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Synthesis of Non-Natural Cyclic Amino Acids from Available Unsaturated Tertiary Amines

I. D. Titanyuk and I. P. Beletskaya

Lomonosov Moscow State University, Moscow, 119992 Russia
e-mail: i-titan@yandex.ru

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Abstract—New approach is developed to the synthesis of cyclic amino acids derivatives. Unsaturated tertiary amines react with ethyl diazoacetate under the catalysis by copper catalyst $Cu(F_3acac)_2$ leading to the formation of products of [2,3]-sigmatropic rearrangement which via the metathesis of double bonds undergo a ring closure. The subsequent hydrogenation of compounds obtained furnished esters of 6- and 7-membered cyclic α-amino acids. Besides the racemic also optically active compounds were obtained, in particular, esters of (*R*)- and (*S*)-pipecolic acid.

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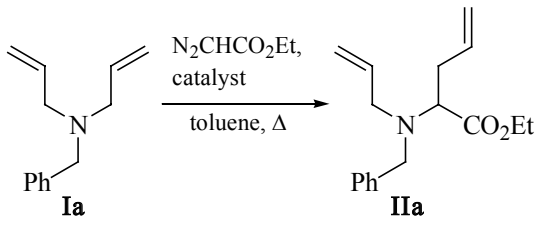
Amino acids are widely employed in all fields of chemistry and biochemistry. However the use of cyclic amino acid comes mainly to the naturally existing L-proline whereas the other chiral homologs appear to be too expensive for wide application for they require complicated, frequently nontrivial, procedures of organic synthesis. The ring closing metathesis (RCM) developed by Grabbs [1] made it possible to prepare cyclic compounds from acyclic dienes. This method provides a possibility to carry out a synthesis of complex molecules containing a large number of various functional groups [2]. In certain cases cyclic amino acids were obtained by olefins metathesis in sufficiently large yields [3–5]. However in these procedures a serious problem consisted in the synthesis of compounds that were the precursors of the metathesis reaction. These precursors are acyclic α-amino acids containing two multiple bonds. One among the known simple methodsof introduction of a double bond into amino acids is a spontaneous [2,3]-sigmatropic rearrangement of nitrogen ylides. Several examples were described of nitrogen ylides generation from ethyl diazoacetate and tertiary N-allylamines in the presence of rhodium catalysts $Rh_6(CO)_{16}$ or $Rh_2(OAc)_4$ [6]. These intermediates underwent the [2,3]-sigmatropic rearrangement forming derivatives of 2-amino-4-pentenic acid. Proceeding from these facts we suggested that the presence in the tertiary amine of the second unsaturated alkyl group would make it possible to obtain in one stage the derivatives of 2-amino-4-pentenic acid which would be suitable for further metathesis. Inasmuch as further the unsaturated cyclic amino acids should be converted into saturated, it was important to have in the initial tertiary amine a substituent readily eliminated by hydrogenation (e.g., a benzyl group). In this report we for the first time describe a method providing a possibility to obtain non-natural cyclic amino acids by the following reaction sequence: [2,3]-sigmatropic rearrangement–metathesis–hydrogenation. As a result the target 6- and 7-membered cyclic amino acids were prepared, both racemic and optically pure.

We started the research from the investigation of the reaction between ethyl diazoacetate and N,N-diallylbenzylamine (**Ia**) (Scheme 1). $Rh_2(OAc)_4$ is the most common catalyst used in transformations of diazo compounds, it has been frequently used for obtaining nitrogen ylides and performing their [2,3]-sigmatropic rearrangement [7, 8]. However the reaction of 5 equiv of amine **Ia** and 5 mol% of $Rh_2(OAc)_4$ with ethyl diazoacetate in toluene resulted in ethyl 2-(*N*-allyl-*N*-benzylamino)pent-4-enoate (**IIa**) in 15–19% yield (see the table, runs nos. *1*, *2*). Further search for the optimum catalyst for this reaction showed that inexpensive copper catalysts were more efficient than the rhodium catalysts, although they required a higher heating temperature to start the reaction (com-

Scheme 1.



