Supporting Information

Vanadium Catalyzed Asymmetric Epoxidation of Homoallylic Alcohols

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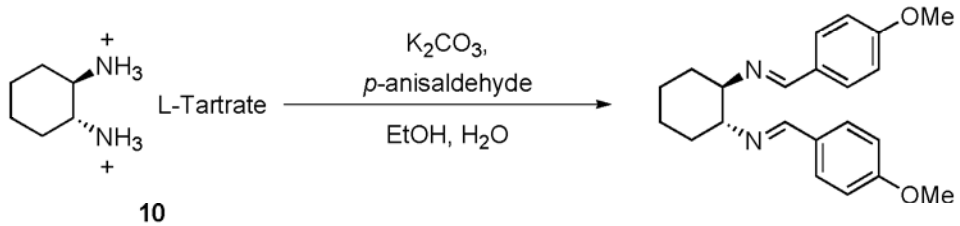
General.

Infrared (IR) spectra were recorded on a Nicolet 20 SXB FTIR. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. Chemical shift values (δ) are expressed in ppm downfield relative to internal standard (tetramethylsilane at 0 ppm). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer and are expressed in ppm using solvent as the internal standard ($CDCl_3$ at 77.0 ppm). Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector and capillary columns of γ-TA (0.25 mm $\times$ 50m), B-DP (0.25 mm $\times$ 20m) using nitrogen as carrier gas. High-performance liquid chromatography (HPLC) was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary columns (Chiracel, AD-H 0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. High-resolution electro spray ionization (HRMS-ESI) mass spectra were obtained on a Micromass Q-Tof-2, Quadrupole Time of Flight mass spectrometer at the University of Illinois Research Resources Center in positive mode.

All reactions were carried out in oven-dried glassware with magnetic stirring unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on Merck pre-coated TLC plates (silica gel 60 GF254, 0.25mm). Flash chromatography was performed on silica gel E. Merck 9385. Toluene ($PhCH_3$) was purchased from Acros as anhydrous solvents. *N,N*-diisopropylethylamine and triethylamine were stored over KOH pellets. Homoallylic alcohols were purchased from commercial vendors or have been previously prepared by reported procedures and characterized.

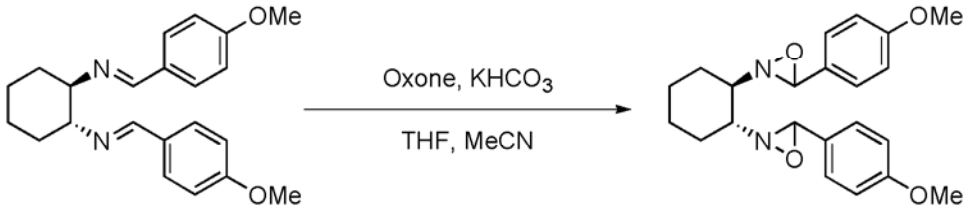
Preparation of (*R,R*)-*N,N'*-*Bis*-(4-methoxybenzylidene)-cyclohexane-1,2-diimine.



10

A mixture of diammonium salt (**10**) (26.4 g, 100 mmol), K_2CO_3 (27.6 g, 200 mmol), and de-ionized water (130 mL) was stirred until dissolution was achieved, and then ethanol (420 mL) was added. The resulting cloudy mixture was heated to reflux, and a solution of *p*-anisaldehyde (27.5 g, 200 mmol) in ethanol (40 mL) was added in a steady stream over 30 min. The yellow slurry was stirred at reflux for 5 h before heating was discontinued. The reaction mixture was cooled to room temperature, and the water phase was separated and discarded. The organic phase was concentrated and dissolved in dichloromethane. It was then removed any trace of water, dried over Na_2SO_4 and filtered. The filtrate was removed solvent to provide crude diimine as light yellow solid, which was purified by recrystalization from dichloromethane and hexanes as white solid (31.5 g, 90% yield). FTIR (film) υ_{max} 2929, 2855, 1643, 1606, 1579, 1512, 1463, 1303, 1250, 1165, 1032, 831 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 2 H), 7.52 (d, J = 8.8 Hz, 4 H), 6.82 (d, J = 8.8 Hz, 4 H), 3.78 (s, 6 H), 3.37-3.32 (m, 2 H), 1.87-1.77 (m, 6 H), 1.49-1.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (C), 160.5 (CH), 129.7 (CH), 114.0 (CH), 74.0 (CH_3), 55.5 (CH), 33.3 (CH_2), 24.8 (CH_2); HRMS-ESI calcd for $C_{22}H_{27}O_6N_2$ $[M+H]^+$ 351.2073, found 351.2076.

