

Convenient Synthesis of Building–Blocks for Pyridine/Piperidine–Decorated Crown Ethers

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Dedicated to Academician Oleg N. Chupakhin on the occasion of his 80th birthday

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A convenient way to 1-(pyridin-2-yl)ethan-1,2-diol, 2-(oxiran-2-yl)pyridine and two diastereomeric forms of 1-(piperidin-2-yl)ethan-1,2-diol, valuable building-blocks for the synthesis of functionalized crown ethers, has been developed. It is based on the Wagner oxidation or NBS-mediated epoxydation of 2-vinylpyridine, and the Schwenk-Papa reduction of 1-(pyridin-2-yl)ethan-1,2-diol, accompanied by fractional crystallization of a diastereo-meric mixture of the target product.

Keywords: 2-Vinylpyridine, piperidine, epoxidation, hydroxylation, reduction.

Усовершенствованный синтез билдинг–блоков для получения краун–эфиров с пиридиновыми или пиперидиновыми фрагментами

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Разработаны эффективные пути получения ключевых интермедиатов для синтеза краун-эфиров, содержащих пиридиновые и пиперидиновые фрагменты, основанные на вицинальном гидроксировании и восстановлении или эпоксидировании 2-винилпиридина.

Ключевые слова: 2-Винилпиридин, пиперидин, эпоксидирование, гидроксирование, восстановление.

Introduction

This work is dedicated to development of new scalable synthetic pathways to pyridinyl and piperidinyl substituted ethane-1,2-diols and oxiranes, namely: 1-(pyridin-2-yl)ethane-1,2-diol,^[1] 2-(oxiran-2-yl)pyridine^[2] and two diastereomeric forms of 1-(piperidin-2-yl)ethane-1,2-diol.^[3] Although, these compounds are well-known, they have never been regarded as promising starting materials for the synthesis of novel chiral macrocyclic compounds, the properties of which can be varied in a wide range, depending on configuration of their stereogenic centres and a degree of stereoregularity in decoration of the cyclic polyether core with incorporative fragments of nitrogen heterocycles. Meanwhile, nitrogen atoms of both pyridine and piperidine fragments are able to form an additional host cavity, superimposed on the crown ether macrocycle. Some macrocyclic compounds of this family appear to be an intriguing alternative to the known coronands and macrocyclic antibiotics (Figure 1).

As far as the template synthesis of crown ethers is not a costly and tedious procedure, we have focused on development of a safe and convenient pathway to the above mentioned pyridine and/or piperidine derivatives. Despite all these compounds were described in the literature, we have experienced severe problems, while trying to reproduce the procedures for their synthesis. This prompted us to develop new procedures for their preparation, which are capable to satisfy the demands of the ongoing template synthesis of macrocycles, based on using these scaffolds.^[1]

Experimental

IR spectra were recorded on a Specord M-82 spectrometer in Nujol mulls, and wave numbers, ν , were expressed in cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a AV Bruker (600 MHz) spectrometer, and shifts, δ , are given in ppm downfield from TMS as an internal standard. TLC analyses were performed on Merck's (Darmstadt, Germany) DC-alufolien with Kieselgel 60 F₂₅₄. HPLC-MS and HPLC-MS/MS analyses were carried out on a Agilent 1200 Instrument HPLC system comprising a vacuum degasser, quaternary gradient pump, an autosampler, and a diode array UV-vis and ELSD detectors. HPLC methods for 1-(pyridin-2-yl)ethane-1,2-diol and its reduction products: Method A: $\lambda = 200$ nm and ELSD-detector; Reprosil-Pur Basic C18 (250×4.6 mm; 5 μm); isocratic method: 0-5 min 113 μl of trifluoroacetic acid in 1 l of water; linear gradient method: 5-20 min from 100 % 113 μl of trifluoroacetic acid in 1 l of water to 113 μl of trifluoroacetic acid in 1 l of acetonitrile; flow 1 ml/min. Method B: $\lambda = 200$ nm and ELSD-detector; Reprosil-Pur Basic C18 (250×4.6 mm; 5 μm) with a Phenomenex pre-column; linear gradient method: 0-20 min from 0 to 90 % of acetonitrile in 10 mM ammonium acetate in water. Melting points were determined using a Buchi M-535 instrument. Elemental analyses were performed on a Vario EL Cube instrument.

