Supporting Information

syn-Selective Epoxidation of Chiral Terminal Allylic Alcohols with a Titanium Salalen Catalyst and Hydrogen Peroxide

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1. Materials and Instrumentation

1.1. Materials

All commercial reagents were used as received. Candida antarctica lipases A and B were bought in immobilized form from Merck Sigma-Aldrich. Anhydrous solvents were distilled and dried prior use over sodium or CaH$_2$. The Ti-catalysts 2 and ent-2 were synthesized according to the literature. The allylic alcohols were synthesized according to the literature procedure by Breit and Grünanger, and the analytic data for undec-1-en-3-ol (rac-3a), pentadec-1-en-3-ol (rac-3f), 1-cyclohexylprop-2-en-1-ol (rac-3c), 4,4-dimethylpent-1-en-3-ol (rac-3d), and 1-phenylbut-3-en-2-ol (rac-3b) are in agreement with the literature. α-Vinylbenzyl alcohol (rac-3e) was bought from Merck Sigma-Aldrich. For the assignment of the configuration of the epoxy alcohols, they were synthesized from the racemic allylic alcohols by epoxidation with mCPBA, as well as from the enantiopure allylic alcohols, if necessary.

1.2. Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance I 300, a Bruker Avance 499, or a Bruker Avance III 500 instrument in CDCl$_3$ at ambient temperature. Chemical shifts (δ) are reported in ppm and are relative to the tetramethylsilane (TMS) signal (1H) or solvent signals (13C). Coupling constants were reported in Hz with the following abbreviations for multiplicities: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded on a Shimadzu IRAffinity-1 spectrometer with ATR technique. Wave numbers were reported in cm$^{-1}$ and the intensities of absorption bands are indicated by the following abbreviations: s = strong, m = medium, w = weak. GC-MS analysis was done on an Agilent Technologies 7890A instrument with injector and autosampler, and an Agilent Technologies 5975C Triple-Axis Detector. A HP-5 MS column (length: 30.0 m, inner diameter: 0.25 mm, film thickness: 0.25 μm) was used with H$_2$ as carriers gas and the following temperature program 50 °C, 5 min, 20 °C/min to 280 °C, 10 min. HR-GC-MS analysis was done on a Thermo Scientific Exactive GC with an Orbitrap Analyser. Chiral HPLC analysis was done on a HITACHI-Chromaster system with pump (5160), autosampler (5260), column oven (5310) and detector (5430), and a Daicel Chiracel OD-H column (length: 25 cm, inner diameter: 4.6 mm). Chiral GC analysis was done on an Agilent Technologies 6890N instrument with injector 7683B, autosampler and a Chirasil-Dex CB column (length: 25.0 m, inner diameter: 250 μm, film thickness: 0.25 μm) or a Hydrodex β-3-P (length: 25.0 m, inner diameter: 250 μm, film thickness: 0.25 μm). Melting points were measured on an Apotec instrument of Kleinfeld Labortechnik, and are uncorrected. Elemental Analyses (EA) were performed on an Elementar Vario MICRO cube from Elementar Analysysteme GmbH.
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2. Experimental Procedures

2.1. General procedure for the configurational assignment of the epoxy alcohols 4a-e

First, the racemic allylic alcohols rac-3a-e were subjected to epoxidation with mCPBA (see 2.2, "general procedure B"), affording mixtures of diastereomeric racemates. These racemic mixtures were assigned as syn and anti by \(^1\)H NMR, according to Mihelich and Sharpless et al.\(^5\) The NMR assignment of syn/anti to the major/minor racemates was then transferred to the GC- and HPLC-analyses. For the assignment of absolute configurations, the enantiomerically pure allylic alcohols 3a-e were epoxidized.

2.2. General preparative procedures

General procedure A: Enzymatic kinetic resolution of the allylic alcohols rac-3a-e

The kinetic resolution was carried out according to the procedure of Porto et al.\(^6\) To a solution of the racemic allylic alcohol (3.77 mmol, 1.00 eq) in 30 mL \(n\)-hexane (HPLC grade), 120 mg of immobilized lipase was added. Vinyl acetate (37.8 mmol, 10.0 eq) was then added, and the reaction mixture was shaken at 150 rpm at room temperature in a stoppered 100 mL Erlenmeyer flask. The reaction was monitored via chiral GC. Upon complete consumption of one of the allylic alcohol substrates, the enzyme was filtered off and washed four times with 30 mL cyclohexane. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography on silica.

General procedure B: Epoxidation of allylic alcohols with mCPBA

To a solution of the racemic allylic alcohol (1.78 mmol, 1.00 eq) in 20 mL dichloromethane was added mCPBA (ca. 75% peracid) (500 mg, ca. 2.20 mmol, ca. 1.25 eq). When the TLC control indicated full consumption of the allylic alcohol, the reaction was quenched with 20 mL sat. aq. \(Na_2S_2O_3\) solution or 20 mL sat. aq. \(Na_2SO_3\) solution. The phases were separated, and the aqueous phase was extracted three times with 15 mL dichloromethane. The combined organic phases were dried over MgSO\(_4\) or Na\(_2\)SO\(_4\), filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica.

2.3. Preparation of enantiopure allylic alcohols

Kinetic resolution of racemic undec-1-en-3-ol (rac-3a)

The kinetic resolution was performed on a 3.77 mmol scale according to general procedure A. The product (R)-undec-1-en-3-ol (3a) was obtained as a colorless liquid. Yield: 296 mg (1.74 mmol, 46%); \(R_s = 0.26\) (SiO\(_2\), cHex:EtOAc = 6:1); \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta [ppm] = 5.87\ (ddd, \ J = 16.9, 10.4, 6.2 \text{ Hz}; 1H), 5.22\ (dt, \ J = 17.2, 1.5 \text{ Hz}; 1H), 5.10\ (dt, \ J = 10.4, 1.4 \text{ Hz}; 1H), 4.10\ (q, \ J = 6.4 \text{ Hz}; 1H), 1.60 – 1.20 (m, 14H), 0.93 – 0.83 (m, 3H). Analytical data are in agreement with the literature.\(^2\) The enantiomeric excess was determined to be >99% by chiral GC (Lipodex A; 93 °C isothermal 45 min, 10 °C/min to 130 °C, isothermal 30 min, 10 °C/min to 180 °C isothermal 5 min; flow 1.0 mL/min; \(\tau_R = \text{minor, (S)}-3a\) = 39.2 min; [major, (R)] 3a = 40.3 min).
The product (S)-undec-1-en-3-yl acetate (ent-3a-Ac) was obtained as a colorless liquid. Yield: 400 mg (1.88 mmol, 50%); Rf = 0.80 (SiO2; cHex:EtOAc = 6:1); 1H-NMR (300 MHz, CDCl3) δ [ppm] = 5.77 (ddd, J = 17.0, 10.5, 6.3 Hz; 1H), 5.32 – 5.11 (m, 3H), 2.06 (s; 3H), 1.73 – 1.48 (m; 2H), 1.40 – 1.16 (m; 12H), 0.94 – 0.81 (m; 3H). Analytical data are in agreement with the literature.[9] The enantiomeric excess was determined to be 94% after hydrolysis of the acetate to the alcohol ent-3a by chiral GC (Chiralsil DEX CB; see analytical details above).

### Kinetic resolution of 1-phenylbut-3-en-2-ol (rac-3b)

The kinetic resolution was performed on a 1.00 mmol scale according to general procedure A.

The product (R)-1-phenylbut-3-en-2-ol (3b) was obtained as a colorless liquid. Yield: 37 mg (0.25 mmol, 23%); Rf = 0.17 (SiO2, pentane:EtOAc = 6:1); 1H-NMR (300 MHz, CDCl3) δ [ppm] = 7.36 – 7.28 (m; 2H), 7.28 – 7.20 (m; 3H), 5.94 (ddd, J = 17.2, 10.5, 5.8 Hz; 1H), 5.25 (dt, J = 17.2, 1.4 Hz; 1H), 5.13 (dt, J = 10.5, 1.4 Hz; 1H), 4.36 (ddd, J = 7.9, 5.6, 4.0 Hz; 1H), 2.89 (dd, J = 13.6, 5.2 Hz; 1H), 2.79 (dd, J = 13.6, 7.9 Hz; 1H), 1.61 (d, J = 4.0 Hz; 1H). Analytical data are in agreement with the literature.[9] The enantiomeric excess was determined to be >99% by chiral GC (Chiralsil-DEX CB; 100 °C isothermal 30 min, 10 °C/min to 180 °C isothermal 5 min; flow 2.0 mL/min; tR = [major (R)-3b] = 20.5 min; [minor (S)-3b] = 22.1 min).

The product (S)-1-phenylbut-3-en-2-yl acetate (ent-3b-Ac) was obtained as a colorless liquid. Yield: 118 mg (620 µmol, 57%); Rf = 0.61 (SiO2, pentane:EtOAc = 6:1); 1H-NMR (500 MHz, CDCl3) δ [ppm] = 7.32 – 7.24 (m; 2H), 7.24 – 7.15 (m; 3H), 5.81 (ddd, J = 17.0, 10.5, 6.2 Hz; 1H), 5.51 – 5.42 (m; 1H), 5.20 (dt, J = 17.2, 1.3 Hz; 1H), 5.15 (dt, J = 10.5, 1.2 Hz; 1H), 2.96 (dd, J = 13.7, 7.4 Hz; 1H), 2.88 (dd, J = 13.7, 6.3 Hz; 1H), 2.01 (s; 3H). Analytical data are in agreement with the literature.[9] The enantiomeric excess was determined to be 45% by chiral GC (Chiralsil-DEX CB; 100 °C isothermal 30 min, 10 °C/min to 180 °C isothermal 5 min; flow 2.0 mL/min; tR = [minor (R)-3b-Ac] = 13.1 min; [major (S)-ent-3b-Ac] = 15.0 min).

### Kinetic resolution of racemic 1-cyclohexylprop-2-en-1-ol (rac-3c)

The kinetic resolution was performed on a 1.00 mmol scale according to general procedure A.

