Tetrahedron: *Asymmetry* xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Acylative kinetic resolution of racemic heterocyclic amines with (*R*)-2-phenoxypropionyl chloride

Sergey A. Vakarov [a], Dmitry A. Gruzdev [a], Evgeny N. Chulakov [a], Liliya Sh. Sadretdinova [a], Andrey A. Tumashov [a], Marina G. Pervova [a], Marina A. Ezhikova [a], Mikhail I. Kodess [a,b], Galina L. Levit [a,*], Victor P. Krasnov [a], Valery N. Charushin [a,b]

[a] *Postovsky Institute of Organic Synthesis of RAS (Ural Branch), 22/20 S. Kovalevskoy/Akademicheskaya St., Ekaterinburg 620990, Russia*
[b] *Ural Federal University, 19 Mira St., Ekaterinburg 620002, Russia*

ARTICLE INFO

Article history:
Received 31 August 2016
Accepted 7 October 2016
Available online xxxx

ABSTRACT

The acylative kinetic resolution of racemic heterocyclic amines such as 3,4-dihydro-3-methyl-2*H*-[1,4]benzoxazines, 3,4-dihydro-3-methyl-2*H*-[1,4]benzothiazine, 2-methyl-1,2,3,4-tetrahydro-quinolines and 2-methylindoline with enantiopure (*R*)-2-phenoxypropionyl chloride has been studied. It has been found that acylation of 3,4-dihydro-3-methyl-2*H*-[1,4]benzothiazine proceeds with the best stereoselectively when compared with other racemic amines. An efficient method for the preparation of (*S*)-3,4-dihydro-3-methyl-2*H*-[1,4]benzothiazine (99.4% *ee*) via a kinetic resolution protocol was developed. The possibility of recycling (*R*)-2-phenoxypropionic acid has been demonstrated.

1. Introduction

The development of efficient methods for the synthesis of enantiopure amines is one of the priorities of modern organic synthesis. In order to obtain individual enantiomers, the kinetic resolution of a racemate is often used. Kinetic resolution is based on the difference in the reaction rates of individual enantiomers with a chiral non-racemic agent.[1] This approach allows for stereoisomerically enriched reaction products and an unreacted substrate to be obtained. The kinetic resolution of racemic amines is most frequently carried out by acylation in the presence of enzymes and synthetic acyl-transfer catalysts, as well as under the action of chiral acylating agents.[2]

Over the last few years, we have performed a detailed study on the acylative kinetic resolution of racemic amines over the course of diastereoselective acylation with acyl chlorides of chiral acids, such as 2-arylpropionic acids[3] and *N*-protected amino acids.[4] Recently, we have demonstrated that the acylation of racemic amines **1a** and **1b** with racemic 2-phenoxy carbonyl chlorides **2a–c** (Scheme 1) proceeds with high diastereoselectivity,[5] exceeding that in the acylation of the studied amines with 2-arylpropionyl chlorides. Thus, the diastereoisomeric ratio (*dr*) of the amide formed reached 499 in the acylation of racemic amine **1a** with acyl chloride **2b** in toluene at −20 °C.[5] It should be noted that 2-phenoxypropionyl chloride **2a**, the derivative of L-lactic acid, is the most easily available in enantiomerically pure form among the studied 2-phenoxy carbonyl chlorides.

Herein our aim was to study the kinetic resolution of racemic heterocyclic amines **1a–f** with enantiopure (*R*)-2-phenoxypropionyl chloride (*R*)-**2a**, as well as the possibility of the preparation of some enantiomerically pure amines via a kinetic resolution protocol with acyl chloride (*R*)-**2a** (Scheme 1).

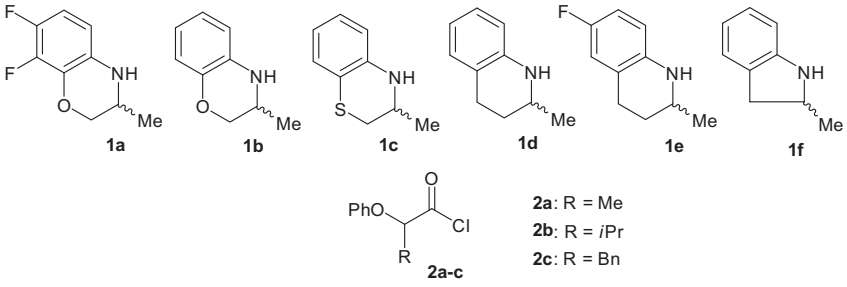
2. Results and discussion

In order to obtain enantiopure amines (*ee* >99%) via kinetic resolution with chiral resolving agents, the latter are required to be of a particularly high enantiomeric purity, therefore, we have developed a process for the preparation of enantiopure (*R*)-2-phenoxypropionic acid (*R*)-**5** (Scheme 2).

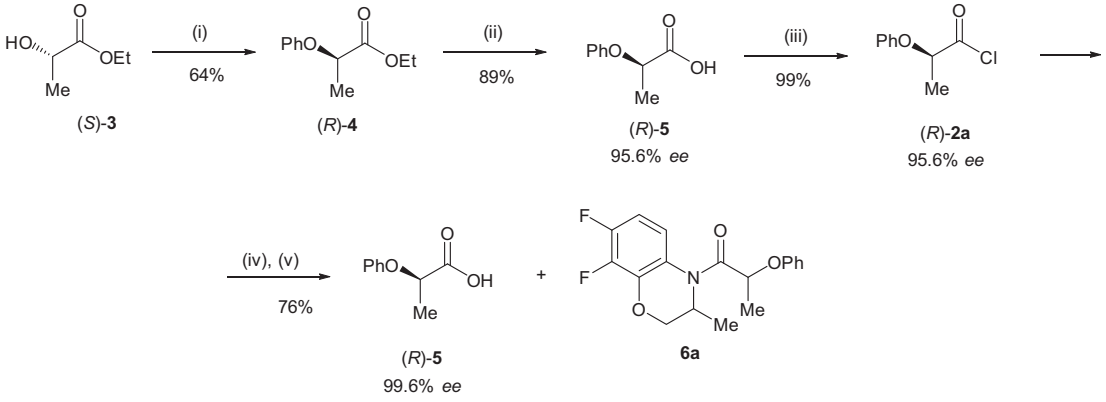
Commercially available enantiomerically pure ethyl L-lactate (*S*)-**3** was used as the starting material; the interaction of compound (*S*)-**3** with phenol in the presence of diisopropyl azodicarboxylate (DIAD) and triphenylphosphine by the Mitsunobu reaction (Scheme 2) resulted in ethyl (*R*)-2-phenoxypropionate (*R*)-**4**. It is known that this approach allows for the esters of (*R*)-2-aryloxy carboxylic acids to be obtained with high enantiomeric purity.[6] The alkaline hydrolysis of compound (*R*)-**4** afforded acid (*R*)-**5** with 95.6% *ee* according to the chiral HPLC (Chiralpak AD column). Thus, minor racemization was observed over the course of the Mitsunobu reaction between ethyl L-lactate

* Corresponding author.
E-mail address: ca512@ios.uran.ru (G.L. Levit).

http://dx.doi.org/10.1016/j.tetasy.2016.10.004
0957-4166/



Scheme 1. Racemic amines **1a–f** and 2-phenoxy carbonyl chlorides **2a–c**.