Preparation of Dioxaziridine 11.

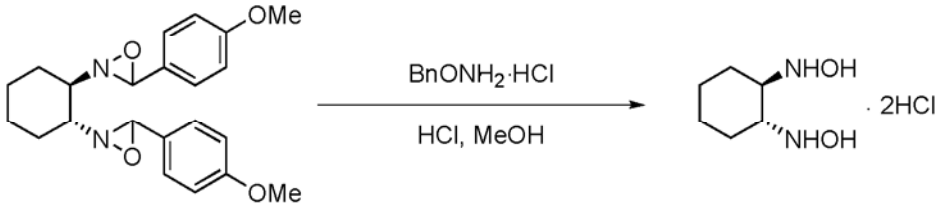


11

To a stirred solution of diimine (10.5 g, 30.0 mmol) in MeCN (180 mL) and THF (360 mL), at room temperature, was added an aqueous solution (300 mL) of $KHCO_3$ (50.5 g, 504 mmol) followed by an aqueous solution (300 mL) of Oxone (44 g, 72 mmol). After stirring for 3 h, the reaction mixture was diluted with CH_2Cl_2 (600 mL). The biphasic mixture was separated and the aqueous portion was extracted with

CH_2Cl_2 (2 x 100 mL) and the combined organic extracts was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to provide crude dioxaziridine **11** (10.3 g, 90% yield) as light yellow solid, which was used in the following step without further purification. Pure product, which was applied to determine the structure, was obtained by recrystalization from dichloromethane and hexane as white solid: FTIR (film) υ_{max} 2935, 1615, 1517, 1309, 1456, 1437, 1310, 1252, 1171, 1031, 821 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.81-6.78 (m, 4 H), 6.58-6.54 (m, 4 H), 4.37 (s, 2 H), 3.78 (s, 6 H), 2.39-2.37(m, 2 H), 2.21-2.18 (m, 2 H), 1.83-1.80 (m, 2 H), 1.58-1.51 (m, 2 H), 1.31-1.27 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7 (C), 129.0 (CH), 126.5 (C), 113.8 (CH), 81.6 (CH), 72.4 (CH_3/CH), 55.4 (CH_3/CH), 30.3 (CH_2), 24.1 (CH_2); HRMS-ESI calcd for $C_{22}H_{26}O_4N_2Na$ $[M+Na]^+$ 405.1788, found 405.1790.

Preparation of Dihydroxylamine dihydrochloride.

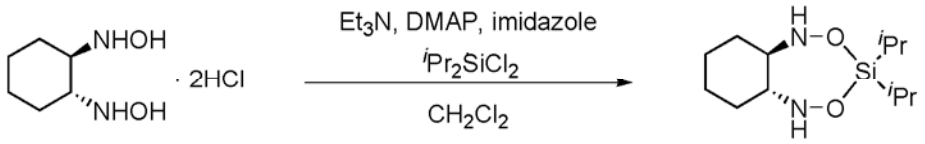


11

To a mixture of the unpurified product **11** (10.3 g) obtained from the previous oxidation reaction and benzyloxyhydroxyl amine hydrochloride (8.80 g, 55.1 mmol) was treated with anhydrous methanol (250 mL), and then 1 M HCl in MeOH (94 mL, 94 mmol) was added immediately. The resulting mixture was stirred for 20 minutes. The reaction mixture was then concentrated under reduced pressure to dryness. Et_2O (200 mL) and de-ionized water (100 mL) was added. The bi-layer was separated and the organic part was extracted with de-ionized water (20 mL). Combined aqueous portion was washed with Et_2O (2 x 100 mL). The aqueous portion was concentrated to 60-75 mL and the resulting white solid ($BnONH_2$.HCl) was filtered off, then filtrate was concentrated under reduced pressure to provide *bis*-hydroxylamine dihydrochloride (6.10 g) as an oily solid, which contained 5-10% of $BnONH_2$.HCl. This material was utilized in the next step without any purification: ^1H NMR (400 MHz, D_2O) δ 3.66-3.62 (m, 2 H), 2.02-1.98 (m, 2 H), 1.69-1.66 (m, 2 H), 1.41-1.37

(m, 4 H), 1.20-1.15 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 58.6 (CH), 25.1 (CH_2), 22.1 (CH_2).

