

Electronic Supplementary Information

Instantaneous Room-Temperature and Highly Enantioselective $\text{ArTi}(\text{O-}i\text{-Pr})_3$

Additions to Aldehydes for the Synthesis of Diarylmethanols

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Table of Contents

I.	Experimental Section	S3
I.1	General Remarks	S3
I.2	General Procedures for the Synthesis of ArTi(O-<i>i</i>-Pr)₃	S3
I.3	General Procedures for the Asymmetric ArTi(O-<i>i</i>-Pr)₃ Addition Reaction of Aldehydes	S3
II.	Reaction Conditions, HPLC Conditions and Chromatograms, ¹H and ¹³C NMR Spectroscopic Data of ArTi(O-<i>i</i>-Pr)₃ Addition Products of Aldehydes	S4
II.1.	(<i>R</i>)-(2-Methyl-phenyl)-phenyl-methanol ((<i>R</i>)- 9a)	S4
II.2.	(<i>R</i>)-(4-Methyl-phenyl)-phenyl-methanol ((<i>R</i>)- 9b)	S5
II.3.	(<i>R</i>)-(2-Methoxyphenyl)-phenyl-methanol ((<i>R</i>)- 9c)	S6
II.4.	(<i>R</i>)-(3-Methoxy-phenyl)-phenyl-methanol ((<i>R</i>)- 9d)	S7
II.5.	(<i>R</i>)-(4-Methoxy-phenyl)-phenyl-methanol ((<i>R</i>)- 9e)	S8
II.6.	(<i>R</i>)-Naphthalen-1-yl-phenyl-methanol ((<i>R</i>)- 9f)	S9
II.7.	(<i>R</i>)-Naphthalen-2-yl-phenyl-methanol ((<i>R</i>)- 9g)	S10
II.8.	(<i>R</i>)-(2-Chloro-phenyl)-phenyl-methanol ((<i>R</i>)- 9h)	S11
II.9.	(<i>R</i>)-(3-Chloro-phenyl)-phenyl-methanol ((<i>R</i>)- 9i)	S12
II.10.	(<i>R</i>)-(4-Chloro-phenyl)-phenyl-methanol ((<i>R</i>)- 9j)	S13
II.11.	(<i>R</i>)-Phenyl-(4-trifluoromethylphenyl)-methanol ((<i>R</i>)- 9k)	S14
II.12.	(<i>S</i>)-(<i>E</i>)-1,3-Diphenyl-prop-2-en-1-ol ((<i>S</i>)- 9l)	S15
II.13.	(<i>R</i>)-(Furan-2-yl)-phenyl-methanol ((<i>R</i>)- 9m)	S16
II.14.	(<i>S</i>)-1-Phenyl-pentan-1-ol ((<i>S</i>)- 9n)	S17
II.15.	(<i>S</i>)-2-methyl-1-phenyl-propan-1-ol ((<i>S</i>)- 9o)	S18
II.16.	(<i>S</i>)-2,2-Dimethyl-1-phenyl-propan-1-ol ((<i>S</i>)- 9p)	S19
II.17.	(<i>S</i>)-(4-Methyl-phenyl)-phenyl-methanol ((<i>S</i>)- 9b)	S20
II.18.	(<i>S</i>)-(4-Methoxy-phenyl)-phenyl-methanol ((<i>S</i>)- 9e)	S21
II.19.	(<i>S</i>)-(Naphthalen-2-yl)-phenyl-methanol ((<i>S</i>)- 9g)	S22
II.20.	(<i>S</i>)-(4-Chloro-phenyl)-phenyl-methanol ((<i>S</i>)- 9l)	S23
II.21.	(<i>S</i>)-(4-bromo-phenyl)-phenyl-methanol ((<i>S</i>)- 9q)	S24
III.	Linear Effect Study of PhTi(O-<i>i</i>-Pr)₃ Additions to 2-Naphthylaldehyde Catalyzed by <i>rac</i>-H₈-BINOL or <i>x</i> mol% (<i>R</i>)-H₈-BINOL	S25
III.1.	HPLC Conditions and Chromatograms of Linear Effect Study	S25
III.2.	Ee Values of (<i>R</i>)- 9g of the Linear Effect Study	S26
III.3.	The Reaction Condition and HPLC Chromatogram of the Autocatalysis Study	S26
IV.	References	S27

I. Experimental Section

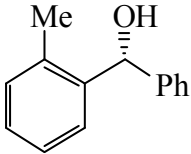
I.1. General Remarks. $\text{ArTi}(\text{O-}i\text{-Pr})_3$,¹ (1*R*,2*R*)-*N,N'*-bis(trifluoromethylsulfonyl)-1,2-cyclohexanediamine (2),² 1,2:5,6-di-*O*-isopropylidene-*D*-mannitol (3),³ $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (4),⁴ and $[\text{Ti}\{\text{H}_8\text{-}(R)\text{-BINOLate}\}(\text{O-}i\text{-Pr})_2]_x$ ((*R*)-7)⁵ were prepared according to literature procedures. $\text{Ti}(\text{O-}i\text{-Pr})_4$ was freshly distilled prior to use. (*S*)-BINOL ((*S*)-5) and (*R*)-H₈-BINOL ((*R*)-6) were obtained commercially. All syntheses and manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Solvents were dried by refluxing for at least 24 h over P₂O₅ (dichloromethane) or sodium/benzophenone (THF, *n*-hexane or toluene) and were freshly distilled prior to use. ¹H NMR spectra were obtained with a Varian Mercury-400 (400 MHz) spectrometer, and ¹³C NMR spectra were recorded with the Varian Mercury-400 (100.70 MHz). ¹H and ¹³C chemical shifts were measured relative to TMS as the internal reference.

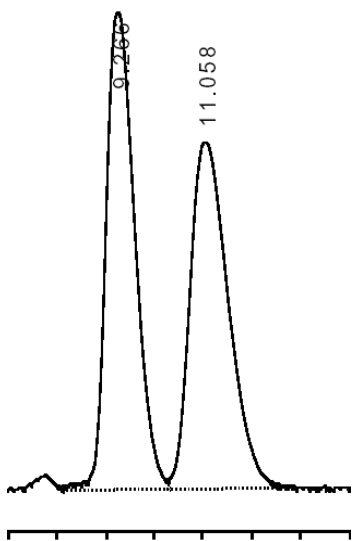
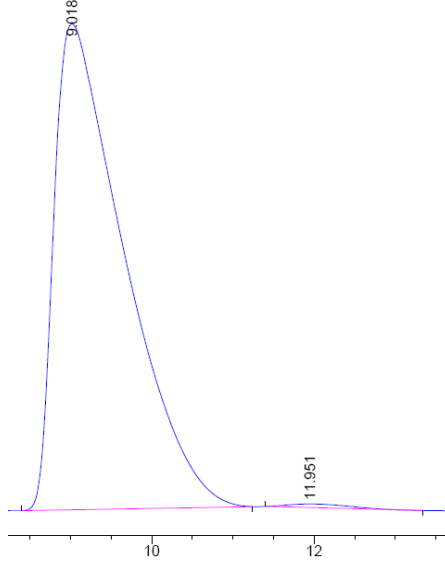
I.2. General Procedures for the Synthesis of $\text{ArTi}(\text{O-}i\text{-Pr})_3$.¹ A 2-necked 250 mL round-bottomed flask equipped with a condenser, a magnetic stir bar and an addition funnel was charged magnesium turning (2.40 g, 100 mmol). Under a nitrogen atmosphere, 100 mL THF was added to the flask and aryl bromide (120 mmol) in 50 mL THF was transferred into the addition funnel. The THF solution of aryl bromide was added slowly to the reaction flask, and the reaction mixture was controlled under gentle refluxing using an ice-bath if necessary. After the reaction completed, the resulted Grignard reagent was cooled to 0 °C. In another 2-necked 500 mL round-bottomed flask under a nitrogen atmosphere, a solution of $\text{Ti}(\text{O-}i\text{-Pr})_4$ (22.4 mL, 75.0 mmol) in 50 mL THF at 0 °C was added TiCl_4 (2.8 mL, 25.0 mmol). The resulted solution was warmed to room temperature and stirred for 30 min, giving a $\text{ClTi}(\text{O-}i\text{-Pr})_3$ solution (100 mmol). The $\text{ClTi}(\text{O-}i\text{-Pr})_3$ solution was cooled to 0 °C, and, to this solution, the ice-cold Grignard solution was transferred via a cannula. The reaction mixture was warmed to room temperature and was allowed to react for 3 h. The volatile material was removed completely under reduced pressures, and, under a nitrogen atmosphere, the residue was extracted with *n*-hexane (3 × 200 mL). The combined hexane solution was concentrated and was cooled to -20 °C, furnishing crystalline product of the $\text{ArTi}(\text{O-}i\text{-Pr})_3$.

