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4,5-Dihydroisoxazoles in the Synthesis of New Metallomesogens

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Abstract—A new approach to the synthesis of metallomesogens containing β-enaminoketone fragments as chelating moieties was developed. The corresponding enaminoketone was synthesized by the oxidation of 3-(4'-butoxybiphenyl-4-yl)-5-pentyl-4,5-dihydroisoxazole to 3-(4'-butoxybiphenyl-4-yl)-5-pentyl-4,5-isoxazole, followed by opening of the isoxazole ring. The reaction of the enaminoketone with copper(II) and nickel(II) acetates gave the target mesogenic metal complexes.

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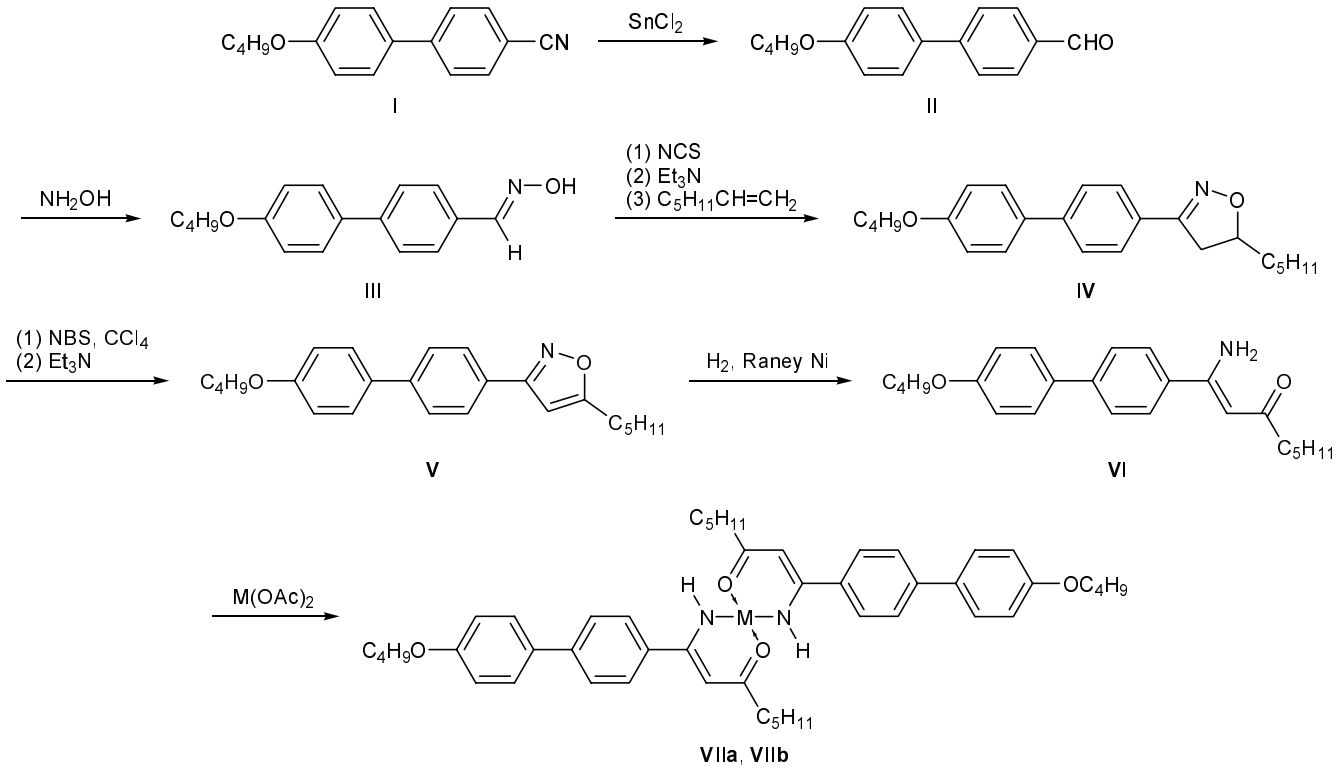
Metallomesogens occupy a specific place among a large number of presently known liquid crystalline substances [1–3]. These liquid crystals are coordination compounds of metal cations with various organic chelating ligands. Their specific physical properties give rise to a variety of applications in modern electronics. In particular, metallomesogens were proposed to be used as components of liquid crystalline compositions for luminescent display devices [4] and for preparation of optical glasses with required properties [3]. Copper, nickel, palladium, zinc, platinum, and lanthanide cations are used most frequently as complexing metals in the synthesis of metallomesogens [1–6], and chelating ligands are based on various β-difunctional organic compounds [2–8]. While analyzing the structure and physical properties of metallomesogens, recently synthesized compounds containing β-enaminoketone fragments as chelating moieties attracted our attention [9–11]. It is known [12] that β-enaminoketone fragment can be built up via reductive cleavage of isoxazole ring; the latter can be obtained from the corresponding 4,5-dihydroisoxazole.