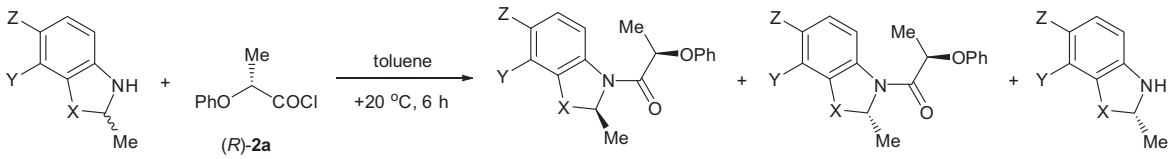
Reagents and conditions: (i) PhOH, DIAD, PPh_3, toluene; (ii) 2M NaOH, EtOH, 4 °C, 24 h; (iii) $(COCl)_2$, CH_2Cl_2, rt; (iv) *rac*-**1a** (0.15 equiv.), $PhNEt_2$ (0.15 equiv.), toluene, rt; (v) Na_2CO_3, H_2O-MeOH

Scheme 2. Preparation of enantiopure (*R*)-2-phenoxypropionic acid (*R*)-**5**.

and phenol and subsequent alkaline hydrolysis of the ester group. Therefore, we studied the possibility of enantiomeric enrichment of scalemic acid (*R*)-**5**. We examined two methods. The first consisted of the double recrystallization of sodium salt of acid (*R*)-**5** from acetone similar to the described procedure.[7] As a result, enantiopure acid (*R*)-**5** (99.4% *ee*) was isolated in low yield (17%).

The second approach was based on the reaction of acyl chloride (*R*)-**2a** [obtained from acid (*R*)-**5** (95.6% *ee*)] with a lack of racemic amine **1a** (0.15 equiv) in the presence of *N*,*N*-diethylaniline ($PhNEt_2$, 0.15 equiv) as an acceptor of HCl (Scheme 2). A theoretical rationale of the possibility of increasing the *ee* value of an enantioimpure substance using a racemic reagent in kinetic resolution was provided.[8] In our case, the formation of a mixture of diastereoisomeric amides **6a** occurred, and acyl chloride (*R*)-**2a** taken in an excess remained unreacted. After isolation of unreacted (*R*)-**2a** from the reaction mixture and subsequent treatment with aqueous solution of Na_2CO_3, we obtained acid (*R*)-**5** (99.6% *ee*, 76% yield), which was further used as a chiral resolving agent.

The acylation of racemic amines **1a–f** with acyl chloride (*R*)-**2a** was carried out in a 2:1 amine:acyl chloride molar ratio at +20 °C for 6 h (Scheme 3). The initial concentration of racemic amine was 0.1 M. Each experiment was carried out in two parallel runs. Previously we have shown that toluene is the solvent of choice for the kinetic resolution of racemic methylbenzoxazines **1a** and **1b** with 2-phenoxy carbonyl chlorides;[5] hence the acylation was carried out in that solvent. After the appropriate treatment, mixtures of diastereoisomeric amides **6a–f** and unreacted enantiomerically enriched amines **1a–f** were isolated from the reaction mixture. The diastereomeric excess (*de*) of the resulting amides was determined by GC or reversed-phase HPLC; the enantiomeric



1a, **6a**: X = OCH_2, Y = Z = F
1b, **6b**: X = OCH_2, Y = Z = H
1c, **6c**: X = SCH_2, Y = Z = H
1d, **6d**: X = $(CH_2)_2$, Y = Z = H
1e, **6e**: X = $(CH_2)_2$, Y = H, Z = F
1f, **6f**: X = CH_2, Y = Z = H

Scheme 3. Kinetic resolution of racemic amines **1a–f** with enantiopure acyl chloride (*R*)-**2a**.

Table 1
Stereoselectivity results of the kinetic resolution of racemic amines **1a–f** with acyl chloride (*R*)-**2a** in toluene at +20 °C[a]

Entry	Amine	(*S*,*R*)-Amide, *de* (%)[b]	(*R*)-Amine, *ee* (%)[c]	Conversion *C* (%)[d]	Selectivity factor *s*[e]
1	**1a**	**6a**, 91.8	87.4	49	67
2	**1b**	**6b**, 84.1	69.8	45	24
3	**1c**	**6c**, 94.2	91.6	49	111
4	**1c**	**6c**, 95.5	87.4	48	135[f]
5	**1d**	**6d**, 74.0	66.7	47	13
7	**1e**	**6e**, 60.4	53.0	48	6.1
8	**1f**	**6f**, 8.8[g]	4.6	34	1.3

[a] Average values for two parallel runs are presented.
[b] Determined by GC (see Section 4).
[c] Determined by chiral HPLC (see Section 4).
[d] $C = ee_{amine}/(ee_{amine} + de_{amide})$.[1]
[e] Selectivity factor, $s = k_{fast}/k_{slow} = \ln[(1 - C)(1 - ee_{amine})]/\ln[(1 - C)(1 + ee_{amine})]$.[1]
[f] Reaction temperature −20 °C.
[g] Determined by RP-HPLC (see Section 4).

excess (*ee*) of unreacted amines was determined by chiral HPLC on a Chiralcel OD-H column (Table 1). Based on these data, we calculated the conversion of the starting racemate (*C*, %) and the selectivity factor *s* (Kagan's factor), i.e., the ratio of the rate constants of the enantiomers. As a result of the acylation, the predominant formation of diastereomerically enriched amides **6a–f** and unreacted enantiomerically enriched amines **1a–f** occurred. As shown by chiral HPLC, the (*R*)-amines were prevailed in the isolated unreacted amines **1a–f**. From this it follows that acyl chloride (*R*)-**2a** reacted faster with (*S*)-amines, and amides **6a–f** were enriched in (*S*,*R*)-diastereomers.

The predominant diastereoisomeric amides (*S*,*R*)-**6a–e** (Scheme 3) were isolated from the reaction mixtures by recrystallization or flash column chromatography. We also managed to isolate the minor amide (*R*,*R*)-**6f** from the reaction mixture by flash column chromatography. In the case of crystalline amides (*S*,*R*)-**6c** and (*S*,*R*)-**6e**, the absolute configuration was confirmed by X-ray diffraction from the known configuration of the acyl fragment (Figs. 1 and 2).

