

Preparation of single-crystals of triglycine sulfate (TGS: $(\text{NH}_2\text{CH}_2\text{CO}_2\text{H})_3\cdot\text{H}_2\text{SO}_4$)

To a suspension of glycine (0.72 mol, 54 g) in distilled water (230 mL), conc. sulfuric acid (13 mL) was added dropwise. After complete dissolution of glycine by heating of the mixture at 60 °C, the resulting solution was slowly concentrated in Petri dishes at room temperature. After several days, single crystals of TGS (size: 1-2 cm) could be obtained. Picking one well-shaped crystal and placing it as a seed in a newly prepared solution of glycine and sulfuric acid, TGS grew to a diameter of 4-5 cm in several days.

Application of an electric field to a TGS crystal

A TGS crystal was sliced to ca 7–8 mm thickness perpendicular to the *b*-axis to give {010} surfaces. The surface was polished to almost flat with emery paper. The sliced crystal with a thickness of ca 6 mm was placed in a 1 kV applied electric field (0.17 kV/mm) by attaching conductive Cu tape to the {010} faces. The electric field was maintained for 2–3 day, during which the crystal was heated on a hot plate warmed to ca 60 °C (Curie temperature of the TGS: ca. 49 °C) and gradually cooled (1 °C/hour) to room temperature under the application of the electric field.

Asymmetric autocatalysis triggered by a chiral TGS crystal (Table 1, run 1)

A mixture of *M*-TGS (0.88g) and aldehyde **1** (4.7 mg, 0.025 mmol) was ground with a mortar and pestle to a fine powder. To this powder, toluene (0.06 mL) and 1 M *i*-Pr₂Zn solution (0.15 mmol, 0.15 mL) was added dropwise over a period of 2 h at –10 °C. To the mixture, a 1 M solution of *i*-Pr₂Zn (0.15 mmol, 0.15 mL) was added dropwise over 2 h at –10 °C, then the mixture was stirred overnight at 0 °C. After the addition of toluene (0.75 mL) and 1 M solution of *i*-Pr₂Zn (0.3 mmol, 0.3 mL), aldehyde **1** (0.1 mmol, 18.8 mg) in toluene (0.75 mL) was added at 0 °C dropwise over a period of 1 h. After stirring for an additional 2 h at 0 °C, the reaction was quenched with a 2:1 (v/v) mixture of saturated aqueous ammonium chloride (NH₄Cl) and saturated aqueous ammonia (NH₃), then the mixture was extracted with EtOAc. Purification by column chromatography (SiO₂; eluent: hexane/EtOAc = 2:1 (v/v)) gave (*S*)-pyrimidyl alkanol **2** with 65% ee (21.1 mg) in 73% yield. The absolute configuration and ee of **2** were analyzed using HPLC on a chiral stationary phase (column: Chiralpak IB, 4.6 mm × 250 mm, eluent: 5% isopropyl alcohol in hexane, 1 mL/min; retention time: 8.2 min for (*S*)-**2**, and 10.8 min for (*R*)-**2**).

Fig. S1 Ortep drawing of (*M*)-triglycine sulfate (CCDC 1993618). Ellipsoids were drawn in 50% probability. Colorless block ($0.44 \times 0.39 \times 0.34 \text{ mm}^3$), monoclinic space group $P2_1$, $a = 9.4396 \text{ \AA}$, $b = 12.6268 \text{ \AA}$, $c = 5.6979 \text{ \AA}$, $\beta = 110.395^\circ$, $V = 636.57 \text{ \AA}^3$, $Z = 2$, $\lambda (\text{MoK}\alpha) = 0.71075 \text{ \AA}$, $\rho = 1.687 \text{ g/cm}^3$, $\mu (\text{MoK}\alpha) = 3.13 \text{ cm}^{-1}$, 11091 reflections measured ($T = 100 \text{ K}$, $2.314^\circ < \theta < 32.234^\circ$), numbers of independent data collected, 4334, numbers of independent data used for refinement, 4143, $R1 = 0.0295 (I > 2\sigma(I))$, $R = 0.0319$, $wR2 = 0.0770$, and $\text{GOF} = 1.052$, absolute Flack parameter = 0.04(6).

