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Self-disproportionation of enantiomers of α-trifluoromethyl lactic acid amides via sublimation

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ABSTRACT

Preparation of racemic and enantiomerically enriched α-trifluoromethyl lactic acid amide [NHPh, NH(4-Cl-C_6H_5), NHBn, NH*t*-Bu] derivatives have been developed. Ph, 4-Cl-C_6H_5, and *tert*-Bu derivatives were found to have substantial magnitude of the self-disproportionation of enantiomers (SDE) via sublimation. For example, when the optically enriched Ph, 4-Cl-C_6H_5, and *tert*-Bu amide derivatives were subjected to sublimation under kinetic conditions (Petri dish in open air), the enantiomeric excess of the remainder has noticeably increased. On the other hand, the SDE of Bn amide derivative by sublimation resulted in almost no change in the optical purity of the remainder. These preliminary results on the SDE of the compounds under study, as well as their excellent chemical and physico-chemical characteristics, render these amide derivatives as readily available and very promising substrates for systematic study of SDE via sublimation.

1. Introduction

Biomolecular homochirality on Earth is still not fully explained and keeps on attracting multidisciplinary research interest [1]. One of the possible scenarios is generation of slightly enantiomerically enriched compounds by, for example, parity violation [2], circular polarized light [3], asymmetric adsorption on spontaneously formed chiral inorganic crystals of random handedness [4], absolute asymmetric synthesis [5], including asymmetric autocatalysis [6–8]. Other sources of generation of non-racemic compounds in the Cosmos or on Earth have also been suggested [9]. Further evolution of thus slightly enantiomerically enriched compounds to highly enantiomerically enriched, ideally homochiral, fractions seems to be virtually inevitable process due to the self-disproportionation of enantiomers (SDE) [10]. SDE is defined as a transformation of an enantiomerically enriched system resulting in the formation of fractions of a different, as compared with the original, proportion of the enantiomers. Thus, the ultimate outcome of SDE is a complete separation of racemate [11] from the excess enantiomer. Since SDE is of fundamentally general nature and can be observed under any physical processes. Thus, the most known and widely used example of SDE is a routine crystallization of enantiomerically enriched compound resulting, ideally, in racemic and optically pure fractions [12]. On the other hand, the SDE via other typical physical processes such as, e.g.: distillation/evaporation [13,14], sublimation [10,15,16], achiral chromatography [17], gravitational field [18] are substantially less known and virtually unstudied. Here, again, we would like to emphasize the fundamentally general nature of SDE as it always takes place under any physico-chemical processes. One of the reasons of the current lack of knowledge in this area is that most of the researchers are unaware of this phenomenon and therefore it goes unnoticed in routine everyday laboratory experiments.

We believe that fluorinated molecules possess a significant potential of SDE phenomenon of highly noticeable magnitude due to their unique properties, as compared with non-fluorinated counterparts, such as: increased density and viscosity, dipole–dipole and hydrogen-bonding intermolecular interactions, and lowered surface tension, refractive index, and dielectric constants [19–21]. Of particular interest are compounds containing a

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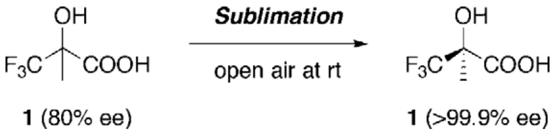


Scheme 1.

trifluoromethyl group which additionally impacts the pattern of intermolecular interactions because of its strong steric [22] and electrostatic [23] demands. For example, we and others have found remarkably high magnitude of the SDE possibly induced by a trifluoromethyl group. For instance, isopropyl 3,3,3-trifluorolactate shows a dramatic magnitude of SDE via distillation while non-fluorinated lactate did not show any measurable SDE phenomenon under the same conditions [14]. Recently, we have discovered that a trifluoromethyl group directly bonded to a stereogenic center can induce significant magnitude of SDE during chromatography on achiral silica-gel stationary phase using achiral eluent [17b–d]. Furthermore, we have found that racemic crystals of α-(trifluoromethyl)lactic acid (**1**) sublime at substantially higher rates, compared with the optically pure form, leading to appreciable magnitude of SDE via sublimation [10]. Thus, optical purification to the homochiral state of enantiomerically enriched samples of the compound **1** was achieved under ultimately simple conditions: just leaving the compound on a bench in open air (Scheme 1). This remarkable preliminary result prompts us to investigate a possible SDE of other molecules containing trifluoromethyl group [16]. As a part of the work, it is quite natural to investigate some new derivatives of the relatively high volatile compound **1**. In this communication we report synthesis of amide derivatives of α-trifluoromethyl lactic acid in racemic and enantiomerically enriched form, as well as preliminary results on their SDE via sublimation.