monly 80–100°C). In the presence of copper powder, CuI, or copper acetylacetonate compound **IIa** formed in moderate yields (see the table, runs nos. *3–9*). However the use as a catalyst of the copper trifluoroacetylacetonate $Cu(F_3acac)_2$ allowed obtaining ester **IIa** in ~70% yield. Further we used this catalyst in all reactions. Some special features of performing this reaction are worth mentioning. To obtain the best yield a large concentration of amine and its excess with respect to ethyl diazoacetate is required. We usually used 5-fold excess of amine **Ia** without solvent, and 4 equiv of the initial compound we succeeded to recover. It was also important to introduce the ethyl diazoacetate to the reaction mixture very slowly, over 3 h, therefore it was dissolved in a large volume of CH_2Cl_2 and was gradually added to amine **Ia–Ic** heated at high temperature. Therewith the dichloromethane was distilled off from the reaction mixture.

Yield of ethyl 2-(*N*-allyl-*N*-benzylamino)pent-4-enoate (**IIa**) in reaction of *N,N*-diallylbenzylamine (**Ia**) with ethyl diazoacetate[a]

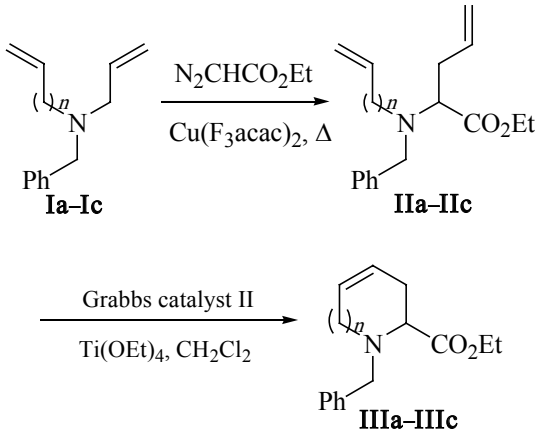
Run no.	Catalyst	mol%	*T*, °C	Yield, %[b]
1	$Rh_2(OAc)_4$	5	50	15
2	$Rh_2(OAc)_4$	5	100	19
3	$Cu(acac)_2$	10	50	–[c]
4	$Cu(acac)_2$	10	80	–[c]
5	$Cu(acac)_2$	10	100	34
6	Cu powder	10	80	–[c]
7	Cu powder	10	100	39
8	CuI	10	80	–[c]
9	CuI	10	100	30
10	$Cu[MeC(O)CHC(O)CF_3]_2$	10	100	50
11[d]	$Cu[MeC(O)CHC(O)CF_3]_2$	10	100	69

[a] Reaction conditions: 5 equiv of **Ia**, 1 equiv of N_2CHCO_2Et, catalyst, toluene.
[b] Yield of the isolated reaction product.
[c] Reaction does not occur.
[d] Without solvent.

The same protocol was used with *N*-allyl-*N*-benzylalkenamines **Ib, Ic**. The reaction products **IIb** and **IIc** were obtained in 61 and 57% yield respectively.

The olefin metathesis is known to be very sensitive to the presence in the molecule of nucleophilic centers, in particular, like amino group. The attempt to carry out the metathesis of compound **IIa** in the presence of Grabbs catalysts I and II gave only trace amounts of cyclic amine **IIIa**. However the addition into the reaction mixture of titanium ethylate $Ti(OEt)_4$ that was a strong Lewis acid and suppressed the nucleophilicity of the nitrogen atom [8] allowed us the isolation of compound **IIIa** in 34% yield with Grabbs catalyst I and in 80% yield with Grabbs catalyst II. Under similar conditions with the help of Grabbs catalyst II we obtained from ester **IIb** the ester of cyclic amino acid **IIIb** containing a seven-membered ring in 78% yield. Regretfully, we failed to obtain in plausible yield the eight-membered cycle **IIIc**. Its signals in the mixture with other compounds of acyclic structure were observed in the NMR spectra.

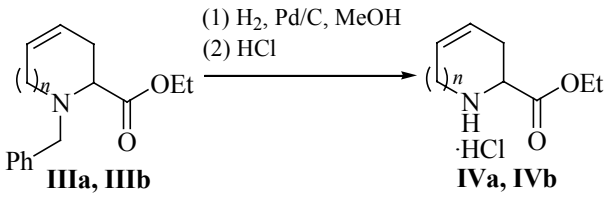
Scheme 2.



n = 1 (**a**), 2 (**b**), 3 (**c**).

