Electronic Supplementary Information (ESI):

Preparation of single crystal of pyrimidine-5-carbaldehyde 1:
Pyrimidine-5-carbaldehyde **1** *ca*. 10 mg was dissolved in 1 mL of acetone in sample tube. Vapor diffusion method with hexane under room temperature afforded single crystal of carbaldehyde **1** with enough quality for single crystal X-ray structural analysis and X-ray diffraction analysis.

Solid–vapor phase absolute asymmetric synthesis of 5-pyrimidyl alkanol 2:
Pyrimidine-5-carbaldehyde **1** was sublimed at 100 °C under vacuum. Sublimed powder crystals of the carbaldehyde **1** (1.5 mg) were placed in slender glass tubes (30 mm × 4 mm ID). These slender tubes were placed into larger glass tubes (40 mm × 11 mm ID), which were then placed in a desiccator (93 mm × 85 mm ID) filled with argon gas. One experimental set comprised 10 or 11 samples of carbaldehyde **1**. A 1 M solution of *i*-Pr_2Zn in toluene (3 mL) was placed in a reaction vessel (15 mm × 33 mm ID) in the desiccator. Pyrimidine-5-carbaldehyde **1** was exposed to *i*-Pr_2Zn vapor for 16 h at room temperature. The reaction was quenched with 1 M hydrochloric acid. The reaction mixture was dissolved in ethyl acetate and water, then extracted with ethyl acetate. The organic layer was passed through silica gel NH_2 using ethyl acetate as eluent. The molar ratio of carbaldehyde **1** and alkanol **2** was determined using gas chromatography (GC) (Phenomenex Zebron ZB-5HT, 30 m × 0.25 mm ID × 0.25 μm; T = 150 °C until 300 °C, with an increment of 20 °C/min; N_2 flow rate 1.0 mL/min; retention time 3.7 min for **1** and 5.6 min for **2**). Calibration revealed that the molar ratio of **1** and **2** was essentially the same as the ratio of peak areas of **1** and **2** determined by GC. The absolute configurations and ee of pyrimidyl alkanol **2** were determined using supercritical fluid chromatography (SFC) on a chiral stationary phase (Daicel Chiralpak IB column, 250 × 4.6 mm ID; eluent 9% methanol in CO_2 (*v*/*v*); flow rate 3.3 mL/min; 254 nm UV detector; retention time 1.8 min for (*S*)-**2** and 2.1 min for (*R*)-**2**).

Table S1. Absolute asymmetric synthesis of pyrimidyl alkanol **2** from powder crystals of pyrimidine-5-carbaldehyde **1** and vapor of diisopropylzinc in conjunction with asymmetric autocatalysis.

Run[a]	Molar ratio of **1** : **2**[b]	Alkanol **2**[c]	
		ee [%]	Config.
C23	47 : 53	5.0	*S*
C24	55 : 45	7.8	*R*
C25	56 : 44	2.0	*R*
C26	55 : 45	9.0	*S*
C27	54 : 46	0.8	*R*
C28	62 : 38	4.5	*R*
C29	70 : 30	6.3	*S*
C30	55 : 45	0.2	*(S)*
C31	61 : 39	4.4	*S*
C32	49 : 51	7.1	*S*
C33	71 : 29	24.1	*R*
D34	39 : 61	2.2	*S*
D35	62 : 38	13.4	*S*
D36	50 : 50	5.0	*R*
D37	39 : 61	3.3	*R*
D38	38 : 62	2.6	*R*
D39	36 : 64	3.3	*R*
D40	33 : 67	5.7	*R*
D41	17 : 83	14.4	*S*
D42	16 : 84	4.9	*R*
D43	8 : 92	1.7	*S*
D44	19 : 81	3.2	*S*
E45	78 : 22	5.6	*S*
E46	13 : 87	9.5	*R*
E47	66 : 34	1.2	*R*
E48	56 : 44	0.5	*S*
E49	70 : 30	5.8	*S*
E50	43 : 57	0.1	*(S)*
E51	55 : 45	0.7	*R*
E52	43 : 57	1.9	*S*
E53	48 : 52	1.6	*S*