2. Results and discussion

Under standard condition, racemic and optically pure α-(trifluoromethyl)lactic acid amide derivatives **3a**–**d** were prepared from (*R*/*S*)- or (*S*)-**2** (Table 1). It should be noted that no racemization occurred under the reaction conditions. Since the obtained amide derivatives **3a**–**c**, except for the compound **3d**, have relatively low volatility at rt under atmospheric pressure, SDE experiments by sublimation of these derivatives should be conducted at higher temperature. It should be emphasized that all compounds **3a**–**d** have profound thermal and chemical stability therefore the corresponding SDE experiments by sublimation are not contaminated by any sort of chemical decomposition.

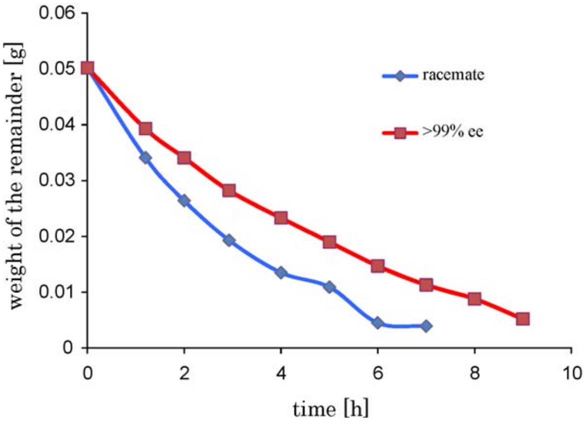
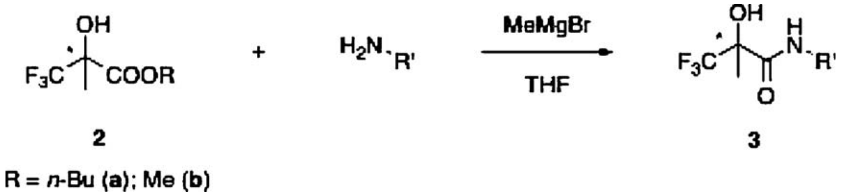


Fig. 1. Sublimation of racemate and >99% ee 3a at 80 °C.

As we always suggest to perform for the initial study of SDE via sublimation [10], the racemic and optically pure samples of **3a**–**c** were sublimed separately on a Petri dish under open air condition (Figs. 1–3). Similarly to the previously reported results for α-CF_3-lactic acid **1** [10] and 3,3,3-trifluorolactic acid isopropyl ester [14], racemic crystals (*R*/*S*)-**3a**–**c** sublimed faster than enantiomerically pure crystals (*S*)-**3a**–**c**. The initial rates of sublimation of racemate and optically pure **3a**–**c** are summarized in Table 2. The phenyl amide derivatives **3a** and **3b** showed significant differences in the sublimation rates of racemate and the optically pure forms. The (*R*/*S*)-**3a** and (*R*/*S*)-**3c** sublime about 1.4 and 1.6 times faster than the corresponding enantiomerically pure counterparts, respectively. These differences in the rates are as large as the case of α-CF_3-lactic acid itself (~1.5 times) [10], suggesting that the SDE of these new derivatives via sublimation should have a substantial, practically useful magnitude and that the sublimed material of the samples of various enantiomeric purity might undergo optical depletion while the remainder is expected to be more enantiomerically enriched. On the other hand, in the case of compound **3c**, though the racemate sublime faster than the optical pure form, similar to other cases, the rates of sublimation were comparable, suggesting the SDE of **3c** via sublimation might be of low magnitude, making it more difficult to separate the corresponding racemate from the excess enantiomer.

With these preliminary results in hand, we decided to perform SDE experiments of **3a**–**d** via sublimation. All the enantiomerically

Table 1
Synthesis of α-trifluoromethyl lactic acid amides.