The hydrogenation of esters of unsaturated cyclic amino acids **IIIa** and **IIIb** was performed with molecular hydrogen in the presence of catalyst Pd/C (5 mol%) in methanol. Simultaneously with the hydrogenation of the double bond the benzyl group was removed (Scheme 3). The hydrogenation products **IVa** and **IVb** were isolated in nearly quantitative yield.

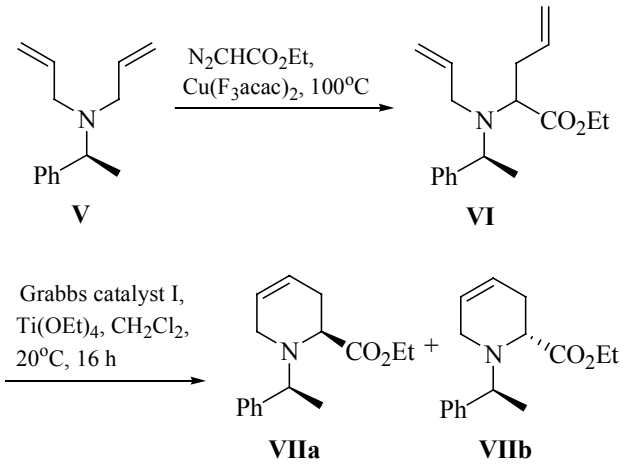
Scheme 3.



n = 1 (**a**), 2 (**b**)

In order to obtain enantiomerically pure derivatives of cyclic amino acids we applied the known (*S*)-N,N-diallyl-1-phenylethylamine (**V**) [9]. The sterical hindrances at the nitrogen atom from the methyl group strongly affected the yield in the reaction with ethyl diazoacetate. Compound **VI** was isolated only in 19% yield as an inseparable mixture of diastereomers. In the presence of $Ti(OEt)_4$ using Grabbs catalyst I we converted compound **VI** into the cyclic unsaturated amino acid as a mixture of diastereomers **VII** and **VIIb** in the ratio 1:1 and an overall yield 82% (Scheme 4). The isomers were easily separated by column chromatography.

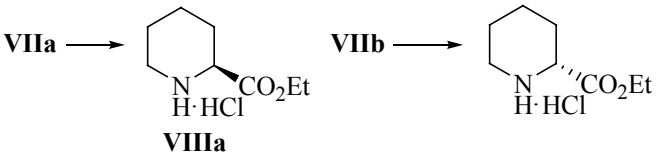
Scheme 4.



Each of diastereomers **VIIa** and **VIIb** was subjected to hydrogenation, and as a result optically active ethyl esters of (*R*)- and (*S*)-pipecolic acid were isolated in the form of hydrochlorides (Scheme 5).

The absolute configuration of ethers obtained was estimated after hydrolysis with 6 N HCl by comparison of the optical properties of obtained enantiomers of free amino acid with the published data. The comparison showed that from compound **VIIa** formed (–)-(*S*)-pipecolic acid, $[\alpha]_D^{22}$ –25.8° (*c* 0.2, H_2O) {$[\alpha]_D^{25}$ –26.3° (*c* 1, H_2O) [10]}, and

Scheme 5.



from compound **VIIb**, (+)-(*R*)-pipecolicaя qandCлOta, $[\alpha]_D^{22}$ +26.0° (*c* 0.2, H_2O) {$[\alpha]_D^{25}$ +26.3° (*c* 1, H_2O) [10]}.

Hence by the use of the three-stage sequence [2,3]-sigmatropic rearrangement–metathesis–hydrogenation we obtained esters of 6- and 7-membered cyclic non-natural amino acids, both racemic and optically pure.

EXPERIMENTAL

NMR spectra were registered on spectrometers Bruker AV-300 and AV-400, operating frequencies 300 and 400 MHz (^1H), 75 and 100 MHz (^{13}C). All solvents used in the reactions were dried with appropriate drying agents. The reaction progress was monitored by TLC on plates with silica gel Merck 60 F_{254} (development by UV irradiation or by treating with cerium molibdate solution in 5% solution of H_2SO_4). In the column chromatography silica gel Merck 60 (230–400 mesh ASTM) was used.