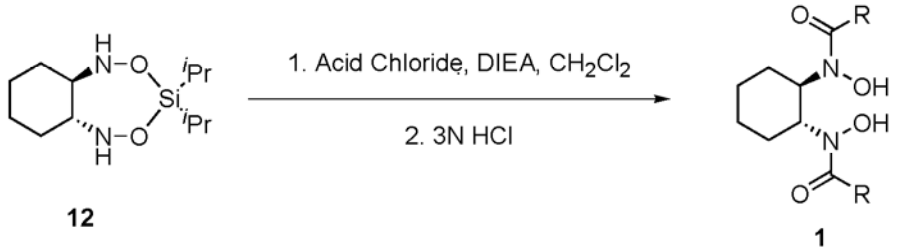
Preparation of *O*-protected Dihydroxylamine 12.



12

To a stirred suspension of unpurified *bis*-hydroxylamine dihydrochloride **11** (6.10 g) obtained from the previous reaction in CH_2Cl_2 (100 mL) under nitrogen at room temperature was added Et_3N (11.1 mL, 76.8 mmol). After 1 h, to the resulting cloudy white suspension, DMAP (180 mg, 1.47 mmol), imidazole (2.00 g, 29.4 mmol) followed by triethylsilyl chloride (5.00 mL, 27.7 mmol) were added and stirring was continued 2 h, and then poured into an aqueous solution of $NaHCO_3$ (5.16 g, 61.4 mmol) and extracted with EtOAc (2 x 100 mL). The combined organic extracts was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in a small amount of dichloromethane and filtered through a small plug of silica gel by washing with the mixture of EtOAc/hexanes (5:95) to provide **12** (3.85 g), which was used in the following step without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (br, 2 H), 2.83-2.77 (m, 2 H), 1.76-1.74 (m, 2 H), 1.54-1.50 (m, 2 H), 1.30-1.26 (m, 2H), 1.12-1.03 (m, 16 H).

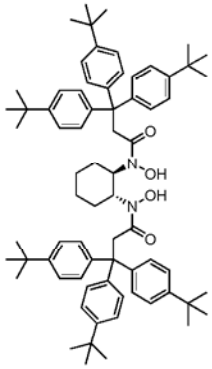
General procedure for preparation of *Bis*-hydroxamic acids (1c, 1d).



12 **1**

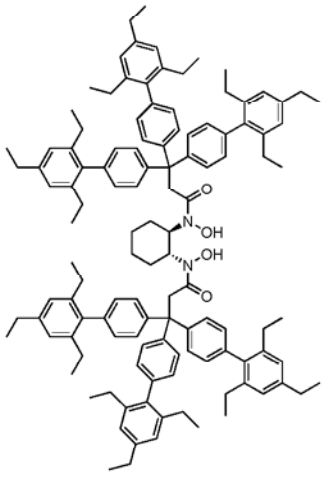
To a stirred solution of **12** (570 mg, ~2.0 mmol) obtained from the previous reaction and DIEA (1.04 mL, 6.00 mmol) in CH_2Cl_2 (20 mL) was added acid chloride (6.00 mmol, dissolved in 10 mL CH_2Cl_2) under nitrogen. After 72 h, the reaction mixture

was treated with 3N HCl (or 1M HCl/MeOH). After stirring for 30 min the reaction mixture was extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel to provide the *bis*-hydroxamic acid.