I.3. General Procedures for the Asymmetric $\text{ArTi}(\text{O-}i\text{-Pr})_3$ Addition Reaction of Aldehydes. Under a dry nitrogen atmosphere, $[\{(R)\text{-H}_8\text{-BINOLate}\}\text{Ti}(\text{O-}i\text{-Pr})_2]_x$ (0.0230 g, 0.0500 mmol) and $\text{ArTi}(\text{O-}i\text{-Pr})_3$ (0.600 mmol) were dissolved in 3 mL of dry THF at room temperature followed by an addition of an aldehyde (0.50 mmol) in 1 mL THF. The mixture was reacted at room temperature for 1 min and quenched with 2 M NaOH (1 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL), and the combined organic phase was dried over MgSO_4 , filtered and concentrated. The residue was purified by column chromatography to give the secondary alcohol. Enantiomeric excesses of products were determined by HPLC using suitable chiral columns.

II. Reaction Conditions, HPLC Conditions and Chromatograms, ^1H and ^{13}C NMR Spectroscopic Data of $\text{ArTi}(\text{O-}i\text{-Pr})_3$ Addition Products of Aldehydes

II.1. (*R*)-(2-Methyl-phenyl)-phenyl-methanol (*R*-9a) (Table 2, entry 1):⁶

	Column:	Chiralcel OB-H,
	Eluent:	Hexane/IPA = 94/6
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	9.3 min (<i>R</i>), 11.1 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	9.266	11.058	Time	9.018	11.951
Height(mAU)	45759	33122	Height(mAU)	116.064	0.8067
Area(mAU-s)	1752158	1714148	Area(mAU-s)	6954.3242	45.0987
Area%	50.548	49.451	Area%	99.3557	0.6443

Catalytic Reaction Conditions:

2-methylbenzaldehyde: 0.50 mmol, $[\text{Ti}\{(R)\text{-H}_8\text{-BINOLate}\}(\text{O-}i\text{-Pr})_2]_x$: 0.050 mmol,
 $\text{PhTi}(\text{O-}i\text{-Pr})_3$: 0.60 mmol, rt, THF: 4 mL, 1 min

Spectrum Data:

^1H NMR (400 MHz, CDCl_3): δ 7.47-7.45 (m, 1H), 7.28-7.10 (m, 8H), 5.88 (s, 1H), 2.56 (br, 1H), 2.18 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 142.8, 141.4, 135.2, 130.4, 128.3, 127.42, 127.37, 127.0, 126.2, 126.0, 73.2, 19.3 ppm.

II.2. (*R*)-(4-Methyl-phenyl)-phenyl-methanol (9b) (Table 2, entry 2):^{6,7}

	Column:	Chiralcel OB-H
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	9.839 min (<i>R</i>), 12.305 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
Peak No.	1	2	Peak No.	1	2
Time	9.839	12.305	Time	9.526	13.647
Height(mAU)	33.884	24.974	Height(mAU)	127.0562	3.8227
Area(mAU-s)	1163.255	1124.632	Area(mAU-s)	4767.7788	155.1563
Area%	50.844	49.156	Area%	96.8483	3.1517

Catalytic Reaction Conditions:

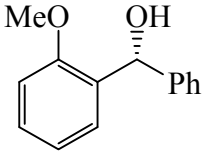
4-methylbenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

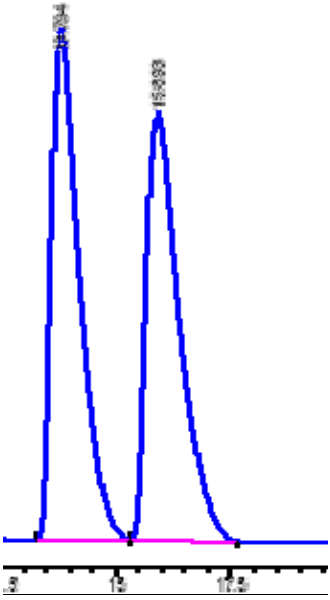
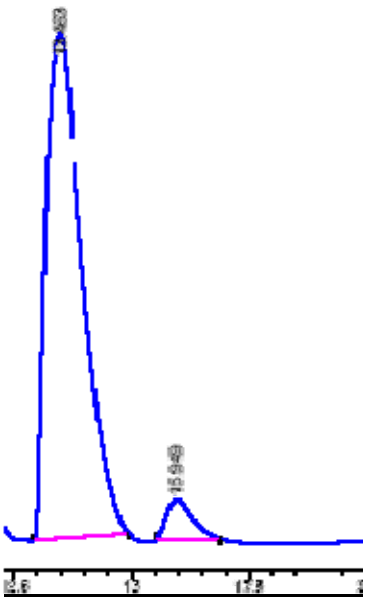
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.32-7.09 (m, 9H), 5.69 (s, 1H), 2.51 (br, 1H), 2.29 (s, 3H)
 ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.3, 141.3, 137.5, 129.5, 128.7, 127.7, 126.9, 126.8, 76.3,
 21.4 ppm.

II.3. (*R*)-(2-Methoxyphenyl)-phenyl-methanol (**9c**) (Table 2, entry 3):^{6,7}

	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	13.794 min (<i>R</i>), 15.893 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	13.794	15.893	Time	13.463	15.949
Height(mAU)	67.91636	56.82853	Height(mAU)	245.97577	19.37109
Area(mAU-s)	2843.10132	2820.24780	Area(mAU-s)	1.31814e4	736.16962
Area%	50.2018	49.7982	Area%	94.7105	5.2895

Catalytic Reaction Conditions:

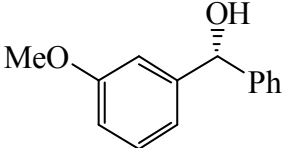
2-methoxybenzaldehyde: 0.50 mmol, [Ti{(R)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

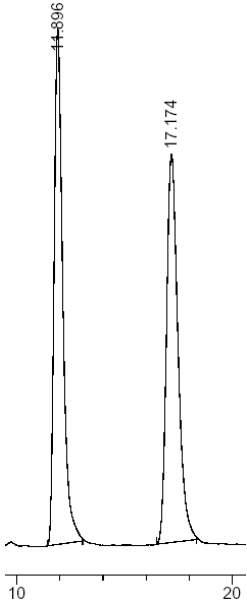
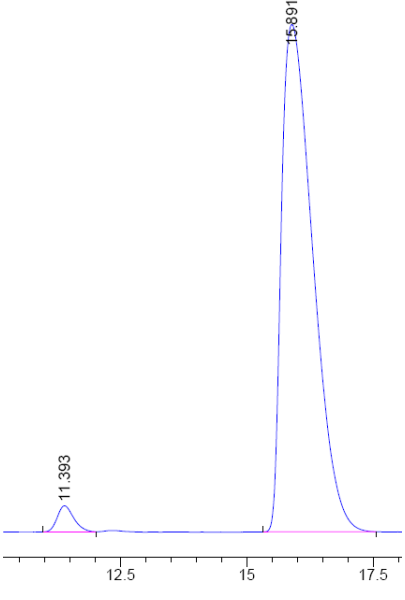
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.41-7.21 (m, 7H), 6.97-6.89 (m, 2H), 6.07 (d, *J* = 13.2 Hz, 1H), 3.82 (s, 3H), 3.06 (d, *J* = 5.6 Hz, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.8, 143.3, 132.0, 128.7, 128.2, 127.9, 127.2, 126.6, 120.8, 110.8, 72.3, 55.4 ppm.

