Electronic supplementary information (ESI):

Table S1 (Continuation of Table 1). The absolute handedness and the value of ee in *p*-tolylglycine nitrile **4** obtained from Strecker reaction under aqueous condition.

Entry	α-Aminonitrile **4**	
	ee [a] / % (Config.)	Yield [b] (%)
9	99 (L)	70
10	99 (L)	63
11	99 (D)	58
12	3 (L)	55
13	99 (L)	52
14	14 (D)	56
15	99 (L)	65
16	>99 (D)	54
17	99 (L)	61
18	>99 (D)	67
19	99 (D)	43
20	17 (L)	49
21	99 (D)	41
22	99 (L)	58
23	98 (D)	65

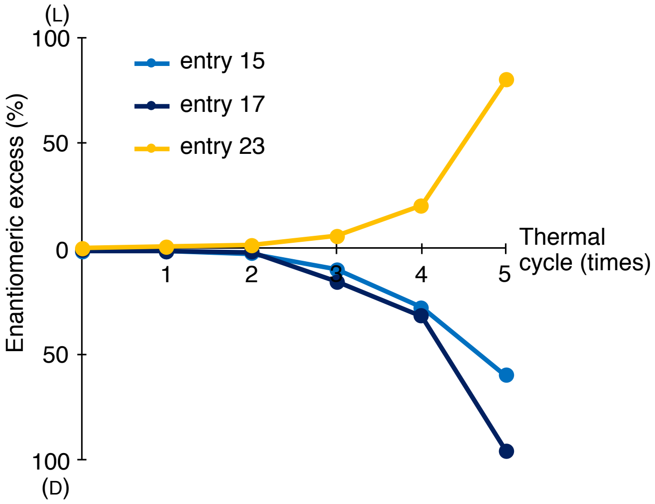
[a] The ee value was determined by high performance liquid chromatography (HPLC) on a chiral stationary phase. [b] The isolated yield of crystalline product by the filtration. The product in the filtrate was not included.

Table S2. The progress of Strecker reaction by the analysis of suspended solid.

Time / h	Suspended solids	
	Molar ratio [a] of **3** / **4**	ee [b] / % of **4**
0	–	–
24	>95 / <5	–
48	38 / 62	96
72	<5 / >95	99 [c]

[a] Determined by ^{1}H-NMR. [b] Determined by chiral HPLC analysis. [c] The chemical yield was 65%, which was indicated in Table 1, Entry 1.

Table S3. Generation and amplification of solid-state ee of **2**.



Entry # of Table 2	ee /% of suspended **4** (Configuration)					Yield[c] / %
	1st	2nd	3rd	4th	5th	
1	BDL	BDL	12 (L)	26 (L)	71 (L)	38
2	BDL	2.1 (D)	2.5 (D)	17 (D)	96 (D)	40
15	BDL	2.3 (D)	10 (D)	28 (D)	60 (D)	42
17	BDL	BDL	15.6 (D)	32 (D)	96 (D)	49
23	BDL	BDL	6.0 (L)	20 (L)	80 (L)	32

[a] The reaction was gradually proceeded for ca. three days and the product was obtained without heating-cooling cycles. [b] The ee was determined by using HPLC with a chiral stationary phase. [c] The solid product **3** was isolated by the filtration of reaction mixture and its recovered yield was described here. The product **3** in the solution-phase was not isolated. [d] In these entries, initially obtained methanol suspension was separated in four portions after the complete dissolution, then each solid 3 was submitted to the thermal cycles to obtain enantiomerically enriched **3**.

Table S4 (Continuation of Table 2). The absolute handedness and ee of aminonitrile **4** obtained from Strecker reaction in MeOH followed by the heating-cooling cycle.