1c

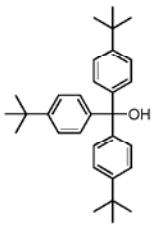
1c: Yield, 45%; white solid: R_f 0.50 (EtOAc/hexanes, 1:6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br, 2 H), 7.23-7.21 (m, 12 H), 7.16-7.14 (m, 12 H), 4.23-4.20 (m, 2 H), 4.13-4.11 (m, 2 H), 3.67-3.64 (m, 2 H), 1.60-1.00 (m, 8 H), 1.27 (s, 54 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 (C=O), 148.3 (C), 144.2 (C), 129.0 (CH), 124.4 (CH), 55.0 (C), 54.9 (CH), 42.3 (CH_2), 34.3 (C), 31.4 (CH_3), 27.4 (CH_2), 24.3 (CH_2). HRMS-ESI calcd for $C_{72}H_{95}O_4N_2$ $[M+H]^+$ 1051.7286, found 1051.7267.



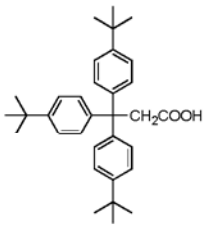
1d

1d: Yield, 40%; white solid: R_f 0.45 (EtOAc/hexanes, 1:6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2 H), 7.29-7.27 (m, 12 H), 7.04-7.01 (m, 12 H), 6.93 (s, 12H), 4.51 (d, J = 16.4 Hz, 2 H), 4.11-4.10 (m, 2 H), 3.73 (d, J = 16.4 Hz, 2 H), 2.65 (q, J = 7.6 Hz, 12 H), 2.32 (q, J = 7.5 Hz, 24 H), 1.78-1.74 (m, 6 H), 1.28 (q, J = 7.6 Hz, 18 H), 1.22-1.20 (m, 2 H), 0.99 (t, J = 7.5 Hz, 36 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7 (C=O), 145.6 (C), 143.1 (C), 142.1 (C), 138.2 (C), 137.8 (C), 129.2 (CH), 128.9 (CH), 125.1 (CH), 55.7 (C), 54.8 (CH), 43.7 (CH_2), 28.6 (CH_2), 27.6 (CH_2) 26.9 (CH_2), 24.4 (CH_2), 15.5 (CH_3), 15.4 (CH_3); HRMS-ESI calcd for $C_{120}H_{143}O_4N_2$ $[M+H]^+$ 1676.1042, found 1676.1040.

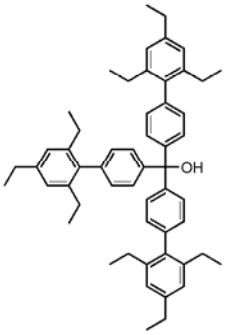
Preparation of Carboxylic acids for Ligand 1c and 1d.



The corresponding alcohol of ligand **1c** was prepared from 1-Bromo-4-*tert*-butylbenzene: To a stirred solution of 1-Bromo-4-*tert*-butylbenzene (29.8 g, 140 mmol) in anhydrous THF (150 mL) under nitrogen at –78°C was added *tert*-BuLi (165mL, 1.7M solution in pentane, 280 mmol) slowly. This solution was then allowed warm to rt. Then diethyl carbonate (5.5g, 46.6 mmol) was added slowly at rt and stirring was kept for 1h. Water was then added to quench the reaction. 3N HCl was added to acidify the mixture, which was then extracted by ether, dried over Na_2SO_4. Solvent was then removed to provide crude product, which was then purified by recrystalization from ether and hexanes. Yield, 80%; White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 6 H), 7.20-7.18 (m, 6 H), 2.75 (br, 1 H), 1.31 (s, 27 H).

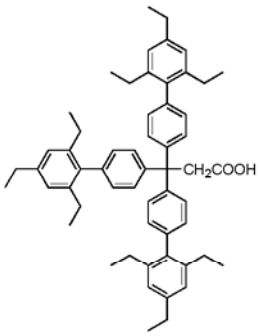


To a stirred solution of AcOH (90 mL), Ac_2O (30 mL) and malonic acid (11.76 g, 113 mmol) was heated to 110°C under N_2. To this mixture, a mixture of alcohol (4.84 g, 11.3 mmol) and malonic acid (11.76 g, 113 mmol) was added portionwise. Additional malonic acid (11.76 g, 113 mmol) was then added followed by AcOH (30 mL). Heating was kept 1.5 h. The mixture was then allowed to warm to rt and poured into saturated KOH solution (pH was kept as 9 ~ 10). The precipitate was filtered and was purified by flash column chromatography on silica gel. Yield, 75%; white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (m, 6 H), 7.04-7.02 (m, 6 H), 3.50 (s, 2 H), 1.29 (m, 27 H).



