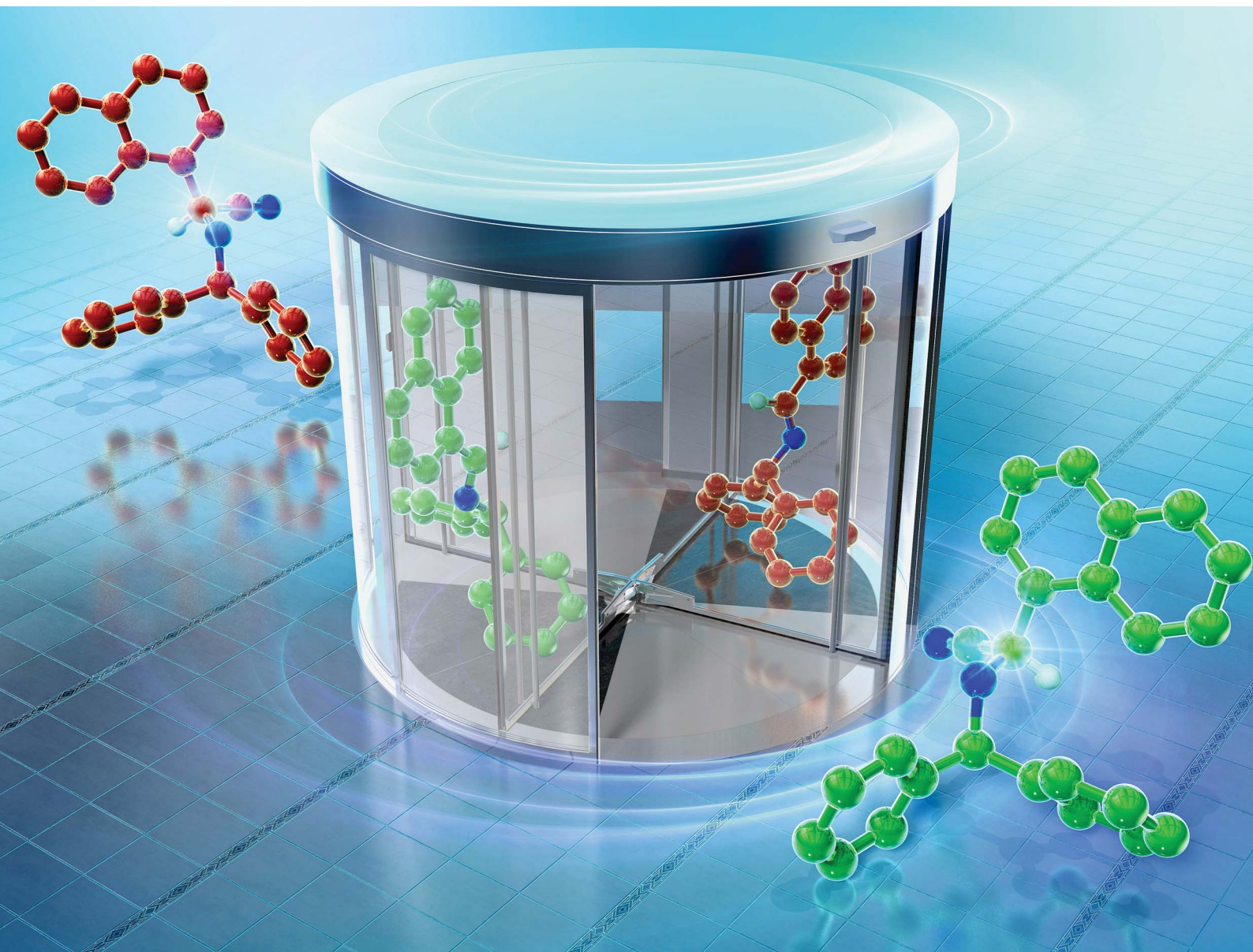


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# Chirally and chemically reversible Strecker reaction†

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In the pursuit of a credible mechanism for the abiotic synthesis of  $\alpha$ -amino acids, solid-state asymmetric Strecker/retro-Strecker reactions have been demonstrated. Asymmetric addition of cyanide to enantiomorphic crystals of achiral imines proceeded to produce enantioenriched aminonitriles. Moreover, dehydrocyanation of enantioenriched aminonitriles gave chiral crystals of achiral imines stereoselectively. We found, for the first time to the best of our knowledge, a stereoinversion of the synthetic intermediates imine and aminonitrile in the sequence of reactions including HCN addition and elimination. Thus, the reversible Strecker reaction is expected to be a focus of research on the origin of chirality.