II.4. (*R*)-(3-Methoxy-phenyl)-phenyl-methanol ((*R*)-9d) (Table 2, entry 4):⁶

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	11.9 min (<i>S</i>), 17.2 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	11.896	17.174	Time	11.393	15.891
Height(mAU)	19.37487	14.59871	Height(mAU)	9.8379	189.8791
Area(mAU-s)	539.12671	537.62329	Area(mAU-s)	226.0272	8193.6816
Area%	50.0698	49.9302	Area%	2.6845	97.3155

Catalytic Reaction Conditions:

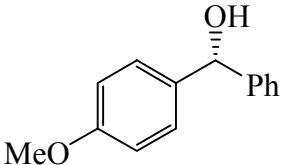
3-methoxybenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

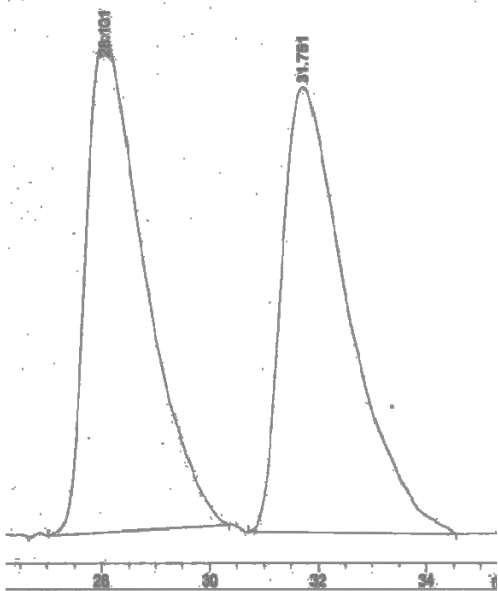
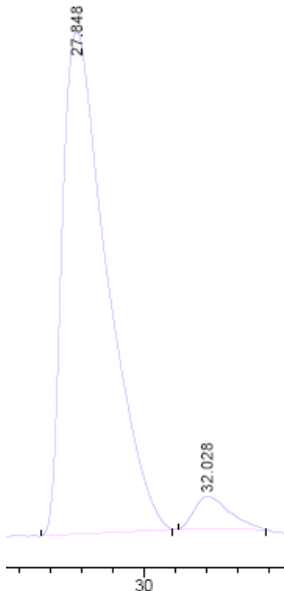
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.33-7.18 (m, 6H), 6.91-6.88 (m, 2H), 6.77-6.74 (m, 1H),
 5.69 (s, 1H), 3.71 (s, 3H), 2.78 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.6, 145.4, 143.6, 129.4, 128.3, 127.4, 126.4, 118.8, 112.8,
 112.0, 75.9, 55.0 ppm.

II.5. (*R*)-(4-Methoxy-phenyl)-phenyl-methanol ((*R*)-9e) (Table 2, entry 5):⁶⁻⁹

	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	28.101 min (<i>R</i>), 31.751 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	28.101	31.751	Time	27.848	32.028
Height(mAU)	20.89861	18.67842	Height(mAU)	28.57123	1.86357
Area(mAU-s)	1571.78979	1584.48865	Area(mAU-s)	2840.67187	149.77913
Area%	49.799	50.201	Area%	94.9914	5.0086

Catalytic Reaction Conditions:

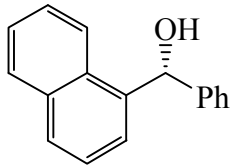
4-methoxybenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.0150 mmol, PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

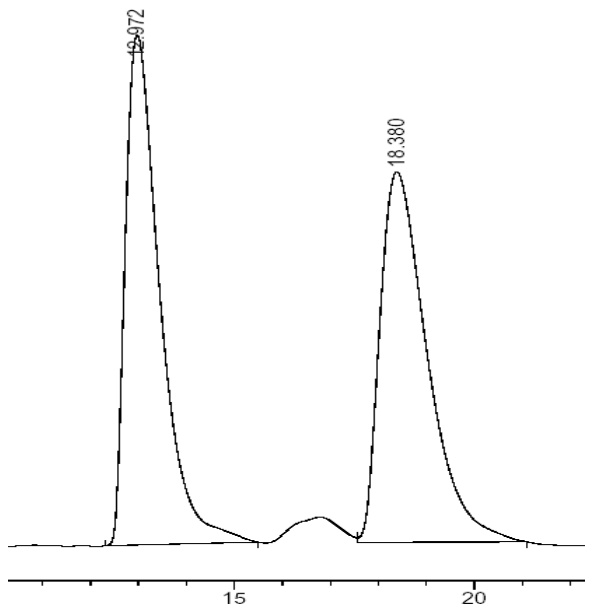
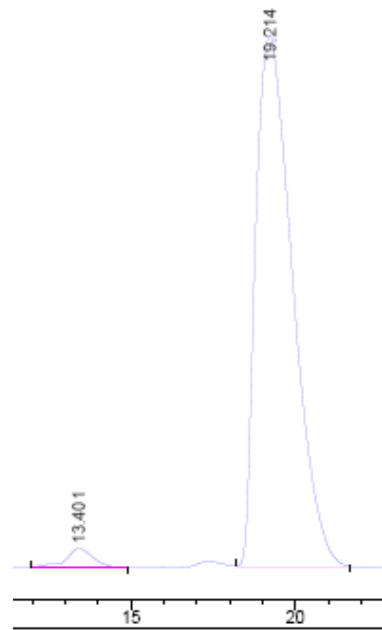
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.36-7.24 (m, 7H), 6.86-6.83 (m, 2H), 5.76 (s, 1H), 3.76 (s, 3H), 2.33 (br, 1H) ppm.

¹³C{¹H} NMR (400 MHz, CDCl₃): δ 159.0, 144.0, 136.2, 128.4, 127.9, 127.4, 126.4, 113.8, 75.7, 55.2 ppm.

II.6. (*R*)-Naphthalen-1-yl-phenyl-methanol ((*R*)-9f) (Table 2, entry 6):^{6,7}

	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 80/20
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	12.972 min (<i>S</i>), 18.380 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	12.972	18.380	Time	13.401	19.214
Height(mAU)	280.200	203.455	Height(mAU)	6.31342	175.13702
Area(mAU-s)	1.40 x 10 ⁴	1.39 x 10 ⁴	Area(mAU-s)	363.30765	1.36 x 10 ⁻⁴
Area%	50.2435	49.7565	Area%	2.5990	97.4010

Catalytic Reaction Conditions:

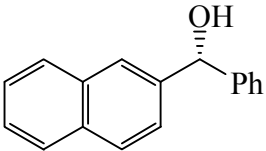
1-naphthylaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.0250 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

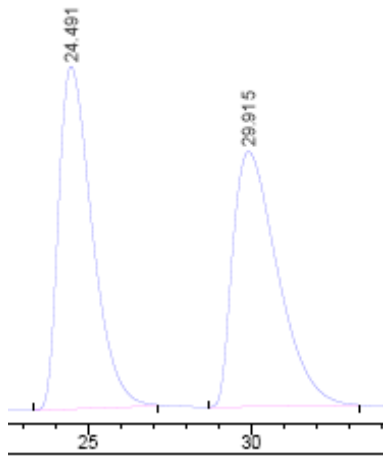
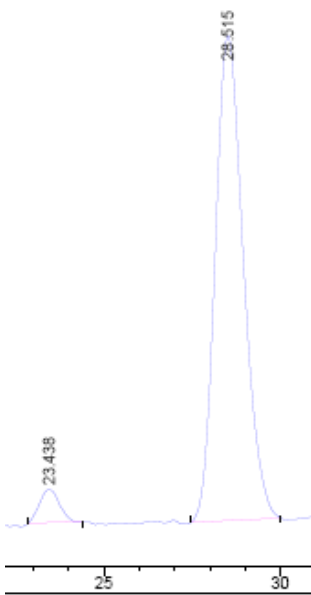
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 8.04-7.24 (m, 12H), 6.53 (d, *J* = 3.2 Hz, 1H), 2.38 (d, *J* = 3.6 Hz, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.1, 138.8, 134.0, 130.7, 128.8, 128.52, 128.49, 127.7, 127.0, 126.1, 125.6, 125.3, 124.6, 124.0, 73.7 ppm.

II.7. (*R*)-Naphthalen-2-yl-phenyl-methanol (*R*-9g) (Table 2, entry 7):⁶

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	24.491 min (<i>S</i>), 29.915 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	24.491	29.915	Time	23.438	28.515
Height(mAU)	562.46753	419.05048	Height(mAU)	1.36497	20.19909
Area(mAU-s)	4.02 x 10 ⁴	3.99 x 10 ⁴	Area(mAU-s)	53.83646	1120.45483
Area%	50.1250	49.8750	Area%	4.5846	95.4154

Catalytic Reaction Conditions:

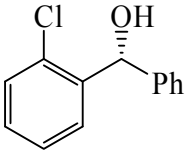
2-naphthylaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.0250 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

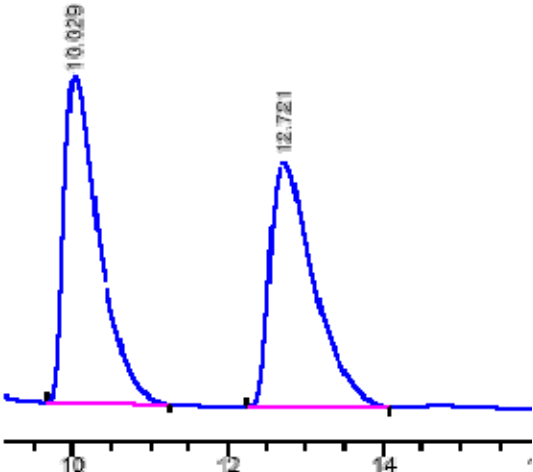
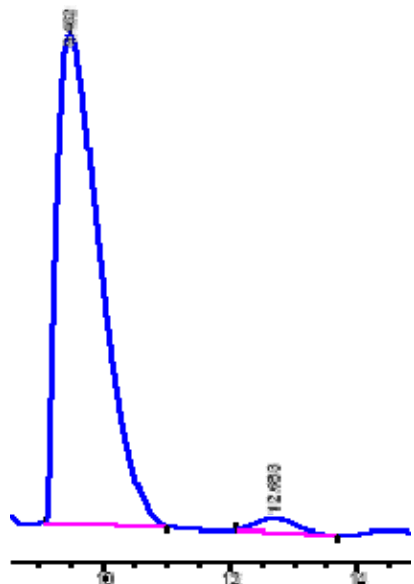
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.77 (m, 4H), 7.49-7.24 (m, 8H), 5.99 (d, *J* = 3.2 Hz, 1H), 2.39 (d, *J* = 3.6 Hz, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.6, 141.1, 133.3, 132.9, 128.5, 128.3, 128.1, 127.7, 126.7, 126.2, 126.0, 125.0, 124.8, 76.4 ppm.

