Supporting Information for:

Vanadium-Catalyzed Asymmetric Oxidation of α -Hydroxy Esters Using Molecular Oxygen as Stoichiometric Oxidant

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Materials and Methods. Solvents for surveys in Table 1 and Table S1 were freshly distilled before use. Acetone for the vanadium-catalyzed asymmetric oxidation reactions was used as received from EMD Chemicals. VO(OiPr)₃, VO(acac)₂, VOCl₃, and V₂O₅ were purchased from Aldrich Chemical and used without further purification. Salicylaldehyde derivatives and chiral amino alcohols were purchased from Aldrich Chemical, except 3-(1-adamantyl)-5-methylsalicylaldehyde¹ and 3-*tert*-butyl-5-nitrosalicylaldehyde.² Chiral ligands employed in Table 1 were prepared by condensation of the corresponding aldehydes and amino alcohols in methanol.³ Available racemic α -hydroxy esters were purchased from commercial vendors and purified as necessary before use. Non-commercially available α -hydroxy esters were prepared as described below. Available enantiopure α -hydroxy esters were purchased from commercial vendors for analytical comparison. Oxygen and nitrogen atmospheres were maintained via a Tygon gas line vented through an oil bubbler. Argon and hydrogen atmospheres were maintained via balloon pressure. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F₂₅₄ TLC plates. Flash column chromatography was carried out on Merck 60 silica gel (32-63 μ m). ¹H and ¹³C NMR spectra were recorded with Bruker AVB-400, AVQ-400, and AV-300 spectrometers and referenced to CHCl₃ (7.26 ppm) unless otherwise noted. ⁵¹V NMR spectra were recorded with a Bruker AVB-400 spectrometer in acetone-*d*₆ and referenced to VOCl₃ (0 ppm) as an external standard. X-band EPR spectra were recorded in acetone solution using a 5 mm o.d. quartz tube with a Bruker EMX-300 spectrometer operating at ambient temperature. Analytical chiral HPLC was performed with a Shimadzu VP Series Chiral HPLC with detection at 210, 254, and 280 nm using Chiralcel OJ and OD columns. Analytical GC was carried out with a Hewlett Packard HP 6850 GC equipped with an Agilent DB-WAX (30.0 m x 0.25 mm) column for achiral separation and a Chiraldex G-TA (30.0 m x 0.25 mm) column for chiral separation.

CAUTION: Organic solvents under oxygen atmosphere are extremely flammable. Although we have never experienced an accident, caution should always be exhibited to avoid ignition.

¹ Dossetter, A.G.; Jamison, T.F.; Jacobsen, E.N. *Angew. Chem. Int. Ed.* **1999**, 38, 2398.

² Cogan, D.A.; Liu, G.; Kim, K.; Backes, B.J.; Ellman, J.A. *J. Am. Chem. Soc.* **1998**, 120, 8011.

³ Liu, G.; Cogan, D.A.; Ellman, J.A. *J. Am. Chem. Soc.* **1997**, 119, 9913.

General Procedure for the Asymmetric Oxidation

Reaction of Ethyl Mandelate - Ligand Screening

Experiments.

A 2-dram vial equipped with a magnetic stir bar was charged with powdered molecular sieves (3ÅMS, 0.15 g) then purged with a flow of oxygen. A solution of the appropriate ligand (0.025 mmol, 0.11 equiv, Figure S1) in dry acetonitrile (0.5 mL) was delivered via syringe. $VO(OiPr)_3$ (4.7 μ L, 0.020 mmol, 0.08 equiv) was then added via syringe, and the resulting dark mixture was stirred under oxygen for 10 min. ($\pm$)-Ethyl mandelate (50 mg, 0.25 mmol) and hexamethylbenzene (5 mg, internal standard) were then introduced via syringe as a solution in dry acetonitrile (0.5 mL). The reaction mixture was stirred at ambient temperature for 3 h, and then filtered over silica with diethyl ether eluent. The filtrate was analyzed directly by chiral GC for conversion and enantiomeric excess (Chiraldex G-TA; 90 °C hold 0 min, then 10 °C/min to 140 °C; 2.0 mL/min He carrier gas), t_R 9.60 min (*S*-alcohol), 10.02 min (*R*-alcohol), 10.96 (ketone).

Figure S1. Chiral Salicylaldehyde Ligands for Vanadium-Catalyzed Asymmetric Oxidation

General Procedure for the Asymmetric Oxidation Reaction of Ethyl Mandelate – Solvent and Vanadium

Source Screening Experiments (Table S1).

A 2-dram vial containing a magnetic stir bar was charged with powdered molecular sieves (3ÅMS, 0.15 g) as necessary. A solution of ligand **1** (0.025 mmol, 0.11 equiv) in 0.5 mL of solvent was then delivered via syringe, followed by the vanadium species (0.020 mmol, 0.08 equiv). The resulting mixture was stirred under oxygen for 15 min. ($\pm$)-Ethyl mandelate (50 mg, 0.25 mmol) and hexamethylbenzene (5 mg, internal standard) were then introduced via syringe as a solution in solvent (0.5 mL). The reaction mixture was stirred at ambient temperature for 3 h, and then filtered over silica with diethyl ether eluent. The filtrate was directly analyzed by chiral GC for conversion and enantiomeric excess (Chiraldex G-TA; 90

°C hold 0 min, then 10 °C/min to 140 °C hold 10 min; 2.0 mL/min He carrier gas), t_R 9.60 min (*S*-alcohol), 10.02 min (*R*-alcohol), 10.96 (ketone).

Table S1. Effect of Solvent and Vanadium Source on the Kinetic Resolution of Ethyl Mandelate^a

1 atm. O₂, rt

entry	conditions	conversion ^b	ee ROH	s ^c
1.	MeCN, VO(<i>i</i> OPr) ₃ , 3ÅMS	49.8	86.1	39
2.	CH ₂ Cl ₂ , VO(<i>i</i> OPr) ₃ , 3ÅMS	16.4	18.3	36
3.	PhMe, VO(<i>i</i> OPr) ₃ , 3ÅMS	15.0	16.1	27
4.	Acetone, VO(<i>i</i> OPr) ₃ , no sieves	27.6	42.0	> 50
5.	Acetone, VO(acac) ₂ , no sieves	26.3	30.2	16
6.	Acetone, V ₂ O ₅ , no sieves	< 5	--	--
7.	Acetone, VOSO ₄ , no sieves	< 5	--	--

^a Conditions: 8 mol% vanadium, 10 mol% **1**, 1 atm O₂, 0.25 M in solvent, 4 h. Conversion and ee determined by chiral GC analysis of reaction mixture. ^c s = $k_{rel}(\text{fast/slow}) = \ln[(1-C)(1-ee)]/\ln[(1-C)(1+ee)]$.

