Supporting Information for

Hydrolytic Kinetic Resolution of Epoxides Catalyzed by Chromium(III)-endo,endo-2,5-diaminonorbornane-salen [Cr(III)-DIANANE-salen] Complexes. Improved Activity, Low Catalyst Loading

Albrecht Berkessel* and Erkan Ertürk

Institut für Organische Chemie der Universität zu Köln, Greinstrasse 4, D-50939 Köln, Germany
Fax: +49-221-470-5102, E-mail: berkessel@uni-koeln.de

General Remarks:
EI mass spectra were measured on a Hewlett-Packard HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector using GC-MS (column: HP-5, 25 m, 0.25 mm ID; inj.: 250 °C (split modus); det.: 250 °C (FID); He, 1.0 ml-min⁻¹ (constant flow modus); oven: 35 °C (5 min), 20 °C-min⁻¹ , 280 °C (10 min)). Optical rotations were measured on a Perkin Elmer 343 plus polarimeter with sodium (λ = 589 nm) and mercury lamp, and registered as follows: [α]T°Cλ (c = g/100 ml, solvent). Enantiomeric excesses were determined using a Hewlett-Packard HP 6890 GC system equipped with chiral capillary GC columns. Chiral GC conditions are given individually below. All epoxides were purified by distillation prior to use. THF was distilled from sodium/benzophenone. Reaction mixtures were filtered through a short plug of neutral alumina to remove residual water, and were carefully concentrated by rotary evaporation to remove the solvent (THF) before isolating the products by (vacuum) distillation.
(R)-Epoxoctane [10a] and (S)-1,2-octanediol [11a] (Table 2, entry 1):

\[
\begin{array}{c}
\text{(+/-)} \\
rac-10a
\end{array}
\xrightarrow{\text{9 (0.50 mol%)}}
\begin{array}{c}
\text{H}_2\text{O (0.55 eq), THF, 0 °C → rt}, 24 \text{ h} \\
n-C_6\text{H}_{13} \text{O} \xrightarrow{\text{+}} n-C_6\text{H}_{13} \text{O} + n-C_6\text{H}_{13} \text{OH}
\end{array}
\begin{array}{c}
\text{rac-10a} \\
10a \\
11a
\end{array}
\]

A 10 ml round-bottomed flask, equipped with a stir bar, was charged with the catalyst 9 (39 mg, 50 µmol, 0.50 mol%). Racemic 1,2-epoxoctane (rac-10a, 1.282 g, 1.528 ml, 10.00 mmol, 1.00 eq) and THF (100 µl) were successively added. The solution was cooled to 0 °C in an ice bath, and H₂O (99 µl, 5.50 mmol, 0.55 eq) was added in one portion. The ice bath was removed and the reaction mixture was allowed to warm to rt. After stirring for 24 h at rt, the reaction was stopped. After filtration of the mixture through a short plug of neutral alumina, and removing the solvent carefully by rotary evaporation, (R)-1,2-epoxoctane (10a, 590 mg, 4.60 mmol, 46 %, >99 % ee) was isolated via Kugelrohr-distillation (50 °C/0.1 mbar). After changing the recipient of the Kugelrohr device, the diol 11a (730 mg, 5.00 mmol, 50 %, >95 % ee) was also isolated under reduced pressure (150 °C/2x10⁻² mbar).

GC (chiral): WCOT-FS, CP Chirasil-Dex CB, 25 m, 0.25 mm ID; inj.: 180 °C (split modus); det.: 180 °C; He, 1.8 ml·min⁻¹ (constant flow modus); oven: 60 °C (48 min), 5 °C·min⁻¹, 120 °C (35 min), 15 °C·min⁻¹, 160 °C (3 min).

\[\tau_R = 40.1 \text{ min}, \ 10a \ ((R)-1,2-epoxoctane)\]
\[\tau_R = 41.2 \text{ min}, \ ent-10a \ ((S)-1,2-epoxoctane)\]
\[\tau_R = 84.9 \text{ min}, \ 11a \ ((S)-1,2-octanediol)\]
\[\tau_R = 87.3 \text{ min}, \ ent-11a \ ((R)-1,2-octanediol)\]

