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Stereoselective Synthesis of (7a*S*)-1-Methylenehexahydro-1*H*-pyrrolizine and (–)-Heliotridane from *N*-Diphenylmethyl-(*S*)-proline Ethyl Ester

I. L. Lysenko and O. G. Kulinkovich

Belarussian State University, pr. Skoriny 4, Minsk, 220050 Belarus

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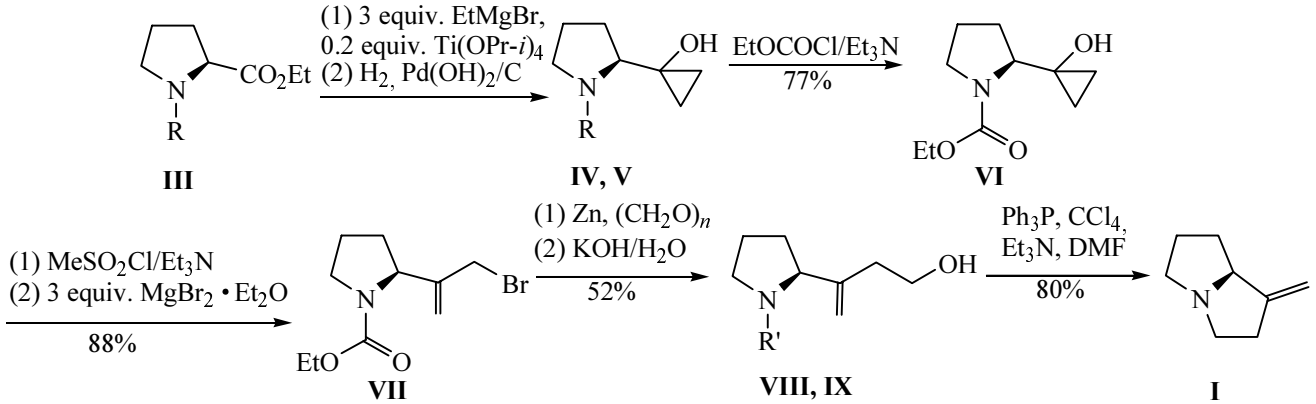
Abstract—Alkaloid (7a*S*)-1-methylenehexahydro-1*H*-pyrrolizine was synthesized from *N*-diphenylmethyl-(*S*)-proline ethyl ester by cyclopropanation of the ester group with ethylmagnesium bromide in the presence of titanium tetraisopropoxide, replacement of the protecting group on the nitrogen atom, and cationic cyclopropyl–allyl isomerization of (*S*)-1-(1-ethoxycarbonylpyrrolidin-2-yl)cyclopropyl sulfonate into the corresponding allyl bromide. Stereoselective reduction of (7a*S*)-1-methylenehexahydro-1*H*-pyrrolizine with sodium tetrahydridoborate in the presence of nickel chloride afforded (–)-heliotridane [(1*S*,7a*S*)-1-methylhexahydro-1*H*-pyrrolizine] in high yield.

Substituted cyclopropanols have found increasing application as intermediate products in organic synthesis due mainly to the development of convenient procedures for their preparation and transformation into compounds belonging to other classes via opening of the three-membered ring [1, 2]. We recently found [3, 4] that *N*-benzyl-α-amino acid esters smoothly react with ethylmagnesium bromide in the presence of titanium tetraisopropoxide to give the corresponding 1-aminoalkylcyclopropanols [5]. Thus, isomerization of the cyclopropanation product obtained from *N*-diphenylmethylpipecolic acid ethyl ester gave the corresponding ethyl ketone, and the subsequent stereoselective reduction of the carbonyl group therein afforded (±)-α- and (±)-β-conhydrins [4]. The present article describes an effective procedure for the synthesis of (7a*S*)-1-methylenehexahydro-1*H*-pyrrolizine (**I**) which is the major alkaloid isolable from *Crotalaria Anagiroides* [6] and *Crotalaria Damarensis* [7], as well as of a necine base, (–)-heliotridane (**II**) [8], which is based on cationic cyclopropyl–allyl isomerization of the cyclopropanation product of *N*-diphenylmethyl-(*S*)-proline ethyl ester (**III**). The synthesis of racemic 1-methylenehexahydro-1*H*-pyrrolizine was reported previously [9]; however, an attempt to isolate particular enantiomers through the corresponding tartrates gave compound **I** with a poor optical purity.