The product (S)-1-cyclohexylprop-2-en-1-ol (3c) was obtained as a colorless liquid. Yield: 64 mg (0.46 mmol, 46%); Rf = 0.20 (SiO2, cHex:EtOAc = 10:1); 1H-NMR (500 MHz, CDCl3) δ [ppm] = 5.87 (ddd, J = 17.1, 10.4, 6.6 Hz; 1H), 5.20 (dt, J = 17.3, 1.5 Hz; 1H), 5.14 (dt, J = 10.4, 1.5 Hz; 1H), 3.85 (m; 1H), 1.91 – 1.60 (m; 5H), 1.49 – 1.33 (m; 2H), 1.32 – 0.91 (m; 5H). Analytical data are in agreement with the literature.[9] The enantiomeric excess was determined to be >99% by chiral GC (Chiralsil-DEX CB; 85 °C isothermal 45 min, 10 °C/min to 140 °C isothermal 20 min, 10 °C/min to 180 °C isothermal 5 min; flow 1.2 mL/min; tR = [minor (R)-3c] = 40.6 min; [major (S)-3c] = 42.2 min).

The product (R)-1-cyclohexylprop-2-en-1-yl acetate (ent-3c-Ac) was obtained as a colorless liquid. Yield: 85 mg (0.47 mmol, 46%); Rf = 0.44 (SiO2, cHex:EtOAc = 10:1); 1H-NMR (500 MHz, CDCl3) δ [ppm] = 5.75 (ddd, J = 17.3, 10.5, 6.9 Hz; 1H), 5.24 – 5.15 (m; 2H), 5.04 (t, J = 6.8 Hz; 1H), 2.06 (s; 3H), 1.80 – 1.61 (m; 5H), 1.61 – 1.47 (m; 1H), 1.32 – 1.06 (m; 3H), 1.06 – 0.91 (m; 2H). Analytical data are in agreement with the literature.[9] The enantiomeric excess was determined to be >99% after hydrolysis of the acetate to the alcohol ent-3c by chiral GC (Chiralsil-DEX CB; see analytical details above).
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**Kinetic resolution of racemic 4,4-dimethylpent-1-en-3-ol (rac-3d)**

The kinetic resolution was performed on a 1.75 mmol scale according to general procedure A.

The product (R)-4,4-dimethylpent-1-en-3-ol acetate (ent-3d-Ac) was obtained as a colorless liquid. Yield: 171 mg (1.09 mmol, 63%); R<sub>1</sub> = 0.20 (SiO<sub>2</sub>, n-Hex:EtOAc = 6:1); ¹H-NMR (500 MHz, CDCl<sub>3</sub>) δ [ppm] = 5.85 – 7.34 (m, 4H), 7.30 – 7.27 (m, 1 H), 6.10 – 6.01 (m, 1 H), 5.35 (d, J = 17.8 Hz, 1H), 5.21 – 5.18 (m, 2H), 1.99 (d, J = 3.8 Hz, 1H); Analytical data are in agreement with the racemic mixture and literature.<sup>[6]</sup> The enantiomeric excess was determined to be >99% by chiral GC (Chiralsil-DEX CB; 40 °C isothermal 1 min, 2 °C/min to 130 °C, 20 °C/min to 170 °C isothermal 5 min; flow 1.0 mL/min; τ<sub>R</sub> = [minor (R)-3e] = 42.4 min; [major (S)-3e] = 43.2 min).

**Kinetic resolution of racemic α-vinylbenzyl alcohol (rac-3e)**

The kinetic resolution was performed on a 11.2 mmol scale according to general procedure A.

The product (R)-α-vinylbenzyl alcohol (3e) was obtained as a colorless liquid. Yield: 620 mg (4.62 mmol, 41%); R<sub>1</sub> = 0.52 (SiO<sub>2</sub>, n-Hex:EtOAc = 4:1); ¹H-NMR (500 MHz, CDCl<sub>3</sub>) δ [ppm] = 7.38 – 7.28 (m, 5H), 6.27 (dt, J = 3.8 Hz, 1H), 6.05 – 5.97 (m, 1H), 5.32 – 5.22 (m, 2H), 2.11 (s, 3H); Analytical data are in agreement with the literature.<sup>[6]</sup> The enantiomeric excess was determined to be >99% by chiral GC (Chirasil-DEX CB; 40 °C isothermal 1 min, 2 °C/min to 130 °C, 20 °C/min to 170 °C isothermal 5 min; flow 1.0 mL/min; τ<sub>R</sub> = [minor (R)-3e] = 34.6 min; [major (S)-3e] = 36.2 min).

**Kinetic resolution of racemic pentadec-1-en-3-ol (rac-3f)**

The kinetic resolution was performed on a 11.7 mmol scale according to general procedure A.

The product (R)-pentadec-1-en-3-ol (3f) was obtained as a colorless solid, m.p. 33-35 °C (m.p. ref.<sup>[11]</sup>; 28-30 °C) Yield: 1.21 g (5.34 mmol, 46%); R<sub>1</sub> = 0.30 (SiO<sub>2</sub>, n-Hex:EtOAc = 6:1); ¹H-NMR (300 MHz, CDCl<sub>3</sub>) δ [ppm] = 5.86 (dd, J = 16.9, 10.4, 6.2 Hz, 1H), 5.21 (dt, J = 17.2, 1.4 Hz, 1H), 5.09 (dt, J = 10.3, 1.2 Hz, 1H), 4.09 (qt, J = 6.3, 1.2 Hz, 1H), 1.59 – 1.45 (m, 2H), 1.45 – 1.14 (m, 21H), 0.87 (t, J = 6.7 Hz, 3H); Analytical data are in agreement with the literature.<sup>[3]</sup> The enantiomeric excess was determined to be >99% by chiral HPLC after derivatization with 3,5-dinitrobenzyl chloride (Daicel Chiralcel OD-H; n-hexane/isopropanol = 98:2; flow = 1.0 mL/min, 18 °C, fixed 210 nm; τ<sub>R</sub> = [major (R)-3f] = 13.8 min; [minor (S)-3f] = 18.3 min).
Preparation of (S)-(3-methoxyallyl)cyclohexane (6)

Under inert atmosphere, a solution of 140 mg (S)-1-cyclohexylprop-2-en-1-ol (3c, 1.00 mmol, 1.00 eq) in 2 mL THF was cooled to 0 °C. Sodium hydride [48 mg (60% in mineral oil), 2.00 mmol, 2.00 eq] was added, and the mixture was stirred at rt for 30 min. Methyl iodide (213 mg, 1.50 mmol, 1.50 eq) was then added, and the reaction mixture was stirred for 3 h. The reaction was quenched by addition of 10 mL sat. aq. NH₄Cl-solution. The aqueous phase was extracted with dichloromethane (3x10 mL). The combined organic phases were washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography on silica gel (cHex:DCM = 7.3 to 100% DCM). The product was obtained as a colorless liquid. Yield: 140 mg. (0.91 mmol, 91%); R₆ = 0.56 (SiO₂, cHex:EtOAc = 10:1); ¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 3.76 (ddt, J = 17.3, 10.5, 7.7 Hz; 1H, H2), 2.53 (dd, J = 7.7, 4.4 Hz; 1H, H1a), 1.61 (m; 2H, H8a, H9a), 1.47 (m; 1H, H4a), 1.42 (m; 1H, H5a), 1.28 – 1.18 (m; 5H, 2H, H6a, H7a), 0.89 (m; 3H, H6b, H7b, H8b). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm] = 71.8 (1C, CH), 68.5 (1C, CH), 55.5 (1C, CH), 54.7 (1C, CH₂), 45.3 (1C, CH₂), 34.6 (1C, CH₂), 33.6 (1C, CH₂), 32.0 (2C, CH₂), 29.8 (2x1C, CH₂), 29.6 (2C, CH₂), 29.4 (2C, CH₂), 25.4 (2C, CH₂), 22.8 (2C, CH₂), 14.3 (2C, CH₃).

IR (ATR): v [cm⁻¹] = 3439 (br), 2955 (m), 2922 (s), 2855 (s), 1458 (w), 1377 (w), 1254 (w), 1086 (m), 974 (w), 817 (w); Analytical data: m/z = 153.3 (M⁺), 122.1 (M-CH₂O), 107.2, 94.1, 79.1, 71.1 (M-C₆H₁₁), 67.1, 55.1; HR-GC-MS: m/z = 122.10891, theoretical: m/z = 122.10555 (M-CH₂O); Analytical data are in agreement with the literature (¹H-NMR).[12]

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2.4. Preparation of mixtures of the stereoisomers of the epoxy alcohol products

Preparation of racemic syn/anti-1-(oxiran-2-yl)nonan-1-ol (rac-syn/anti-4a)

H₂C═CH₂

H₂C═CH₂

The epoxidation was performed on a 1.76 mmol scale according to general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, with a ratio of the syn/anti-racemates of 56:44. Yield: 304 mg (1.63 mmol, 93%); R₆ = 0.13 (SiO₂, cHex:EtOAc = 6:1).

rac-syn-4a

rac-anti-4a

rac-syn/anti-4a

Preparation of racemic syn/anti-1-(oxiran-2-yl)-2-phenylethan-1-ol (rac-syn/anti-4b)

The epoxidation was performed on a 1.96 mmol scale according to general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, with a ratio of the syn/anti-racemates of 59:41. Yield: 292 mg (1.78 mmol, 91%); R₆ = 0.17 (SiO₂, pentane:EtOAc = 6:1).

rac-syn/anti-4b

rac-anti-4b

syn-Epoxy alcohol rac-syn-4b: ¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 7.36 – 7.28 (m; 2H), 7.28 – 7.21 (m; 3H), 3.72 (dtd, J = 7.3, 6.2, 4.6 Hz; 1H), 3.06 – 3.02 (m; 1H), 2.99 – 2.82 (m; 2H), 2.75 (dd, J = 4.9, 4.0 Hz; 1H), 2.62 (dd, J = 4.9, 2.7 Hz; 1H), f (m, 1H); ¹³C-NMR...
Preparation of racemic syn/anti-cyclohexyl(oxiran-2-yl)methanol (rac-syn/anti-4c)

\[
\text{OH} \quad \xrightarrow{\text{DCM, r.t.}} \quad \text{rac-3c} \quad \xrightarrow{\text{mCPBA}} \quad \text{rac-syn-4c} + \text{rac-anti-4c}
\]

The epoxidation was performed on a 0.66 mmol scale according to general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, with a ratio of the syn/anti-racemates of 57:43. Yield: 150 mg (0.96 mmol, 96%); \( R_t = 0.19 \) (SiO\textsubscript{2}, cHex:EtOAc = 4:1).