The corresponding alcohol of ligand **1d** was prepared from 4'-Bromo-2,4,6-trirethyl-biphenyl: To a stirred solution of 4'-Bromo-2,4,6-trirethyl-biphenyl (44.4 g, 140 mmol) in anhydrous THF (150 mL) under nitrogen at –78°C was added *tert*-BuLi (165mL, 1.7M solution in pentane, 280 mmol) slowly. This solution was then allowed warm to rt. Then diethyl carbonate (5.5g, 46.6 mmol) was added slowly at rt and stirring was kept for 1h. Water was then added to quench the reaction. 3N HCl was added to acidify the mixture, which was

then extracted by ether, dried over Na_2SO_4. Solvent was then removed to provide crude product, which was then purified by recrystalization from ether and hexanes. Yield, 73%; White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 6 H), 7.20-7.18 (m, 6 H), 7.00 (s, 6 H), 3.02 (br, 1 H), 2.69 (q, J = 7.6 Hz, 6 H), 2.38 (q, J = 7.6 Hz, 12 H), 1.32 (t, J = 7.6 Hz, 9 H), 1.06 (t, J = 7.6 Hz, 18 H).



To a stirred solution of AcOH (450 mL), Ac_2O (150 mL) and malonic acid (16.6 g, 160 mmol) was heated to 110°C under N_2. To this mixture, a mixture of alcohol (11.8 g, 15.9 mmol) and malonic acid (16.6 g, 160 mmol) was added portionwise. Additional malonic acid (16.6 g, 160 mmol) was then added followed by AcOH (150 mL). Heating was kept 1.5 h. The mixture was then allowed to warm to rt and poured into saturated KOH solution (pH was kept as 9 ~ 10). The precipitate was filtered and was purified by flash column chromatography on silica gel. Yield, 80%; white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 6 H), 7.13-7.11 (m, 6 H), 6.98 (s, 6 H), 3.89 (s, 2 H), 2.70 (q, J = 7.6 Hz, 6 H), 2.39 (q, J = 8.6 Hz, 12 H), 1.31 (t, J = 7.6 Hz, 9 H), 1.00 (t, J = 7.6 Hz, 18 H).

General procedure for asymmetric epoxidation of homoallylic alcohols in the presence of $VO(OPr^i)_3$ and ligand 1d.

To a solution of **1d** (35.2mg, 0.0210 mmol) in toluene (0.25 mL) was added $VO(OPr^i)_3$ (0.0025 mL, 0.0104 mmol), and the mixture was stirred for 8 h at room temperature. 88% cumene hydroperoxide (CHP) (0.25 mL, 1.50 mmol) and homoallylic alcohol **2** (1.05 mmol) were then added and the stirring was continued at the same temperature for 24 hours. The process of epoxidation was monitored by TLC. The mixture was then allowed to be purified by flash column chromatography on silica gel to provide epoxy alcohol **3**.

3a: Yield, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5 H), 3.88-3.87 (m, 2 H), 3.74 (d, J = 2.1 Hz 1 H), 3.17-3.14 (m, 1 H), 2.14-2.09 (m, 1 H), 1.90-1.85 (m, 1

H), 1.80 (br, 1 H); 96% ee, HPLC (AD-H), Hexanes: ^{i}Propanol = 95:5, flow rate = 1 mL/min, 15.0 min (major), 17.6 min (minor).

3b: Yield, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 5 H), 4.14 (d, J = 4.2 Hz, 1 H), 3.80-3.76 (m, 2 H), 3.42-3.38 (m, 1 H), 1.61-1.51 (m, 3 H); 99% ee, HPLC (AD-H), Hexanes: ^{i}Propanol = 98:2, flow rate = 0.7 mL/min, 54.3 min (major), 57.7 min (minor).