Representative Procedure for the Preparation of Methyl Mandelate Derivatives.

To a solution of *p*-trifluorotolualdehyde (3.14 mL, 23.0 mmol) in tetrahydrofuran (30 mL) was added bis(triphenylphosphine)iododioxorhenium(V) (0.998 g, 1.15 mmol). Trimethylsilylcyanide (4.0 mL, 30.0 mmol) was then added and the resulting purple suspension was heated to 60 °C overnight with stirring. After cooling to room temperature, silica gel was added to the reaction mixture to form a thick slurry and stirred for an additional 30 min. The slurry was filtered over a pad of silica gel (ethyl acetate eluent, 300 mL), and the filtrate was concentrated with a rotary evaporator. Column chromatography (silica gel, 4:1 Hex:EtOAc) afforded the cyanohydrin as a light yellow solid (4.40 g, 95% yield). To a solution of the cyanohydrin (4.40 g, 21.9 mmol) in 25 mL of diethyl ether at 0 °C was added methanol (1.33 mL, 32.8 mmol). The reaction mixture was saturated with hydrochloric acid by bubbling anhydrous HCl(g) through the reaction mixture for 30 min. The reaction mixture was then placed in a freezer (-30 °C) overnight. The resulting white precipitate was subsequently filtered and washed with cold diethyl ether. The white solid was transferred to a 100 mL round bottom flask and left under vacuum for 1 h. Water (130 mL) was then added and the resulting mixture was stirred overnight at ambient temperature. The heterogeneous mixture was filtered and washed with water to yield the α-hydroxy ester as a white solid (3.99 g, 78% yield).

Characterization Data for Entry 2, Table 2. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (m, 2H), 6.89 (m, 2H), 5.13 (s, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.40 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 159.8, 130.5, 127.9, 114.1, 72.5, 55.3, 53.0; Anal. Calc'd for C₁₀H₁₂O₄: C, 61.22; H, 6.16; Found: C, 61.05; H, 6.43. See Table S2 for chiral assay method.

Characterization Data for Entry 3, Table 2. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (m, 2H), 7.57 (m, 2H), 5.25 (d, 1H, $J=4.0$ Hz), 3.78 (s, 3H), 3.55 (d, 1H, $J=4.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 142.0, 130.9, 130.6, 126.9, 125.5, 72.3, 53.4; Anal. Calc'd for $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_3$: C, 51.29; H, 3.87; Found: C, 51.10; H, 3.91. See Table S2 for chiral assay method.

Preparation of Substrate for Entry 4, Table 2. To a 100 mL round bottom flask equipped with a magnetic stir bar containing bis(triphenylphosphine)iododioxorhenium(V)⁴ (1.04 g, 1.2 mmol) was added tiglaldehyde (2.0 g, 24 mmol) as a solution in 50 mL of tetrahydrofuran. Trimethylsilylcyanide (4.8 mL, 36 mmol) was then added and the resulting purple suspension was heated to 60 °C overnight with stirring. After cooling to room temperature, silica gel was added to the reaction mixture to form a thick slurry and stirred for an additional 30 min. The slurry was filtered over a pad of silica gel (diethyl ether eluent, 300 mL), and the filtrate was concentrated with a rotary evaporator. Column chromatography (silica gel, 3:1→2:1 Hex:Et₂O) afforded the allylic cyanohydrin⁵ (1.83 g, 69% yield). To a solution of the cyanohydrin (1.83 g, 16.5 mmol) in 20 mL of diethyl ether at 0 °C was added benzyl alcohol (2.67 g, 24.7 mmol). The reaction mixture was saturated with hydrochloric acid by bubbling anhydrous HCl(g) through the reaction mixture for 45 min. The reaction mixture was then placed in a freezer (-30 °C) overnight. The resulting white precipitate was subsequently filtered and washed with cold diethyl ether. The white solid was transferred to a 100 mL round bottom flask and left under vacuum for 10 min. Distilled water (50 mL) was added and the resulting suspension was stirred for 2 h at room temperature. After extraction with diethyl ether, the α -hydroxy benzyl ester was obtained as a clear oil (2.24 g, 61% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 5H), 5.65 (d, 1H, $J=6.8$ Hz), 5.22 (s, 2H), 4.55 (s, 1H); 1.64 (d, 3H, $J=6.8$ Hz), 1.43 (s, 3H). Chiral GC assay for the trifluoroacetyl derivative of the racemate (Chiraldex G-TA; 90 °C hold 0 min, then 10 °C/min to 140 °C hold 10 min; 2.0 mL/min He carrier gas), t_R 13.99 min, 14.32 min.

Preparation of Substrate for Entry 7, Table 2. To a solution of (±)- α -hydroxy- γ -butyrolactone in 50 mL of methanol was added 0.15 mL of concentrated hydrochloric acid. The resulting colorless solution was heated to reflux overnight. The volatile components of the reaction mixture were then removed with a rotary evaporator, and the residue was partitioned between brine and diethyl ether (3 x 50 mL). The combined organic components were washed with brine and dried (Na_2SO_4). Column chromatography (silica gel, 10:1 EtOAc:Hex) gave the dihydroxy ester as a colorless oil.⁶ ^1H NMR (400 MHz, CDCl_3) δ 4.44 (m, 1H), 3.89-3.77 (m, 2H), 3.78 (s, 3H), 2.66 (br s, 2H), 2.13-1.96 (m, 1H), 1.93-1.87 (m, 1H). The diol (2.25 g, 16.8 mmol) was dissolved in dimethylformamide (15 mL) at 0 °C. To this clear solution was added imidazole (1.32 g, 19.0 mmol), followed by TBSCl (2.66 g, 17.6 mmol) in two portions over 15 min. The reaction mixture was warmed to room temperature overnight with stirring, and then diluted with water and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine and dried (MgSO_4). Column chromatography (silica gel, 3:1

⁴ (a) Cyanohydrin synthesis adapted from: Nolin, K.A.; Toste, F.D. *Unpublished results*. (b) For preparation of $(\text{PPh}_3)_2\text{Re}(\text{O})_2\text{I}$, see: Kennedy-Smith, J.J.; Nolin, K.A.; Gunterman, H.P.; Toste, F.D. *J. Am. Chem. Soc.* **2003**, *125*, 4056.