N-Diphenylmethyl-(*S*)-proline ethyl ester (**III**) was treated with 3 equiv of ethylmagnesium bromide in the presence of 0.2 equiv of titanium tetraisopropoxide at room temperature to obtain 92% of cyclopropanol **IV**.

Scheme 1.



III, **IV**, R = Ph_2CH; **V**, R = H; **VIII**, R' = EtOC(O); **IX**, R' = H.

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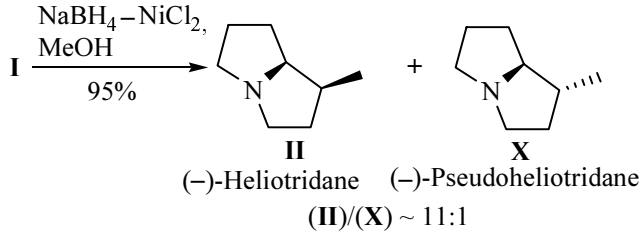
Removal of the protecting diphenylmethyl group from compound **IV** by hydrogenation over palladium catalyst [4, 10] and the subsequent acylation of pyrrolidine **V** with ethyl chloroformate gave substituted cyclopropanol **VI** in a good yield (Scheme 1). The latter was converted into the corresponding methanesulfonate which was subjected to cyclopropyl–allyl rearrangement to allyl bromide **VII** by the action of magnesium bromide in diethyl ether according to the procedure reported in [11]. However, the isomeriza-tion under heterogeneous conditions afforded compound **VII** in a poor yield. Better results were obtained when the reaction was carried out with magnesium bromide–ether complex ($MgBr_2 \cdot Et_2O$) in boiling chloroform. In this case, the reaction mixture was homogeneous, and allyl bromide **VII** was obtained in 88% yield. Compound **VII** was then converted into the corresponding organozinc derivative which was brought into condensation with paraformaldehyde, followed by removal of the protecting group from the nitrogen atom in **VIII**. We thus isolated homoallyl alcohol **IX** in a moderate yield. Intramolecular cyclization of compound **IX** was smoothly effected by the action of triphenylphosphine and carbon tetrachloride in the presence of triethylamine. As a result, (7a*S*)-1-methylenehexahydro-1*H*-pyrrolizine (**I**) was formed; taking into account high volatility of **I**, the product was isolated from the reaction mixture as the corresponding picrate [12].

Culvenor and Smith previously reported [6, 7] that hydrogenation of methylenepyrrolizine **I** over the Adams catalyst or Raney nickel gives a mixture of heliotridane (**II**) and its diastereoisomer **X**, the latter slightly prevailing. We succeeded in effecting a similar transformation with a considerably higher stereoselectivity using the system sodium tetrahydridoborate–nickel(II) chloride in methanol [13] as reducing agent. In this case, the ratio of (–)-heliotridane (**II**) and (–)-pseudoheliotridane (**X**) was 11 : 1 (Scheme 2); it was determined from the intensity ratio of the methyl proton signals in the ^{1}H NMR spectrum of a mixture of the corresponding picrates [14, 15]. Pure (–)-heliotridane picrate was isolated by recrystallization.

Scheme 2.



To conclude, it should be noted that the proposed procedure for efficient transformation of the carboxylic functionality in (*S*)-proline to allyl bromide moiety opens a simple synthetic route to compound **VII** which can be regarded as a promising chiral building block. In the present work it was successfully used to synthesize pyrrolizidine alkaloids **I** and **II**.

EXPERIMENTAL

The ^{1}H NMR spectra of solutions of compounds **I**–**X** in chloroform-*d* were obtained on a Bruker AC 400 instrument (400 MHz). The IR spectra were recorded from solutions in carbon tetrachloride using a Specord 75 IR spectrometer. Diethyl ether and benzene were dried and distilled over metallic sodium; tetrahydrofuran was distilled over lithium tetrahydridoaluminate; paraformaldehyde was dried under reduced pressure over phosphorus(V) oxide.