II.8. (*R*)-(2-Chloro-phenyl)-phenyl-methanol (*R*-9h) (Table 2, entry 8):⁶

	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 80/20
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	10.029 min (<i>R</i>), 12.721 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	10.029	12.721	Time	9.462	12.683
Height(mAU)	35.58539	26.77971	Height(mAU)	205.7819	5.89407
Area(mAU-s)	1097.77649	1059.42090	Area(mAU-s)	9804.27930	254.6468
Area%	50.8890	49.1110	Area%	97.4684	2.5316

Catalytic Reaction Conditions:

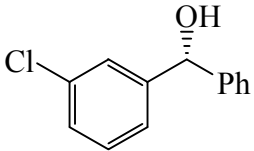
2-chlorobenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

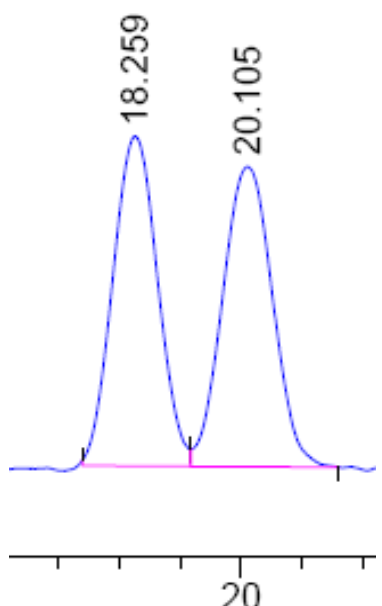
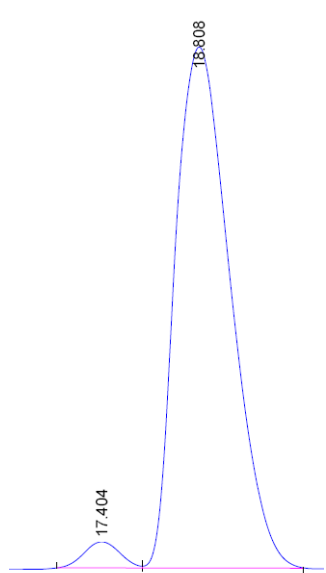
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.58-7.15 (m, 9H), 6.15 (s, 1H), 2.65 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.1, 140.9, 132.4, 129.4, 128.6, 128.4, 127.9, 127.7, 127.0, 126.9, 72.5 ppm.

II.9. (*R*)-(3-Chloro-phenyl)-phenyl-methanol ((*R*)-9i) (Table 2, entry 9):⁶

	Column:	Chiralcel OD-H,
	Eluent:	Hexane/IPA = 98/2
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	18.259 min (<i>R</i>), 20.105 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	18.259	20.105	Time	17.404	18.808
Height(mAU)	7.271	6.611	Height(mAU)	3.6232	72.3607
Area(mAU-s)	370.991	376.603	Area(mAU-s)	130.0882	3964.7949
Area%	49.625	50.375	Area%	3.1768	96.8232

Catalytic Reaction Conditions:

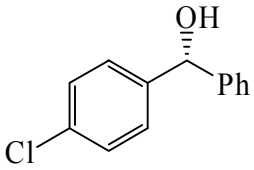
3-chlorobenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

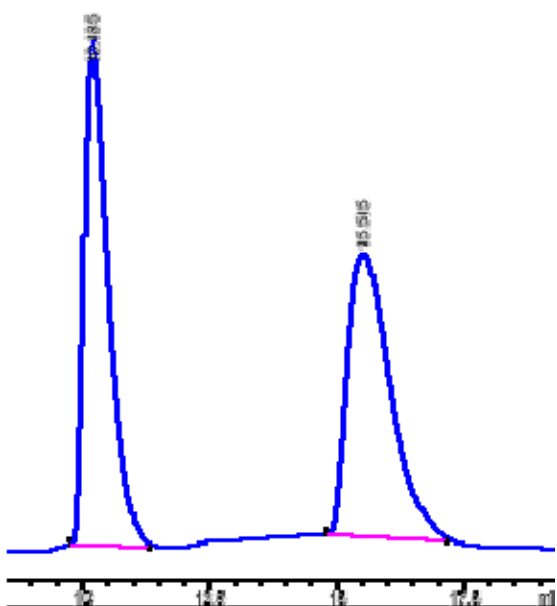
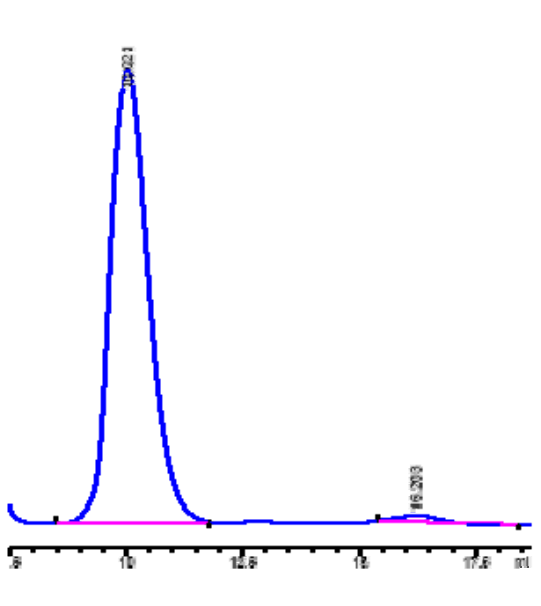
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): 7.35-7.20 (m, 9H), 5.68 (s, 1H), 2.63 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): 145.7, 143.1, 134.3, 129.6, 128.6, 127.8, 127.5, 126.5,
 124.5, 75.5 ppm

II.10. (*R*)-(4-Chloro-phenyl)-phenyl-methanol ((*R*)-9j) (Table 2, entry 10):⁶⁻⁸

	Column:	Chiralcel OB-H,
	Eluent:	Hexane/IPA = 92/8
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	10.185 min (<i>R</i>), 15.515min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	10.185	15.515	Time	10.021	16.203
Height(mAU)	170.29872	95.49712	Height(mAU)	233.51138	3.06891
Area(mAU-s)	5576.95654	5582.49712	Area(mAU-s)	1.33502e4	167.38177
Area%	49.9759	50.0241	Area%	98.7618	1.2382

Catalytic Reaction Conditions:

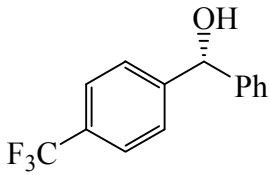
4-chlorobenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

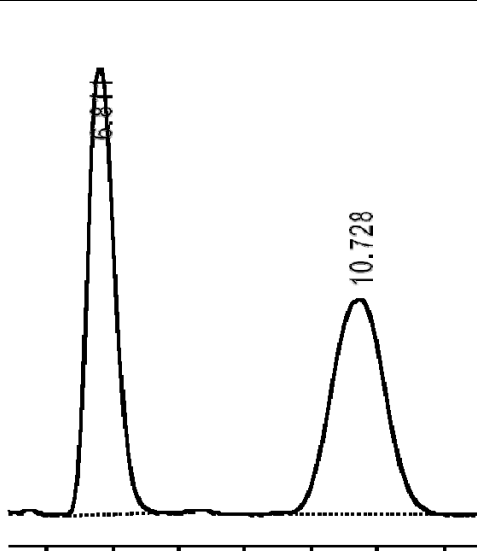
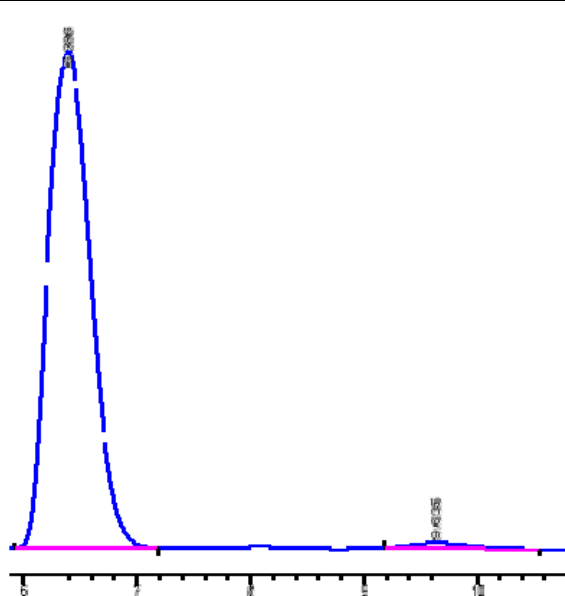
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): 7.35-7.25 (m, 9H), 5.80 (s, 1H), 2.31 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): 143.4, 142.2, 133.3, 128.6, 128.6, 127.9, 127.8, 126.5,
 75.6 ppm.