Reaction of ethyl diazoacetate with tertiary *N*-allylamines. General procedure. Into a flask equipped with a magnetic stirrer, a dropping funnel, and a distillation head with a Liebig condenser was charged 10 mmol of tertiary amine **Ia–Ic**. Into the flask was charged 36.9 mg (0.1 mmol) of copper(II) trifluoroacetylacetonate, and the mixture was heated to 90°C at stirring. From the dropping funnel was added during 3 h 228 mg (2 mmol) of ethyl diazoacetate in 50 ml of anhydrous CH_2Cl_2, therewith the most of dichloromethane was distilled off from the reactor flask through the Liebig condenser into a receiver. On completing the addition the mixture was cooled, and the reaction product **IIa–IIc** was isolated by column chromatography (eluent ethyl acetate–petroleum ether, 1:20 v/v).

Ethyl 2-[allyl(benzyl)amino]pent-4-enoate (IIa). Colorless oily substance. Yield 69%. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t (3H, *J* 7.1 Hz), 2.52 m (2H), 3.25 m (1H), 3.45 m (1H), 3.65 m (2H), 4.11 d (1H, *J* 10.1 Hz), 4.25 m (2H), 5.20 m (4H), 5.80 m (2H), 7.41 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5, 34.2, 53.6, 54.2, 60.1, 61.5, 116.8, 117.3, 126.9, 128.2, 128.7, 135.1, 136.5, 139.9, 172.5. Found, %: C 74.82;

H 8.40; N 5.20. $C_{17}H_{23}NO_2$. Calculated, %: C 74.69; H 8.48; N 5.12.

Ethyl 2-[benzyl(but-3-enyl)amino]pent-4-enoate (IIb). Colorless oily substance. Yield 61%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t (3H, *J* 7.1 Hz), 2.25 m (2H), 2.45 m (1H), 2.50 m (2H), 2.58 m (1H), 3.45 t (1H, *J* 8.3 Hz), 3.62 AB system (1H, *J* 12.0 Hz), 3.98 AB system (1H, *J* 12.0 Hz), 4.23 m (2H), 5.10 m (4H), 5.60 m (2H), 7.31 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5, 33.1, 34.4, 50.3, 55.1, 60.1, 62.3, 115.5, 116.7, 126.9, 128.2, 128.7, 135.2, 136.8, 140.1, 172.5. Found, %: C 75.43; H 8.68; N 4.67. $C_{18}H_{25}NO_2$. Calculated, %: C 75.22; H 8.77; N 4.87.

Ethyl 2-[benzyl(pent-4-enyl)amino]pent-4-enoate (IIc). Colorless oily substance. Yield 57%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, *J* 7.1 Hz), 1.66 m (2H), 1.98 m (1H), 2.07 m (1H), 2.45 m (1H), 2.52 m (2H), 2.62 m (1H), 3.45 t (1H, *J* 8.3 Hz), 3.60 AB system (1H, *J* 12.0 Hz), 3.95 AB system (1H, *J* 12.0 Hz), 4.23 m (2H), 5.0 m (4H), 5.60 m (2H), 7.33 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5, 27.6, 33.3, 34.3, 50.2, 55.1, 60.0, 62.3, 114.4, 116.7, 126.8, 128.1, 128.7, 135.2, 138.7, 140.2, 172.5. Found, %: C 75.53; H 9.25; N 4.84. $C_{19}H_{27}NO_2$. Calculated, %: C 75.71; H 9.03; N 4.65.

Ethyl 2-{allyl[(*S*)-1-phenylethyl]amino}pent-4-enoate (VI). Colorless oily substance. Yield 19%, inseparable mixture of diastereomers. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 + 1.25–1.33 (6H), 2.40–2.52 m (2H), 2.76 + 2.90 + 3.20 (2H), 3.30–3.65 m (3H), 3.80 + 4.0–4.35 (2H), 5.0–5.3 m (4H), 5.40 + 5.70 (2H), 7.15–7.41 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.2, 14.6, 19.1, 19.9, 35.2, 39.5, 50.0, 53.0, 53.3, 59.4, 60.0, 60.3, 61.3, 67.4, 68.0, 115.1, 116.3, 116.8, 117.1, 126.9, 127.7, 127.9, 128.2, 135.2, 135.5, 136.4, 138.1, 139.2, 172.1. Found, %: C 75.33; H 8.78; N 4.64. $C_{18}H_{25}NO_2$. Calculated, %: C 75.22; H 8.77; N 4.87.