⁵ Hayashi, M.; Miyamoto, Y.; Inoue, T.; Oguni, N. *J. Org. Chem.* **1993**, *58*, 1515.

⁶ Hayashi, Y.; Yamaguchi, J.; Shoji, M. *Tetrahedron* **2002**, *58*, 9839.

Hex:Et₂O) gave the siloxy ester as a clear, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.73 (m, 1H), 3.82 (m, 2H), 3.78 (s, 3H), 3.34 (br s, 1H), 2.06 (m, 1H), 1.87 (m, 1H), 0.89 (s, 9H), 0.06 (s, 6H). See Table S2 for chiral assay method. A sample of enantiopure siloxy ester for analytical comparison purposes was prepared from (*R*)-(+)-α-hydroxy-γ-butyrolactone by an identical procedure.

Preparation of Substrate for Entry 8, Table 2. A 50 wt% solution of ethyl glyoxylate in toluene (10 mL, ~ 49 mmol) was heated to reflux under argon for 4 h. The solution was then cooled to 0 °C and α-methylstyrene (9.75 mL, 75 mmol) was added via syringe. Diethylaluminum chloride (25 mL, 1M in hexane) was added slowly. The reaction mixture was warmed to room temperature overnight with rapid stirring. A saturated aqueous solution of sodium sulfate was added slowly at 0 °C and the resulting white precipitate was filtered. The clear filtrate was partitioned between brine and EtOAc (3 x 150 mL). The combined organic layers were washed with brine, dried (MgSO₄) and concentrated. Column chromatography (silica gel, 3:1 Hex:Et₂O) afforded the homoallylic alcohol as a colorless oil (2.44 g, 55% yield). See Table S2 for chiral assay method. Spectral data were consistent with reported literature values.⁷

Preparation of Substrate for Entry 9, Table 2. To a solution of benzoic acid (0.61 g, 5.0 mmol) in tetrahydrofuran (5.0 mL) was added via syringe benzaldehyde (0.51 mL, 5.0 mmol) followed by *tert*-butylisocyanide (0.59 mL, 5.0 mmol). The reaction mixture was heated to 50 °C with stirring for 16 h. The resulting colorless mixture was cooled to room temperature, diluted with EtOAc, and transferred to a separatory funnel. The organic layer was washed with a saturated aqueous solution of NaHCO₃ (3 x 50 mL), dried (MgSO₄), and concentrated to give a white solid, which was dissolved in methanol (25 mL). To the solution was added NaOH (0.205 g, 5.1 mmol), and the resulting mixture was heated at reflux for 2 h. The solvent was removed by rotary evaporation. The residue was partitioned between EtOAc and a saturated aqueous solution of NaHCO₃ and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 50 mL) and the combine organic layers were washed with brine and dried (Na₂SO₄). Column chromatography (silica gel, 2:1 Hex:EtOAc) gave the product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (m, 5H), 5.90 (br s, 1H), 4.87 (s, 1H), 3.85 (br s, 1H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 139.9, 128.9, 128.6, 126.9, 74.2, 51.5, 28.7. See Table S2 for chiral assay method.

General Procedure for the Oxidative Kinetic Resolution of Secondary Alcohols – Table 2. To a 100 mL round bottom flask equipped with magnetic stir bar was added ligand **1** (110 mg, 0.33 mmol, 5.5 mol%) followed by acetone (15.0 mL) at ambient temperature to form a yellow solution. VO(O^{*i*}Pr)₃ (70 μL, 0.30 mmol, 5 mol%) was then added, and the resulting dark solution was stirred under an atmosphere of oxygen for 15 min. The alcohol (6.00 mmol, 1.0 equiv) was then added via syringe as a solution in 15.0 mL of acetone with 50 mg of an inert internal standard (hexamethylbenzene or durene). Aliquots of the reaction mixture were removed via syringe at intervals to monitor for percent conversion and enantiomeric excess. Each aliquot (0.1 mL) was filtered over a 3-cm Pasteur pipette silica gel column (diethyl ether eluent), and the filtrate was analyzed by TLC, GC, and HPLC as necessary

⁷ Evans, D.A.; Burgey, C.S.; Paras, N.A.; Vojkovsky, T.; Tregay, S.W. *J. Am. Chem. Soc.* **1998**, *120*, 5824.

(see Table S2 for details). Upon completion of the reaction (~ 50 % conversion), silica gel was added to the reaction mixture to form a thick slurry, which was stirred for 30 min. The slurry was then filtered over a pad of silica gel (diethyl ether eluent, 500 mL). The filtrate was concentrated on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel (see Table S3 for details).

Table S2. Methods for the Determination of Percent Conversion and Enantiomeric Excess.

Entry	Assay	Method	Conditions	Retention Time (min)	
				Alcohol	Ketone
1	a.) conversion	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 140 °C, 9 min
	b.) ee			9.61 minor (S) 10.02 major (R)	10.96
2	a.) conversion	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 150 °C, 20 min
	b.) ee	HPLC Chiralcel OD	10 % <i>i</i> PrOH/Hexane 1.0 mL/min	16.90 14.47 minor (S) 27.48 major (R)	23.10
3	a.) conversion	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 115 °C, 16 min
	b.) ee			17.05 minor (S) 17.45 major (R)	13.82
4	a.) conversion	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 150 °C, 20 min
	b.) ee	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 140 °C, 9 min	R= H 17.64; 18.18 (not fully resolved) R= -COCF ₃ 13.99 minor (S) 14.32 major (R)	23.52
5	a.) conversion	GC Chiraldex G-TA	90 °C, 20 min
	b.) ee			R= -COCF ₃ 8.97 major (R) 9.24 minor (S)	N/A
6	a.) conversion	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 80 °C, 20 min
	b.) ee			14.40 minor (S) 15.49 major (R)	17.03
7	a.) conversion	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 145 °C, 10 min
	b.) ee	GC Chiraldex G-TA	90 °C, 0 min 10 °C/min to 110 °C, 20 min	R=H 7.98 R= -COCF ₃ 8.97 major (R) 9.24 minor (S)	7.26
8	a.) conversion	GC Agilent DB-WAX	40 °C, 0 min 10 °C/min to 200 °C
	b.) ee	HPLC Chiralcel OJ	7% <i>i</i> PrOH/Hexane 1.0 mL/min	13.80 15.67 minor (S) 23.22 major (R)	15.04
9	a.) conversion	Calculated from recovered mass	90 °C, 0 min 10 °C/min to 140 °C, 9 min
	b.) ee	GC Chiraldex G-TA		R= -COCF ₃ 13.99 minor (S) 14.32 major (R)	N/A

Table S3. Details of Preparative Scale Resolution Experiments.

