ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 12, pp. 1755–1768. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.R. Ranyuk, A.D. Averin, N.V. Lukashev, A.K. Buryak, I.P. Beletskaya, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 12, pp. 1765–1776.

Palladium-Catalyzed Amination in the Synthesis and Modification of Acyclic Oxadiamino Cholane Derivatives

E. R. Ranyuk[a], A. D. Averin[a], N. V. Lukashev[a], A. K. Buryak[b], and I. P. Beletskaya[a]

[a] *Faculty of Chemistry, Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia*
e-mail: averin@org.chem.msu.ru; beletska@org.chem.msu.ru

[b] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*

Received April 10, 2009

Abstract—Palladium-catalyzed reactions of 24-(haloaryloxy)cholanes and 3,24-bis(haloaryloxy)cholanes with excess oxadiamines gave the corresponding mono- and bis(oxadiamino)-substituted cholanes which were subjected to palladium-catalyzed arylation with 1,3-dibromobenzene, 2,6-dibromopyridine, 1,8-dichloroanthracene, 9-bromoanthracene, 1-chloroanthracene, and 1-chloroanthraquinone. The results of these reactions were found to strongly depend on the haloarene nature. The arylation with 1,3-dibromobenzene and 2,6-dibromopyridine led to the formation of new macrocyclic compounds containing one cholane, one arene, and two oxadiamine fragments.

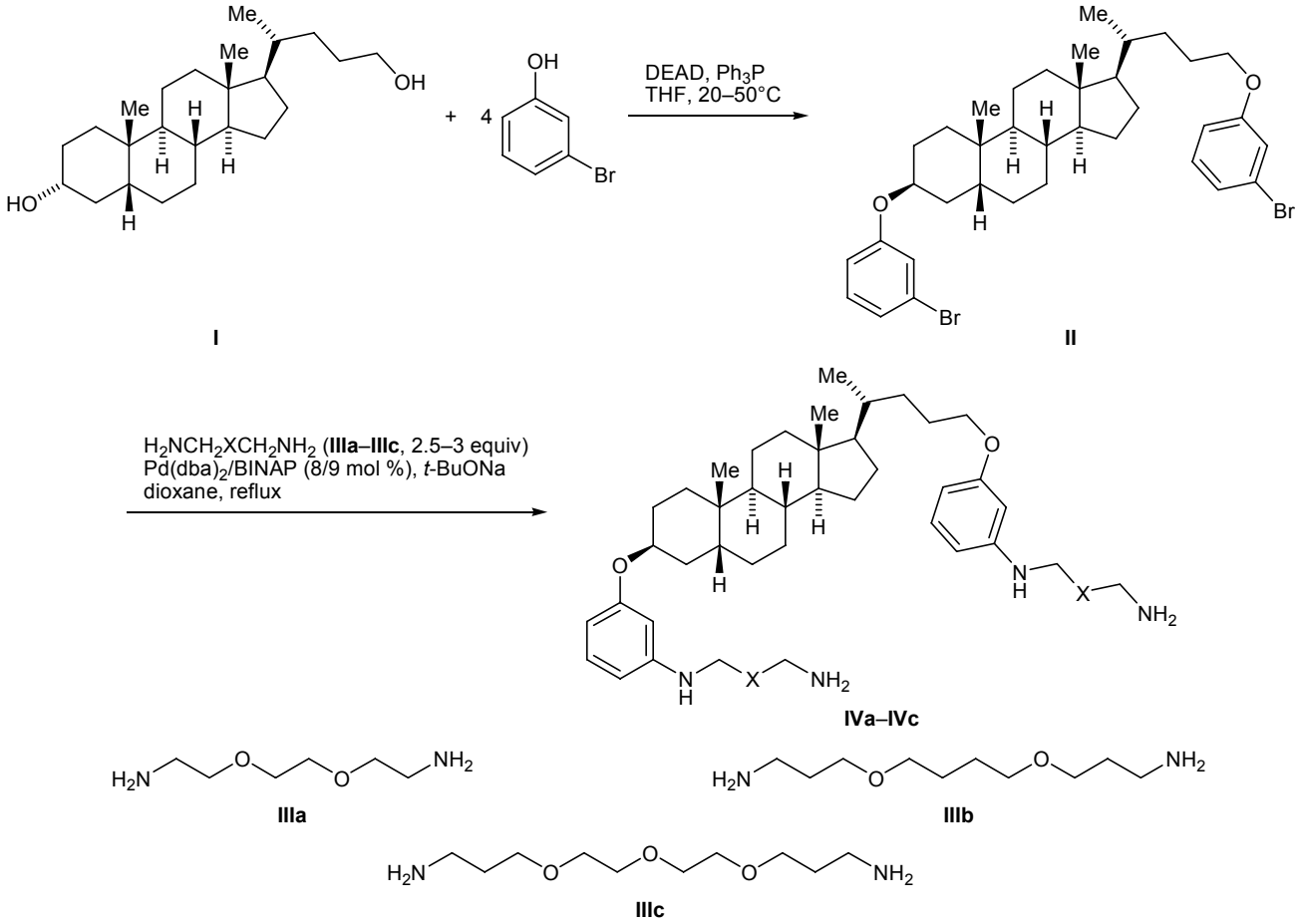
DOI: 10.1134/S1070428009120021

We recently developed an efficient procedure for the synthesis of macrocyclic compounds containing steroid and polyamine fragments via palladium-catalyzed amination of 3,24-bis(haloaryloxy)cholanes [1–5]. This procedure can also be used to obtain derivatives with linear polyamine chains appended to steroid fragment. Steroidal compounds with polyamine substituents on C^3 and C^{17} were found to ensure ion transport through lipid membranes. An analog of the natural polyamine Squalamine was reported to effectively transfer some anions [6], and amphiphilic polyamine dendrimers prepared from cholestamine were shown to be promising as transmembrane ion-transporting agents [7]. Squalamine exhibits biological activity against Gram-negative and Gram-positive bacteria [8], as well as antiangiogenic activity [9], and replacement of the triamine spermidine fragment by tetraamine spermine moiety considerably enhances the activity toward various microorganisms [10]. Polyamine substituents are generally introduced by reductive amination of 3-oxo steroids [11, 12]. Therefore, in the present work attempts were made to synthesize mono- and bis(polyamino)-substituted steroid derivatives via palladium-catalyzed amination and perform their further modification with a view to obtain novel macrocyclic compounds.

In the first step of our study we synthesized 3,24-bis(3-bromophenoxy)cholane (**II**) by the Mitsunobu reaction of cholane-3,24-diol (**I**) with 3-bromophenol, following the procedure described previously [1]. Reactions of **II** with 2.5–3 equiv of polyoxadiamines **IIIa**–**IIIc** gave the corresponding bis-amino derivatives **IVa**–**IVc** (Scheme 1). These reactions were carried out using the catalytic system $Pd(dba)_2$/BINAP (8/9 mol %) which turned out to be efficient in the syntheses of macrocyclic compounds described previously, but the reactant concentration was higher ($c \approx 0.1$ M) to avoid possible cyclization. The reaction mixtures were heated for 7 h under reflux. In almost all cases, compounds **IVa**–**IVc** were formed in nearly quantitative yields (according to the ^1H and ^{13}C NMR data) and were isolated from the reaction mixtures by column chromatography on silica gel in 40, 72, and 82% yield, respectively.

We also tried to synthesize unsymmetrical macrocycles consisting of one steroid, one arene, and two polyamine fragments. For this purpose, bis-amino-substituted steroids **IVa**–**IVc** were treated with various dihaloarenes (1,3-dibromobenzene, 2,6-dibromopyridine, and 1,8-dichloroanthracene). However, no desired cyclic compounds were formed from bisamines **IV** prepared *in situ*, but complex mixtures of products with different structures were obtained. Therefore, our further study was performed using as model compound **IVc** which can be readily isolated by chromatography. The reactions were carried out by

Scheme 1.

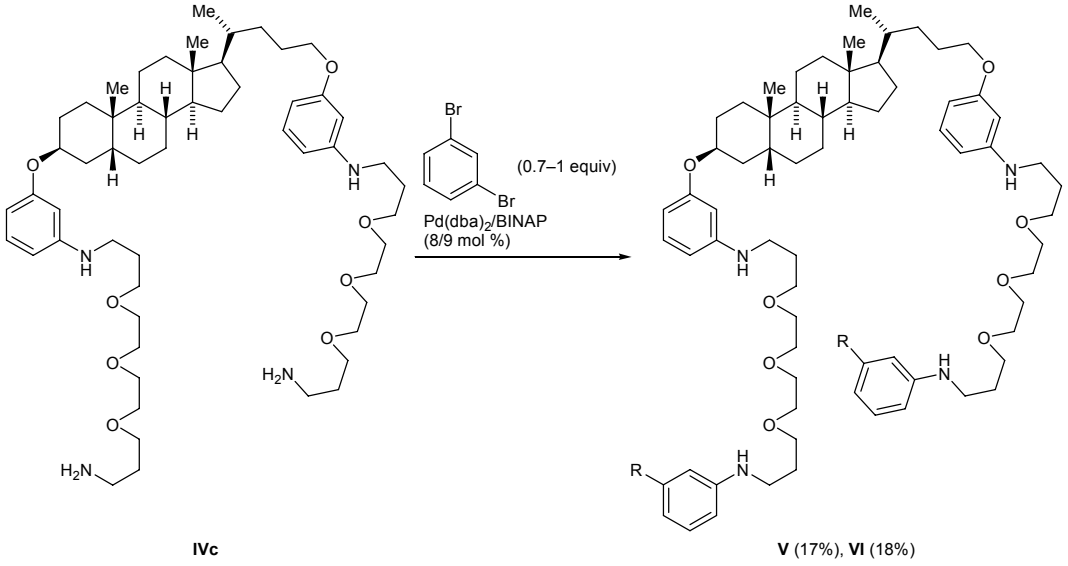


heating dilute solutions ($c \approx 0.02$ M) of the reactants in boiling dioxane over a period of 18 h. In the reaction of **IVc** with an equimolar amount of 1,3-dibromobenzene, acyclic bis-arylamino derivative **V** was formed instead of the expected cyclic product; it was isolated in 17% yield. No cyclic compound was isolated when the reaction was carried out wit insufficient *m*-dibromobenzene (0.7 equiv) to suppress bis-arylation process. Surprisingly, in this case we isolated 18% of linear bis-arylamino compound **VI** formed as a result of hydrodebromination of the bromophenylamino fragments in **V** (Scheme 2). Analogous bis-anthryl derivative **VII** was obtained in the reaction of **IVc** with 1,8-dichloroanthracene as potential ring-closing moiety. It was isolated in 33% yield. We succeeded in synthesizing the desired unsymmetrical macrocycle only by the reaction of **IVc** with 2,6-dibromopyridine, but the yield of **VIII** was as poor as 4%.

Taking into account difficulties encountered while attempting to synthesize macrocyclic compounds from bis-amino-substituted steroid, my examined an alternative synthetic pathway using compound **II** and bis-amino-substituted arenes as starting compounds. Initially, we prepared individual 1,3-disubstituted benzene **IX** and 2,6-disubstituted pyridine **X** in 56 and 27% yield, respectively, by palladium-catalyzed amination of 1,3-dibromobenzene and 2,6-dibromopyridine with 2.5 equiv of trioxadiamine **IIIc**. The reactions of **IX** and **X** with steroid **II** afforded the desired macrocycles **XI** and **VIII** in 21 and 20% yield, respectively (Scheme 3).

