Supplementary material (ESI) for Chemical Communications
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Occurrence of spontaneous resolution of ketoprofen with a racemic crystal structure by simple crystallization under nonequilibrium preferential enrichment conditions

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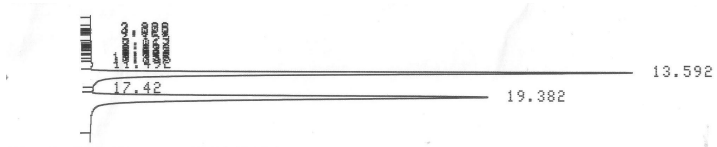
Electronic Supplementary Information

(a)

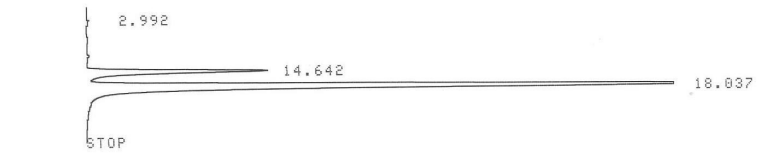


CHROMATOGRAM 4 MEMORIZED

CHROMATOPAC C-R6A FILE 1
SAMPLE NO 0 METHOD 61
REPORT NO 2818

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	11.492	8055			0.2679	
2	13.592	1493584	S		49.6659	
3	19.382	1505623	V		50.0662	
	TOTAL	3007262			100	

(b)



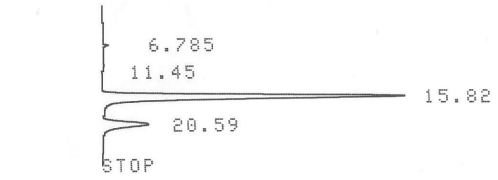
CHROMATOGRAM 3 MEMORIZED

S- 64.4%ee

CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 12251

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	14.642	575828			17.7792	
2	18.037	2662946	V		82.2208	
	TOTAL	3238774			100	

(c)



CHROMATOGRAM 2 MEMORIZED

CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 12365

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	15.82	647139			83.7815	
2	20.59	125274			16.2185	
	TOTAL	772413			100	

Fig. S1 HPLC chromatograms of ketoprofen. (a) *RS* (0% *ee*), (b) *S*-rich (64% *ee*), and (c) *R*-rich (68% *ee*). The *ee* values were determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralcel OJ, 0.40 x 25 cm), a mixture of hexane, 2-propanol, and acetic acid (900:100:5) as the mobile phase at a flow rate of 1.0 mL/min at 30°C, and UV-vis spectrometer (254 nm) as the detector.

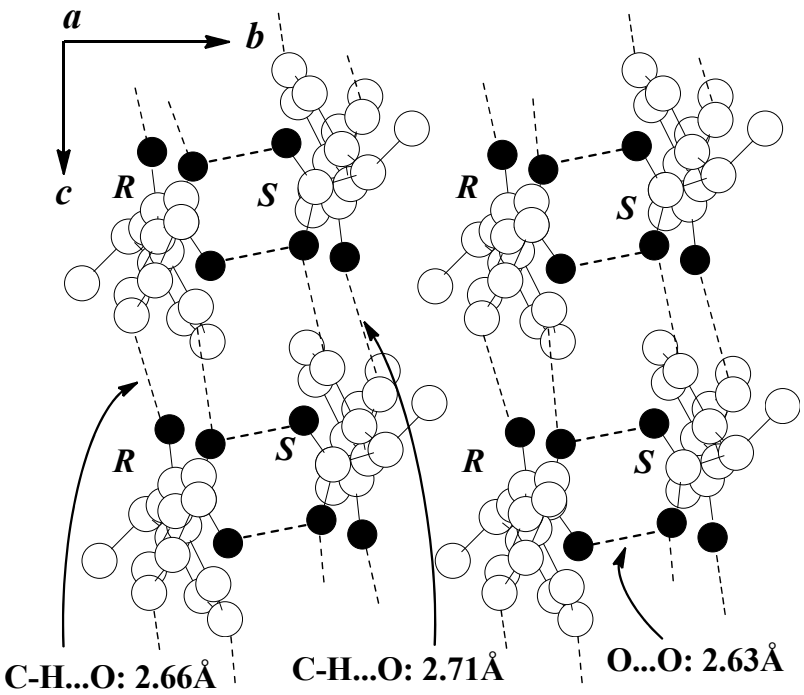


Fig. S2 Crystal structure of (*RS*)-ketoprofen. A view down the *a*-axis.