1-(Pyridin-2-yl)ethane-1,2-diol, $\text{C}_7\text{H}_9\text{NO}_2$, (3). A saturated aqueous solution of 440 g (2.78 mol) of potassium permanganate was slowly dosed to a chilled solution of 300 ml (292 g, 2.78 mol) of 2-vinylpyridine in 5 l of acetone. An addition of the permanganate solution was accompanied by vigorous stirring of the reaction mixture and maintaining the inner temperature below 5 °C. After all the solution of potassium permanganate has been added, the reaction mixture was treated with 1500 ml of isopropanol and left at 0-5 °C overnight. The precipitated manganese dioxide was filtered off and filtrate was acidified to pH=5-6 with conc. sulphuric acid and treated

with 40 g of activated carbon. An excess acetone was distilled off at ordinary pressure and an aqueous solution was adjusted to pH=7 with solid potassium carbonate, filtered and evaporated to dryness under the diminished pressure. The resulting pasty mass was boiled with 2 l of ethanol, sucked from the precipitate of potassium sulphate and the stripped down from the solvent under reduced pressure. The dark semi-solid residue was extracted with 2 l of chloroform, filtered from the insoluble matter and concentrated to the residual volume of 800 ml. Upon stirring and cooling to -20 °C overnight, the solution deposited a crop of fine crystalline product, which was filtered off and washed with a little cold chloroform. This was recrystallized from chloroform one more time in a similar manner, giving the target product as smelly beige crystals. Yield - 250 g (65 %). M. p. 98-99.5 °C. Found: C 60.82, H 6.90, N 10.35 %. $\text{C}_7\text{H}_9\text{NO}_2$ requires C 60.42, H 6.52, N 10.07. ^1H NMR and ^{13}C NMR spectral data are in agreement with literature values.^[4]

2-(Oxiran-2-yl)pyridine, $\text{C}_7\text{H}_7\text{NO}$. *N*-Bromosuccinimide (450 g, 2.53 mol) was added portion-wise to a stirred solution of 250 ml (244 g, 2.32 mol) of 2-vinylpyridine in a mixture of 850 ml of tetrahydrofuran, 135 ml (142 g, 2.36 mol) of acetic acid and 2850 ml of water. During the addition of *N*-bromosuccinimide the temperature of the reaction mixture gradually raised from 24 to 34.5 °C. After stirring for additional 2 h, the reaction mixture cooled down to 27.5 °C and was treated with 655 g (4.74 mol) of solid potassium carbonate. During this operation pH of the solution reached 9-10. The whole mixture was stirred for an additional 30 min, and the resulting reddish-brown solution was thoroughly extracted with trichloroethylene (3×1 l). The combined organic extracts were dried over anhydrous sodium sulphate, filtered and quenched with 500 ml of diphenyloxide (vacuum distillation of the target product always results in a violent, explosion-like decomposition without the addition of diphenyloxide). Trichloroethylene was removed under diminished pressure and the target product was distilled *in vacuo* with a short Vigreux column, yielding 210 g (73 %) of a yellowish oil with characteristic odor. B.p. 102 °C (13 Torr). $n_D^{22} = 1.5365$. This product is unstable and readily turns into a mixture of polymers after a week at room temperature, even when stored in a sealed ampoule. Found: C 69.41, H 5.82, N 11.56 %. $\text{C}_7\text{H}_7\text{NO}$ requires C 69.80, H 6.10, N 11.73. ^1H NMR and ^{13}C NMR spectral data are in agreement with literature values.^[5]