II.11. (*R*)-Phenyl-(4-trifluoromethylphenyl)-methanol ((*R*)-9k) (Table 2, entry 11):⁶

	Column:	Chiralcel OB-H
	Eluent:	Hexane/IPA = 94/6
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	6.811 min (<i>R</i>), 10.728 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	6.811	10.728	Time	6.386	9.635
Height(mAU)	367614	177379	Height(mAU)	257.82782	3.07813
Area(mAU-s)	9539451	9568137	Area(mAU-s)	6686.23877	115.37144
Area%	49.924	50.075	Area%	98.3038	1.6962

Catalytic Reaction Conditions:

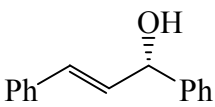
4-trifluoromethylbenzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol, PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

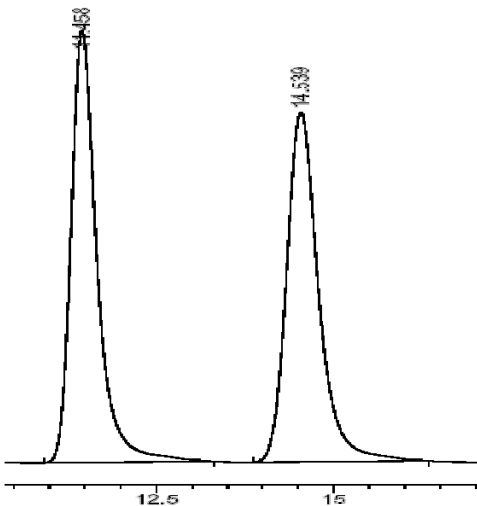
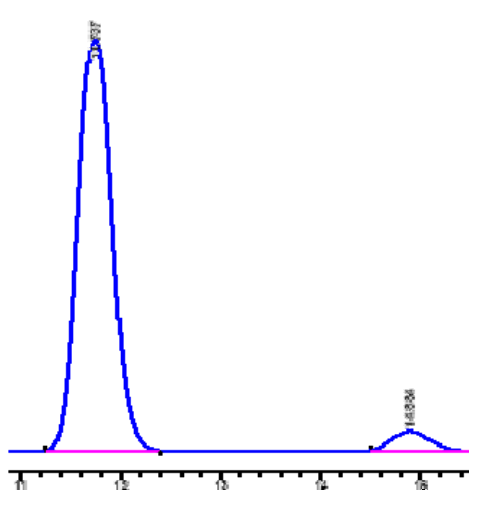
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.60-7.25 (m, 9H), 5.88 (s, 1H), 2.36 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.5, 143.2, 129.6 (q, *J* = 31.8 Hz), 128.7, 128.0, 126.61, 126.57, 125.3 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 270 Hz), 75.6 ppm.

II.12. (*S*)-(*E*)-1,3-Diphenyl-prop-2-en-1-ol ((*S*)-9l) (Table 2, entry 12):⁶

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 88/12
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	11.458 min (<i>S</i>), 14.539 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	11.458	14.539	Time	11.737	14.884
Height(mAU)	788.50482	637.28748	Height(mAU)	2579.0183	125.96530
Area(mAU-s)	2.0002×10^4	1.9941×10^4	Area(mAU-s)	6.23416e4	3384.52441
Area%	50.076	49.924	Area%	94.8506	5.1494

Catalytic Reaction Conditions:

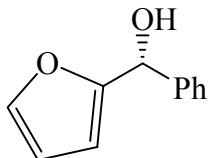
cinnamaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

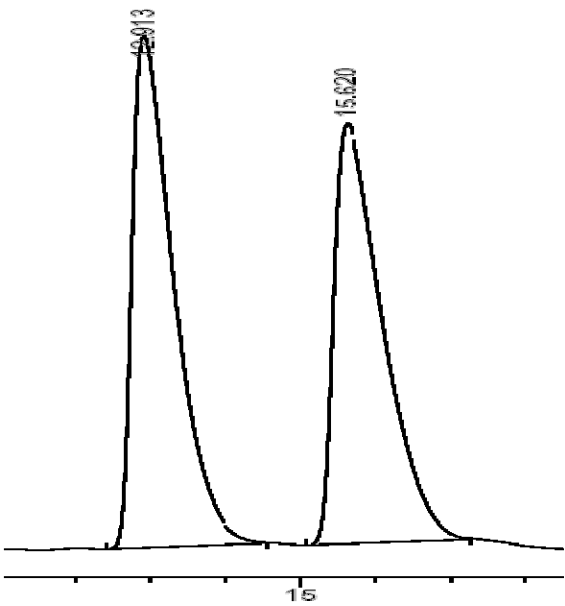
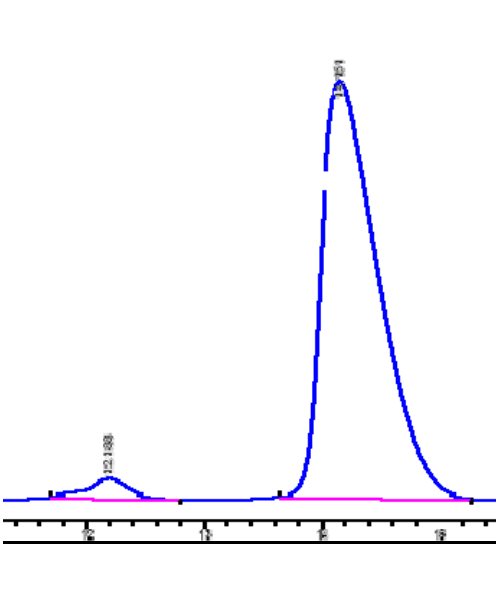
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.45-7.22 (m, 10H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.71-6.36 (m, 1H), 5.39 (dd, *J* = 3.2, 6.8 Hz, 1H), 2.07 (d, *J* = 3.6 Hz, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.7, 136.5, 131.5, 130.5, 128.6, 128.5, 127.7, 126.6, 126.3, 75.0 ppm

II.13. (*R*)-(Furan-2-yl)-phenyl-methanol ((*R*)-9m) (Table 2, entry 13):⁶

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	12.913 min (<i>S</i>), 15.620 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	12.913	15.620	Time	12.188	14.151
Height(mAU)	178.42395	146.73128	Height(mAU)	9.63425	200.87593
Area(mAU-s)	6797.8076	6656.7915	Area(mAU-s)	242.05536	6700.58301
Area%	50.5240	49.4760	Area%	3.4865	96.5135

Catalytic Reaction Conditions:

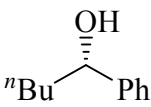
2-furylaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

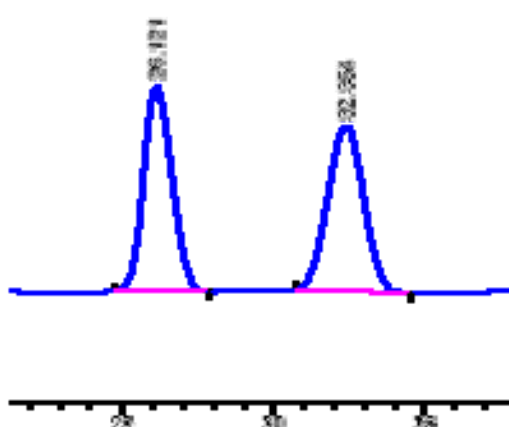
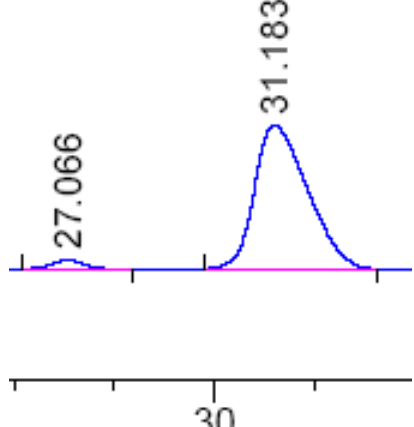
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.44-7.28 (m, 6H), 6.31 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.10 (dd, *J* = 4.0, 0.8 Hz, 1H), 5.80 (d, *J* = 2.4 Hz, 1H), 2.56 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.0, 142.5, 140.8, 128.4, 128.0, 126.6, 110.2, 107.4, 70.1 ppm.