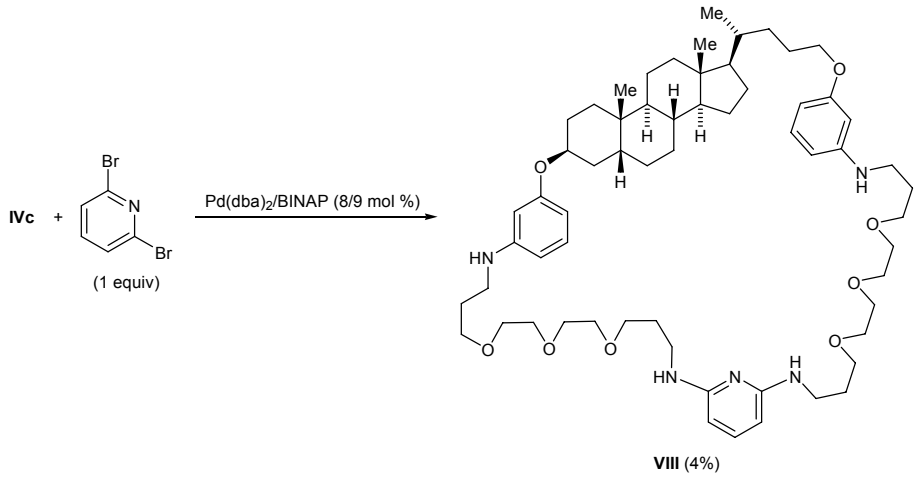
Acyclic polyamino derivatives of bis(pyridyloxy)-cholane were synthesized using 24-(6-chloropyridin-2-yloxy)cholane (**XII**) which was prepared from cholane-3,24-diol according to the procedure described in [3, 4]. Compound **XII** was treated with 2 equiv of trioxadiamine **IIIc** in the presence of 8/9 mol % of $Pd(dba)_2$/BINAP at a reactant concentration of 0.1 M in boiling dioxane (reaction time 4 h). We thus obtained compound **XIII**, which was isolated in 66% yield (Scheme 4). The reaction of **XII** with 2 equiv of tetraamine **IIId** gave 14% of bis-steroid derivative

Scheme 2.

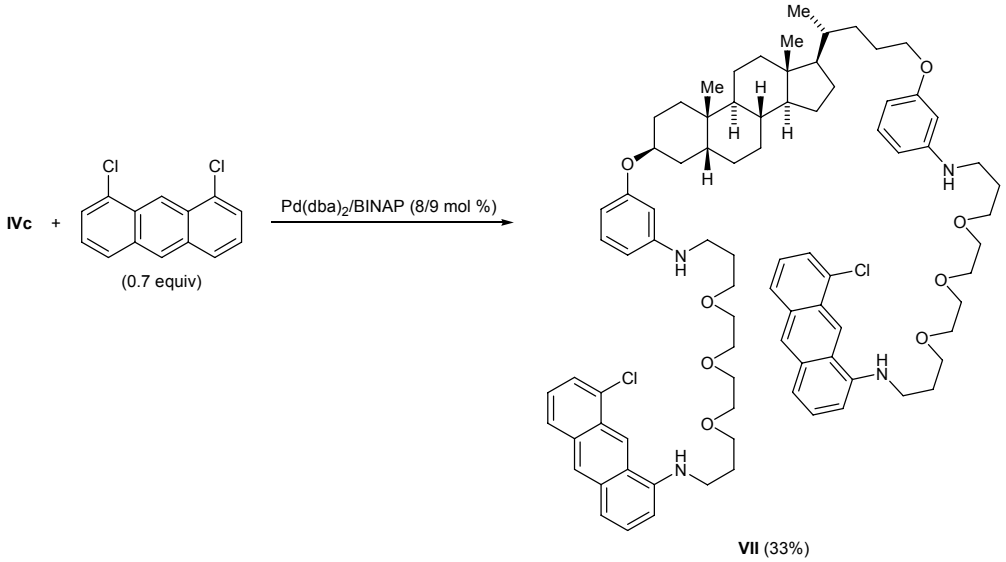


IVc **V** (17%), **VI** (18%)

V, R = Br; **VI**, R = H.

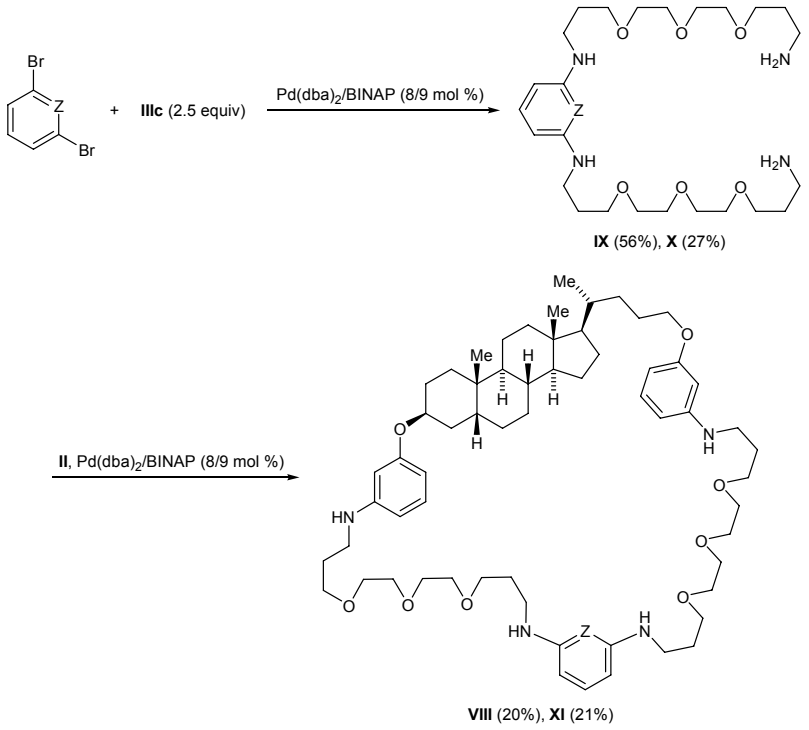


VIII (4%)



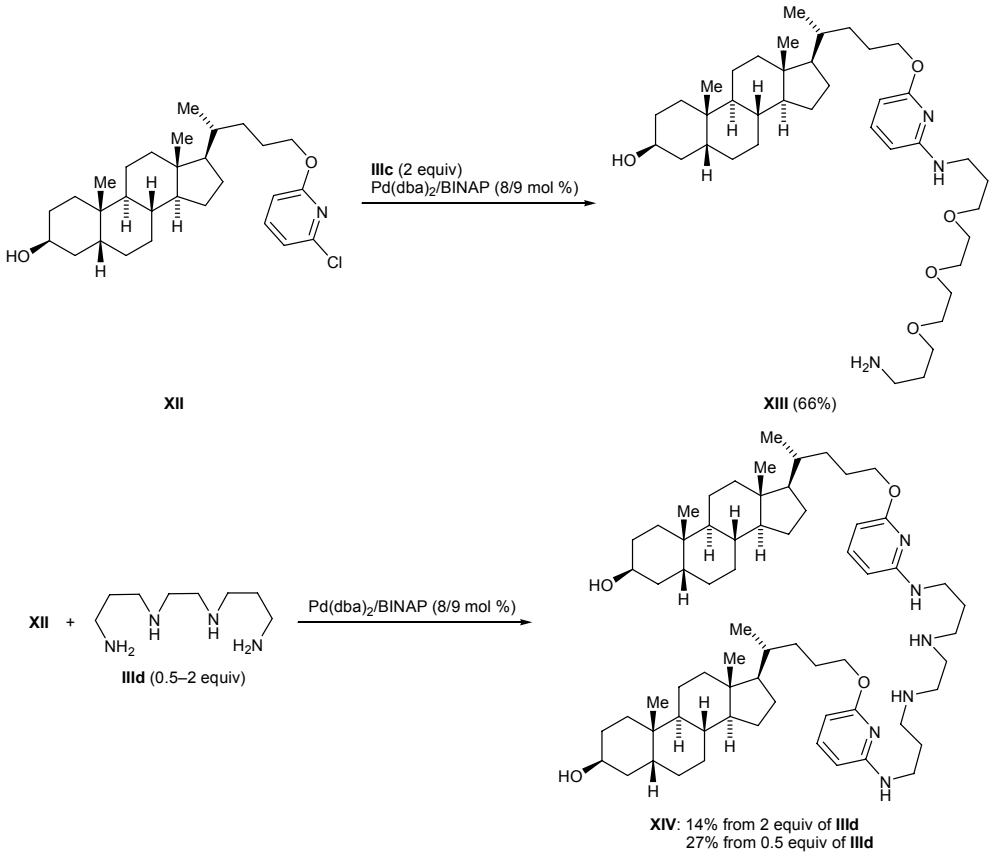
VII (33%)

Scheme 3.