## Introduction

Biological systems are composed of molecules with a specific handedness such as seen in *L*-amino acids and *D*-sugars. Since the discovery of molecular chirality by Pasteur,<sup>1</sup> the origin and amplification of chirality have been long-standing mysteries closely related to the chemical origin of life.<sup>2</sup> Several chiral factors and processes have been proposed and investigated as possible candidates for the origin of chirality,<sup>3</sup> and chiral crystallization of achiral compounds<sup>3b,4</sup> is one of the possibilities. Initiated by the pioneering work of Schmidt *et al.*,<sup>5</sup> stereospecific reactions utilizing a chiral crystal of achiral compounds as a substrate have been demonstrated.<sup>6</sup> Their utilization as heterogeneous chiral triggers for asymmetric autocatalysis, *i.e.*, the Soai reaction,<sup>7</sup> has also been reported.<sup>8</sup> To the best of our knowledge, there are no reports on asymmetric HCN addition using this strategy.

Meanwhile, Strecker synthesis has long been considered to be one of the way that  $\alpha$ -amino acids are abiotically synthesized.<sup>9</sup> Because chiral aminonitrile intermediates<sup>10</sup> hydrolyze to amino acids, asymmetric HCN addition<sup>11</sup> determines the molecular handedness. Thus, research on chirality of the sequence of reactions involving cyanide addition and elimination would be a challenge but might expand our knowledge of biological homochirality as exemplified by  $\alpha$ -amino acids.

We have reported on the spontaneous absolute asymmetric Strecker synthesis based on the spontaneous crystallization of

aminonitriles (Fig. 1).<sup>12a,b</sup> In addition to the total spontaneous resolution of aminonitriles as a result of a three-component Strecker reaction, the enantiopurity of aminonitriles can be improved significantly. Because corresponding amino acids can act as chiral triggers for the amplification of their own chiral intermediate, the process represents the replication of chiral  $\alpha$ -amino acids.<sup>12c,d</sup> The oriented prochirality of imines,<sup>12e</sup> chiral isotopomers<sup>12f</sup> and chiral crystal of the related racemate<sup>12g</sup> can be responsible for the generation and amplification of enantioenriched aminonitriles.

Here, we report on asymmetric addition of HCN to a chiral crystal of achiral imines to afford highly enantioenriched aminonitriles in conjunction with an amplification of chirality

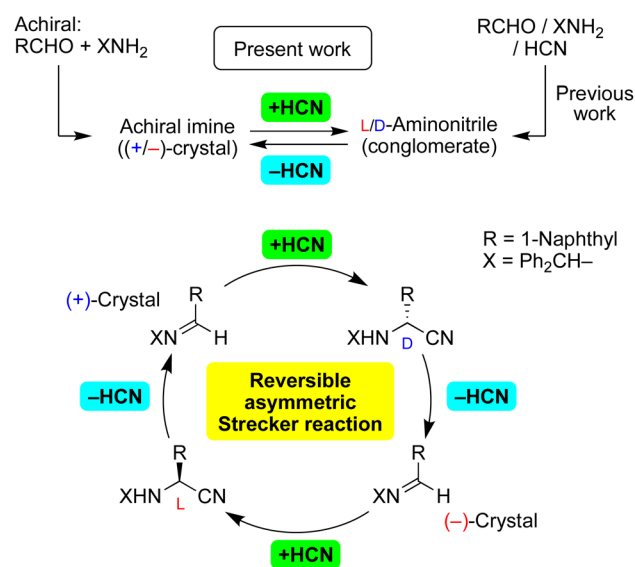


Fig. 1 Concept of the current work.

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(Fig. 1). In the reverse reaction, dehydrocyanation<sup>13</sup> proceeded stereoselectively with the loss of a stereocenter to give the corresponding enantiomorphic crystals of achiral imines. Furthermore, the inversion of the enantiomorphic crystals of an achiral compound was observed for the first time; therefore, the (+)-crystal of the imine was transformed to its enantiomorphic (−)-crystal by carrying out HCN addition and then elimination and *vice versa*. In addition, the sequence of stereoselective reactions without stereoinversion was also investigated using other substrates. Note a requirement of the current methods being chiral crystallization (conglomerate formation) of achiral or racemic compounds, observed in only *ca.* 10% of crystalline compounds.