Entry	Amount	Time	Conversion	Chromatography	Alcohol	Mass	ee	s	Ketone	Mass
1.	1.08 g (6.00 mmol)	10 h	51%	10:1 $\rightarrow$ 3:1 Hex:Et ₂ O		535 mg (49%)	99%	>50		478 mg (45%)
2.	1.18 g (6.00 mmol)	5.5 h	62%	4:1 $\rightarrow$ 1:1 Hex:Et ₂ O		448 mg (38%)	95%	13		355 mg (31%)
3.	1.41 g (6.00 mmol)	4.0 h	57%	19:1 $\rightarrow$ 4:1 Hex:EtOAc		495 mg (35%)	98%	29		707 mg (51%)
4.	1.32 g (6.00 mmol)	16 h	57%	20:1 $\rightarrow$ 1:1 Hex:Et ₂ O		594 mg (45%)	92%	18		585 mg (45%)
5.	0.525 g (2.62 mmol)	5.0 h	47%	5:1 $\rightarrow$ 3:1 Hex:Et ₂ O		280 mg (53%)	50%	6		165 mg (32%)
6.	1.05 g (6.00 mmol)	90 h	55%	25:1 $\rightarrow$ 3:1 Hex:Et ₂ O		394 mg (37%)	98%	30		498 mg (49%)
7.	1.49 g (6.00 mmol)	144 h	51%	10:1 $\rightarrow$ 3:1 Hex:Et ₂ O		716 mg (48%)	90%	42		694 mg (47%)
8.	1.32 g (6.00 mmol)	72 h	48%	8:1 $\rightarrow$ 3:1 Hex:Et ₂ O		629 mg (48%)	90%	34		525 mg (40%)
9. ^a	0.13 g (0.63 mmol)	16 h	52%	4:1 $\rightarrow$ 2:1 Hex:Et ₂ O		63 mg (48%)	72%	12		63 mg (49%)

^a- Reaction conducted at 40 °C.

Preparation of *syn*- and *anti*-benzyl-2-hydroxy-3-methylpentanoate - (±)-2 and (±)-4.

To a solution of the allylic alcohol (860 mg, 3.9 mmol) in dry toluene (16 mL) under argon was added (PPh₃)₃RhCl (360 mg, 0.39 mmol). The reaction flask was vacuum evacuated and filled with H₂ three times. The reaction mixture was warmed to 65 °C and the temperature maintained with stirring overnight. The reaction mixture was concentrated with a rotary evaporator, and the residue was chromatographed (silica gel, 5:1 Hex: Et₂O) to give diastereomer (±)-2 followed by diastereomer (±)-4. Repeated column chromatography was necessary to obtain pure samples of the individual diastereomers.

Characterization Data for (±)-2. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (m, 5H), 5.22 (m, 2H), 4.23 (app s, 1H), 2.79 (br s, 1H), 1.84 (m, 1H), 1.52 (m, 1H), 1.29 (m, 1H), 0.96 (t, 3H, *J*=7.2 Hz), 0.78 (d, 3H, *J*=7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 175.3, 135.2, 128.6, 128.5, 128.4, 73.0, 67.3, 38.5, 25.9, 13.1, 11.8; Chiral GC assay for racemic sample (Chiraldex G-TA; 90 °C hold 0 min, then 10 °C/min to 150 °C hold 20 min; 2.0 mL/min He carrier gas), *t*_R 14.56 min, 14.77 min.

Characterization Data for (±)-4. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (m, 5H), 5.21 (m, 2H), 4.12 (d, 1H, *J*=4.8 Hz), 2.78 (br s, 1H), 1.83 (m, 1 H), 1.46-1.17 (m, 2H), 0.97 (d, 3H, *J*=7.2 Hz), 0.86 (t, 3H, *J*=7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 135.5, 128.9, 128.8, 128.7, 75.1, 67.5, 39.4, 23.9, 15.7, 12.0; Chiral GC assay for racemic sample (Chiraldex G-TA; 90 °C hold 0 min, then 10 °C/min to 145 °C hold 20 min; 2.0 mL/min He carrier gas), *t*_R 16.58 min, 16.83 min.

Asymmetric Oxidation of *syn*-benzyl-2-hydroxy-3-methylpentanoate - (±)-2.

To a 10 mL round bottom flask equipped with magnetic stir bar at ambient temperature was added ligand **1** (11.6 mg, 0.035 mmol, 5.5 mol%) followed by acetone (1.6 mL) to form a yellow solution. VO(OiPr)₃ (7.6 μL, 0.032 mmol, 5 mol%) was then added, and the resulting dark solution was stirred under an atmosphere of oxygen for 10 min. The alcohol (140 mg, 0.63 mmol) was then added via syringe as a solution in 1.6 mL of acetone. The reaction mixture was maintained at 40 °C for 18 h with stirring. The solvent was then removed with a rotary evaporator and the residue was purified by column chromatography (silica gel, 6:1 → 3:1 Hex:Et₂O) to give (*R*)-**3** (65 mg, 47 % yield) followed by (2*R*,3*S*)-**2** (70 mg, 50% yield). Enantiomeric excess of **2** was determined by chiral GC (Chiraldex G-TA; 90 °C hold 0 min, then 10 °C/min to 150 °C hold 20 min; 2.0 mL/min He carrier gas), *t*_R 14.56 min (minor, (2*S*,3*R*)), 14.77 min (major, (2*R*,3*S*)). Enantiomeric excess of **3** was determined by chiral HPLC (Chiralcel OJ column, 99:1 hexanes:isopropanol, 1 mL/min) *t*_R 22.46 min (minor, (*S*)), 25.93 min (major, (*R*)); Absolute stereochemistry of compound (*R*)-**3** was assigned by comparison of HPLC

retention times with compound (*S*)-**3**, see below for details. Absolute stereochemistry of compound (2*R*,3*S*)-**2** was assigned as a consequence of the assignment of (*R*)-**3**.