Esters of unsaturated cyclic racemic amino acids. General procedure. In 10 ml of anhydrous CH_2Cl_2 was dissolved 1 mmol of compound **IIa–IIc** and 284 mg (1 mmol) of titanium(IV) ethylate, to the solution was added 20 mg (0.05 mmol) of Grabbs catalyst II, and the mixture was stirred in a closed flask under an argon atmosphere at room temperature over 16 h. Then the solution was evaporated in a vacuum on a rotary evaporator, and the residue was subjected to chromatography on silica gel (eluent ethyl acetate–petroleum ether, 1 : 10 v/v).

Ethyl 1-benzyl-1,2,3,6-tetrahydropyridine-2-carboxylate (IIIa). Colorless oily substance. Yield 80%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, *J* 7.1 Hz), 2.50 m (2H), 3.17 m (1H), 3.46 m (1H), 3.58 m (1H), 3.82 AB system (1H, *J* 9 Hz), 3.92 AB system (1H, *J* 9 Hz), 4.25 q (2H, *J* 7.0 Hz), 5.71 br.s (2H), 7.31 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5, 28.6, 48.8, 58.1, 59.4, 67.6, 122.4, 125.7, 127.1, 128.3, 128.9, 138.7, 172.6. Found, %: C 73.32; H 7.84, N 5.59. $C_{15}H_{19}NO_2$. Calculated, %: C 73.44; H 7.81; N 5.71.

Ethyl 1-benzyl-2,3,6,7-tetrahydro-1*H*-azepine-2-carboxylate (IIIb). Colorless oily substance. Yield 78%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, *J* 7.1 Hz), 2.20 m (1H), 2.40 m (1H), 2.55 m (1H), 2.75 m (2H), 3.20 m (1H), 3.65 d (1H, *J* 8.1 Hz), 3.85 s (2H), 4.19 m (2H), 5.75 m (1H), 5.81 m (1H), 7.26 m (1H), 7.33 t (2H, *J* 8.5 Hz), 7.43 d (2H, *J* 8.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.3, 27.7, 30.0, 48.5, 58.7, 60.3, 64.8, 127.0, 127.8, 128.2, 128.8, 132.2, 139.4, 173.4. Found, %: C 74.18; H 8.20; N 5.35. $C_{16}H_{21}NO_2$. Calculated, %: C 74.10; H 8.16; N 5.40.

Ethyl *R*- and *S*-piperidine-2-carboxylates. In 10 ml of anhydrous CH_2Cl_2 was dissolved 250 mg oif compound **VI** and 284 mg (1 mmol) of titanium(IV) ethylate, to the solution was added 20 mg (0.05 mmol) of Grabbs catalyst II, and the mixture was stirred in a closed flask under an argon atmosphere at room temperature over 16 h. Then the solution was evaporated in a vacuum on a rotary evaporator, and the residue was subjected to chromatography on silica gel (eluent ethyl acetate–petroleum ether, 1 : 10 v/v).

First compound **VIIb** was eluted, then compound **VIIa**.

Ethyl (*S*)-1-[(*S*)-1-phenylethyl]-1,2,3,6-tetrahydropyridine-2-carboxylate (VIIa). Yield 41%. Colorless oily substance, R_f 0.2, $[\alpha]_D^{22}$ –101.05° (*c* 0.5, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, *J* 7.1 Hz), 1.42 d (3H, *J* 8.0 Hz), 2.30 m (1H), 2.44 m (1H), 3.38 AB system (1H, *J* 9 Hz), 3.60 s (2H), 4.21 m (2H + 1H), 5.45 m (1H), 5.55 m (1H), 7.21–7.40 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.3, 22.1, 29.1, 45.7, 55.4, 59.8, 61.8, 122.4, 126.2, 127.1, 127.3, 128.5, 145.3, 173.1.

