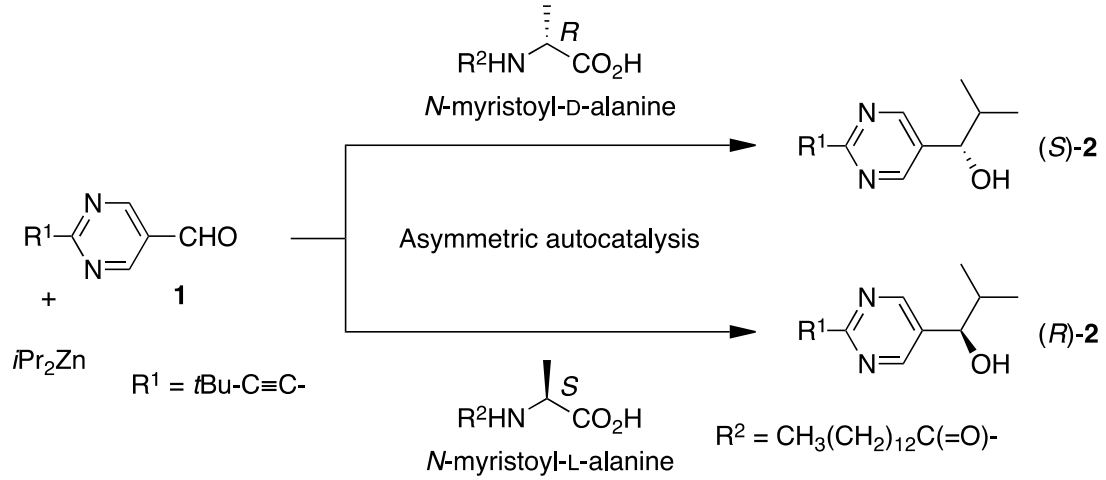
1. Asymmetric autocatalysis initiated with *N*-myristoyl alanine.

The direction of asymmetric induction has been examined employing *N*-myristoyl alanine[1] as a chiral initiator of asymmetric autocatalysis (Table S1). As a result of asymmetric autocatalysis, *N*-myristoyl-D-alanine induced the formation of (*S*)-pyrimidyl alkanol **2** with a high ee value, and *N*-myristoyl-L-alanine promoted the production of enantiomerically enriched (*R*)-alkanol **2**, respectively.

Table S1. Asymmetric autocatalysis initiated with *N*-myristoyl alanine.[a]



Entry	Config. of *N*-myristoyl alanine	5-Pyrimidyl alkanol **2**		
		Yield (%)[b]	ee (%)[c]	Config.
1	D	87	94	*S*
2	L	91	93	*R*
3	D	93	93	*S*
4	L	86	90	*R*

[a] The aldehyde 1 and diisopropylzinc were added in three separate portions in the presence of *N*-myristoyl alanine. [b] Isolated yield. [c] The ee was determined using HPLC employing a chiral stationary phase.

[S1] Asymmetric autocatalysis induced by chiral amino acids: a) T. Shibata, J. Yamamoto, N. Matsumoto, S. Yonekubo, S. Osanai, K. Soai, *J. Am. Chem. Soc.* **1998**, *120*, 12157–12158; b) I. Sato, Y. Ohgo, H. Igarashi, D. Nishiyama, T. Kawasaki, K. Soai, *J. Organomet. Chem*. **2007**, *692*, 1783–1787.

2. Determination of ee of chiral mesoporous silica.

The enrichment of the handedness of chiral mesoporous silica (Sample A, B, C, D and E) were determined from the SEM images. Determination of the ee of Sample C was shown in Figure S1.

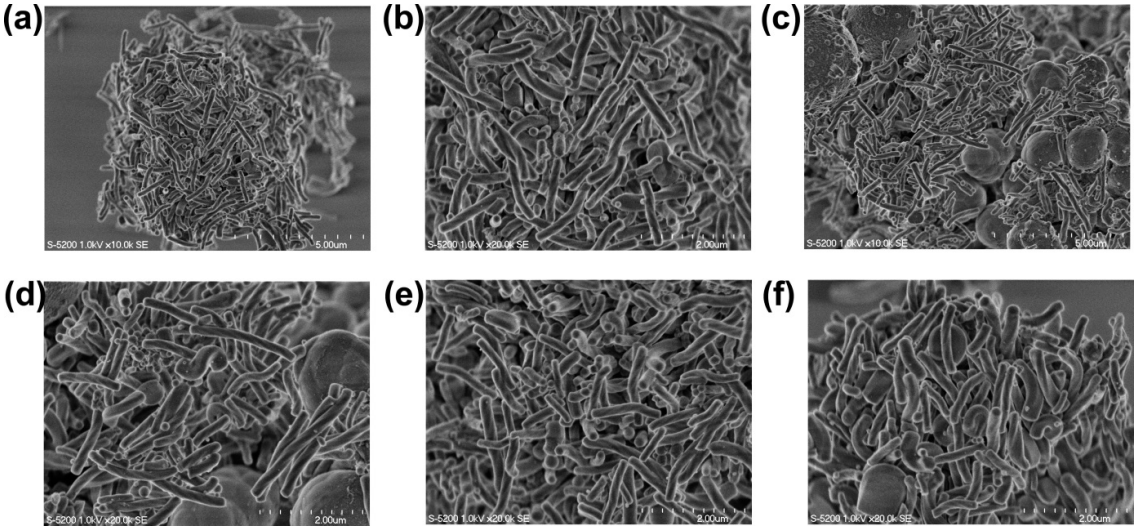


Figure S1. SEM images of right-handed enriched (*P*)-helical mesoporous silica (Sample C) used as chiral initiators of asymmetric autocatalysis shown in Table 1, Entries 7 and 8. The numbers of (*P*)- and (*M*)-helical silica in each images are (a) (*P*) : (*M*) = 36 : 21, (b) 44 : 25, (c) 65 : 22, (d) 30 : 18, (e) 47 : 18, (f) 46 : 14. Therefore, the ee of Sample C was calculated to be 39% ee (*P*) from the total numbers of 268 (*P*)- and 118 (*M*)-mesoporous silica.