As can be seen from the data presented in Table 1, acylation of racemic 3-methylbenzoxazines **1a** and **1b** with acyl chloride (*R*)-**2a** proceeded with high stereoselectivity (selectivity factor *s* 67 and 24, respectively), with the acylation of amine **1a** being more selective. These data are comparable to the previously published stereochemical results of acylation of racemic amines **1a** and **1b** with

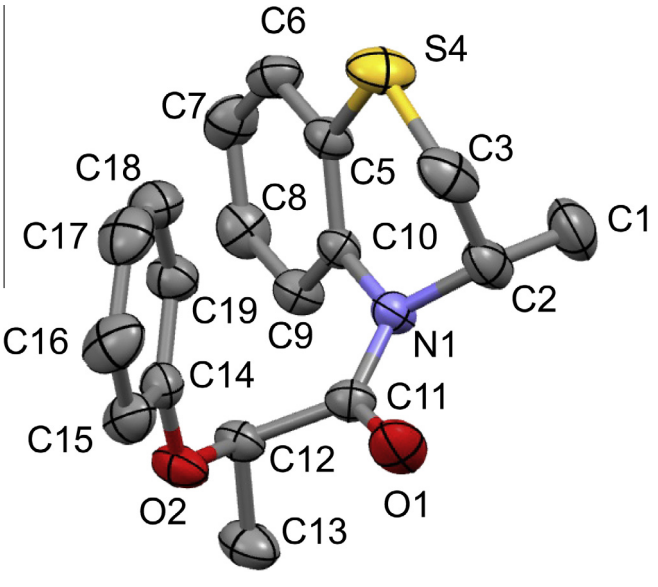


Figure 1. Structure of amide (*S*,*R*)-**6c** (thermal ellipsoids of 50% probability).

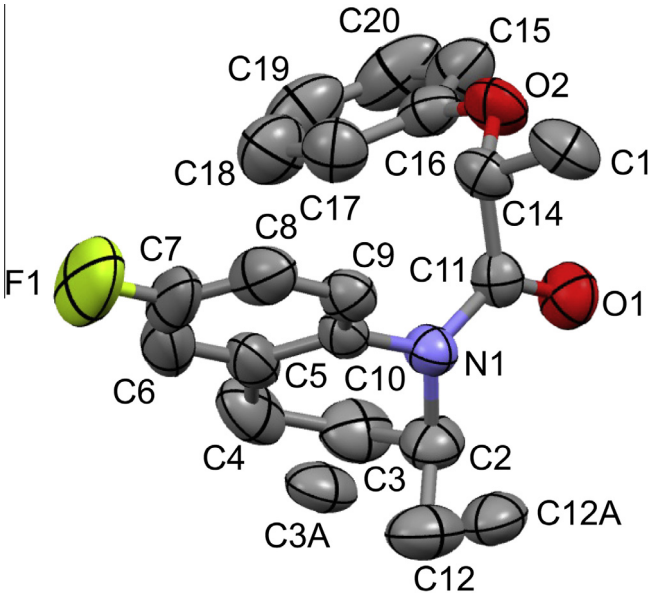


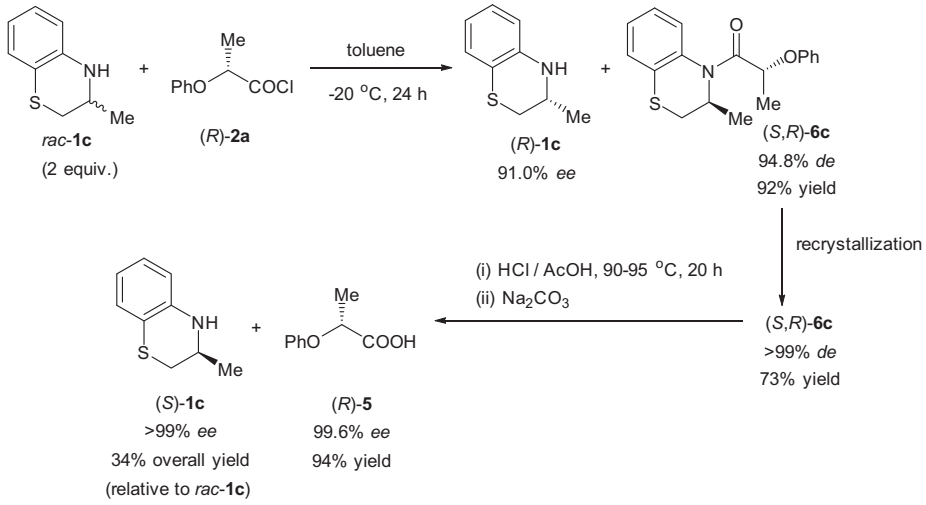
Figure 2. Structure of amide (*S*,*R*)-**6e** (thermal ellipsoids of 50% probability).

racemic acyl chloride **2a** under the same conditions (selectivity factor *s* was 55 and 35, respectively).[5]

Replacement of the oxygen atom in the amine molecule **1b** by the sulfur atom (amine **1c**) significantly increased the stereoselectivity of acylation. Thus, the kinetic resolution of 3-methyl-dihydrobenzothiazine **1c** with acyl chloride (*R*)-**2a** at +20 °C led to amide (*S*,*R*)-**6c** with 94.2% *de* (selectivity factor *s* 111).

Acylation of racemic quinoline derivatives **1d** and **1e** took place with substantially lower selectivity than the acylation of amines **1a–c**: the selectivity factor *s* did not exceed 13. The kinetic resolution of racemic 2-methylindoline **1f** with acyl chloride (*R*)-**2a** was inefficient (*de* of (*S*,*R*)-**6f** was 8.8%, *s* 1.3). In the case of acylation of racemic amine **1c** with acyl chloride (*R*)-**2a**, lowering the reaction temperature to −20 °C made it possible to increase the stereoselectivity of the process (*de* of (*S*,*R*)-**6c** 95.5%, *s* 135). These kinetic resolution conditions were selected to develop a preparative method for the (*S*)-enantiomer of amine **1c**.

Thus, in order to obtain amine (*S*)-**1c**, we carried out the kinetic resolution of racemic 3,4-dihydro-3-methyl-2*H*-[1,4]benzothiazine **1c** with acyl chloride (*R*)-**2a** in toluene at −20 °C for 24 h, which resulted in amide (*S*,*R*)-**6c** with 94.8% *de* and unreacted amine (*R*)-**1c** (91.0% *ee*) (Scheme 4). The subsequent recrystallization of amide (*S*,*R*)-**6c** from a hexane–EtOAc mixture gave diastereomerically pure amide (*S*,*R*)-**6c** (>99.9% *de*) in 73% yield. Acidic hydrolysis



Scheme 4. Preparation of amine (*S*)-**1c** via kinetic resolution with acyl chloride (*R*)-**2a**.

of the latter in a mixture of glacial AcOH and concentrated HCl (1:1) was carried out at 90–95 °C for 20 h resulted in enantiopure amine (*S*)-**1c** (according to chiral HPLC) in 34% overall yield (relative to the starting racemate). In addition, the (*R*)-enantiomer of 2-phenoxypropionic acid **5** was isolated in 94% yield from the hydrolysis products. Chiral HPLC of acid (*R*)-**5** (99.6% *ee*) showed that there was no racemization of the acyl fragment either during the acylation of amine **1c** or the hydrolysis of amide **6c**. Hence, the isolated acid (*R*)-**5** can be recycled to obtain enantiopure acyl chloride (*R*)-**2a**.