II.14. (S)-1-Phenyl-pentan-1-ol ((S)-9n) (Table 2, entry 14):⁶

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 99.5/0.5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	26.121 min (<i>R</i>), 32.354 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	26.121	32.354	Time	27.066	31.183
Height(mAU)	17.76250	14.28900	Height(mAU)	2.26377	35.53828
Area(mAU-s)	1146.18652	1178.7867	Area(mAU-s)	116.88503	2634.56323
Area%	49.2989	50.7011	Area%	4.2481	95.7519

Catalytic Reaction Conditions:

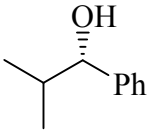
pentanal: 0.50 mmol, [Ti{(R)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

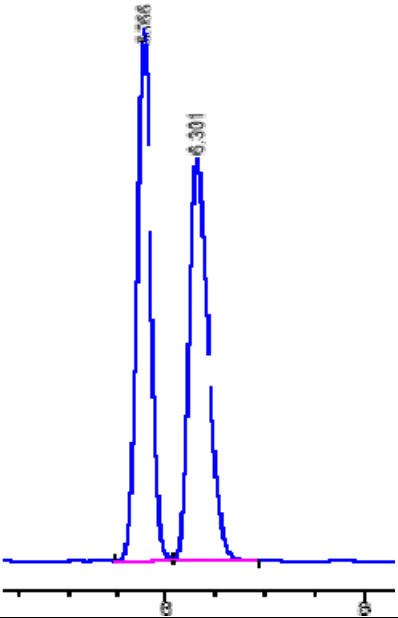
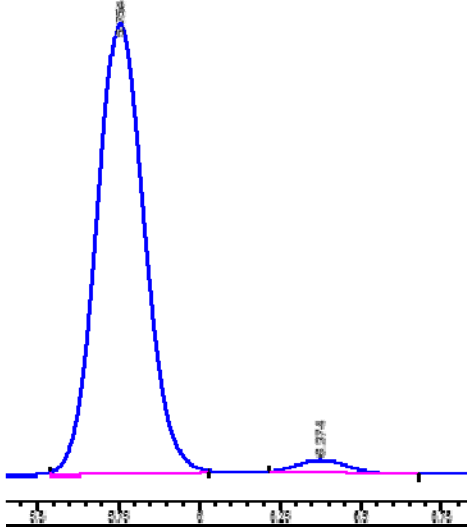
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.35-7.24 (m, 5H), 4.64-4.61 (m, 1H), 2.02 (br, 1H),
 1.81-1.67 (m, 2H), 1.40-1.21 (m, 4H), 0.89-0.85 (m, 3H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.9, 128.4, 127.4, 125.5, 74.6, 38.8, 27.9, 22.5, 13.9
 ppm.

II.15. (S)-2-methyl-1-phenyl-propan-1-ol ((S)-9o) (Table 2, entry 15):⁶

	Column:	Chiralcel OD-H
	Eluent:	Hexane/IPA = 98/2
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	5.766 min (<i>S</i>), 6.301 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	5.766	6.301	Time	5.754	6.374
Height(mAU)	153.62849	116.72093	Height(mAU)	161.34369	4.32873
Area(mAU-s)	1603.4288	1609.57263	Area(mAU-s)	1665.5638	45.42761
Area%	49.9044	50.0956	Area%	97.3450	2.6550

Catalytic Reaction Conditions:

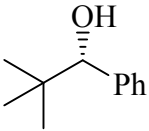
isobutyraldehyde: 0.50 mmol, [Ti{(R)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

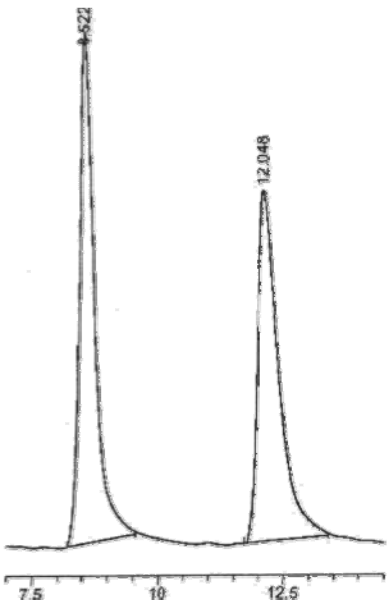
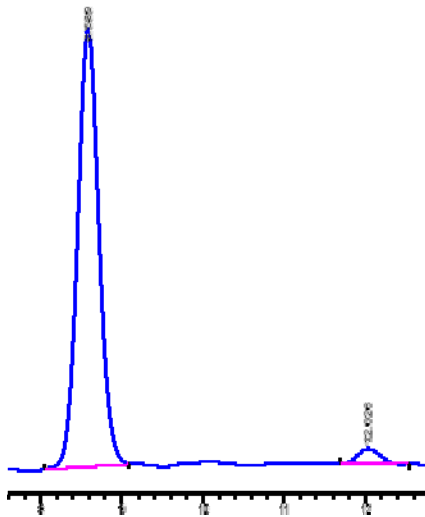
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.35-7.24 (m, 5H), 4.34 (m, 1H), 1.99-1.91 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.6, 128.1, 127.3, 126.5, 80.0, 35.2, 19.0, 18.2 ppm.

II.16. (*S*)-2,2-Dimethyl-1-phenyl-propan-1-ol ((*S*)-9p) (Table 2, entry 16):⁶

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 99/1
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	8.522 min (<i>S</i>), 12.048 min (<i>R</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	8.522	12.048	Time	8.589	12.026
Height(mAU)	59.37840	40.73387	Height(mAU)	1121.4054	38.51155
Area(mAU-s)	1219.93262	1208.75183	Area(mAU-s)	60.99925	2.08175
Area%	50.2302	49.7698	Area%	96.6798	3.3202

Catalytic Reaction Conditions:

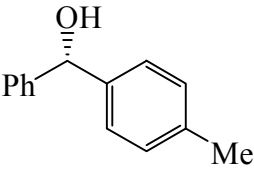
pivalaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 PhTi(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.


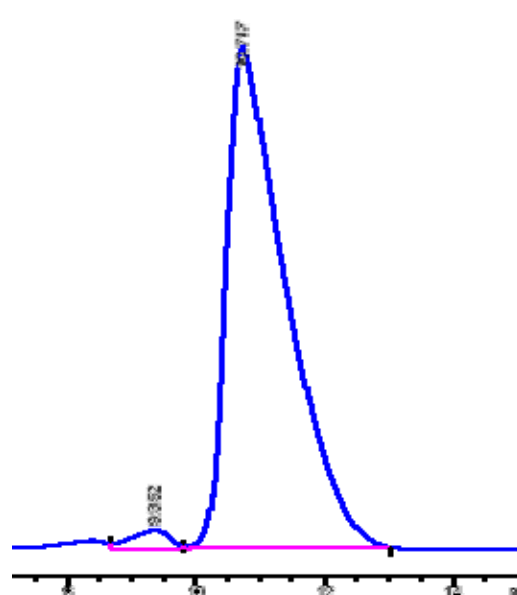
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.23-7.18 (m, 5H), 4.30 (d, *J* = 2.8 Hz, 1H), 1.87 (d, *J* = 2.8 Hz, 1H), 0.90 (s, 9H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.2, 127.6, 127.5, 127.2, 82.4, 35.6, 25.9 ppm.