Mixture of the epoxy alcohols rac-syn/anti-4c: 1H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) [ppm] = 3.66-3.60 (m; 1 H), 3.19 (dd, \( J = 11.7, 5.8 \) Hz; 1 H), 3.11 – 3.07 (m; 1 H), 3.07 – 3.02 (m; 1 H), 2.85 (dt, \( J = 5.3, 3.3 \) Hz; 2 H), 2.77 (dd, \( J = 5.0, 4.1 \) Hz; 1 H), 2.72 (dd, \( J = 5.0, 2.8 \) Hz; 1 H), 1.98 – 1.63 (m; 10 H), 1.64 – 1.51 (m; 2 H), 1.35 – 1.01 (m; 10 H); Analytical data are in agreement with the literature.\[15\]

Preparation of racemic syn/anti-2,2-dimethyl-1-(oxiran-2-yl)propan-1-ol (rac-syn/anti-4d)

\[
\text{\( \beta \)BuOH} \quad \xrightarrow{\text{DCM, r.t.}} \quad \text{rac-3d} \quad \xrightarrow{\text{mCPBA}} \quad \text{rac-syn-4d} + \text{rac-anti-4d}
\]

The epoxidation was performed on a 0.66 mmol scale according to general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, with a ratio of the syn/anti-racemates of 48:52. Yield: 72 mg (0.56 mmol, 84%); \( R_t = 0.23 \) (SiO\textsubscript{2}, cHex:EtOAc = 4:1).

Mixture of the epoxy alcohols rac-syn/anti-4d: 1H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) [ppm] = 3.52 (d, \( J = 2.9 \) Hz; 1 H), 3.17 – 3.03 (m; 3 H), 2.87 – 2.80 (m; 2 H), 2.76 (dd, \( J = 5.1, 4.0 \) Hz; 1 H), 2.70 (dd, \( J = 5.0, 2.6 \) Hz; 1 H), 1.73 (brs; 2 H), 1.00 (s; 18 H).

Preparation of racemic syn-anti-1-(oxiran-2-yl)-phenyl methanol (rac-syn/anti-4e)

\[
\text{CH} \quad \xrightarrow{\text{DCM, r.t.}} \quad \text{rac-3e} \quad \xrightarrow{\text{mCPBA}} \quad \text{rac-syn-4e} + \text{rac-anti-4e}
\]

The epoxidation was performed on a 2.24 mmol scale after general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, as a diastereomeric mixture with a ratio of the syn/anti-racemates of 1:1. Yield: 264 mg (1.89 mmol, 84%); \( R_t = 0.13 \) (SiO\textsubscript{2}, cHex:EtOAc = 4:1).

Mixture of the epoxy alcohols rac-syn/anti-4e: 1H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) [ppm] = 7.45 – 7.30 (m; 10 H), 4.94 (d, \( J = 2.5 \) Hz, 1 H, H-3\textsubscript{anti}), 4.48 (t, \( J = 4.7 \) Hz, 1H, H-3\textsubscript{syn}), 3.25 – 3.21 (m; 2 H), 2.97 (dd, \( J = 5.0, 2.8 \) Hz, 1 H), 2.88 – 2.82 (m; 2 H), 2.78 – 2.75 (m; 1 H), 2.47 (d, \( J = 4.0 \) Hz, 1 H), 2.29 (s, 1 H).\[15\]

IR (ATR): \( \nu \) [cm\textsuperscript{-1}] = 3435 (b), 3062 (w), 2997 (w), 1982 (w), 1254 (w), 1196 (w), 1040 (m), 1024 (m), 926 (m), 912 (m), 741 (s), 698 (s); GC-MS: \( t_{R} = 10.4 \) min, m/z = 150.1 (M), 117.1, 107.1 (M-C\textsubscript{2}O), 91.1, 79.1, 63.1, 51.1.

SUPPORTING INFORMATION

(75 MHz, CDCl\textsubscript{3}) \( \delta \) [ppm] = 137.3 (1C, Cq), 129.5 (2C, CH\textsubscript{2}), 128.7 (2C, CH\textsubscript{2}), 126.8 (1C, CH), 72.4 (1C, CH), 54.7 (1C, CH), 45.2 (1C, CH\textsubscript{2}), 41.2 (1C, CH\textsubscript{2}); Analytical data are in agreement with the literature.\[14\]

anti-Epoxy alcohol rac-anti-4b: 1H-NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) [ppm] = 7.36 – 7.28 (m; 2 H), 7.28 – 7.21 (m; 3 H), 4.01 (dt, \( J = 7.9, 4.5, 2.9 \) Hz; 1 H), 3.06 – 3.02 (m; 1 H), 2.99 – 2.92 (m; 2 H), 2.60 (dd, \( J = 5.0, 2.7 \) Hz; 1 H), 2.75 (dd, \( J = 4.9, 4.0 \) Hz; 1 H), 1.89 – 1.85 (m; 1 H); 13C-NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) [ppm] = 137.3 (1C, Cq), 129.5 (2C, CH\textsubscript{2}), 128.7 (2C, CH\textsubscript{2}), 128.8 (1C, CH), 69.9 (1C, CH), 54.2 (1C, CH), 44.0 (1C, CH\textsubscript{2}), 40.2 (1C, CH\textsubscript{2}); Analytical data are in agreement with the literature.\[14\]

IR (ATR): \( \nu \) [cm\textsuperscript{-1}] = 3424 (br), 3061 (w), 2999 (w), 2922 (w), 1495 (w), 1454 (w), 1254 (w), 1105 (w), 1080 (w), 1043 (w), 1032 (w), 989 (w), 926 (w), 912 (w), 885 (m), 870 (w), 849 (w), 831 (w), 746 (m), 698 (s); GC-MS: \( t_{R} = 10.4 \) min, m/z = 164.1 (M), 146.1 (M–H\textsubscript{2}O), 128.1, 118.1, 103.1, 92.1, 91.1 (M–C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}).
Preparation of racemic syn/anti-1-(oxiran-2-yl)tridecan-1-ol (rac-syn/anti-4f)

The epoxidation was performed on a 1.60 mmol scale according to general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, with a ratio of the syn/anti-racemates of 56:44. Yield: 344 mg (1.42 mmol, 89%); Rf = 0.26 (SiO2, cHex:EtOAc = 4:1).

syn-Epoxy alcohol rac-syn-4f: 1H-NMR (300 MHz, CDCl3) δ [ppm] = 3.48 – 3.38 (m; 1H), 2.98 (td, J = 4.5, 2.7 Hz; 1H), 2.84 – 2.79 (m; 1H), 2.75 – 2.71 (m; 1H), 1.90 – 1.84 (m; 1H), 1.66 – 1.19 (m; 22H), 0.88 (t, J = 6.9 Hz; 3H); Analytical data are in agreement with the literature.[5]

anti-Epoxy alcohol rac-anti-4f: 1H-NMR (300 MHz, CDCl3) δ [ppm] = 3.84 (ddt, J = 7.4, 4.9, 2.7 Hz; 1H), 3.02 (q, J = 3.3 Hz; 1H), 2.84 – 2.79 (m; 1H), 2.75 – 2.71 (m; 1H), 1.83 – 1.79 (m; 1H), 1.66 – 1.19 (m; 22H), 0.88 (t, J = 6.9 Hz; 3H); Analytical data are in agreement with the literature.[5]

13C-NMR (75 MHz, CDCl3) δ [ppm] = 71.8 (1C, CH), 68.5 (1C, CH), 55.5 (1C, CH), 54.7 (1C, CH2), 45.3 (1C, CH2), 34.6 (1C, CH2), 33.6 (1C, CH2), 32.1 (2C, CH3), 29.8 (10C, CH3), 29.7 (2C, CH3), 29.5 (2C, CH3), 25.4 (2C, CH2), 22.8 (2C, CH2), 14.3 (2C, CH2).

IR (ATR): ν [cm⁻¹] = 3339 (br), 2955 (w), 2914 (s), 2874 (w), 2849 (s), 1466 (w), 1256 (w), 1111 (w), 1072 (w), 966 (w), 935 (w), 901 (w), 878 (w), 854 (m), 754 (w), 719 (m), 662 (w); GC-MS: τR = 13.7 min, m/z = 208.3 (M–H2O), 199.2 (M–C2H5O), 125.0, 111.1, 97.2, 83.1.

Preparation of racemic syn/anti-2-(cyclohexyl(methoxy)methyl)oxirane (syn/anti-rac-7)

The epoxidation was performed on a 1.24 mmol scale according to general procedure B. The mixture of stereoisomeric products was obtained as a colorless liquid, with a ratio of the syn/anti-racemates of 42:58. Yield: 208 mg (1.23 mmol, 98%); Rf = 0.25 (SiO2, cHex:EtOAc = 10:1).

Mixture of the epoxy alcohols rac-syn/anti-7: 1H-NMR (300 MHz, CDCl3) δ [ppm] = 3.47 (s; 3H), 3.38 (s; 3H), 3.00 – 2.92 (m; 2H), 2.82 – 2.72 (m; 4H), 2.57 – 2.51 (m; 1H), 2.51 – 2.46 (m; 1H), 1.92 – 1.52 (m; 12H), 1.32 – 1.00 (m; 10H).