**Optical rotation of 10a:**
\[\alpha^{20}_D = +7.36^\circ \ (c = 1.15, \text{CHCl}_3); \text{lit.}^{[1]}: \alpha^{22}_D = +7.4^\circ \ (c = 4.50, \text{CHCl}_3)\]

**Optical rotation of 11a:**
\[\alpha^{20}_D = -13.2^\circ \ (c = 3.0, \text{EtOH}); \text{lit.}^{[2]}: \alpha^{20}_D = -16.4^\circ \ (c = 2.20, \text{EtOH})\]
(R)-Propylene oxide [10b] and (S)-1,2-propanediol [11b] (Table 2, entry 2):

\[
\begin{align*}
\text{H}_3\text{C} & \quad \xrightarrow{\text{9 (0.05 mol\%)} \quad \text{H}_2\text{O (0.55 eq), 1 °C, 34 h}} \quad \text{H}_3\text{C} \\
\text{(+/−) rac-10b} & \quad + \quad \text{H}_3\text{C} \quad \text{OH} \\
\text{10b} & \quad \text{11b}
\end{align*}
\]

A 10 ml round-bottomed flask, equipped with a stir bar, was charged with the catalyst 9 (31 mg, 40.00 µmol, 0.05 mol%) and racemic propylene oxide (rac-10b, 4.464 g, 5.6 ml, 80.00 mmol, 1.00 eq) was added into the flask. The mixture was cooled to 1 °C, H₂O (792 µl, 44.00 mmol, 0.55 eq) was added, and the flask was capped with a rubber septum. After stirring the reaction mixture at 1 °C for 34 h, (R)-propylene oxide (10b, 2.11 g, 36.00 mmol, 45 %, >99 % ee) was isolated by bulb-to-bulb distillation into a flask cooled in a dry ice-PrOH mixture (-78 °C). (S)-1,2-Propanediol (11b, 2.90 g, 38.00 mmol, 48 %, >99 % ee) was subsequently isolated by Kugelrohr-distillation (70 °C/0.1 mbar).

GC (chiral): Chiraldex α-TA, 30 m, 0.25 mm ID; inj.: 130 °C (split modus); det.: 150 °C; N₂, 0.41 bar (10 min), 1 bar-min⁻¹, 1 bar (26.41 min); oven: 30 °C (10 min), 10 °C⋅min⁻¹, 100 °C (20 min)
\[\tau_R = 8.29 \text{ min}, \text{10b (}(R)\text{-propylene oxide)}\]
\[\tau_R = 9.31 \text{ min}, \text{ent-10b (}(S)\text{-propylene oxide)}\]

GC (chiral): WCOT-FS, CP Chirasil-Dex CB, 25 m, 0.25 mm ID; inj.: 180 °C (split modus); det.: 180 °C; N₂, 1.2 ml-min⁻¹ (constant flow modus); oven: 60 °C (45 min), 15 °C⋅min⁻¹, 160 °C (3 min).
\[\tau_R = 35.69 \text{ min}, \text{11b (}(S)\text{-1,2-propanediol)}\]
\[\tau_R = 37.46 \text{ min}, \text{ent-11b (}(R)\text{-1,2-propanediol)}\]

Optical rotation of 10b :
\[\alpha^{23}_{D} = +11.9^{\circ} \text{ (neat)}; \text{lit.}^{[3]}: \alpha^{23}_{D} = +11.6^{\circ} \text{ (neat)}\]

Optical rotation of 11b :
\[\alpha^{23}_{D} = +14.8^{\circ} \text{ (neat)}; \text{lit.}^{[3]}: \alpha^{23}_{D} = +17.2^{\circ} \text{ (neat)}\]
(S)-Epichlorohydrin [10c] and (R)-3-chloro-1,2-propanediol [11c] (Table 2, entry 3):