3. Conclusion

Herein, we have studied the acylative kinetic resolution of racemic heterocyclic amines with the acyl chloride of enantiopure (*R*)-2-phenoxypropionic acid. It has been found that acylation of 3,4-dihydro-3-methyl-2*H*-[1,4]benzothiazine proceeds with the best stereoselectively when compared with other racemic amines. An efficient method for the preparation of the (*S*)-enantiomer of 3,4-dihydro-3-methyl-2*H*-[1,4]benzothiazine via a kinetic resolution protocol using (*R*)-2-phenoxypropionyl chloride has been developed. We have also demonstrated the possibility of recycling (*R*)-2-phenoxypropionic acid, the product of the acidic hydrolysis of the diastereoisomerically pure amide.

4. Experimental

4.1. General

Racemic 7,8-difluoro-3,4-dihydro-3-methyl-2*H*-[1,4]-benzoxazine **1a** and 3,4-dihydro-3-methyl-2*H*-[1,4]-benzoxazine **1b**,[9] 3,4-dihydro-3-methyl-2*H*-[1,4]-benzothiazine **1c**,[4g] 2-methyl-1,2,3,4-tetrahydroquinoline **1d**,[10] and 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline **1e**,[3e] were obtained according to the literature procedures. Other reagents are commercially available. The solvents were dried according to standard methods[11] and used freshly prepared. Flash column chromatography was performed using Silica gel 60 (230–400 mesh) (Alfa Aesar, UK). Melting points were obtained on a SMP3 apparatus (Barloworld Scientific, UK) and are uncorrected. Optical rotations were measured on a Perkin Elmer M341 polarimeter. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 500 spectrometer with tetramethylsilane and hexafluorobenzene as the internal standards. The NMR spectra of amides **6a**–**f** were recorded in DMSO-d_6 at 100 °C; the NMR spectra of other compounds, at ambient temperature. Elemental analysis was performed using Perkin Elmer 2400 II or EuroVector EA3000 analyzers. The high-resolution mass spectra of amides (*S*,*R*)-**6d**, (*S*,*R*)-**6f**, (*R*,*R*)-**6f** and amine (*S*)-**1c** were obtained on a Bruker maXis Impact HD mass spectrometer, electrospray ionization with direct sample inlet (flow rate 4 L/min).

GC analyses of amides **6a**–**e** were performed using a Shimadzu GC-2010 instrument with a ZB-5 quartz capillary column (30 m × 0.25 mm × 0.25 μm); initial column temperature 40 °C (3 min), programming with a rate of 10 K/min up to 280 °C (30 min); oven temperature 250 °C, detector temperature 300 °C; nitrogen as a carrier gas, flow rate 1.0 mL/min, split ratio 1:30.

Analytical chiral HPLC of amines **1a**–**f** was performed on a Knauer Smartline-1100 instrument using a Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm; 0.6 mL/min flow rate, *n*-hexane–^{i}PrOH 40:1 for amine **1a** ($\tau_{(R)\text{-}\mathbf{1a}}$ 12.3–12.5 min, $\tau_{(S)\text{-}\mathbf{1a}}$ 16.3–16.5 min); 1.0 mL/min flow rate, *n*-hexane–^{i}PrOH–MeOH 100:1:1 for amines **1b**, **d**, **e** ($\tau_{(R)\text{-}\mathbf{1b}}$ 12.6–12.8 min, $\tau_{(S)\text{-}\mathbf{1b}}$ 13.4–13.6 min; $\tau_{(R)\text{-}\mathbf{1d}}$ 6.5–6.7 min, $\tau_{(S)\text{-}\mathbf{1d}}$ 7.2–7.4 min; $\tau_{(R)\text{-}\mathbf{1e}}$ 6.0–6.2 min, $\tau_{(S)\text{-}\mathbf{1e}}$ 8.1–8.3 min); 1.0 mL/min flow rate, *n*-hexane–^{i}PrOH–MeOH 100:1:0.5 for amine **1c** ($\tau_{(R)\text{-}\mathbf{1c}}$ 16.3–16.8 min, $\tau_{(S)\text{-}\mathbf{1c}}$ 17.1–17.5 min). Analytical chiral HPLC of amine **1f** was performed after pre-column derivatization with benzoyl chloride;[4g] *n*-hexane–^{i}PrOH 20:1 ($\tau_{(S)\text{-Bz-}\mathbf{1f}}$ 12.5 min, $\tau_{(R)\text{-Bz-}\mathbf{1f}}$ 19.5 min). Analytical chiral HPLC of acid (*R*)-**5** was performed on a Knauer Smartline-1100 instrument using a Chiralpak AD column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate; *n*-hexane–^{i}PrOH–TFA 20:1:0.02 ($\tau_{(S)\text{-}\mathbf{5}}$ 7.1–7.3 min, $\tau_{(R)\text{-}\mathbf{5}}$ 9.1–9.5 min). Analytical reversed-phase HPLC of amide **6f** was performed on an Agilent 1100 instrument using a Phenomenex Luna C 18(2) column (250 × 4.6 mm), detection at 220 nm, 0.8 mL/min flow rate; MeCN–H_2O 7:3 ($\tau_{(S,R)\text{-}\mathbf{6f}}$ 8.05–8.07 min, $\tau_{(R,R)\text{-}\mathbf{6f}}$ 8.85–8.86 min).