II.17. (*S*)-(4-Methyl-phenyl)-phenyl-methanol ((*S*)-9b) (Table 2, entry 17):^{6,7}

	Column:	Chiralcel OB-H
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	8.738 min (<i>R</i>), 10.921 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	8.738	10.921	Time	9.352	10.717
Height(mAU)	201.78398	153.31110	Height(mAU)	9.01436	237.03903
Area(mAU-s)	8576.84473	8444.35059	Area(mAU-s)	369.15567	1.53842e4
Area%	50.3892	49.6108	Area%	2.3433	97.6567

Catalytic Reaction Conditions:

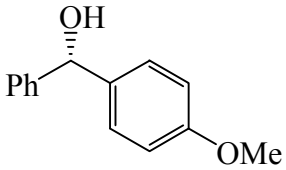
benzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 (4-MeC₆H₄)Ti(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

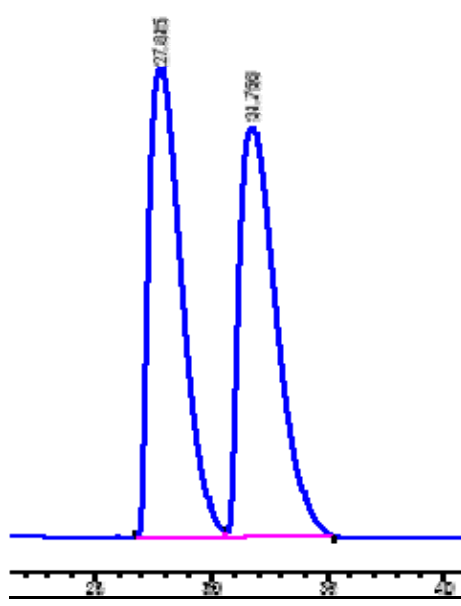

Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.36-7.12 (m, 9H), 5.77 (d, 1H), 2.32 (s, 3H), 2.27 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.0, 141.0, 137.2, 129.2, 128.4, 127.4, 126.5, 126.5, 76.1, 21.1 ppm.

II.18. (S)-(4-Methoxy-phenyl)-phenyl-methanol ((S)-9e) (Table 2, entry 18):^{6,7}

	Column:	Chiralcel OJ
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	27.815 min (<i>R</i>), 31.756 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	27.815	31.756	Time	28.837	31.359
Height(mAU)	62.56820	54.77216	Height(mAU)	6.13610	116.24293
Area(mAU-s)	6033.6665	6032.40625	Area(mAU-s)	386.10165	155928e4
Area%	50.0052	49.9948	Area%	2.4163	97.5837

Catalytic Reaction Conditions:

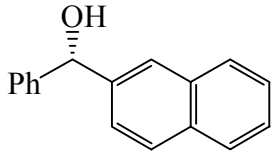
benzaldehyde: 0.50 mmol, [Ti{(R)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 (4-MeOC₆H₄)Ti(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

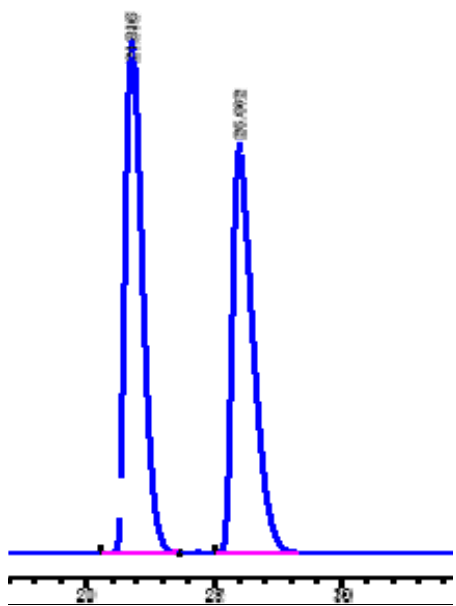
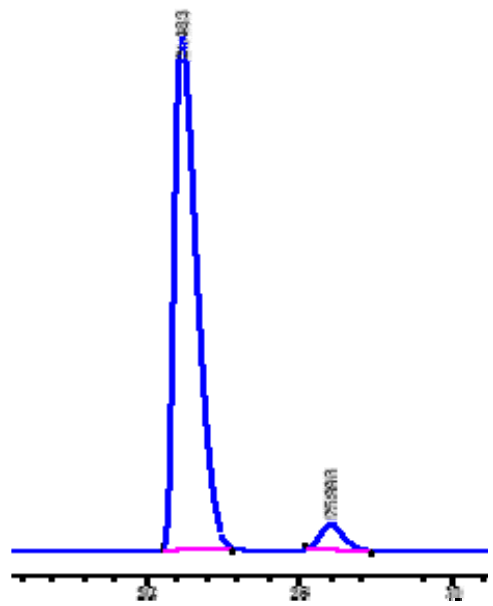
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.36-7.24 (m, 7H), 6.86-6.83 (m, 2H), 5.76 (s, 1H), 3.76 (s, 3H), 2.33 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.0, 144.0, 136.2, 128.4, 127.9, 127.4, 126.4, 113.8, 75.7, 55.2 ppm.

II.19. (*S*)-(Naphthalen-2-yl)-phenyl-methanol ((*S*)-9g) (Table 2, entry 19):⁶

	Column: Chiralcel OD Eluent: Hexane/IPA = 95/5 Flow rate: 1 mL/min Detector: UV, 254 nm Retention time: 21.816 min (<i>S</i>), 25.992 min (<i>R</i>)
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Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	21.816	25.992	Time	21.183	25.993
Height(mAU))	619.91327	494.12964	Height(mAU)	1446.8031	70.42558
Area(mAU-s)	2.84732e4	2.85523e4	Area(mAU-s)	7.17725e4	3742.83813
Area%	49.9306	50.0694	Area%	95.0436	4.9564

Catalytic Reaction Conditions:

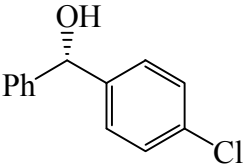
benzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
(2-naphthyl)Ti(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

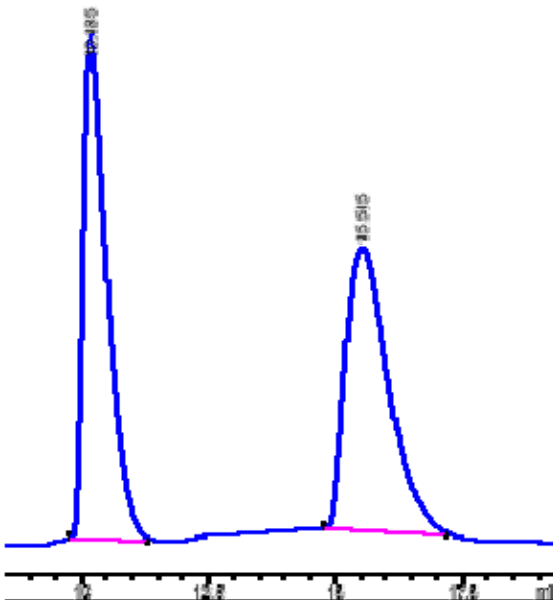
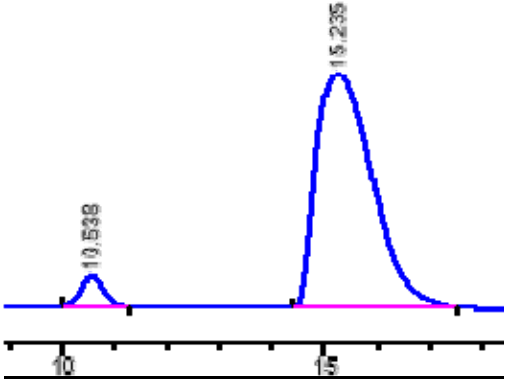
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.77 (m, 4H), 7.49-7.24 (m, 8H), 5.99 (d, *J* = 3.2 Hz, 1H), 2.39 (d, *J* = 3.6 Hz, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.6, 141.1, 133.3, 132.9, 128.5, 128.3, 128.1, 127.7, 126.7, 126.2, 126.0, 125.0, 124.8, 76.4 ppm.

II.20. (*S*)-(4-Chloro-phenyl)-phenyl-methanol ((*S*)-91) (Table 2, entry 20):^{6,7}

	Column:	Chiralcel OB-H,
	Eluent:	Hexane/IPA = 92/8
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	10.185 min (<i>R</i>), 15.515 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	10.185	15.515	Time	10.538	15.235
Height(mAU)	170.29872	95.49712	Height(mAU)	20.74713	159.25754
Area(mAU-s)	5576.95654	5582.4971	Area(mAU-s)	607.11108	1.17942e4
Area%	49.9759	50.0241	Area%	4.8955	95.1045

Catalytic Reaction Conditions:

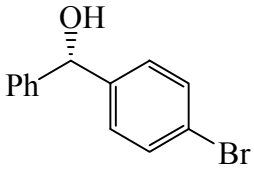
benzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 (4-ClC₆H₄)Ti(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

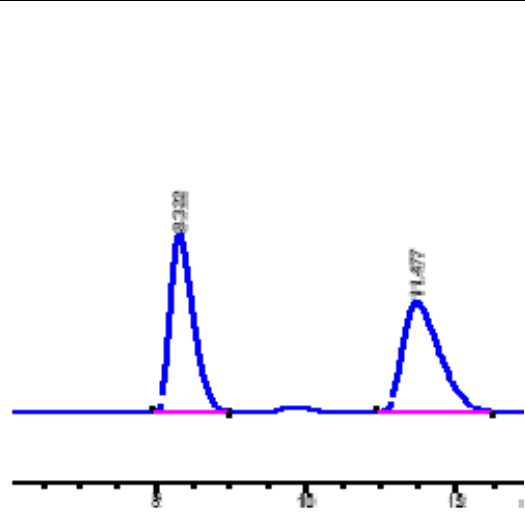
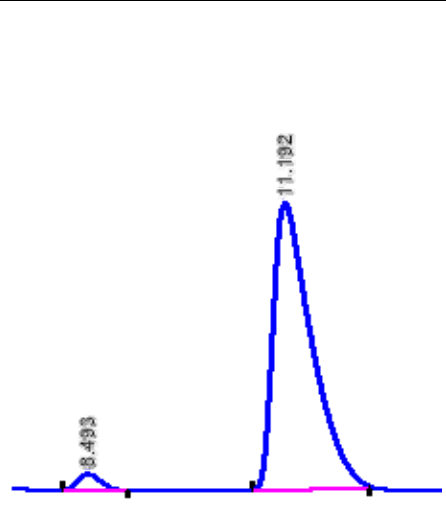
Spectrum Data:

¹H NMR (400 MHz, CDCl₃): δ 7.35-7.25 (m, 9H), 5.80 (s, 1H), 2.31 (br, 1H) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.4, 142.2, 133.3, 128.6, 128.6, 127.9, 127.8, 126.5, 75.6 ppm.

