

Supplementary information for:

Tuning enantioselectivity for crystallization-induced asymmetric synthesis of a conglomerating oxo-rhenium(V) complex

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Experimental

General data: Optical rotations were measured for samples in acetonitrile solution at 25 °C and concentrations close to $c = 0,05$ g/100 mL on a Jasco DIP-1000 digital Polarimeter at $\lambda = 589$ nm (sodium D line). ^1H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using a CD_2Cl_2 solvent as lock and internal reference (^1H). All preparations were performed under dry, oxygen-free nitrogen.

Starting materials: Solvents and regular reagents obtained from commercial sources (Aldrich) were used without further purification. The ligand $\text{HP}(\text{OCMe}_2\text{CMe}_2\text{O})_2$ (HP~O) and the complexes *cis*- $[\text{ReOCl}_2(\text{P}^{\sim}\text{O})\text{py}]$ (*cis*-**1**) and *trans*- $[\text{ReOCl}_2(\text{P}^{\sim}\text{O})\text{OPP}_3]$ were prepared according to literature procedures.¹

Experimental Section: Crystallization-induced asymmetric synthesis, reactions (1) and (2) in Scheme 1, was carried out similarly to the literature procedures.²

The substrates relevant to reaction (1) (*trans*- $\text{ReOCl}_2(\text{OEt})\text{py}_2$ 0.05 g, 0.1 mmol) and $\text{HP}(\text{OCMe}_2\text{CMe}_2\text{O})_2$ (0.08 g, 0.3 mmol, HP~O) or reaction (2) (*trans*- $\text{ReOCl}_2(\text{P}^{\sim}\text{O})\text{OPPh}_3$ 0.05 g, 0.061 mmol; py 5 μL , 0.062 mmol), with the addition of appropriate amounts of finely ground seeds of *C*-(+)-*cis*-**1** (*cis*- $[\text{ReOCl}_2(\text{P}^{\sim}\text{O})\text{py}]$ 2–7 mg, 0.003–0.011 mmol, *ee* = +99.5%) were placed with the respective solvents (9 mL) in a 50 mL Schlenk flask under nitrogen. The flask, equipped with an octagonal Teflon® stir-bar (16 x 7 mm), a condenser, and an oil pressure equalizer, was placed in an heated oil bath. The reaction mixture was boiled and powerfully stirred (ca. 1100 rpm, with IKA® RET digi-visc) for either 1 h or a longer time. These preparations afford the major sparingly soluble product *cis*-**1** and the minor readily soluble product *trans*-**1**, as the only rhenium products. To follow the reaction progress, occasionally three small samples (0.2 mL) of the reaction suspension were collected in NMR tubes, and the volatiles were evaporated to dryness (by means of freeze–thaw cycles under vacuum). The residue was weighed and dissolved in CD_2Cl_2 in order to record the NMR spectra and evaluate the yield and composition of the sample by assessment of the integral intensity of resonance signals of the ligand's Me groups $(\text{OCMe}_2\text{CMe}_2\text{O})\text{POCMe}_2\text{CMe}_2\text{O}^{(1-)} = \text{P}^{\sim}\text{O}$). Finally, the sample was diluted with CH_2Cl_2 in a volumetric flask (5 mL) to measure optical rotation and to assess enantiomeric excess (*ee*). The specific rotation was $[\alpha]_{589} = +1380$ (c 0.05 g per 100 mL in CH_2Cl_2) for the pure enantiomer *C*-(+)-*cis*-**1**. The results were averaged from experiments repeated at least twice. To evaluate intrinsic *ee* values of the product after deduction of the seeds initially added were calculated using following formulas: $ee_{\text{meas.}} = 2x_{(+)\text{cis}} - 100$ and $ee_{\text{corr.}} = (x_{(+)\text{prod}} - x_{(-)\text{prod}}) / (x_{(+)\text{prod}} + x_{(-)\text{prod}})$, where $x_{(+)\text{cis}} = x_{(+)\text{prod}} + x_{(+)\text{Re}}$ and $x_{(+)\text{cis}}$ is the resulting whole mole fraction of the *C*-(+)-*cis*-**1** enantiomer after the reaction, $x_{(+)\text{prod}}$, $x_{(-)\text{prod}}$ are mole fractions of newly formed product (*C*-(+)-*cis*-**1** and *A*-(-)-*cis*-**1** enantiomers respectively), and $x_{(+)\text{Re}}$ is mole fraction of added seeds.