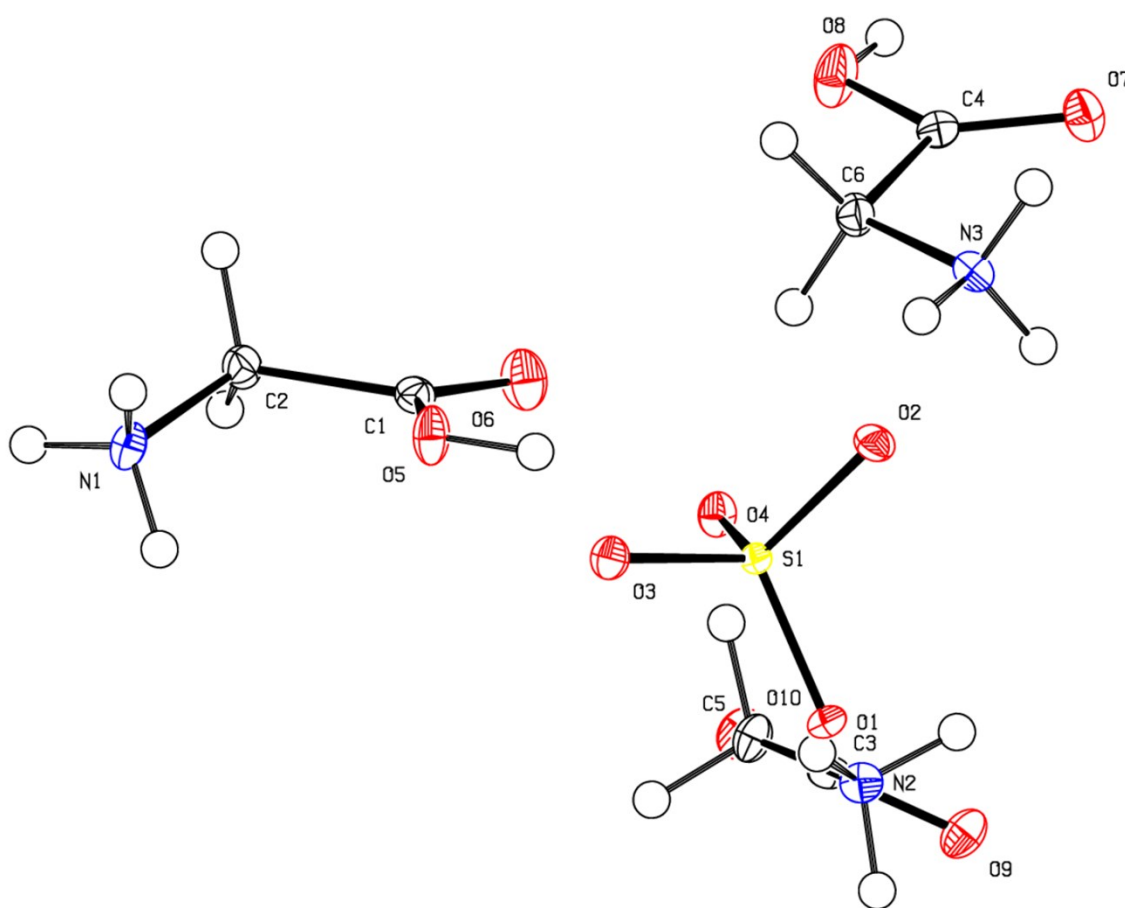


Fig. S2 Ortep drawing of (*P*)-triglycine sulfate (CCDC 1993609). Ellipsoids were drawn in 50% probability. Colorless block ($0.49 \times 0.40 \times 0.16 \text{ mm}^3$), monoclinic space group $P2_1$, $a = 9.4482 \text{ \AA}$, $b = 12.6347 \text{ \AA}$, $c = 5.7085 \text{ \AA}$, $\beta = 110.407^\circ$, $V = 638.68 \text{ \AA}^3$, $Z = 2$, $\lambda (\text{MoK}\alpha) = 0.71075 \text{ \AA}$, $\rho = 1.689 \text{ g/cm}^3$, $\mu (\text{MoK}\alpha) = 3.1 \text{ cm}^{-1}$, 11132 reflections measured ($T = 100 \text{ K}$, $3.225^\circ < \theta < 32.242^\circ$), numbers of independent data collected, 4269, numbers of independent data used for refinement, 4123, $R_1 = 0.0243$ ($I > 2\sigma(I)$), $R = 0.0260$, $wR_2 = 0.0656$, and GOF = 1.055, absolute Flack parameter = 0.06(6).