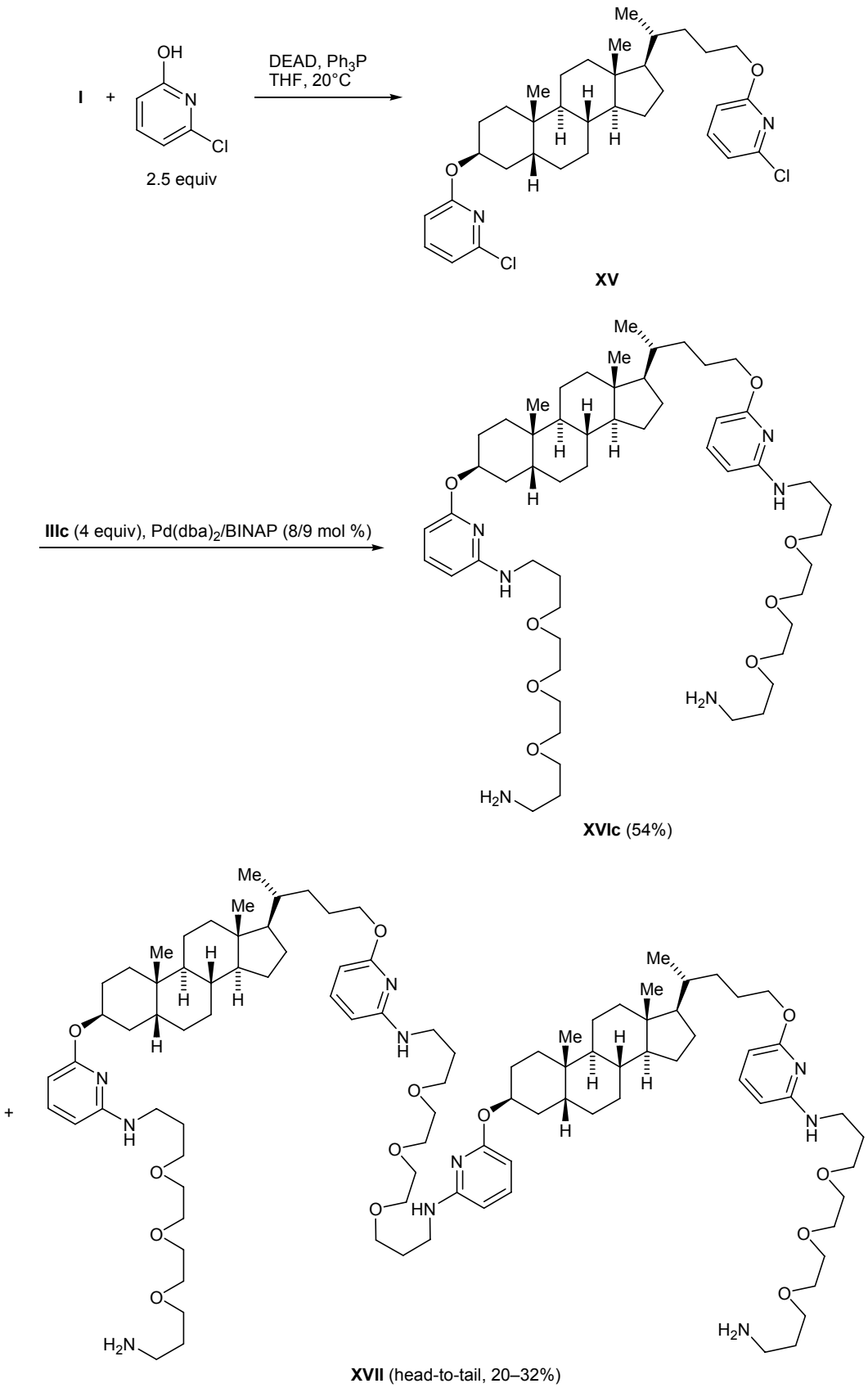


VIII, **X**, Z = N; **IX**, **XI**, Z = CH.

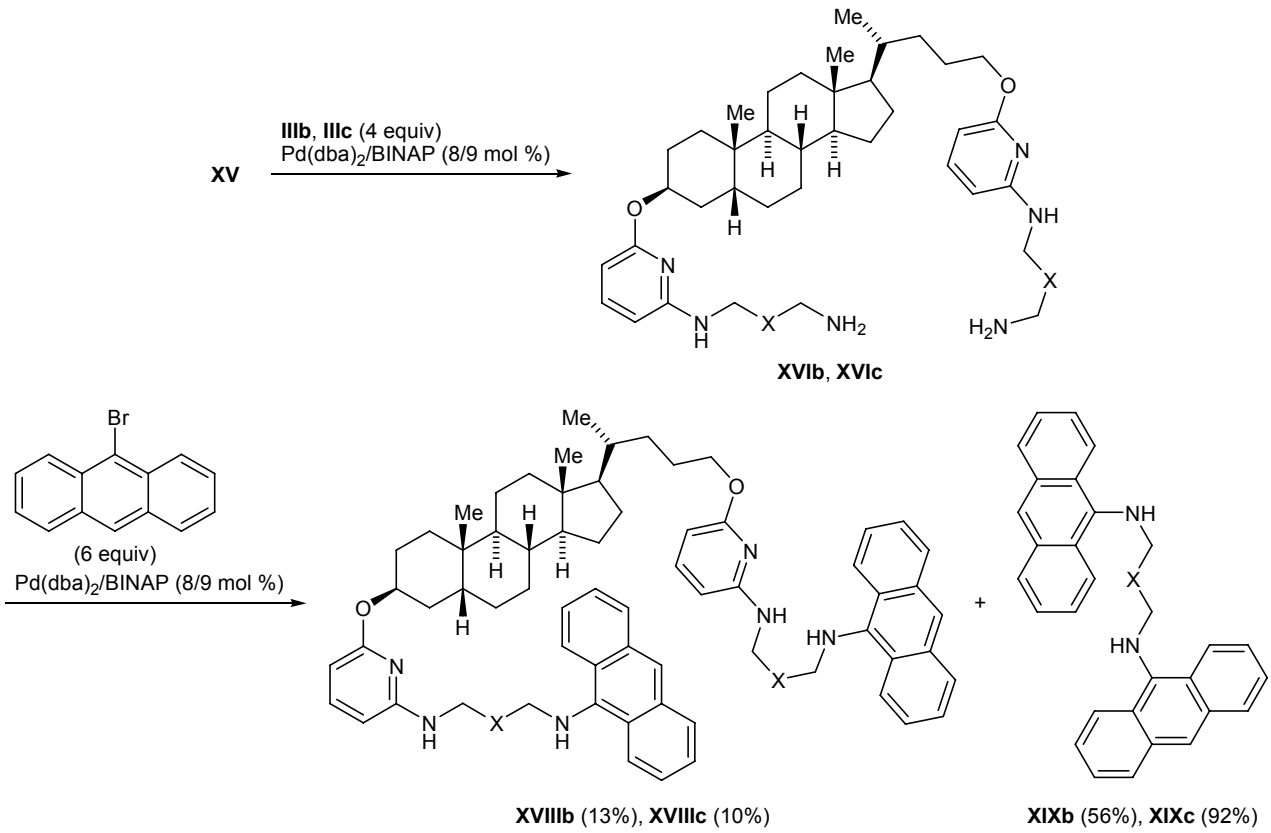
Scheme 4.



Scheme 5.


I
2.5 equiv
DEAD, Ph3P
THF, 20°C
XV
IIIc (4 equiv), Pd(dba)2/BINAP (8/9 mol %)
XVIc (54%)
XVII (head-to-tail, 20–32%)

Scheme 6.



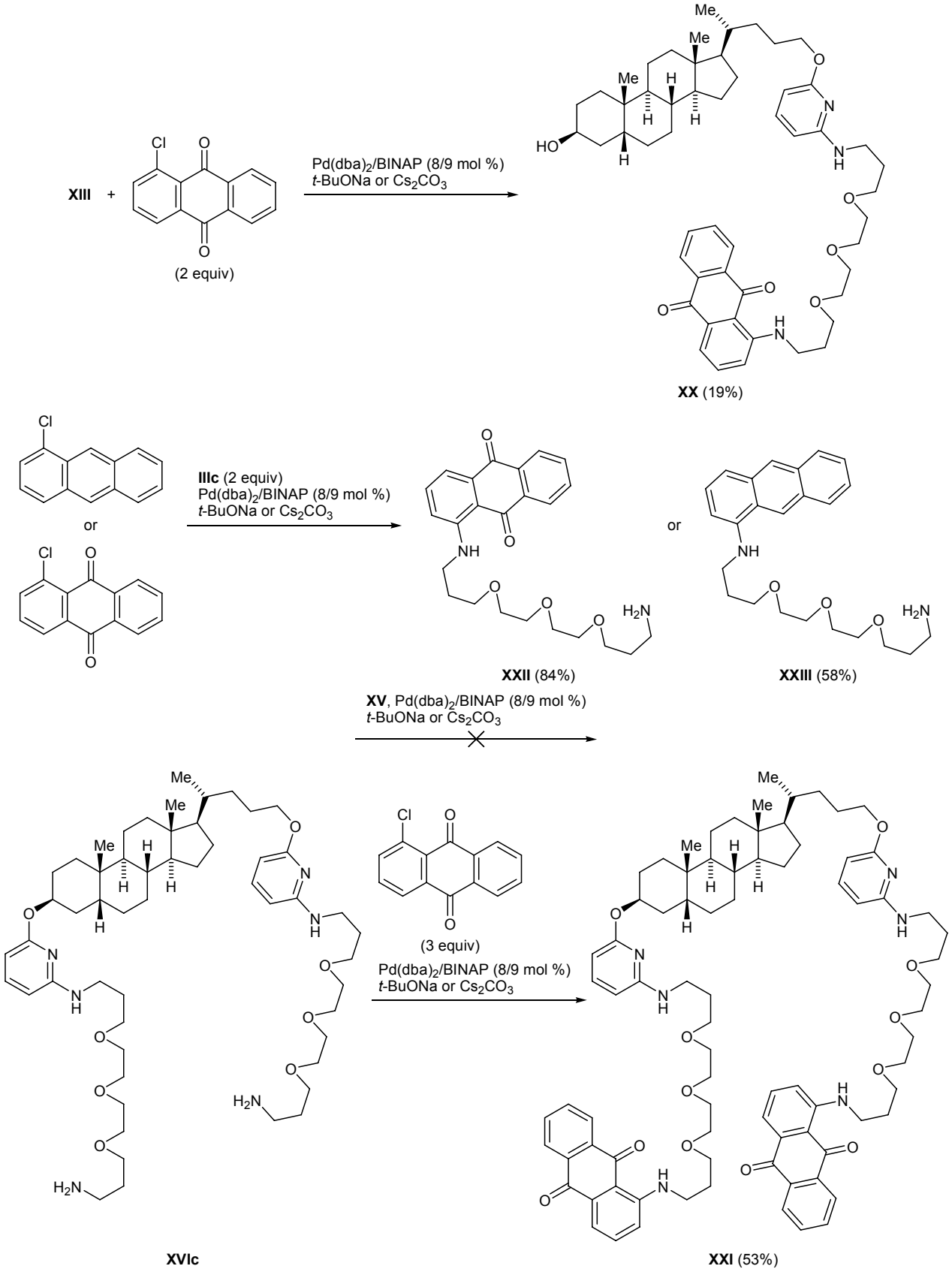
XIV instead of expected analogous mono-aminopyridyloxycholane. Compound **XIV** was synthesized in a higher yield (27%) by reaction of the same compounds at a **XII**:**IIId** ratio of 2:1 Compounds like **XIV** can be used in regioselective (head-to-head) syntheses of cyclic dimers.

Bis(trioxaaminopyridyloxy)-substituted cholane **XVIc** was synthesized in 54% yield by reaction of 3,24-bis(6-chloropyridin-2-yloxy)cholane (**XV**), which was prepared from cholane-3,24-diol (**I**) [3, 4], with 4 equiv of trioxadiamine **IIIc** at a reactant concentration of 0.05 M. It was noted that increase of the reactant concentration to 0.1 or 0.2 M or the use of a smaller amount of diamine **IIIc** (3 equiv) leads to sharp reduction of the yield of **XVIc** and the formation of three regioisomeric linear oligomer **XVII** (head-to-head, head-to-tail, and tail-to-tail; only one of the possible regioisomers is shown in Scheme 5).

We tried to modify the primary amino groups in disubstituted cholane derivatives **XVI** by introduction of aryl fragments, such as anthracene and anthraquinone, taking into account that anthracene and anthraquinone derivatives are characterized by strong absorption and emission bands in the electronic spectra. Compounds containing aminoanthracene and aminoanthraquinone fragments attract interest as potential optical sensors. Initially, we tried to synthesize such compounds by reaction of quite reactive 9-bromoanthracene with cholane derivatives **XVIb** and **XVIc** prepared *in situ*. We thus isolated the corresponding bis(anthrylamino) derivatives **XVIIIb** and **XVIIIc** in poor yields (13 and 10%, respectively; Scheme 6), presumably because of difficulties in chromatographic separation of the target products from *N*,*N*′-bisanthrylpolyoxadiamines **XIXb** and **XIXc**. Therefore, it was necessary to isolate cholane derivatives **XVI** as individual substances in order to perform their subsequent modifications.