Entry	α-Aminonitrile **4**		Thermal cycle
	ee[a] (%)	Yield[b] (%)	
11	94 (L)	21	5
12	40 (L)	25	7
13	38 (D)	29	5
14	95 (L)	16	5
15	60 (D)	42	5
16	2.8 (L)	43	4
17	96 (D)	49	5
18	78 (D)	43	6
19	4.0 (L)	49	4
20	6.2 (D)	48	4
21	18 (L)	46	4
22	51 (D)	33	5
23	80 (L)	32	5
24	40 (D)	35	6
25	11 (D)	38	6

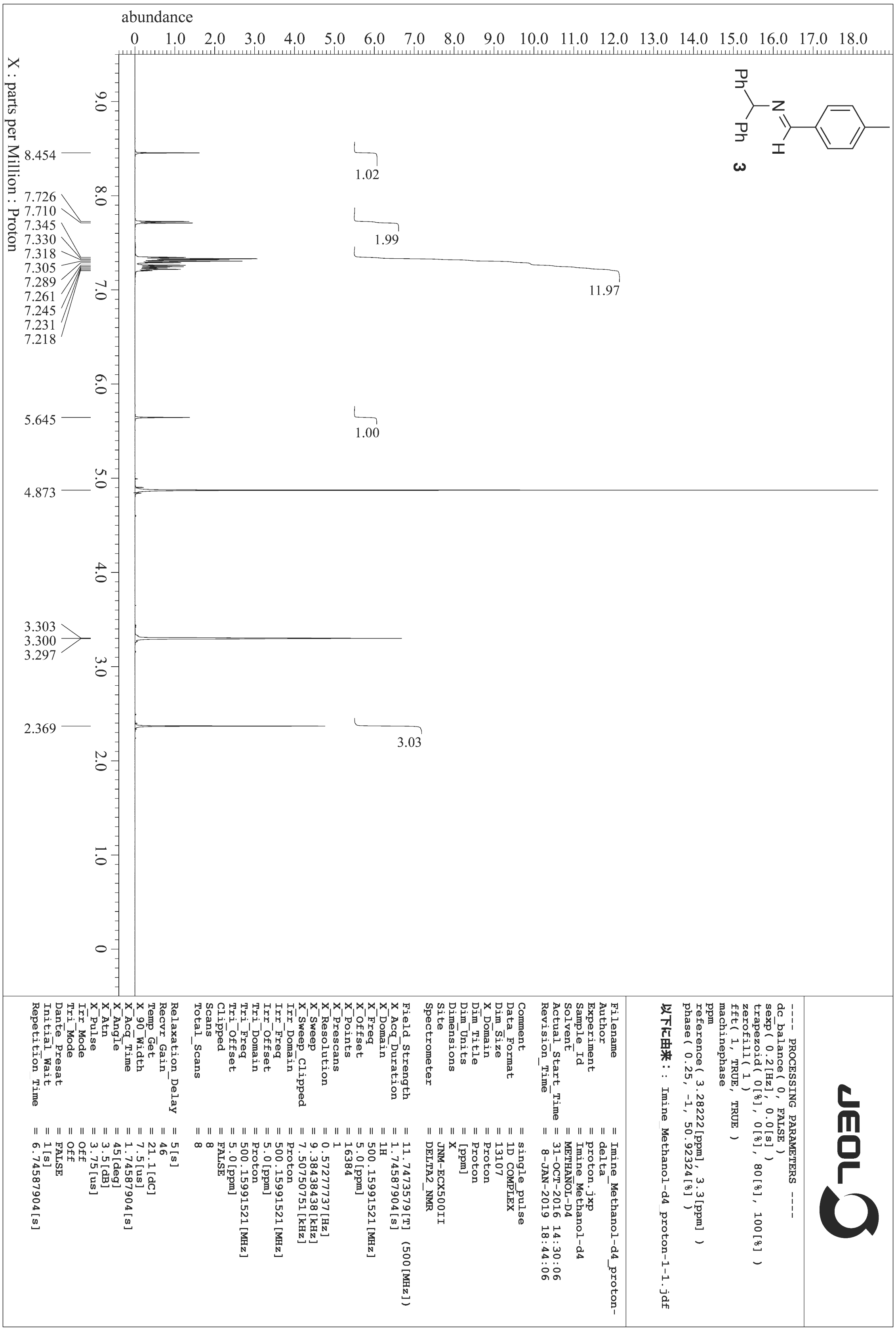
[a] The ee was determined by using HPLC with a chiral stationary phase. [b] The solid product **3** was isolated by the filtration of reaction mixture and its recovered yield was described here. The product **3** in the solution-phase was not isolated. [c] Generation and amplification of ee was monitored as shown in Fig. 3b. [d] After the precipitation of **4**, the suspension was stirred for 13 h and dissolved by the addition of $CHCl_3$, which was separated into two portions. Then after the concentration, thermal cycle was applied to the suspension of resulting solid **4** in 1 M DBU in methanol, independently. [e] After the precipitation of **4**, the suspension was stirred for 15 h, which was divided into four portions in the same procedure in entries 5 and 6. Then the thermal cycle was conducted independently.