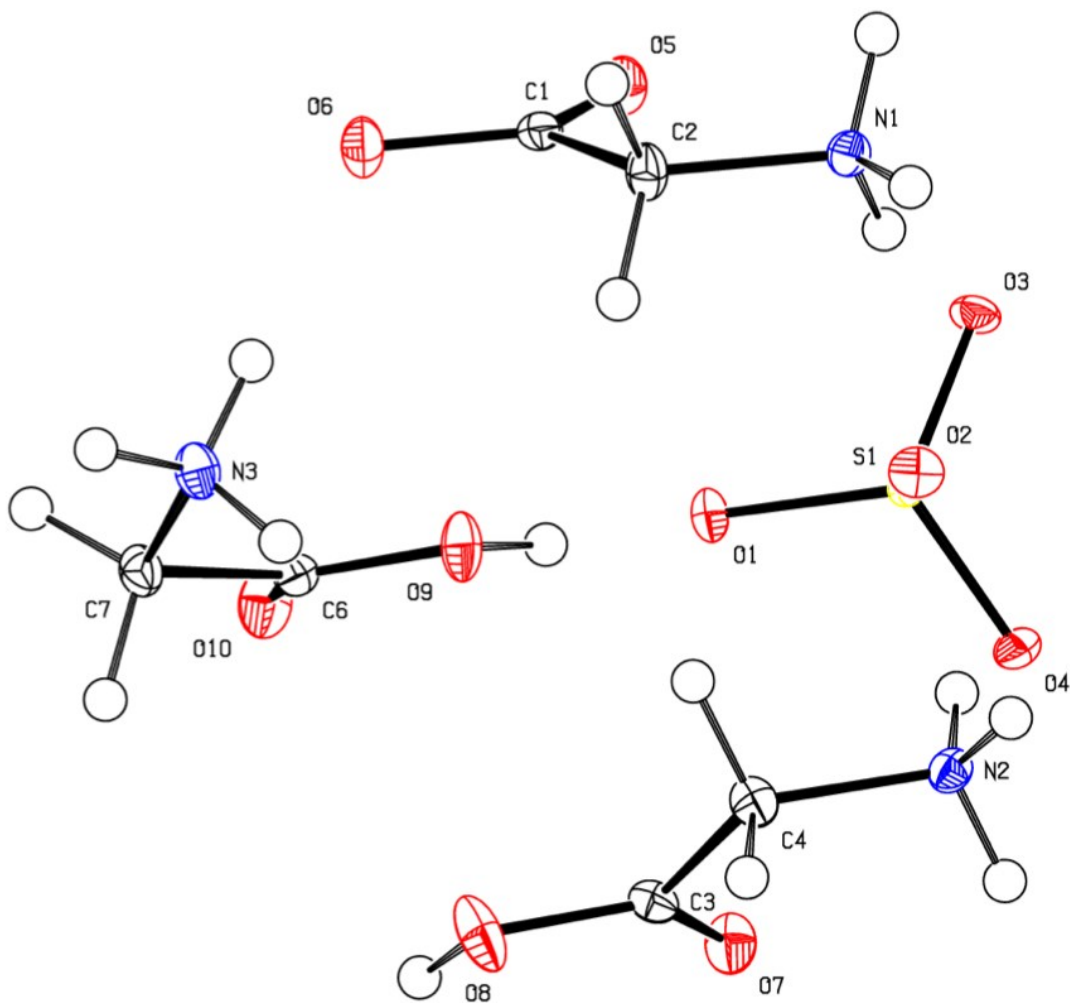


Fig. S3 Powdered TGS (particle size, 1–20 μm).