Entry	2	R′=	Yield [%]
1	(*R*/*S*)-**2a**	Ph	90 (**3a**)
2	(*S*)-**2b**		81 (**3a**)
5	(*R*/*S*)-**2a**	4-Cl-C_6H_5	66 (**3b**)
6	(*S*)-**2b**		10 (**3b**)
3	(*R*/*S*)-**2a**	Bn	92 (**3c**)
4	(*S*)-**2b**		74 (**3c**)
7	(*R*/*S*)-**2a**	*tert*-Bu	91 (**3d**)
8	(*S*)-**2b**		32 (**3d**)

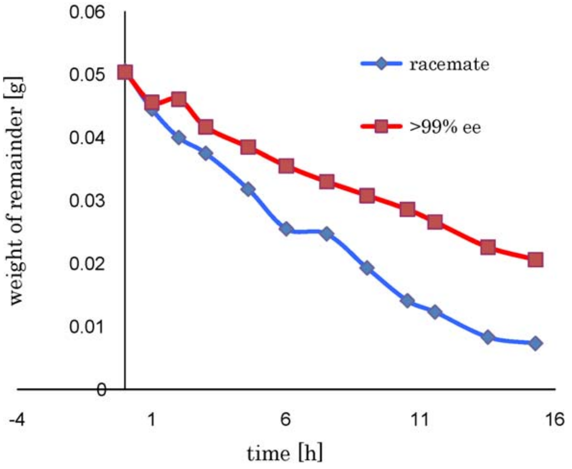


Fig. 2. Sublimation of racemate and >99% ee 3b at 80 °C.

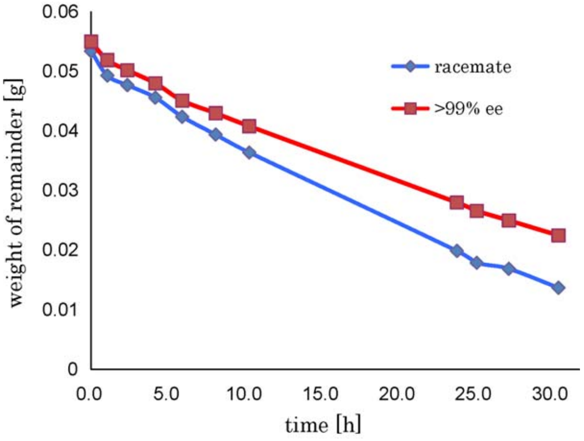


Fig. 3. Sublimation of racemate and >99% ee 3c at 60 °C.

enriched samples under study were prepared by mixing and well grinding (*R*/*S*)-**3** and (*S*)-**3** before the SDE experiments, and spreading the samples as evenly as possible on a Petri dish.

SDE experiments of **3a** and **3b** via sublimation were conducted at 80 °C starting with 87.5 and 76.9% ee, respectively (Figs. 4 and 5). As is anticipated above, in general, the optical purity of the remainder kept increasing: in the case of **3b**, the enantiomeric excess reached to >99% ee after 23 h. In the SDE experiment of α-trifluoromethyl lactic acid **1** via sublimation [10], 80% of the sample (initial optical purity: 80% ee) had sublimed when the optical purity of the remainder reached to >99% ee after 56 h. On the other hand, in the case of **3b**, due to the sublimation at the higher temperature, the less amount of the optically pure product was obtained: 93% of **3b** sublimed after 23 h. As one may assume, more preoperatively attractive optical purification via sublimation should be conducted at lower temperatures, which was not the goal of present study. At some points in the graphs, the enantiomeric excess of the remainder looks decreasing. But, this could stem from the unevenness of surface of samples for sublimation as well as non-homogeneous distribution of enantiomerically pure and racemic crystals derived from the manual spreading of the samples on Petri dishes and/or the manual samplings for determination of the optical purity of the remainder.

Table 2
Rates of sublimation of (*R*/*S*)- and (*S*)-3.