(7a*S*)-1-Methylenehexahydro-1*H*-pyrrolizine (I). A mixture of 0.58 g (4.1 mmol) of compound **IX**, 2.15 g (8.2 mmol) of triphenylphosphine, 0.8 ml (8.3 mmol) of carbon tetrachloride, and 1.14 ml (8.2 mmol) of triethylamine in 9 ml of dimethylformamide was stirred for 48 h at room temperature, 4 ml of 2 M hydrochloric acod was added, and the solvent was distilled off on stirring under reduced pressure at a temperature not exceeding 60°C (oil bath). Water, 5 ml, was added to the residue, and the mixture was extracted with methylene chloride (3 × 5 ml). Potassium hydroxide, 2 g, was added to the aqueous phase, and the product was extracted into diethyl ether (3 × 5 ml). The extract was dried over solid potassium hydroxide, the solvent was distilled off under atmospheric pressure, and a solution of 1.0 g (4.3 mmol) of picric acid in 4 ml of a 1 : 1 mixture of ethanol with diethyl ether was added to the residue. The precipitate was filtered off, washed with 1 ml of a cold ethanol–diethyl ether mixture (1 : 1), and dried under reduced pressure. We thus isolated 1.15 g (80%) of compound **I** picrate as fine yellow crystals with mp 217.5–218.5°C (from ethanol); published data [7]: mp 218–219°C. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.96–2.16 m (2H), 2.20–2.30 m (1H), 2.43–2.53 m (1H), 2.75–2.85 m (1H), 2.89–3.00 m (1H), 3.04–3.14 m (2H), 3.76–3.86 m (1H), 3.87–3.97 m (1H), 3.71–3.79 m (1H), 5.13 d (1H, *J* = 2.3 Hz), 5.26 d (1H, *J* = 2.1 Hz), 8.87 s (2H), 11.82 br.s (1H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.05, 31.09, 31.68, 53.40, 55.23, 69.49, 110.29, 126.55, 128.36, 141.63, 144.60, 162.18. (7a*S*)-1-Methylene-hexahydro-1*H*-pyrrolizine (**I**) was isolated from the

picrate by treatment with aqueous alkali. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.53–1.63 m (1H), 1.7–1.85 m (2H), 2.02–2.12 m (1H), 2.45–2.70 m (4H), 2.95–3.1 m (2H), 3.8–3.3.86 m (1H), 4.82 s (1H), 4.94 s (1H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.60, 32.32, 32.68, 52.76, 54.28, 67.61, 104.56, 154.71.

(–)-Heliotridane (II). Powdered sodium tetrahydridoborate, 10 mg (0.26 mmol), was added in portions under stirring to a solution of 10 mg (0.08 mmol) of compound **I** and 20 mg (0.08 mmol) of nickel(II) chloride hexahydrate in 0.4 ml of methanol. The mixture was stirred for 10 min, 1 ml of diethyl ether was added, and the precipitate was filtered off. Picric acid, 20 mg (0.08 mmol), was added to the filtrate, the solvent was removed under reduced pressure, and ^{1}H NMR spectrum of the dry residue was recorded. The intensity ratio of the methyl proton signals at δ 1.14 {(–)-heliotridane picrate; cf. [14]} and 1.20 ppm {(–)-pseudoheliotridane picrate; cf. [15]} was 11 : 1. The resulting mixture of **II** and **X** was recrystallized from 0.5 ml of ethanol to isolate 25 mg (81%) of (–)-heliotridane **II** picrate with mp 245–246°C (from ethanol); published data [16]: mp 245.5–246°C. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.14 d (3H, J = 6.5 Hz), 1.68–1.82 m (2H), 2.04–2.24 m (4H), 2.63 oct (1H, J = 6.5 Hz), 2.74–2.86 m (1H), 3.12 d.d (1H, J_1 = 12, J_2 = 7 Hz), 3.68 sept (1H, J = 6.2 Hz), 4.0–4.1 m (1H), 4.24–4.34 m (1H), 8.89 s (2H), 11.42 br.s (1H) (cf. [14]).

