

Electronic Supplementary Information for:

Reversal Phenomenon of Enantioface Selectivity by the Cooperative Operation of Two Chiral Catalysts

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(1) Enantioselective addition of *i*-Pr₂Zn to pyrimidine-5-carbaldehyde **1 (Table 1, entry 49):** A 0.0625 M solution of (1*R*,2*S*)-DMNE **3** (1.6 mL, 0.1 mmol) in hexane and a 0.0625 M solution of (*R*)-PEAE **4** (4.8 mL, 0.3 mmol) in hexane and hexane (8.3 mL) was mixed in the flask. And then, *i*-Pr₂Zn (1.3 mL of 1 M hexane solution, 1.3 mmol) was added dropwise at 0 °C. After stirring for 0.5 h, pyrimidine-5-carbaldehyde **1** (94.1 mg, 0.5 mmol) via a powder dropping funnel at 0 °C. And the mixture was stirred overnight. A part of the reaction mixture (1 mL) was transferred to another reaction vessel by syringe, and *i*-Pr₂Zn (0.25 mL of 1 M toluene solution, 0.25 mmol) and toluene (2.75 mL) solution of aldehyde **1** (23.5 mg, 0.125 mmol) were added at 0 °C, and the reaction mixture was stirred for 2.5 h. Moreover, after the addition of toluene (8 mL), *i*-Pr₂Zn (1.0 mL of 1 M toluene solution, 1.0 mmol) and toluene (3.0 mL) solution of **1** (94.1 mg, 0.5 mmol) were added dropwise at 0 °C, and the mixture was stirred for 2 h. The reaction was quenched with a mixture of 30% aqueous ammonia and saturated aqueous ammonium chloride (2/1, *v/v*) solution (10 mL). The mixture was extracted using CHCl₃ three times. The combined organic layers were dried over anhydrous sodium sulfate and evaporated *in vacuo*. Purification of the residue using silica gel column chromatography (hexane / ethyl acetate = 3/1, *v/v*) gave (*S*)-5-pyrimidyl alkanol **2** (137.3 mg, 0.591 mmol) with 95.2% ee. The yield was calculated to be 91% by subtracting the amount of autocatalyst **2** loading from the amount of isolated **2**. The ee value was determined by HPLC using a chiral stationary phase (Daicel Chiralpak IB column (250 x 4.6 Φ mm ID), eluent = 5% 2-propanol in hexane, flow rate 1.0 mL min⁻¹, 254 nm UV detector, retention time 10.8 min for (*S*)-**2**, 14.8 min for (*R*)-**2**).