Electronic Supplementary Information (ESI):

Typical procedure for asymmetric autocatalysis initiated by γ-glycine (Table 1, entry 1):

An enantiomorphic crystal of γ-glycine (right-handed, space group: $P3_1$, CD(+)215_{KBr}, 37.5 mg, 0.5 mmol) was ground into a fine powder together with pyrimidine-5-carbaldehyde **1** (9.4 mg, 0.05 mmol) using a pestle and mortar. After drying under reduced pressure, 1 M toluene solution of *i*-Pr_2Zn (0.4 mL, 0.4 mmol) was slowly added dropwise over a period of 2 h at 0 °C. After the mixture was stirred for 12 h and following addition of toluene (1 mL), 1M toluene solution of *i*-Pr_2Zn (0.3 mL, 0.3 mmol) and aldehyde 1 (18.8 mg, 0.1 mmol) dissolved in toluene (0.5 mL) were then added dropwise over a period of 2 h at 0 °C. The reaction was quenched with a mixture of 30% aqueous ammonia and a saturated aqueous ammonium chloride (2/1, *v*/*v*) solution (5 mL). The mixture was extracted three times using ethyl acetate. 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 = 2/1, *v*/*v*) gave (*R*)-5-pyrimidyl alkanol **2** with 68% ee in 73% yield. 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, 254 nm UV detector, retention time 10.2 min for (*S*)-**2**, 13.6 min for (*R*)-**2**).

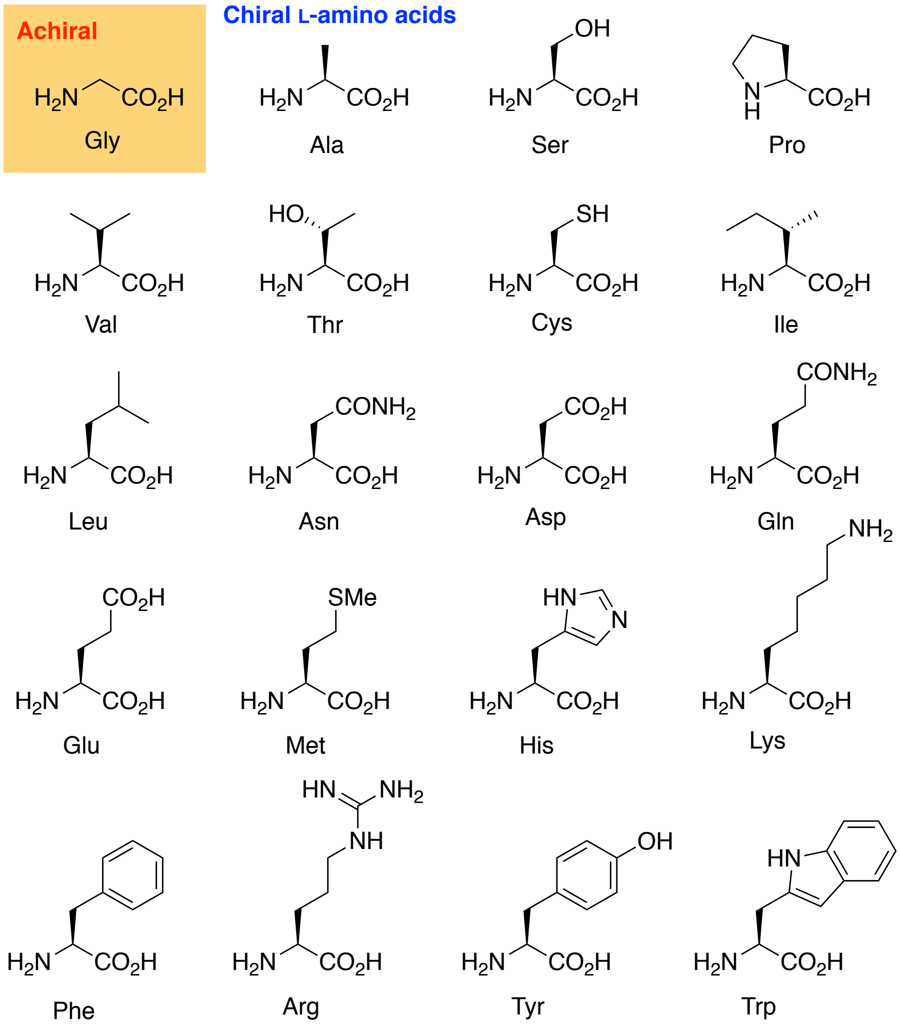

Fig. S1. The chemical structures of 20 natural amino acids. Only glycine is achiral and the rest of 19 are L-configuration.