(–)-Heliotridane (**II**) was isolated from the picrate by the action of aqueous alkali. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.98 d (3H, J = 7 Hz), 1.28–1.44 m (2H), 1.52–1.76 m (3H), 1.77–1.88 m (1H), 2.24 d.sext (1H, J_1 = 10, J_2 = 7 Hz), 2.44 t.d (1H, J_1 = 10, J_2 = 6 Hz), 2.54 d.d.d (1H, J_1 = 11, J_2 = 7.5, J_3 = 3.5 Hz), 2.96 d.d.d (1H, J_1 = 11, J_2 = 9, J_3 = 6 Hz), 3.14 d.d.d (1H, J_1 = 10, J_2 = 7, J_3 = 3 Hz), 3.39 d.t (1H, J_1 = 9.5, J_2 = 7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.11, 26.53, 26.68, 32.07, 35.64, 54.42, 56.48, 68.32.

***N*-Diphenylmethyl-(*S*)-proline ethyl ester (III).** A mixture of 16.1 g (112.5 mmol) of (*S*)-proline ethyl ester, 27.66 g (112 mmol) diphenylmethyl bromide, 11 g (130 mmol) of sodium hydrogen carbonate, and 40 ml of toluene was heated for 4 h under reflux with simultaneous removal of water, the precipitate of inorganic salts was filtered off, and the solvent was removed under reduced pressure. The residue was distilled in a vacuum to isolate 31.67 g (91%) of compound **III**, bp 166–169°C (1–2 mm), $[\alpha]_D^{17}$ = –79° (c = 10, Et_2O). IR spectrum: ν C=O 1720 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.10 t (3H, J = 7 Hz), 1.76–2.26 m (4H), 2.56–2.74 m (1H), 2.92–3.08 m (1H), 3.4–3.54 m (1H), 3.92 q (2H, J = 7 Hz), 4.80 s (1H), 7.08–7.34 m (6H), 7.36–7.56 m (4H). Found, %: C 77.59; H 7.37. $C_{20}H_{23}NO_2$. Calculated, %: C 77.71; H 7.45.

1-[(2*S*)-1-Diphenylmethylpyrrolidin-2-yl]cyclopropanol (IV). A 1 M solution of ethylmagnesium bromide in diethyl ether, 15 ml (15 mmol), was added over a period of 40–60 min under stirring at room temperature to a solution of 1.51 g (5 mmol) of ester **III** and 0.28 ml (1 mmol) of titanium tetraisopropoxide in 15 ml of diethyl ether. The mixture was left overnight, cooled to 0°C, treated with 12 ml of 2 M hydrochloric acid, and stirred for 2–4 h at room temperature. The organic phase was separated, the oily material was dissolved in 10 ml of methylene chloride, and the aqueous phase was additionally treated with methylene chloride (2 × 10 ml). The extracts were combined, washed in succession with saturated aqueous solutions of sodium chloride (5 ml) and sodium hydrogen carbonate (5 ml), and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure to obtain 1.35 g (92%) of compound **IV** with $[\alpha]_D^{20}$ = –22.4° (c = 10, Et_2O). IR spectrum: ν OH 3455 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.04 d.d.d (1H, J_1 = 11, J_2 = 6, J_3 = 5 Hz), 0.24 d.d.d (1H, J_1 = 11, J_2 = 6, J_3 = 5 Hz), 0.54 d.d.d (1H, J_1 = 11, J_2 = 6, J_3 = 5 Hz), 0.74 d.d.d (1H, J_1 = 11, J_2 = 6, J_3 = 5 Hz), 1.5–2.10 m (5H), 2.40–2.56 m (2H), 3.02–3.18 m (1H), 5.14 s (1H), 7.12–7.44 s (10H). Found, %: C 81.98; H 7.81. $C_{20}H_{23}NO$. Calculated, %: C 81.91; H 7.92.

