Highly Regio- and Stereoselective Rearrangement of Epoxides to Aldehydes Catalyzed by High-Valent Metalloporphyrin Complex, Cr(TPP)OTf

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Supporting Information

General. ^1H - and ^{13}C -NMR spectra were recorded on a JEOL JNM-EX270, JNM-AL300, and JNM-GSX400 spectrometer. The chemical shifts were reported in ppm relative to CHCl_3 ($\delta = 7.26$) for ^1H -NMR and relative to the central CDCl_3 resonance ($\delta = 77.0$) for ^{13}C -NMR. UV-visible absorption spectra were measured with a Hitachi U-3210 spectrophotometer. IR spectra were recorded on a JASCO FT/IR-7000 spectrophotometer. Optical rotation was measured on a JASCO DIP-4 polarimeter. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer. Cyclic voltammetry was carried out at 25°C using BAS CV-50W electrochemical analyzer: working electrode, BAS-GCE glassy carbon disk (7.07 mm^2 area); counter electrode, Pt wire (0.1 mm diameter); reference electrode, Ag wire (1 mm diameter). Chiral HPLC analysis was performed on a JASCO GULLIVER-series instrument.

Materials. Merck kiesel-gel 60 and Merck kiesel-gel 60 F_{254} were employed for silica gel column and thin layer chromatographies, respectively. 1,2-Dichloroethane and toluene were distilled from P_2O_5 . THF and dioxane were distilled from benzophenone ketyl under a nitrogen atmosphere. Iron(III), manganese(III) and chromium(III) tetraphenylporphyrin complexes, $\text{Fe}(\text{TPP})\text{ClO}_4$,¹ $\text{Mn}(\text{TPP})\text{ClO}_4$,² $\text{Cr}(\text{TPP})\text{ClO}_4$,³ and $\text{Cr}(\text{TPP})\text{Cl}$,⁴ were prepared by the literature methods. Salen complexes, (*S,S*)-(+)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino manganese(III) and chromium(III) triflates, $\text{Mn}(\text{salen})\text{OTf}$ and $\text{Cr}(\text{salen})\text{OTf}$, were prepared from the corresponding metallosalen chlorides, $\text{Mn}(\text{salen})\text{Cl}$ and $\text{Cr}(\text{salen})\text{Cl}$, respectively, by a counter ion exchange reaction using AgOTf in THF. Other chemicals were commercial products and were used without further purifications unless otherwise stated.

Preparation of tetraphenylporphynatochromium (III) Triflate, Cr(TPP)OTf. All glassware and a stirrer bar were dried overnight in an oven at 130°C and assembled while still warm. In two necked flask fitted with condenser was placed $\text{Cr}(\text{TPP})\text{Cl}$ (140 mg, 0.2 mmol). The flask was sealed with septum, then was evacuated and backfilled with Ar. To the solid $\text{Cr}(\text{TPP})\text{Cl}$ was added anhydrous THF (30 mL), and the mixture was refluxed for 10 min. To the refluxing solution was added AgOTf (62 mg, 0.24 mmol) in one portion, and the reaction mixture was continued to reflux under Ar until no $\text{Cr}(\text{TPP})\text{Cl}$ was found in the UV-visible spectrum of the solution (ca. 3h): absorption maxima shifted gradually from 603 and 450 nm to 598 and 452 nm, respectively, during the axial ligand exchange reaction. The reaction mixture was allowed to cool to room temperature and then filtered through a Celite. The filtrate was concentrated under a reduced pressure, and the resulting residue was purified by recrystallization from CH_2Cl_2 –hexane (twice time) to give $\text{Cr}(\text{TPP})\text{OTf}$ as a dark green solid (77 mg, 46 %). UV-visible spectrum, cyclic voltammogram and IR spectrum are shown in Fig. 1, Fig. 2 and Fig. 3 on pages S8, S9, and S10, respectively. Anal. Calcd for $\text{C}_{45}\text{H}_{28}\text{N}_4\text{F}_3\text{O}_3\text{SCr} \cdot 1/2\text{H}_2\text{O}$: C, 65.69; H, 3.55; N, 6.81. Found: C, 65.75; H, 3.48; N, 6.82.