2.5. Catalytic Epoxidations

General procedure for catalytic epoxidations

A 5 mL reaction tube with a stirring bar (10 mm x 5 mm) was charged with the allylic alcohol (100 µmol, 1.00 eq), diphenyl ether (100 µmol, 1.00 eq, internal standard), 7.2 mg titanium salalen catalyst 2 (5 µmol, 0.05 eq) and 0.5 mL solvent. No inert atmosphere was applied. The solution was thermostated to 20 °C and stirred at 400 rpm. After 15 min, an aliquot (10 µL) was withdrawn with an Eppendorf pipette, passed through cotton/MgSO4:MnO2 (in a Pasteur pipette), and eluted with ethyl acetate. The epoxidation was then started by the addition of aqueous H2O2 (8.5 µL, 150 µmol, 1.50 eq, 50 % w/w in water) with an Eppendorf pipette. Aliquots were withdrawn in regular intervals, treated like the tₐ-sample, and analyzed by chiral GC. For the NMR-characterization of the product epoxy alcohols 4a to 4e, the reaction mixtures were filtered through a small pad of MgSO4:MnO2. Solvents were removed from the filtrate under reduced pressure, and the residue was purified by flash column chromatography on silica.
2.5.1. Kinetic resolution of the allylic alcohol rac-3a by catalytic epoxidation

This kinetic resolution of racemic undec-1-en-3-ol (rac-3a) was performed on a 100 µmol scale according to the general procedure for catalytic epoxidations using 2.8 µL H₂O₂ (50 µmol, 0.50 eq). The aliquots withdrawn were analyzed by chiral GC (Lipodex A; 93 °C isothermal 45 min, 10 °C/min to 130 °C, isothermal 30 min, 10 °C/min to 180 °C, isothermal 5 min; flow 1.0 mL/min; \( \tau_R = [\text{major (S)-3a}] = 39.2 \text{ min}; [\text{minor (R)-3a}] = 40.3 \text{ min}; (\text{Ph}_2\text{O}) = 49.9 \text{ min}; [\text{minor syn-(S,S)-4a}] = 59.5; [\text{major anti-(R,S)-4a}] = 59.9 \text{ min}; [\text{minor anti-(S,R)-4a}] = 60.5 \text{ min}; [\text{major syn-(R,R)-4a}] = 61.3 \text{ min}.)

Table S1. Kinetic resolution of racemic undec-1-en-3-ol (rac-3a).

| Entry | solvent | time | conversion allylic alcohol[^a] | ee allylic alcohol[^a] | yield epoxy alcohol[^a] | ee epoxy alcohol[^a] | \( \text{dr syn:anti epoxy alcohol}[^a] \) |
|-------|---------|------|-------------------------------|-----------------------|------------------------|----------------------|--------------------------------|
| 1     | DCM     | 2 h  | 0%                            | 1%                    | 1%                     | >99%                 | n.d.                           |
|       |         |      |                               |                       |                        |                      |                                 |
|       |         | 4 h  | 7%                            | 7%                    | 7%                     | >99%                 | 9.8:1                          |
|       |         | 20 h | 40%                           | 39%                   | 30%                    | 96%                  | 7.8:1                          |
|       |         | 24 h | 40%                           | 41%                   | 30%                    | 97%                  | 8.0:1                          |
|       |         | 48 h | 41%                           | 42%                   | 32%                    | 97%                  | 7.9:1                          |
| 2     | MeCN    | 2 h  | 7%                            | 0%                    | 0%                     | n.d.                 | n.d.                           |
|       |         |      |                               |                       |                        |                      |                                 |
|       |         | 4 h  | 9%                            | 0%                    | 1%                     | >99%                 | 4.4:1                          |
|       |         | 20 h | 26%                           | 14%                   | 18%                    | 93%                  | 4.1:1                          |
|       |         | 24 h | 31%                           | 18%                   | 20%                    | 96%                  | 4.3:1                          |
|       |         | 48 h | 51%                           | 42%                   | 41%                    | 94%                  | 3.3:1                          |

[^a] Determined by GC on chiral stationary phase. [^b] Enantiomeric excess of major diastereomer, i.e. syn-epoxy alcohol.
2.5.2. Optimization of the catalytic epoxidation of enantiopure undec-1-en-3-ol (3a): solvent screening

The catalytic epoxidation was performed on a 100 µmol scale, using the enantiopure undec-1-en-3-ol (R)-3a as the substrate. According to the general procedure for catalytic epoxidations, 8.5 µL H₂O₂ (150 µmol, 1.50 eq) in different solvents were employed. Aliquots were analyzed by chiral GC (Figure S1).

![Figure S1](image1.png)

**Figure S1.** Yields of the epoxide (R)-4a in various solvents; dr >99:1 in all cases, except in EtOH as solvent (dr 30:1 after 48 h).

2.5.3. Optimization of the catalytic epoxidation of enantiopure undec-1-en-3-ol (3a): catalyst loading

The catalytic epoxidation was performed on a 100 µmol scale, using the enantiopure undec-1-en-3-ol (R)-3a as the substrate. According to the general procedure for catalytic epoxidations, 8.5 µL H₂O₂ (150 µmol, 1.50 eq) were employed in chloroform as solvent, at different catalyst loadings (1-5 mol-%). Aliquots were analyzed by chiral GC (Figure S2).

![Figure S2](image2.png)

**Figure S2.** Yields of the epoxide 4a at different catalyst loadings; dr > 99:1 in all cases; full conversion after 24 h for all three catalyst loadings.
2.5.4. Optimization of the catalytic epoxidation of enantiopure undec-1-en-3-ol (3a): additives

The catalytic epoxidation was performed on a 100 µmol scale, using the enantiopure undec-1-en-3-ol (R)-3a as the substrate. According to the general procedure for catalytic epoxidations, 8.5 µL H$_2$O$_2$ (150 µmol, 1.50 eq) were employed. DCE was used as solvent, with and without the additives PFBA (pentfluorobenzoic acid) or DTBP (2,6-di-tert-butyl pyridine) being added (10 µmol, 0.10 eq). Aliquots were analyzed by chiral GC (Figure S3).

Figure S3. Yields of the epoxide 4a in the presence/absence of additives; dr > 99:1 in all cases; full conversion after 24 h in all cases.
2.5.5. Catalytic epoxidation of the enantiopure allylic alcohols 3a-e

According to the general procedure for catalytic epoxidations, reactions were performed on a 100 µmol scale, using the enantiopure allylic alcohols 3a-e as the substrate. Chloroform was used as solvent.

Table S2. Summary of catalytic epoxidation of different allylic alcohols.

| Entry | Substrate, R = | Ti-catalyst (mol %) | H₂O₂ (eq) | Epoxide yield [%] (reaction time) | ee[^a] | dₐ[^a,b] |
|-------|---------------|---------------------|-----------|---------------------------------|--------|---------|
| 1     | 3a, R = n-C₈H₁₇ | 5                   | 1.5       | 91 (48 h)                       | >99%   | >99:1   |
| 2     | 3a, R = n-C₈H₁₇ | 2.5                 | 1.5       | 82 (24 h)                       | >99%   | >99:1   |
| 3     | 3a, R = n-C₈H₁₇ | 1                   | 1.5       | 88 (48 h)                       | >99%   | >99:1   |
| 4     | 3b, R = Bn      | 5                   | 1.5       | 86 (48 h)                       | >99%   | >99:1   |
| 5     | 3c, R = c-C₆H₁₁ | 5                   | 1.5       | 93 (48 h)                       | >99%   | >99:1   |
| 6     | 3c, R = c-C₆H₁₁ | 1                   | 1.5       | 70 (48 h)                       | >99%   | >99:1   |
| 7     | 3c, R = c-C₆H₁₁ | 1                   | 4.5[^b]  | 85 (48 h)                       | 88 (72 h) | >99%   | >99:1   |
| 8     | 3d, R = t-C₄H₉[^d] | 5                  | 1.5       | 85 (48 h)                       | >99%   | 98:2    |
| 9     | 3d, R = t-C₄H₉[^d] | 5                  | 3[^b]    | 97 (48 h)                       | >99%   | 98.2    |
| 10    | 3d, R = t-C₄H₉[^d] | 10                 | 1.5       | 97 (48 h)                       | 99 (72 h) | >99%   | 98:2    |
| 11    | 3e, R = Ph      | 5                   | 1.5       | 90 (24 h)                       | >99%   | >99:1   |

[^a] Determined by GC on chiral stationary phase. [^b] 1.5 eq H₂O₂ every 24 h. [^c] syn:anti. [^d] The allylic alcohol 3d used as substrate had 98 % ee.
2.5.6. Epoxidation of enantiopure undec-1-en-3-ol (3a) with the titanium salalen catalyst ent-2

A reaction tube with a stirring bar (10 mm x 5 mm) was charged with the salalen ligand ent-1 (6.5 mg, 10 µmol, 0.10 eq) and transferred into a glovebox. Ti(OiPr)₄ (2.8 mg, 10 µmol, 0.10 eq) was added, together with 0.5 mL DCM. After 2 h, all volatiles were removed under reduced pressure. Then, 16.9 mg (R)-undec-1-en-3-ol (3a, 100 µmol, 1.00 eq), 16.1 mg diphenyl ether (95 µmol, 0.95 eq) and 0.5 mL CHCl₃ were added. The solution was thermostated to 20 °C and stirred at 400 rpm (no inert atmosphere applied). After 15 min, an aliquot (10 µL) was withdrawn with an Eppendorf pipette, passed through cotton/MgSO₄:MnO₂ (in a Pasteur pipette), and eluted with ethyl acetate. The epoxidation was then started by the addition of aqueous H₂O₂ (8.5 µL, 150 µmol, 1.50 eq, 50 % w/w in water) with an Eppendorf pipette. Aliquots were withdrawn in regular intervals, treated like the t₀-sample, and analyzed by chiral GC (Table S3).

Table S3. Time course of the catalytic epoxidation of (R)-undec-1-en-3-ol (3a) with the titanium salalen catalyst ent-2.

| Entry | Reaction time [h] | Conversion [%][a] | Yield of 4a [%][a] | dr[anti:13] |
|-------|------------------|------------------|-------------------|------------|
| 1     | 1                | 7                | 2                 | 1:13       |
| 2     | 2                | 15               | 6                 | 1:13       |
| 3     | 3                | 22               | 11                | 1:14       |
| 4     | 4                | 31               | 16                | 1:15       |
| 5     | 5                | 38               | 21                | 1:15       |
| 6     | 24               | 92               | 70                | 1:18       |
| 7     | 48               | 95               | 77                | 1:18       |

[a] Determined by GC on chiral stationary phase. [b] syn:anti.