1-[(2*S*)-Pyrrolidin-2-yl]cyclopropanol (V). A solution of 5.86 g (20 mmol) of compound **IV** in 50 ml of methanol containing 0.50 g of 20% $Pd(OH)_2$/C was stirred under a hydrogen pressure of 1 atm until hydrogen was no longer absorbed (500 ml, 22 mmol). The catalyst was filtered off, the filtrate was evaporated under reduced pressure, 10 ml of hexane was added to the residue, the mixture was cooled to –10°C, and the precipitate was filtered off, washed on a filter with a small amount of cold diethyl ether, and dried under reduced pressure. Yield 2.16 g (85%), colorless leaflets, mp 48–50°C, $[\alpha]_D^{16}$ = –19.5° (c = 4, MeOH). ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.40–0.56 m (2H), 0.70–0.82 m (2H), 1.62–1.96 m (4H), 2.80–3.14 m (3H), 4.30 br.s (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 10.78, 12.97, 25.45, 27.11, 46.26, 54.82, 65.25. Found, %: C 66.11; H 10.30. $C_7H_{13}NO$. Calculated, %: C 66.07; H 10.33.

Ethyl (2*S*)-2-(1-hydroxycyclopropyl)-1-pyrrolidinecarboxylate (VI). Ethyl chloroformate, 1.61 ml (16.5 mmol), was added dropwise to a solution of 2.0 g

(15.7 mmol) of compound **V** and 2.4 ml (17.3 mmol) of triethylamine in 40 ml of methylene chloride, cooled to –20°C. The mixture was stirred for 1 h at room temperature, 10 ml of 1 M hydrochloric acid was added, and the organic phase was separated, washed with 10 ml of a saturated solution of sodium hydrogen carbonate, and dried over sodium sulfate. The drying agent was separated, the solvent was removed under reduced pressure, and the residue was subjected to chromatography on silica gel using first benzene and then benzene–diethyl ether (1 : 1) as eluent. Yield 2.83 g (90%). $[\alpha]_D^{16}$ = –53° (*c* = 10, Et_2O). IR spectrum, ν, cm^{-1}: 3573 (O–H), 3387 (O–H), 1653 (C=O). ^1H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.33–0.41 m (1H), 0.58–0.67 m (1H), 0.68–0.76 m (2H), 1.20 t (3H, *J* = 7 Hz), 1.60–1.78 m (1H), 1.8–2.2 m (3H), 3.2–3.58 m (3H), 3.8–3.72 m (1H), 4.0–4.12 m (2H). Found, %: C 60.38; H 8.52. $C_{10}H_{17}NO_3$. Calculated, %: C 60.25; H 8.65.

Ethyl (2*S*)-2-(1-bromomethylvinyl)-1-pyrrolidinecarboxylate (VII). A solution of 3.48 g (17.5 mmol) of compound **VI** and 7.3 ml (52.5 mmol) of triethylamine in 30 ml of diethyl ether was cooled to –10°C, and 2.0 ml (26.3 mmol) of methanesulfonyl chloride was added dropwise. When the addition was complete, the cooling bath was removed, the mixture was stirred for 2 h at room temperature, and 20 ml of water was added. The organic phase was separated, washed with 10 ml of 2 M hydrochloric acid and 10 ml of a saturated solution of sodium hydrogen carbonate, and dried over sodium sulfate. Removal of the solvent under reduced pressure gave 4.81 g (99%) of crude ethyl (2*S*)-2-(1-methylsulfonyloxycyclopropyl)-1-pyrrolidinecarboxylate. The product was dissolved in 20 ml of chloroform, and solid magnesium bromide–ether complex [prepared from 1.26 g (52 mmol) of magnesium and 4.5 ml (52 mmol) of 1,2-dibromoethane in 20 ml of diethyl ether, followed by vacuum distillation of the solvent] was added. The mixture was heated for 1 h under reflux with stirring (oil bath, 80°C), cooled to 0°C, and treated with 10 ml of water on stirring. The organic phase was separated, the aqueous phase was extracted with 5 ml of chloroform, and the combined extracts were washed in succession with 5 ml of 1 M hydrochloric acid and 5 ml of a saturated solution of sodium hydrogen carbonate, dried over sodium sulfate, and evaporated. The residue was subjected to flash chromatography on silica gel using benzene–diethyl ether (first 10 : 1 and then 1 : 1) as eluent. Yield 4.08 g (89%), yellowish oily substance, $[\alpha]_D^{16}$ = –13° (*c* = 10, Et_2O). IR spectrum: ν(C=O) 1680 cm^{-1}. ^1H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.18–1.32 m (3H), 1.80–2.00 m (3H), 2.08–2.20 m (1H), 3.44–3.60 m (2H), 3.90–4.20 m (4H), 4.48–4.56 m (1H), 4.98–5.12 m (1H), 5.20–5.32 m (1H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.66, 31.90, 33.46, 46.73, 59.10, 61.00, 64.90, 114.70, 146.20, 158.67. Found, %: C 45.82; H 6.15. $C_{10}H_{16}BrNO_2$. Calculated, %: C 45.65; H 6.32.