Preparation of epoxides: Optical active epoxy silyl ethers **1b**, **1f**⁵ and **1g**⁶ were prepared by the reported methods. Other epoxides were prepared according to either of following procedures: (1) simple epoxidation of olefins with MCPBA; (2) VO(acac)₂-catalyzed epoxidation of allylic alcohols with *tert*-BuOOH.⁵ The absolute configuration of epoxides **1b**, **1g** was determined by comparison of the optical rotations with those of authentic samples.^{5, 6}

trans-1-(tert-Butyldimethylsiloxy)-3-phenyl-2-propene oxide (1a)⁵: ¹H-NMR (270 MHz, CDCl₃), ¹H-NMR (300 MHz, CDCl₃), δ 7.27-7.39 (5H, m, Ph), 3.97 (1H, dd, *J* = 3.1 and 12.1 Hz, CHOSi), 3.83 (1H, dd, *J* = 4.4 and 12.1 Hz, CHOSi), 3.81 (1H, d, *J* = 2.4 Hz, PhCH), 3.13-3.17 (1H, m, CH₂CH-O), 0.93 (9H, s, ^{*t*}Bu), 0.11 and 0.12 (each 3H, s, (CH₃)₂Si).

2,2-Dimethyl-3-(triphenylsiloxy)methyloxirane: ¹H-NMR (270 MHz, CDCl₃), δ 7.35-7.66 (15H, m, Ph₃), 3.94 (1H, dd, *J* = 5.6 and 11.2 Hz, CHOSi), 3.84 (1H, dd, *J* = 5.6 and 11.2 Hz, CHOSi), 3.00 (1H, t, *J* = 5.6 Hz, CH-O), 1.29 and 1.34 (each 3H, s, (CH₃)₂C); ¹³C-NMR (100.4 MHz, CDCl₃), δ 135.24, 133.67, 130.02, 127.80, 63.59, 62.82, 24.76, 18.84; IR(KBr) ν / cm⁻¹: 3068, 3054, 3044, 2986, 2952, 2936, 1591, 1487, 1458, 1429, 1381, 1267, 1247, 1139, 1118, 1073, 1054, 1029, 998, 866, 826, 779, 743, 714, 704, 679; Exact mass Calcd for C₂₃H₂₄O₂Si: 360.1546, Found: 360.1543; Anal. Calcd for C₂₃H₂₄O₂Si: C, 76.62; H, 6.71 Found: C, 76.52; H, 6.80.

8-(tert-Butyldimethylsiloxy)-2,6-dimethyl-2-octene oxide⁵: ¹H-NMR (270 MHz, CDCl₃), δ 3.56-3.63 (2H, m, CH₂OSi), 2.64 (1H, t, *J* = 6.1 Hz, CH-O), 1.22 and 1.26 (each 3H, s, (CH₃)₂C), 1.18-1.56 (7H, m, CH and 3CH₂), 0.85 (3H, d, *J* = 8.9 Hz, CH₃-CH), 0.84 (9H, s, ^{*t*}Bu), -0.05 and 0.00 (each 3H, s, (CH₃)₂Si).

1-Cyclohexyliden-1-hexene oxide: ¹H-NMR (270 MHz, CDCl₃), δ 2.70 (1H, t, *J* = 5.9 Hz, CH-O), 1.20-1.80 (16H, m, 8CH₂), 0.92 (3H, t, *J* = 6.9 Hz, CH₃).

1-Phenylcyclohexene oxide: ¹H-NMR (270 MHz, CDCl₃), δ 7.21-7.41 (5H, m, Ph), 3.06 (1H, t, *J* = 2.2 Hz, CH-O), 1.96-2.34 (4H, m, 2CH₂), 1.23-1.67 (4H, m, 2CH₂).

1b: [α]_D²³ +27.9 ° (*c* 1.12, CHCl₃, >99% ee) [lit.⁵ [α]_D²⁴ +27.6 ° (*c* 1.10, CHCl₃, 98% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 7.27-7.39 (5H, m, Ph), 3.97 (1H, dd, *J* = 3.1 and 12.1 Hz, CHOSi), 3.83 (1H, dd, *J* = 4.4 and 12.1 Hz, CHOSi), 3.81 (1H, d, *J* = 2.4 Hz, PhCH), 3.13-3.17 (1H, m, CH₂CH-O), 0.93 (9H, s, ^{*t*}Bu), 0.11 and 0.12 (each 3H, s, (CH₃)₂Si). The ee was determined by ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (-)-MTPA chloride.