2.5.7. Epoxidation of (S)-(1-methoxyallyl)cyclohexane (6)

The catalytic epoxidation was performed on a 100 µmol scale, using the enantiopure allylic ether (S)-(1-methoxyallyl)cyclohexane (6) as the substrate. According to the general procedure for catalytic epoxidations, various amounts of H₂O₂ (150 µmol, 1.50 eq) were employed in different chloroform or DCE as solvent. Aliquots were analyzed by chiral GC (Table S4). The configuration of the product 7 was verified by O-methylation of enantiopure (R,R)-cyclohexyl(oxiran-2-yl)methanol (4c) and comparison of the NMR and GC data.

Table S4. Catalytic epoxidation of (S)-(1-methoxyallyl)cyclohexane (6) under various conditions.

| Entry | Solvent | Ti-catalyst [2] [mol %] | H₂O₂ [eq] | Epoxide yield [%](reaction time) | ee[%] | dr[anti] |
|-------|---------|------------------------|-----------|---------------------------------|-------|---------|
| 1     | CHCl₃   | 5                      | 1.5       | 24 (48 h)                       | >99%  | >99:1   |
| 2     | CHCl₃   | 5                      | 7.5[b]    | 33 (48 h) 49 (168 h)            | >99%  | >99:1   |
| 3     | CHCl₃   | 10                     | 3[c]      | 46 (48 h) 48 (168 h)            | >99%  | >99:1   |
| 4     | DCE     | 5                      | 3[c]      | 68 (48 h) 71 (168 h)            | >99%  | >99:1   |

[a] Determined by GC on chiral stationary phase. [b] 1.5 eq H₂O₂ every 24 h. [c] 2nd portion H₂O₂ after 48 h. [d] syn:anti.
2.6. Analytical data of hitherto unknown epoxide products

**(R)-2,2-Dimethyl-1-(2-oxiran-2-yl)propan-1-ol (4d)**

Pale yellow liquid; \( R_f = 0.29 \) (SiO\(_2\), n-pentane:Et\(_2\)O = 7:3); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 3.13 – 3.09 (m; 1H, H2), 3.09 – 3.05 (m; 1H, H3), 2.82 (dd, \( \Delta H_{AB} = 5.0 \) Hz, \( \Delta H_{AB} = 4.0 \) Hz; 1H, H1b), 2.69 (dd, \( \Delta H_{AB} = 5.0 \), \( \Delta H_{AB} = 2.8 \) Hz; 1H, H1a), 1.99 (s, 1H, OH), 1.00 (s; 9H, H5 – 7); \(^13\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 78.4 (1C, C3), 52.1 (1C, C2), 45.4 (1C, C1), 34.9 (1C, C4), 25.8 (3C, C5 – 7); IR (ATR): \( \nu \) [cm\(^{-1}\)] = 3461 (br), 2956 (s), 2871 (s), 1704 (w), 1481 (s), 1417 (w), 1397 (m), 1365 (s), 1287 (w), 1256 (s), 1187 (s), 1135 (w), 1107 (s), 1061 (s), 1011 (s), 990 (w), 928 (s), 904 (s), 880 (s), 846 (s), 809 (m), 767 (m), 745 (m), 672 (m), 526 (s); GC-MS: \( \tau_R = 6.5 \) min, m/z = 129.9 (M), 115.1 (M-CH\(_3\)), 98.1 (M-CH\(_2\)O), 85.1, 74.1, 69.1, 57.1 (C\(_4\)H\(_9\)).

**(R)-2-(3-Cyclohexyl(methoxy)methyl)oxirane (7)**

Colorless liquid; \( R_f = 0.25 \) (SiO\(_2\), cHex:EtOAc = 10:1); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 3.46 (s; 3H, H10), 2.96 (ddd, \( \Delta H_{AB} = 4.2 \) Hz, \( \Delta H_{AB} = 2.8 \) Hz; 1H, H2), 2.77 (dd, \( \Delta H_{AB} = 4.9 \) Hz, \( \Delta H_{AB} = 4.3 \) Hz; 1H, H1b), 2.55 – 2.50 (m; 1H, H3), 2.48 (dd, \( \Delta H_{AB} = 4.9 \) Hz, \( \Delta H_{AB} = 2.8 \) Hz; 1H, H1a), 1.89 – 1.82 (m; 1H, H5), 1.78 – 1.69 (m; 3H, H6, H8, H9), 1.69 – 1.62 (m; 1H, H7), 1.62 – 1.50 (m; 1H, H4), 1.29 – 0.99 (m; 5H, H5, H6, H7, H8, H9); \(^13\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 87.1 (1C, C3), 58.6 (1C, C10), 53.7 (1C, C2), 43.6 (1C, C1), 41.4 (1C, C4), 29.3 (1C, C5), 29.2 (1C, C9), 26.6 (1C, C7), 26.4 (1C, C5), 26.3 (1C, C8); IR (ATR): \( \nu \) [cm\(^{-1}\)] = 3046 (w), 2980 (w), 2924 (s), 2853 (s), 2826 (m), 1450 (s), 1410 (w), 1310 (w), 1255 (w), 1185 (w), 1144 (w), 1102 (s), 1085 (s), 976 (m), 967 (m), 912 (s), 886 (s), 854 (s), 838 (s), 815 (s), 795 (w), 690 (w), 671 (w), 618 (m), 515 (s); GC-MS: \( \tau_R = 10.1 \) min, m/z = 152.0 (M-H\(_2\)O), 138.1 (M-CH\(_2\)O), 127.1 (M-C\(_4\)H\(_8\)O), 95.1, 87.0 (M-C\(_6\)H\(_11\)), 79.1, 67.1, 55.1; HR-GC-MS: \( \tau_R = 14.41 \) min, measured: m/z = 127.11160, theoretical: m/z 127.11229 (M-C\(_2\)H\(_4\)O); elemental analysis calcd (%) for C\(_{10}\)H\(_{18}\)O\(_2\): C, 70.55; H, 10.66; found: C, 70.38; H, 10.55.
2.7. Synthesis of the THF-building block 8

Synthesis of (R)-1-[(R)-oxiran-2-yl]tridecan-1-ol (4f)

(4f)-Pentadec-1-en-3-ol (3f) (453 mg, 2.00 mmol, 1.00 eq), 81 mg diphenyl ether (0.48 mmol, 0.25 eq) and 58 mg of the titanium salalen catalyst 2 (0.04 mmol, 0.02 eq) were dissolved in 10 mL chloroform. No inert atmosphere was applied. The solution was thermostated to 20 °C, and 170.5 µL H₂O₂ (3.00 mmol, 1.50 eq, 50% w/w in water) were added. The biphasic mixture was stirred at 20 °C for 48 h. The reaction mixture was then passed through MgSO₄; IR (ATR): 1891 (w), 1823 (w), 1590 (w), 1464 (m), 1428 (s), 1391 (w), 1362 (w), 1275 (s), 1242 (s), 1193 (w), 1125 (s), 1068 (m), 1031 (w), 963 (s), 889 (s), 3662 (w), 3362 (br), 3291 (br), 2962 (w), 2916 (s), 2849 (s), 1473 (s), 1463 (s), 1404 (m), 1338 (s), 1255 (w), 1125 (m), 1068 (m), 1031 (w), 963 (s), 889 (s), 784 (s), 752 (s), 720 (s), 664 (m), 648 (m), 541 (w), 509 (w); GC-MS: τᵣ = 13.7 min, m/z = 208.3 (M⁻H₂O₂), 199.1 (M-C₆H₄ / M-C₇H₇O₂), 166.2, 152.1, 137.3, 125.1 (C₈H₇O₂), 111.2 (C₆H₅O), 83.1 (C₄H₈O), 69.1 (C₄H₈O), 55.1; Analytic data are in agreement with the literature.^[3]

Synthesis of tert-butyl[(R)-1-[(R)-oxiran-2-yl]tridecyl]oxy)diphenylsilane (9)

The reaction was carried out according to a modified procedure by Trost and Rey.[17] (R)-1-[(R)-oxiran-2-yl]tridecan-1-ol (4f) (408 mg, 1.68 mmol, 1.00 eq) was dissolved in 7 mL DCM. No inert atmosphere was applied. The solution was cooled to 0 °C, and 344 µL tert-butyl(chloro)diphenylsilane (2.02 mmol, 1.20 eq) were added. The reaction mixture was cooled to 0 °C, and 344 µL tert-butyldiphenylsilane (9) (2.02 mmol, 1.20 eq) were added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was then diluted with 20 mL DCM and washed with 20 mL water. The aqueous phase was extracted twice with 10 mL DCM. The combined organic phases were washed with brine, dried over MgSO₄, filtered, and the solvent was evaporated under reduced pressure. The product was obtained as a colorless liquid. Yield: 784 mg (1.63 mmol, 97%); Rf = 0.26 (SiO₂, hex:DCM = 7:3); ¹H-NMR (500 MHz, CDCl₃) δ [ppm] = 7.77 – 7.64 (m, 4H, H₂1, H₂5, H₂7, H₃1), 7.46 – 7.40 (m, 2H, H₂3 + H₂9), 7.40 – 7.32 (m, 4H, H₂2, H₂4, H₂8, H₃0), 3.36 (dd, J₄₋₃ = J₃₋₂ = 6.3 Hz; 1H, H₃), 3.05 (dd, J₅₋₄ = 6.7 Hz, J₃₋₂ = 4.1 Hz, J₂₋₁ = J₁₋₂ = 2.7 Hz; 1H, H₁a), 2.72 (dd, J₂₋₁ = J₁₋₂ = 4.9 Hz, J₂₋₁ = J₁₋₂ = 4.2 Hz; 1H, H₁b), 2.47 (dd, J₂₋₁ = J₁₋₂ = 4.9 Hz, J₁₋₂ = J₀₋₁ = 2.7 Hz; 1H, H₁a), 1.55 – 1.42 (m; 2H, H₄), 1.38 – 1.00 (m; 20H, H₅₋₇, H₈₋₁₀, H₁₁₋₁₃), 0.90 (t, J₃₋₂ = 7.0 Hz; 2H, H₁₅), 1.3C-NMR (125 MHz, CDCl₃) δ [ppm] = 136.1 (2C, C₂₁, C₂5), 136.1 (2C, C₂₇, C₃₁), 134.4 (1C, C₂₀), 134.1 (1C, C₂₆), 129.7 (1C, C₂₉), 129.7 (1C, C₂₉), 127.6 (2C, C₂₂, C₂₄), 127.5 (2C, C₂₈, C₃₀), 75.3 (1C, C₃), 55.8 (1C, C₅), 45.0 (1C, C₇), 34.9 (1C, C₉), 32.1 (1C, C₁₃), 29.8 (1C, C₁₇), 29.8 (1C, C₁₉), 29.8 (1C, C₁₉), 29.7 (1C, C₁₉), 29.7 (1C, C₁₉), 29.6 (1C, C₁₉), 29.5 (1C, C₁₉), 27.2 (3C, C₁₇₋₁₉), 25.0 (1C, C₅), 22.9 (1C, C₁₄), 19.6 (1C, C₁₆), 14.3 (1C, C₁₅); IR (ATR): ν [cm⁻¹] = 3662 (w), 3072 (w), 3049 (w), 2924 (s), 2854 (s), 1958 (w), 1891 (w), 1823 (w), 1590 (w), 1464 (m), 1428 (s), 1391 (w), 1362 (w), 1308 (w), 1257 (w), 1105 (s), 1071 (s), 999 (w), 929 (w), 844 (m), 719 (m), 708 (s), 611 (s), 507 (s); GC-MS: τᵣ = 16.8 min, m/z = 503.1, 465.3 (M-CH₃), 423.3 (M-C₁₇H₅), 393.3, 345.2, 225.1 (M-C₁₆H₇O₃), 199.1, 165.0, 139.0; elemental analysis calcd (%) for C₃₉H₉₁O₇Si: C, 77.44; H, 10.06; found: C, 77.45; H, 10.08; Analytic data are in agreement with the literature.^[18]
SUPPORTING INFORMATION