In fact, compounds **XIII** and **XVIc** reacted with 1-chloroanthraquinone to afford target products **XX** and **XXI** (Scheme 7) in 19 and 53% yield, respectively. However, we failed to isolate analogous products in the reactions of the same cholane derivatives with 1-chloroanthracene. Alternative approach based on the reaction of *N*-monoaryl-substituted diamines **XXII** and **XXIII** with steroid **XV** was also inefficient: the conversion of the initial compounds was as low as 5 and 30%, respectively, after heating for 15 h under

Scheme 7.


XIII
(2 equiv)
Pd(dba)2/BINAP (8/9 mol %)
t-BuONa or Cs2CO3
XX (19%)
or
IIIc (2 equiv)
Pd(dba)2/BINAP (8/9 mol %)
t-BuONa or Cs2CO3
XXII (84%)
or
XXIII (58%)
XV, Pd(dba)2/BINAP (8/9 mol %)
t-BuONa or Cs2CO3
(3 equiv)
Pd(dba)2/BINAP (8/9 mol %)
t-BuONa or Cs2CO3
XVIc
XXI (53%)

reflux. These findings indicated that introduction of an aryl group into terminal amino group considerably affects the reactivity of the remaining free amino group.

Thus we demonstrated the possibility for catalytic synthesis of linear mono- and bis-polyoxaamino-substituted cholane derivatives, their transformation into macrocyclic compounds, and arylation with halo arenes. The results of the examined reactions were shown to depend on the structure of the initial compounds, so that the scope of their application was determined.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 instrument at 400 and 100.6 MHz, respectively. The mass spectra (MALDI TOF) were obtained on a Bruker Daltonics Ultraflex spectrometer using 1,8,9-trihydroxyanthracene as matrix. Commercially available lithocholic acid (3α-hydroxy-5β-cholan-24-oic acid), sodium tetrahydridoborate, boron trifluoride–ether complex, diethyl azodicarboxylate, 3-bromophenol, 6-chloropyridin-2-ol, 1,3-dibromobenzene, 2,6-dibromopyridine, 1,8-dichloroanthraquinone, 1-chloroanthraquinone, 9-bromoanthracene, polyoxa-(aza)diamines **IIIa**–**IIId**, BINAP, sodium *tert*-butoxide, and cesium carbonate were used without additional purification; triphenylphosphine was recrystallized from ethanol; THF and dioxane were distilled first over alkali and then over metallic sodium, diethyl ether was distilled over alkali; methylene chloride and methanol were purified by distillation. Silica gel with a grain size of 40–60 μm (from Fluka) was used for chromatography.

(3α,5β)-Cholane-3,24-diol (**I**) was synthesized by reduction of lithocholic acid with diborane in THF, and (3β,5β)-3,24-bis(3-bromophenoxy)cholane (**II**) was prepared from (3α,5β)-cholane-3,24-diol (**I**), according to the procedures described in [1]; (3α,5β)-24-(6-chloropyridin-2-yloxy)cholane (**XII**) and (3β,5β)-3,24-bis(6-chloropyridin-2-yloxy)cholane (**XV**) were obtained from (3α,5β)-cholane-3,24-diol (**I**) as reported in [3, 4]; 1,8-dichloroanthracene and 1-chloroanthracene were synthesized by reduction of 1,8-dichloroanhtraquinone and 1-chloroanthraquinone, respectively, with zinc in ammonia [13]; bis(dibenzylideneacetonato)palladium(II) was prepared as described in [14]. *N*,*N*′-Bis(13-amino-4,7,10-trioxatridecyl)benzene-1,3-diamine (**IX**) [15] and *N*,*N*′-bis(13-amino-4,7,10-trioxatridecyl)pyridine-2,6-diamine (**X**) [16] were synthesized as described previously.

Bis(polyoxaaminoaryloxy)-substituted cholanes IVa–IVc (*general procedure*). A 25-ml two-necked flask was filled with argon and charged with the corresponding reactants (see below). The mixture was heated for 5–8 h under reflux and cooled, the precipitate of sodium bromide was filtered off, and the filtrate was evaporated. The solid or oily residue was purified by chromatography on silica gel.

***N*-{2-[2-(2-Aminoethoxy)ethoxy]ethyl}-3-({(3β,5β,17α,20*S*)-3-[3-({2-[2-(2-aminoethoxy)-ethoxy]ethyl}amino)phenoxy]cholan-24-yl}oxy)-aniline (IVa)** was synthesized from 470 mg (0.7 mmol) of compound **II** and 259 mg (1.75 mmol) of dioxadiamine **IIIa** in the presence of 32 mg of $Pd(dba)_2$, 39 mg of BINAP, and 270 mg (2.8 mmol) of sodium *tert*-butoxide in 6 ml of anhydrous dioxane (reaction time 7 h). Eluent CH_2Cl_2–MeOH, 5:1. Yield 225 mg (40%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.64 s (3H), 0.93 d (3H, ^3J = 6.6 Hz), 0.96 s (3H), 0.99–2.00 m (28H), 2.85 br.s (4H), 3.25 t (4H, ^3J = 4.8 Hz), 3.49 br.s (4H), 3.59 s (8H), 3.66 t (4H, ^3J = 5.0 Hz), 3.81–3.89 m (2H), 4.52 br.s (1H), 6.15–6.28 m (6H), 7.00 t (1H, ^3J = 7.8 Hz), 7.02 t (1H, ^3J 7.9 = Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.6 (1C), 21.0 (1C), 23.8 (1C), 24.2 (1C), 24.6 (1C), 25.9 (1C), 26.2 (1C), 26.6 (1C), 28.2 (1C), 30.4 (1C), 32.0 (1C), 34.8 (1C), 35.5 (1C), 35.6 (1C), 36.9 (1C), 39.9 (1C), 40.2 (1C), 41.1 (1C), 42.7 (1C), 43.4 (2C), 56.1 (1C), 56.6 (1C), 68.2 (1C), 69.6 (2C), 69.6 (2C), 70.1 (4C), 71.9 (2C), 72.3 (1C), 99.5 (1C), 101.2 (1C), 103.2 (1C), 104.8 (1C), 105.8 (1C), 106.0 (1C), 129.7 (1C), 129.8 (1C), 149.5 (1C), 149.6 (1C), 158.9 (1C), 160.3 (1C). Mass spectrum: *m*/*z* 807.48 $[M + H]^+$.

***N*-{3-[4-(3-Aminopropoxy)butoxy]propyl}-3-({24-[3-({3-[4-(3-aminopropoxy)butoxy]propyl}-amino)phenoxy]cholan-3-yl}oxy)aniline (IVb)** was synthesized from 140 mg (0.21 mmol) of compound **II** and 129 mg (0.63 mmol) of dioxadiamine **IIIb** in the presence of 10 mg of $Pd(dba)_2$, 12 mg of BINAP, and 70 mg (0.73 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 8 h). Eluent CH_2Cl_2–MeOH (5:1), CH_2Cl_2–MeOH–aq. NH_3 (10:3:1). Yield 138 mg (72%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.65 s (3H), 0.93 d (3H, ^3J = 6.2 Hz), 0.96 s (3H), 1.02–2.03 m (44H), 3.18 br.s (8H), 3.43 br.s (4H), 3.45 br.s (4H), 3.50–3.58 m (8H),

3.86 br.s (2H), 4.53 s (1H), 6.12–6.25 m (6H), 7.01 t (1H, ^3J = 7.7 Hz), 7.02 t (1H, ^3J = 7.8 Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.1 (1C), 18.6 (1C), 21.1 (1C), 23.8 (1C), 24.2 (1C), 24.7 (1C), 25.9 (1C), 26.3 (1C), 26.4 (4C), 26.6 (1C), 28.3 (1C), 29.3 (2C), 29.4 (2C), 30.5 (2C), 32.1 (1C), 34.8 (1C), 35.5 (1C), 35.7 (1C), 37.0 (1C), 39.2 (2C), 40.0 (1C), 40.3 (1C), 41.9 (2C), 42.7 (1C), 56.2 (1C), 56.6 (1C), 68.2 (1C), 68.9 (2C), 69.3 (2C), 70.7 (2C), 70.9 (2C), 72.3 (1C), 99.2 (1C), 100.7 (1C), 102.8 (1C), 104.6 (1C), 105.5 (1C), 105.8 (1C), 129.8 (2C), 149.8 (1C), 149.9 (1C), 159.0 (1C), 160.4 (1C). Mass spectrum: *m*/*z* 919.48 $[M]^+$.

***N*-(3-{2-[2-(3-Aminopropoxy)ethoxy]ethoxy}-propyl)-3-([(3β,5β,17α,20*S*)-24-{3-[(3-{2-[2-(3-aminopropoxy)ethoxy]ethoxy}propyl)amino]-phenoxy}cholan-3-yl]oxy)aniline (IVc)** was synthesized from 908 mg (1.35 mmol) of compound **II** and 1.189 g (5.4 mmol) of trioxadiamine **IIIc** in the presence of 62 mg of $Pd(dba)_2$, 76 mg of BINAP, and 520 mg (5.4 mmol) of sodium *tert*-butoxide in 13 ml of anhydrous dioxane (reaction time 8 h). Eluent CH_2Cl_2–MeOH, 5:1. Yield 1.05 g (82%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.63 s (3H), 0.92 d (3H, ^3J = 6.6 Hz), 0.95 s (3H), 0.98–2.02 m (28H), 1.84 br.s (4H), 1.89 quint (4H, ^3J = 6.3 Hz), 2.99 t (4H, ^3J = 5.5 Hz), 3.18 t (4H, ^3J = 5.7 Hz), 3.55–3.66 m (24H), 3.82–3.88 m (2H), 4.52 br.s (1H), 6.10–6.26 m (6H), 6.99 t (1H, ^3J = 7.8 Hz), 7.00 t (1H, ^3J = 8.0 Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.6 (1C), 21.0 (1C), 23.8 (1C), 24.1 (1C), 24.6 (1C), 25.9 (1C), 26.2 (1C), 26.5 (1C), 28.1 (1C), 28.2 (2C), 29.0 (2C), 30.4 (2C), 32.1 (1C), 34.8 (1C), 35.5 (1C), 35.6 (1C), 36.9 (1C), 39.7 (2C), 40.0 (1C), 40.2 (1C), 41.6 (2C), 42.7 (1C), 56.1 (1C), 56.6 (1C), 68.2 (1C), 69.6 (2C), 69.8 (2C), 69.9 (2C), 70.0 (4C), 70.4 (2C), 72.2 (1C), 99.5 (1C), 101.1 (1C), 103.0 (1C), 104.7 (1C), 105.8 (1C), 106.1 (1C), 129.7 (1C), 129.7 (1C), 149.8 (1C), 149.9 (1C), 158.9 (1C), 160.3 (1C). Mass spectrum: *m*/*z* 951.60 $[M + H]^+$.

The other compounds were synthesized and isolated in a similar way.