## Results and discussion

We carried out a chiral crystallization of achiral imine **1** synthesized from 1-naphthaldehyde and benzhydramine (Fig. 2a). The handedness of crystal **1** was determined from solid-state circular dichroism (CD) spectroscopy with a KBr matrix; one crystal showed a positive Cotton effect at a wavelength of 340 nm (CD(+)340<sub>KBr</sub>) and the other showed a negative effect (CD(−)340<sub>KBr</sub>) (Fig. 2b). When the dehydrative condensation of 1-naphthaldehyde and benzhydramine proceeded, enantioenriched powder-like crystal **1** formed spontaneously under stirred conditions<sup>3c,14</sup> (Table S1†). The crystal was determined to belong to the chiral space group *P*<sub>2</sub><sub>1</sub> (Fig. 2c) and the relationship between the absolute configuration of the crystal **1** and its CD was determined (Table S2†).

Because the solid-state CD of **1** was quite reproducible when carefully preparing a fixed and translucent KBr disc, the enantioenrichment of **1** could be characterized from the value of ΔCD at 340 nm. Because the enantiomeric excess (ee) of

suspended solid **1** can be enhanced by vigorously stirring the mixture<sup>3d,15</sup> (Fig. S1†), the maximum ΔCD value of 201 mdeg at 340 nm was considered as that with 100% ee. The linearity between the ΔCD and ee was checked by mixing enantiomorphic crystals at various proportions (Fig. S2†).<sup>16</sup>

The chiral crystal of achiral imine **1** was subjected to an asymmetric HCN addition by exposing the crystal to HCN vapor. Due to dissolution of **1** causing the disappearance of the chirality, HCN and **1** were stored separately in sealed reaction vials (Fig. S3†). We then added DBU, HCN, methanol and toluene to the product of the vapor-phase reaction to prepare a suspension of **2** with an enantiomeric imbalance corresponding to the asymmetric hydrocyanation. Due to the tendency of aminonitrile **2** to form a conglomerate, asymmetric amplification was applied to this suspension as in the previous report (see the figure in Table 1).<sup>12d</sup> The results are summarized in Tables 1 and S3.† When a powder of [CD(−)340<sub>KBr</sub>]-**1** was treated with HCN, *L*-aminonitrile **2** with >99% ee was synthesized in 67% yield (Table 1, series I, entry 1). In contrast, addition of HCN to [CD(+)-340<sub>KBr</sub>]-**1** gave *D*-**2** with >99% ee in 60% yield (entry 2). The stereochemical relationships were reproducible as confirmed in entries 3 and 4.

Table 1 Asymmetric addition of HCN to a chiral crystal of achiral imine **1**

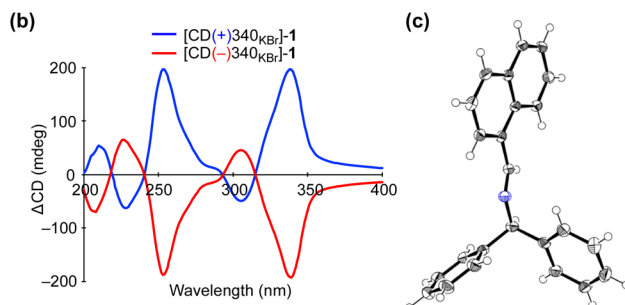
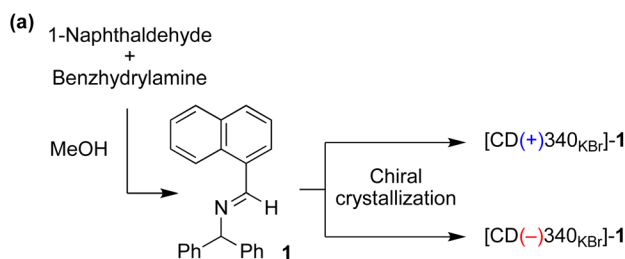
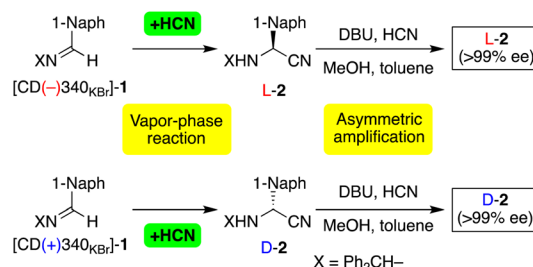


Fig. 2 (a) Chiral crystallization of achiral imine **1**. (b) Solid-state CD spectrum of **1**. (c) Single-crystal X-ray structure of **1** (CCDC 2224018†).