1c: $[\alpha]_D^{23} -27.5^\circ$ (*c* 0.98, CHCl₃, >99% ee) [lit.⁵ $[\alpha]_D^{24} -26.8^\circ$ (*c* 1.04, CHCl₃, 98% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 7.27-7.39 (5H, m, Ph), 3.97 (1H, dd, *J* = 3.1 and 12.1 Hz, CHOSi), 3.83 (1H, dd, *J* = 4.4 and 12.1 Hz, CHOSi), 3.81 (1H, d, *J* = 2.4 Hz, PhCH), 3.13-3.17 (1H, m, CH₂CH-O), 0.93 (9H, s, ^tBu), 0.11 and 0.12 (each 3H, s, (CH₃)₂Si). The ee was determined by ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (–)-MTPA chloride.

1d: $[\alpha]_D^{23} -23.5^\circ$ (*c* 1.05, CHCl₃, 96% ee) [lit.⁵ $[\alpha]_D^{24} -23.9^\circ$ (*c* 1.22, CHCl₃, 98% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 7.20-7.37 (5H, m, Ph), 3.89 (1H, dq, *J* = 4.2 and 6.3 Hz, CHOSi), 3.82 (1H, d, *J* = 2.1 Hz, PhCH), 2.92 (1H, dd, *J* = 2.1 and 4.2 Hz, CH-O), 1.29 (3H, d, *J* = 6.3 Hz, CH₃), 0.90 (9H, s, ^tBu), 0.08 and 0.09 (each 3H, s, (CH₃)₂Si). The ee was determined by HPLC analysis (DAICEL CHIRACEL OD-H, 2-propanol/hexane 0.3/1000, flow rate 0.5 mL/min, *t*_R 17.9 min (minor isomer) and 22.0 min (major isomer), detection at 220 nm).

1e: $[\alpha]_D^{23} = -4.80^\circ$ (*c* 1.04, CHCl₃, >99% ee), [lit.⁵ $[\alpha]_D^{24} = -4.57^\circ$ (*c* 1.00, CHCl₃, 95% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 5.10 (1H, br t, CH=C), 3.73 (2H, dd, *J* = 1.2 and 5.3 Hz, CH₂OSi), 2.90 (1H, t, *J* = 5.3 Hz, CH-O), 2.08 (2H, q, *J* = 7.2 Hz, CH₂-CH=C), 1.61 and 1.68 (each 3H, s, (CH₃)₂C=CH), 1.40-1.65 (2H, m, CH₂C-O), 1.27 (3H, s, CH₃C-O), 0.91 (9H, s, ^tBu), 0.08 and 0.09 (each 3H, s, (CH₃)₂Si). The ee was determined by ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (+)-MTPA chloride.

1f: $[\alpha]_D^{23} = +4.18^\circ$ (*c* 0.97, CHCl₃, 93% ee), [lit.⁵ $[\alpha]_D^{26} = +4.03^\circ$ (*c* 1.07, CHCl₃, 90% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 5.10 (1H, br t, CH=C), 3.77 (1H, dd, *J* = 5.1 and 11.7 Hz, CHOSi), 3.69 (1H, dd, *J* = 5.7 and 11.7 Hz, CHOSi), 2.88 (1H, t, *J* = 5.1 Hz, CH-O), 2.11 (2H, q, *J* = 7.8 Hz, CH₂-CH=C), 1.61 and 1.69 (each 3H, s, (CH₃)₂C=CH), 1.40-1.64 (2H, m, CH₂C-O), 1.32 (3H, s, CH₃C-O), 0.91 (9H, s, ^tBu), 0.08 and 0.09 (each 3H, s, (CH₃)₂Si). The ee was determined by ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (+)-MTPA chloride.

1g: $[\alpha]_D^{23} = -24.8^\circ$ (*c* 1.04, CHCl₃), [lit.⁶ $[\alpha]_D^{26} = -24.8^\circ$ (*c* 1.83, CHCl₃, >99% ee)]; ¹H-NMR (300 MHz, CDCl₃): δ 7.27-7.59 (20H, m, Ph), 4.08 (2H, s, CH₂OSi), 2.94 (1H, d, *J* = 8.6 Hz, CH-O), 0.92-0.99 (4H, m, CH₃ and CH(CH₃)₂), 0.74 (3H, d, *J* = 6.6 Hz, CH₃). The ee was determined by ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (–)-MTPA chloride.

Typical procedure for the Cr(TPP)OTf-catalyzed rearrangements of epoxides to aldehydes.

