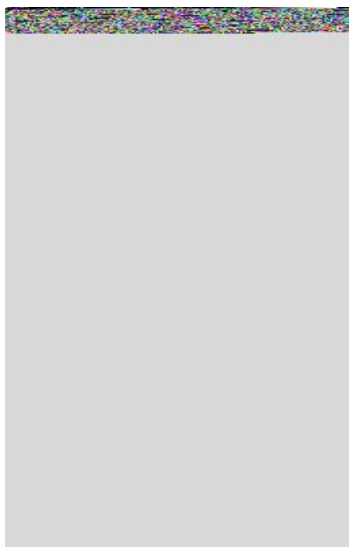
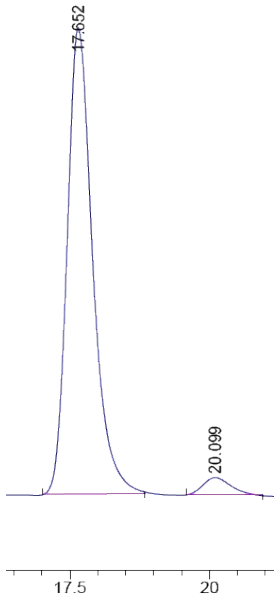


**Catalytic Reaction Conditions:**

2'-acetonaphthone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>*i*</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

22. 1-(4-Chlorophenyl)-1-phenyl-ethanol (**4l'**) (Table 2, entry 22, 91% ee)

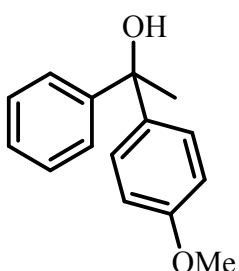
	Column:	Chiralcel OD-H
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	18.197 min, 20.087 min

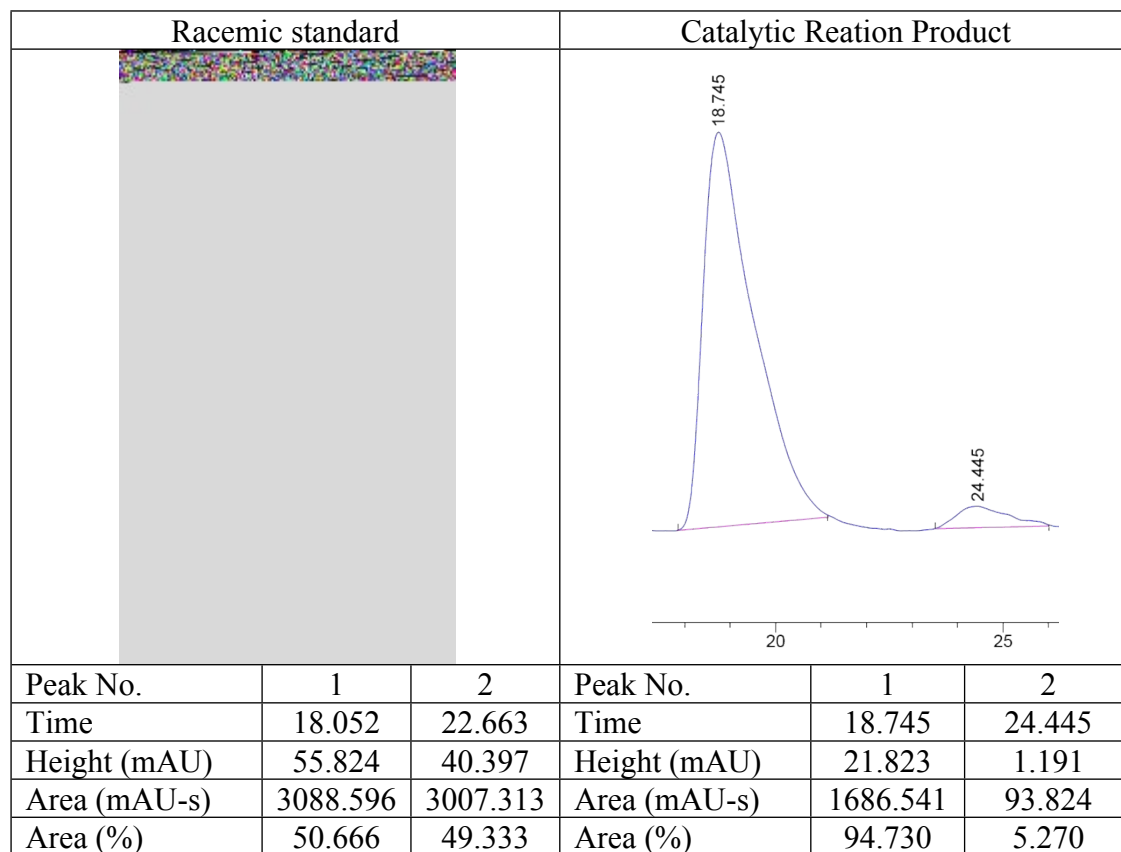
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	18.197	20.087	Time	17.652	20.099
Height (mAU)	66.275	62.460	Height (mAU)	46.255	1.772
Area (mAU-s)	2972.738	2991.497	Area (mAU-s)	1466.223	64.259
Area (%)	49.843	50.157	Area (%)	95.801	4.199