A solution of the Cr(III) complex 9 (31 mg, 40 µmol, 0.05 mmol%) and racemic epichlorohydrin (rac-10c, 7.40 g, 6.26 ml, 80.00 mmol, 1.00 eq) in THF (0.8 ml) was placed into 25 ml round-bottomed and was cooled to 0 °C in an ice bath. H₂O (792 µl, 44.00 mmol, 0.55 eq) was added in one portion. After stirring for 20 min., the ice bath was removed, the mixture was allowed to warm to rt and was stirred for another 42 h at rt. After filtration of the mixture through a short plug of neutral alumina and careful removal of the solvent by rotary evaporation, (S)-epichlorohydrin (10c, 3.38 g, 36.50 mmol, 46 %, >99 % ee) was distilled off under reduced pressure (53 °C/87 mbar) and collected in (-78 °C) recipient. The residue was diluted with 100 ml n-hexane/EtOAc (5:3), and treated with 30 ml H₂O and the resulting mixture was filtered to remove solids. The layers were separated and the organic phase was extracted with H₂O (2 x 30 ml). The organic phases were discarded. The combined aqueous layers were concentrated by rotary evaporation (65 °C/20 mbar) to yield (R)-3-chloro-1,2-propanediol (11c, 4.26 g, 38.80 mmol, 49 %, >95 % ee).

GC (chiral): Chiraldex γ-TA, 20 m, 0.25 mm ID; inj.: 170 °C (split modus); det.: 180 °C; N₂, 1.0 ml·min⁻¹ (constant flow modus); oven: 40 °C (8 min), 5 °C·min⁻¹, 75 °C (20 min), 15 °C·min⁻¹, 160 °C (2 min)

τᵣ = 4.33 min, 10c ((S)-epichlorohydrin)
τᵣ = 5.12 min, ent-10c ((R)-epichlorohydrin)
τᵣ = 26.87 min, ent-11c ((S)-3-chloro-1,2-propanediol)
τᵣ = 27.13 min, 11c ((R)-3-chloro-1,2-propanediol)

Optical rotation of 10c:
[α]²⁰⁻D = +35.7° (c = 3.00, MeOH); lit.[⁴]: [α]²³⁻D = +35.5° (c = 3.44, MeOH)

Optical rotation of 11c:
[α]²³⁻D = -1.14° (neat); lit.[³]: [α]²₃⁻D = -1.24° (neat)
(R)-1,2-Epoxyhexane [10d] and (S)-1,2-hexanediol [11d] (Table 2, entry 4):

\[
\text{n-C}_4\text{H}_9\text{O} \quad \xrightarrow{9 \text{(0.20 mol%)}} \quad \text{H}_2\text{O} \text{(0.55 eq), } 0^\circ\text{C} \rightarrow \text{rt, 26 h}} \quad \text{n-C}_4\text{H}_9\text{O} + \text{n-C}_4\text{H}_9\text{OH} \quad (+/-) \text{rac-10d}
\]

The catalyst 9 (39 mg, 50 µmol, 0.20 mol%) and racemic 1,2-epoxyhexane (rac-10d, 2.504 g, 3.013 ml, 25.00 mmol, 1.00 eq) were placed in a 25 ml round-bottomed flask. The mixture was cooled to 0 °C in an ice bath. H₂O (248 µl, 13.75 mmol, 0.55 eq) was added to the mixture. After stirring for 20 min. at 0 °C, the ice bath was removed, the mixture was allowed to warm to rt, and it was stirred for 26 h at rt. The mixture was filtered through a short plug of neutral alumina. (R)-1,2-Epoxyhexane (10d, 1.150 g, 11.50 mmol, 46 %, >99 % ee) was isolated by Kugelrohr-distillation (60 °C/1.0 mbar) and (S)-1,2-hexanediol (11d, 1.50 g, 12.70 mmol, 51 %, >95 % ee) was also isolated by Kugelrohr-distillation (120 °C/2x10⁻² mbar) from the reaction flask.