The catalyst Cr(TPP)OTf were dried over silica gel for 10h under reduced pressure (1 mmHg) at 100°C just before its use. To a solution of epoxides **1** (1 mmol) in freshly distilled 1,2-dichloroethane (5 mL) was added Cr(TPP)OTf (0.01 mmol). The mixture was heated to reflux under Ar. After completion of the reaction (monitored by tlc analysis), the reaction mixture was concentrated under a reduced pressure. The residue was passed through a silica gel short column (1:3 AcOEt–hexane) to remove the catalyst. The eluate was concentrated in vacuo, and the residue was chromatographed on silica-gel (1:3 AcOEt–hexane) to give aldehydes **3**. The absolute configuration of the products was determined by comparison of the optical rotations with those of authentic samples.^{5, 6}

3b: $[\alpha]_D^{23} +32.6^\circ$ (*c* 1.03, CHCl₃, >99% ee) [lit.⁵ $[\alpha]_D^{22} +32.3^\circ$ (*c* 1.00, CHCl₃, 98% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 9.84 (1H, d, *J* = 2.0 Hz, CHO), 7.22-7.41 (5H, m, Ph), 4.25 (1H, dd, *J* = 7.3 and 10.1 Hz, CHOSi), 3.98 (1H, dd, *J* = 5.7 and 10.1 Hz, CHOSi), 3.75 (1H, br t, *J* = 6.6 Hz, PhCH), 0.85 (9H, s, ^tBu), -0.01 and 0.01 (each 3H, s, (CH₃)₂Si). The ee was determined by HPLC analysis after the conversion of aldehyde **3b** to the corresponding alcohol with NaBH₄ and then to the benzoic ester with PhCOCl, DMAP, and Et₃N (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/500, flow rate 0.5 mL/min, *t*_R 18.3 min (minor isomer) and 19.4 min (major isomer), detection at 220 nm).

3c: $[\alpha]_D^{23} -32.5^\circ$ (*c* 1.15, CHCl₃, >99% ee) [lit.⁵ $[\alpha]_D^{21} -31.8^\circ$ (*c* 1.00, CHCl₃, 98% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 9.84 (1H, d, *J* = 2.0 Hz, CHO), 7.22-7.41 (5H, m, Ph), 4.25 (1H, dd, *J* = 7.3 and 10.1 Hz, CHOSi), 3.97 (1H, dd, *J* = 5.7 and 10.1 Hz, CHOSi), 3.75 (1H, br t, *J* = 6.5 Hz, PhCH), 0.85 (9H, s, ^tBu), -0.01 and 0.01 (each 3H, s, (CH₃)₂Si). The ee was determined by HPLC analysis after the conversion of aldehyde **3c** to the corresponding alcohol with NaBH₄ and then to the benzoic ester with PhCOCl, DMAP, and Et₃N (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/500, flow rate 0.5 mL/min, *t*_R 18.1 min (major isomer) and 19.7 min (minor isomer), detection at 220 nm).

3d: $[\alpha]_D^{23} = +64.0^\circ$ (*c* 1.07, CHCl₃, 96% ee), [lit.⁵ $[\alpha]_D^{22} = +64.8^\circ$ (*c* 1.12, CHCl₃), 98% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 9.88 (1H, d, *J* = 3.3 Hz, CHO), 7.20-7.39 (5H, m, Ph), 4.50 (1H, dq, *J* = 6.1 and 8.4 Hz, CHOSi), 3.53 (1H, dd, *J* = 3.3 and 8.4 Hz, CHCHO), 1.07 (3H, d, *J* = 6.1 Hz, CH₃), 0.89 (9H, s, ^tBu), 0.08 and 0.09 (each 3H, s, (CH₃)₂Si). The ee was determined by HPLC analysis after the conversion of aldehyde **3d** to the corresponding alcohol with NaBH₄ and then to the benzoic ester with PhCOCl, DMAP, and Et₃N (DAICEL CHIRACEL OD-H, 2-propanol/hexane 0.2/500, flow rate 0.5 mL/min, *t*_R 29.4 min (major isomer) and 31.0 min (minor isomer), detection at 220 nm).

