Supplementary Material (ESI) for Chemical Communications

A Simple Explanation of the Enhancement or Depletion of the Enantiomeric Excess in Fractional Sublimation of Enantiomerically Enriched Amino Acids.

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Electronic Supplementary Information (ESI)
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To determine the reproducibility of the sublimations, five similar experiments were performed starting from (DL + L) samples with a starting *ee* of 9%. The *ee* of the sublimates range between 30 and 36 %. (Table S1). The differences were attributed to the precision of the determination of the *ee* and the variation (±20%) of the sublimed amount. The difference between two *ee* of sublimates for experiments starting from the same *ee* has never been higher than 9 % (±5%).

Table S1: *ee* after sublimation under standard procedure of a DL + L mixture of leucine.

Entry	Starting *ee*	*ee* sublimate
1	9	36
2	9	30
3	9	34
4	9	34
5	9	30

Table S2: Starting *ee* and *ee* of the sublimate of DL and L mixtures of leucine.[a]

Entry	Starting *ee* (%)	*ee* sublimate (%)
1	0	0
2	5	36
3	10	42
4	20	42
5	30	44
6	40	48
7	50	48
8	60	54
9	70	52
10	80	52
11	90	61
12	95	65
13	100	100

[a] The samples were cautiously prepared by grinding appropriate amounts of L- and DL-leucine (1 g) for 10 min in a mortar.

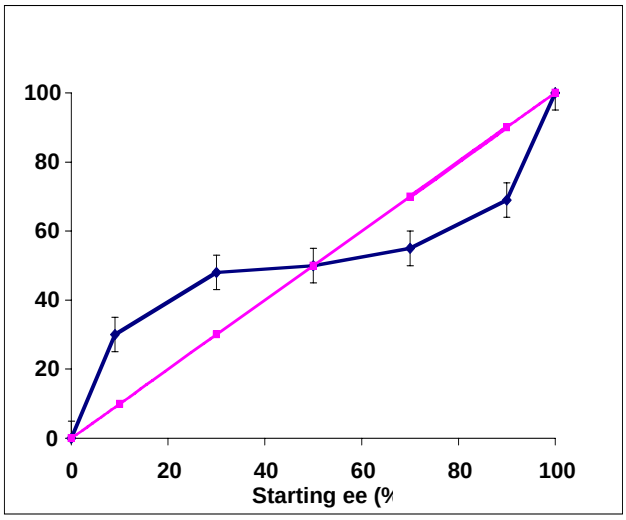

Fig. S1. *ee* of the sublimate versus *ee* of the starting material of DL + D leucine.

Experimental section

Materials. Standard sublimation apparatus were purchased from Aldrich. Amino acids were purchased from Aldrich except L-leucine (Alfa-Aesar).

Sublimation of leucine. A mixture of 1g of enantiomers (D and L) or racemate and enantiomer (DL and L) or (DL and D) of leucine were cautiously ground in a mortar for about 10 min. The mixture was then cautiously introduced in the sublimation apparatus with a funnel to avoid deposition on the walls. The sublimation apparatus was connected to a vacuum pump and the gas phase was evacuated. The bottom of the apparatus (3 cm) was introduced in an oil bath (θ: 120°C). 0.5-1 % (5-10 mg) of the starting material was sublimed after 16 hours at 120 °C under 0.1 mbar. The sublimate was collected from the cold finger by dissolution of the amino acid in aqueous hydrochloric acid (1N). Water was then removed *in vacuo* and the solid was dried *in vacuo* for 30 min at room temperature. Alanine and proline were partially sublimed in similar conditions (16 hours at 120°C).
The amount of starting material (1 g) was only different in experiments using two sublimation apparatus as indicated on Table 3. 5-10 mg of sublimates were obtained for each, independently of the starting amounts.

Derivatization of an amino acid. In a 5mL flask were introduced under nitrogen about 10 mg of amino acid (11 mmol, 1eq), 2mL of dry THF, 34 µL of pyridine (42 mmol, 3 equiv.) and a large excess of ethyl chloroformate (44 µL, 4.4 equiv.). The mixture was stirred for 1h at room temperature. About 50µL of the mixture was then quenched with 1mL of HCl 1N. Ethyl ether (1 mL) was added to extract the derivatized amino acid before to inject it in GC for analysis.

A sample of each starting mixture and each sublimate was derivatized and the *ee* was determined by GC. GC analysis was performed on a CHIRALDEX^{TM} G-BP capillary column. The samples of the starting mixtures showed the absence of racemization or enantioenrichment in these conditions.