Asymmetric Oxidation of *anti*-benzyl-2-hydroxy-3-methylpentanoate - (±)-4**.** To a 10 mL round bottom flask equipped with magnetic stir bar at ambient temperature was

added ligand **1** (11.6 mg, 0.035 mmol, 5.5 mol%) followed by acetone (1.6 mL) to form a yellow solution. VO(O*i*Pr)₃ (7.6 μL, 0.032 mmol, 5 mol%) was then added, and the resulting dark solution was stirred under an atmosphere of oxygen for 10 min. The alcohol (140 mg, 0.63 mmol) was then added via syringe as a solution in 1.6 mL of acetone. The reaction mixture was maintained at 40 °C for 18 h with stirring. The solvent was then removed by rotary evaporation and the residue was purified by column chromatography (silica gel, 6:1→3:1 Hex:Et₂O) to give (*S*)-**3** (66 mg, 48% yield) followed by (2*R*,3*R*)-**4** (69 mg, 49% yield). Enantiomeric excess of **4** was determined by chiral GC (Chiraldex G-TA; 90 °C hold 0 min, then 10 °C/min to 145 °C hold 20 min; 2.0 mL/min He carrier gas), *t*_R 16.58 min (minor, (2*S*,3*S*)), 16.83 min (major, (2*R*,3*R*)). Enantiomeric excess of **3** was determined by chiral HPLC (Chiralcel OJ column, 99:1 hexanes:isopropanol, 1 mL/min) *t*_R 22.53 min (major, (*S*)), 25.98 min (minor, (*R*)). Absolute stereochemistry of compound **4** was assigned by comparison of optical rotation data to literature value: [α]_D = +2.7 (c 2.0, CHCl₃), (lit.⁸ [α]_D = -4.1 (c 2.0, CHCl₃)). Absolute stereochemistry of compound **3** was assigned as a consequence of the assignment of compound **4**.

Characterization Data for **3.** ¹H NMR (400 MHz, CDCl₃) δ 7.37 (m, 5H), 5.28 (s, 2H), 3.13 (m, 1H), 1.73 (m, 1H), 1.42 (m, 1H), 1.12 (d, 3H, *J*=7.2 Hz), 0.90 (t, 3H, *J*=7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 161.8, 134.6, 128.7, 128.6, 128.5, 67.7, 43.7, 24.8, 14.5, 12.3; Chiral HPLC assay for racemic sample (Chiralcel OJ column, 99:1 hexanes:isopropanol, 1 mL/min) *t*_R 22.49 min, 25.95 min.

Preparation of Chlorovanadate **5.** To a solution of VOCl₃ (44 μL, 0.465 mmol) in dry THF (15 mL) at room temperature was slowly added ligand **1** as a solution in THF (5 mL). The dark reaction mixture was stirred at room temperature for 30 min and then concentrated with a rotary evaporator to a black residue. Hexanes (10 mL) was added and the mixture was left to stand for 30 min. Filtration of the mixture afforded chlorovanadate **5** (167 mg, 82% yield) as a black solid. Spectral data were consistent with reported literature values.⁹ ⁵¹V NMR (131.53 MHz, CD₂Cl₂) δ -432 ppm.

Stoichiometric Reaction of (*S*)-Ethyl Mandelate and Chlorovanadate **5.** A 5 mL portion of acetone-*d*₆ was degassed via successive freeze-pump-thaw cycles in a 10 mL Schlenk flask and used in the following procedure. The following manipulations were conducted in an inert

⁸ Shin, I.; Lee, M.-r.; Lee, J.; Jung, M.; Lee, W.; Yoon, J. *J. Org. Chem.* **2000**, *65*, 7667.

⁹ Blum, S.A.; Bergman, R.G.; Ellman, J.A. *J. Org. Chem.* **2003**, *68*, 150.

atmosphere (N₂) glove box using oven-dried glassware. Spectra (NMR, EPR) were recorded in solution using air-tight spectroscopy tubes. Chlorovanadate **5** (130 mg, 0.30 mmol) was dissolved in 3.0 mL of acetone-*d*₆, a ⁵¹V NMR spectrum of which shows a signal at δ -438 ppm. (*S*)-(+)-Ethyl mandelate (54 mg, 0.30 mmol) was added as a solid and the dark reaction mixture was stirred at room temperature for 18 h, over the course of which the reaction mixture became green. An aliquot of the green reaction mixture was analyzed by NMR and EPR spectroscopy. A ¹H NMR spectrum indicated partial consumption of ethyl mandelate. ⁵¹V NMR of the aliquot showed no signals in the range +2500 to -2000 ppm. An X-band EPR spectrum exhibited an eight line signal (g= 1.97, Figure S2). The green reaction mixture was subsequently exposed to an atmosphere of oxygen and stirred at room temperature for an additional 12 h, over the course of which the reaction mixture became dark in color. Analysis of an aliquot of the mixture by ¹H NMR indicated complete consumption of ethyl mandelate and ⁵¹V NMR spectra show regeneration of a signal at δ -438 ppm.

Figure S2. EPR spectrum of Vanadium Intermediate After Single Turnover.