We previously synthesized various liquid crystalline substances on the basis of 4,5-dihydroisoxazoles [13–15]. Therefore, in the present work we planned to use 4,5-dihydroisoxazoles as key intermediate products to prepare new metallomesogens having β-enaminoketone fragments. We anticipated to obtain the desired β-enaminoketones from the corresponding 4,5-dihydroisoxazoles by converting them into isoxazoles and subjecting the latter to reductive fission.

As starting compound we used commercially available 4'-butoxybiphenyl-4-carbonitrile (**I**). Stephen's reduction [16, 17] of the cyano group in **I** with tin(II) chloride, followed by hydrolysis of the resulting imine gave aldehyde **II** in about 80% yield. Aldehyde **II** was treated with hydroxylamine hydrochloride in the presence of sodium acetate to obtain oxime **III** in quantitative yield. The structure of compounds **II** and **III** unambiguously follows from their IR and ^{1}H NMR spectra. The IR spectrum of **II** contained absorption bands due to the aldehyde group at 1695 (C=O) and 2735 cm^{-1} (C–H), while no absorption at 2230 cm^{-1} typical of cyano group in initial nitrile **I** was present. In the ^{1}H NMR spectrum of **II**, the aldehyde proton signal appeared as a singlet at δ 10.15 ppm. Compound **III** characteristically showed in the IR spectrum O–H absorption bands at 3575 and 3460–3125 cm^{-1}, while carbonyl absorption was lacking.

In the next step, oxime **III** was treated with *N*-chlorosuccinimide and triethylamine to generate the corresponding nitrile oxide, and 1,3-dipolar cycloaddition of the latter to 1-heptene afforded 89% of 4,5-dihydroisoxazole derivative **IV**. The structure of **IV** was confirmed by the spectral data. The ^{1}H NMR spectrum of **IV** contained multiplet signals from both aromatic protons and those of the pentyl group. Protons on C^4 in the dihydroisoxazole ring gave two one-proton doublets of doublets at δ 3.02 and 3.42 ppm. The 5-H signal appeared as a one-proton multiplet in a weaker field, at δ 4.72–4.79 ppm. The intensity ratio of the C^{4}H$_2$ and C^{5}H signals indicates regioselective addition

Scheme 1.



VII, M = Ni (**a**), Cu (**b**).

of nitrile oxide to 1-heptene to give just 3-aryl-5-pentyl-4,5-dihydroisoxazole derivative **IV** rather than isomeric 3-aryl-4-pentyl-4,5-dihydroisoxazole.

It was then necessary to oxidize the dihydroisoxazole ring in **IV** to isoxazole. Several preparative procedures for effecting such transformation are known [12, 18, 19]. We used the two-step procedure developed previously [18]; it includes bromination of a substituted 4,5-dihydroisoxazole with *N*-bromosuccinimide (NBS) and subsequent dehydrobromination of a mixture of 4- and 5-bromo-4,5-dihydroisoxazoles thus formed. By reaction of compound **IV** with NBS, followed by treatment with triethylamine, we obtained a mixture of isoxazole derivative **V** and unreacted dihydroisoxazole **IV** at a ratio of 4:1. In the ^{1}H NMR spectrum of the product mixture we observed a singlet at δ 6.59 ppm from the 4-H proton in **V**. Protons of the biphenyl fragment in molecule **V** appeared as downfield doublets characteristic of 1,4-disubstituted benzene rings. These data showed that the formation of isoxazole **V** was not accompanied by side transformations of the aromatic rings.

