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Electronic Supplementary Information (ESI)

General comments

Enantioenriched α-(*p*-tolyl)glycine (**2**) was prepared by the previously reported method.[18] *p*-Tolualdehyde (**3**), benzhydrylamine (**4**), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and methanol used in the present work were purified by the distillations of commercial sources before use. Hydrogen cyanide (HCN) was prepared from the reaction between H_2SO_4 and KCN (or NaCN) in water and isolated by the distillations.

Asymmetric induction of aminonitrile 1 by amino acid 2 followed by the amplification of solid ee (Table 1, entry 3): L-(*p*-Tolyl)glycine **2** with *ca*. 50% ee (46.5% ee from Chiral HPLC analysis) was prepared by mixing L-**2** (110.5 mg, 97% ee) and D-**2** (37.0 mg, 97% ee). To a solution of L-**2** (83.4 mg, *ca*. 50% ee) in 1 M DBU solution of MeOH (2.4 mL) were added *p*-tolualdehyde (118 μL, 1.0 mmol), benzhydrylamine (173 μL, 1.0 mmol) and HCN (120 μL, 3.0 mmol) at room temperature. The crystallization of solid **1** was observed in 12 hours. After stirring the suspension for 2 days, the mixture allowed to warm to 50 °C dissolving apparently 80 to 90% of suspended solid **1**. Before the complete dissolution of **1**, the power of heating bath was shut off to cool to room temperature gradually for a period of >1 hour in accordance with lowering of the water bath temperature. After additional four temperature cycles, solid **1** was collected by a vacuum filtration and its ethereal solution was passed through silica gel. L-Aminonitrile **1** (131.7 mg, 0.42 mmol) with 99.1% ee was isolated in 42% yield. The filtrate was purified with silica gel column chromatography (hexane/ether = 3/1, *v/v*) to afford **1** (74 mg, 0.24 mmol) as a colorless solid in 24% yield.

Preparation of L and D-solid 1 with ca. 0.05% ee and following amplification in solid-phase ee: To a suspension of sodium sulfate (4.4 g) in CH_2Cl_2, (30 mL), were added *p*-tolualdehyde (2.0 g, 16.6 mmol) and benzhydrylamine (3.06 g, 16.6 mmol) at room temperature and the mixture was stirred for 1 day. After the filtration of the reaction mixture through celite, the solution was concentrated *in vacuo* to afford crude imine as colorless solid, and which was submitted to the next reaction without further purification. To a solution of crude imine and DBU (124 μL, 0.84 mmol) in toluene (50

mL) was added HCN (1.96 mL, 50 mmol) at room temperature. After stirring for 7 hours, 1 M HCl (30 mL) was added to the reaction mixture and was extracted with ether (3 times). The combined organic layer was dried over sodium sulfate and ether was removed *in vacuo*. Without crystallization of **1**, the residue was purified with silica gel column chromatography (hexane/ether = 3/1 (*v/v*)) to afford racemic conglomerate **1** (4.84 g, 15.5 mmol) as colorless solid in the 2 steps yield of 93%. After racemic conglomerate **1** was ground into a fine powder, D-solid **1** (1.0 mg, >99.5% ee) was added to racemic conglomerate **1** (2.00 g, 6.4 mmol) and was ground again using motor and pestle to afford a fine powder of D-**1** with *ca*. 0.05% ee. The resulting powder of D-**1** (280.5 mg, 0.9 mmol) was suspended in 1 M DBU solution of methanol (2.4 mL) in the presence of HCN (73 μL, 1.85 mmol) with stirring. The mixture was submitted to the thermal cycles to afford enantiomerically amplified D-**1** after the isolation procedure mentioned above.

Stereoselective reactive crystallization of D-1 using seed crystal: To a 1 M DBU solution of methanol (192 mL) were added *p*-tolualdehyde (7.55 mL, 64 mmol), benzhydrylamine (11.0 mL, 64 mmol) and HCN (8.29 mL, 208 mmol) at room temperature. After stirring the mixture for 1.5 hours, D-seed **1** (80 mg, 0.26 mmol) with >99.5% ee was added. After stirring for 12 hours, *p*-tolualdehyde (**3**) (3.78 mL, 32 mmol), benzhydrylamine (**4**) (5.50 mL, 32 mmol) and HCN (1.26 mL, 32 mmol) were added. It was repeated total four times to add three reagents (each 32 mmol) to the reaction mixture after stirring for >2 hours. Solid product **1** was collected by a vacuum filtration and washed with small amount of cold MeOH to afford D-**1** (46.5 g, 149 mmol) with >99.5% ee in 76% isolated yield.