Preparation of Cyclopropane (±)-6. To a suspension of lithium aluminum hydride (0.29 g, 7.7 mmol) in dry Et₂O (15 mL) at 0 °C under nitrogen was added dropwise *trans*-2-phenylcyclopropane-1-

carboxylic acid (1.0 g, 6.17 mmol) as a solution in 10 mL of dry Et₂O. The reaction mixture was stirred at 0 °C for 3 h, and then quenched by slow addition of a saturated solution of Rochelle's salt. The mixture was extracted with ether (3 x 50 mL) and the combined organic layers washed with brine, concentrated, and dried (MgSO₄) to give the cyclopropyl alcohol as a colorless oil. The alcohol in CH₂Cl₂ (15 mL) was added dropwise to a premixed (1.5 h, -78 °C) solution of oxalyl chloride (0.81 mL, 9.26 mmol) and dimethylsulfoxide (1.75 mL, 24.7 mmol) in CH₂Cl₂ at -78 °C, and then stirred for 1 h. Triethylamine (8.4 mL, 60.17 mmol) was then added dropwise at -78 °C, and the reaction mixture was subsequently warmed to room temperature with stirring overnight. The reaction mixture was quenched by addition of an aqueous solution of 0.1 M HCl, and extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layers were washed with an aqueous solution of 0.1 M HCl and brine and then concentrated and dried

(MgSO₄). Column chromatography (silica gel, 10:1→5:1 Hex:Et₂O) gave the cyclopropyl aldehyde as a colorless oil, which solidified to a white solid upon refrigeration. The aldehyde was dissolved in 12 mL of tetrahydrofuran, to which was added bis(triphenylphosphine)iododioxorhenium(V) (260 mg, 0.30 mmol) followed by trimethylsilylcyanide (1.2 mL, 9.0 mmol). The purple reaction mixture was heated to 60 °C for 3 h, then cooled to room temperature. Silica gel was added to the reaction mixture to form a thick slurry and stirred for an additional 30 min. The slurry was filtered over a pad of silica gel (diethyl ether eluent, 100 mL), and the filtrate concentrated with a rotary evaporator. Column chromatography (silica gel, 10:1→1:1 Hex:Et₂O) afforded the cyclopropyl cyanohydrin (3.5:1 *dr*, NMR) as a light yellow oil. The following resonance were observed for the mixture of diastereomers: ¹H NMR (400 MHz, CDCl₃) δ 7.29 (m, 2H), 7.21 (m, 1H), 7.11 (m, 2H), 4.50 (d, 1H, *J*=6.4 Hz, minor diastereomer), 4.42 (d, 1H, *J*=6.4 Hz, major diastereomer), 2.15 (m, 1H), 1.67 (m, 1H), 1.25-1.13 (m, 2H). The cyanohydrin was dissolved in 5 mL of methanol and cooled to 0 °C. The solution was saturated with hydrochloric acid by bubbling anhydrous HCl through the reaction mixture for 30 min. The reaction mixture was placed in a freezer overnight (-30 °C). The volatile components were removed by rotary evaporation and the yellow residue was stirred with distilled water at room temperature for 30 min. The aqueous mixture was extracted with diethyl ether (3 x 30 mL), and the combined organic layers were washed with a saturated aqueous solution of NaHCO₃ and brine, and then dried (Na₂SO₄). Column chromatography (silica gel, 2:1 Hex:Et₂O) gave cyclopropyl methyl ester, a light yellow oil, as a 1:1 mixture of diastereomers (325 mg, 26% over 4 steps). See below for spectral data.

Asymmetric Oxidation of Cyclopropane (±)-6.

To a 2-dram vial equipped with a magnetic stir bar was added ligand **1** (8.4 mg, 0.025 mmol) followed by 0.6 mL of acetone. VO(OiPr)₃ (4.7 μL, 0.020 mmol) was added via syringe and the dark mixture was stirred under oxygen for 10 min. Cyclopropane (±)-**6** (50 mg, 0.25 mmol) was added as a solution in 0.6 mL of acetone. The reaction mixture was stirred under oxygen at room temperature for 30 h. An aliquot (0.1 mL) of the crude reaction mixture was removed via syringe and filtered over a 3-cm Pasteur pipette column of silica gel (diethyl ether eluent). The filtrate was treated with trifluoroacetic anhydride and analyzed by chiral GC. The remaining crude reaction mixture was concentrated by rotary evaporation and analyzed by ¹H NMR spectroscopy. The only signals other than catalyst observed in the ¹H NMR spectrum were verified to belong to compounds **6** and **7** by chromatographic isolation (silica gel, 5:1→2:1 Hex:Et₂O).

Characterization Data for **6**.

The following resonances were observed for the 1:1 mixture of diastereomers of **6**: ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.24 (m, 4H), 7.19-7.15 (m, 2H), 7.10-7.07 (m, 4H), 4.10 (d, 1H, *J*=6.0 Hz), 4.03 (d, 1H, *J*=6.0 Hz), 3.84 (s, 3H), 3.82 (s, 3H), 2.14 (m, 1H), 2.04 (m, 1H), 1.45 (m, 2H), 1.22 (m, 1H), 1.12 (1H), 0.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 175.1, 175.0, 141.8 (2), 128.3 (2), 126.1, 126.0, 125.8 (2), 71.3, 70.8, 52.8, 52.7, 25.6 (2), 19.5 (2), 12.0, 11.3; Chiral GC assay of the trifluoroacetyl derivative of the racemate (Chiraldex G-TA, 90 °C hold 0 min, then 10 °C/min to 130 °C hold 30

min; 2.0 mL/min He carrier gas), t_R diastereomer **A**: 16.93 min (major), 17.22 min (minor); t_R diastereomer **B**: 18.33 min (major), 18.73 min (minor).

Characterization Data for 7. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.22 (m, 3H), 7.13 (m, 2H), 3.89 (s, 3H), 3.04 (m, 1H), 2.72 (m, 1H), 1.88 (m, 1H), 1.66 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.8, 161.2, 139.1, 128.6, 127.0, 126.2, 53.11, 32.7, 29.6, 21.6; Chiral GC assay for the racemic sample (Chiraldex G-TA, 90 °C hold 0 min, then 10 °C/min to 130 °C hold 30 min; 2.0 mL/min He carrier gas), t_R 38.35 min, 40.03 min.