Compounds **IV** and **V** were brought into further syntheses without separation. Catalytic hydrogenation of the heteroring in substituted isoxazoles is known to give the corresponding enaminoketones [12], while substituted 4,5-dihydroisoxazoles are converted into β-hydroxy ketones under analogous conditions [20]. Hydrogenation of the obtained mixture of isoxazole **V** and dihydroisoxazole **IV** over Raney nickel afforded enaminoketone **VI** in 90% yield (calculated on isoxazole **V**); compound **VI** was separated from ring opening products of dihydroisoxazole **IV** by column chromatography. The structure of enaminoketone **VI** was confirmed by the UV, IR, and ^{1}H NMR spectra. The presence in molecule **VI** of a conjugated system including the aromatic rings, double C=C bond, and ketone group is supported by the UV spectrum which contains an absorption maximum at λ 334 nm. The conjugated C=C–C=O bond sequence gives rise to strong absorption bands at 1600, 1525, and 1480 cm^{-1} in the IR spectrum. Enaminoketone **VI** displayed in the ^{1}H NMR a singlet at δ 5.75 ppm due to olefinic proton; methylene protons in the α-position with respect to the carbonyl group appeared as a triplet at δ 2.48 ppm. The amino group is characterized by two broadened singlets at δ 8.31 and 10.74 ppm in the ^{1}H NMR spectrum and IR absorption bands at 3475 and 3335–3100 cm^{-1}.

In the final step, coordination compounds **VIIa** and **VIIb** were obtained by reaction of enaminoketone **VI** with nickel(II) and copper(II) acetates, respectively. Copper and nickel were selected as complexing metals, taking into account that Ni^{2+} and Cu^{2+} ions with bidentate ligands form square–planar complexes [2, 8, 11]. Planar coordination entity was expected to ensure planar structure of the whole molecule, which is a necessary condition for liquid crystalline properties. Complexes **VIIa** and **VIIb** are colored substances, which are readily soluble in such solvents as chloroform, carbon tetrachloride, dioxane, and benzene. Their structure was confirmed by the spectral data. The UV spectra of **VIIa** and **VIIb** contained absorption maxima at λ 299 and 298 nm, respectively. These maxima are most likely to belong to their biphenyl fragments. In the IR spectra of **VIIa** and **VIIb**, the conjugated C=C–C=O bond system gives rise to strong absorption in the region 1600–1480 cm^{-1}. In addition, absorption bands due to stretching vibrations of the N–H bond were observed at 3335 (**VIIa**) and 3345 cm^{-1} (**VIIb**). In the ^1H NMR spectrum of nickel complex **VIIa**, the vinyl proton signal of the ligand was located at δ 5.30 ppm, and the NH signal appeared as a broadened singlet at δ 5.50 ppm. The ^1H NMR spectrum of copper complex **VIIb** was characterized by appreciable broadening and distortion of signals, which are typical of coordination compounds formed by paramagnetic metal ions, including Cu^{2+} [6]. Although analysis and interpretation of the spectrum of **VIIb** was complicated, the observed pattern may be regarded as an additional proof for the formation of copper complex. It should be emphasized that enaminoketone complexes **VIIa** and **VIIb** differ from those described previously [9–11], for the latter contain no free N–H bonds which are expected to strongly affect their properties as liquid crystals.

Phase transition study showed that both complexes **VIIa** and **VIIb** possess liquid crystalline properties: they formed nematic phase in a wide temperature range. The temperature of formation of nematic phase by nickel complex **VIIa** was lower than the corresponding temperature for copper complex **VIIb**. Moreover, nickel complex **VIIa** turned out to be more thermally stable than copper complex **VIIb**. The latter underwent partial decomposition on heating to the temperature corresponding to clarification of mesophase and higher.

Thus the results of our study showed that 4,5-dihydroisoxazole derivatives may be used as starting compounds for the synthesis of novel metallomesogens which are enaminoketone nickel and copper complexes. Studies on the application of the developed approach to the synthesis of other metallomesogens are now in progress, and their results will be reported later.