3c: Yield, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82-3.76 (m, 2 H), 2.90-2.85 (m, 1 H), 2.78-2.74 (m, 1 H), 2.00-1.90 (m, 1 H), 1.76-1.63 (m, 1 H), 1.58 (br, 1 H), 1.00 (t, J = 16.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.8 (CH_2), 56.5 (CH), 56.5 (CH), 34.3 (CH_2), 25.9 (CH_2), 9.8 (CH_3); 93% ee, GC (γ-TA), injection 120°C, column 100°C, pressure 100Kpa, 41.8 min (major) (***3R, 4R***), 45.3 min (minor) (***3S, 4S***).

3d: Yield, 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80-3.79 (m, 2 H), 2.87-2.86 (m, 1 H), 2.81-2.80 (m, 1 H), 2.01-1.92 (m, 1 H), 1.91 (br, 1 H), 1.71-1.65 (m, 1 H), 1.55-1.52 (m, 2 H), 1.44-1.40 (m, 2 H), 1.34-1.30 (m, 4 H), 0.92 (t, J = 5.8 Hz, 3 H); 96% ee, GC (γ-TA), injection 120°C, column 100°C, pressure 100Kpa, 36.7 min (major), 38.0 min (minor).

3e: Yield, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80-3.79 (m, 2 H), 2.87-2.86 (m, 1 H), 2.81-2.80 (m, 1 H), 2.04-1.94 (m, 1 H), 1.90 (br, 1 H), 1.73-1.63 (m, 1 H), 1.55-1.52 (m, 2 H), 1.45-1.43 (m, 2 H), 1.36-1.30 (m, 6 H), 0.90 (t, J = 6.6 Hz, 3 H); 98% ee, GC (γ-TA), injection 120°C, column 100°C, pressure 100Kpa, 61.8 min (major), 63.0 min (minor).

3f: Yield, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84-3.81 (m, 2 H), 3.10-3.09 (m, 1 H), 2.91-2.89 (m, 1 H), 2.16 (br, 1 H), 1.85-1.83 (m, 1 H), 1.70-1.67 (m, 1 H), 1.58-1.50 (m, 2 H), 1.05 (t, J = 7.6 Hz, 3 H); 95% ee, GC (γ-TA), injection 120°C, column 100°C, pressure 100Kpa, 29.6 min (minor) (***3S, 4R***), 36.8 min (major) (***3R, 4S***).

3g: Yield, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90-3.84 (m, 2 H), 3.11-3.08 (m, 1 H), 2.97-2.96 (m, 1 H), 1.89-1.87 (m, 2 H), 1.72-1.70 (m, 1 H), 1.54-1.50 (m, 4 H),

1.00 (t, J = 7.6 Hz, 3 H); 97% ee, GC (γ-TA), injection 140°C, column 120°C, pressure 100Kpa, 18.4 min (minor), 19.6 min (major).

3h: Yield, 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90-3.85 (m, 2 H), 3.11-3.08 (m, 1 H), 2.96-2.95 (m, 1 H), 1.86-1.85 (m, 2 H), 1.70-1.67 (m, 1 H), 1.56-1.38 (m, 6 H), 0.94 (t, J = 7.5 Hz, 3 H); 99% ee, GC (γ-TA), injection 140°C, column 120°C, pressure 100Kpa, 26.1 min (minor), 28.4 min (major).

3i: Yield, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80-3.78 (m, 2 H), 3.50 (br, 1 H), 3.10-3.07 (m, 1 H), 2.96-2.95 (m, 1 H), 1.85-1.83 (m, 1 H), 1.69-1.66 (m, 1 H), 1.54-1.52 (m, 4 H), 1.36-1.33 (m, 4 H), 0.92 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.2 (CH_2), 56.9 (CH), 54.9 (CH), 31.4 (CH_2), 30.6 (CH_2), 27.8 (CH_2), 26.1 (CH_2); 22.5 (CH_2), 13.9 (CH_3); 99% ee, GC (γ-TA), injection 140°C, column 120°C, pressure 100Kpa, 41.8 min (minor), 45.1 min (major).

Procedure for kinetic resolution of homoallylic alcohols in the presence of $VO(OPr^i)_3$ and ligand 1d.