3e from silyl ether of epoxy geraniol: $[\alpha]_D^{23} = +6.78^\circ$ (*c* 1.06, CHCl₃, >99% ee), [lit.⁵ $[\alpha]_D^{24} = +6.45^\circ$ (*c* 1.00, CHCl₃), 95% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 9.56 (1H, s, CHO), 5.06 (1H, br t, CH=C), 3.68 (1H, d, *J* = 9.9 Hz, CHOSi), 3.57 (1H, d, *J* = 9.9 Hz, CHOSi), 1.85-1.96 (2H, m, CH₂-CH=C), 1.58 and 1.67 (each 3H, s, (CH₃)₂C=CH), 1.41-1.63 (2H, m, CH₂-C-CHO), 1.04 (3H, s, CH₃), 0.87 (9H, s, ^tBu), 0.03 (6H, s, (CH₃)₂Si). The ee was determined by HPLC analysis after the conversion of aldehyde **3e** to the corresponding alcohol with NaBH₄ and then to the *p*-nitrobenzoic ester with *p*-NO₂-PhCOCl, DMAP, and Et₃N (DAICEL CHIRACEL OD-H, 2-propanol/hexane 1/500, flow rate 0.4 mL/min, *t*_R 19.4 min (major isomer) and 20.2 min (minor isomer), detection at 250 nm).

3e from silyl ether of epoxy nerol: $[\alpha]_D^{23} = +6.35^\circ$ (*c* 1.04, CHCl₃, 93% ee), [lit.⁵ $[\alpha]_D^{24} = +6.45^\circ$ (*c* 1.00, CHCl₃), 95% ee)]; ¹H-NMR (300 MHz, CDCl₃), δ 9.56 (1H, s, CHO), 5.06 (1H, br t, CH=C), 3.68 (1H, d, *J* = 9.9 Hz, CHOSi), 3.57 (1H, d, *J* = 9.9 Hz, CHOSi), 1.85-1.95 (2H, m, CH₂-CH=C), 1.58 and 1.68 (each 3H, s, (CH₃)₂C=CH), 1.41-1.64 (2H, m, CH₂-C-CHO), 1.04 (3H, s, CH₃), 0.87 (9H, s, ^tBu), 0.03 (6H, s, (CH₃)₂Si). The ee was determined by HPLC analysis after the conversion of aldehyde **3e** to the corresponding alcohol with NaBH₄ and then to the

p-nitrobenzoic ester with *p*-NO₂-PhCOCl, DMAP, and Et₃N (DAICEL CHIRACEL OD-H, 2-propanol/hexane 1/500, flow rate 0.4 mL/min, *t*_R 19.1 min (major isomer) and 19.9 min (minor isomer), detection at 220 nm).

3g: $[\alpha]_{\text{D}}^{23} = -27.9^\circ$ (*c* 1.12, CHCl₃, 97% ee), [lit.⁶ $[\alpha]_{\text{D}}^{26} = -28.5^\circ$ (*c* 0.29, CHCl₃), >99% ee]; ¹H NMR (300 MHz, CDCl₃): δ 9.80 (1H, s, CHO), 7.07-7.66 (20H, m, Ph), 4.28 (1H, d, *J* = 10.5 Hz, CHOSi), 4.25 (1H, d, *J* = 10.5 Hz, CHOSi), 2.74 (1H, septet, *J* = 6.8 Hz, CH(CH₃)₂), 0.89 (3H, d, *J* = 6.8 Hz, CH₃), 0.81 (3H, d, *J* = 6.8 Hz, CH₃). The ee was determined by HPLC analysis after the conversion of aldehyde **3g** to the corresponding alcohol with NaBH₄ (DAICEL CHIRACEL OD-H, 2-propanol/hexane 0.2/500, flow rate 0.4 mL/min, *t*_R 14.2 min (minor isomer) and 15.0 min (major isomer), detection at 220 nm).

References

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Fig. 1 Absorption spectrum of $\text{Cr}(\text{TPP})\text{OTf}$ in CH_2Cl_2 .

Fig. 2 Cyclic voltammogram of Cr(TPP)OTf.

Conditions: 5 mM Cr(TPP)OTf; CH₂Cl₂; 0.1M Bu₄NClO₄; 100 mV/sec; 25°C; glassy carbon working electrode; Pt counter electrode; Ag/AgCl wire reference electrode.

Fig. 3 IR spectrum of Cr(TPP)OTf in KBr.

Determination of the optical purity of 1b (>99% ee): ^1H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (-)-MTPA chloride.

Determination of the optical purity of 1c (>99% ee): ^1H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (-)-MTPA chloride.

The ee was determined by HPLC analysis (see S31).

Determination of the optical purity of **1e** (>99% ee): ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (+)-MTPA chloride.

Determination of the optical purity of 1f (93% ee): ¹H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (+)-MTPA chloride.