EXPERIMENTAL

The melting points and phase transition temperatures were determined on a melting point apparatus coupled with a polarizing microscope. The IR spectra were recorded on a Specord 75IR spectrometer from solutions in chloroform placed in KBr cells. The electron absorption spectra were measured in the λ range from 220 to 900 nm on a Specord M40 spectrophotometer. The ^1H NMR spectra were obtained on a Bruker Avance 400 instrument (400 MHz) using HMDS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Kieselgel 60 F_{254} plates (Merck).

4'-Butoxybiphenyl-4-carbaldehyde (II). A mixture of 3.34 g (17.6 mmol) of anhydrous $SnCl_2$ and 40 ml of ethyl acetate was saturated at 0°C with dry hydrogen chloride, and a solution of 2.0 g (7.97 mmol) of 4'-butoxybiphenyl-4-carbonitrile (**I**) in 45 ml of ethyl acetate, saturated with hydrogen chloride, was added on cooling to 0°C. Hydrogen chloride was passed through the resulting mixture over a period of 10 min, maintaining the temperature at 0°C. The mixture was kept for 4 days at 2–4°C, the precipitate was filtered off, washed with ethyl acetate on a filter, and dissolved in 100 ml of water, and the aqueous solution was extracted with ethyl acetate (3 × 50 ml). The extracts were combined and washed in succession with water (5 × 50 ml), a saturated solution of sodium carbonate (2 × 30 ml), and a saturated solution of sodium chloride (30 ml). The organic solution was dried over sodium sulfate, the solvent was removed under reduced pressure, and the residue was recrystallized from 2-propanol. Yield 1.61 g (79.5%). Phase transition temperatures, °C: (Cr) 85.5 (N) 86.5 (I). IR spectrum, ν, cm^{-1}: 3005 ($C–H_{arom}$); 2955, 2930, 2870 ($C–H_{alk}$); 2735 ($C–H_{ald}$); 1695 (C=O); 1600, 1515, 1490 ($C=C_{arom}$). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.89 t (3H, CH_3, J = 7.0 Hz); 1.43 sext (2H, CH_2, J = 7.0 Hz); 1.71 quint (2H, CH_2, J = 7.0 Hz); 3.67 t (2H, OCH_2, J = 7.0 Hz); 7.17 d (2H, J = 8.5 Hz), 7.73 d (2H, J = 8.5 Hz), 7.81 d (2H, J = 8.5 Hz), and 8.02 d (2H, J = 8.5 Hz) (H_{arom}); 10.15 s (1H, CHO).

4'-Butoxybiphenyl-4-carbaldehyde oxime (III). A solution of 15.0 g (59.1 mmol) of aldehyde **II** in 150 ml of 2-propanol was heated to the boiling point,

and a solution of 4.5 g (64.7 mmol) of hydroxylamine hydrochloride and 8.8 g (64.7 mmol) of sodium acetate trihydrate in 25 ml of water was added dropwise over a period of 40 min. The mixture was then heated for 1 h under reflux, diluted with 80 ml of water, and cooled to 4°C, and the precipitate was filtered off. Yield 15.7 g (99.8%). Phase transition temperatures, °C: (Cr) 163 (N) 169 (I). UV spectrum (CH_3OH): λ_{max} 295 nm. IR spectrum, ν, cm^{-1}: 3575, 3460–3125 (O–H); 3000 (C–H_{arom}); 2955, 2930, 2865 (C–H_{alk}); 1600, 1495 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.98 t (3H, CH_3, J = 7.0 Hz); 1.50 sext (2H, CH_2, J = 7.0 Hz); 1.78 quint (2H, CH_2, J = 7.0 Hz); 3.99 t (2H, OCH_2, J = 7.0 Hz); 6.96 d (2H, J = 8.5 Hz), 7.52 d (2H, J = 8.5 Hz), 7.56 d (2H, J = 8.5 Hz), and 7.61 d (2H, J = 8.5 Hz) (H_{arom}); 8.11 br.s (1H, OH); 8.16 s (1H, CH=N).