To a solution of **1d** (35.2 mg, 0.0210 mmol) in toluene (0.25 mL) was added $VO(OPr^i)_3$ (0.0025 mL, 0.0104 mmol), and the mixture was stirred for 8 h at room temperature. 88% cumene hydroperoxide (CHP) (0.37 mL, 1.47 mmol) and homoallylic alcohol **4** (racemic, 2.10 mmol) were then added and stirring was continued at the same temperature for 30 h. [The process of conversion was monitored by GC: Detailed information of determining the ee values of the homoallylic alcohol **4** and the epoxy alcohol **5** was provided as following.] Saturated aqueous Na_2SO_3 was added when the conversion reached 50%, and the mixture was stirred for 1 h at 0 °C. The mixture was then allowed to warm to room temperature, extracted with Et_2O, dried over Na_2SO_4 and concentrated under reduced pressure. The remaining residue was purified by flash column chromatography on silica gel to provide the homoallylic alcohols **4** and the epoxy alcohols **5**.

4a: Yield, 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54-5.51 (m, 1 H), 5.12-5.07 (m, 1 H), 3.48 (br, 1 H), 3.35-3.31 (m, 1 H), 2.70-2.68 (m, 1 H), 2.11-2.08 (m, 2 H), 1.58

(br, 1 H), 1.00-0.94 (m, 6 H); 95% ee, GC (B-DP), injection 100°C, column 80°C, pressure 100Kpa, 4.8 min (major) (***R***), 5.2 min (minor) (***S***).

(9a, which was prepared from Methyl (*S*)-(-)-3-hydroxy-2-methylpropionate by reported procedure, was obtained as a mixture of *(Z)*-(*R*)-2-Methyl-hex-3-en-1-ol and *(E)*-(*R*)-2-Methyl-hex-3-en-1-ol (95:5). The retention time was 4.8 min and 5.0 min respectively based on conditions: GC (B-DP), injection 100°C, column 80°C, pressure 100Kpa.)

5a: Yield, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80-3.76 (m, 1 H), 3.68-3.66 (m, 1 H), 2.92-2.89 (m, 1 H), 2.83-2.80 (m, 1 H), 2.00-1.90 (m, 1 H), 1.70 (br, 1 H), 1.63-1.55 (m, 2 H), 1.09 (t, *J* = 7.5 Hz, 3 H), 0.99 (d, *J* = 6.9 Hz, 3 H); 95% ee, GC (B-DP), injection 150°C, column 130°C, pressure 100Kpa, 16.4 min (minor), 17.2 min (major).

4b: Yield, 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56-5.53 (m, 1 H), 5.14-5.09 (m, 1 H), 3.48 (br, 1 H), 3.39-3.45 (m, 1 H), 2.70-2.68 (m, 1 H), 2.11-2.08 (m, 2 H), 1.58 (br, 1 H), 1.00-0.94 (m, 6 H); 96% ee, GC (B-DP), injection 110°C, column 80°C, pressure 100Kpa, 15.9 min (major) (***R***), 16.7 min (minor) (***S***).

(9b, which was prepared from Methyl (*S*)-(-)-3-hydroxy-2-methylpropionate by reported procedure, was obtained as a mixture of *(Z)*-(*R*)-2-Methyl-oct-3-en-1-ol and *(E)*-(*R*)-2-Methyl-oct-3-en-1-ol (97:3). The retention time was 15.9 min and 16.9 min respectively based on conditions: GC (B-DP), injection 110°C, column 80°C, pressure 100Kpa.)

5b: Yield, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80-3.76 (m, 1 H), 3.68-3.66 (m, 1 H), 2.92-2.89 (m, 1 H), 2.83-2.80 (m, 1 H), 2.00-1.90 (m, 1 H), 1.70 (br, 1 H), 1.63-1.55 (m, 2 H), 1.09 (t, *J* = 7.5 Hz, 3 H), 0.99 (d, *J* = 6.9 Hz, 3 H); 97% ee, GC (B-DP), injection 130°C, column 110°C, pressure 100Kpa, 23.4 min (major), 25.6 min (minor).

Proposed Model of the Asymmetric Epoxidation of Homoallylic Alcohols Catalyzed by the Complex of Vanadium and Ligand 1d