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Resolution of 1-[2-carboxy-6-(trifluoromethyl)phenyl]-1*H*-pyrrole-2-carboxylic acid with methyl (*R*)-2-phenylglycinate, reciprocal resolution and second order asymmetric transformation

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ABSTRACT

A novel, highly efficient method has been developed for the separation of the optical isomers of 1-[2-carboxy-6-(trifluoromethyl)phenyl]-1*H*-pyrrole-2-carboxylic acid with methyl (*R*)-2-phenylglycinate. The structural aspects of chiral discrimination have been discussed via comparison of the molecular structures and the packing energies of the diastereoisomeric salts determined by single crystal X-ray diffraction measurements. Reciprocal resolution and a new, highly efficient second order asymmetric transformation of racemic methyl 2-phenylglycinate with the pure enantiomer of the previously resolved atropisomeric carboxylic acid are also reported.

1. Introduction

1-Phenylpyrrole derivatives are known as important building blocks for antibiotics,[1,2] antiviral,[3] and cytostatic[4] compounds. Recently, mineralcorticoid receptor antagonist effects of atropisomeric 1-phenylpyrrole derivatives have been recognized.[5] Optically active 1-phenylpyrrole derivatives have also been used as chiral reagents, ligands, and organocatalysts.[6] A useful intermediate of the synthesis of atropisomeric 1-phenylpyrrole derivatives was prepared several years ago in our laboratory. The pure enantiomers of 1-[2-carboxy-6-(trifluoro-methyl)phenyl]-1*H*-pyrrole-2-carboxylic acid **1** were prepared from the racemate via diastereoisomeric salt formation which is one of the easiest methods for the separation of carboxylic acid enantiomers.[7] (*R*)-α-Methylbenzylamine **2**, (*S*)-α-naphthylethylamine, (*S*)-α-hydroxymethylbenzylamine, and (*R*,*R*)-2-amino-1-phenyl-1,3-propanediol were tested for the separation of the isomers of **1**, and the best result was achieved with (*R*)-α-methylbenzylamine. In this case the efficiency ('*S*') of the resolution ('*S*' = yield × ee × 0.01)[8] of (*R*)-**1** was about 0.28 (ee 95%, yield 30%) and the single enantiomer of **1** could only be obtained after recrystallization of the primary diastereoisomeric salt causing a further decrease in the yield. The absolute configuration of the carboxylic acid enantiomers was determined from the single crystal X-ray diffraction measurements of the diastereoisomeric salts.[7]

In order to find a more efficient resolution method for racemic dicarboxylic acid **1**, detailed experimental studies were carried out and are reported herein.

2. Results and discussion

2.1. Highly selective method for the resolution of (*R*,*S*)-1

As a result of resolution trials, we have found that methyl (*R*)-2-phenylglycinate (*R*)-**3** was a much better resolving agent for **1** than amine **2**. Diastereoisomeric salt formation was accomplished in ethanol and after 2 h of crystallization, the precipitated diastereoisomeric salt contained the (−)-(*S*)-**1** enantiomer in excellent enantiomeric purity (ee >96%). The optically active acid was liberated in a dichloromethane/water mixture with aqueous sodium carbonate followed by phase separation. Compound (*S*)-**1** was isolated from the aqueous solution by acidification with 15% hydrochloride acid solution and filtration in good yield (Scheme 1).

The (*R*)-**1** isomer (ee >99%) was obtained by recrystallization of (*R* > *S*)-**1** (ee 80%), which was regenerated from the filtrate of the salt formation reaction. The recrystallization was carried out in ethyl acetate. The resolving agent could also be regenerated from the organic phases of the diastereoisomeric salt decomposition and the filtrate decomposition in good yield (85%).

The effect of the amount of resolving agent was also studied. The results are collected in Table 1. We observed that better enantiomer separation could be achieved with an equivalent amount of resolving agent than with the half equivalent method. The

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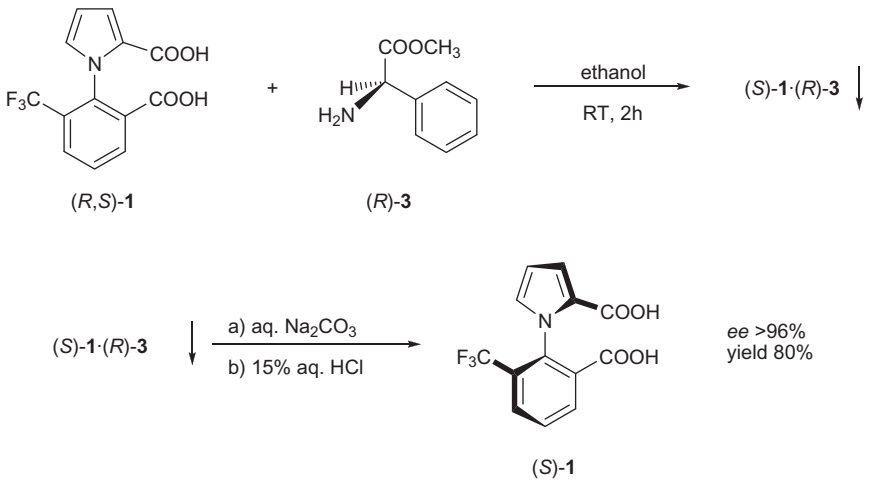


Scheme 1. Resolution of racemic **1** with methyl (*R*)-2-phenylglycinate (*R*)-**3**.

Table 1
Resolution of **1** in case of different molar ratios[a]

Resolving agent	Molar ratio	Diastereoisomeric salt		Efficiency ('*S*')
		Yield[b] (%)	de (config)[c] (%)	
(*R*)-**3**	1:0.5	70	95 (*S*)	0.67
(*R*)-**3**	1:1	85	96 (*S*)	0.82

[a] Crystallization was carried out for 2 h in ethanol.
[b] Yields were calculated to the half of the racemate.
[c] Configuration of **1** in the diastereoisomeric salt.

efficiency of the optimized resolution was high ('*S*' = 0.82), with it being almost three times better than the previously reported method.

2.2. Single-crystal X-ray diffraction, PXD and DSC studies

Previous X-ray studies proved the absolute configuration of the (+)-(*R*)-**1**·(*R*)-**2**[7] salt.

We prepared single crystals from the new (*S*)-**1**·(*R*)-**3** diastereoisomeric salt for X-ray studies by crystallization from methanol. The structure of the (*S*)-**1**·(*R*)-**3** salt is shown in the ORTEP-like diagram[9] in Figure 1. To compare the crystal structure of these two diastereoisomeric salts, one has to invert the (+)-(*R*)-**1**·(*R*)-**2**[7] structure into the mirror image (*S*)-**1**-(*S*)-**2** structure. Such a comparison may shed some light on the details of the chiral discrimination process during separation of the atropisomers of **1**.

Unit cell data for these crystals can be seen in Table 2, and include the previously reported (*R*)-**1**·(*R*)-**2** salt. From a comparison of the two data series, the similarity of the two diastereoisomeric salt crystals is apparent. It is noteworthy that the (*S*)-**1**·(*R*)-**3** salt has a larger density indicating a somewhat bigger thermodynamic stability.

The packing energies[10,11] were calculated[12] for the (*S*)-**1**·(*R*)-**3** and (*S*)-**1**·(*S*)-**2** salts as well using normalized hydrogen positions. The total packing energy is −272.7 kJ/mol in the (*S*)-**1**·(*R*)-**3** crystal, while it is −250.8 kJ/mol in the (*S*)-**1**·(*S*)-**2** case. The total packing energy difference of 21.9 kJ/mol between the two crystal structures is partitioned the following way. The **1** molecules have a similar interaction energies (−151.3 and −156.7 kJ/mol) in the two crystal. However, the difference is larger between the two cationic components **3** (−116.0 kJ/mol) and **2** (−99.5 kJ/mol), amounting to approximately 2/3rd of the total energy difference between the two salt pairs crystal structures. Thus the chemical change from α-methylbenzylamine **2** for the phenylglycine methyl ester **3** is re-

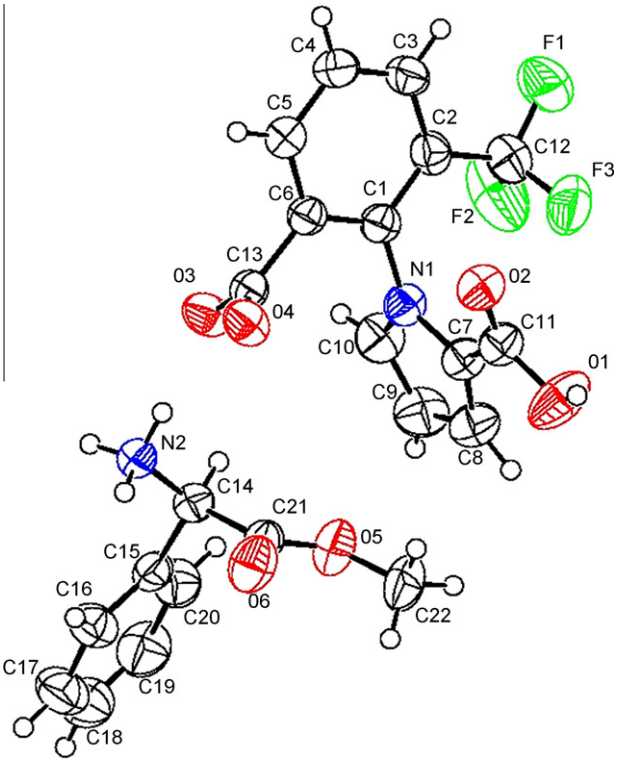


Figure 1. (*S*)-**1**·(*R*)-**3** salt crystal structure with atomic numbering and 50% probability anisotropic displacement ellipsoids for non-H atoms.[9]

Table 2
Crystallographic cell data for (*S*)-**1**·(*R*)-**3** and (*R*)-**1**·(*R*)-**2** crystals

	(*S*)-**1**·(*R*)-**3**	(*R*)-**1**·(*R*)-**2**[7]
Formula	$C_{22}H_{19}F_3N_2O_6$	$C_{21}H_{19}F_3N_2O_4$
Molecular weight	464.39	420.38
Space group	$P2_1$	$P2_1$
a (Å)	11.9804(5)	12.3977(12)
b (Å)	7.8115(3)	7.4905(14)
c (Å)	12.9927(5)	12.5196(14)
β (°)	118.25(2)	118.95(6)
V (Å^3)	1071.1(1)	1017.4(2)
Z	2	2
D_x (g cm^{-3})	1.440	1.372

flected in the respective packing energies of the crystals. It seems that the resolution effectivity may be correlated to the packing energy differences, with the (*S*)-**1**·(*R*)-**3** crystal structure being more stable by ca. 22 kJ/mol than the (*S*)-**1**·(*S*)-**2** one. A comparison of the related molecular positions from a fit of 13 C and N atoms of **1** molecules of the two crystal structures also shows distinct changes in the substituent alignments, although the salt H-bridges are virtually identical in terms of geometry and energy aspects (Fig. 2).

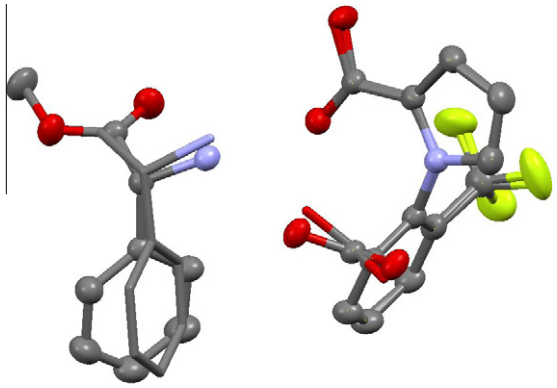


Figure 2. The overlay fit[10] of all C and N atoms of (*S*)-**1** and the inverted (*R*)-**1** from the (*S*)-**1**·(*R*)-**3** and from the inverted (*R*)-**1**·(*R*)-**2** salt. The former salt pair is shown with 30% displacement probabilities, while the latter is a stick model.[9]

Attempts to prepare single crystals from the more soluble (*R*)-**1**·(*R*)-**3** salt were unsuccessful, as amorphous solid material was formed during the evaporation of the solvent under reduced pressure. Differences between (*S*)-**1**·(*R*)-**3** and (*R*)-**1**·(*R*)-**3** diastereoisomeric salts were investigated by powder XRD and DSC methods. Powder XRD studies of the salts have shown that (*R*)-**1**·(*R*)-**3** is amorphous having no peaks in the diffractogram, however the powder XRD analysis curve of the (*S*)-**1**·(*R*)-**3** salt suggests a crystalline solid (Fig. 3).

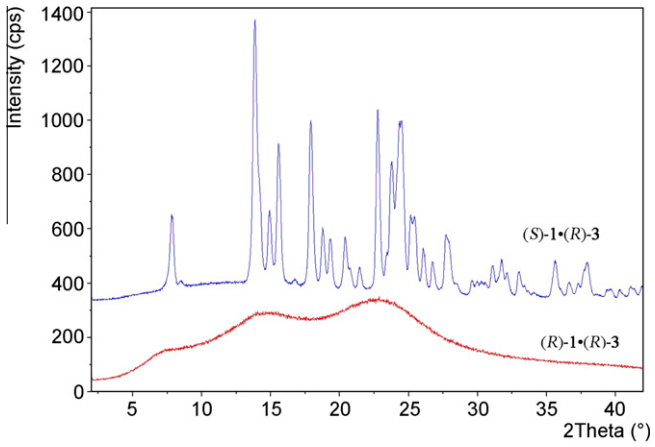


Figure 3. The powder XRD spectrum of (*S*)-**1**·(*R*)-**3** and (*R*)-**1**·(*R*)-**3** salts.

The measured and the calculated powder XRD analysis curves show a good agreement. From the DSC studies, similar results were obtained. The less soluble (*S*)-**1**·(*R*)-**3** salt melted at 191 °C, but it decomposed before completion of the melting. The DSC analysis curve of (*R*)-**1**·(*R*)-**3** salt showed a small, wide endothermic peak followed by a big exothermic peak at about 120 °C. This means that this salt decomposed at a much lower temperature than the less soluble one. Such a difference between the two diastereoisomeric salts (*S*)-**1**·(*R*)-**3** and (*R*)-**1**·(*R*)-**3** clarify the observed high efficiency of the new resolution method.

2.3. Effect of the duration of the crystallization on the efficiency of the resolution

We observed that the enantiomeric excess of **1** in the crystalline diastereoisomeric salt strongly depends on the duration of the crystallization. Thus, practically pure (−)-(*S*)-**1** (ee >96%) could be isolated when the salt was filtered off after 2 h, while the ee decreased with increasing crystallization time and racemic **1** was isolated from the salt after 2 weeks.

In order to determine the process of the decreasing enantiomeric purity and the optimal duration of the crystallization a series of experiments were carried out. We found that the enantiomeric excess is very good and in fact increased slightly over a short period; however after 8 h the ee decreased dramatically. After 330 h, the enantiomeric purity was only 4.7% (Fig. 4 and Table 3).

The observed phenomenon can be rationalized by taking into consideration the stereochemical stability of the resolving agent (*R*)-**3**. It is known from the literature that the esters of 2-phenylglycine are stable *in substantia* but slow racemisation occurs in solution, in the presence of acids (e.g., tartaric acid).[13] The rate of racemisation dramatically increases if the amino group is converted into a Schiff base (the addition of acetone or other oxo compounds into the reaction mixture).[13,14]

Under the applied experimental conditions, racemisation of compound **3** was observed without changing the stoichiometry of the diastereoisomeric salt. A 1:1 mixture of (*S*)-**1**·(*R*)-**3** and

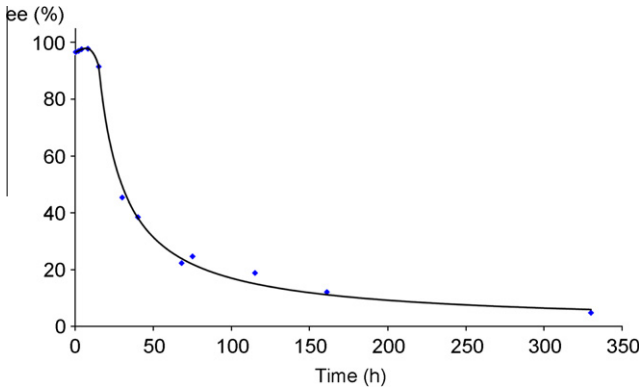


Figure 4. Effect of the duration of the crystallization on the ee of (*S*)-**1** in the (*S*)-**1**·(*R*)-**3** salt.

Table 3
Change of the ee of (*S*)-**1** in the diastereoisomeric salt (*S*)-**1**·(*R*)-**3** during crystallization

Time[a] (h)	ee[b] (%)	'S'
0.25	96.6	0.82
1	97	0.81
4	97.6	0.82
8	97.8	0.82
15	91.5	0.77
30	45.3	0.49
40	38.5	0.40
68	22.3	0.25
75	24.6	0.32
115	18.8	0.23
161	12.1	0.14
330	4.7	0.05

[a] Independent experiments.
[b] ee was determined by HPLC analysis using a chiral stationary phase (Chiralpak AD–H).

(*R*)-**1**·(*S*)-**3** salts was in the solid phase after a prolonged crystallization time. It should be mentioned that the transesterification of compound **3** did not occur in the ethanolic solution within the 161 h reaction time.

2.4. Application of optically active 1 as a resolving agent

In reciprocal resolution the roles of substrate and resolving agent are interchanged, that is resolution of a racemic mixture of a compound used in the primary process as the resolving agent is attempted with one of the enantiomers of the compound, which had been originally subjected to resolution.

Reciprocal resolution of (*R*,*S*)-**3** with (*S*)-**1** was accomplished in methanol. When the diastereoisomeric salt was filtered after 2.5 h of crystallization, the enantiomeric excess was moderate and the yield was poor. When increasing the duration of the crystallization the diastereoisomeric salt contained more of the (*R*)-**3** enantiomer. Finally, after 360 h the salt crystallized in good yield and it contained practically pure (*R*)-**3** (ee 99%, Scheme 2).

Higher than 50% yield of the diastereoisomeric salt (in this case the yield was calculated with regards to the whole amount of the racemate) was due to a second order asymmetric transformation of **3**. In order to improve the yield of the diastereoisomeric salt (*S*)-**1**·(*R*)-**3**, further studies were carried out by changing the solvent. We found that the yield of the desired salt was at its highest when toluene was used as a solvent; the addition of acetone accelerated the racemisation of methyl (*S*)-2-phenylglycinate resulting in better enantiomeric excesses in the crystallized diastereoisomeric salt. When 30% of acetone was used, the enantiomeric purity of (*R*)-**3** was higher, however the yield decreased. The addition of 10% of water resulted in 92% yield and the ee of (*R*)-**3** in the salt was as high as it was in the absence of water ('*S*' = 0.87). The results of the reciprocal resolution and the second order asymmetric transformation are summarized in Table 4.

From the experimental data we concluded that optically active **1** can be used as an efficient resolving agent for the separation of methyl 2-phenylglycinate enantiomers and the second order asymmetric transformation could be achieved by prolonged reaction time or by the addition of acetone into the reaction mixture. The atropisomeric dicarboxylic acid was stereochemically stable under the conditions of the second order asymmetric transformation (40 °C, 40 h) and it was regenerated in good yield. The optimal conditions of such a transformation were a toluene–acetone–water solvent mixture, 20 h and 40 °C. Under these conditions we obtained (*R*)-**3** from the crystalline diastereoisomeric salt in 92% yield and >95% enantiomeric excess. The mechanism of this second order asymmetric transformation with an equivalent amount of optically active **1** related to the racemate of methyl 2-phenylglycinate is shown in Scheme 3.

3. Conclusion

On the basis of our experimental results, we conclude that 1-[2-carboxy-6-(trifluoromethyl)phenyl]-1*H*-pyrrole-2-carboxylic acid **1** and methyl 2-phenylglycinate **3** are good resolving agents for each other. Within this pair of compounds, the stereochemical stability of **3** determines the applicable duration of the crystallization of the diastereoisomeric salts, and it can be used to govern the outcome of the resolution processes.

Thus, one should separate the crystalline diastereoisomeric salt from the reaction mixture of (*R*,*S*)-**1** and (*R*)-**3** within 2–3 h in order to obtain the (*S*)-**1**·(*R*)-**3** diastereoisomeric salt in high de. In this case, the efficiency of the resolution is excellent ('*S*' = 0.87), much better then that of the previously published method, where (*S*)- or (*R*)-**2** was used as resolving agent ('*S*' = 0.28). A comparison of the X-ray crystal structures and the packing energies of the two diastereoisomeric salts (*S*)-**1**·(*R*)-**3** and (*S*)-**1**·(*S*)-**2** showed a very similar H-bridge system in the salts and larger packing energy difference between the cationic species of the salts. Furthermore, the diastereoisomeric pair, that is (*R*)-**1**·(*S*)-**2** of (*S*)-**1**·(*S*)-**2** could easily be isolated in crystalline form while the diastereoisomeric pair, that is (*R*)-**1**·(*R*)-**3** of (*S*)-**1**·(*R*)-**3** remained amorphous under the conditions investigated, showing a bigger difference between the latter mentioned pairs of diastereoisomeric salts. All of the above mentioned differences may explain the much higher efficiency of the resolution accomplished with (*R*)-**3** compared to the previously described one (with (*S*)-**2**).

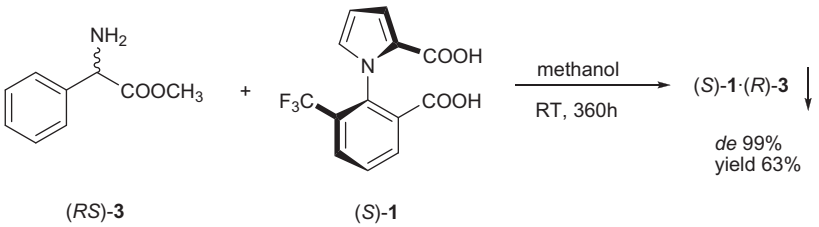
On the other hand, the reciprocal resolution and, as a more useful method, second order asymmetric transformation of (*R*,*S*)-**3** with a pure enantiomer of **1**, could be accomplished when a prolonged crystallization time was used and/or the racemisation of the enantiomers of **3** was accelerated with an additive (acetone), in toluene solution. Practically pure (*R*)-**3** (ee >95%) could also be isolated from the diastereoisomeric salt in high yield (92%, calculated to the whole amount of racemic **3**) when the reaction mixture contained 10% of water.

All of the aforementioned results demonstrate that optically active atropisomeric dicarboxylic acid **1** can be prepared easily and, in addition to its application as a chiral precursor of other atropisomeric 1-phenylpyrrole derivatives,[6] it can also be used as an excellent resolving agent.

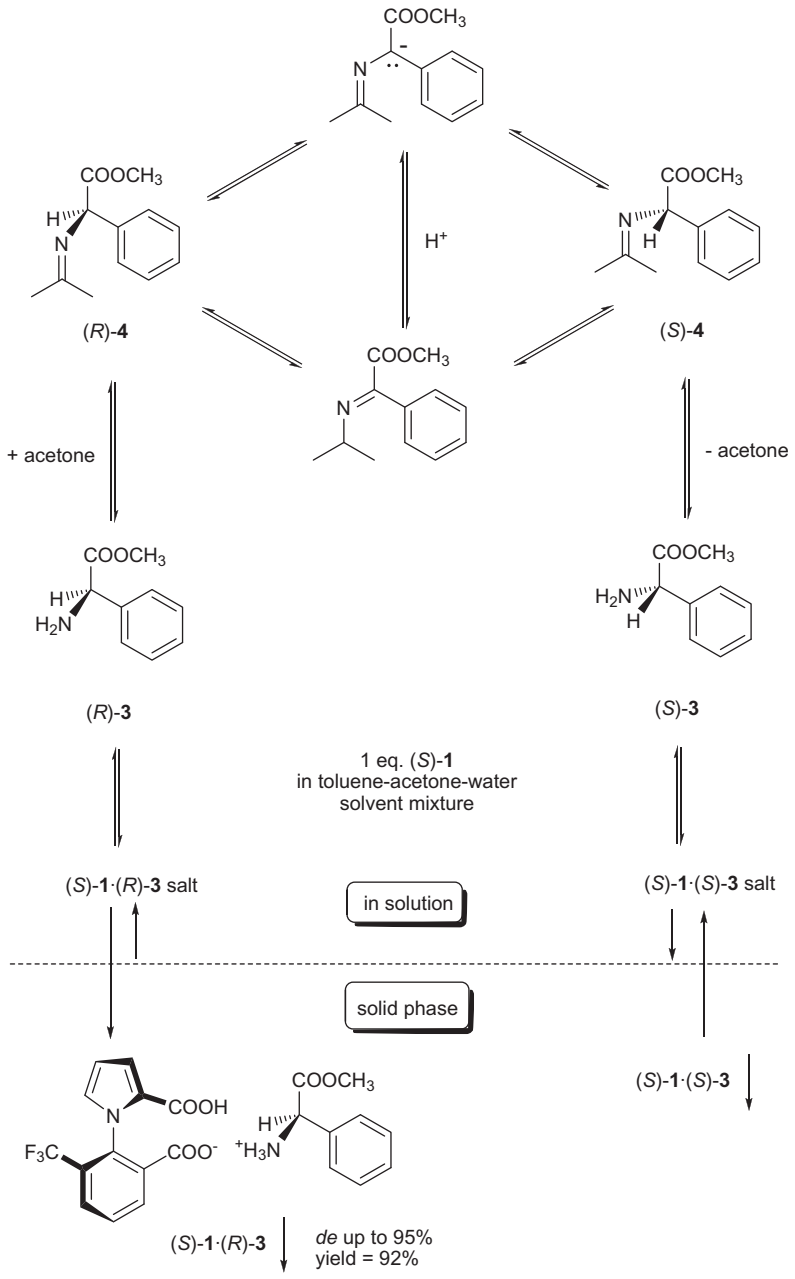
Table 4
Results of the reciprocal resolution and the second order asymmetric transformation of (*R*,*S*)-**3**[a]

Entry	Solvent	Yield[b] (%) (*S*)-**1**·(*R*)-**3**	ee[c] (%) (*R*)-**3**	Time (h)	'*S*'
1[e]	MeOH	40[d]	83	2.5	0.33
2[e]	MeOH	63	99	360	0.62
3	Tol/Ac 10/3	95	50	3	0.48
4	Tol/Ac 10/3	95	90	20	0.86
5	Tol/Ac 10/3	96	90	40	0.86
6	Tol/Ac 10/4	86	93	20	0.82
7	Tol/Ac 10/5	82	95	20	0.78
8[f]	Tol/Ac 10/5	92	95	20	0.87

[a] All reactions were carried out in 0.34 M solution at 40 °C.
[b] Yield was calculated to the whole amount of the racemate.
[c] ee was determined by HPLC analysis using a chiral stationary phase (Kromasil 5-AmyCoat).
[d] Yield was calculated to the half of the racemate.
[e] 25 °C.
[f] 10 mol % water was added.



Scheme 2. Reciprocal resolution of racemic **3** with an equivalent amount of (*S*)-**1**.



Scheme 3. Second order asymmetric transformation of methyl 2-phenylglycinate **3**.

4. Experimental

4.1. General

All commercial starting materials were purchased from Sigma–Aldrich and Merk-Schuchardt and were used without further purification.

Routine ^{1}H NMR spectra were recorded in DMSO-d_6 solution on a BRUKER AV 300 spectrometer. Proton chemical shifts are reported in ppm relative to the solvent (δ_{DMSO} = 2.50 ppm). IR spectra were recorded on an appliance type PERKIN ELMER 1600 with a Fourier Transformer. Data are given in cm^{-1}. The specific rotations of the optically active samples were determined on a PERKIN ELMER 245 MC polarimeter using a sodium lamp (589 nm).

Powder X-ray diffraction patterns were recorded with a PANalytical X'pert Pro MPD (PANalytical Bv., The Netherlands) multipurpose X-ray diffractometer using Cu-K$_\alpha$ radiation, Ni filter, X'celerator detector, and 'zero background' single crystal silicon sample holder in the range of $2\theta = 2$–42°. Differential scanning calorimetry (DSC) measurements were performed using a DSC 2920 device (TA Instruments Inc., USA). The samples (1–8 mg) were measured in sealed Al-pans at a heating rate of 10 K/min.

4.2. Resolution of dicarboxylic acid 1; a typical example

Racemic dicarboxylic acid **1** (0.5 g, 1.67 mmol) was dissolved in ethanol (5 mL) and methyl (*R*)-2-phenylglycinate (0.276 g, 1.67 mmol) was added to it. The clear solution of the mixture was stirred at room temperature and after a short time it was seeded with the crystals of the (*S*)-**1**·(*R*)-**3** salt. The diastereoisomeric salt was filtered off after 2 h crystallization. The crystals were washed with cold ethanol and dried to yield 0.33 g of a white solid (85%).

The salt was suspended in water (1 mL) and a saturated sodium carbonate solution (5 mL) was poured into it. The resolving agent was extracted with dichloromethane (3 × 5.0 mL), then the aqueous solution was acidified with hydrochloric acid solution until pH 1. After half an hour of stirring at 5 °C, the precipitate was filtered off, washed with ice water and dried. Thus optically active **1** was obtained (0.20 g, 80%, ee 96%), $[\alpha]_D^{25} = -43.1$ (*c* 1.0, EtOH).

The optically active dicarboxylic acid samples **1** were quantitatively converted into their bismethyl esters before HPLC analysis. HPLC measurements were carried out on Chiralpak AD–H column (5 μm, 250 × 4.6 mm), eluent hexane/2-propanol = 98/2, 0.8 mL/min, UV detector 256 nm, 20 °C, retention time for (*S*)-**1** ester: 9.8 min, for (*R*)-**1** ester: 11.3 min.

4.2.1. 1-[2-Carboxy-6-(trifluoromethyl)phenyl]-1*H*-pyrrole-2-carboxylic acid methyl 2-phenylglycinate salt (after 161 h crystallization)

IR (KBr, cm^{-1}): 3481, 3122, 2854, 2635, 2502, 2080, 1994, 1750, 1676, 1529, 1433, 1316, 1252, 1131. ^1H NMR (DMSO-d_6, 300 MHz) δ_H (ppm): 7.94 (1H, d, *J* = 7.8 Hz), 7.90 (1H, d, *J* = 7.8 Hz), 7.41–7.35 (5H, m), 6.81 (1H, s), 6.74 (1H, dd, *J* = 2.1, 3.3 Hz), 6.19 (1H, t, *J* = 3.2 Hz), 4.89 (1H, s), 3.65 (3H, s). Anal. Calcd for $C_{22}H_{19}F_3N_2O_6$ (464.39): C, 56.90; H, 4.12; N, 6.03. Found: C, 56.86; H, 3.90; N, 6.13.

4.3. Enantiomeric enrichment of the dicarboxylic acid 1 from the filtrate of the resolution; a typical example

An enantiomeric mixture of (*R* > *S*)-**1** was isolated from the filtrate of the diastereoisomeric salt formation reaction. The solvent was evaporated, and the residue was worked up in an analogous way to the work-up procedure of the crystalline diastereoisomeric salt (see Section 4.2). Pure (*R*)-**1** isomer was obtained by recrystallization of (*R* > *S*)-**1** (0.25 g, 0.84 mmol, ee 80%) from ethyl acetate (1 mL). The crystalline product was 0.185 g (74%, ee >99%).

4.4. Second order asymmetric transformation of methyl 2-phenylglycinate 3; a typical example

Racemic methyl 2-phenylglycinate **3** (0.276 g, 1.67 mmol) was dissolved in toluene (3 mL) and (*S*)-1-[2-carboxy-6-(trifluoromethyl)phenyl]-1*H*-pyrrole-2-carboxylic acid (*S*)-**1** (0.5 g, 1.67 mmol, ee >99%) in acetone (1.5 mL) was added to it. Water (0.5 mL) was poured into the reaction mixture and stirred at 40 °C. The diastereoisomeric salt (*S*)-**1**·(*R*)-**3** was filtered off after 20 h. The crystals were washed with toluene and dried to yield 0.714 g of a white solid (92%).

The salt was suspended in water (2 mL) after which saturated sodium carbonate solution (10 mL) was added. Amine was extracted with dichloromethane (3 × 8.0 mL) and then the organic phase was dried over sodium sulfate. The organic solvent was evaporated. Thus optically active **3** was obtained (0.248 g, 90%, ee 95%), $[\alpha]_D^{25} = -154$ (*c* 1.0, EtOH).

The filtrate of the diastereoisomeric salt formation was concentrated under reduced pressure and then was added to an aqueous solution of the salt decomposition. It was then acidified with hydrochloric acid until pH 1. After half an hour of stirring at 5 °C, the precipitate was filtered off, washed with ice water and dried. Thus optically active **1** was recovered (0.45 g, 90%, ee >99%).

The HPLC measurements of optically active amino ester samples **3** were carried out on Kromasil 5-AmyCoat column (5 μm, 250 × 4.6 mm), eluent hexane/2-propanol = 90/10, 0.5 mL/min, UV detector 222 nm, 20 °C, retention time for (*S*)-**3**: 18.4 min., for (*R*)-**3**: 22.0 min.

4.5. Crystal structure determination

A selected single crystal (0.4 × 0.3 × 0.2 mm) of (*S*)-**1**·(*R*)-**3** was mounted on a Rigaku R-AXIS RAPID diffractometer (graphite monochromator Cu-K_α radiation, $\lambda = 1.54187$ Å). Data collection was performed at room temperatures ($T = 295 \pm 2$ K). Crystal data for (*S*)-**1**·(*R*)-**3**: $C_{22}H_{19}F_3N_2O_6$, Fwt.: 464.39, colorless, chunk, monoclinic, space group $P2_1$, $a = 11.9804(5)$ Å, $b = 7.8115(3)$ Å, $c = 12.9927(5)$ Å, $\beta = 118.252(2)°$, $V = 1071.07(7)$ Å^3, $Z = 2$, $D_x = 1.440$ g/cm^3. Initial structure model was obtained by SHELXS-97, completed by successive difference Fourier syntheses and refined to convergence by SHELXL-97.[15] Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded $R_1 = 0.0356$ and $wR^2 = 0.0982$ for 1332 [$I > 2s(I)$] and $R_1 = 0.0375$ and $wR^2 = 0.1002$ for all (3395) intensity data, (number of parameters = 302, goodness-of-fit = 1.070, extinction coefficient = 0.0052(7), absolute structure parameter $x = 0.05(15)$).

CCDC 844299 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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