Chromatogram – Table 2, Entry 1 (racemic)

Data File D:\HPCHEM\1\DATA\ALEX\JUN12005.D

Sample Name: +/-mandelate

```
=====
Injection Date   : 6/12/04 6:13:00 PM      Seq. Line :    1
Sample Name     : +/-mandelate             Vial       :    3
Acq. Operator   : ALEX                     Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\MAND2.M
Last changed    : 5/28/04 9:24:53 AM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\BDS6.M
Last changed    : 10/20/04 6:45:38 PM by BDS
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.612	MM	0.0491	23.08471	7.84093	49.91447
2	10.021	MM	0.0503	23.16382	7.66774	50.08553

Totals : 46.24853 15.50867

Chromatogram – Table 2, Entry 1 (resolved)

Data File D:\HPCHEM\1\DATA\ALEX\JUL15006.D

Sample Name: ar5-020e

```
=====
Injection Date   : 7/16/04 12:56:14 AM      Seq. Line :    1
Sample Name     : ar5-020e                 Vial       :    5
Acq. Operator   : Alex                     Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\MAND2.M
Last changed    : 6/17/04 10:26:31 PM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\BDS6.M
Last changed    : 10/20/04 6:49:57 PM by BDS
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
=====
```

Chromatogram – Table 2, Entry 2 (racemic)

Sample ID:	OMe mandalate
Filename:	C:\EZStart\Projects\Default\Data\Christine\8-23-2004
11-56-51 AMCOMM_OD9010IP.met.dat	Method:
C:\EZStart\Projects\Default\Method\Christine\CMM_OD9010IP.met	
Injection volume:	10 uL

Description: {Data Description}

1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
15.248	33524934	49.553
27.208	34130149	50.447

2: 254 nm, 4 nm Results

Retention Time	Area	Area Percent
15.248	1860630	50.168
27.208	1848133	49.832

Chromatogram – Table 2, Entry 2 (resolved)

Sample ID:	Isolated p-OMe alcohol
Filename:	C:\EZStart\Projects\Default\Data\Christine\9-7-2004
8-36-48 PMCMM_OD9010IP.met.dat	Method:
C:\EZStart\Projects\Default\Method\Christine\CMM_OD9010IP.met	
Injection volume:	10 uL

Description: {Data Description}

1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
14.796	1250105	2.405
27.280	50720679	97.595

2: 254 nm, 4 nm Results

Retention Time	Area	Area Percent
14.792	78492	2.726
27.284	2801256	97.274

Chromatogram – Table 2, Entry 3 (racemic)

Data File D:\HPCHEM\1\DATA\CMM\OCT28001.D

Sample Name: CF3sub+std_t=0

```
=====
Injection Date   : 10/28/04 2:51:34 PM      Seq. Line :    1
Sample Name      : CF3sub+std_t=0          Vial       :    1
Acq. Operator    : Christine                Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method      : D:\HPCHEM\1\METHODS\MAND4.M
Last changed     : 7/29/04 10:50:01 AM by Christine
Analysis Method  : D:\HPCHEM\1\METHODS\SHUTDWN.M
Last changed     : 11/3/04 1:50:02 PM by Christine
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	16.952	MM	0.1226	160.54803	21.82233	49.76093
2	17.369	MM	0.1350	162.09070	20.00441	50.23907

Chromatogram – Table 2, Entry 3 (resolved)

Data File D:\HPCHEM\1\DATA\CMM\OCT28004.D

Sample Name: CF3sub+std_t=4h

```
=====
Injection Date   : 10/28/04 6:53:23 PM      Seq. Line :    1
Sample Name      : CF3sub+std_t=4h          Vial       :    1
Acq. Operator    : Christine                Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method      : D:\HPCHEM\1\METHODS\MAND4.M
Last changed     : 7/29/04 10:50:01 AM by Christine
Analysis Method  : D:\HPCHEM\1\METHODS\SHUTDWN.M
Last changed     : 11/3/04 1:50:02 PM by Christine
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	17.069	MM	0.1230	1.15159	1.56010e-1	0.88540
2	17.394	MM	0.1360	128.91240	15.80259	99.11460

Chromatogram – Table 2, Entry 4 (racemic)

Data File D:\HPCHEM\1\DATA\ALEX\OCT20001.D

Sample Name: ar5-067_COCHF3

```
=====
Injection Date   : 10/20/04 8:46:05 PM      Seq. Line :    1
Sample Name     : ar5-067_COCHF3          Vial       :    3
Acq. Operator   : Alex                    Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\MAND2.M
Last changed    : 6/17/04 10:26:31 PM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\BDS6.M
Last changed    : 10/20/04 9:35:33 PM by BDS
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.997	MM	0.0791	154.74883	32.60118	50.24927
2	14.315	MM	0.0948	153.21353	26.93303	49.75073

Totals : 307.96236 59.53421

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 4 (resolved)

Data File D:\HPCHEM\1\DATA\ALEX\AUG17006.D

Sample Name: ar5-069d_COCHF3

```
=====
Injection Date   : 8/18/04 2:52:43 AM      Seq. Line :    2
Sample Name     : ar5-069d_COCHF3          Vial       :    6
Acq. Operator   : Alex                    Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\MAND2.M
Last changed    : 6/17/04 10:26:31 PM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\DIAS6.M
Last changed    : 8/18/04 4:41:26 AM by Christine
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.987	MM	0.0827	1.69400	3.41467e-1	4.16316
2	14.321	MM	0.0940	38.99617	6.91718	95.83684

Totals : 40.69017 7.25864

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 5 (racemic)

Data File D:\HPCHEM\1\DATA\ALEX\JUL19003.D

Sample Name: butyne

```
=====
Injection Date   : 7/19/04 3:28:25 PM      Seq. Line :    3
Sample Name     : butyne                  Vial       :    3
Acq. Operator   : Alex                   Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\BUTYNE.M
Last changed    : 6/12/04 2:09:26 PM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\BUTYNE.M
Last changed    : 7/19/04 5:15:12 PM by Alex
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.973	MM	0.0733	80.17105	18.21972	50.03213
2	9.239	MM	0.0724	80.06808	18.42226	49.96787

Totals : 160.23913 36.64197

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 5 (resolved)

Data File D:\HPCHEM\1\DATA\ALEX\OCT25002.D

Sample Name: ar5-101-COCF3

```
=====
Injection Date   : 10/26/04 12:14:44 AM    Seq. Line :    1
Sample Name     : ar5-101-COCF3          Vial       :    8
Acq. Operator   : Alex                   Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\BUTYNE.M
Last changed    : 10/26/04 12:26:07 AM by Alex
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\BDS6.M
Last changed    : 10/26/04 12:31:31 AM by BDS
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.991	MM	0.0748	9.77987	2.17793	74.22043
2	9.264	MM	0.0801	3.39692	7.06860e-1	25.77957

Chromatogram – Table 2, Entry 6 (racemic)

Data File D:\HPCHEM\1\DATA\ALEX\JUL04004.D

Sample Name: ar5-017a