Entry <sup>a</sup>	Imine <b>1</b>	Aminonitrile <b>2</b>	
		% ee (config.) <sup>b</sup>	Yield <sup>c</sup>
<b>Series I</b>			
1	CD(−)340 <sub>KBr</sub>	>99 (L)	67
2	CD(+)-340 <sub>KBr</sub>	>99 (D)	60
3	CD(−)340 <sub>KBr</sub>	>99 (L)	53
4	CD(+)-340 <sub>KBr</sub>	>99 (D)	56
<b>Series II<sup>d</sup></b>			
5	CD(−)340 <sub>KBr</sub>	7 (L)	18
6	CD(+)-340 <sub>KBr</sub>	7 (D)	23
7 <sup>e</sup>	CD(−)340 <sub>KBr</sub>	2 (L)	34

<sup>a</sup> Asymmetric amplification of **2** was carried out after the vapor-phase reaction in series I was carried out. <sup>b</sup> Determined using HPLC on a chiral stationary phase. The absolute configuration of **2** (CCDC 2224019) was reconfirmed by derivatizing it to α-(1-naphthyl)glycine (**5**) (Fig. S5). <sup>c</sup> Each value in series I indicates the isolated yield (%) of **2**, whereas each value in series II indicates the reaction conversion (%), which was determined using <sup>1</sup>H NMR from the molar ratio of **1** to **2**. <sup>d</sup> Chiral crystal **1** was ground into a fine powder together with Na<sub>2</sub>SO<sub>4</sub>. <sup>e</sup> Chiral crystal **1** was ground into a fine powder together with KCN and then the mixture was exposed to acetic acid vapor.



The enantioenrichment of **2** was monitored as shown in Fig. S4;† the initially slight enantioimbalance of suspended **2** continuously increased to finally achieve an ee >99% when carrying out thermal cycling. In this heating-cooling cycles,<sup>12c</sup> nearly equimolar amounts of D- and L-**2** dissolved during heating to afford a reduced amount of suspended **2** with amplified ee. Then, cooling-induced deracemization of **2** occurred, *i.e.*, the crystal recovered during gradual crystal growth without a decrease in the amplified ee.

In series II, the enantioselectivity of the HCN addition was examined without asymmetric amplification. In this series, chiral crystal **1** was finely ground together with Na<sub>2</sub>SO<sub>4</sub> to expand the reactive chiral surface, which was exposed to HCN. When [CD(−)340<sub>KBr</sub>]-**1** was subjected to HCN addition, L-**2** with 7% ee formed with an 18% reaction conversion. In contrast, the [CD(+340<sub>KBr</sub>)-**1** enantiomorph gave the oppositely configured D-**2** (entries 5 and 6). As shown in entry 7, when [CD(−)340<sub>KBr</sub>]-**1** was ground with KCN and the resulting mixture was exposed to acetic acid vapor, L-**2** was obtained with 2% ee<sup>12f</sup> with the same stereoselectivity. Because fine powder **1** was exposed to HCN vapor, the addition reaction occurred under heterogeneous conditions of a random orientation of **1**. Thus, enantiomeric crystals **1** were responsible for the present asymmetric Strecker reaction.

The ability of enantioenriched **2** to be hydrolyzed to the corresponding amino acid, α-(1-naphthyl)glycine (**5**),<sup>12d</sup> allowed chiral crystallization of achiral imine to be connected with production of enantioenriched α-amino acid *via* a Strecker reaction and asymmetric amplification.

Next, the retro-Strecker reaction of enantioenriched aminonitrile **2** was examined (Table 2). Guillemin *et al.* reported carrying out the dehydrocyanation of aminonitriles to give imines by utilizing KOH *in vacuo*.<sup>13</sup> After the investigation, we found K<sub>2</sub>CO<sub>3</sub> to be an appropriate solid base for the present transformation of *N*-benzhydryl substrates. Thus, enantioenriched **2** was ground into a fine powder with K<sub>2</sub>CO<sub>3</sub> and the mixture was heated at 50 °C *in vacuo*. It was found to give imine **1** with the elimination of HCN and without any side reaction detected. After the removal of K<sub>2</sub>CO<sub>3</sub>, the optical properties and crystal structure of the resulting **1** were analyzed. Solid-state CD spectra (see the figure in Table 2) and a powder XRD pattern (Fig. S6†) indicated the formation of essentially the same crystal of **1** as that obtained from recrystallization from the solvent.