Determination of the optical purity of 1g (>99% ee): ^1H NMR analysis of the Mosher ester derived from the corresponding epoxy alcohol with (–)-MTPA chloride.

The ee was determined by HPLC analysis (see S32).

3c (> 99% ee)

The ee was determined by HPLC analysis (see S33).

The ee was determined by HPLC analysis (see S34).

**3e (>99% ee) from
silyl ether of epoxy
geraniol**

The ee was determined by HPLC analysis (see S35).

**3e (93% ee) from
silyl ether of epoxy
nerol**

The ee was determined by HPLC analysis (see S36).

The ee was determined by HPLC analysis (see S37).

Determination of the optical purity of 1d (96% ee).

Chiral HPLC: Daicel CHIRALCEL OD-H, 1000:0.3 Hexane:2-Propanol, 0.5 mL/min, 220 nm

racemic (erythro >99%)

No.	Rt (min)	Area	Area Percent
1	17.56	5078678.6	50.7795
2	21.72	4922756.2	49.2205
total		10001435	100

96% ee

No.	Rt (min)	Area	Area Percent
1	17.93	195193.4	2.0069
2	21.97	9530802.4	97.9931
total		9725995.8	100

Determination of the optical purity of **3b** (>99% ee).

Chiral HPLC: Daicel CHIRALPAK AD-H, 500:1 Hexane:2-Propanol, 0.5 mL/min, 220 nm

racemic

No.	Rt (min)	Area	Area Percent
1	18.31	11144141.4	50.2385
2	19.65	11038345.8	49.7615
total		22182487.2	100

>99% ee

No.	Rt (min)	Area	Area Percent
1	19.44	12979321	100
total		12979321	100

Determination of the optical purity of 3c (>99% ee).

Chiral HPLC: Daicel CHIRALPAK AD-H, 500:1 Hexane:2-Propanol, 0.5 mL/min, 220 nm

racemic

No.	Rt (min)	Area	Area Percent
1	18.31	11144141.4	50.2385
2	19.65	11038345.8	49.7615
total		22182487.2	100

>99% *ee*

No.	Rt (min)	Area	Area Percent
1	18.09	16672528.4	100
total		16672528.4	100

Determination of the optical purity of 3d (96% ee).

Chiral HPLC: Daicel CHIRALCEL OD-H, 500:0.2 Hexane:2-Propanol, 0.5 mL/min, 220 nm

racemic (65:35 erythro:threo mixture)

No.	Rt (min)	Area	Area Percent
1	29.1	2379737.22	17.1213
2	30.73	2467469.47	17.7525
3	32.86	4548955.97	32.728
4	37.79	4503116.14	32.3982
total		13899278.8	100

96% ee

No.	Rt (min)	Area	Area Percent
1	29.36	6937901.4	98.2005
2	30.96	127135.3	1.7995
total		7065036.7	100

Determination of the optical purity of 3e (>99% ee) prepared from silyl ether of epoxy geraniol.

Chiral HPLC: Daicel CHIRALCEL OD-H, 500:1 Hexane:2-Propanol, 0.4 mL/min, 250 nm

racemic

No.	Rt (min)	Area	Area Percent
1	19.4	2425742.45	49.2108
2	20.19	2503546.38	50.7892
total		4929288.8	100

>99% ee

No.	Rt (min)	Area	Area Percent
1	19.09	8171320.2	322505
total		8171320.2	322505

Determination of the optical purity of 3e (93% ee) prepared from silyl ether of epoxy nerol.

Chiral HPLC: Daicel CHIRALCEL OD-H, 500:1 Hexane:2-Propanol, 0.4 mL/min, 250 nm

racemic

No.	Rt (min)	Area	Area Percent
1	19.4	2425742.45	49.2108
2	20.19	2503546.38	50.7892
total		4929288.8	100

93% ee

No.	Rt (min)	Area	Area Percent
1	19.08	12290710.8	96.3908
2	19.89	460207.6	3.6092
total		12750918.4	100

Determination of the optical purity of 3g (97% ee).

Chiral HPLC: Daicel CHIRALCEL OD-H, 500:0.2 Hexane:2-Propanol, 0.4 mL/min, 220 nm

racemic

No.	Rt (min)	Area	Area Percent
1	14.28	11930335.6	50.8026
2	14.99	11553359	49.1974
total		23483694.6	100

97% ee

No.	Rt (min)	Area	Area Percent
1	14.22	67404.8	1.3529
2	14.97	4914853.2	98.6471
total		4982258	100