Compound	Rates of (*R*/*S*)-**3** [g/h]	Rates of (*S*)-**3** [g/h]
3a	0.0106	0.0075
3b	0.0033	0.0021
3c	0.0016	0.0014

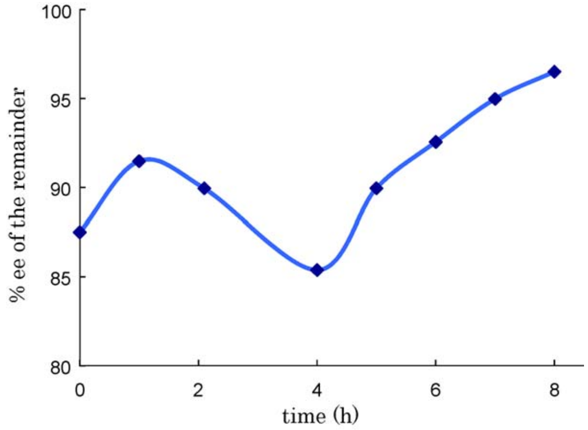


Fig. 4. SDE of 3a (87.5% ee) at 80 °C. Time dependent change of % ee of the remainder.

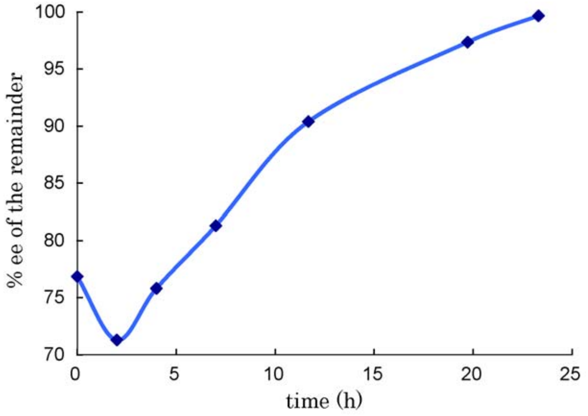


Fig. 5. SDE of 3b (76.9% ee) at 80 °C. Time dependent change of % ee of the remainder.

Judging from the small difference in the rates of sublimation of compound **3c** (See, Table 2), the SDE of **3c** via sublimation seems not to be effective for optical purification of this compound. In fact, the enantiomeric excess of the remainder did not change much in the SDE experiment of **3c** by sublimation (Fig. 6). This result

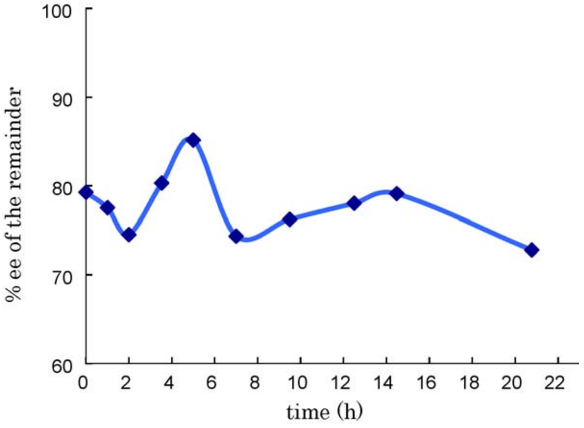


Fig. 6. SDE of 3c (79.3% ee) at 60 °C. Time dependent change of % ee of the remainder.

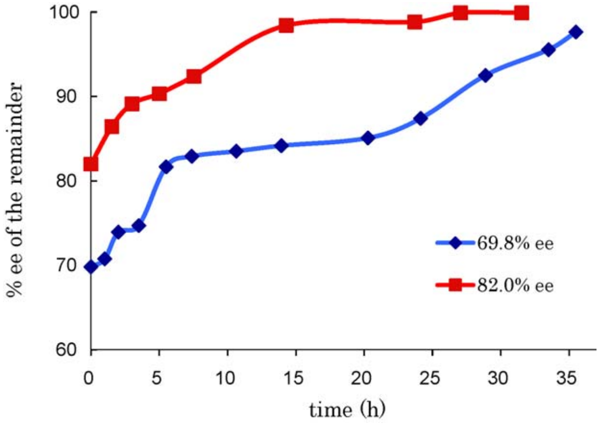


Fig. 7. SDE of 3d at rt. Time dependent change of % ee of the remainder.

implies the differences in the rates of sublimation obtained separately for racemate and optically pure forms could be used for estimation of magnitude of the SDE via sublimation and therefore efficiency of this approach for optical purifications.

The *tert*-Bu amide **3d** has a relatively high volatility: it can sublime efficiently at rt under normal pressure. The SDE experiments by sublimation, starting with 69.8 and 82.0% ee, resulted in the increase of the optical purity of the remainder up to 98 and >99% ee, respectively. The latter case has as good efficiency as the case of α-trifluoromethyl lactic acid itself [14] with only half amount of the sublimation time: 78% of the amide **3d** had sublimed when the optical purity of the remainder reached to >99% ee after 27 h (Fig. 7).