***N*-[3-(2-{2-[3-(3-Bromophenylamino)propoxy]-ethoxy}ethoxy)propyl]-3-{[(3β,5β)-24-(3-{[3-(2-{2-[3-(3-bromophenylamino)propoxy]ethoxy}ethoxy)-propyl]amino}phenoxy)cholan-3-yl]oxy}aniline (V)** was synthesized from 214 mg (0.225 mmol) of compound **IVc** and 53 mg (0.225 mmol) of 1,3-dibromobenzene in the presence of 11 mg of $Pd(dba)_2$, 13 mg of BINAP, and 90 mg (0.92 mmol) of sodium *tert*-butoxide in 11 ml of anhydrous dioxane (reaction time 18 h). Eluent CH_2Cl_2–MeOH, 100:1. Yield 24 mg (17%), transparent light yellow oily substance which slowly crystallized on storage. ^{1}H NMR spectrum, δ, ppm: 0.66 s (3H), 0.95 d (3H, ^3J = 6.3 Hz), 0.97 s (3H), 0.98–2.02 m (28H), 1.86 quint (8H, ^3J = 6.3 Hz), 3.16–3.24 m (8H), 3.55–3.70 m (24H), 3.84–3.91 m (2H), 4.17 br.s (4H), 4.54 br.s (1H), 6.13–6.25 m (6H), 6.47 d.d (2H, ^3J = 8.1, ^4J = 2.1 Hz), 6.71 br.s (2H), 6.75 d (2H, ^3J = 8.1 Hz), 6.97 t (2H, ^3J = 8.0 Hz), 7.02 t (1H, ^3J = 7.9 Hz), 7.03 t (1H, ^3J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.1 (1C), 18.6 (1C), 21.1 (1C), 23.9 (1C), 24.2 (1C), 24.7 (1C), 26.0 (1C), 26.3 (1C), 26.6 (1C), 28.3 (1C), 28.9 (2C), 29.2 (2C), 29.2 (2C), 32.2 (1C), 34.9 (1C), 35.5 (1C), 35.7 (1C), 37.0 (1C), 40.1 (1C), 40.3 (1C), 41.8 (4C), 42.8 (1C), 56.3 (1C), 56.7 (1C), 68.3 (1C), 69.8 (2C), 69.8 (2C), 70.3 (4C), 70.7 (4C), 72.3 (1C), 99.3 (1C), 101.0 (1C), 102.8 (1C), 104.4 (1C), 105.6 (1C), 105.8 (1C), 111.4 (2C), 115.1 (2C), 119.5 (2C), 123.2 (2C), 129.7 (1C), 129.8 (1C), 130.4 (2C), 149.9 (3C), 150.0 (1C), 159.0 (1C), 160.4 (1C).

***N*-(3-{2-[2-(3-Phenylaminopropoxy)ethoxy]-ethoxy}propyl)-3-([(3β,5β)-24-{3-[(3-{2-[2-(3-phenylaminopropoxy)ethoxy]ethoxy}propyl)amino]-phenoxy}cholan-3-yl]oxy)aniline (VI)** was synthesized from 334 mg (0.35 mmol) of compound **IVc** and 55 mg (0.23 mmol) of 1,3-dibromobenzene in the presence of 11 mg of $Pd(dba)_2$, 13 mg of BINAP, and 90 mg (0.92 mmol) of sodium *tert*-butoxide in 11 ml of anhydrous dioxane (reaction time 18 h). Eluent CH_2Cl_2–MeOH, 100:1. Yield 23 mg (18%), transparent light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.66 s (3H), 0.94 d (3H, ^3J = 6.6 Hz), 0.97 s (3H), 0.99–2.03 m (28H), 1.86 quint (4H, ^3J = 5.7 Hz), 1.88 quint (4H, ^3J = 5.7 Hz), 3.22 t (8H, ^3J = 6.6 Hz), 3.54–3.69 m (24H), 3.83–3.93 m (2H), 4.54 br.s (1H), 6.08–6.26 m (6H), 6.59 d (4H, ^3J = 8.6 Hz), 6.66 t (2H, ^3J = 7.4 Hz), 7.02 t (1H, ^3J = 8.3 Hz), 7.03 t (1H, ^3J = 8.1 Hz), 7.15 t (4H, ^3J = 7.8 Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.1 (1C), 18.6 (1C), 21.1 (1C), 23.8 (1C), 24.2 (1C), 24.9 (1C), 26.0 (1C), 26.3 (1C), 26.6 (1C), 28.3 (1C), 29.1 (2C), 30.4 (2C), 30.5 (2C), 32.1 (1C), 34.9 (1C), 35.5 (1C), 35.7 (1C), 37.0 (1C), 40.0 (1C), 40.3 (1C), 41.7 (4C), 42.7 (1C), 56.2 (1C), 56.6 (1C), 68.3 (1C), 69.7 (4C), 70.3 (4C), 70.6 (4C), 72.3 (1C), 99.2 (1C), 100.9 (1C), 102.7 (1C), 104.3 (1C), 105.6 (1C), 105.8 (1C), 112.7 (4C), 117.0 (2C),

129.2 (4C), 129.7 (1C), 129.8 (1C), 148.5 (2C), 149.9 (1C), 150.0 (1C), 158.9 (1C), 160.4 (1C).

***N*-(8-Chloroanthracen-1-yl)-3-[2-(2-{3-[3-({(3β,5β)-24-[3-({3-[2-(2-{3-[(8-chloroanthracen-1-yl)amino]propoxy}ethoxy)ethoxy]propyl}amino)-phenoxy]cholan-3-yl}oxy)phenylamino]propoxy}-ethoxy)ethoxy]propane-1-amine (VII)** was synthesized from 334 mg (0.35 mmol) of compound **IVc** and 57 mg (0.23 mmol) of 1,8-dichloroanthracene in the presence of 11 mg of $Pd(dba)_2$, 13 mg of BINAP, and 90 mg (0.92 mmol) of sodium *tert*-butoxide in 11 ml of anhydrous dioxane (reaction time 18 h). Eluent CH_2Cl_2–MeOH, 100:1. Yield 52 mg (33%), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 0.66 s (3H), 0.94 d (3H, ^3J = 5.8 Hz), 0.97 s (3H), 1.78 quint (4H, ^3J = 6.1 Hz), 1.00–2.07 (28H), 2.12 quint (4H, ^3J = 6.1 Hz), 3.14 t (4H, ^3J = 6.4 Hz), 3.46 t (4H, ^3J = 5.4 Hz), 3.55–3.77 m (24H), 3.83–3.90 m (2H), 4.52 br.s (1H), 6.08–6.28 m (6H), 6.49 d (2H, ^3J = 6.6 Hz), 7.02 t (1H, ^3J = 8.2 Hz), 7.03 t (1H, ^3J = 8.0 Hz), 7.28–7.58 m (6H), 7.95 d (2H, ^3J = 9.1 Hz), 8.00 d (2H, ^3J = 8.6 Hz), 8.33 s (2H), 8.39 s (2H); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.1 (1C), 18.6 (1C), 21.08 (1C), 23.8 (1C), 24.2 (1C), 24.7 (1C), 26.0 (1C), 26.2 (1C), 26.6 (1C), 28.3 (1C), 28.9 (2C), 29.1 (1C), 29.1 (1C), 30.5 (2C), 32.1 (1C), 34.8 (1C), 35.5 (1C), 35.6 (1C), 37.0 (1C), 40.0 (1C), 40.2 (1C), 41.7 (2C), 42.7 (1C), 42.8 (2C), 56.2 (1C), 56.6 (1C), 68.3 (1C), 69.6 (2C), 70.1 (2C), 70.2 (2C), 70.5 (2C), 70.6 (2C), 70.6 (2C), 72.3 (1C), 99.2 (1C), 100.9 (1C), 101.4 (2C), 102.7 (1C), 104.3 (1C), 105.6 (1C), 105.8 (1C), 116.9 (2C), 118.9 (2C), 123.8 (2C), 124.8 (2C), 125.4 (2C), 126.3 (2C), 127.7 (2C), 128.4 (2C), 129.7 (1C), 129.8 (1C), 130.8 (2C), 131.5 (2C), 132.0 (2C), 132.6 (2C), 143.6 (2C), 149.9 (1C), 149.9 (1C), 159.0 (1C), 160.4 (1C).

Macrocyclic compound (VIII). *a*. The reaction was carried out with 214 mg (0.23 mmol) of compound **IVc** and 53 mg (0.23 mmol) of 2,6-dibromopyridine in the presence of 11 mg of $Pd(dba)_2$, 13 mg of BINAP, and 90 mg (0.92 mmol) of sodium *tert*-butoxide in 11 ml of anhydrous dioxane (reaction time 18 h). Eluent CH_2Cl_2–MeOH, 25:1. Yield 9 mg (4%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.65 s (3H), 0.94 d (3H, ^3J = 6.4 Hz), 0.96 s (3H), 0.99–2.01 m (28H), 1.86 q (8H, ^3J = 5.8 Hz), 3.20 q (4H, ^3J = 6.3 Hz), 3.27 t (4H, ^3J = 6.3 Hz), 3.51–3.69 m (24H), 3.83–3.91 m (2H), 4.53 br.s (1H), 5.67 d (2H, ^3J = 7.8 Hz), 6.11–6.27 m (6H), 6.98–7.06 m (2H), 7.22 t (1H, ^3J = 7.8 Hz); signals from NH protons were not assigned unambiguously.

b. Compound **VIII** was synthesized from 68 mg (0.1 mmol) of cholane derivative **II** and 52 mg (0.1 mmol) of 2,6-disubstituted pyridine **X** in the presence of 4.5 mg of $Pd(dba)_2$, 5.5 mg of BINAP, and 30 mg (0.3 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane (reaction time 20 h). Eluent CH_2Cl_2–MeOH, 25:1. Yield 21 mg (20%).

Macrocyclic compound (XI) was synthesized from 200 mg (0.3 mmol) of compound **II** and 154 mg (0.3 mmol) of 1,3-disubstituted benzene **IX** in the presence of 14 mg of $Pd(dba)_2$, 17 mg of BINAP, and 86 mg (0.9 mmol) of sodium *tert*-butoxide in 15 ml of anhydrous dioxane (reaction time 29 h). Eluent CH_2Cl_2–MeOH, 25:1. Yield 63 mg (21%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.66 s (3H), 0.94 d (3H, ^3J = 6.4 Hz), 0.97 s (3H), 1.01–2.01 m (28H), 1.86 br.s (8H), 3.18 t (4H, ^3J = 5.9 Hz), 3.19 t (4H, ^3J = 5.8 Hz), 3.55–3.61 m (16H), 3.63–3.68 m (8H), 3.87 br.s (2H), 4.54 s (1H), 5.85 s (1H), 5.97 d (2H, ^3J = 7.8 Hz), 6.13–6.25 m (6H), 6.94 t (1H, ^3J = 7.9 Hz), 7.02 t (1H, ^3J = 7.7 Hz), 7.03 t (1H, ^3J = 7.7 Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.6 (1C), 21.1 (1C), 23.8 (1C), 24.2 (1C), 24.6 (1C), 25.9 (1C), 26.2 (1C), 26.6 (1C), 28.2 (1C), 29.0 (2C), 29.3 (2C), 30.4 (2C), 32.1 (1C), 34.8 (1C), 35.5 (1C), 35.6 (1C), 36.9 (1C), 40.0 (1C), 40.2 (1C), 41.5 (2C), 41.6 (2C), 42.7 (1C), 56.2 (1C), 56.6 (1C), 68.2 (1C), 69.6 (2C), 69.7 (2C), 70.2 (4C), 70.6 (4C), 72.2 (1C), 97.0 (1C), 99.1 (1C), 100.8 (1C), 102.5 (2C), 102.6 (1C), 104.2 (1C), 105.6 (1C), 105.8 (1C), 129.7 (1C), 129.8 (2C), 149.6 (2C), 149.8 (1C), 149.9 (1C), 158.9 (1C), 160.3 (1C).