```
=====
Injection Date   : 7/4/04 12:38:33 PM      Seq. Line :    2
Sample Name     : ar5-017a                Vial       :    3
Acq. Operator   : Alex                    Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method      : D:\HPCHEM\1\METHODS\LEUCIC.M
Last changed     : 7/4/04 12:06:52 PM by ALEX
Analysis Method  : D:\HPCHEM\1\METHODS\BDS6.M
Last changed     : 10/20/04 8:54:38 PM by BDS
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.291	MM	0.1254	360.01190	47.85465	49.98230
2	15.383	MM	0.1473	360.26682	40.77335	50.01770

Totals : 720.27872 88.62800

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 6 (resolved)

Data File D:\HPCHEM\1\DATA\ALEX\JUL18001.D

Sample Name: ar5-019e

```
=====
Injection Date   : 7/18/04 2:41:48 PM      Seq. Line :    1
Sample Name     : ar5-019e                Vial       :    1
Acq. Operator   : Alex                    Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method      : D:\HPCHEM\1\METHODS\LEUCIC.M
Last changed     : 7/6/04 11:48:01 AM by ALEX
Analysis Method  : D:\HPCHEM\1\METHODS\BDS6.M
Last changed     : 10/20/04 8:54:38 PM by BDS
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.455	MM	0.1706	1.06885	1.04414e-1	1.95730
2	15.512	MM	0.1287	53.53937	6.93476	98.04270

Totals : 54.60822 7.03918

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 7 (racemic)

Data File D:\HPCHEM\1\DATA\ALEX\JUL30006.D

Sample Name: ar5-034-COCF3

```
=====
Injection Date   : 7/30/04 7:44:03 PM      Seq. Line :    2
Sample Name     : ar5-034-COCF3           Vial       :    7
Acq. Operator   : Alex                   Inj        :    1
                                           Inj Volume : 1 µl
Acq. Method     : D:\HPCHEM\1\METHODS\G-OTBS.M
Last changed    : 7/30/04 7:02:25 PM by Christine
Analysis Method : D:\HPCHEM\1\METHODS\MAND3.M
Last changed    : 7/31/04 2:18:33 PM by Christine
                  (modified after loading)
=====
```

Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.758	MM	0.0816	63.19650	12.90050	49.80486
2	11.039	MM	0.0822	63.69172	12.91580	50.19514

Totals : 126.88822 25.81630

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 7 (resolved)

File D:\HPCHEM\1\DATA\ALEX\AUG06003.D

Sample Name: ar5-041d-COCF3

```
=====
Injection Date   : 8/6/04 2:42:12 PM      Seq. Line :    3
Sample Name     : ar5-041d-COCF3         Vial       :    2
Acq. Operator   : Alex                   Inj        :    1
                                           Inj Volume : 1 µl
Acq. Method     : D:\HPCHEM\1\METHODS\G-OTBS.M
Last changed    : 7/30/04 7:02:25 PM by Christine
Analysis Method : D:\HPCHEM\1\METHODS\CPROP.M
Last changed    : 8/6/04 4:05:48 PM by Christine
                  (modified after loading)
=====
```

Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.752	MM	0.0813	49.20158	10.08814	94.92925
2	11.021	MM	0.0838	2.62816	5.22703e-1	5.07075

Totals : 51.82973 10.61085

Results obtained with enhanced integrator!

*** End of Report ***

Chromatogram – Table 2, Entry 8 (racemic)

Sample ID:	ar5-076
Filename:	C:\EZStart\Projects\Default\Data\Alex\9-1-2004
4-43-39 PMar_OJ9307IP.met.dat	Method:
C:\EZStart\Projects\Default\Method\Alex\ar_OJ9307IP.met	
Injection volume:	5 uL

Description: {Data Description}

1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
16.948	14452165	50.004
26.612	14449724	49.996

2: 254 nm, 4 nm Results

Retention Time	Area	Area Percent
16.948	7163960	49.671
26.612	7258836	50.329

Chromatogram – Table 2, Entry 8 (resolved)

Sample ID:	ar5-099
Filename:	C:\EZStart\Projects\Default\Data\Alex\10-21-2004
6-24-50 PMar_OJ9307IP.met.dat	Method:
C:\EZStart\Projects\Default\Method\Alex\ar_OJ9307IP.met	
Injection volume:	5 uL

Description: {Data Description}

1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
11.816	2085338	4.779
13.832	41552311	95.221

2: 254 nm, 4 nm Results

Retention Time	Area	Area Percent
11.812	1229942	5.612
13.832	20684512	94.388

Chromatogram – Table 2, Entry 9 (racemic)

Data File D:\HPCHEM\1\DATA\ALEX\NOV15001.D

Sample Name: ar5-116a-COCF3

```
=====
Injection Date   : 11/15/04 12:47:04 PM      Seq. Line :    1
Sample Name     : ar5-116a-COCF3            Vial       :    2
Acq. Operator   : Alex                      Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\MAND2.M
Last changed    : 6/17/04 10:26:31 PM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\SHUTDWN.M
Last changed    : 12/14/04 4:14:08 PM by Alex
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.826	BB	0.0542	44.71612	12.96230	50.10311
2	10.999	BB	0.0512	44.53208	12.91915	49.89689

```
Totals :                      89.24820  25.88145
```

Chromatogram – Table 2, Entry 8 (resolved)

Data File D:\HPCHEM\1\DATA\ALEX\DEC02001.D

Sample Name: ar5-135

```
=====
Injection Date   : 12/4/04 8:08:25 PM      Seq. Line :    1
Sample Name     : ar5-135                  Vial       :    1
Acq. Operator   : Alex                      Inj        :    1
                                           Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\1\METHODS\MAND2.M
Last changed    : 6/17/04 10:26:31 PM by ALEX
Analysis Method : D:\HPCHEM\1\METHODS\SHUTDWN.M
Last changed    : 12/14/04 4:14:08 PM by Alex
                  (modified after loading)
=====
```

Area Percent Report

```
=====
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
=====
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.809	MM	0.0559	27.04097	8.05861	13.63011
2	11.010	MM	0.0601	171.35043	47.49542	86.36989

```
Totals :                      198.39140  55.55404
```