GC (chiral): Chiraldex γ-TA, 20 m, 0.25 mm ID; inj.: 170 °C (split modus); det.: 180 °C; N₂, 1.0 ml·min⁻¹ (constant flow modus); oven: 40 °C (7 min), 5 °C·min⁻¹, 85 °C (11 min), 15 °C·min⁻¹, 150 °C (2 min)

\[\tau_R = 3.4 \text{ min, } \text{ent-10d } ((S)-1,2\text{-epoxyhexane)}\]

\[\tau_R = 3.7 \text{ min, 10d } ((R)-\text{epoxyhexane)}\]

\[\tau_R = 21.4 \text{ min, } \text{ent-11d } ((R)-1,2\text{-hexanediol)}\]

\[\tau_R = 22.0 \text{ min, 11c } ((S)-1,2\text{-hexanediol)}\]

**Optical rotation of 10d:**

\[\left[\alpha\right]_{D}^{20} = +10.9^\circ \text{ (c = 1.07, CHCl}_3\text{)}; \text{lit.}^{[5]}: \left[\alpha\right]_{D}^{20} = +9.1^\circ \text{ (c = 1.00, CHCl}_3\text{)}\]

**Optical rotation of 11d:**

\[\left[\alpha\right]_{D}^{20} = -17.0^\circ \text{ (c = 1.095, EtOH); lit.}^{[6]}: \left[\alpha\right]_{D}^{20} = -17.5^\circ \text{ (c = 13, EtOH)}\]
(R)-Vinylcyclohexane oxide [10e] and (S)-2-cyclohexyl-1,2-ethanediol [11e] (Table 2, entry 5):

A 10 ml round-bottomed flask was charged with the catalyst 9 (27 mg, 34 µmol, 0.20 mol%). The catalyst 9 was then dissolved in racemic vinylcyclohexane oxide (rac-10e, 2.145 g, 17.00 mmol, 1.00 eq) and THF (130 µl). The reaction mixture was cooled in an ice bath, and H₂O (168 µl, 9.35 mmol, 0.55 eq) was added in one portion. After stirring for 15 min. at 0 °C, the ice bath was removed and the mixture was allowed to warm to rt. After 54 h at rt, the mixture was filtered through a short plug of neutral alumina, and it was carefully concentrated by rotary evaporation. (R)-Vinylcyclohexane oxide (10e, 920 mg, 7.30 mmol, 43 %, >99 % ee) was isolated by Kugelrohr-distillation (60 °C/0.2 mbar) from the reaction mixture. (S)-2-Cyclohexyl-1,2-ethanediol (11e, 1.215 g, 8.43 mmol, 50 %, 96 % ee) was also isolated from the residue by Kugelrohr-distillation (150 °C/5x10⁻² mbar).

GC (chiral): Chrompak Hydrodex β-3P, 25 m, 0.25 mm ID; inj.: 185 °C (split modus); det.: 200 °C; N₂, 12 psi column head pressure (constant flow modus); oven: 60 °C (28 min), 6 °C·min⁻¹, 130 °C (20 min), 15 °C·min⁻¹, 160 °C (2 min)

τᵣ = 21.8 min, 10e ((R)-vinylcyclohexane oxide)
τᵣ = 22.8 min, ent-10e ((S)-vinylcyclohexane oxide)

The separation of the diol enantiomers (11e and ent-11e) and the determination of enantiomeric excess for the diol 11e was accomplished after conversion to the bis-trifluoroacetate ester: In a test tube, 3-4 drops of 11e were dissolved in 5 ml of CH₂Cl₂, and 5-10 drops of trifluoroacetic acid anhydride ((CF₃CO)₂O) were added with ice cooling. After shaking for 30 min., the mixture was quenched with ice, the organic phase was separated and filtered through a short column of neutral alumina. The filtrate was analyzed by chiral GC.
Optical rotation of 10e:
$\left[\alpha\right]^{20}_D = -1.49^\circ$ (c = 1.075, CHCl$_3$); lit.$^{[7]}$: $\left[\alpha\right]^{22}_D = -2.1^\circ$ (c = 0.88, CHCl$_3$)

Optical rotation of 11e:
$\left[\alpha\right]^{20}_D = -3.45^\circ$ (c = 1.22, EtOH); lit.$^{[3]}$: $\left[\alpha\right]^{27}_D = -2.6^\circ$ (c = 1.81, EtOH)

