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Supplementary Material

Optical rotations were measured using Jasco DIP-1000 polarimeter. IR spectra were recorded on a Horiba FT-210 spectrometer. ^1H -NMR spectra were recorded on a Jeol JNM-EX270L (270 MHz) spectrometer with tetramethylsilane as internal standard. Toluene was distilled from calcium hydride, and dried over molecular sieves 4A. All reactions were carried out under an argon atmosphere.

General procedures for the preparation of chiral pyrimidylalcohols **2 a, b** using a chiral catalyst (1*S*, 2*R*)-*N,N*-dipropylnorephedrine (DPNE)⁹: A mixture of DPNE (0.20 mmol) in toluene and (*i*-Pr)₂Zn (2.2 ml of 1 M toluene solution, 2.2 mmol) was stirred for 30 min at 0 °C, then a toluene solution of aldehyde **1 a, b** (1.00 mmol) was added at 0 °C. The reaction mixture was stirred for 24 h at 0 °C, and then quenched by the addition of 1N hydrochloric acid (5 ml) and satd. aq. NaHCO₃ (15 ml) at 0 °C. The mixture was filtered using celite and the filtrate was extracted with ethyl acetate. The extract was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. Purification of the crude on silica gel TLC (thin-layer chromatography) gave pyrimidyl alcohol **2 a, b** (0.77 mmol, 0.79 mmol respectively).

(*S*)-2-Methyl-1-(5-pyrimidyl)-1-propanol (**2 a**) (92.6% ee) Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel OD). Eluent: 2% 2-propanol in hexane; flow rate: 1.0 ml/min; 254 nm UV detector;

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retention time 34.8 min for *S* isomer, 45.7 min for *R* isomer. $[\alpha]_D^{25}$ -31.2° (*c* 1.01, MeOH). FT-IR (Neat) 3400 cm^{-1} . ^1H NMR (270 MHz, CDCl_3) δ (ppm) = 0.89 (d, $J = 6.9\text{ Hz}$, 3H), 0.98 (d, $J = 6.9\text{ Hz}$, 3H), 1.91-2.06 (m, 1H), 3.55 (bs, 1H), 4.51 (d, $J = 6.3\text{ Hz}$, 1H), 8.67 (s, 2H), 9.06 (s, 1H). HRMS m/z for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$, calcd 152.0951, found 152.0955.

(*S*)-2-Methyl-1-(2-methyl-5-pyrimidyl)-1-propanol (2b) (94.8% ee) Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel OD). Eluent: 2% 2-propanol in hexane; flow rate: 1.0 ml/min; 254 nm UV detector; retention time 34.8 min for *R* isomer and 38.2 min for *S* isomer. $[\alpha]_D^{25}$ -37.5° (*c* 1.02, MeOH). FT-IR (Neat) 3363 cm^{-1} . ^1H NMR (270 MHz, CDCl_3) δ (ppm) = 0.87 (d, $J = 6.9\text{ Hz}$, 3H), 0.97 (d, $J = 6.9\text{ Hz}$, 3H), 1.92-2.10 (m, 1H), 2.72 (s, 3H), 2.89 (bs, 1H), 4.45 (d, $J = 5.9\text{ Hz}$, 1H), 8.53 (s, 2H). HRMS m/z for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}$, calcd 166.1107, found 166.1109.

2-Ethylpyrimidine-5-carbaldehyde was prepared by the literature procedures¹⁴ using ethylamidine hydrochloride. FT-IR (Neat) 1709 cm^{-1} . ^1H NMR (270 MHz, CDCl_3) δ (ppm) = 1.41 (t, $J = 7.6\text{ Hz}$, 3H), 3.11 (q, $J = 7.6\text{ Hz}$, 2H), 9.11 (s, 2H), 10.13 (s, 1H). HRMS m/z for $\text{C}_7\text{H}_8\text{N}_2\text{O}$, calcd 136.0637, found 136.0635.