E54	31 : 69	7.0	*S*
E55	65 : 35	3.2	*R*
F56	84 : 16	2.6	*R*
F57	77 : 23	0.1	*(S)*
F58	86 : 14	2.6	*R*
F59	80 : 20	1.6	*R*
F60	83 : 17	3.9	*R*
F61	79 : 21	3.3	*S*
F62	78 : 22	2.3	*R*
F63	88 : 12	2.8	*S*
F64	80 : 20	7.6	*S*
F65	79 : 21	1.1	*R*
F66	67 : 33	0.5	*R*
G67	48 : 52	4.4	*R*
G68	61 : 39	4.9	*R*
G69	44 : 56	9.5	*R*
G70	50 : 50	2.7	*R*
G71	41 : 59	2.1	*S*
G72	24 : 76	1.4	*S*
G73	48 : 52	1.9	*S*
G74	54 : 46	9.0	*R*
G75	15 : 85	1.5	*S*
G76	48 : 52	3.0	*S*
G77	63 : 37	10.1	*S*
H78	71 : 29	2.6	*S*
H79	74 : 26	5.1	*R*
H80	72 : 28	6.9	*S*
H81	79 : 21	3.4	*R*
H82	89 : 11	12.6[d]	*R*
H83	67 : 33	5.2	*R*
H84	88 : 12	4.6	*S*
H85	67 : 33	6.0	*S*
H86	69 : 31	0.7	*S*
H87	57 : 43	0.2	*(S)*
H88	48 : 52	5.7	*S*
I89	93 : 7	2.2	*S*

I90	88 : 12	3.0	*S*
I91	86 : 14	0.5	*S*
I92	84 : 16	1.1	*R*
I93	94 : 6	4.0	*R*
I94	88 : 12	0.3	*(S)*
I95	81 : 19	0.7	*S*
I96	88 : 12	1.4	*S*
I97	92 : 8	1.2	*R*
I98	85 : 15	1.4	*R*
J99	87 : 13	0.3	*(R)*
J100	88 : 12	0.5	*R*
J101	91 : 9	0.1	*(R)*
J102	89 : 11	3.1	*R*
J103	86 : 14	1.2	*R*
J104	83 : 17	2.3	*R*
J105	92 : 8	0.2	*(S)*
J106	91 : 9	5.0	*S*
J107	89 : 11	2.6	*R*
J108	87 : 13	4.4	*S*
K109	86 : 14	3.4	*S*
K110	75 : 25	1.2	*S*
K111	83 : 17	3.7	*R*
K112	89 : 11	1.2	*R*
K113	78 : 22	1.5	*R*
K114	83 : 17	0.2	*(R)*
K115	80 : 20	0.1	*(R)*
K116	78 : 22	0.9	*S*
K117	72 : 28	2.3	*R*
K118	71 : 29	4.9	*S*
L119	81 : 19	6.1	*S*
L120	90 : 10	4.7	*S*
L121	88 : 12	2.8	*S*
L122	73 : 27	1.8	*R*
L123	93 : 7	6.0	*S*
L124	88 : 12	4.1	*R*
L125	84 : 16	3.4	*R*