(R)-3,3-Dimethylbutene oxide [10f] and (S)-3,3-dimethylbutane-1,2-diol [11f] (Table 2, entry 6):

\[
\begin{align*}
\text{t-C}_4\text{H}_9\text{O} & \quad + \quad \text{t-C}_4\text{H}_9\text{OH} \\
\text{rac-10f} & \quad \text{rac-1,2-hexanediol, THF, rt, 42 h} \\
\text{10f} & \quad \text{11f}
\end{align*}
\]

In a 10 ml round-bottomed flask, the catalyst 9 (98 mg, 125 µmol, 2.50 mol%) was dissolved in racemic tert.-butyl oxirane (rac-10f, 591 mg, 5.00 mmol, 1.00 eq), rac-1,2-hexanediol (500 µl), and THF (300 µl). After stirring for 5 min. at rt, H$_2$O (54 µl, 3.00 mmol, 0.60 eq) was added in one portion. The reaction mixture was stirred for 42 h at rt. After filtration of the mixture through a short plug of neutral alumina and careful removal of the solvent by rotary evaporation, (R)-3,3-dimethylbutene oxide (10f, 230 mg, 2.40 mmol, 46 %, >95 % ee) was obtained by Kugelrohr-distillation (0.3 mbar/40-50 °C). After changing the recipient of the Kugelrohr device, the residual liquid was distilled and (S)-3,3-dimethyl-1,2-butanediol (11f, 90 % ee, yield was not determined) was obtained as a mixture with rac-1,2-hexanediol.

GC (chiral): Chiraldex $\gamma$-TA, 20 m, 0.25 mm ID; inj.: 170 °C (split modus); det.: 180 °C; N$_2$, 1.0 ml-min$^{-1}$ (constant flow modus); oven: 75 °C (25 min), 15 °C-min$^{-1}$, 150 °C (3 min)

$\tau_R = 13.3$ min, ent-11eD ((R)-bis-trifluoroacetate of ent-11e)

$\tau_R = 15.5$ min, 11eD ((S)- bis-trifluoroacetate of 11e)

GC (chiral): Chiraldex $\gamma$-TA, 20 m, 0.25 mm ID; inj.: 150 °C (split modus); det.: 180 °C; N$_2$, 1.0 ml-min$^{-1}$ (constant flow modus); oven: 30 °C (10 min), 5 °C-min$^{-1}$, 80 °C (11 min), 15 °C-min$^{-1}$, 160 °C (2 min)

$\tau_R = 3.15$ min, 10f ((R)-3,3-dimethylbutene oxide)

$\tau_R = 3.46$ min, ent-10f ((S)-3,3-dimethylbutene oxide)
The separation of the diol enantiomers (11f and ent-11f) and the determination of enantiomeric excess for the diol 11f was accomplished after conversion to the bis-trifluoroacetate esters: In a test tube, 3-4 drops of 11f were dissolved in 5 ml CH₂Cl₂, and 5-10 drops of trifluoroacetic acid anhydride ((CF₃CO)₂O) were added with ice cooling. After shaking for 30 min., the mixture was quenched with ice, the organic phase was separated and filtered through a short column on neutral alumina. The filtrate was analyzed by chiral GC.

\[
\begin{align*}
(+) &- \text{C}_4\text{H}_9 \quad \text{OH} \\
\text{OH} &\quad \text{(CF}_3\text{CO)}_2\text{O} \\
\text{t-C}_4\text{H}_9 &\quad \text{OCO(CF}_3) \\
\text{OCO(CF}_3) &+ \quad \text{t-C}_4\text{H}_9 \\
(+) &- \text{C}_4\text{H}_9 \quad \text{OH} \\
\text{OH} &\quad \text{(CF}_3\text{CO)}_2\text{O} \\
\text{t-C}_4\text{H}_9 &\quad \text{OCO(CF}_3) \\
\text{OCO(CF}_3) &+ \quad \text{t-C}_4\text{H}_9 \\
\end{align*}
\]

GC (chiral): Chiraldex γ-TA, 20 m, 0.25 mm ID; inj.: 150 °C (split modus); det.: 180 °C; N₂, 0.8 ml·min⁻¹ (constant flow modus); oven: 30 °C (10 min), 5 °C·min⁻¹, 80 °C (11 min), 15 °C·min⁻¹, 160 °C (2 min)

\[\tau_R = 15.91 \text{ min, } \text{ent-11fD } ((R)-\text{bis-trifluoroacetate of } \text{ent-11f}) \]

\[\tau_R = 17.25 \text{ min, } \text{11fD } ((S)-\text{bis-trifluoroacetate of } \text{11f}) \]