¹ Głowiak, T.; Rybak, W. K.; Skarżyńska, A., *Polyhedron* 2000, **19**, 2667–2672.

² W. K. Rybak, *Tetrahedron: Asymmetry* 2008, **19**, 2234–2239.

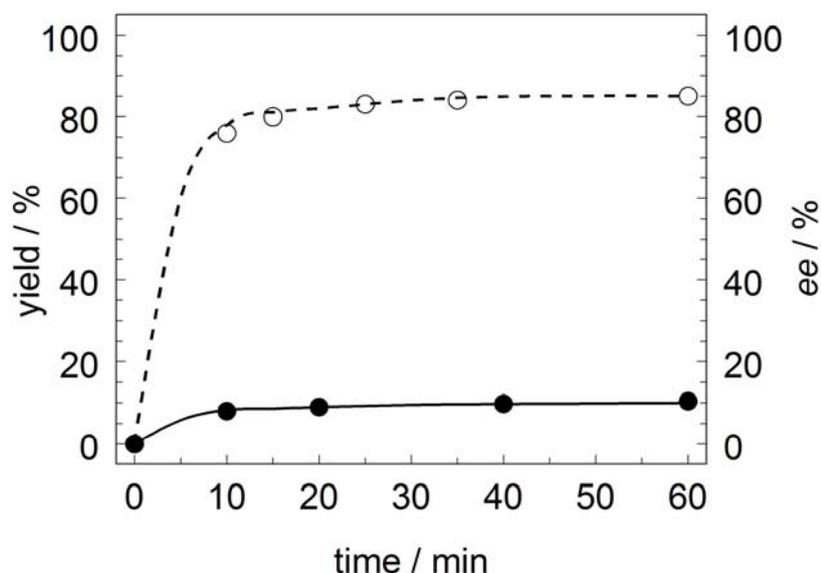


Figure S1. Reaction yield (outline circles, broken line, left axis) and enantiomeric excess (solid circles, solid line, right axis) of *cis*-**1** vs. time in the isomerization reaction of *trans*-**1** ($\text{ReOCl}_2\text{P}^{\sim}\text{O}$)py (0.050 g, 0.081 mmol), carried out in boiling partially miscible solvents, *n*-octane / MeCN (6 / 3 mL), with vigorous stirring and seeds (0.0044 g, $X_{(+)\text{Re}} = 8\%$) of *C*-(+)-*cis*-**1** ($ee = +99.5\%$) added initially. The relatively fast isomerization and poor chiral amplification at similar reaction conditions as in the synthesis (Figure 1) does not play a consequential role in the symmetry-breaking synthesis under study.

