Electronic Supplementary Information (ESI) for:

Asymmetric autocatalysis initiated by achiral nucleic acid base adeninde:
Implications on the origin of homochirality of biomolecules

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1. Stirred crystallization of adeninium dinitrate **1**

Adenine (2 g) was dissolved in 4.6 M aqueous nitric acid (140 mL) at 45 °C. The temperature was gradually lowered at room temperature with stirring. The crystals were filtered and precipitate was dried in vacuo to give the powder-like crystal of 1.

2. Single crystallization of adeninium dinitrate **1**

Adenine (0.7 g) was dissolved in 4.6 M aqueous nitric acid (140 mL) at 45 °C. The single crystals of 1 were appeared, after the slow evaporation of the solvent at room temperature under ambient pressure.

3. The X-ray powder diffraction patterns of powder-like crystal **1**

The data were collected on a Rigaku Rint 2500 X-ray diffractometer with Cu Kα radiation.

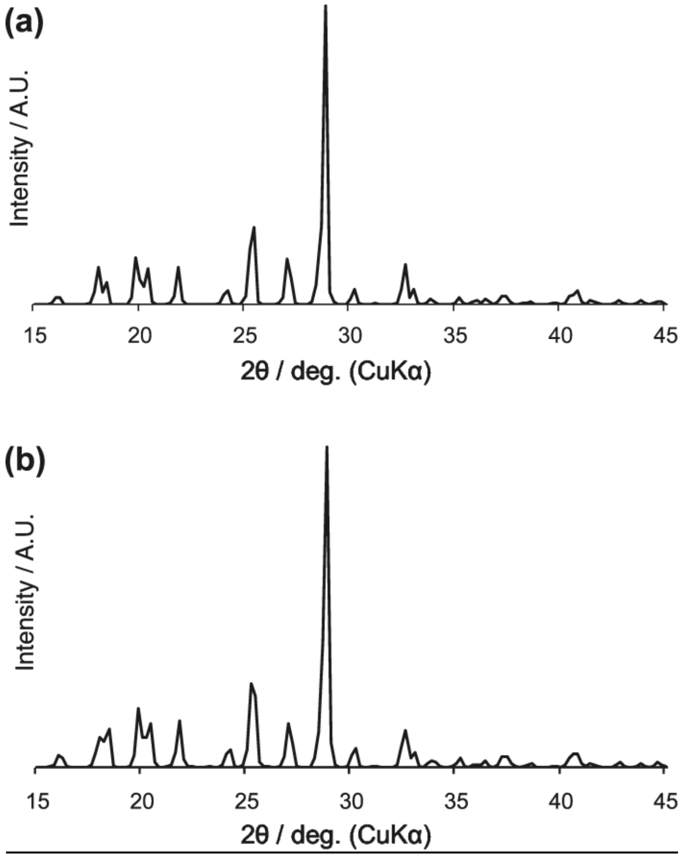

Fig. S1. (a) Simulated pattern from single crystal data. (b) Powder-like crystal **1** obtained from stirred crystallization (observed pattern).

4. Typical experimental procedure for asymmetric autocatalysis (Table 1, entry 2)

A crystal of adeninium dinitrate **1** was ground into a fine powder using an agate pestle and mortar. Toluene solution of *i*-Pr_2Zn (0.08 mL, 0.08 mmol) was added dropwise at 0 °C with stirring to a mixture of finely powdered crystal of [CD(+)250_{Nujol}]-**1** (19.6 mg, 0.075 mmol) and aldehyde **2** (4.7 mg, 0.025 mmol). After stirring overnight at 0 °C, toluene (0.75 mL) was added to the mixture, and then toluene solution of *i*-Pr_2Zn (0.3 mL, 0.3 mmol) was added dropwise over a period of 1 h. Then, toluene (0.75 mL) solution of aldehyde **2** (18.8 mg, 0.1 mmol) was slowly added dropwise over a period of 1.5 h. After stirring for 3 h at 0 °C, toluene (5.0 mL) and toluene solution of *i*-Pr_2Zn (0.8 mL, 0.8 mmol) were added successively. Then, toluene (2.0 mL) solution of **2** (75.3 mg, 0.4 mmol) was added dropwise over a period of 1.5 h and the mixture was stirred for 1 h at 0 °C. Once again, toluene (14.0 mL) and toluene solution of *i*-Pr_2Zn (1.6 mL, 1.6 mmol) were added, and toluene (4.0 mL) solution of **2** (150.6 mg, 0.8 mmol) was added dropwise over a period of 1.5 h. After the mixture was stirred for 1 h at 0 °C, the reaction was quenched using a mixture of 30% aqueous ammonia and a saturated aqueous ammonium chloride (2/1, *v*/*v*) solution (10 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 = 3/1, *v*/*v*) gave (*R*)-5-pyrimidyl alkanol **3** with 88.7% ee in 89.4% 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 11.4 min for (*S*)-**3**, 15.6 min for (*R*)-**3**).