L126	85 : 15	5.2	*R*
L127	83 : 17	3.6	*R*
L128	88 : 12	2.8	*R*
L129	91 : 9	27.2	*S*

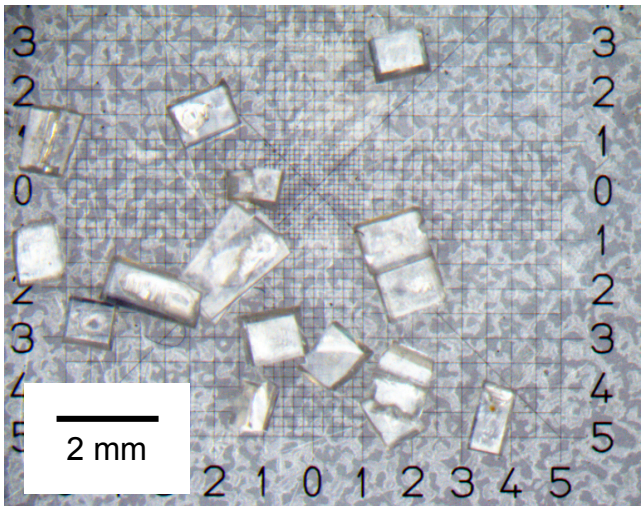
[a] In the series A–L, each set of reactions was run simultaneously in the same desiccator. Each glass tube was used in only one reaction.

[b] Determined using GC.

[c] Determined using supercritical fluid chromatography (SFC) analysis on a chiral stationary phase.

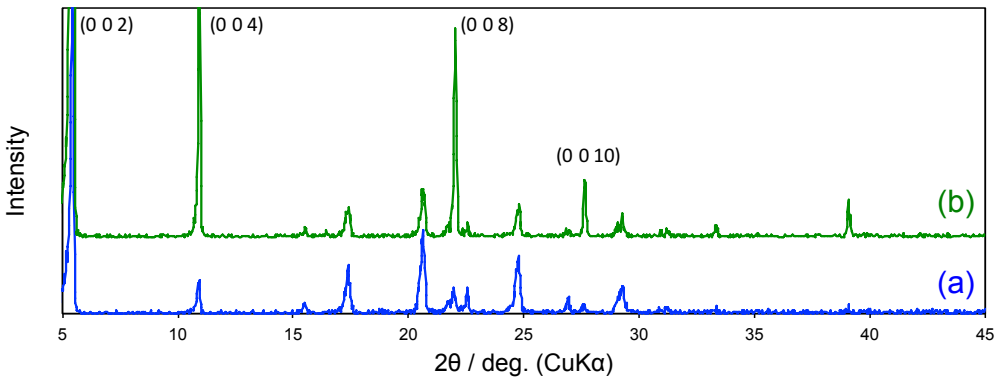
[d] Chiral SFC chromatogram was shown in Fig. 3S.

Fig. S1. Single crystal of pyrimidine-5-carbaldehyde **1**.



Powder X-ray diffractometry (XRD) of crystals of pyrimidine-5-carbaldehyde 1: It can be seen that the diffraction peaks at 5.5°, 10.9°, 22.0°, 27.6°, 33.3°, and 39.1° correspond to (0 0 2), (0 0 4), (0 0 8), (0 0 10), (0 0 12), and (0 0 14) crystal planes respectively.

Fig. S2. X-ray powder diffraction patterns. (a) Single crystal of pyrimidine-5-carbaldehyde **1** ($P2_1/n$: observed pattern). (b) Sublimated powder crystal of carbaldehyde **1** (observed pattern).



Chi-squared test: Chi-squared test for goodness of fit (χ_{GF}^2) and Chi-squared test for independence (χ_I^2) were shown in Tables S2 and S3, respectively. The results affording alkanol **2** with <0.5% ee were excluded.

Table S2. Chi-squared test for goodness of fit (χ_{GF}^2).

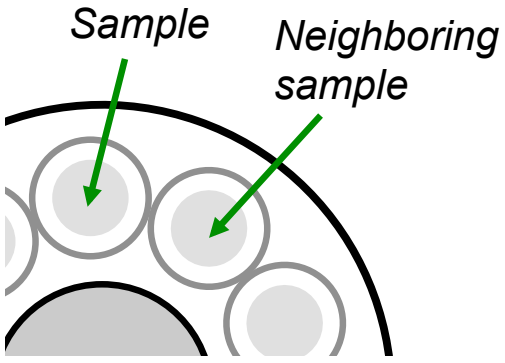
	Pyrimidyl alkanol **2**[a]		Total
	R	*S*	
Observed frequency $\mathbf{O_i}$	61	58	119
Theoretical probability	0.5	0.5	1
Theoretical frequency $\mathbf{E_i}$	59.5	59.5	119

$$\chi_{GF}{}^2 = \sum_{i=1}^{k} \frac{(O_i - E_i)^2}{E_i} = 0.07563$$

(Significant probability: p = 0.78)

Table S3. Chi-squared test for independence (χ_I^2).