Single-crystallization of γ-glycine: Glycine (6.0 g) was dissolved in 28-30% aqueous ammonia (20 mL) by stirring for 5 h at room temperature. After the filtration, the filtrate was concentrated under an ambient atmosphere to form the single-crystal of γ-glycine (Figure S2).

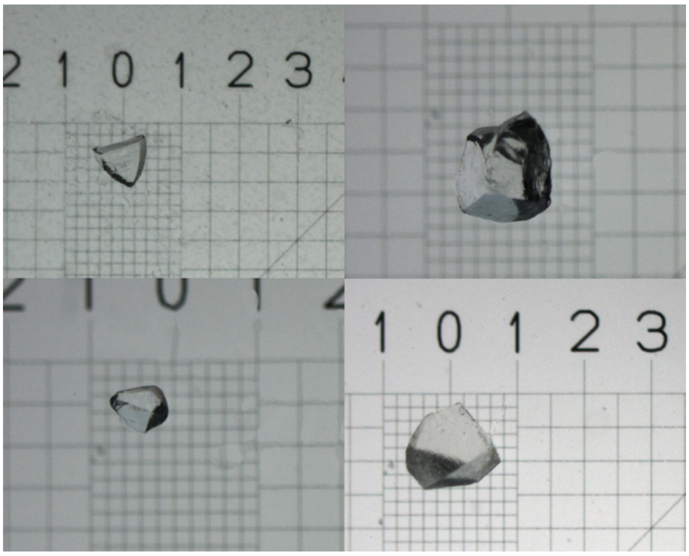

Fig. S2. Photos of single-crystals of γ-glycine.

Table S1. Single-crystal X-ray structure analysis of γ-glycine.

Entry	Flack parameter	Parsons Z	Hooft Y	R1	wR	Space group	CD[a]
1	–0.2 (2)	–0.24 (14)	–0.29 (13)	3.41	9.27	$P3_1$	(+)
2	–0.08 (15)	–0.37 (8)	–0.01 (12)	2.81	8.22	$P3_1$	(+)
3	–0.12 (19)	–0.16 (8)	–0.18 (10)	2.78	7.58	$P3_1$	(+)
4	0.11 (12)	0.07 (11)	0.07 (10)	3.34	8.05	$P3_1$	(+)
5	–0.1 (3)	0.03 (11)	–0.02 (16)	4.03	10.37	$P3_1$	(+)
6	0.27 (16)	0.22 (9)	0.23 (12)	3.64	8.74	$P3_1$	(+)
7	0.04 (19)	–0.56 (14)	0.10 (18)	4.84	12.08	$P3_1$	(+)
8	–0.5 (3)	0.35 (7)	–0.3 (2)	3.17	8.11	$P3_2$	(–)
9	0.15 (19)	0.02 (10)	0.09 (11)	2.88	7.52	$P3_2$	(–)
10	–0.08 (15)	–0.02 (10)	0.00 (10)	3.02	7.78	$P3_2$	(–)

[a] Observed sigh of Cotton effect in solid-state CD with KBr disk at 215 nm.

Preparation of KBr pellet: After determination of absolute structure of γ-glycine by X-ray single-crystal analysis, the single crystal itself (0.1 mg) was ground in fine powder together with KBr (27 mg). The pellet for solid-state CD was prepared from this powderd mixture.

Formation of enantioenriched powder-like crystals of γ-glycine: Glycine (6.0 g) was dissolved in 28-30% aqueous ammonia (20 mL) by stirring for 5 h at room temperature. After the filtration and addition of seed crystal whose absolute structure was determined by X-ray analysis, the mixture was vigorously stirred with glass beads under ambient atmosphere for 6 d to form the powder-like crystal of γ-glycine.

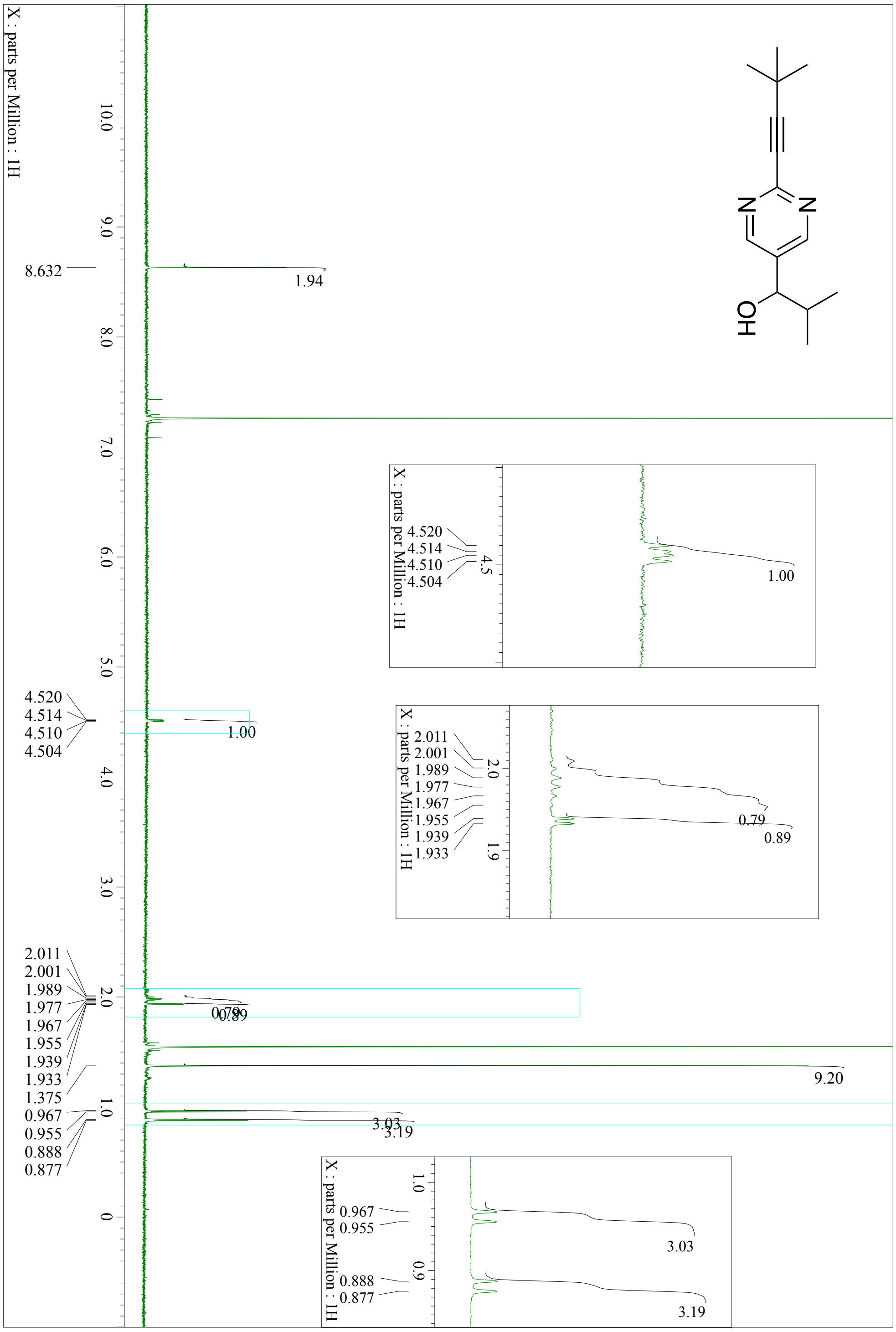

Fig. S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 7.26 ppm for residual $CHCl_3$) of 5-pyrimidyl alkanol **2**: δ 0.883 ppm (d, J = 6.6 Hz, 3H), 0.961 (d, J = 6.6, 3H), 1.375 (s, 9H), 1.36 (d, J = 3.0, 1H), 1.99 (m, 1H), 4.51 (dd, J = 3.0, 5.0, 1H), 8.63 (s, 2H).

See also the following reference: T. Shibata, S. Yonekubo, K. Soai *Angew. Chem. Int. Ed.* **1999**, *38*, 659-661.