The stereochemical outcomes of this retro-Strecker reaction are summarized in Tables 2 and S4.† When L-**2** with >99% ee was subjected to dehydrocyanation, imine **1** with positive CD at 340 nm was isolated in 71% yield (Table 2, entry 1). From the value of ΔCD (+90 mdeg), the crystal ee was calculated to be 45% (see also Fig. S2†). In contrast, [CD(−)340<sub>KBr</sub>]-**1** with a ΔCD value of −89 mdeg (45% ee) was formed from D-**2** with 89% ee (entry 2). As seen in entries 3 and 4, dehydrocyanation occurred stereoselectively to produce chiral crystal **1**, even when using, respectively, L- and D-**2**, each with a slightly lower ee value of 67%. Thus, a chiral crystal of achiral imine **1** could be synthesized enantioselectively by carrying out a dehydrocyanation of enantioenriched **2**.

Table 2 Stereoselective dehydrocyanation of enantioenriched aminonitrile **2**

Entry <sup>a</sup>	% ee (config) of <b>2</b>	Aminonitrile <b>2</b>		
		ΔCD <sup>b</sup>	% ee <sup>c</sup>	Yield <sup>d</sup>
1	>99 (L)	+90	45	71
2	89 (D)	−89	45	70
3	67 (L)	+48	24	—
4	67 (D)	−55	28	—

<sup>a</sup> Aminonitrile **2** was ground into a fine powder together with K<sub>2</sub>CO<sub>3</sub> and heated at 50 °C *in vacuo* (<0.2 kPa). <sup>b</sup> Sign and value (mdeg) of the solid-state CD at 340 nm. <sup>c</sup> Each value was obtained from the corresponding calibration curve (Fig. S2). <sup>d</sup> Isolated yield (%) of solid **1**.

An unprecedented reversal of chirality was observed in the present transformations (Fig. 1). That is, addition of HCN to [CD(−)340<sub>KBr</sub>]-imine **1** gave L-aminonitrile **2**, and then dehydrocyanation of L-**2** gave the opposite [CD(+340<sub>KBr</sub>)-**1**. Thus, chiral crystallization-induced stereoinversion was realized between enantiomorphs of **1**, and of course, between L- and D-**2**.

The current asymmetric cyanide addition and dehydrocyanation were checked using substrates **3** and **4** with the 2-furyl substituent<sup>17</sup> (Fig. 3). Achiral imine **3** formed from furfural and benzhydrylamine (Fig. 3a) and crystallized in the chiral space group *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub> (Fig. 3b). The enantiomorphs of **3** were identified from a solid-state CD study, in which large positive and negative Cotton effects were observed at a wavelength of 300 nm (Fig. 3c).

A chiral enantioenriched crystal of achiral **3** ([CD(−)300<sub>KBr</sub>]-**3**) was subjected to a reaction with vapor-phase HCN (Fig. 3d). When the reaction conversion was 6%, L-aminonitrile **4** with an ee of up to 15% was found to have formed. While allowing the reaction to continue further appeared to have resulted in a decrease in enantioselectivity, the stereochemical relationships between the enantiomeric crystals **3** and the absolute configuration of **4** remained constant and reproducible, as shown in Table S5.†

Next, retro-Strecker reactions were investigated (Fig. 3e and Table S6†) using asymmetrically synthesized **4** (ref. 18) (Fig. S7†). Dehydrocyanations of L- and D-**4** were found to give [CD(−)300<sub>KBr</sub>]- and [CD(+300<sub>KBr</sub>)-**3**, respectively. The solid-state CD spectra (see the figure in Table S6†) and XRD pattern