1-(Piperidin-2-yl)ethane-1,2-diol, $\text{C}_7\text{H}_{15}\text{NO}_2$. Nickel-aluminium alloy (50/50, wt/wt; 480 g) was added portion-wise to a mixture of vigorously stirred solutions of 200 g (1.44 mol) 1-(pyridin-2-yl)ethane-1,2-diol in 5.2 l of tetrahydrofuran and 1.2 kg (~18 mol; assay ~84.5 % KOH) of potassium hydroxide in 4.8 l of water. After the exothermic reaction had ceased, the reaction mixture was left overnight at room temperature. The solution was removed by decantation and the Raney nickel catalyst was immediately covered with 500 ml of *n*-butanol. An upper organic layer was separated from an aqueous solution, and the former was returned to the reaction flask. The resulting mixture was vigorously stirred for 15-20 minutes and the above mentioned procedure was repeated. The aqueous phase and Raney nickel catalyst were extracted three times with *n*-butanol in a similar manner. All the *n*-butanol extracts were collected together, while an aqueous phase was discarded. The combined *n*-butanol solutions were evaporated at the diminished pressure and the residue was mixed with tetrahydrofuran layer, boiled with potassium hydroxide pellets stripped from the solvent under the ordinary pressure. A technical grade product obtained in this manner was fractionated *in vacuo*, resulting the colourless oil [b.p. 126-131 °C (1 Torr)] with pungent mouse-like odour, which solidified upon standing at room temperature (m.p. 66-67 °C). This was completely dissolved in a large amount of boiling methyl *t*-butyl ether and the resulting solution was concentrated at ordinary pressure until an opalescence appeared. Upon stirring and cooling to room temperature, the first crop (35 g) of the higher melting β -racemate precipitated from the solution. After concentration of the mother liquor to one-third of its initial volume, crystallization

of the second crop (25 g) of β -racemate deposited from the solution. The resulting filtrate was evaporated to dryness and the residue was dissolved in boiling diethyl ether. Concentration of this solution until the appearance of the turbidity and further stirring and cooling to room temperature, yielded 64 g of the lower melting α -racemate of the target compound. Additional crops (11 g) of this material were obtained by several further concentration of the mother liquor. Total yield of β -racemate is 60 g (29 %). M.p. 99-100 °C. (Lit. 99-100 °C^[6]) Found: C 58.01, H 10.50, N 9.47 %. $C_7H_{15}NO_2$ requires C 57.90, H 10.41, N 9.65. Total yield of α -racemate is 75 g (36 %). M.p. 77-78 °C. (Lit. 77-78 °C^[6]) Found: C 58.00, H 10.62, N 9.44 %. $C_7H_{15}NO_2$ requires C 57.90, H 10.41, N 9.65. ¹H NMR and ¹³C NMR spectral data for both products are in agreement with literature values.^[7]

Hydrogenation of 1-(pyridin-2-yl)ethane-1,2-diol. 1-(Pyridin-2-yl)ethane-1,2-diol (500 mg), 100 mg of catalyst (5 % palladium supported on carbon "Sibunit" or 5 % ruthenium supported on coal) and 10 ml of glacial acetic acid were loaded to steel autoclave equipped a mixer, manometer and thermocouple. The hydrogenation was carried out at 75-80 °C and at 50 bar of hydrogen pressure for 5-6 hours.

Results and Discussion

1-(2-Pyridin-2-yl)ethane-1,2-diol has first been reported by F.E. Cislack^[8] and, since that time, several synthetic pathways have been developed for its production. Most of them use 2-(pyridin-2-yl)ethanol (or 2-vinylpyridine) as a starting material.

While trying to reproduce the method of Cislack, we have faced with the problem to cause dehydration of 2-(pyridin-2-yl)ethanol, and to obtain the corresponding diol and its diacetate, since the reaction was accompanied by esterification of the diol on treatment with acetic acid. All attempts to distil the intermediate 1-(pyridin-2-yl)ethan-1,2-diyl diacetate in vacuum have failed, since they resulted in the formation of a huge amount of tarry material, together with small amounts of 1-(pyridin-2-yl)ethenyl acetate and 1-(pyridin-2-yl)ethan-1-one. Only traces of 1-(pyridin-2-yl)ethan-1,2-diyl diacetate were identified in the distillate, in spite of many runs of this reactions.

A straightforward method of the Wagner vicinal hydroxylation makes it an attractive synthetic route to convert 2-vinylpyridine into the desired 1-(pyridin-2-yl)ethane-1,2-diol. It has been stated that the pioneer procedure reported by Haas and co-authors^[9] allows to isolate the target compound in pure state only after the column chromatography in 40 % yield.^[10] Addition of magnesium sulphate during the permanganate oxidation gave a less pure product in a lower yield.^[11] The original procedure of Haas, as well as its improved version, proved to be hard to reproduce. On the one hand, a slimy precipitate of hydrated manganese dioxide proved to be hardly separable from an aqueous solution. On the other hand, chromatographic purification of 1-(pyridin-2-yl)ethane-1,2-diol was accompanied by local overheats of the column, thus leading to a poor separation. This is why we have used an acetone-water mixture, instead of water, to carry out an oxidation process. This allowed us to carry out the Wagner oxidation reaction under monophasic conditions, to remove the precipitated manganese dioxide easily by filtration, and to isolate the target product in a pure form after two recrystallizations from chloroform in 65 % yield (Figure 2).