3-(4'-Butoxybiphenyl-4-yl)-5-pentyl-4,5-dihydroisoxazole (IV). *N*-Chlorosuccinimide, 7.1 g (53.2 mmol), was added over a period of 1 h to a solution of 13.0 g (48.3 mmol) of oxime **III** in 100 ml of dimethylformamide under stirring at 8–10°C (after addition of the first portion of NCS, the mixture was purged with gaseous phase collected over concentrated hydrochloric acid). The mixture was then stirred for 1 h at 10–15°C, cooled to 0–3°C, 13.6 ml (96.7 mmol) of 1-heptene was added, and a solution of 7.5 ml (54.0 mmol) of triethylamine in 20 ml of dimethylformamide was added. The mixture was stirred for 12 h at room temperature, and 100 ml of chloroform and 60 ml of dilute (1:5) hydrochloric acid were added. The organic phase was separated, and the aqueous phase was extracted with chloroform (2×100 ml). The extracts were combined with the organic phase and washed with water (2×70 ml), most part of the solvent was removed under reduced pressure, the residue was diluted with water, and the precipitate was filtered off. Yield 15.7 g (89%). Phase transition temperatures, °C: (Cr) 181 (Sm*A*) 220 (I). UV spectrum (C_2H_5OH): λ_{max} 301 nm. IR spectrum, ν, cm^{-1}: 3010 (C–H_{arom}); 2955, 2930, 2875 (C–H_{alk}); 1600, 1500 (C=C_{arom}). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.84 t (3H, CH_3, J = 7.0 Hz); 0.89 t (3H, CH_3, J = 7.0 Hz); 1.20–1.28 m (4H), 1.34–1.49 m (4H), 1.55–1.62 m (1H), and 1.67–1.80 m (3H) (CH_2); 3.02 d.d (1H, J_1 = 8.5, J_2 = 16.5 Hz) and 3.42 d.d (1H, J_1 = 10.5, J_2 = 16.5 Hz) (C^4H_2); 3.97 t (2H, OCH_2, J = 6.5 Hz); 4.72–4.79 m (1H, 5-H); 7.17 d (2H, J = 9.0 Hz), 7.75 d (2H, J = 9.0 Hz), 7.78 d (2H, J = 8.5 Hz), and 7.95 d (2H, J = 8.5 Hz) (H_{arom}).

3-(4'-Butoxybiphenyl-4-yl)-5-pentylisoxazole (V). A mixture of 4.0 g (11.0 mmol) of dihydroisoxazole **IV**, 2.15 g (12.1 mmol) of *N*-bromosuccinimide, and 100 ml of carbon tetrachloride was heated for 4 h under reflux. The mixture was cooled, 15 ml (10.8 mmol) of triethylamine was added, the mixture was heated for 11 h under reflux and cooled, and 95 ml of dilute (1:5) hydrochloric acid was added. The organic phase was separated, washed with water (2×40 ml), and dried over magnesium sulfate, the solvent was removed under reduced pressure, and the residue was recrystallized from 2-propanol–methyl ethyl ketone. We thus obtained 3.41 g of a mixture of isoxazole **V** and initial dihydroisoxazole **IV** at a ratio of 4:1. Yield of isoxazole **V** 69%. UV spectrum (C_2H_5OH): λ_{max} 295 nm. IR spectrum, ν, cm^{-1}: 3000 (C–H_{arom}); 2955, 2930, 2865 (C–H_{alk}); 1600, 1495 (C=C_{arom}); 1280, 1170 (C–O). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.73 t (3H, CH_3, J = 7.0 Hz); 0.80 t (3H, CH_3, J = 7.0 Hz); 1.08–1.20 m (4H), 1.35 sext (2H, J = 7.0 Hz), 1.54 quint (2H, J = 7.0 Hz), 1.63 quint (2H, J = 7.0 Hz), and 2.64 t (2H, J = 7.0 Hz) (CH_2); 3.88 t (2H, OCH_2, J = 7.0 Hz); 6.59 s (1H, 4-H); 7.08 d (2H, J = 8.5 Hz), 7.66 d (2H, J = 8.5 Hz), 7.74 d (2H, J = 8.5 Hz), and 8.09 d (2H, J = 8.5 Hz) (H_{arom}).