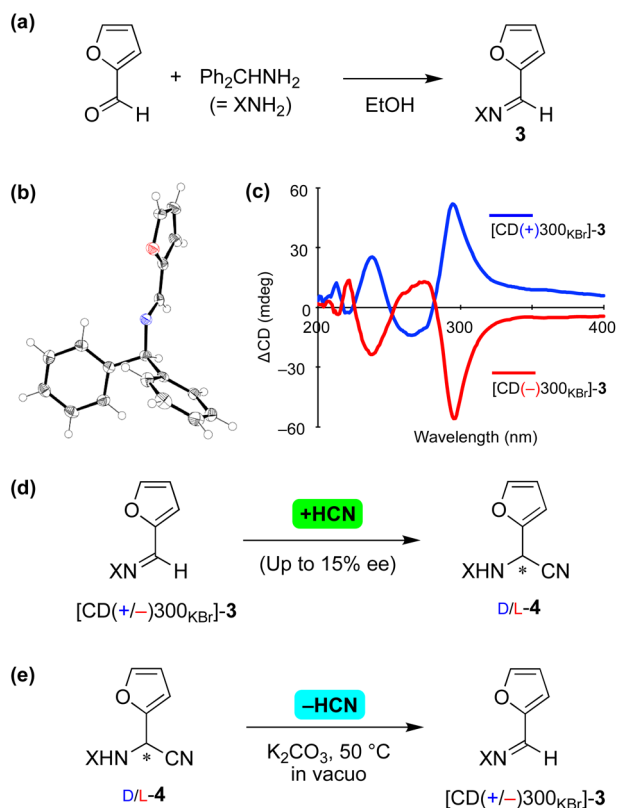


Fig. 3 Reversible asymmetric Strecker reaction between imine **3** and aminonitrile **4** with a 2-furyl substituent. (a) Synthesis of imine **3**. (b) Single-crystal X-ray structure of  $[\text{CD}(+)\text{300}_{\text{KBr}}]\text{-3}$  (CCDC 2224020†). (c) Solid-state CD spectrum of **3**. (d) Asymmetric vapor-phase addition of HCN to imine **3**. (e) Stereoselective retro-Strecker reaction of **4** (CCDC 2224021†).

(Fig. S8†) of product **3** indicated the formation of essentially the same crystal **3** ( $P2_12_12_1$ ) as that obtained as a result of recrystallization from the solvent. Note that stereoinversion was not observed in the reactions between **3** and **4**, even though cyanide addition and elimination occurred in an enantioselective manner.

In the crystal structures of **1** and **3**, a weak interaction between the imine and adjacent aromatic rings of neighboring

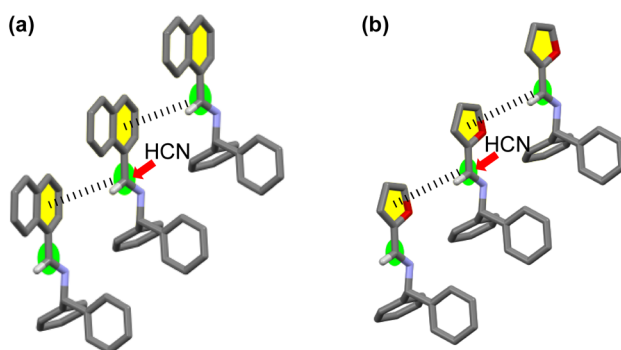


Fig. 4 Enantioselectivity of the addition of HCN to (a)  $[\text{CD}(+)\text{340}_{\text{KBr}}]\text{-1}$  and (b)  $[\text{CD}(+)\text{300}_{\text{KBr}}]\text{-3}$  to form **D-2** and **-4**, respectively.

molecules<sup>49</sup> was observed (Fig. 4). Thus, HCN might approach preferentially from the side of the molecule opposite these interactions, consistent with the stereochemical outcomes observed for the additions of cyanide to **1** and **3**. Comparing the patterns of the CD curves of **1** and **3** indicated a similarity of their crystal systems, a feature supporting the assumption that asymmetric induction occurred in similar manners for the additions of HCN to **1** and **3**.

When dehydrocyanation of **2** was performed in the presence of 10 mol% of **1** with mismatched enantiomeric crystals as seeds, enantiomeric crystals of imine **1** with the same chirality as that of the seeds was formed in a highly enantioselective manner (Fig. S9†). Thus, the initial selective formation of the crystal of the imine may have occurred on the chiral surface of the aminonitrile, with this surface acting as a chiral seed for further dehydrocyanation. The mechanism of dehydrocyanations as a selective process is now under investigation.

## Conclusions

In conclusion, asymmetric addition of cyanide to a chiral crystal of achiral imines has been demonstrated for the first time to the best of our knowledge. Moreover, asymmetric dehydrocyanation of enantioenriched aminonitrile was realized and stereo-inversion of a chiral crystal formed from an achiral compound has also been achieved for the first time to the best of our knowledge. The present reversible asymmetric transformations, while requiring chiral crystallization (conglomerate formation) of the substrate, would nevertheless be expected to help investigators better understand the mechanism of abiotic synthesis of enantioenriched amino acids.

## Author contributions

T. K. conceptualized the project and designed the experiments. Y. M., Y. T., Y. M. and A. K. carried out the experiments and analyzed the data. T. K. wrote the manuscript with contributions from all authors.

## Conflicts of interest

There are no conflicts to declare.

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