(*S*)-1-(2-Ethyl-5-pyrimidyl)-1-propanol (88.5% ee) Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel OD-H). Eluent: 2% 2-propanol in hexane; flow rate: 1.0 ml/min; 254 nm UV detector; retention time 11.5 min for *R* isomer and 13.0 min for *S* isomer. $[\alpha]_D^{25}$ -37.7° (*c* 1.15, MeOH).

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FT-IR (Neat) 3311 cm^{-1} . ^1H NMR (270 MHz, CDCl_3) δ (ppm) = 0.97 (t, $J = 7.4$ Hz, 3H), 1.36 (t, $J = 7.6$ Hz, 3H), 1.82 (m, 2H), 2.45 (bs, 1H), 2.99 (q, $J = 7.6$ Hz, 3H), 4.67 (t, $J = 6.3$ Hz, 1H), 8.64 (s, 2H). HRMS m/z for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}$, calcd 166.1107, found 166.1112.

Plot of yield against reaction time in the automultiplication reaction using (*S*)-**2a** with 92.6% ee as a chiral catalyst is shown in Fig. 2 (see also ref. 12). The reaction rate is obviously accelerated during the initial 2.5 hours, which suggests that the present reaction is autocatalytic during the period.

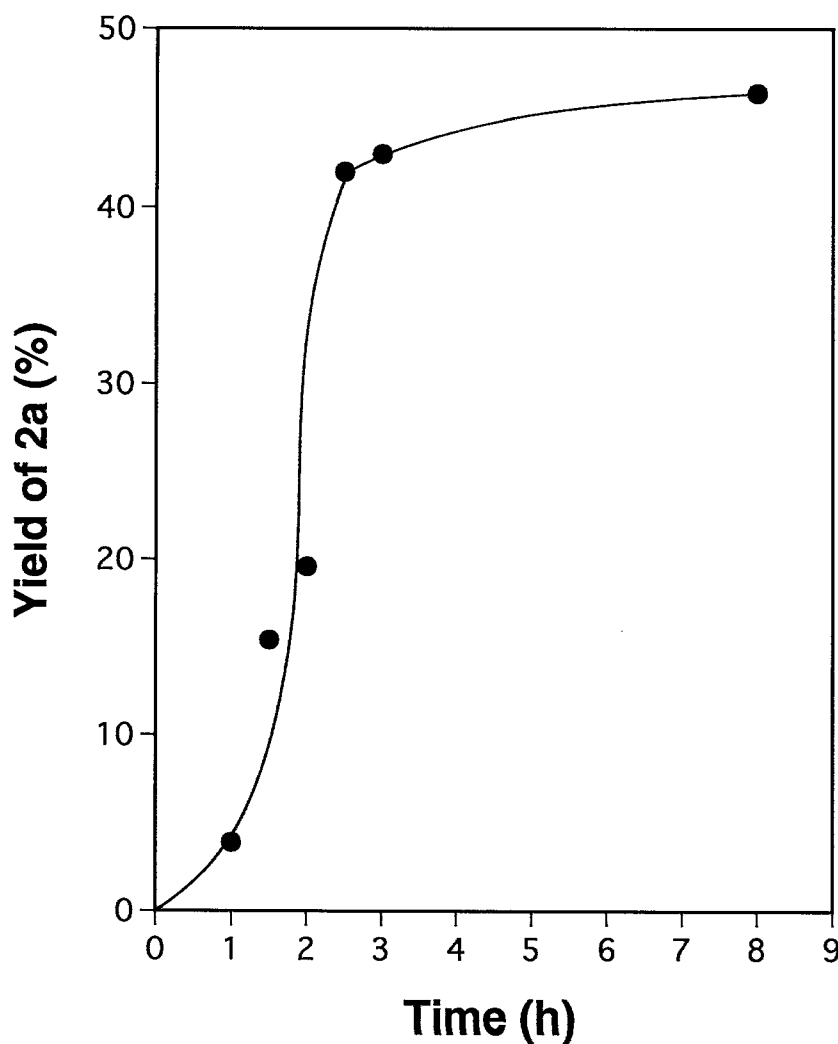


Fig. 2. Relationship between the reaction time and the yield of **2a**.