Supporting information for :

Original use of the *same* heterogeneous chiral catalyst batch to promote *different* asymmetric reactions

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General methods and materials

All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. MTBE and CH₂Cl₂ were distilled before use from calcium hydride. The aldehydes and cyclohexene oxide were distilled before use, Danishefsky's diene, trimethylsilylazide and dimethylzinc (as a 1.2 M solution in toluene) were engaged as received from commercial sources. The synthesis of cat-1 and (*poly*)cat-1 is described in ref [1]. ¹H NMR spectra and ¹³C NMR spectra were recorded on either a Bruker AM 360 (360 MHz), AM 300 (300 MHz) or AM 250 (250 MHz) instrument with samples dissolved in CDCl₃ and data are reported in ppm with the solvent signal as reference (7.27 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR). Optical rotations were measured in solution in 10 cm cells at the sodium D line using a PERKIN ELMER 241 polarimeter. Mass spectra were recorded on a Finnigan MAT 95 S spectrometer. HPLC analyses were carried out on a separation product pomp P100 chromatograph equipped with an UV100 detector using an ODH column. GC analyses were carried out on a GC430 Varian equipped with a FID detector and a split/splitless injector.

Ring opening of epoxides

Homogeneous conditions

A schlenk tube was charged with catalyst cat-1 (13.7 mg, 2 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuum-argon cycles. MTBE (330 μ L) and cyclohexene oxide (1 mmol) were introduced with a syringe. The resulting solution was stirred at room temperature and then trimethylsilylazide (197 μ L, 1.5 mmol) was introduced. The mixture was stirred for 72 h. The solvents were removed under reduced pressure. The

residue was purified by celite filtration for the determination of the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous conditions

A schlenk tube was charged with catalyst (*poly*)cat-1 (27.4 mg, 4 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuum-argon cycles. MTBE (330 μ L) and cyclohexene oxide (1 mmol) were introduced with a syringe. The resulting solution was stirred at room temperature and then trimethylsilylazide (197 μ L, 1.5 mmol) was introduced. The mixture was stirred for 72 h. It was then filtered with a filtering syringe and the solvents were removed under reduced pressure. The residue was purified by celite filtration for the determination of the yield of the reaction and the enantiomeric excess of the product.

(1R,2R)-1-azido-2-trimethylsiloxycyclohexane

Colourless oil, $[\alpha]^{20}_{D}$ + 18.5 (*c* 0.99, CHCl₃) for 58 % ee, lit **1** $[\alpha]^{23}$ - 22.4 (*c* 2.87, CHCl₃) for 93 % ee material. The ee was determined by GC analysis using a chiral column Chiraldex B-PM (50m x 0.25mm x 0.25µm, 120 °C) which resolved both enantiomers ($t_{R(major)} = 9.5$ min, $t_{R(minor)} = 9.8$ min). The absolute stereochemistry was assigned as (*1R,2R*)-based on comparison of the measured rotation with the literature (see ref [2]). ¹H NMR (250 MHz, CDCl₃) δ 3.49-3.37 (m, 1H), 3.21-3.08 (m, 1H), 1.96-1.81 (m, 2H), 1.71-1.57 (m, 2H), 1.41-1.02 (m, 4H), 0.14 (s, 9H). ¹³C NMR (90 MHz, CDCl₃) δ 75.1, 66.6, 34.5, 30.4, 24.0, 23.8, -0.1). MS (IE) : 170 (32), 143 (21), 142 (69), 129 (26), 118 (29), 75 (86), 73 (100), 45(15).

Dimethylzinc alkylation

Homogeneous conditions

A schlenk tube was charged with catalyst cat-1 (13.7 mg, 2 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuum-argon cycles. MTBE (2 mL) and benzaldehyde (1 mmol) were introduced with a syringe. After 5 min dimethylzinc (2M solution in toluene) was then introduced (1 mL, 2 mmol). The resulting solution was stirred at room temperature for 24 h. It was then treated with water. The solution was then filtered and the aqueous layer was extracted with Et₂O. The organic layer was dried over MgSO₄ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous conditions

A schlenk tube was charged with catalyst (*poly*)cat-1 (27.4 mg, 4 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuum-argon cycles. MTBE (2

mL) and the benzaldehyde (1 mmol) were then introduced with a syringe. After 5 min dimethylzinc (2M solution in toluene) was then introduced (1 mL, 2 mmol). The resulting suspension was stirred at room temperature for 24 h. It was then filtered with a filtering syringe and water was added in the filtrate. The solution was then filtered and the aqueous layer was extracted with Et_2O . The organic layer was dried over MgSO₄ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product.

(S)-1-Phenyl-ethanol

Solvent for flash chromatography : pentane/diethylether 7/3. Colourless oil, $[\alpha]^{20}_{D} - 46.7$ (*c* 0.98, CHCl₃) for 88 % ee, $[\alpha]_{D} + 45.2$ (*c* 1.01, CH₂Cl₂, ref[3]) for 93 % ee material. The ee was determined by HPLC analysis using an ODH column (hexane/isopropanol 98/2, 1.0 mL/min) which resolved both enantiomers ($t_{R(minor)} = 15.1 \text{ min}$, $t_{R(major)} = 18.7 \text{ min}$). The absolute stereochemistry was assigned as (*S*)-based on comparison of the measured rotation with the literature (see ref [4]). ¹H NMR (360 MHz, CDCl₃) δ 7.38 (d, *J* = 4.9 Hz, 2H), 7.38-7.26 (m, 3H), 4.86 (q, *J* = 7.7 Hz, 1H), 2.56 (bs, 1H), 1.49 (d, *J* = 7.7 Hz, 3H). ¹³C NMR (90 MHz, CDCl₃) δ 145.8, 2 x 128.3, 127.3, 2 x 125.3, 70.1, 25.0. MS (IE) : 179 (70), 122 (42), 107 (100), 77 (38).

Recycling procedure

After each run, catalyst (*poly*)cat-1 was washed with MTBE and dried under vacuum. New substrates and solvents for the next reaction were then added for its reuse. In the case of Henry reaction, the catalyst was washed with water before being reused in the ring opening reaction.

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