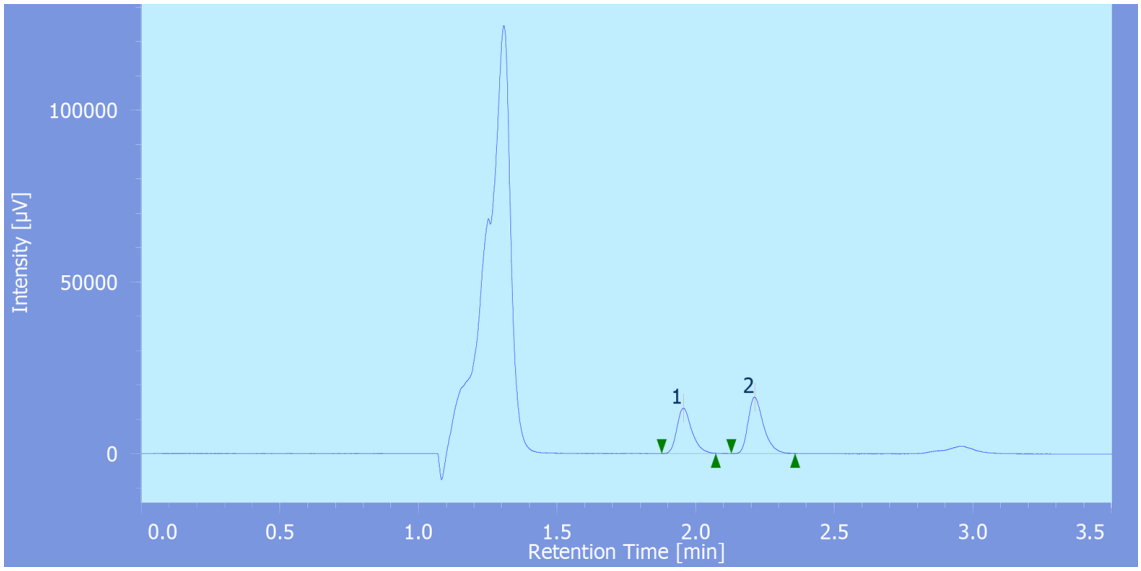
		Neighboring sample		Total
		R	*S*	
Sample	*R*	32	29	61
	S	29	29	58
	Total	61	58	119



$$\chi_I{}^2 = \sum_i \sum_j \frac{\left(f_{ij} - \frac{f_{i.}f_{.j}}{n}\right)^2}{\frac{f_{i.}f_{.j}}{n}} = 0.07196$$

(Significant probability: p = 0.79)

Fig. S3. Chiral SFC chromatogram of the reaction mixture (Table S1, run H82). The reaction mixture was analyzed after working up. SFC conditions: column, Daicel Chiralpak IB (250 × 4.6 mm ID); eluent, 9% methanol in CO_2 (*v*/*v*); flow rate, 3.3 mL/min; detection, 254 nm UV detector; retention time (t_R) 1.96 min for (*S*)-alkanol **2** and 2.21 min for (*R*)-alkanol **2**). The areas of 43.687% for (*S*)-**2** and 56.313% for (*R*)-**2**, thus, analysed product is *R*-configured alkanol **2** with 12.6% ee.



Peak #	Alkanol	t_R (min)	area (µV·sec)	area (%)	height (µV)	height (%)
1	(*S*)-**2**	1.955	49232	43.687	13192	44.543
2	(*R*)-**2**	2.213	63460	56.313	16425	55.313