Optical rotation of 10f:

\[\alpha_{25}^D = -9.5^\circ \quad (c = 1.30, \text{CHCl}_3) \]

lit.^[8]: \[\alpha_{25}^D = -18.4^\circ \quad (c = 1.80, \text{PhH}) \]

(R)-Styrene oxide [10g] and (S)-2-phenyl-1,2-ethanediol [11g] (Table 2, entry 7):

\[
\begin{align*}
\text{Ph} &\quad \text{O} \\
\text{H}_2\text{O} (0.70 \text{ eq}, \text{THF}, \text{rt}, 34 \text{ h}) &\quad \text{Ph} \\
(+) &- \text{C}_4\text{H}_9 \quad \text{OH} \\
\text{OH} &\quad \text{(CF}_3\text{CO)}_2\text{O} \\
\text{t-C}_4\text{H}_9 &\quad \text{OCO(CF}_3) \\
\text{OCO(CF}_3) &+ \quad \text{t-C}_4\text{H}_9 \\
\text{Ph} &\quad \text{O} \\
\text{OH} &\quad \text{OH} \\
\text{Ph} &\quad \text{OH} \\
\text{OH} &\quad \text{OH} \\
\end{align*}
\]

The catalyst 9 (19.5 mg, 25 µmol, 2.50 mol%) was placed in a screw cap test tube. Racemic styrene oxide (120 mg, 114 µl, 1.00 mmol, 1.00 eq) and THF (114 µl) were successively added. After stirring the solution for 5 min., H₂O (12.6 µl, 0.70 mmol, 0.70 eq) was added in one portion, and the tube was sealed with a screwcap. The mixture was allowed to stir for 4 h at rt, and bromobenzene (157 mg, 105 µl, 1.00 mmol, 1.00 eq) was added as internal standard. Samples were periodically withdrawn, filtered through neutral alumina, and analyzed by chiral GC.
<table>
<thead>
<tr>
<th>Time [h]</th>
<th>Yield of 10g [%]</th>
<th>ee of 10g [%]</th>
<th>Yield of 11g [%]</th>
<th>ee of 11g [%]</th>
</tr>
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<tr>
<td>34</td>
<td>20</td>
<td>97</td>
<td>53</td>
<td>88</td>
</tr>
</tbody>
</table>

GC (chiral): Chiraldex γ-TA, 20 m, 0.25 mm ID; inj.: 170 °C (split modus); det.: 180 °C; N₂, 1.0 ml·min⁻¹ (constant flow modus); oven: 100 °C (4.5 min), 5 °C·min⁻¹, 110 °C (30 min), 15 °C·min⁻¹, 160 °C (2 min)

τᵣ = 1.3 min, bromobenzene

τᵣ = 2.6 min, ent-10g ((S)-styrene oxide)

τᵣ = 3.0 min, 10g ((R)-styrene oxide)

τᵣ = 24.3 min, ent-11g ((R)-2-phenyl-1,2-ethanediol)

τᵣ = 24.7 min, 11g ((S)-2-phenyl-1,2-ethanediol)

(S)-Methyl glycidate [10h] and (R)-2,3-dihydroxypropionic acid methyl ester [11h]

(Table 2, entry 8):

\[
\text{H}_2\text{C}=\text{O} \xrightarrow{\text{H}_2\text{O} (0.60 \text{ eq}), \text{THF, rt, 48 h}} \text{H}_3\text{C}=\text{O} \quad \text{+} \quad \text{H}_3\text{C}=\text{O} + \text{H}_3\text{C}=\text{O} \quad \text{OH} \quad \text{OH}
\]