In summary, the rates of sublimation in Table 2 and above preliminary results of SDE experiments via sublimation clearly demonstrate that phenyl and *tert*-Bu amide derivatives of α-trifluoromethyl lactic acid **3a**,**b**,**d** are quite useful substrates for systematic study of SDE via sublimation while the benzyl derivative **3c** is not suitable for SDE via sublimation. Thus, compounds **3a**,**b**,**d** are easily available in racemic and enantiomerically enriched forms, highly crystalline and reasonably volatile. Moreover, compounds **3a**,**b**,**d** are chemically and configurationally stable and their study of SDE via sublimation is not complicated by any problems with chemical decomposition, which is very important factor in collecting reliable and reproducible results. All these important features render compounds **3a**,**b**,**d**, and most probably other amide derivatives of α-(trifluoromethyl)lactic acid **1**, as very useful substrates for systematic study of SDE via sublimation and its practical applications. These results add also an additional support for our hypothesis that compounds containing $-CF_3$ group directly bonded to a stereogenic carbon center are prone to induce a SDE effect ([10,16,17b–d]), plus some papers from this issue).

3. Experimental

3.1. General

Unless otherwise stated, all reagents and solvents were obtained from commercial suppliers and used without further purification. All the reactions were carried out under N_2 atmospheric conditions. Unless indicated ^{1}H and ^{13}C NMR spectra, were taken in $CDCl_3$ solutions at 299.95 and 75.42 MHz, respectively. Chemical shifts for ^{1}H and ^{13}C NMR refer to TMS as the internal standard. Chemical shifts for ^{19}F NMR refer to $CFCl_3$ as the internal standard. A Micromass Q-TOF was used to measure the time-of-flight electro-spray mass spectra in positive ion mode (TOF-ESIMS^{+}). All new compounds were characterized by ^{1}H, ^{13}C and ^{19}F NMR, high-resolution mass spectrometry (HRMS-ESI), and melting point, when applicable.

The optical purity of **3a** and **3b** was determined by HPLC (AD: 25 cm × 0.5 cm). The flow rate of solvent (*n*-hexane/*i*-PrOH = 95/5) was set at 1.0 mL/min. The retention times of compound **3a** were 9.6 and 12.6 min. The retention times of compound **3b** were 10.6 and 13.9 min. The optical purity of **3c** was determined by HPLC (OA-4500: 25 cm × 0.5 cm). The flow rate of solvent (*n*-hexane/CH_2Cl_2/EtOH = 82/15/3) was set at 1.0 mL/min. The retention times of compound **3c** were 16 and 17 min. The enantiomeric excess of the compound **3d** was determined by GC (CYCLOSIL-β column: 30 m × 0.25 mm × 0.25 μm). The initial temperature was set at 50 °C for 5 min, then increased the temperature at 10 °C/min. The final temperature was set at 150 °C for 5 min. The total time for a measurement was set as 20 min. The retention times of compound **3d** were 14.7 and 14.9 min.

3.2. General synthetic procedure of α-trifluoromethyl lactic acid amides 3a–d

To a THF solution containing amine (5.0 equiv.), was added MeMgBr (5.0 equiv.) slowly at 0 °C under N_2 atmosphere, and the reaction mixture was stirred at that temperature for 30 min. Then, THF solution of ester **2a** or **2b** was added slowly. The reaction mixture was stirred overnight. Then, 1N HCl aq was added to the reaction mixture, and THF was removed under vacuum. The organic layer was extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous $MgSO_4$. After filtration, evaporation of solvents and silica-gel column, the desired compound **3** was obtained in good yield.

*__3a__ and **3c** were recrystallized from toluene/*n*-hexane solution before the further use. **3b** was recrystallized from benzene/*n*-hexane solution before the further use. **3d** was recrystallized from CH_2Cl_2/*n*-hexane solution before the further use.