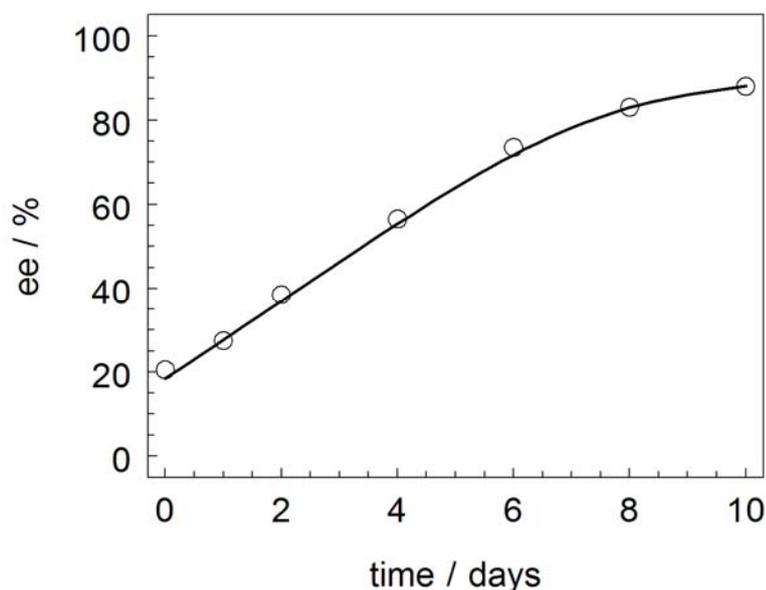


Figure S2. Time evolution of enantiomeric excess for non-racemic suspension of *cis*-**1** (0.050 g, 0.061 mmol) under prolonged vigorous stirring and boiling in partially miscible solvents, octane / MeCN (6 / 3 mL). Over 10 days, the rotation power of the solid samples slowly increases from $ee = 20\%$ to $ee = 85\%$, which indicates a very slow asymmetric transformation *rac-cis*-**1** due to *cis-trans* isomerization reaction. However, the rate of this asymmetric transformation is incomparably low (days vs. minutes) in relation to the rate of the asymmetric synthesis under study.

It might be noteworthy that similar asymmetric transformation (enantiomerization) in toluene is approximately two times slower (see the reference 4a) than in acetonitrile phase of partially miscible solvents. This

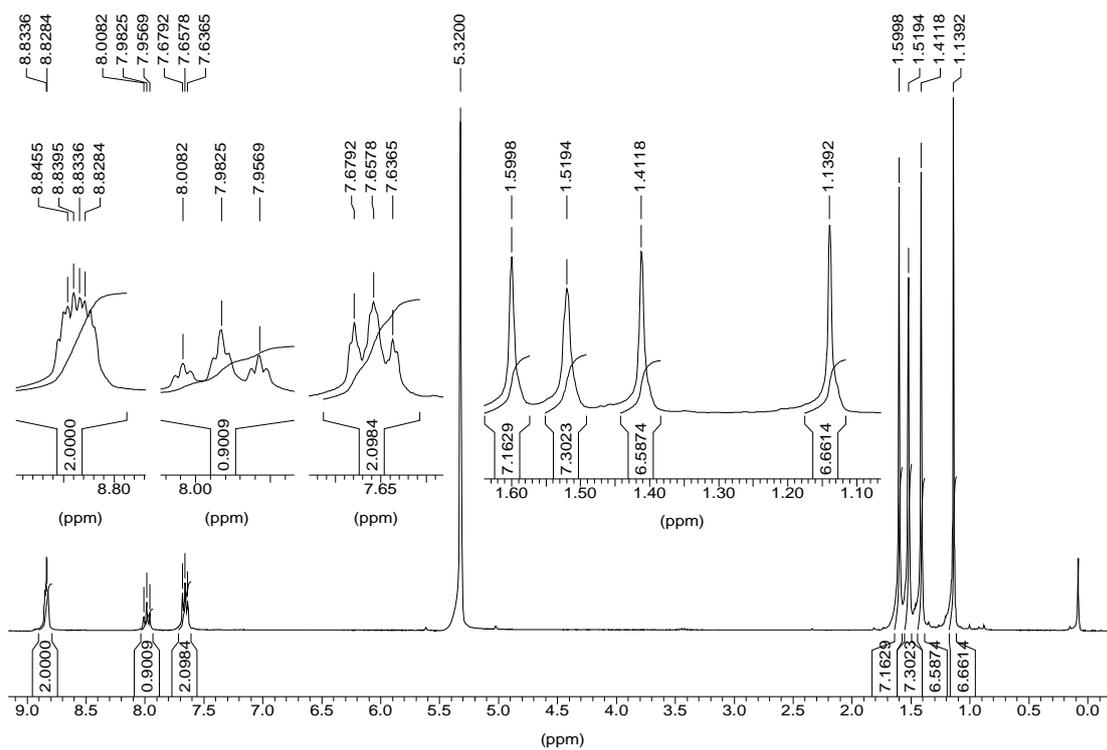


Figure S5. ^1H NMR spectrum of the *trans*-1 product recorded in CD_2Cl_2 solution.