(3α,5β)-24-{3-[(3-{2-[2-(3-Aminopropoxy)-ethoxy]ethoxy}propyl)amino]phenoxy}cholan-3-ol (XIII) was synthesized from 280 mg (0.59 mmol) of compound **XII** and 260 mg (1.18 mmol) of trioxadiamine **IIIc** in the presence of 27 mg of $Pd(dba)_2$, 33 mg of BINAP, and 115 mg (1.18 mmol) of sodium *tert*-butoxide in 6 ml of anhydrous dioxane (reaction time 4 h). Eluent CH_2Cl_2–MeOH (5:1, 2.5:1), CH_2Cl_2–MeOH–aq. NH_3 (100:20:1, 100:20:2). Yield 257 mg (66%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.54 s (3H), 0.80 s (3H), 0.83 d (3H, ^3J = 7.0 Hz), 0.90–1.90 m (32H), 2.66 t (2H, ^3J = 6.1 Hz), 3.24 t (2H, ^3J = 5.6 Hz), 3.44 t (2H, ^3J = 6.3 Hz), 3.46–3.50 m (6H), 3.52–3.56 m (4H), 3.56–3.60 m (1H), 4.03 br.s (2H), 5.81 d (1H, ^3J = 7.6 Hz),

5.84 d (1H, ^3J = 8.0 Hz), 7.18 t (1H, ^3J = 7.8 Hz); signals from NH and OH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 11.8 (1C), 18.4 (1C), 20.6 (1C), 23.2 (1C), 24.0 (1C), 25.5 (1C), 26.2 (1C), 27.0 (1C), 28.0 (1C), 29.1 (1C), 29.4 (1C), 30.3 (1C), 31.9 (1C), 33.0 (1C), 34.3 (1C), 35.2 (1C), 35.3 (1C), 35.6 (1C), 36.2 (1C), 39.3 (1C), 40.0 (1C), 40.2 (1C), 41.9 (1C), 42.4 (1C), 55.9 (1C), 56.3 (1C), 65.8 (1C), 69.2 (2C), 69.9 (2C), 70.3 (2C), 70.7 (1C), 96.7 (1C), 97.3 (1C), 139.5 (1C), 157.7 (1C), 163.2 (1C). Mass spectrum: *m*/*z* 657.74 $[M]^+$.

(3α,5β,3′α,5′β)-24,24′-[Ethane-1,2-diyldi(iminopropane-3,1-diyliminopyridine-6,2-diyloxy)]bis(cholan-3-ol) (XIV) was synthesized from 460 mg (0.97 mmol) of compound **XII** and 85 mg (0.5 mmol) of tetraamine **IIId** in the presence of 22 mg of $Pd(dba)_2$, 27 mg of BINAP, and 140 mg (1.45 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane (reaction time 6 h). Eluent CH_2Cl_2–MeOH–aq. NH_3 (100:20:1, 100:20:2, 100:20:3). Yield 140 mg (27%), light yellow crystalline powder, mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 0.59 s (6H), 0.86 s (6H), 0.88 d (6H, ^3J = 6.8 Hz), 0.95–1.95 m (60H), 2.82 t (4H, ^3J = 5.7 Hz), 2.96 s (4H), 3.31 br.s (4H), 3.52–3.60 m (2H), 3.98–4.08 m (4H), 4.70 br.s (2H), 5.89 d (2H, ^3J = 7.7 Hz), 5.93 d (2H, ^3J = 7.8 Hz), 7.23 t (2H, ^3J = 7.8 Hz); signals from two NH protons ($CH_2N\mathbf{H}CH_2$) were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 11.9 (2C), 18.5 (2C), 20.7 (2C), 23.3 (2C), 24.1 (2C), 25.7 (2C), 26.3 (2C), 27.1 (2C), 27.7 (2C), 28.2 (2C), 30.4 (2C), 32.0 (2C), 34.4 (2C), 35.3 (2C), 35.5 (2C), 35.7 (2C), 36.3 (2C), 39.3 (2C), 40.1 (2C), 40.3 (2C), 42.0 (2C), 42.6 (2C), 46.4 (4C), 56.0 (2C), 56.4 (2C), 66.4 (2C), 71.5 (2C), 96.1 (2C), 98.6 (2C), 139.8 (2C), 157.8 (2C), 163.3 (2C). Mass spectrum: *m*/*z* 1049.09 $[M]^+$.

6,6′-[(3β,5β)-Cholane-3,24-diyldi(oxy)]bis(*N*-{3-[4-(3-aminopropoxy)butoxy]propyl}pyridin-2-amine) (XVIb) was synthesized from 290 mg (0.49 mmol) of compound **XV** and 400 mg (1.96 mmol) of dioxadiamine **IIIb** in the presence of 23 mg of $Pd(dba)_2$, 27 mg of BINAP, and 140 mg (1.5 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane. Yield 90% (in the reaction mixture). The product was brought into reaction with 9-bromoanthracene without isolation. ^{1}H NMR spectrum, δ, ppm: 0.60 s (3H), 0.89 d (3H, ^3J = 6.6 Hz), 0.92 s (3H), 0.96–1.95 m (36H), 1.65 quint (4H, ^3J = 6.5 Hz), 1.81 quint (4H, ^3J = 5.5 Hz), 2.73 t (4H, ^3J = 6.8 Hz), 3.24–3.31 m (4H), 3.35–3.49 m (16H), 4.04–4.12 m (2H), 4.63 t (1H, ^3J = 5.0 Hz), 4.66 t (1H, ^3J = 5.1 Hz), 5.13 s (1H), 5.82 d (1H, ^3J = 7.9 Hz), 5.85 d (1H, ^3J = 7.8 Hz), 5.91 d (2H, ^3J = 7.8 Hz), 7.24 t (1H, ^3J = 7.8 Hz), 7.25 t (1H, ^3J = 7.8 Hz); signals from protons in the primary amino groups were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.5 (1C), 21.0 (1C), 23.7 (1C), 24.1 (1C), 24.9 (1C), 25.7 (1C), 26.2 (1C), 26.4 (4C), 26.5 (1C), 28.2 (1C), 29.4 (2C), 30.6 (2C), 32.1 (1C), 33.4 (2C), 34.8 (1C), 35.4 (1C), 35.6 (1C), 37.1 (1C), 39.6 (2C), 39.9 (1C), 40.0 (2C), 40.2 (1C), 42.6 (1C), 56.2 (1C), 56.6 (1C), 66.0 (1C), 68.8 (2C), 69.0 (2C), 70.1 (1C), 70.6 (2C), 70.7 (2C), 96.8 (1C), 97.0 (1C), 97.2 (1C), 98.0 (1C), 139.6 (1C), 139.7 (1C), 157.8 (2C), 162.8 (1C), 163.4 (1C). Mass spectrum: *m*/*z* 920.87 $[M]^+$.

6,6′-[(3β,5β)-Cholane-3,24-diyldi(oxy)]bis[*N*-(3-{2-[2-(3-aminopropoxy)ethoxy]ethoxy}propyl)pyridin-2-amine] (XVIc). *a*. The reaction was carried out with 693 mg (1.18 mmol) of compound **XV** and 1.04 g (4.72 mmol) of trioxadiamine **IIIc** in the presence of 54 mg of $Pd(dba)_2$, 66 mg of BINAP, and 340 mg (3.5 mmol) of sodium *tert*-butoxide in 24 ml of anhydrous dioxane (reaction time 4 h). Eluent CH_2Cl_2–MeOH (5:1, 2.5:1),. Yield 605 mg (54%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H), 0.85 d (3H, ^3J = 6.4 Hz), 0.88 s (3H), 0.92–1.91 m (28H), 1.62 quint (4H, ^3J = 6.6 Hz), 1.77 quint (4H, ^3J = 5.7 Hz), 2.68 t (4H, ^3J = 6.8 Hz), 3.25 br.s (4H), 3.45 t (4H, ^3J = 6.2 Hz), 3.47–3.51 m (12H), 3.53–3.57 m (8H), 3.99–4.09 m (2H), 4.72 t (1H, ^3J = 4.6 Hz), 4.76 t (1H, ^3J = 5.7 Hz), 5.09 s (1H), 5.79 d (1H, ^3J = 7.8 Hz), 5.82 d (1H, ^3J = 7.9 Hz), 5.86 d (2H, ^3J = 7.8 Hz), 7.19 t (1H, ^3J = 7.8 Hz), 7.20 t (1H, ^3J = 7.8 Hz); signals from protons in the primary amino groups were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 11.8 (1C), 18.4 (1C), 20.8 (1C), 23.6 (1C), 24.0 (1C), 24.7 (1C), 25.5 (1C), 26.0 (1C), 26.4 (1C), 28.0 (1C), 29.1 (2C), 30.5 (2C), 31.9 (1C), 33.1 (2C), 34.6 (1C), 35.3 (1C), 35.4 (1C), 36.9 (1C), 39.3 (2C), 39.4 (2C), 39.7 (1C), 40.0 (1C), 42.5 (1C), 56.0 (1C), 56.4 (1C), 65.8 (1C), 69.2 (4C), 69.9 (4C), 70.3 (5C), 96.6 (1C), 96.9 (1C), 97.3 (1C), 97.6 (1C), 139.4 (1C), 139.5 (1C), 157.7 (2C), 162.6 (1C), 163.2 (1C). Mass spectrum: *m*/*z* 952.89 $[M]^+$.

b. The reaction of 290 mg (0.47 mmol) of compound **XV** with 310 mg (1.41 mmol) trioxadiamine **IIIc** in the presence of 22 mg of $Pd(dba)_2$, 26 mg of BINAP, and 135 mg (1.4 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane (7 h under reflux) gave 125 mg (32%) of acyclic oligomer **XVII** as by-product. Eluent CH_2Cl_2–MeOH (2.5:1), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 0.63 s

(6H), 0.91 d (6H, ^3J = 6.3 Hz), 0.94 s (6H), 0.96–2.00 m (68H), 3.14 br.s (4H), 3.30 br.s (8H), 3.58 br.s (36H), 4.01–4.13 m (4H), 4.66 br.s (2H), 4.71 br.s (2H), 5.10 s and 5.13 s (1H each), 5.85–5.99 m (8H), 7.27 t (4H, ^3J = 7.7 Hz); signals from protons in the primary amino groups were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 12.0 (2C), 18.6 (2C), 21.0 (2C), 23.8 (2C), 24.2 (2C), 24.9 (2C), 25.7 (2C), 26.2 (2C), 26.6 (2C), 28.2 (2C); 29.0, 29.1, and 29.2 (6C); 30.7 (4C), 32.1 (2C), 34.8 (2C), 35.5 (2C), 35.6 (2C), 37.1 (2C); 39.3, 39.4, and 39.7 (6C); 39.9 (2C), 40.2 (2C), 42.7 (2C), 56.2 (2C), 56.6 (2C), 66.1 (2C), 69.3 (2C), 69.4 (2C), 69.8 (8C), 70.1 (2C), 70.2 (2C), 70.3 (2C), 70.5 (2C), 96.1 (1C), 96.9 (1C), 97.1 (1C), 97.4 (1C), 97.5 (1C), 97.7 (1C), 97.9 (1C), 98.2 (1C), 139.8 and 139.9 (4C), 158.0 (2C), 162.8 (2C), 163.4 (2C). Mass spectrum: *m*/*z* 1685.38 $[M]^+$.