2-(Oxiran-2-yl)pyridine can also be regarded as a synthetic precursor of 1-(pyridin-2-yl)ethane-1,2-diol. It can be converted into the latter by an acidic or enzymatic hydrolysis, but it has not been known definitely, whether this protocol may be scalable or not.^[5,12,13] The next part of our studies discloses a practical route to this compound. While trying to reproduce the method, described by Thurkauf and co-authors,^[14] we have discovered some surprising features. The first one is that the target product proved to be unstable under vacuum-distillation conditions, and it underwent violent, explosion-like decomposition. It is worth to mention, that a considerable amount of succinimide, which has gone into the organic extract due to use of dioxane, as a co-solvent, and ethyl acetate, as extractant, favours this process. Anyway, yields of 2-(oxiran-2-yl)pyridine never exceeded 50-55 %. In order to improve this method, several modifications, which appear to be crucial for the synthesis, have been undertaken. They include: i) replacement of dioxane for tetrahydrofuran, and use of potassium carbonate instead of sodium carbonate during the reaction; ii) use of trichloroethylene instead of ethyl acetate, as extractant; iii) dilution of organic extracts with diphenyloxide, before to remove trichloroethylene, and to do vacuum-distillation of the target compound. All these improvements allowed us to increase yields up to 73 % and avoid a plausible risk for the procedure of vacuum-distillation of the resulting pyridine derivative (Figure 3).

Finally, we had to carry out hydrogenation of 1-(pyridin-2-yl)ethane-1,2-diol into 1-(piperidin-2-yl)ethane-1,2-diol. It is noteworthy, that this compound, firstly reported in 1966, is still an object of particular interest in respect to the stereoselective preparation of its individual stereoisomers.^[7,15,16] Unfortunately, all procedures described in the literature are of theoretical, but not practical value.

While trying to hydrogenate 1-(pyridin-2-yl)ethane-1,2-diol hydrochloride in aqueous media according to the method of Hardie and co-authors,^[17] we have observed no absorption of hydrogen at a pressure up to 130 bar and temperature of 110 °C. Also we tried to do hydrogenation in the presence of the Adams catalyst, and found that the results obtained were in a full agreement with the pioneer data of Adams, who stated, that platinum dioxide was effective for reduction of the pyridine ring under anhydrous conditions.^[18]

An attempt to carry out the above mentioned hydrogenation procedure with a mixture of palladium on charcoal and platinum oxide, according to the method of Jacobson and co-authors,^[10] was also unsuccessful. The reaction gave a complex mixture of an unchanged starting material, together with 2-ethylpyridine and 2-(pyridin-2-yl)ethanol, as major products. No reduction of the pyridine ring has been observed.

The following results have been obtained for reduction of 1-(pyridin-2-yl)ethane-1,2-diol in anhydrous organic solvents (ethanol, *n*-butanol and acetic acid) using 5 % palladium on sibunit or 5 % ruthenium on carbon. In case of the first catalyst no reduction was observed in *n*-butanol (7.5 bar, 110 °C) after 5 hours, while in acetic acid the predominant dehydration proved to occur after 5-6 hours, 9.5 bar positive pressure of hydrogen and 120 or 75 °C. The target reduction product was also detected. Some progress in the hydrogenation reaction has also been observed, when

the reaction was carried out in ethanol at 70 °C and positive pressure of hydrogen of 35 Bar.

A more complete reduction was achieved with the above mentioned catalysts in acetic acid, at 40-50 °C and positive pressure of hydrogen 50 Bar. While carrying out the HPLC-MS and HPLC-MS/MS analysis of the reaction mixture with trifluoroacetic acid-water-acetonitrile, as a mobile phase, three main components were registered by ELSD detector (UV-detection appeared to be a less informative, due to a very low extinction of the target piperidine derivatives relative to acetic acid and other contaminants): $t_R = 2.731$ min (4.341 %), $t_R = 4.940$ min (82.599 %) and $t_R = 13.672$ min (11.414 %). These data concern the palladium-catalyzed reduction. The main component exhibits a peak of 146 on mass-detector (in case of MS/MS-analysis two characteristic ions, related to mono- or double-dehydration, 128.0 and 110.1, respectively, were recognized as the main ones), corresponding to the target compound, but it was also “infected” with the ions of a higher molecular weight - 271.5 and 400.4 (together with its fragment - 255.2). It was not clear, however, whether these ions were generated during an ionization process, or they simply resemble the undivided components. While performing the same analysis, using an ammonium acetate buffer solution together with acetonitrile, as a mobile phase, it was clearly seen for both ruthenium and palladium catalyzed reductions, that three main components were detected in each sample: $t_R = 2.847$ min (19.513 %), $t_R = 5.324$ min (36.274 %) and $t_R = 6.604$ min (27.612 %) - for palladium-catalyzed reaction and $t_R = 2.855$ min (24.281 %), $t_R = 5.328$ min (39.759 %) and $t_R = 6.611$ min (28.546 %) - for ruthenium-catalyzed process. It is noteworthy, that these data were very similar to each other, and the above mentioned peaks were assigned as follows, according to MS and MS/MS-data: the target product (146) - corresponding to the peak with $t_R \sim 6.61$ min, contaminant 1 (271.3) - corresponding to the peak with $t_R \sim 5.33$ min and contaminant 2 (400.4) - corresponding to the peak with $t_R \sim 2.85$ min. Taking into consideration the ability of primary and secondary amines to undergo alkylation with alcohols in the presence of hydrogenation-dehydrogenation catalysts, together with a higher reaction ability of primary alcohols in this side-reaction, we have suggested the structures of self-alkylation products to the above mentioned contaminants. So, the equation of this process seems to respond the following scheme (Figure 4).

After the negative experience, we have to pay our attention to an opportunity to use the Schwenk-Papa reaction, exploiting nickel-aluminium alloy in an aqueous alkali solution as a reductive agent.^[19] This method was successfully used for hydrogenation of a variety of substituted pyridines, however we have failed to do it with 2-isopropylpyridine and 2-(pyridin-2-yl)ethan-1-ol. Fortunately, this method appears to be quite effective and selective in regard to reduction of 1-(pyridin-2-yl)ethane-1,2-diol, but a large amount of mineral salts, which are present in a dilute water solution, together with miscibility of the target product with water, make the work-up procedure to be a very tedious one.^[6] To overcome this difficulties, we have turned to a mixed water-organic medium and, finally, extracted the target product from an aqueous matrix with *n*-butanol. These improvements led us to a simple and

effective protocol for the hydrogenation reaction, which avoids use of both high pressure and an external source of hydrogen. Moreover, to exclude the step of separation of two racemic mixtures of the target product, *via* formation and fractional crystallization and subsequent hydrolysis of their diphenylketals,^[17] we have simply resolved them by subsequent fractional crystallizations from methyl *tert*-butyl and diethyl ethers (Figure 5).

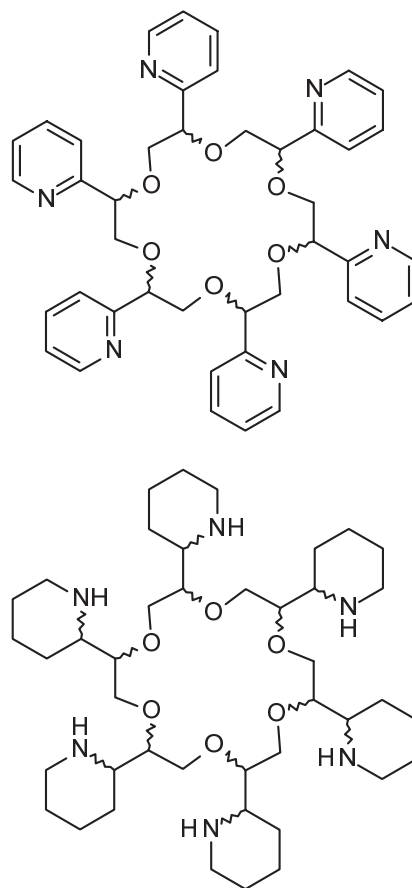


Figure 1. General structure of pyridine/piperidine-decorated crown ether.

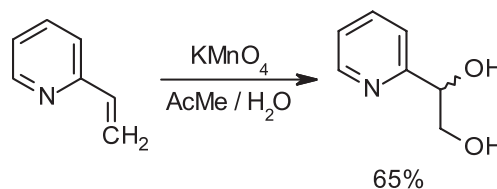


Figure 2. The Wagner oxidation of 2-vinylpyridine.

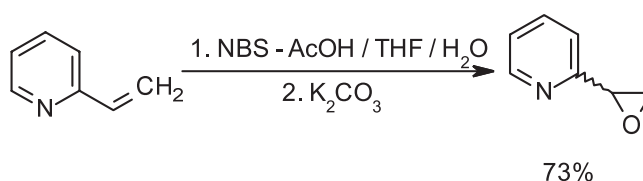


Figure 3. NBS-mediated epoxidation of 2-vinylpyridine.

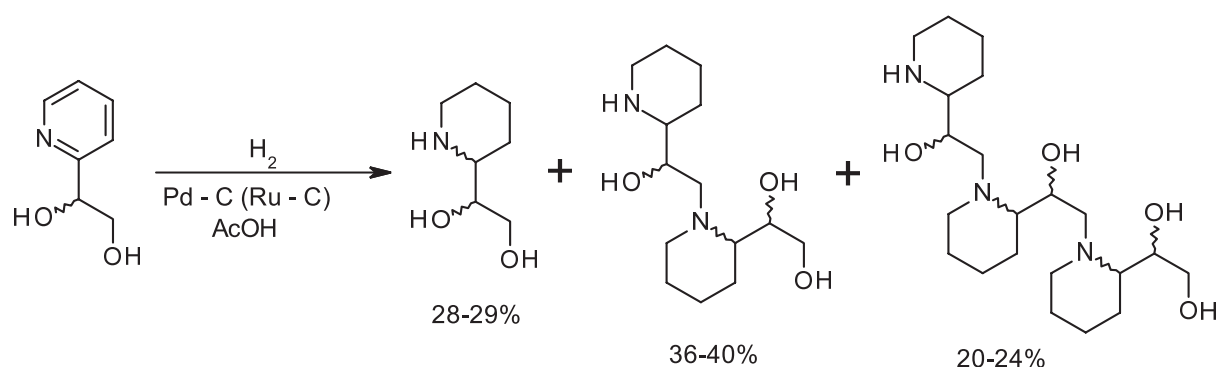


Figure 4. Catalytic reduction of 1-(pyridin-2-yl)ethane-1,2-diol.

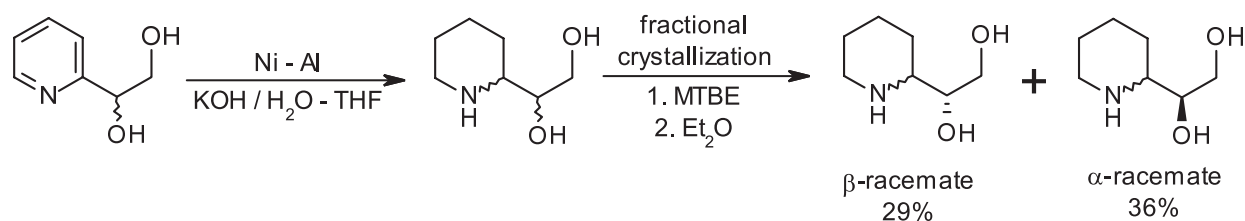


Figure 5. The Schwenk-Papa reduction and diastereomer separation of 1-(piperidin-2-yl)ethane-1,2-diol.

Conclusions

1-(Pyridine-2-yl)ethane-1,2-diol, 2-(oxirane-2-yl)pyridine and 1-(piperidine-2-yl)ethane-1,2-diol are considered as valuable starting materials for construction of crown ethers, decorated with pyridine and/or piperidine rings. Use of these compounds allows a particular feature of the target macrocycles - the formation of an additional cavity, formed by nitrogen atoms of pyridine and/or piperidine heterocycles. Novel procedures for preparation of the above mentioned building-blocks have been developed, in order to provide scalable and convenient methods for their production in amounts, needed for preparation of a library of the target chiral cyclic oligoethers.

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