Synthesis of (5R,6R)-6-[(tert-butylidiphenylsilyloxy)octadec-1-en-5-ol (10)

The reaction was carried out according to a modified procedure by Trost and Rey.[17] tert-butyl[(R)-1-[(R)-oxiran-2-yl](tridecyl)oxy]diphenylsilane (9) (723 mg, 1.50 mmol, 1.00 eq) was dissolved in 15 mL dry THF under argon atmosphere. 50 mg Cul (0.26 mmol, 0.17 eq) was added, and the suspension was cooled to −78 °C. Allylmagnesium bromide (4.5 mL, 4.50 mmol, 3.00 eq, 1M solution in Et₂O) was added in a dropwise manner, with stirring. The reaction mixture was allowed to warm to rt, and was left stirring for 1 h. The reaction mixture was then cooled to 0 °C and quenched with 20 mL sat. aq. NaH₂O₄-solution. The phases were separated, and the aqueous phase was extracted twice with 20 mL diethyl ether. The combined organic phases were washed with brine, dried over MgSO₄, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica (chX:EtOAc = 24:1). The product was obtained as a colorless liquid. Yield: 662 mg (1.27 mmol, 84%); Rₙ = 0.30 (SiO₂, chX:EtOAc = 24:1); ¹H-NMR (500 MHz, CDCl₃) δ [ppm] = 7.72 – 7.66 (m; 4H, H₂4, H₂8, H₃0, H₃4), 7.46 – 7.41 (m; 2H, H₂6, H₃2), 7.41 – 7.34 (m; 4H, H₂5, H₂7, H₃1, H₃3), 5.79 (ddt, J₂H₂₁-H₂₃ = 16.9 Hz, J₂H₂₃-H₂₅ = 10.2 Hz, J₂H₂₁-H₂₅ = 6.6 Hz; 1H, H₂), 5.01 – 4.96 (m; 1H, H₄a), 4.96 – 4.92 (m; 1H, H₁b), 3.61 – 3.54 (m; 1H, H₆), 3.54 – 3.46 (m; 1H, H₅), 2.22 (d, J₂H₂₃-H₂₅ = 7.1 Hz; 1H, OH), 2.20 – 2.11 (m; 1H, H₃), 2.08 – 1.97 (m; 1H, H₃), 1.64 – 1.53 (m; 2H, H₄, H₇), 1.53 – 1.40 (m; 1H, H₄), 1.39 – 0.93 (m; 21 H, H₇-H₁₇), 1.08 (s; 9H, H₂₀-2₂), 0.90 (t, J = 7.0 Hz; 3H, H₁₈); ¹³C-NMR (125 MHz, CDCl₃) δ [ppm] = 138.5 (1C, C₅), 136.0 (2C, C₂₄, C₂₈), 135.9 (2C, C₃₀, C₃₄), 134.1 (1C, C₂₃), 133.5 (1C, C₂₉), 129.8 (1C, C₂₆), 129.7 (1C, C₃₂), 127.7 (2C, C₂₅, C₂₇), 127.5 (2C, C₃₁, C₃₃), 114.6 (1C, C₁), 76.3 (1C, C₆), 72.2 (1C, C₅), 33.4 (1C, C₇), 33.2 (1C, C₄), 32.0 (1C, C₁₆), 30.1 (1C, C₃), 29.8 (C₂₈), 29.8 (C₂₇), 29.6 (C₂₆), 29.6 (C₂₉), 29.5 (C₂₅), 29.5 (C₂₇), 27.3 (C₂₀-2₂), 25.0 (1C, C₈), 22.8 (1C, C₁₇), 19.6 (1C, C₁₉), 14.2 (1C, C₁₈); IR (ATR): v [cm⁻¹] = 3578 (w), 3073 (w), 3051 (w), 2924 (s), 2854 (s), 1957 (w), 1889 (w), 1823 (w), 1641 (w), 1590 (w), 1570 (w), 1464 (w), 1428 (w), 1390 (w), 1378 (w), 1362 (w), 1306 (w), 1261 (w), 1190 (w), 1110 (s), 1074 (br), 998 (m), 910 (m), 821 (m), 739 (m), 700 (m).

Synthesis of (2R,5R)-5-[(R)-1-[(tert-butylidiphenylsilyloxy)tridecyl]tetrahydrofuluran-2-yl]methanol (8)
SUPPORTING INFORMATION

3. HPLC and GC-Methods

3.1. Allylic alcohols and related compounds

| Structure | $\tau_R$ | Chromatography and Method |
|-----------|---------|---------------------------|
| \[
\begin{array}{c}
\text{OH} \\
\text{H}_7\text{C}_8 \\
\text{3a}
\end{array}
\] | $\tau_S = 39.2$ min (S) \[
\tau_R = 40.3$ min (R)
| GC, Lipodex A 
split = 50:1; split flow = 50 mL/min, $N_2$; 
flow 1.0 mL/min; 93 °C isothermal 45 min, 10 °C/min to 130 °C isothermal 30 min, 10 °C/min to 180 °C isothermal 5 min. |

GC of rac-undec-1-en-3-ol (rac-3a):

GC of the allylic alcohol 3a, from the kinetic resolution of rac-undec-1-en-3-ol (rac-3a) with the enzyme CAL B, after 19 h:

GC of ent-3a, obtained from undec-1-en-3-yl acetate (ent-3a-Ac) after ester hydrolysis:
### SUPPORTING INFORMATION

| Structure | $\tau_R$ | Chromatography and Method |
|-----------|---------|---------------------------|
| [Image of structure](3b) | $\tau_R = 13.1$ min $3b$-Ac ($R$) $\tau_R = 15.0$ min ent-$3b$-Ac ($S$) $\tau_R = 20.5$ min $3b$ ($R$) $\tau_R = 22.1$ min ent-$3b$ ($S$) | GC, Chirasil-Dex CB split = 80:1; split flow = 160.0 mL/min, N$_2$; flow 2.0 mL/min; 100 °C isothermal 30 min, 10 °C/min to 180 °C isothermal 10 min. |

**GC of rac-1-phenylbut-3-en-2-ol (rac-3b):**

![GC trace of rac-3b](image)

**GC of the allylic alcohol 3b, plus the acetates 3b-Ac and ent-3b-Ac, from the kinetic resolution of rac-1-phenylbut-3-en-2-ol (rac-3b) with the enzyme CAL B, after 48 h:**

![GC trace of allylic alcohol and acetates](image)
GC of rac-1-phenylbut-3-en-2-yl acetate (rac-3b-Ac)
### GC of rac-1-cyclohexylprop-2-en-1-ol (rac-3c):

| Structure | $t_R$ | Chromatography and Method |
|-----------|-------|---------------------------|
| ![Structure](image) 3c | $t_R = 40.6\text{ min (R)}$ $t_R = 42.2\text{ min (S)}$ | GC, Chirasil-Dex CB split = 80:1; split flow = 97.9 mL/min, $N_2$; flow 1.2 mL/min; 85 °C isothermal 45 min, 10 °C/min to 140 °C isothermal 20 min, 10 °C/min to 180 °C isothermal 5 min. |

GC of the allylic alcohol 3c, from the kinetic resolution of rac-1-cyclohexylprop-2-en-1-ol (rac-3c) with the enzyme CAL B, after 20 h:

![GC of allylic alcohol 3c](image)

GC of ent-3c, obtained from 1-cyclohexyllalyl acetate (ent-3c-Ac) after ester hydrolysis:

![GC of ent-3c](image)
### GC of rac-4,4-dimethylpent-1-en-3-ol (rac-3d):

| Structure | Retention Time ($\tau_R$) | Chromatography and Method |
|-----------|---------------------------|---------------------------|
| ![Structure](image) | $\tau_R = 29.7$ min ($R$) $\tau_R = 31.6$ min ($S$) | GC, Chirasil-Dex CB split = 80:1; split flow = 116.6 mL/min, $N_2$; flow 1.5 mL/min; 50 °C isothermal 38 min, 10 °C/min to 140 °C isothermal 20 min, 10 °C/min to 180 °C isothermal 5 min. |

GC of the allylic alcohol 3d, from the kinetic resolution of rac-4,4-dimethylpent-1-en-3-ol (rac-3d) with the enzyme CAL A, after 16 h:

GC of ent-3d (+3d as minor component), obtained from 4,4-dimethylpent-1-en-3-yl acetate (ent-3d-Ac) after ester hydrolysis:
Chromatography and Method

| Structure | $\tau_R$ | Chromatography and Method |
|-----------|---------|---------------------------|
| | $\tau_R = 34.6$ min $3\text{e-Ac} (S)$; $\tau_R = 36.2$ min $\text{ent-3e-Ac} (R)$; $\tau_R = 42.4$ min $\text{ent-3e} (R)$; $\tau_R = 43.2$ min $3\text{e} (S)$. | Chirasil-DEX CB split = 50:1; split flow = 50 mL/min, N$_2$; flow 1.0 mL/min; 40 °C isothermal 1 min, 2 °C/min to 130 °C, 20 °C/min to 170 °C isothermal 5 min. |

GC of rac-α-vinylbenzyl alcohol (rac-3e):

GC of the allylic alcohol 3e plus the acetate $\text{ent-3e-Ac}$ from the kinetic resolution of rac-α-vinylbenzyl alcohol (rac-3e) with the enzyme CAL B, after 48 h:

GC of rac-1-phenyl-2-propenyl acetate (rac-3e-Ac):
HPL-Chromatogram of rac-pentadec-1-en-3-ol (rac-3f) after derivatization with 3,5-dinitrobenzoyl chloride:

HPL-Chromatogram of the allylic alcohol 3f, from the kinetic resolution of rac-pentadec-1-en-3-ol (rac-3f) with the enzyme CAL B, after 24 h and derivatization with 3,5-dinitrobenzoyl chloride:
3.2. *syn/anti*-Epoxy alcohols obtained from *m*CPBA oxidation of racemic allylic alcohols, and *syn*-epoxy alcohols obtained from catalytic epoxidations with the titanium salalen catalyst 2

| Structure | \( t_R \) | Chromatography and Method |
|-----------|-----------|--------------------------|
| \[
\text{OH} \\
(2R,3R)-4a
\] | \( t_R = 39.2 \text{ min (S)-3a;} \) | GC, Lipodex A \( \text{split} = 50:1; \text{split flow} = 50 \text{ mL/min, N}_2\); flow 1.0 mL/min; 93 °C isothermal 45 min, 10 °C/min to 130 °C isothermal 30 min, 10 °C/min to 180 °C isothermal 5 min. |
| \[
\text{OH} \\
(2S,3R)-4a
\] | \( t_R = 40.3 \text{ min (R)-3a;} \) |
| \[
\text{OH} \\
(2S,3S)-4a
\] | \( t_R = 49.9 \text{ min (Ph}_2\text{O);} \) |
| \[
\text{OH} \\
(2R,3S)-4a
\] | \( t_R = 59.5 \text{ min (2S,3S)-4a;} \) |
| \[
\text{OH} \\
(2S,3R)-4a
\] | \( t_R = 59.9 \text{ min (2R,3S)-4a;} \) |
| \[
\text{OH} \\
(2R,3R)-4a
\] | \( t_R = 60.5 \text{ min (2S,3R)-4a;} \) |
| \[
\text{OH} \\
(2S,3R)-4a
\] | \( t_R = 61.3 \text{ min (2R,3R)-4a.} \) |

GC obtained from the epoxidation of the allylic alcohol rac-3a with *m*CPBA (overview):

GC obtained from the epoxidation of the allylic alcohol rac-3a with *m*CPBA (epoxy alcohol region):
GC obtained from the epoxidation of the allylic alcohol 3a with the titanium salalen catalyst 2 (epoxy alcohol region):

GC obtained from the epoxidation of the allylic alcohol 3a with the titanium salalen catalyst ent-2 (epoxy alcohol region):
GC obtained from the kinetic resolution of rac-undec-1-en-3-ol (rac-3a) with the titanium salalen catalyst 2 after 24 h in DCM:

[Graph of GC obtained from the kinetic resolution of rac-undec-1-en-3-ol (rac-3a) with the titanium salalen catalyst 2 after 24 h in DCM.]

GC obtained from the kinetic resolution of rac-undec-1-en-3-ol (rac-3a) with the titanium salalen catalyst 2 after 24 h in acetonitrile:

[Graph of GC obtained from the kinetic resolution of rac-undec-1-en-3-ol (rac-3a) with the titanium salalen catalyst 2 after 24 h in acetonitrile.]
SUPPORTING INFORMATION

| Structure | \( \tau_R \) | Chromatography and Method |
|-----------|-------------|---------------------------|
| \( (2R,3R)\)-4b | 28.1 min (2R,3S)-4b; 28.7 min (2S,3R)-4b and (2S,3S)-4b; 30.2 min (2R,3R)-4b. | GC, Lipodex A split = 50:1; split flow = 50 mL/min, \( N_2 \); flow 1.0 mL/min; 120 °C isothermal 32 min, 10 °C/min to 180 °C isothermal 5 min. |
| \( (2S,3R)\)-4b |             |                           |

GC obtained from the epoxidation of the allylic alcohol \( \text{rac-3b} \) with \( m \text{CPBA} \) (epoxy alcohol region):

![GC epoxidation rac-3b with mCPBA](image1)

GC obtained from the epoxidation of the allylic alcohol \( 3\text{b} \) with \( m \text{CPBA} \) (epoxy alcohol region):

![GC epoxidation 3b with mCPBA](image2)
GC obtained from the epoxidation of the allylic alcohol 3b with the titanium salalen catalyst 2 (epoxy alcohol region):

| Structure | $\tau_R$ | Chromatography and Method |
|-----------|----------|---------------------------|
| (2R,3R)-4c | $\tau_R = 43.3$ min (2S,3S)-4c; $\tau_R = 47.1$ min (2R,3S)-4c and (2R,3R)-4c; $\tau_R = 51.1$ min (2S,3R)-4c. | GC, Chirasil-Dex CB split = 80:1; split flow = 125.3 mL/min, N₂; flow 1.6 mL/min; 100 °C isothermal 55 min, 10 °C/min to 180 °C isothermal 5 min. |
| (2S,3R)-4c |

GC obtained from the epoxidation of the allylic alcohol rac-3c with mCPBA (epoxy alcohol region):
GC obtained from the epoxidation of the allylic alcohol \(3c\) with \(m\)CPBA (epoxy alcohol region):

GC obtained from the epoxidation of the allylic alcohol \(3c\) with the titanium salalen catalyst \(2\) (epoxy alcohol region):

GC obtained from the crystal of the epoxy alcohol \(4c\) used for X-ray crystallography (epoxy alcohol region):
| Structure | $\tau_R$ | Chromatography and Method |
|-----------|---------|---------------------------|
| (2R,3R)-4d | $\tau_R = 16.4$ min (2S,3S)-4d; $\tau_R = 17.8$ min (2R,3R)-4d; $\tau_R = 19.8$ min anti/4d; $\tau_R = 21.6$ min anti/4d. | GC, Chirasil-Dex CB split = 80:1; split flow = 100.2 mL/min, $N_2$; flow 1.3 mL/min; 80 °C isothermal 30 min, 10 °C/min to 100 °C isothermal 25 min, 10 °C/min to 180 °C isothermal 5 min. |
| (2S,3R)-4d | | |

GC obtained from the epoxidation of the allylic alcohol rac 3d with mCPBA (epoxy alcohol region):

![GC trace rac 3d](image1)

GC obtained from the epoxidation of the allylic alcohol 3d (98 % ee) with the titanium salalen catalyst 2 (epoxy alcohol region):

![GC trace 3d](image2)
GC obtained from the epoxidation of the allylic alcohol rac-3e with mCPBA (epoxy alcohol region):

| Structure | $\tau_R$ | Chromatography and Method |
|-----------|----------|---------------------------|
| (2R,3R)-4e | $\tau_R = 25.4$ min ($\text{Ph}_2\text{O}$) | Hydrodex $\beta$-3-P |
| (2S,3R)-4e | $\tau_R = 48.4$ min ((2S,3S)-4e or (2R,3S)-4e) | split = 50:1; split flow = 50 mL/min, $\text{N}_2$; flow |
| (2R,3S)-4e | $\tau_R = 48.6$ min ((2R,3S)-4e or (2S,3S)-4e) | 1.0 mL/min; 165 °C isothermal 65 min, |
| (2S,3S)-4e | $\tau_R = 48.8$ min ((2S,3R)-4e) | 10 °C/min to 160 °C isothermal 5 min. |
| (2R,3R)-4e | $\tau_R = 49.5$ min ((2R,3R)-4e). |  |

GC obtained from the epoxidation of the allylic alcohol 3e with mCPBA (epoxy alcohol region):
GC obtained from the epoxidation of the allylic alcohol 3e with the titanium salalen catalyst 2 (epoxy alcohol region):

![Graph showing GC results](image)

| Structure       | TR       | Chromatography and Method |
|-----------------|----------|---------------------------|
| ![Structure Image](image) |          |                           |
| (2R,3R)-7       | TR = 41.5 min (2S,3R)-7; TR = 44.0 min (2R,3R)-7. | Chirasil-Dex CB
split = 80:1; split flow = 97.9 mL/min, N2;
flow 1.2 mL/min; 85 °C isothermal
50 min, 10 °C/min to 100 °C,
isothermal 16 min,
10 °C/min to 180 °C,
isothermal 5 min. |
| (2S,3R)-7       |          |                           |

GC obtained from the epoxidation of the methyl ether 6 with mCPBA (epoxy ether region):

![Graph showing GC results](image)
GC obtained from the epoxidation of the methyl ether 6 with the titanium salalen catalyst 2 (epoxy ether region):

GC of the methyl ether 7 obtained from the methylation of the epoxy alcohol 4c (epoxy ether region):
4. NMR-Spectra

4.1. Allylic alcohols and related compounds

$^1$H-NMR (300 MHz) of (R)-undec-1-en-3-ol (3a) in CDCl$_3$

$^1$H-NMR (500 MHz) of (R)-1-phenylbut-3-en-2-ol (3b) in CDCl$_3$
$^1$H-NMR (500 MHz) of (S)-1-cyclohexylprop-2-en-1-ol (3c) in CDCl$_3$
$^1$H-NMR (500MHz) of (S)-α-vinylbenzyl alcohol (3e) in CDCl$_3$
$^{13}$C-NMR (75 MHz) of (S)-α-vinylbenzyl alcohol (3e) in CDCl$_3$

