



Supporting Information

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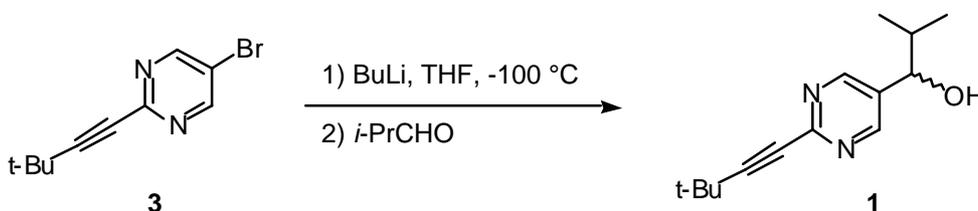
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Practically Complete Amplification of Chirality from Extremely Low (order $10^{-5}\%$) Enantiomeric Excess to Greater Than 99.5% Enantiomeric Excess by Asymmetric Autocatalysis

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Synthesis of racemic 2-alkynyl-5-pyrimidyl alkanol (1**).**



A 1.6 M hexane solution of butyllithium (1.3 mL, 2.0 mmol) was added at $-100\text{ }^{\circ}\text{C}$ to THF (20 mL) solution of 2-alkynyl-5-bromopyrimidine **3** (478 mg, 2.0 mmol), and the mixture was stirred for 5 min. 2-Methylpropanal (437 mg, 6.0 mmol) was added, and the mixture was stirred for 5 min. The reaction was quenched with water (15mL). The mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Purification of the residue by silica gel chromatography (eluent, hexane:ethyl acetate = 3 : 1 *v/v*) gave pyrimidyl alkanol **1** (136 mg, 29%).

Preparation of (*R*)-1** with *ca.* 0.00005% *ee.*** A standardized 2.6×10^{-6} M ethyl acetate (or benzene) solution of (*R*)-**1** was made using 1.2 mg of (*R*)-**1** (>99.5% *ee*) instead of (*S*)-**1** according to the procedure (see ref. 9) described in the text (ref. 9). The solution

(50 μ L) was added to the ethyl acetate (or benzene) solution of racemic **1** (60.8 mg). Then, a part of the solution was transferred to another flask, and the removal of solvent gave (*R*)-**1** with *ca.* 0.00005% *ee* (8.2 mg). Dissolution of the whole (*R*)-**1** in 3.6 mL of cumene produced 9.8×10^{-3} M cumene solution of (*R*)-**1** with *ca.* 0.00005% *ee*.

Typical experimental procedure for the synthesis of (*S*)-1** with very high *ee* (Table 1, run 2).** A 1.0 M toluene solution of *i*Pr₂Zn (0.75 mL, 0.75 mmol) was added at 0 °C to cumene solution (10 mL) of (*S*)-**1** with 57% *ee* (2.3 mg, 0.01 mmol), and the mixture was stirred for 15 min. A toluene solution (5 mL) of aldehyde **2** (94.1 mg, 0.50 mmol) was then added over a period of 1.5 h using a microfeeder. The mixture was stirred at 0 °C for additional 1.5 h, and the reaction was quenched with hydrochloric acid (1.0 M, 4 mL), and satd. aq. sodium hydrogencarbonate (13 mL) was then added. The mixture was filtered using Celite, and the filtrate was extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Purification of the residue by silica gel chromatography (eluent, hexane:ethyl acetate = 3 : 1 *v/v*) gave (*S*)-**1** (114 mg, 0.49 mmol) with 99% *ee*, which contained both the initial and the newly formed **1**. The yield of the newly formed **1** was 96%.

Typical experimental procedure of asymmetric autocatalysis using pyrimidyl alkanol **1 with 0.0005% *ee* (Table 1, run 9).** A 1.0 M cumene solution of *i*Pr₂Zn (0.1 mL, 0.1 mmol) was added at 0 °C to 1.3 mL cumene solution of (*S*)-**1** with *ca.* 0.0005% *ee* (2.9 mg, 0.013 mmol), and the mixture was stirred for 10 min. A cumene (1 mL) solution of aldehyde **2** (9.4 mg, 0.05 mmol) was then added over a period of 30 min, and the mixture was stirred for 1.5 h at 0 °C. Cumene (2.9 mL), *i*Pr₂Zn (0.4 mmol, 0.4

mL of 1.0 M cumene solution), and a cumene solution (1.5 mL) of aldehyde **2** (37.6 mg, 0.2 mmol) were added successively, and the reaction mixture was stirred for 1.5 h. The cumene (15.9 mL), *i*Pr₂Zn (1.6 mmol, 1.6 mL of 1.0 M cumene solution) and a cumene solution (4 mL) of aldehyde **2** (150 mg, 0.8 mmol) were then added successively, and the mixture was stirred at 0 °C for another 18 h. The reaction was quenched with hydrochloric acid (1.0 M, 4 mL), and satd. aq. sodium hydrogencarbonate (13 mL) was then added. The mixture was filtered using Celite, and the filtrate was extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Purification of the residue by silica gel chromatography (eluent, hexane: ethyl acetate = 3 : 1 v/v) gave (*S*)-pyrimidyl alkanol **2** (236 mg) with 76% *ee*. The yield of the newly formed (*S*)-**1** was 95% which was calculated by subtraction of the amount of **1** initially used.