Ethyl (*R*)-1-[(*S*)-1-phenylethyl]-1,2,3,6-tetrahydropyridine-2-carboxylate (VIIb). Yield 41%. Colorless oily substance, R_f 0.4, $[\alpha]_D^{22}$ +19.0° (*c* 0.5, $CHCl_3$) ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, *J* 7.1 Hz), 1.37 d (3H, *J* 8.0 Hz), 2.50 m (1H), 2.65 m (1H), 3.00 AB system (1H, *J* 9 Hz), 3.26 AB system (1H, *J* 9 Hz), 3.98 q (1H, *J* 8.0 Hz), 4.08 d (1H, *J* 9.1 Hz), 4.22 m (2H), 5.62 m (1H), 5.72 m (1H), 7.21 m (1H), 7.33 t (2H, *J* 8.5 Hz),

7.39 d (2H, *J* 8.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.4, 21.1, 29.1, 47.3, 54.2, 59.9, 62.1, 121.8, 126.2, 126.8, 127.2, 128.3, 145.9, 173.5.

Esters of saturated cyclic amino acids. *General procedure.* To a solution of compound **IIIa, IIIb** or **VIIa, VIIb** in 10 ml of methanol was added 5 mol% of palladium on carbon (5% Pd), then a rubber ball filled with hydrogen was connected to the flask, and the mixture was stirred in the hydrogen atmosphere for 4 h at room temperature. After the total disappearance of the initial compound (TLC monitoring) the reaction mixture was filtered, acidified to pH 2, and evaporated in a vacuum on a rotary evaporator. The residue was washed with ethyl acetate and dried in a vacuum for 30 min.

Ethyl 1-piperidine-2-carboxylate hydrochloride (IVa). Colorless crystals. Yield 92%. ^{1}H NMR spectrum (D_2O), δ, ppm: 1.30 t (3H, *J* 7.1 Hz), 1.50–1.70 m (3H), 1.8 m (2H), 2.50 m (1H), 3.08 t (1H, *J* 12 Hz), 3.45 d (1H, *J* 12 Hz), 4.00 d (1H, *J* 12 Hz), 4.25 q (2H, *J* 7.0 Hz). ^{13}C NMR spectrum (D_2O), δ, ppm: 13.2, 21.2, 25.6, 44.1, 56.9, 63.5, 169.7. Found, %: C 49.70; H 8.40; N 7.14. $C_8H_{16}ClNO_2$. Calculated, %: C 49.61; H 8.33; N 7.23.

Ethyl 1-azacycloheptane-2-carboxylate hydrochloride (IVb). Colorless oily substance. Yield 90%. ^{1}H NMR spectrum (D_2O), δ, ppm: 1.15 t (3H, *J* 7.1 Hz), 1.30–1.80 m (7H), 2.20 m (1H), 3.12 m (1H), 3.25 m (1H), 4.00 d (1H, *J* 11 Hz), 4.15 q (2H, *J* 7.0 Hz). ^{13}C NMR spectrum (D_2O), δ, ppm: 13.3, 21.2, 24.6, 25.1, 43.8, 56.8, 63.3, 169.3. Found, %: C 41.95; H 8.62, N 6.65. $C_9H_{18}ClNO_2$. Calculated, %: C 52.05; H 8.74; N 6.74.

Ethyl (*S*)-(–)-1-piperidine-2-carboxylate hydrochloride was obtained by hydrogenation of compound **VIIa**. Yield 80%, $[\alpha]_D^{22}$ –2.1° (*c* 0.15, H_2O). ^{1}H and ^{13}C NMR spectra are identical to those of compound **IVa**.

Ethyl (*R*)-(+)-1-piperidine-2-carboxylate hydrochloride was obtained by hydrogenation of compound **VIIb**. Yield 80%, $[\alpha]_D^{22}$ +1.82° (*c* 0.2, H_2O). ^{1}H and ^{13}C NMR spectra are identical to those of compound **IVb**.

Hydrolysis of ethyl esters of (*R*)- and (*S*)-piperidine-2-carboxylic acid. The hydrochloride of ethyl (*R*)- or (*S*)-piperidine-2-carboxylate was dissolved in 6 N HCl and was heated at 90°C for 6 h. The pH of the solution was adjusted at 5.5 by gradual adding water solution of $NaHCO_3$, then the solution was evaporated to dryness on a rotary evaporator. According to the ^{1}H NMR spectra the free acid in both cases formed in the quantitative yield.

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