(+/−) rac-10h

10h

11h

The catalyst 9 (97.5 mg, 125 µmol, 2.50 mol%) was placed in a 10 ml round-bottomed flask, together with racemic methyl glycidate (rac-10h, 511 mg, 5.00 mmol, 1.00 eq) and THF (250 µl). After stirring for 5 min. at rt, H₂O (54 µl, 3.00 mmol, 0.60 eq) was added in one portion. The mixture was stirred for 48 h at rt. After filtration of the mixture through a short plug of neutral alumina and careful removal of the solvent by rotary evaporation, (S)-methyl glycidate (10h, 190 mg, 1.86 mmol, 37 %, >99 % ee) was obtained by Kugelrohr-distillation (50 °C/2-5 mbar). After changing the recipient of the Kugelrohr device, (R)-2,3-dihydroxypropionic acid methyl ester (11h, 290 mg, 48 %, 88 % ee) was subsequently isolated by Kugelrohr-distillation in vacuo (90 °C/5.5×10⁻² mbar).

GC (chiral): Chiraldex γ-TA, 20 m, 0.25 mm ID; inj.: 170 °C (split modus); det.: 180 °C; N₂, 1.0 ml·min⁻¹ (constant flow modus); oven: 55 °C (3 min), 6 °C·min⁻¹, 85 °C (30 min), 15 °C·min⁻¹, 160 °C (2 min)

τᵣ = 5.64 min, ent-10h ((R)-methyl glycidate)
\[ \tau_R = 7.18 \text{ min}, \ 10h \ (\text{methyl glycidate}) \]
\[ \tau_R = 16.55 \text{ min}, \ 11h \text{ and } \text{ent-11h} \ (\text{no GC separation of enantiomers}) \]

The separation of the diol enantiomers (11h and ent-11h) and the determination of enantiomeric excess for the diol 11h was accomplished after conversion to its acetonide:

In a test tube, 3-4 drops of 11h and a catalytic amount of p-toluene sulfonic acid (TsOH) were dissolved in 5 ml CH$_2$Cl$_2$. Then, 5-10 drops of 2,2-dimethoxypropane (18) were added. After shaking for 30 min., the mixture was directly analyzed by chiral GC.

![Diol Acetonide Reaction](image)

GC (chiral): WCOT-FS, CP Chirasil Dex CB, 25 m, 0.25 mm ID; inj.: 180 °C (split modus); det.: 180 °C; N$_2$, 1.1 ml-min$^{-1}$ (constant flow modus); oven: 60 °C (5 min), 2 °C-min$^{-1}$, 100 °C (5 min), 10 °C-min$^{-1}$, 160 °C (3 min)

\[ \tau_R = 24.88 \text{ min}, \text{ent-11hD} \ (\text{acetonide of ent-11h}) \]
\[ \tau_R = 26.45 \text{ min}, \text{11hD} \ (\text{acetonide of 11h}) \]

Optical rotation of 10h:

\[ [\alpha]^{31}_D = -9.47^\circ \ (c = 1.13, \text{MeOH}); \text{lit.}\[9]: [\alpha]^{31}_D = -9.8^\circ \ (c = 1.01, \text{MeOH}) \]

Optical rotation of 11h:

\[ [\alpha]^{25}_D = +10.07^\circ \ (c = 1.125, \text{CHCl}_3); \text{lit.}\[10]: [\alpha]^{31}_D = +4.1^\circ \ (c = 1.7, \text{CHCl}_3) \]

(R)-3-Bromo-1,2-propanediol [11i] (Table 2, entry 9):

![Bromo Propanediol Reaction](image)

The catalyst 9 (78 mg, 100 µmol, 1.00 mol%), racemic epibromohydrin (rac-10i, 1.370 g, 10.00 mmol, 1.00 eq) and THF (750 µl) were placed in a 10 ml round-bottomed flask. After stirring for 5 min. in an ice bath, H$_2$O (270 µl, 15.00 mmol, 1.50 eq) was added in one
portion. After stirring for 10 min., the ice bath was removed and the reaction mixture was allowed to warm to rt. The mixture was stirred for another 22 h at rt. The mixture was filtered through a short column of neutral alumina (flushing with ethyl acetate), and the filtrate was concentrated by rotary evaporation. (R)-3-Bromo-1,2-propanediol (11i, 1.400 g, 9.00 mmol, 90 %, 94 % ee) was obtained by Kugelrohr-distillation (120 °C/4.5x10⁻² mbar).