Crystallographic data for compounds (*S*,*R*)-**6c** and (*S*,*R*)-**6e** have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 1484576 and 1485429). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.2. Ethyl (*R*)-2-phenoxypropionate (*R*)-4

A solution of diisopropyl azodicarboxylate (5.25 g, 24.5 mmol) in toluene (50 mL) was added dropwise to a solution of ethyl L-lac-

tate (2.89 g, 24.5 mmol), phenol (2.31 g, 24.5 mmol) and triphenylphosphine (6.43 g, 24.5 mmol) in toluene (100 mL) under stirring at −20 °C. The reaction mixture was stirred at −20 °C for 2 h, then at room temperature for 48 h, and then evaporated to dryness under reduced pressure. The residue was treated with hexane (50 mL), the precipitate was filtered off and then washed with hexane (50 mL). The mother liquor and washings were evaporated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent hexane–ethyl acetate) to afford 3.05 g (64%) of compound (*R*)-**4** as colorless oil. $[\alpha]_D^{20}$ = +46.6 (*c* 1.0, MeOH) {lit.[12] $[\alpha]_D^{20}$ = +47.2 (*c* 0.5, MeOH); 99% *ee*}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (3H, t, *J* = 7.1 Hz, $COOCH_2$-$\underline{CH_3}$); 1.62 (3H, d, *J* = 6.8 Hz, 2-Me); 4.22 (2H, q, *J* = 7.1 Hz, OCH_2); 4.74 (1H, q, *J* = 6.8 Hz, CH); 6.88 (2H, dd, *J* = 8.7, 1.0 Hz, H*o*); 6.97 (1H, tt, *J* = 7.4, 1.0 Hz, H*p*); 7.27 (2H, dd, *J* = 8.7, 7.4 Hz, H*m*). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.10; 18.55; 61.23; 72.60; 115.10; 121.53; 129.50; 157.59; 172.25. Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.01; H, 7.07.

4.3. (*R*)-2-Phenoxypropionic acid (*R*)-5

At first, 2 M NaOH (5.2 mL, 10.4 mmol) was added dropwise to a solution of compound (*R*)-**4** (1.01 g, 5.2 mmol) in ethanol (20 mL) with stirring at 4 °C. The reaction mixture was stirred at room temperature for 24 h, and then evaporated to dryness under reduced pressure. The residue was dissolved in water (40 mL), washed with ethyl ether (2 × 10 mL), acidified with 4 M HCl to pH 1–2 and extracted with ethyl ether (4 × 20 mL). The organic layers were washed with saturated aqueous NaCl (2 × 40 mL), dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was recrystallized from hexane to yield 0.77 g (89%) of compound (*R*)-**5** as a colorless solid, mp 86–88 °C (hexane) (lit. 85–87 °C,[12] 83 °C[13]); $[\alpha]_D^{20}$ = +16.2 (*c* 0.6, $CHCl_3$) {lit.[13] $[\alpha]_D^{20}$ = +19 (*c* 1.0, $CHCl_3$)}. HPLC (Chiralpak AD, *n*-hexane–^{i}PrOH–TFA 20:1:0.02): 95.6% *ee*. Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.06. Found: C, 64.95; H, 6.24. ^{1}H and ^{13}C NMR spectra were identical to those published for (*S*)-**5**.[14]

4.4. (*R*)-2-Phenoxypropionyl chloride (*R*)-2a

Oxalyl chloride (1.09 mL, 12.5 mmol) was added to a solution of acid (*R*)-**5** (0.83 g, 5 mmol) and DMF (5 μL) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temperature for 6 h, and then evaporated to dryness under reduced pressure. The residue was dried over P_2O_5 in vacuo to afford 0.92 g (99%) of compound (*R*)-**2a** as a yellowish oil, which had an unpleasant odor. Anal. Calcd for $C_9H_9ClO_2$: C, 58.55; H, 4.91. Found: C, 58.78; H, 5.07. ^{1}H NMR spectrum was identical to that published for racemic chloride **2a**.[5]

4.5. Enantiomeric enrichment of scalemic acid (*R*)-5 (95.6% *ee*)

Method A: At first, NaOH (0.25 g, 6.25 mmol) was added to a solution of acid (*R*)-**5** (2.00 g, 12.0 mmol) in acetone (26 mL). The reaction mixture was stirred at room temperature until complete dissolution of NaOH and then evaporated. The residue was washed with chloroform (2 × 15 mL), recrystallized from acetone, and then dissolved in water (10 mL). The aqueous solution was acidified with 4 M HCl to pH 1–2 at cooling (+4 °C), and then extracted with chloroform (4 × 10 mL). The organic layers were washed with saturated aqueous NaCl (4 × 20 mL), dried over $MgSO_4$ and evaporated to dryness under reduced pressure to afford 0.34 g (17%) of (*R*)-**5** as a colorless powder, mp 86–88 °C; $[\alpha]_D^{20}$ = +20.4 (*c* 1.0, $CHCl_3$). HPLC (Chiralpak AD, *n*-hexane–^{i}PrOH–TFA 20:1:0.02): 99.4% *ee*.

Method B: A solution of amine (*RS*)-**1b** (0.28 g, 0.15 mmol) and $PhNEt_2$ (0.22 g, 1.5 mmol) in toluene (20 mL) was added to a solution of acyl chloride **2a** (1.84 g, 10 mmol) [obtained from scalemic acid (*R*)-**3**, 96.5% *ee*] in toluene (30 mL). The reaction mixture was kept at room temperature for 24 h and then evaporated to dryness under reduced pressure. Acetonitrile (20 mL) and saturated aqueous Na_2CO_3 (20 mL) were added to the residue and the reaction mixture was stirred vigorously for 1 h, after which acetonitrile was removed under reduced pressure, and the aqueous solution was washed with chloroform (4 × 15 mL), acidified with 4 M HCl to pH 1–2 and extracted with chloroform (4 × 10 mL). The organic layers were washed with saturated aqueous NaCl (4 × 20 mL), dried over $MgSO_4$ and evaporated to dryness under reduced pressure to afford 1.26 g (76%) of acid (*R*)-**5** as a colorless solid, mp 88–90 °C; $[\alpha]_D^{20}$ = +21.1 (*c* 1.0, $CHCl_3$). HPLC (Chiralpak AD, *n*-hexane–^{i}PrOH–TFA 20:1:0.02): 99.6% *ee*. Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.06. Found: C, 65.18; H, 6.25.

4.6. Kinetic resolution of racemic amines 1a–f. General procedure

A solution of acyl chloride (*R*)-**2a** (92 mg, 0.5 mmol) in toluene (5 mL) was added to a solution of amine **1a** (**1b**–**f**) (1.0 mmol) in toluene (5 mL) under stirring at +20 °C. The reaction mixture was kept in a thermostat at +20 °C for 6 h and then successively washed with 4 M HCl (2 × 4 mL), saturated aqueous NaCl (4 × 5 mL), 5% $NaHCO_3$ (2 × 5 mL), and water (2 × 5 mL). The mixture was then dried over $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was analyzed by GC or RP-HPLC, then recrystallized to yield the major (*S*,*R*)-diastereoisomers of amides **6a**–**6f**. Acidic aqueous solutions (after washing with 4 M HCl) were collected, alkalized with Na_2CO_3 to pH ~9 and extracted with chloroform (2 × 5 mL); the organic layers were washed with water (2 × 5 mL), dried over $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was analyzed by chiral HPLC (in the case of amine **1e**, the residue was treated with benzoyl chloride prior to RP-HPLC as described in Ref. 4g). Each experiment was performed in duplicate.