***N*-(3-{4-[3-(9-Anthrylamino)propoxy]butoxy}propyl)-6-{[(3β,5β)-24-({6-[(3-{4-[3-(9-anthrylamino)propoxy]butoxy}propyl)amino]pyridin-2-yl}oxy)cholan-3-yl]oxy}pyridin-2-amine (XVIIIb)** was synthesized from compound **XVIb** (prepared *in situ*) and 830 mg (3.2 mmol) of 9-bromoanthracene in the presence of 34 mg of $Pd(dba)_2$, 41 mg of BINAP, and 420 mg (4.3 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane (reaction time 4 h). Eluent CH_2Cl_2–MeOH (25:1). Yield 82 mg (13%, calculated on the initial compound **XV** taken for the preparation of 0.49 mol of **XVIb**), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 0.64 s (3H), 0.92 d (3H, ^3J = 4.9 Hz), 0.96 s (3H), 0.98–1.95 m (36H), 2.00 quint (4H, ^3J = 5.9 Hz), 2.12 quint (4H, ^3J = 6.2 Hz), 3.25–3.34 m (8H), 3.36–3.70 m (16H), 4.08–4.18 m (2H), 4.68 br.s (4H), 5.16 s (1H), 5.86 d (1H, ^3J = 8.1 Hz), 5.89 d (1H, ^3J = 8.1 Hz), 5.97 d (2H, ^3J = 7.6 Hz), 7.25–7.31 m (2H), 7.38–7.45 m (8H), 7.91–7.97 m (4H), 8.10 s (2H), 8.25–8.30 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.6 (1C), 21.1 (1C), 23.8 (1C), 24.2 (1C), 25.0 (1C), 25.8 (1C), 26.3 (1C), 26.5 (1C), 26.6 (4C), 28.2 (1C), 29.5 (3C), 30.7 (2C), 32.1 (1C), 34.9 (1C), 35.5 (1C), 35.7 (1C), 37.1 (1C), 40.0 (1C), 40.1 (2C), 40.3 (1C), 42.7 (1C), 50.5 (2C), 56.2 (1C), 56.6 (1C), 66.1 (1C), 69.1 (2C), 70.1 (2C), 70.3 (1C), 70.7 (2C), 71.1 (2C), 96.9 (1C), 97.1 (1C), 97.3 (1C), 98.1 (1C), 121.0 (2C), 123.2 (4C), 124.5 (4C), 125.1 (4C), 125.3 (4C), 128.8 (4C), 132.3 (4C), 139.8 (2C), 142.2 (2C), 157.9 (2C), 162.9 (1C), 163.5 (1C). Mass spectrum: *m*/*z* 1272.18 $[M]^+$.

***N*,*N*′-{3,3′-[Butane-1,4-diyldi(oxy)]bis(propane-3,1-diyl)}di(anthracen-9-amine) (XIXb)** was isolated as the major product in the synthesis of compound **XVIIIb**. Eluent CH_2Cl_2–MeOH, 100:1. Yield 304 mg (56%), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 1.80 br.s (4H), 2.00 quint (4H, ^3J = 6.0 Hz), 3.49 t (4H, ^3J = 6.2 Hz), 3.54–3.57 m (4H), 3.66 t (4H, ^3J = 5.8 Hz), 7.40–7.46 m (8H), 7.93–7.98 m (4H), 8.10 s (2H), 8.26–8.32 m (4H); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 26.7 (2C), 30.8 (2C), 50.4 (2C), 70.1 (2C), 71.1 (2C), 121.0 (2C), 123.2 (4C), 124.4 (4C), 125.1 (4C), 125.2 (4C), 128.8 (4C), 132.3 (4C), 142.2 (2C). Mass spectrum: *m*/*z* 556.47 $[M]^+$.

***N*-[3-(2-{2-[3-(9-Anthrylamino)propoxy]ethoxy}ethoxy)propyl]-6-({(3β,5β)-24-[(6-{[3-(2-{2-[3-(9-anthrylamino)propoxy]ethoxy}ethoxy)propyl]amino}pyridin-2-yl)oxy]cholan-3-yl}oxy)pyridin-2-amine (XVIIIc)** was synthesized from compound **XVIc** (prepared *in situ*) and 830 mg (3.2 mmol) of 9-bromoanthracene in the presence of 34 mg of $Pd(dba)_2$, 41 mg of BINAP, and 420 mg (4.3 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane (reaction time 4 h). Eluent CH_2Cl_2–MeOH, 50:1. Yield 62 mg (10%, calculated on the initial compound **XV** taken for the synthesis of 0.49 mol of diamine **XVIc**), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 0.64 s (3H), 0.93 d (3H, ^3J = 6.3 Hz), 0.96 s (3H), 0.99–2.00 m (32H), 2.01 quint (4H, ^3J = 6.1 Hz), 3.25 q (4H, ^3J = 6.7 Hz), 3.33 q (4H, ^3J = 6.7 Hz), 3.44–3.75 m (24H), 4.08–4.16 m (2H), 4.63 br.s (2H), 4.69 br.s (2H), 5.17 s (1H), 5.83 d (1H, ^3J = 7.8 Hz), 5.87 d (1H, ^3J = 7.8 Hz), 5.97 d (2H, ^3J = 7.7 Hz), 7.26 d (1H, ^3J = 7.8 Hz), 7.27 d (1H, ^3J = 7.8 Hz), 7.40–7.45 m (8H), 7.93–7.97 m (4H), 8.09 s (2H), 8.27–8.31 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.6 (1C), 21.0 (1C), 23.8 (1C), 24.2 (1C), 24.9 (1C), 25.7 (1C), 26.2 (1C), 26.6 (1C), 28.2 (1C), 29.3 (2C), 30.7 (4C), 32.1 (1C), 34.8 (1C), 35.5 (1C), 35.6 (1C), 37.1 (1C), 39.7 (1C), 39.9 (2C), 40.2 (1C), 42.7 (1C), 50.3 (2C), 56.2 (1C), 56.6 (1C), 66.1 (1C), 69.4 (2C), 70.1 (2C), 70.2 (2C), 70.4 (1C), 70.5 (2C), 70.6 (4C), 97.0 (1C), 97.1 (1C), 97.5 (1C), 97.9 (1C), 120.9 (2C), 123.3 (4C), 124.4 (4C), 125.1 (4C), 125.2 (4C), 128.8 (4C), 132.3 (4C), 139.8 (2C), 142.2 (2C), 157.9 (2C), 162.8 (1C), 163.4 (1C). Mass spectrum: *m*/*z* 1305.01 $[M]^+$.

***N*,*N*′-{3,3′-[2,2′-Oxydi(ethane-2,1-diyl)di(oxy)]di(propane-3,1-diyl)}bis(anthracen-9-amine) (XIXc)** was isolated as the major product in the synthesis of compound **XVIIIc**. Eluent CH_2Cl_2–MeOH, 500:1. Yield 515 mg (92%), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 1.95 quint (4H, ^3J = 6.1 Hz), 3.47 t (4H, ^3J = 6.3 Hz), 3.61–3.65 m (8H),

3.70–3.75 m (4H), 7.41–7.49 m (8H), 7.94–7.99 m (4H), 8.11 s (2H), 8.28–8.34 m (4H); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 30.6 (2C), 50.2 (2C), 70.2 (2C), 70.3 (2C), 70.5 (2C), 120.8 (2C), 123.2 (4C), 124.3 (4C), 125.0 (4C), 125.1 (4C), 128.7 (4C), 132.2 (4C), 142.2 (2C). Mass spectrum: *m*/*z* 572.47 $[M]^+$.

1-({3-[2-(2-{3-[(6-{[(3α,5β)-3-Hydroxycholan-24-yl]oxy}pyridin-2-yl)amino]propoxy}ethoxy)ethoxy]-propyl}amino)-9,10-dihydroanthracene-9,10-dione (XX) was synthesized from 180 mg of compound **XIII** and 133 mg (0.55 mmol) of 1-chloroanthraquinone in the presence of 12 mg of $Pd(dba)_2$, 15 mg of BINAP, and 176 mg (0.54 mmol) of cesium carbonate in 6.75 ml of anhydrous dioxane (reaction time 24 h). Eluent CH_2Cl_2–MeOH, 100:1. Yield 33 mg (19%), dark red oily substance. ^{1}H NMR spectrum, δ, ppm: 0.60 s (3H), 0.88 s (3H), 0.90 d (3H, ^3J = 6.4 Hz), 0.93–1.95 m (29H), 1.85 quint (2H, ^3J = 6.2 Hz), 2.00 quint (2H, ^3J = 6.5 Hz), 3.32 q (2H, ^3J = 6.1 Hz), 3.44 q (2H, ^3J = 6.3 Hz), 3.54–3.70 m (13H), 4.05–4.15 m (2H), 4.66 t (1H, ^3J = 5.3 Hz), 5.88 d (1H, ^3J = 7.9 Hz), 5.93 d (1H, ^3J = 7.8 Hz), 7.07 d (1H, ^3J = 8.3 Hz), 7.27 t (1H, ^3J = 7.9 Hz), 7.50 t (1H, ^3J = 7.9 Hz), 7.56 d.d (1H, ^3J = 7.2, ^4J = 0.9 Hz), 7.67 t.d (1H, ^3J = 7.6, ^4J = 1.3 Hz), 7.73 t.d (1H, ^3J = 7.5, ^4J = 1.2 Hz), 8.21 d.d (1H, ^3J = 7.6, ^4J = 0.9 Hz), 8.25 d.d (1H, ^3J = 7.6, ^4J = 0.9 Hz), 9.77 t (1H, ^3J = 5.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.0 (1C), 18.6 (1C), 20.7 (1C), 23.4 (1C), 23.5 (1C), 24.2 (1C), 25.8 (1C), 26.3 (1C), 27.1 (1C), 28.2 (1C), 28.7 (1C), 29.3 (2C), 32.1 (1C), 32.6 (1C), 34.7 (1C), 35.3 (1C), 35.6 (1C), 35.8 (1C), 39.8 (1C), 40.0 (1C), 40.1 (1C), 40.2 (1C), 42.6 (1C), 56.2 (1C), 56.4 (1C), 66.1 (1C), 66.5 (1C), 68.6 (1C), 69.4 (1C), 70.2 (1C), 70.4 (1C), 70.6 (2C), 97.0 (1C), 97.4 (1C), 112.9 (1C), 115.5 (1C), 117.9 (1C), 126.5 (1C), 126.6 (1C), 132.8 (1C), 133.0 (1C), 133.9 (1C), 134.6 (1C), 135.0 (1C), 135.2 (1C), 139.8 (1C), 151.8 (1C), 157.9 (1C), 163.5 (1C), 183.8 (1C), 184.8 (1C). Mass spectrum: *m*/*z* 863.55 $[M]^+$.

1-{[3-(2-{2-[3-({6-([(3β,5β)-24-{[6-({3-[2-(2-{3-[(9,10-Dioxo-9,10-dihydroanthracen-1-yl)amino]-propoxy}ethoxy)ethoxy]propyl}amino)pyridin-2-yl]-oxy}cholan-3-yl]oxy)pyridin-2-yl}amino)propoxy]-ethoxy}ethoxy)propyl]amino}-9,10-dihydroanthracene-9,10-dione (XXI) was synthesized from 220 mg (0.23 mmol) of compound **XVIc** and 168 mg (0.7 mmol) of 1-chloroanthraquinone in the presence of 11 mg of $Pd(dba)_2$, 13 mg of BINAP, and 300 mg (0.9 mmol) of cesium carbonate in 5.75 ml of anhydrous dioxane (reaction time 24 h). Eluent CH_2Cl_2–MeOH, 100:1. Yield 166 mg (53%), dark red oily substance. ^{1}H NMR spectrum, δ, ppm: 0.60 s (3H), 0.89 d (3H, ^3J = 6.4 Hz), 0.92 s (3H), 0.95–1.94 m (28H), 1.83 quint (2H, ^3J = 6.3 Hz), 1.84 quint (2H, ^3J = 6.1 Hz), 1.98 quint (4H, ^3J = 6.3 Hz), 3.31 q (4H, ^3J = 5.9 Hz), 3.40 q (4H, ^3J = 6.3 Hz), 3.54 t (4H, ^3J = 5.9 Hz), 3.55 t (4H, ^3J = 6.1 Hz), 3.57–3.70 m (16H), 4.04–4.14 m (2H), 4.65 t (2H, ^3J = 5.0 Hz), 4.68 t (2H, ^3J = 4.9 Hz), 5.14 s (1H), 5.85 d (1H, ^3J = 7.9 Hz), 5.88 d (1H, ^3J = 7.9 Hz), 5.92 d (1H, ^3J = 7.8 Hz), 5.93 d (1H, ^3J = 7.8 Hz), 7.02 d (2H, ^3J = 8.4 Hz), 7.25 t (1H, ^3J = 7.9 Hz), 7.26 t (1H, ^3J = 7.8 Hz), 7.45 t (2H, ^3J = 7.9 Hz), 7.52 d.d (2H, ^3J = 7.2, ^4J = 1.2 Hz), 7.64 t (2H, ^3J = 7.4 Hz), 7.70 t.d (2H, ^3J = 7.2, ^4J = 0.7 Hz), 8.17 d.d (2H, ^3J = 7.6, ^4J = 0.9 Hz), 8.20 d.d (2H, ^3J = 7.8, ^4J = 0.9 Hz), 9.72 t (2H, ^3J = 4.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.9 (1C), 18.5 (1C), 21.0 (1C), 23.7 (1C), 24.1 (1C), 24.8 (1C), 25.7 (1C), 26.1 (1C), 26.5 (1C), 28.2 (1C), 29.2 (4C), 30.6 (2C), 32.0 (1C), 34.8 (1C), 35.4 (1C), 35.5 (1C), 37.0 (1C), 39.7 (2C), 39.9 (3C), 40.1 (1C), 42.6 (1C), 56.1 (1C), 56.5 (1C), 66.0 (1C), 68.5 (2C), 69.3 (2C), 70.1 (3C), 70.3 (2C), 70.5 (4C), 96.9 (1C), 97.0 (1C), 97.4 (1C), 97.9 (1C), 112.7 (2C), 115.4 (2C), 117.8 (2C), 126.5 (4C), 132.7 (2C), 132.8 (2C), 133.7 (2C), 134.4 (2C), 134.8 (2C), 135.1 (2C), 139.7 (2C), 151.6 (2C), 157.8 (2C), 162.8 (1C), 163.3 (1C), 183.6 (2C), 184.6 (2C). Mass spectrum: *m*/*z* 1365.11 $[M]^+$.

1-(3-{2-[2-(3-Aminopropoxy)ethoxy]ethoxy}propylamino)-9,10-dihydroanthracene-9,10-dione (XXII) was synthesized from 1 mmol (243 mg) of 1-chloroanthraquinone and 3 mmol (660 mg) of trioxadiamine **IIIc** in the presence of 23 mg of $Pd(dba)_2$, 28 mg of BINAP, and 1 g (3 mmol) of cesium carbonate in 5 ml of anhydrous dioxane (reaction time 8 h). Eluent CH_2Cl_2–MeOH (5:1, 2.5:1). Yield 350 mg (84%), dark red oily substance. ^{1}H NMR spectrum, δ, ppm: 1.68 quint (2H, ^3J = 6.4 Hz), 1.96 quint (2H, ^3J = 6.3 Hz), 2.26 br.s (2H), 2.75 t (2H, ^3J = 6.7 Hz), 3.35–3.42 m (4H), 3.49 t (2H, ^3J = 6.2 Hz), 3.51–3.65 m (8H), 7.02 d.d (1H, ^3J = 8.3, ^4J = 1.3 Hz), 7.45 t (1H, ^3J = 7.7 Hz), 7.49 d.d (1H, ^3J = 7.3, ^4J = 1.5 Hz), 7.62 t.d (1H, ^3J = 7.5, ^4J = 1.6 Hz), 7.68 t.d (1H, ^3J = 7.5, ^4J = 1.5 Hz), 8.15 d.d (1H, ^3J = 7.6, ^4J = 1.1 Hz), 8.18 d.d (1H, ^3J = 7.7, ^4J = 1.1 Hz), 9.69 t (1H, ^3J = 4.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.2 (1C), 32.7 (1C), 39.4 (1C), 39.9 (1C), 68.5 (1C), 69.3 (1C), 70.0 (1C), 70.3 (1C), 70.4 (2C), 112.7 (1C), 115.4 (1C), 117.8 (1C), 126.5 (2C), 132.7 (1C), 132.8 (1C), 133.8 (1C), 134.4 (1C), 134.8 (1C), 135.1 (1C), 151.6 (1C), 183.6 (1C), 184.7 (1C). Mass spectrum: *m*/*z* 426.22 $[M]^+$.

***N*-(3-{2-[2-(3-Aminopropoxy)ethoxy]ethoxy}-propyl)anthracen-1-amine (XXIII)** was synthesized from 1 mmol (213 mg) of 1-chloroanthracene and 3 mmol (660 mg) of trioxadiamine **IIIc** in the presence of 23 mg of $Pd(dba)_2$, 28 mg of BINAP, and 290 mg (3 mmol) of potassium *tert*-butoxide in 5 ml of anhydrous dioxane (reaction time 8 h). Eluent CH_2Cl_2–MeOH (2.5:1), CH_2Cl_2–MeOH–aq. NH_3 (100:20:1). Yield 230 mg (58%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.68 quint (2H, ^3J = 6.0 Hz), 2.08 quint (2H, ^3J = 6.0 Hz), 2.82 t (2H, ^3J = 6.3 Hz), 3.33–3.36 m (4H), 3.39 t (4H, ^3J = 5.9 Hz), 3.47–3.51 m (2H), 3.61 br.s (4H), 3.69 t (2H, ^3J = 5.6 Hz), 5.58 br.s (1H), 6.44 d (1H, ^3J = 6.3 Hz), 7.26–7.41 m (4H), 7.90 d (1H, ^3J = 7.1 Hz), 8.00 d (1H, ^3J = 8.8 Hz), 8.28 s (1H), 8.49 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 28.5 (1C), 33.0 (1C), 39.1 (1C), 42.3 (1C), 69.1 (1C), 69.7 (1C), 69.9 (1C), 70.2 (1C), 70.3 (1C), 70.4 (1C), 101.1 (1C), 116.5 (1C), 118.8 (1C), 123.5 (1C), 124.5 (1C), 125.1 (1C), 126.0 (1C), 126.1 (1C), 127.4 (1C), 128.1 (1C), 130.5 (1C), 131.2 (1C), 132.3 (1C), 143.4 (1C). Mass spectrum: *m*/*z* 396.07 $[M]^+$.

This study was performed under financial support by the Russian Academy of Sciences (program P-8, "Development of Methodology of Organic Synthesis and Design of Compounds with Practically Important Properties"), and by the Russian Foundation for Basic Research (project nos. 06-03-32376, 07-03-00619, 08-03-91308-Ind).

REFERENCES

1. Averin, A.D., Ranyuk, E.R., Lukashev, N.V., and Beletskaya, I.P., *Chem. Eur. J.*, 2005, vol. 11, p. 1730.
2. Lukashev, N.V., Averin, A.D., Latyshev, G.V., Donez, P.A., Ranyuk, E.R., and Beletskaya, I.P., *Pol. J. Chem.*, 2006, vol. 80, p. 559.
3. Averin, A.D., Ranyuk, E.R., Lukashev, N.V., Golub, S.L., Buryak, A.K., and Beletskaya, I.P., *Tetrahedron Lett.*, 2008, vol. 49, p. 1188.
4. Averin, A.D., Ranyuk, E.R., Lukashev, N.V., Buryak, A.K., and Beletskaya, I.P., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 78.
5. Averin, A.D., Uglov, A.N., Ranyuk, E.R., Lukashev, N.V., and Beletskaya, I.P., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 273.
6. Deng, G., Dewa, T., and Regen, S.L., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 8975.
7. Sakai, N. and Matile, S., *Tetrahedron Lett.*, 1997, vol. 38, p. 2613.
8. Moore, K.S., Wehrli, S., Roder, H., Rodgers, M., Forrest, J.M., McCrimmon, D., and Zasloff, M., *Proc. Natl. Acad. Sci. USA*, 1993, vol. 90, p. 1354.
9. Sills, A.K., Jr., Williams, J.I., Tyler, B.M., Epstein, D.S., Sipos, E.P., Davis, J.D., McLane, M.P., Pitchford, S., Cheshire, K., Gannon, F.H., Kinney, W.A., Chao, T.L., Donowitz, M., Laterra, J., Zasloff, M., and Brem, H., *Cancer Res.*, 1998, vol. 58, p. 2784.
10. Rao, M., Shinnar, A.E., Noecker, L.A., Chao, T.L., Feibush, B., Snyder, B., Sharkansky, I., Sarkahian, A., Zhang, X., Jones, S.R., Kinney, W.A., and Zasloff, M., *J. Nat. Prod.*, 2000, vol. 63, p. 631.
11. Shu, Y., Jones, S.R., Kinney, W.A., and Selinsky, B.S., *Steroids*, 2002, vol. 67, p. 291.
12. Khan, S.N., Bae, S.-Y., and Kim, H.-S., *Tetrahedron Lett.*, 2005, vol. 46, p. 7675.
13. Golden, R. and Stock, L.M., *J. Am. Chem. Soc.*, 1972, vol. 94, p. 3080.
14. Ukai, T., Kawazura, H., Ishii, Y., Bonnet, J.J., and Ibers, J.A., *J. Organomet. Chem.*, 1974, vol. 65, p. 253.
15. Averin, A.D., Shukhaev, A.V., Golub, S.L., Buryak, A.K., and Beletskaya, I.P., *Synthesis*, 2007, p. 2995.
16. Averin, A.D., Ulanovskaya, O.A., Pleshkova, N.A., Borisenko, A.A., and Beletskaya, I.P., *Coll. Czech. Chem. Commun.*, 2007, vol. 72, p. 785.