$^1$H-NMR (300 MHz) of (R)-pentadec-1-en-3-ol (3f) in CDCl$_3$
$^{13}$C-NMR (75 MHz) of (R)-pentadec-1-en-3-ol (3f) in CDCl$_3$

$^1$H-NMR (500 MHz) of (S)-(3-methoxyallyl)cyclohexane (6) in CDCl$_3$
$\text{SUPPORTING INFORMATION}$

$\text{\textsuperscript{13}C-NMR (125 MHz) of (S)-(3-methoxyallyl)cyclohexane (6) in CDCl}_3$

$\text{H-NMR (500 MHz) of pentadec-1-en-3-yl acetate (ent-3f-Ac) in CDCl}_3$
4.2. **syn/anti-Epoxy alcohols obtained from mCPBA epoxidation**

$^1$H-NMR (300 MHz) in CDCl$_3$, rac-undecec-1-en-ol (rac 3a) as substrate
$^1$H-NMR (500 MHz) in CDCl$_3$, rac-1-phenylbut-3-en-2-ol (rac-3b) as substrate

$^1$H-NMR (500 MHz) in CDCl$_3$, rac-1-cyclohexylprop-2-en-1-ol (rac-3c) as substrate
$^1$H-NMR (300 MHz) in CDCl$_3$, rac-4,4-dimethylpent-1-en-3-ol (rac-3d) as substrate

$^1$H-NMR (500 MHz) in CDCl$_3$, rac-α-vinylbenzyl alcohol (3e) as substrate
$^{1}$H-NMR (300 MHz) in CDCl$_3$, rac-pentadec-1-en-3-ol (rac-3f) as substrate
4.3. syn-Epoxy alcohols obtained by catalytic epoxidation with the titanium salalen catalyst 2

$^1$H-NMR (300 MHz) in CDCl$_3$, (R)-undecec-1-en-ol (3a) as substrate

$^{13}$C-NMR (75 MHz) in CDCl$_3$, (R)-undecec-1-en-ol (3a) as substrate
$^1$H-NMR (500 MHz) in CDCl$_3$, (R)-1-phenylbut-3-en-2-ol (3b) as substrate:

$^{13}$C-NMR (75MHz) in CDCl$_3$, (R)-1-phenylbut-3-en-2-ol (3b) as substrate:
SUPPORTING INFORMATION

$^{1}$H-NMR (300 MHz) in CDCl$_3$, (S)-1-cyclohexylprop-2-en-1-ol (3c) as substrate

$^{13}$C-NMR (75 MHz) in CDCl$_3$, (S)-1-cyclohexylprop-2-en-1-ol (3c) as substrate
\textsuperscript{1}H-NMR (500 MHz) in CDCl\textsubscript{3}, (S)-4,4-dimethylpent-1-en-3-ol (3d) as substrate

\textsuperscript{13}C-NMR (125 MHz) in CDCl\textsubscript{3}, (S)-4,4-dimethylpent-1-en-3-ol (3d) as substrate
Supporting Information

\(^1\)H-NMR (500 MHz) in CDCl\(_3\), (S)-\(\alpha\)-vinylbenzyl alcohol (3e) as substrate:

\(^{13}\)C-NMR (75MHz) in CDCl\(_3\), (S)-\(\alpha\)-vinylbenzyl alcohol (3e) as substrate:
$^1$H-NMR (500 MHz) in CDCl$_3$, (R)-1-((R)-oxiran-2-yl)tridecan-1-ol (3f) as substrate

$^{13}$C-NMR (125 MHz) in CDCl$_3$, (R)-1-((R)-oxiran-2-yl)tridecan-1-ol (3f) as substrate
$^1$H-NMR (500 MHz) in CDCl$_3$, (S)-(3-methoxyallyl)cyclohexane (6) as substrate

$^{13}$C-NMR (125 MHz) in CDCl$_3$, (S)-(3-methoxyallyl)cyclohexane (6) as substrate
4.4. THF Building block 8 and synthetic intermediates 9 and 10

$^1$H-NMR (500MHz) of tert-butyl(((R)$-1-(($R$)-oxiran-2-yl)tridecyl)oxy)diphenylsilane (9) in CDCl$_3$

$^{13}$C-NMR (125MHz) of tert-butyl(((R)$-1-(($R$)-oxiran-2-yl)tridecyl)oxy)diphenylsilane (9) in CDCl$_3$
\(^1\)H-NMR (500MHz) of (5R,6R)-6-((tert-butyldiphenylsilyl)oxy)octadec-1-en-5-ol (10) in CDCl\(_3\)

\(^{13}\)C-NMR (125MHz) of (5R,6R)-6-((tert-butyldiphenylsilyl)oxy)octadec-1-en-5-ol (10) in CDCl\(_3\)
$^1$H-NMR (500MHz) of ($2R,5R$)-5-($R$)-1-(tert-butyldiphenylsilyl)oxy)tridecyltetrahydrofuran-2-yl)methanol (8) in CDCl$_3$

$^{13}$C-NMR (125MHz) of ($2R,5R$)-5-($R$)-1-(tert-butyldiphenylsilyl)oxy)tridecyltetrahydrofuran-2-yl)methanol (8) in CDCl$_3$
$^1$H-NMR (500MHz) monitoring of the epoxidation/ring closure of intermediate 10 to the THF building block 8 (CDCl$_3$).
5. X-ray Crystallographic Data

5.1. X-Ray crystal structure of (R,R)-cyclohexyl(oxiran-2-yl)methanol (4c)

Crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution in n-pentane.

| Property                              | Value                  |
|---------------------------------------|------------------------|
| CCDC registry number                  | 2132886                |
| Empirical formula                     | C₉H₁₆O₂                 |
| Moiety formula                        | C₉H₁₆O₂                 |
| Formula weight                        | 156.22                 |
| Temperature                           | 150(2) K               |
| Wavelength                            | 1.54178 Å              |
| Crystal system                        | Monoclinic             |
| Space group                           | P2₁                    |
| Unit cell dimensions                  | a = 5.2366(2) Å        |
|                                       | b = 31.8952(10) Å      |
|                                       | c = 10.4186(3) Å       |
| Volume                                | 1740.10(10) Å³         |
| Z                                      | 8                      |
| Density (calculated)                  | 1.193 mg/m³            |
| Absorption coefficient                | 0.656 mm⁻¹             |
| F(000)                                | 688                    |
| Crystal size                          | 2.000 x 0.200 x 0.040 mm³ |
| Theta range for data collection       | 4.243 to 72.235°       |
| Index ranges                          | -5<=h<=6, -39<=k<=39, -12<=l<=12 |
| Reflections collected                 | 35958                  |
| Independent reflections               | 6833 [R(int) = 0.0388]  |
| Completeness to theta = 67.679°       | 99.7 %                 |
| Absorption correction                 | Semi-empirical from equivalents |
| Max. and min. transmission            | 0.7536 and 0.6502      |
| Refinement method                     | Full-matrix least-squares on F² |
| Data / restraints / parameters         | 6833 / 1 / 405         |
| Goodness-of-fit on F²                 | 1.053                  |
| Final R indices [I>2sigma(I)]         | R1 = 0.0269, wR2 = 0.0726 |
| R indices (all data)                  | R1 = 0.0273, wR2 = 0.0728 |
| Absolute structure parameter          | 0.00(3)                |
| Largest diff. peak and hole           | 0.170 and -0.135 eÅ³   |

*Figure S1:* Molecular structure (left) and ORTEP (right, four independent molecules in the unit cell) of the X-ray crystal structure of the epoxy alcohol 4c. Thermal ellipsoids are drawn at 50% probability level.
5.2. X-Ray crystal structure of \((R,R)-1-(oxiran-2-yl)tridecan-1-ol\) (4f)

Crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution in \(n\)-pentane.

- **CCDC registry number**: 2132887
- **Empirical formula**: \(C_{15}H_{30}O_2\)
- **Formula weight**: 242.39
- **Temperature**: 100(2) K
- **Wavelength**: 1.54178 Å
- **Space group**: \(P2_1\)
- **Unit cell dimensions**:
  - \(a = 8.8612(5)\) Å \(\alpha = 90^\circ\)
  - \(b = 4.8888(4)\) Å \(\beta = 90.288(4)^\circ\)
  - \(c = 33.909(2)\) Å \(\gamma = 90^\circ\)
- **Volume**: 1468.95(17) Å\(^3\)
- **Z**: 4
- **Density (calculated)**: 1.096 mg/m\(^3\)
- **Absorption coefficient**: 0.538 mm\(^{-1}\)
- **F(000)**: 544
- **Crystal size**: 0.500 x 0.100 x 0.020 mm\(^3\)
- **Theta range for data collection**: 2.606 to 72.205°
- **Index ranges**: \(-10 \leq h \leq 10, -5 \leq k \leq 6, -41 \leq l \leq 41\)
- **Reflections collected**: 28259
- **Independent reflections**: 5640 \([R(int) = 0.0658]\)
- **Completeness to theta = 67.679°**: 99.9 %
- **Absorption correction**: Semi-empirical from equivalents
- **Max. and min. transmission**: 0.7536 and 0.5828
- **Refinement method**: Full-matrix least-squares on \(F^2\)
- **Data / restraints / parameters**: 5640 / 1 / 317
- **Goodness-of-fit on \(F^2\)**: 1.068
- **Final R indices [I>2sigma(I)]**: \(R1 = 0.0398, wR2 = 0.1072\)
- **R indices (all data)**: \(R1 = 0.0429, wR2 = 0.1093\)
- **Absolute structure parameter**: 0.10(10)
- **Largest diff. peak and hole**: 0.226 and \(-0.206\) e•Å\(^{-3}\)

**Figure S2:** Molecular structure (top) and ORTEP (bottom, two independent molecules in the unit cell) of the X-ray crystal structure of the epoxy alcohol 4f. Thermal ellipsoids are drawn at 50% probability level.
6. References

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