II.21. (*S*)-(4-bromo-phenyl)-phenyl-methanol ((*S*)-9q) (Table 2, entry 21):⁷

	Column:	Chiralcel, OB-H
	Eluent:	Hexane/IPA = 90/10
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	8.322 min (<i>R</i>), 11.477 min (<i>S</i>)

Racemic standard			Catalytic Reaction Product		
					
Peak No.	1	2	Peak No.	1	2
Time	8.322	11.477	Time	8.493	11.192
Height(mAU)	24.99641	15.57013	Height(mAU)	2.45572	43.86544
Area(mAU-s)	519.15289	523.18439	Area(mAU-s)	53.44579	1605.62781
Area%	49.8066	50.1934	Area%	3.2214	96.7786

Catalytic Reaction Conditions:

benzaldehyde: 0.50 mmol, [Ti{(*R*)-H₈-BINOLate}(O-*i*-Pr)₂]_x: 0.050 mmol,
 (4-TMSC₆H₄)Ti(O-*i*-Pr)₃: 0.60 mmol, rt, THF: 4 mL, 1 min.

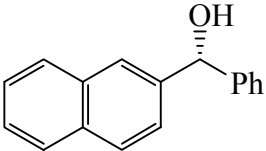
Spectrum Data:

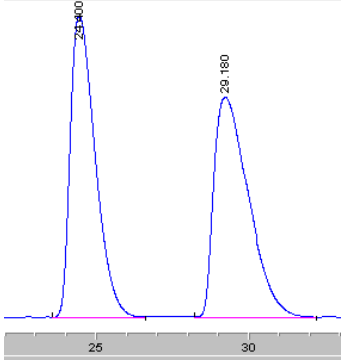
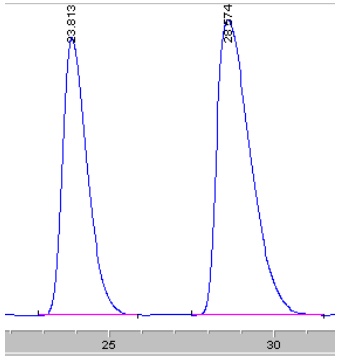
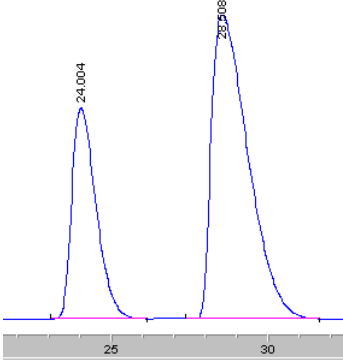
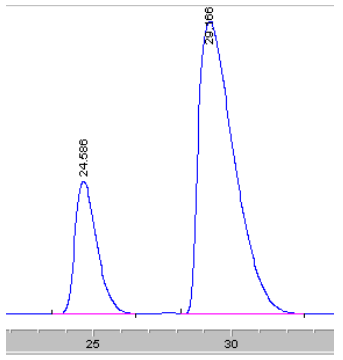
¹H NMR (400 MHz, CDCl₃): δ 7.44-7.21 (m, 9H), 5.74 (s, 1H), 2.40 (br, 1H) ppm.

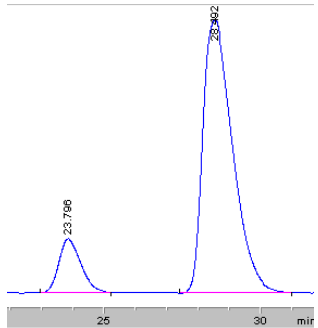
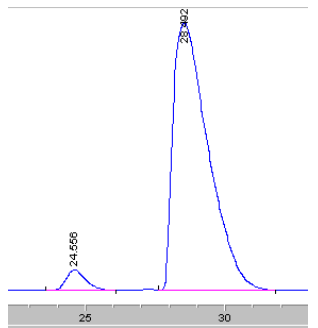
¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.7, 131.5, 128.6, 128.5, 128.2, 127.8, 126.5, 121.4, 75.6 ppm.

III. Linear Effect Study of $\text{PhTi}(\text{O-}i\text{-Pr})_3$ Additions to 2-Naphthylaldehyde Catalyzed by *rac*- $\text{H}_8\text{-BINOL}$ or *x* mol% (*R*)- $\text{H}_8\text{-BINOL}$

III.1. HPLC Conditions and Chromatograms of Linear Effect Study

	Column:	Chiralcel OD
	Eluent:	Hexane/IPA = 95/5
	Flow rate:	1 mL/min
	Detector:	UV, 254 nm
	Retention time:	24.400 min (<i>S</i>), 29.18 min (<i>R</i>)

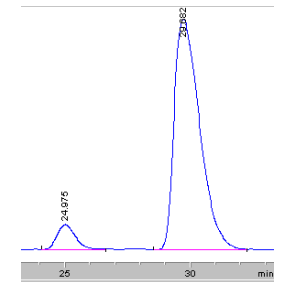
Racemic $\text{H}_8\text{-BINOL}$			20% ee (<i>R</i>)- $\text{H}_8\text{-BINOL}$		
					
Peak No.	1	2	Peak No.	1	2
Time	24.400	29.180	Time	23.813	28.574
Height(mAU)	722.1	527.2	Height(mAU)	397.7	422.9
Area(mAU-s)	40772.4	41814.7	Area(mAU-s)	20800.6	30013.7
Area%	49.369	50.631	Area%	40.935	59.065
40% ee (<i>R</i>)- $\text{H}_8\text{-BINOL}$			60% ee (<i>R</i>)- $\text{H}_8\text{-BINOL}$		
					
Peak No.	1	2	Peak No.	1	2
Time	24.004	28.508	Time	24.586	29.166
Height(mAU)	520.4	748.2	Height(mAU)	404	891.5
Area(mAU-s)	28056.5	60700.5	Area(mAU-s)	22184.6	79364.9
Area%	31.610	68.390	Area%	21.8463	78.154

80% ee (<i>R</i>)-H ₈ -BINOL			100% ee (<i>R</i>)-H ₈ -BINOL		
					
Peak No.	1	2	Peak No.	1	2
Time	23.796	28.492	Time	24.556	28.492
Height(mAU)	48.5	244.1	Height(mAU)	81.4	1061.6
Area(mAU-s)	2361.7	16188.5	Area(mAU-s)	4055.1	92534.7
Area%	12.731	87.269	Area%	4.198	95.802

III.2. Ee Values of (*R*)-9g of Linear Effect Study

Entry	(<i>R</i>)-H ₈ BINOL (mmol)	<i>Rac</i> -H ₈ BINOL (mmol)	ee of (<i>R</i>)-H ₈ -BINOL (%)	Ee of (<i>R</i>)-9g (%)
1	0	0.050	0	1.3
2	0.010	0.040	20	18.1
3	0.020	0.030	40	36.8
4	0.030	0.020	60	56.3
5	0.040	0.010	80	74.5
6	0.050	-	100	91.6

III.3. The Reaction Condition and HPLC Chromatogram of the Autocatalysis Study

0.25 mmol (<i>R</i>)-9g + 0.60 mmol PhTi(O- <i>i</i> -Pr) followed by an addition of 0.25 mmol 8g. The reaction time was 2 h to give a 96% conversion of (<i>R</i>)-9g with an 84.7% ee.		
Peak No.	1	2
Time	24.975	29.682
Height(mAU)	32.7	295
Area(mAU-s)	1730.1	20832.1
Area%	7.668	92.332

IV. References

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