**Catalytic Reaction Conditions:**

1'-acetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

22. 1-(4-Methoxyphenyl)-1-phenyl-ethanol (**4f**) (Table 2, entry 22, 90% 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

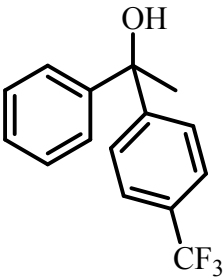


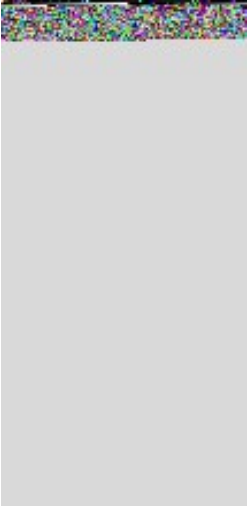
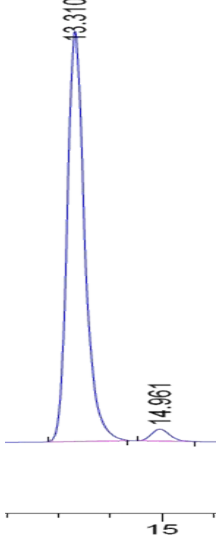
**Catalytic Reaction Conditions:**

1'-acetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.



23. 1-(4-Trifluoromethylphenyl)-1-phenyl-ethanol (**4n'**) (Table 2, entry 23, 93% ee)

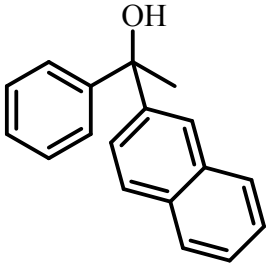
	Column:	Chiralcel AD
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	13.744 min, 15.408 min

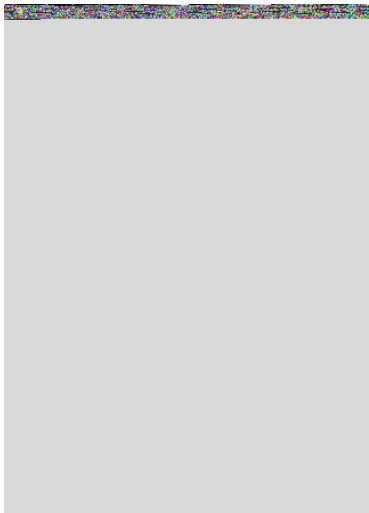
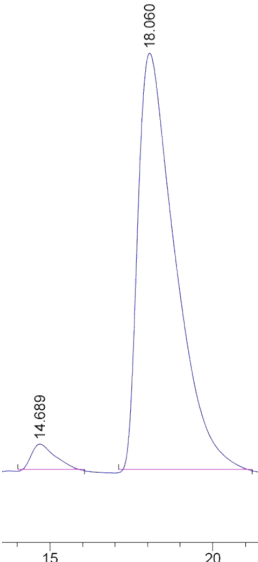
Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	13.744	15.408	Time	13.310	14.961
Height (mAU)	8.2054	7.6166	Height (mAU)	91.494	2.691
Area (mAU-s)	376.8533	360.0422	Area (mAU-s)	2177.172	67.132
Area (%)	51.1407	48.8593	Area (%)	97.009	2.991

**Catalytic Reaction Conditions:**

1'-acetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0 °C, toluene: 5 mL, 24 h.

24. 1-(Naphthalen-2-yl)-1-phenyl-ethanol (**4a'**) (Table 2, entry 24, 92% 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	14.689	18.060
Height (mAU)	731.907	489.963	Height (mAU)	6.328	97.729
Area (mAU-s)	$3.223 \times 10^4$	$3.226 \times 10^4$	Area (mAU-s)	341.546	7840.168
Area (%)	49.973	50.026	Area (%)	4.175	95.825

**Catalytic Reaction Conditions:**

1'-acetophenone: 0.5 mmol, **1h**: 12 mol%, MgBr<sub>2</sub>: 24 mol%, TiPh(O<sup>i</sup>Pr)<sub>3</sub>: 0.95 mmol, 0°C, toluene: 5 mL, 48 h.

## II. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