Table S5 (Continuation of Table 3). Emergence of enantiomeric imbalances of aminonitrile **4** synthesized by the repetition of heating-cooling of the *rac*-**4** obtained from the homogeneous solution without the addition of any chiral materials.

Entry	α-Aminonitrile **3**		Thermal cycle
	ee [a] / % (Config.)	Yield[b] / %	
9	30 (D)	38	8
10	77 (D)	46	7
11	95 (L)	44	8
12	95 (L)	42	8
13	77 (D)	57	9
14	72 (L)	36	7
15	86 (L)	56	9
16	94 (D)	–	11
17	95 (D)	–	11
18	90 (L)	–	11
19	94 (D)	–	11
20	>99.5 (L)	48	9
21	94 (D)	49	9
22	>99 (L)	50	5
23	93 (L)	47	8
24	96 (D)	53	13
25	53 (D)	58	9

[a] The ee was determined by using HPLC with a chiral stationary phase. [b] The solid product **3** was isolated by the filtration of reaction mixture and its recovered yield was described here. The product **3** in the solution-phase was not isolated. [c,d] Strecker reaction was performed in the same reaction vessel. After removal of DBU, the mixture was separated in two portions and submitted to the thermal amplification independently. [e] Methanol was used instead of DBU.

^{1}H NMR spectrum of imine **3** (500 MHz, methanol-d_4, 3.30 ppm)



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fft( 1, TRUE, TRUE )
machinephase
ppm
reference( 3.28222[ppm], 3.3[ppm] )
phase( 0.25, -1, 50.92324[%] )

以下に由来 : Imine_Methanol-d4_proton-1-1.jdf

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Author                = delta
Experiment            = proton.jxp
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Solvent               = METHANOL-D4
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Revision_Time         =  8-JAN-2019 18:44:06

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Spectrometer          = DELTA2_NMR

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X_Sweep_Clipped       = 7.50750751[kHz]
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Irr_Freq              = 500.15991521[MHz]
Irr_Offset            = 5.0[ppm]
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Tri_Freq              = 500.15991521[MHz]
Tri_Offset            = 5.0[ppm]
Clipped               = FALSE
Scans                 = 8
Total_Scans           = 8