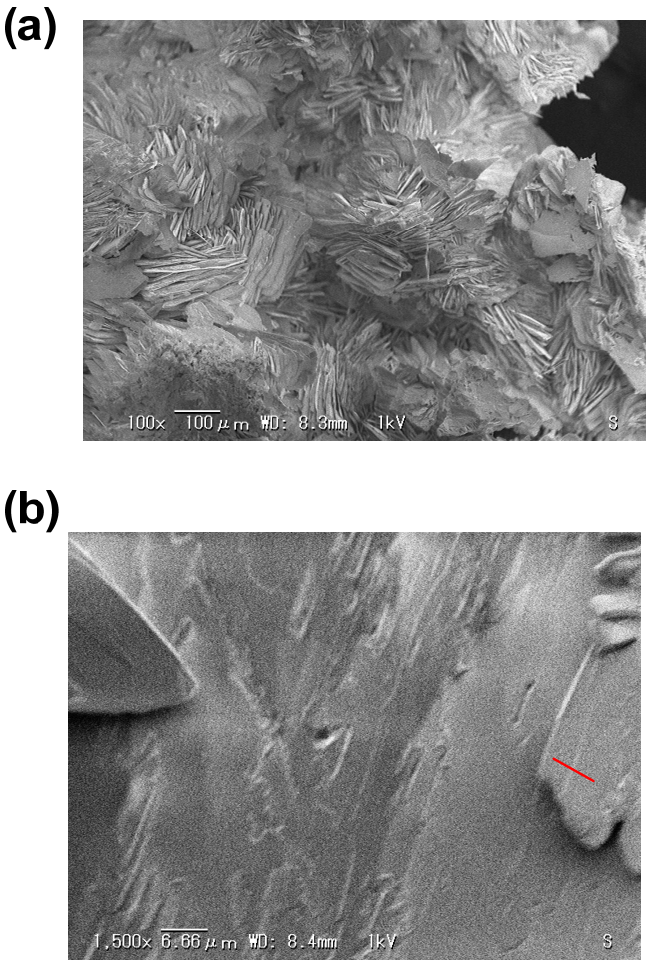


Fig. S3 SEM images of the deposited *S*-rich crystals of 1.2% *ee* after recrystallization of slightly *R*-rich crystal of ketoprofen under the preferential enrichment conditions. The scale bar at the lower left corresponds to (a) 100 μm and (b) 6.6 μm. In panel b, the depth of the hollow along the red line was ca. 1 μm by AFM observation.

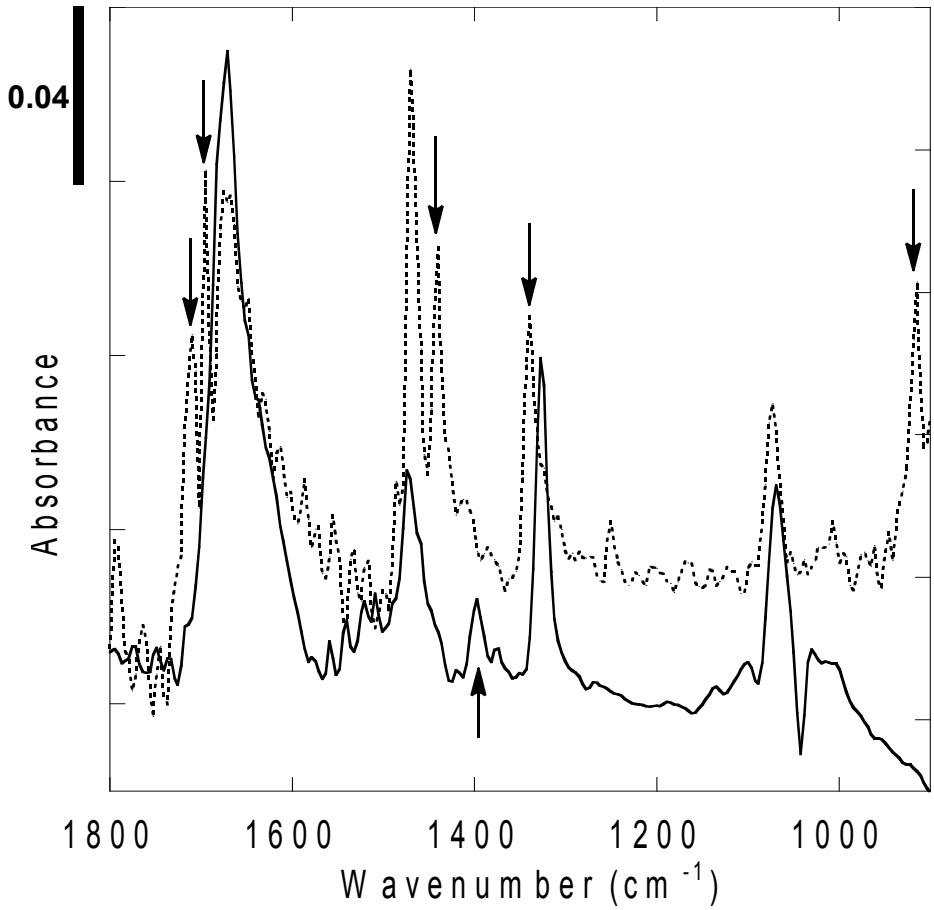


Fig. S4 Comparison of in situ ATR-IR (ReactIR) spectra of ketoprofen. In the supersaturatetd H_2O-EtOH (v/v 1:1) solution of (*RS*)-ketoprofen (solid line) and in the solid state of deposited *S*-rich crystals of 1.2% *ee* (dotted line). The spectral region includes (i) the C=O stretching vibrations of the keto group and (ii) the C=O and C-O stretching vibrations and O-H bending vibrations with respect to the carboxylic acid. The band near 920 cm^{-1} which is observed only in the solid state corresponds to the out-of-plane bending of the bonded O-H, which is characteristic of dimeric carboxylic acids. Arrows indicate the difference in the two spectra.