General methods. All reactions were conducted in flame dried glassware with magnetic stirring under an atmosphere of argon. Toluene and diethyl ether were distilled from sodium/benzophenone ketyl and stored under argon. \( \text{Et}_2\text{Zn} \) (1.1 M solution in toluene) and \( \text{Me}_2\text{Zn} \) (2.0 M solution in toluene) were purchased from Aldrich. Analytical TLC were performed on Alugram SIL G/UV254 silica gel sheets (Macherey-Nagel) with detection by 0.5% phosphomolybdic acid solution in 95% EtOH. Silica gel 60 (Macherey-Nagel 230-400 mesh) was used for flash chromatography. Solvents for extraction and chromatography were HPLC grade.

Optical rotation were measured on a Perkin-Elmer 241 digital polarimeter with a 1 dm cell. \( ^1\text{H} \) NMR spectra were recorded on a Bruker AC-200 spectrometer on \( \text{CDCl}_3 \) solution. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: \( \delta \) 7.26). \( ^{13}\text{C} \) NMR spectra were recorded on a Bruker AC-200 (50 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: \( \delta \) 77.7). Gas chromatography was performed on a Perkin-Elmer 8420 apparatus (FI detector) using a Chromopak fused silica 50 m x 0.25 mm column, coated with CP-Cyclodextrin-B-236-M-19). In all cases, the injector and detector temperature was 250°C and a 0.9 mL / min helium flow was employed.
**General procedure for the regiodivergent parallel kinetic resolution.** A solution of Cu(OTf)$_2$ (10.83 mg, 0.030 mmol) and (R,R,R)-1 (32.3 mg, 0.06 mmol) in anhydrous toluene (4.0 mL) was stirred at r.t. for 40 min. The colorless solution was cooled to -78 °C, and subsequently additioned with a solution of racemic vinyloxepoxide (2.0 mmol) in toluene (1.0 mL) and with 3.0 mmol of R$_2$Zn (solution in toluene). The resulting light yellow solution was quenched with saturated aqueous NH$_4$Cl (5.0 mL) once the reaction reached completion (GC analysis). Extraction with Et$_2$O and evaporation of the dried (MgSO$_4$) organic phase gave the crude product, which was subjected to flash chromatography.

**R-(+)-3-Propyl-2-cyclohexen-1-ol (3a):**

The general procedure was followed employing 220 mg of racemic vinyloxirane 2 (2.0 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), chiral ligand (R,R,R)-1 (32.3 mg, 0.06 mmol) and Et$_2$Zn (2.72 mL, 3.0 mmol). The usual work-up afforded a crude reaction mixture which was subjected to flash chromatography (SiO$_2$) with 10% EtOAc: hexanes to give 129 mg of pure 3a (46%), as a liquid. TLC (15% EtOAc/hexanes) $R_f$=0.14. $[\alpha]_D^\infty$=+43 ($c$=1.0, CHCl$_3$).

The enantiomeric excess of 3a (80%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 110°C, $S$-(-) (minor) $t_R$30.78 min, $R$-(+) (major) $t_R$ 31.72 min.

**(1S, 2S)-(-)-3-Methylidene-2-ethyl-1-cyclohexanol (4a):**

The first eluting fractions of the above described flash chromatography afforded 104 mg of pure 4a (37%) as a liquid. TLC (15% EtOAc/hexanes) $R_f$=0.20. $[\alpha]_D^\infty$=-8.9 ($c$=1.12, CHCl$_3$).

$^1$H NMR δ 4.84 (bs, 1H, methylidene H), 4.73 (bs, 1H, methylidene H), 3.65-3.72 (m, 1H, CH-OH), 1.95-2.21 (m, 3H, allylic-H), 1.38-1.85 (m, 6H, -CH$_2$-), 0.87 (t, 3H, -CH$_3$, $J$=7.3 Hz).

$^{13}$C NMR δ 178.53, 111.60, 73.08, 54.16, 32.53, 30.39, 23.46, 23.32, 12.66.

The enantiomeric excess of 3a (99%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 110 °C, (1R, 2R)-(+) (minor) tᵣ23.44 min, (1S, 2S)-(−) (major) tᵣ 23.87 min.

(R)-(+)−3-Ethyl-2-cyclohexen-1-ol (3b):³

The general procedure was followed employing 110 mg of racemic vinyloxirane 2 (1.0 mmol), Cu(OTf)₂ (5.4 mg, 0.015 mmol), chiral ligand (R,R,R)-1 (16.2 mg, 0.03 mmol) and Me₂Zn (0.75 mL, 1.5 mmol). The usual work-up afforded a crude reaction mixture which was subjected to flash chromatography (SiO₂) with 10% EtOAc: hexanes to give 51 mg of pure 3b (40%), as a liquid. TLC (20% EtOAc/hexanes) Rᵣ=0.21.

The enantiomeric excess of 3b (96%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 115 °C, (S)-(−) (minor) tᵣ35.21 min, (R)-(+) (major) tᵣ 35.67 min.