4.6.1. (*S*,*R*)-7,8-Difluoro-3,4-dihydro-3-methyl-*N*-(2′-phenoxypropionyl)-2*H*-[1,4]benzoxazine (*S*,*R*)-6a

Yield 107 mg (64%) as colorless crystals, mp 97–98 °C (*n*-hexane–ethyl acetate); $[\alpha]_D^{20}$ = +63.5 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{18}H_{17}F_2NO_3$: C, 64.86; H, 5.14; N, 4.20; F, 11.40. Found: C, 64.89; H, 5.20; N, 4.11; F, 11.19. GC >99.8% *de*. Retention times (GC), ^{1}H, ^{13}C and ^{19}F NMR were identical to those published for amide (*R**,*S**)-**6a**.[5]

4.6.2. (*S*,*R*)-3,4-Dihydro-3-methyl-*N*-(2′-phenoxypropionyl)-2*H*-[1,4]benzoxazine (*S*,*R*)-6b

Yield 88 mg (59%) as colorless crystals, mp 121–122 °C (*n*-hexane–ethyl acetate); $[\alpha]_D^{20}$ = +117 (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.70; H, 6.61; N, 4.52. GC >99.8% *de*. Retention times (GC), ^{1}H, ^{13}C and ^{19}F NMR were identical to those published for amide (*R**,*S**)-**6b**.[5]

4.6.3. (*S*,*R*)-3,4-Dihydro-3-methyl-*N*-(2′-phenoxypropionyl)-2*H*-[1,4]benzothiazine (*S*,*R*)-6c

Yield 124 mg (79%) as colorless crystals, mp 126–127 °C (*n*-hexane–ethyl acetate); $[\alpha]_D^{20}$ = +198 (*c* 1.3, $CHCl_3$). GC ($\tau_{(S,R)\text{-}\mathbf{6c}}$ 28.13 min): *de* >99.8%. ^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 1.03 (3H, d, *J* = 6.7 Hz, C^3-CH_3); 1.56 (3H, d, *J* = 6.3 Hz, H-3′); 2.79 (1H, dd, *J* = 12.3, 4.3 Hz, H-2A); 3.22 (1H, dd, *J* = 12.3, 5.8 Hz, H-2B); 5.02 (1H, q, *J* = 6.3 Hz, H-2′); 5.14 (1H, qdd, *J* = 6.3, 5.8, 4.4 Hz, H-3); 6.55 (2H, dd, *J* = 8.7, 1.0 Hz, H*o*); 6.85 (1H, tt, *J* = 7.4, 1.0 Hz, H*p*); 7.10–7.17 (4H, m, H*m*, H6 and H7); 7.24–7.31 (2H, m, H-5 and H8). ^{13}C NMR (126 MHz, DMSO-d_6, 100 °C): δ 16.62; 17.58; 33.54; 45.12; 70.11; 114.57; 120.57; 124.64; 126.15;

126.78; 127.24; 128.61; 130.10; 133.52; 156.51; 169.06. Anal. Calcd for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47; S, 10.23. Found: C, 69.09; H, 6.30; N, 4.42; S, 10.38.

4.6.4. (*S*,*R*)-2-Methyl-*N*-(2′-phenoxypropionyl)-1,2,3,4-tetrahydroquinoline (*S*,*R*)-6d

Yield 27 mg (18%) as a yellow oil after flash column chromatography (*n*-hexane–ethyl acetate, fast eluting diastereomer); $[\alpha]_D^{20}$ = +192 (*c* 0.4, $CHCl_3$). GC ($\tau_{(S,R)\text{-}\mathbf{6d}}$ 26.52 min, $\tau_{(R,R)\text{-}\mathbf{6d}}$ 26.95 min): 96.0% *de*. ^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 1.02 (3H, d, *J* = 6.6 Hz, C^2-CH_3); 1.32 (1H, dddd, *J* = 13.1, 9.4, 6.5, 5.7 Hz, H-3A); 1.55 (3H, d, *J* = 6.3 Hz, H-3′); 2.18 (1H, ddt, *J* = 13.1, 7.3, 5.8 Hz, H-3B); 2.33 (1H, ddd, *J* = 15.3, 9.4, 5.8 Hz, H-4A); 2.61 (1H, dt, *J* = 15.3, 5.8 Hz, H-4B); 4.65 (1H, m, H-2); 5.17 (1H, q, *J* = 6.3 Hz, H-2′); 6.52 (2H, dd, *J* = 8.7, 1.0 Hz, H*o*); 6.85 (1H, tt, *J* = 7.4, 1.0 Hz, H*p*); 7.09–7.14 (3H, m, H*m* and H*quin*); 7.17–7.24 (3H, m, H*quin*). ^{13}C NMR (126 MHz, DMSO-d_6, 100 °C): δ 17.39; 19.01; 24.19; 30.74; 47.37; 70.27; 114.85; 120.63; 124.83; 125.19; 125.68; 127.17; 128.59; 134.14; 135.81; 156.61; 168.80. HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1645. Found: 296.1649.

4.6.5. (*S*,*R*)-6-Fluoro-2-methyl-*N*-(2′-phenoxypropionyl)-1,2,3,4-tetrahydroquinoline (*S*,*R*)-6e

Yield 52 mg (33%) as colorless crystals, mp 118–120 °C (*n*-hexane–ethyl acetate); $[\alpha]_D^{20}$ = +214 (*c* 1.0, $CHCl_3$). GC ($\tau_{(S,R)\text{-}\mathbf{6e}}$ 26.55 min, $\tau_{(R,R)\text{-}\mathbf{6e}}$ 26.75 min): 98.6% *de*. ^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 1.02 (3H, d, *J* = 6.6 Hz, C^2-CH_3); 1.32 (1H, ddt, *J* = 13.2, 9.2, 6.0 Hz, H-3A); 1.53 (3H, d, *J* = 6.3 Hz, H-3′); 2.18 (1H, ddt, *J* = 13.2, 7.2, 6.0 Hz, H-3B); 2.33 (1H, ddd, *J* = 15.4, 9.2, 6.0 Hz, H-4A); 2.63 (1H, dt, *J* = 15.4, 5.7 Hz, H-4B); 4.66 (1H, m, H-2); 5.19 (1H, q, *J* = 6.3 Hz, H-2′), 6.58 (2H, d, *J* = 8.6 Hz, H*o*); 6.87 (1H, tt, *J* = 7.4, 1.0 Hz, H*p*); 6.94 (1H, td, *J* = 8.7, 3.0 Hz, H-7); 7.00 (1H, dd, *J* = 9.0, 3.0 Hz, H-5); 7.14 (2H, dd, J = 8.6, 7.4 Hz, H*m*); 7.29 (1H, dd, *J* = 8.7, 5.2 Hz, H-8). ^{19}F NMR (470 MHz, DMSO-d_6, 100 °C): δ 45.89 (unres. m, F-6). ^{13}C NMR (126 MHz, DMSO-d_6, 100 °C): δ 17.11; 18.87; 24.21; 30.29; 47.34; 70.43; 112.21 (d, *J* = 23.1 Hz); 113.64 (d, *J* = 22.4 Hz); 114.81; 120.64; 126.52 (d, *J* = 8.4 Hz); 128.60; 132.07 (d, *J* = 2.7 Hz); 136.49 (br m); 156.57; 159.20 (d, *J* = 243.1 Hz); 168.74. Anal. Calcd for $C_{19}H_{20}FNO_2$: C, 72.82; H, 6.43; N, 4.47; F, 6.06. Found: C, 72.93; H, 6.38; N, 4.47; F, 5.99.