Ethyl (2*S*)-2-[1-(2-hydroxyethyl)vinyl]-1-pyrrolidinecarboxylate (VIII). A mixture of 1.31 g (5 mmol) of compound **VII**, 0.98 g (15 mmol) of zinc powder, 0.45 g (15 mmol) of paraformaldehyde, and 0.22 ml (2.5 mmol) of 1,2-dibromoethane in 5 ml of tetrahydrofuran was heated for 2 h under reflux with stirring in an argon atmosphere. The mixture was evaporated under reduced pressure, the residue was treated with 5 ml of 1 M hydrochloric acid on stirring, 10 ml of diethyl ether was addded, and the precipitate was filtered off and washed on a filter with 5 ml of diethyl ether. The organic phase was separated from the filtrate, washed with 3 ml of a saturated solution of sodium hydrogen carbonate, and dried over sodium sulfate. By flash chromatography on silica gel using first benzene–diethyl ether (5 : 1) and then diethyl ether as eluent we isolated 0.65 g (61%) of compound **VIII** as a colorless oily substance. $[\alpha]_D^{17}$ = –14° (*c* = 5, Et_2O). IR spectrum, ν, cm^{-1}: 3400 (O–H), 1665 (C=O). ^1H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.15–1.25 m (3H), 1.6–1.75 m (1H), 1.75–2.10 m (3H), 1.15–1.25 m (1H), 2.27–2.30 m (1H), 3.37–3.55 m (3H), 3.67–3.90 m (2H), 4.05–4.15 m (2H), 4.20–4.30 m (1H), 4.85–4.95 m (2H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.65, 23.26, 31.16, 37.25, 46.87, 60.51, 61.04, 110.33, 155.06. Found, %: C 61.95; H 8.98. $C_{11}H_{19}NO_3$. Calculated, %: C 62.11; H 8.83.

3-[(2*S*)-Pyrrolidin-2-yl)-3-buten-1-ol (IX). A mixture of 1.58 g (7.4 mmol) of compound **VIII**, 1.8 g of potassium hydroxide, and 5 ml of a 80% aqueous solution of ethylene glycol was heated for 3 h at the boiling point with stirring. The product was extracted into diethyl ether (3 × 5 ml), and the combined extracts were dried over sodium sulfate, filtered through a layer of activated aluminum oxide, and evaporated under reduced pressure. Yield 0.89 g (85%), colorless oily substance. $[\alpha]_D^{13}$ = –86° (*c* = 5, Et_2O). IR spectrum, ν, cm^{-1}: 3347 (O–H, N–H), 1680 (C=C). ^1H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.65–1.94 m (4H), 2.32 t (2H, *J* = 4.6 Hz), 2.94–3.04 m (2H), 3.44–3.53 m (1H), 3.66–3.75 m (2H), 4.36–4.56 br.s (2H), 4.87 m (1H), 4.94 m (1H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.57, 30.08, 36.48, 46.16, 63.04, 63.14, 114.17, 150.30. Found, %: C 68.04; H 10.71. $C_8H_{15}NO$. Calculated, %: C 67.92; H 10.85.

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