3.3. N-Phenyl-α-trifluoromethyllactyl amide (3a)

^{1}H NMR in $CDCl_3$ δ 1.71 (3H, s), 4.32 (1H, s), 7.15–7.20 (1H, m), 7.32–7.38 (2H, m), 7.51–7.54 (2H, m), 8.49 (1H, s). ^{19}F NMR δ −80.1 (s). ^{13}C NMR δ 20.3, 75.3 (q, *J* = 29 Hz), 120.3, 124.0 (q, *J* = 286 Hz), 129.1, 136.3, 166.2. HRMS (TOF) $[M+H]^{+}$, cald for $[C_{10}H_{10}F_3NO_2+H]^{+}$: 234.0742, found: 234.1124. Mp of racemate: 119 °C, mp of chiral isomer: 135 °C.

3.4. N-4-Chlorophenyl-α-trifluoromethyllactyl amide (3b)

^{1}H NMR in $CDCl_3$ δ 1.77 (3H, s), 3.67 (1H, s), 7.34–7.39 (2H, m), 7.53–7.57 (2H, m), 8.35 (1H, s). ^{19}F NMR δ −80.1 (s). ^{13}C NMR δ 20.5, 77.2 (q, *J* = 27 Hz), 124.0, 125.1 (q, *J* = 285 Hz), 131.3, 135.6, 128.5, 167.0. HRMS (TOF) $[M+H]^{+}$, cald for $[C_{10}H_{10}ClF_3NO_2+H]^{+}$: 268.0352, found: 268.0445. Mp of racemate: 116 °C, mp of chiral isomer: 144 °C.

3.5. N-Benzyl-α-trifluoromethyllactyl amide (3c)

^{1}H NMR in $CDCl_3$ δ 1.61 (3H, s), 3.54 (1H, s), 4.50 (2H, d, *J* = 6.0 Hz), 6.75–7.38 (5H, m) 8.23 (1H, b.m.). ^{19}F NMR δ −80.1 (s). ^{13}C NMR δ 20.3 (d, *J* = 1 Hz), 44.1, 74.5 (q, *J* = 29 Hz), 124.1 (q, *J* = 285 Hz), 127.5, 127.9, 128.9, 136.9, 168.2. HRMS (TOF) $[M+H]^{+}$, cald for $[C_{11}H_{12}F_3NO_2+H]^{+}$: 248.0898, found: 248.1299. mp of racemate: 79 °C, mp of chiral isomer: 71 °C.

3.6. N-tert-Butyl-α-trifluoromethyllactyl amide (3d)

^{1}H NMR in $CDCl_3$ δ 1.39 (9H, s), 1.56 (3H, s), 4.29 (1H, s), 6.01 (1H, s). ^{19}F NMR δ −80.2 (s). ^{13}C NMR δ 20.2 (d, *J* = 1 Hz), 28.3, 52.1, 74.2 (q, J = 29 Hz), 124.2 (q, J = 285 Hz), 167.2. HRMS (TOF) $[M+H]^+$, cald for $[C_8H_{14}F_3NO_2+H]^+$: 214.1055, found: 214.1336. mp of racemate: 125 °C, mp of chiral isomer: 133 °C.

3.7. Determination of rates of sublimation of (R/S)- and (S)-3 on a Petri dish

Sublimation experiment of (*R*/*S*)- and (*S*)-**3** was conducted on a Petri dish (surface area: 20.25π cm^2) at 80 °C for **3a**,**b** and 60 °C for **3c** under atmospheric pressure. Since sublimation rates are affected by various physical factors such as temperature and wind, the experiments with racemate and optically pure compounds were conducted at the same time. After a long time sublimation, time dependent loss of the remainder started curving because the surface area became uneven. Therefore, for the determination of sublimation rates in Table 2, initial rates were used.

3.8. General SDE via sublimation experimental procedure

Just prior to the start of the experiments, various optically enriched samples were prepared by simply mixing racemate and optically pure crystals in appropriate amounts and well grinding of the mixture, following which the optical purity was measured. The optically enriched sample was spread on a Petri dish as flat as possible, and sublimation experiments conducted under atmospheric pressure at 80 °C for **3a**,**b**, 60 °C for **3c** and rt for **3d**. After certain amount of time, the sample (ca. 0.01 g) of the remaining crystals on the Petri dish was taken for determination of its enantiomeric composition. Before the sampling, the remaining crystals on the Petri dish were carefully agitated with a spatula to provide for an even and homogeneous distribution of the remaining compound.

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[11] The term "racemate" as used in this paper refers to crystalline racemate in which the two enantiomers are present in equal quantities in the crystallographic unit. It does not refer the case of conglomerate that is a mechanical mixtures of two pure enantiomers.

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