4.6.6. (*R*,*R*)-2-Methyl-*N*-(2′phenoxypropionyl)-indoline (*R*,*R*)-6f

Yield 25 mg (18%) as a colored oil after flash column chromatography on silica gel (*n*-hexane–ethyl acetate, fast eluting diastereomer); $[\alpha]_D^{20}$ = +1.3 (*c* 0.8, $CHCl_3$). HPLC (Phenomenex Luna C 18 (2), MeCN–H_2O 7:3): 99.6% *de*. ^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 1.22 (3H, d, *J* = 6.4 Hz, C^2-CH_3); 1.52 (3H, d, *J* = 6.4 Hz, H-3′); 2.64 (1H, br d, *J* = 15.9 Hz, H-3A); 3.32 (1H, dd, *J* = 15.9, 8.7 Hz, H-3B); 4.78 (1H, dqd, *J* = 8.6, 6.4, 1.5 Hz, H-2); 5.25 (1H, q, *J* = 6.4 Hz, H-2′); 6.94–6.98 (3H, m, H*p* and H*o*); 7.03 (1H, td, *J* = 7.5, 1.0 Hz, H-5); 7.16 (1H, t, *J* = 7.8 Hz, H-6); 7.24–7.30 (3H, m, H-4 and H*m*); 7.89 (1H, d, *J* = 7.8 Hz, H-7). ^{13}C NMR (126 MHz, DMSO-d_6, 100 °C): δ 16.76; 21.00; 35.55; 54.60; 71.96; 115.46; 116.62; 120.97; 123.39; 124.67; 126.39; 128.99; 130.72; 140.58; 156.61; 167.65. HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1489. Found: 282.1489.

4.6.7. (*S*,*R*)-2-Methyl-*N*-(2′-phenoxypropionyl)-indoline (*S*,*R*)-6f

Yield 38 mg (27%) as a colorless amorphous solid after flash column chromatography on silica gel (*n*-hexane–ethyl acetate, slow eluting diastereomer); $[\alpha]_D^{20}$ = +43.7 (*c* 0.6, $CHCl_3$). HPLC (Phenomenex Luna C 18 (2), MeCN–H_2O 7:3): 98.8% *de*. ^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 1.21 (3H, d, *J* = 6.4 Hz, C^2-CH_3); 1.55 (3H, d, *J* = 6.4 Hz, H-3′); 2.64 (1H, br d, *J* = 15.8 Hz, H-3A); 3.35 (1H, dd, *J* = 15.8, 8.6 Hz, H-3B); 4.72 (1H, dqd, *J* = 8.5, 6.4, 1.3 Hz, H-2); 5.24 (1H, q, *J* = 6.4 Hz, H-2′); 6.92–6.96 (3H, m, H*o* and H*p*); 7.03 (1H, td, *J* = 7.5, 1.0 Hz, H-5); 7.16 (1H, t, *J* = 7.8 Hz, H-6); 7.24–7.29 (3H, m, H*m* and H-4); 7.89 (1H, br d, *J* = 7.8 Hz, H-7). ^{13}C NMR (126 MHz, DMSO-d_6, 100 °C): δ 17.26; 20.84; 35.55; 54.46; 71.76; 115.46 (2C); 116.64; 120.79; 123.35; 124.65; 126.39; 128.88; 130.71; 140.58; 156.70; 167.91. HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1489. Found: 282.1489.

4.7. (*S*)-3,4-Dihydro-3-methyl-2*H*-[1,4]benzothiazine (*S*)-1c

A solution of acyl chloride (*R*)-**2a** (0.92 g, 5 mmol) in toluene (50 mL) was added to a solution of amine **1c** (1.65 g, 10 mmol) in toluene (50 mL) under stirring at −20 °C. The reaction mixture was stirred at −20 °C for 24 h, then successively washed with 4 M HCl (2 × 50 mL), saturated aqueous NaCl (3 × 100 mL), 5% $NaHCO_3$ (2 × 50 mL) and H_2O (2 × 100 mL), dried over $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was recrystallized from *n*-hexane–ethyl acetate to afford 1.25 g (80%) of amide (*S*,*R*)-**6c** (*de* >99.9% according to GC) as colorless crystals.

Amide (*S*,*R*)-**6c** (1.25 g, 4 mmol) was dissolved in glacial acetic acid (9 mL), after which concentrated HCl (9 mL) was added to the resulting solution. The reaction mixture was heated at 90–95 °C for 20 h, then cooled to room temperature, evaporated to half the volume, poured into 4 M HCl (50 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated aqueous NaCl (3 × 20 mL), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (*n*-hexane–ethyl acetate) to yield 0.62 g (94%) of acid (*R*)-**5** as colorless crystals, mp 84–86 °C, $[\alpha]_D^{20}$ = +21.1 (*c* 1.0, $CHCl_3$). HPLC (Chiralpak AD, *n*-hexane–^{i}PrOH–TFA 20:1:0.02): 99.4% *ee*. Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.06. Found: C, 65.03; H, 6.21. ^{1}H and ^{13}C NMR spectra were identical to those published for (*S*)-**5**.[14]

The acidic aqueous layer was alkalized with Na_2CO_3 and extracted with benzene (3 × 10 mL). The organic layers were washed with water (3 × 20 mL), dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel (from *n*-hexane–benzene to benzene) to afford 0.61 g (92%) of amine (*S*)-**1c** as a colorless oil. $[\alpha]_D^{20}$ = −77.8 (*c* 1.0, $CHCl_3$) {lit.[15] $[\alpha]_D^{20}$ = −79.0 (*c* 1.2, $CHCl_3$)}. HPLC (Chiralcel OD-H, *n*-hexane–^{i}PrOH–MeOH 100:1:0.5): >99.9% *ee*. ^{1}H and ^{13}C NMR spectra were identical to those published for (*S*)-**1c**.[15] HRMS (ESI) calcd for $C_9H_{12}NS$ $[M+H]^+$ 166.0685. Found: 166.0687.

Acknowledgments

The authors thank Dr. Pavel A. Slepukhin for performing X-ray diffraction and Dr. Ilya N. Ganebnykh for recording HRMS spectra. The work was financially supported by the Russian Science Foundation (grant 14-13-01077).