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X_Pulse               = 3.75[us]
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Tri_Mode              = Off
Dante_Presat          = FALSE
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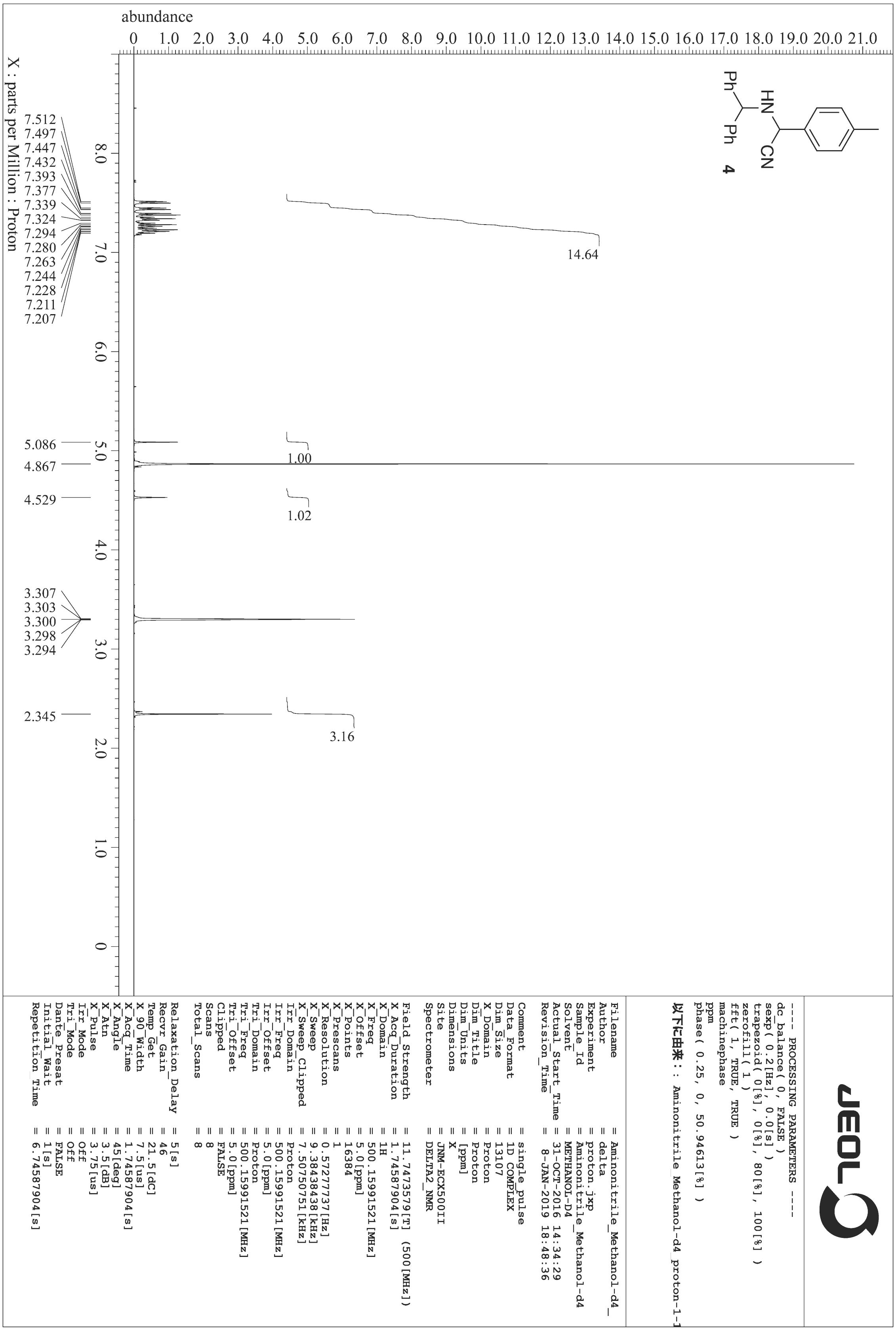
^{1}H NMR spectrum of aminonitrile **4** (500 MHz, methanol-d_4, 3.30 ppm)



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---- PROCESSING PARAMETERS ----
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sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
phase( 0.25, 0, 50.94613[%] )
以下に由来：: Aminonitrile_Methanol-d4_proton-1-1

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Experiment           = proton.jxp
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Revision_Time        =  8-JAN-2019 18:48:36

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X_Domain             = Proton
Dim_Title            = Proton
Dim_Units            = [ppm]
Dimensions           = X
Site                 = JNM-ECX500II
Spectrometer         = DELTA2_NMR

Field_Strength       = 11.7473579[T] (500[MHz])
X_Acq_Duration       = 1.74587904[s]
X_Domain             = 1H
X_Freq               = 500.15991521[MHz]
X_Offset             = 5.0[ppm]
X_Points             = 16384
X_Prescans           = 1
X_Resolution         = 0.57277737[Hz]
X_Sweep              = 9.38438438[kHz]
X_Sweep_Clipped      = 7.50750751[kHz]
Irr_Domain           = Proton
Irr_Freq             = 500.15991521[MHz]
Irr_Offset           = 5.0[ppm]
Tri_Domain           = Proton
Tri_Freq             = 500.15991521[MHz]
Tri_Offset           = 5.0[ppm]
Clipped              = FALSE
Scans                = 8
Total_Scans          = 8

Relaxation_Delay     = 5[s]
Recvr_Gain           = 46
Temp_Get             = 21.5[dC]
X_90_Width           = 7.5[us]
X_Acq_Time           = 1.74587904[s]
X_Angle              = 45[deg]
X_Atn                = 3.5[dB]
X_Pulse              = 3.75[us]
Irr_Mode             = Off
Tri_Mode             = Off
Dante_Presat         = FALSE
Initial_Wait         = 1[s]
Repetition_Time      = 6.74587904[s]
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