Table S1. The numerical data of Figure 3a.

Entry	Config. of **1**	Solid-phase ee of **1** [%]						Yield
		Initial	1st	2nd	3rd	4th	5th	
1	L	*ca.* 5	26	91	>99.5	–	–	54
2	L	*ca.* 0.5	5	22	73	93	99	52
3	L	*ca.* 0.05	2	10	38	93	99	46
4	D	*ca.* 5	16	71	87	96	–	48
5	D	*ca.* 0.5	2	27	87	93	99	51
6	D	*ca.* 0.05	BDL	8	40	85	>99.5	42

BDL: Below the detectable level (<2% ee).

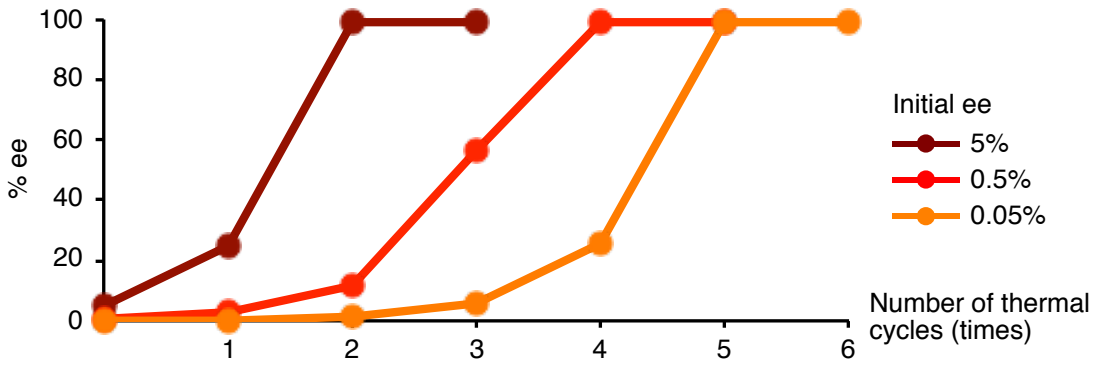

Fig. S1. Simulated amplification of solid-phase ee by the partial (80%) dissolution of racemic conglomerate **1** followed by deracemization *via* crystallization without decrease of enantiopurity.

Table S2. Highly stereoselective reactive crystallization of **1**.

Entry	Addition	Solid **1**		HCN	**3** and **4**	Solvent[a)]
		ee [%]	[mmol]	[mmol]	[mmol]	[mL]
1[b)]	Initial			208	64	192
	1st	>99.5 (D)	0.26			
	2nd			32	32	
	3rd			32	32	
	4th			32	32	
	5th			32	32	
	Total	>99.5 (D)	149 (76%)[c)]	336	192	192
2[b)]	Initial			208	64	192
	1st	>99.5 (L)	0.26			
	2nd			32	32	
	3rd			32	32	
	4th			32	32	
	Total	>99.5 (L)	96 (60%)[c)]	304	160	192
3[d)]	Initial	>99.5 (L)	0.1			
	1st			0.18	0.05	0.4
	2nd			0.18	0.05	–
	3rd			0.23	0.1	0.2
	4th			0.23	0.1	0.2
	5th			0.47	0.2	0.4
	6th			0.47	0.2	0.4
	7th			0.94	0.4	0.8
	8th			0.94	0.4	0.8
	9–18th			$0.2\times10^{\text{times}}$	$0.2\times10^{\text{times}}$	–
	Total	99 (L)	2.5 (72%)[c)]	5.64	3.5	3.2

a) 1 M DBU solution of methanol was used as a reaction solvent.

b) The seed **1** was added to the reaction solution at the initial stage.

c) The isolated yield of solid **1**.

d) The solvent and substrates were added to the seed **1** at the initial stage.