A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2016.10.004.

References

1. Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249–330.
2. (a) Breuer, M.; Ditrich, K.; Habicher, T.; Hauer, B.; Keβeler, M.; Stürmer, R.; Zelinski, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 788–824; (b) Müller, C. E.; Schreiner, P. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 6012–6042; (c) Krasnov, V. P.; Gruzdev, D. A.; Levit, G. L. *Eur. J. Org. Chem.* **2012**, 1471–1493.

3. (a) Charushin, V. N.; Krasnov, V. P.; Levit, G. L.; Korolyova, M. A.; Kodess, M. I.; Chupakhin, O. N.; Kim, M. H.; Lee, H. S.; Park, Y. G.; Kim, K.-C. *Tetrahedron: Asymmetry* **1999**, *10*, 2691–2702; (b) Krasnov, V. P.; Levit, G. L.; Andreyeva, I. N.; Grishakov, A. N.; Charushin, V. N.; Chupakhin, O. N. *Mendeleev Commun.* **2002**, *12*, 27–28; (c) Chulakov, E. N.; Gruzdev, D. A.; Levit, G. L.; Sadretdinova, L. Sh.; Krasnov, V. P.; Charushin, V. N. *Russ. Chem. Bull.* **2011**, *60*, 948–955; (d) Chulakov, E. N.; Levit, G. L.; Tumashov, A. A.; Sadretdinova, L. Sh.; Krasnov, V. P. *Chem. Heterocycl. Compd.* **2012**, *48*, 724–732; (e) Gruzdev, D. A.; Chulakov, E. N.; Levit, G. L.; Ezhikova, M. A.; Kodess, M. I.; Krasnov, V. P. *Tetrahedron: Asymmetry* **2013**, *24*, 1240–1246.
4. (a) Krasnov, V. P.; Levit, G. L.; Bukrina, I. M.; Andreeva, I. N.; Sadretdinova, L. Sh.; Korolyova, M. A.; Kodess, M. I.; Charushin, V. N.; Chupakhin, O. N. *Tetrahedron: Asymmetry* **2003**, *14*, 1985–1988; (b) Krasnov, V. P.; Levit, G. L.; Kodess, M. I.; Charushin, V. N.; Chupakhin, O. N. *Tetrahedron: Asymmetry* **2004**, *15*, 859–862; (c) Gruzdev, D. A.; Levit, G. L.; Krasnov, V. P.; Chulakov, E. N.; Sadretdinova, L. Sh.; Grishakov, A. N.; Ezhikova, M. A.; Kodess, M. I.; Charushin, V. N. *Tetrahedron: Asymmetry* **2010**, *21*, 936–942; (d) Levit, G. L.; Gruzdev, D. A.; Krasnov, V. P.; Chulakov, E. N.; Sadretdinova, L. Sh.; Ezhikova, M. A.; Kodess, M. I.; Charushin, V. N. *Tetrahedron: Asymmetry* **2011**, *22*, 185–189; (e) Gruzdev, D. A.; Levit, G. L.; Kodess, M. I.; Krasnov, V. P. *Chem. Heterocycl. Compd.* **2012**, *48*, 748–757; (f) Gruzdev, D. A.; Levit, G. L.; Krasnov, V. P. *Tetrahedron: Asymmetry* **2012**, *23*, 1640–1646; (g) Gruzdev, D. A.; Vakarov, S. A.; Levit, G. L.; Krasnov, V. P. *Chem. Heterocycl. Compd.* **2014**, *49*, 1795–1807; (h) Vakarov, S. A.; Gruzdev, D. A.; Chulakov, E. N.; Sadretdinova, L. Sh.; Ezhikova, M. A.; Kodess, M. I.; Levit, G. L.; Krasnov, V. P. *Chem. Heterocycl. Compd.* **2014**, *50*, 838–855.
5. Vakarov, S. A.; Gruzdev, D. A.; Sadretdinova, L. Sh.; Chulakov, E. N.; Pervova, M. G.; Ezhikova, M. A.; Kodess, M. I.; Levit, G. L.; Krasnov, V. P. *Tetrahedron: Asymmetry* **2015**, *26*, 312–319.
6. (a) Takamura, M.; Yanagisawa, H.; Kanai, M.; Shibasaki, M. *Chem. Pharm. Bull.* **2002**, *50*, 1118–1121; (b) Shi, Y.-J.; Hughes, D. L.; McNamara, J. M. *Tetrahedron Lett.* **2003**, *44*, 3609–3611; (c) Crassous, P.-A.; Cardinaletti, C.; Carrieri, A.; Bruni, B.; Di Vaira, M.; Gentili, F.; Ghelfi, F.; Giannella, M.; Paris, H.; Piergentili, A.; Quaglia, W.; Schaak, S.; Vesprini, C.; Pigini, M. *J. Med. Chem.* **2007**, *50*, 3964–3968; (d) Fujita, M.; Okuno, S.; Lee, H. J.; Sugimura, T.; Okuyama, T. *Tetrahedron Lett.* **2007**, *48*, 8691–8694; (e) Vartak, A. P.; Crooks, P. A. *Org. Process Res. Dev.* **2009**, *13*, 415–419; (f) Fujita, M.; Wakita, M.; Sugimura, T. *Chem. Commun.* **2011**, 3983–3985.
7. Manimaran, T.; Stahly, G. P. *Tetrahedron: Asymmetry* **1993**, *4*, 1949–1954.
8. Satyanarayana, T.; Kagan, H. B. *Tetrahedron* **2007**, *63*, 6415–6422.
9. Hayakawa, I.; Hiramitsu, T.; Tanaka, Y. EP Patent 47,005, 1982; *Chem. Abstr.* **1982**, *97*, 55821b.
10. Oldham, W.; Johns, I. B. *J. Am. Chem. Soc.* **1939**, *61*, 3289–3291.
11. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 6th ed.; Butterworth Heinemann: USA, 2009.
12. Chen, C.; Zhu, S.-F.; Liu, B.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2007**, *129*, 12616–12617.
13. Tottie, L.; Baeckström, P.; Moberg, C.; Tegenfeldt, J.; Heumann, A. *J. Org. Chem.* **1992**, *57*, 6579–6587.
14. Boyd, E.; Chavda, S.; Eames, J.; Yohannes, Y. *Tetrahedron: Asymmetry* **2007**, *18*, 476–482.
15. Gruzdev, D. A.; Chulakov, E. N.; Sadretdinova, L. Sh.; Kodess, M. I.; Levit, G. L.; Krasnov, V. P. *Tetrahedron: Asymmetry* **2015**, *26*, 186–194.

Please cite this article in press as: Vakarov, S. A.; et al. *Tetrahedron: Asymmetry* (2016), http://dx.doi.org/10.1016/j.tetasy.2016.10.004