1-Amino-1-(4'-butoxybiphenyl-4-yl)oct-1-en-3-one (VI). A suspension of 1 g of Raney nickel in a mixture of 10 ml of methanol and 10 ml of tetrahydrofuran was saturated with hydrogen while stirring over a period of 1 h. A solution of 0.9 g of mixture **V**/**IV** (4:1) in 50 ml of tetrahydrofuran was added, and the mixture was stirred for 2 days under hydrogen (after 24 h, and additional portion of Raney nickel, 1 g, was added). The catalyst was filtered off and washed with 40 ml of tetrahydrofuran on a filter, the solvent was distilled off from the filtrate under reduced pressure, and the residue was applied to a column charged with silica gel. The column was eluted with ethyl acetate–petroleum ether (1:3 to 1:2, gradient elution) to isolate 0.652 g (90% calculated on isoxazole **V**) of compound **VI** with mp 117–118°C (from 2-propanol). UV spectrum, λ_{max}, nm: 339 (C_2H_5OH), 334 (dioxane). IR spectrum, ν, cm^{-1}: 3475, 3335–3100 (N–H); 2995 (C–H_{arom}); 2950, 2925, 2865 (C–H_{alk}); 1600, 1525, 1480. ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.76 t (3H, CH_3, J = 7.0 Hz); 0.79 t (3H, CH_3, J = 7.0 Hz); 1.16–1.30 m (4H), 1.34 sext (2H, J = 7.0 Hz), 1.62 quint (2H, J = 7.0 Hz), and 1.75 quint (2H, J = 7.0 Hz) (CH_2); 2.48 t (2H, C^4H_2, J = 7.0 Hz); 3.86 t (2H, OCH_2, J = 7.0 Hz); 5.75 s (1H, =CH); 7.08 d (2H, J = 9.0 Hz), 7.65 d (2H, J = 9.0 Hz), 7.71 d (2H, J = 8.0 Hz), and 7.90 d (2H, J = 8.0 Hz) (H_{arom}); 8.31 br.s (1H) and 10.74 br.s (1H) (NH_2).

Bis[1-amino-1-(4'-butoxybiphenyl-4-yl)oct-1-en-3-onato]nickel(II) (VIIa). Enaminoketone **VI**, 0.120 g (0.329 mmol), was dissolved in 10 ml of ethanol, 0.044 g (0.177 mmol) of nickel acetate tetrahydrate was added to the solution, and the mixture was heated for 1 min under reflux, diluted with 5 ml of water, and cooled. The precipitate was filtered off and washed on a filter with 20 ml of water and 3 ml of cold ethanol. Yield 0.113 g (87%). Phase transition temperatures, °C: (Cr) 194 (N) 270 (I). UV spectrum (dioxane): λ_{max} 299 nm. IR spectrum, ν, cm^{-1}: 3335 (N–H); 2990 (C–H_{arom}); 2950, 2920, 2865 (C–H_{alk}); 1600, 1565, 1540, 1485, 1425, 1330. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (6H, CH_3, J = 7.0 Hz); 0.98 t (6H, CH_3, J = 7.5 Hz); 1.20–1.35 m (8H), 1.42–1.56 m (8H), and 1.79 quint (4H, J = 7.0 Hz) (CH_2); 2.07 t (4H, CH_2, J = 7.0 Hz); 4.00 t (4H, OCH_2, J = 7.0 Hz); 5.30 d (2H, =CH, J = 3.0 Hz); 5.50 br.s (2H, NH); 6.97 d (4H, J = 9.0 Hz), 7.48–7.54 m (8H), and 7.56 d (4H, J = 8.5 Hz) (H_{arom}).

Bis[1-amino-1-(4'-butoxybiphenyl-4-yl)oct-1-en-3-onato]copper(II) (VIIb) was synthesized in a similar way. Yield 89%. Phase transition temperatures, °C: (Cr) 207 (N) 234 (I, decomp.). UV spectrum (dioxane): λ_{max} 298 nm. IR spectrum, ν, cm^{-1}: 3345 (N–H); 2990 (C–H_{arom}); 2950, 2920, 2865 (C–H_{alk}); 1600, 1565, 1530, 1480, 1425, 1340. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84–1.00 m (3H, CH_3), 0.96 t (3H, CH_3, J = 7 Hz), 1.42–1.56 m and 1.76 quint (J = 7 Hz) (CH_2), 3.95 t (2H, OCH_2, J = 6 Hz), 6.82–6.94 m and 7.40–7.56 m (H_{arom}).

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