(1S, 2S)-(−)-3-Methylidene-2-methyl-1-cyclohexanol (4b):

The first eluting fractions of the above described flash chromatography afforded 47 mg of pure 4b (37%) as a liquid. TLC (20% EtOAc/hexanes) Rᵣ=0.29. [α]D=+27 (c=0.53, CHCl₃). ¹H NMR δ 4.78 (bs, 1H, methylidene-H), 4.69 (bs, 1H, methylidene-H), 3.23 (dt, 1H, -CHOH, J=3.9 and 8.8 Hz), 2.19-2.35 (m, 1H, -CHCH₃), 1.86-2.14 (m, 3H), 1.68-1.83 (m, 1H), 1.31-1.53 (m, 2H), 1.16 (d, 3H, -CH₃, J=6.8 Hz).

¹³C NMR δ 151.30, 108.45, 76.59, 46.30, 35.41, 34.57, 25.22, 15.17.

The enantiomeric excess of 4b (92%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 105 °C, (1R, 2R)-(−) (minor) tᵣ27.72 min, (1S, 2S)-(+) (major) tᵣ 28.14 min.
(1R, 4R)-(+)−4-Ethyl-2-cyclohexen-1-ol (6a):

The general procedure was followed employing 96 mg of racemic vinyloxirane $^5$ (1.0 mmol), Cu(OTf)$_2$ (5.40 mg, 0.015 mmol), chiral ligand (R,R,R)-1 (16.2 mg, 0.03 mmol) and Et$_2$Zn (1.36 mL, 1.5 mmol). The usual work-up afforded a crude reaction mixture which was subjected to flash chromatography (SiO$_2$) with 20% EtOAc: hexanes to give 78 mg of pure 6a (62%) as a liquid.

$^1$H NMR $\delta$ 5.58-5.72 (m, 2H, olefinic-$\mathrm{H}$), 4.32-4.36 (m, 1H, $-\mathrm{CHOH}$), 1.75-2.13 (m, 3H), 1.08-1.47 (m, 4H, $-\mathrm{CH}_2$-$-), 0.88 (t, 3H, $-\mathrm{CH}_2\mathrm{CH}_3, J=7.3$ Hz).

$^{13}$C NMR $\delta$ 135.01, 130.97, 67.75, 37.61, 32.64, 29.26, 27.10, 11.93.


The enantiomeric excess of 6a (34%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 115 °C, (1S, 4S)-(−) (minor) $t_R$25.98 min, (1R, 4R)-(+)−(major) $t_R$ 26.78 min.

(1S, 2S)-(+)−2-Ethyl-3-cyclohexen-1-ol (7a):

The first eluting fractions of the above described flash chromatography afforded 18 mg of pure 7a (14%) as a liquid. $[\alpha]_D^2=+97.4$ (c=1.5, CHCl$_3$).

$^1$H NMR $\delta$ 5.59-5.71 (m, 1H, olefinic-$\mathrm{H}$), 5.47-5.56 (m, 1H, olefinic-$\mathrm{H}$), 3.53-3.67 (m, 1H, $-\mathrm{CHOH}$), 1.77-2.16 (m, 4H), 1.24-1.74 (m, 3H), 0.94 (t, 3H, $-\mathrm{CH}_2\mathrm{CH}_3, J=7.3$ Hz).

$^{13}$C NMR $\delta$ 129.29, 127.12, 71.39, 45.92, 30.61, 26.14, 24.43, 11.55.


The enantiomeric excess of 7a (>98%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 110 °C, (1S, 2S)-(+) (major) $t_R$24.06 min, (1R 2R)-(−) (minor) $t_R$ 24.56 min.
(1R, 4R)-(−)-4-Methyl-2-cyclohexen-1-ol (6b):  

The general procedure was followed employing 192 mg of racemic vinyloxirane 5 (2.0 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), chiral ligand (R,R,R)-1 (32.3 mg, 0.06 mmol) and Et$_2$Zn (2.72 mL, 3.0 mmol). The usual work-up afforded a crude reaction mixture which was repeatedly subjected to flash chromatography (SiO$_2$) with 10% EtOAc: hexanes to give 85 mg of pure 6b (38%) as a liquid. The enantiomeric excess of 6b (64%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 104 °C, (1S,4S)-(−) (minor) t$_R$19.94 min, (1R, 4R)-(+) (major) t$_R$20.72 min.

(1S, 2S)-(−)-2-Methyl-3-cyclohexen-1-ol (7b):  

The first eluting fractions of the above described flash chromatography afforded a total amount of 45 mg of pure 7b (20%) as a liquid. The enantiomeric excess of 7b (>97%) was determined by chiral GC (CP-cyclodex-β-column), isothermal 104 °C, (1S, 2S)-(−) (major) t$_R$19.73 min, (1R, 2R)-(−) (minor) t$_R$20.46 min.

**Determination of Absolute Configurations of 7b:**

To a 60:40 mixture of 6b and 7b (80 mg) in absolute EtOH (7 mL) was added a catalytic amount of Pd on charcoal. The resulting mixture was vigorously stirred overnight under a H$_2$ atmosphere at rt. Filtration through a pad of Celite and evaporation of the organic solvent afforded a crude reaction mixture which was subjected to flash chromatography (SiO$_2$) with 13% EtOAc: hexanes to give 5 mg of pure (1S, 2S)-(−)-2-methylcyclohexanol.

---

[6] The chromatographic separation (SiO2) between 6b and 7b is minimal. Hydrogenation of the double bond (see the demonstration of absolute configuration of 7b) affords the corresponding saturated compounds that are more prone to chromatographic separation.