The separation of the diol enantiomers (11i and ent-11i) and the determination of enantiomeric excess for the diol 11i was accomplished after conversion to its acetonide: In a test tube, 3-4 drops of 11i and a catalytic amount of p-toluene sulfonic acid (TsOH) were dissolved in 5 ml CH₂Cl₂. Then, 5-10 drops of 2,2-dimethoxypropane (18) were added. After shaking for 30 min., the mixture was directly analyzed by chiral GC.

\[
\text{BrH}_2\text{C} \text{OH} + \text{H}_3\text{C} \text{OCH}_3 \xrightarrow{p\text{-TsOH}} \text{BrH}_2\text{C} \text{O} \text{CH}_3 + \text{H}_3\text{C} \text{OCH}_3
\]

GC (chiral): WCOT-FS, CP Chirasil Dex CB, 25 m, 0.25 mm ID; inj.: 180 °C (split modus); det.: 180 °C; N₂, 1.1 ml·min⁻¹ (constant flow modus); oven: 60 °C (5 min), 2 °C·min⁻¹, 100 °C (5 min), 10 °C·min⁻¹, 160 °C (3 min)

\[\tau_R = 27.27 \text{ min}, \text{ent-11iD} ((S)\text{-acetonide of ent-11i})\]

\[\tau_R = 28.49 \text{ min}, \text{11hi} ((R)\text{-acetonide of 11i})\]

Optical rotation of 11i:

\[\left[\alpha\right]_{25}^{D} = -4.95^\circ (c = 2.12, \text{CHCl}_3)\]; lit.\[11\]: \[\left[\alpha\right]_{25}^{D} = -4.0^\circ (c = 1.0, \text{CHCl}_3)\]

HKR of rac-2-methyl-2-n-pentyl oxirane [rac-10j] (Table 3):

\[
\begin{array}{c}
\text{H}_3\text{C} \\
n\text{C}_5\text{H}_{11}
\end{array}
\xrightarrow{17 (2.00 \text{ mol}), \text{H}_2\text{O} (2.00 \text{ eq})}
\begin{array}{c}
\text{H}_3\text{C} \\
n\text{C}_5\text{H}_{11}
\end{array}
\]

A GC vial was charged with the catalyst 17 (13.8 mg, 20 µmol, 2.00 mol%). Then, racemic 2-methyl-2-n-pentyl oxirane (rac-10j, 128 mg, 1.00 mmol, 1.00 eq), racemic 1,2-hexanediol
(100 µl), THF (100 µl), and 1,3-dibromobenzene (47 mg, 24 µl, 0.20 eq, as internal standard) were added. A sample was taken from the mixture and it was analyzed by chiral GC to determine the response factor of rac-10j vs. 1,3-dibromobenzene. By adding H₂O (36 µl, 2.00 mmol, 2.00 eq), the reaction was started. Samples were periodically withdrawn from the reaction mixture, filtered through a short plug of neutral alumina (flushing with ethyl acetate), and analyzed by means of chiral GC to determine the conversion/yield and the enantiomeric excesses of 10j and 11j. The results are summarized in Table 3. The absolute configurations of 10j, ent-10j, 11j, and ent-11j were assigned in analogy to the result of the HKR of rac-10a.

GC (chiral): WCOT-FS, CP Chirasil-Dex CB, 25 m, 0.25 mm ID; inj.: 180 °C (split modus); det.: 180 °C; N₂, 1.1 ml·min⁻¹ (constant flow modus); oven: 85 °C (13 min), 5 °C·min⁻¹, 110 °C (20 min), 15 °C·min⁻¹, 160 °C (3 min).

τᵣ = 9.1 min, 10j

τᵣ = 9.4 min, ent-10j

τᵣ = 21.4 min, 1,3-dibromobenzene

τᵣ = 25.6 min, (R)-1,2-hexanediol or (S)-1,2-hexanediol

τᵣ = 25.9 min, (R)-1,2-hexanediol or (S)-1,2-hexanediol

τᵣ = 31.3 min, ent-11j

τᵣ = 31.8 min, 11j

References:
