Synthesis of macrobicyclic compounds containing aza-crown ether fragments and study of their complexation with zinc and cadmium nitrates*

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N-(3,5-Dibromobenzyl) derivatives of 1-aza-15-crown-5 and 1-aza-18-crown-6 were synthesized in high yields and their palladium-catalyzed amination reactions with various linear polyamines were studied. As a result, macrobicyclic compounds were obtained in yields up to 56%. The complexation of some macrocycles with zinc and cadmium nitrates was studied by NMR titration.

Key words: macrocycles, amination, homogenous transition metal catalysis, aza-crown ethers, polyamines, complexation, NMR titration.

Palladium-catalyzed amination of dihalobenzenes with polyamines and oxadiamines has been applied successfully by us for the synthesis of the nitrogen- and oxygen-containing macrocycles. As a result, the compounds containing one or two aromatic rings and polyamine fragments have been prepared.[1] Several examples of analogous compounds derived from *o*- and *p*-phenylenediamines containing two oxadiamine chains are known, which have been synthesized by non-catalytic methods.[2,3] It has been shown that these compounds exhibit complexation selectivity towards the Pb^{II} ions and, to some extent, the Dy^{III} ions; at the same time, they bind weakly the alkali metals. The macrobicyclic compounds containing two aza-crown ether fragments are of considerable interest due to their remarkable coordination properties. A convenient synthetic approach to various bi- and polycyclic compounds of this type, *viz.*, cryptands and supercryptands based on aza-crown ethers, was first developed by Krakowiak at the beginning of the 1990s using simple nucleophilic substitution reactions.[4—6] The majority of the currently known bis(aza-crown) ethers contain two isolated macrocyclic fragments positioned symmetrically relative to the aromatic,[7,8] metallocene,[9] porphyrin,[10] or calixarene[11] spacers. They can also serve as a basis for more complex macrocycles, among which calix-crown ethers are most common.[12—14] For the design of the metal-ion sensors, such fluorophores as coronene,[12] perylene,[13] anthracene,[14] coumarin,[15] and boron dipyrromethene complexes[16] are incorporated into the molecule, these substituents can be bound to the aza-macrocycles through linkers or constitute a part of the macrocycle. Bis(aza-crown) ethers have been studied as the sensors for the Na^{I}, K^{I}, Cs^{I}, Ba^{II}, Ag^{I}, Zn^{II}, and Cd^{II} ions.[13,14,16] In the vast majority of studies, the syntheses of almost all compounds were carried out using non-catalytic methods. Palladium-catalyzed N-arylation of aza-crown ether was first used by Witulski for the preparation of the *N*-anthryl derivative.[17] In the present work, we described the use of the catalytic amination of the aza-crown ether derivatives for the synthesis of a series of macrobicyclic compounds with two different macrocycles connected through a flexible benzyl-type linker, which allows changing the distance between the ring cavities for creation of the cooperative effect upon complexation.

Results and Discussion

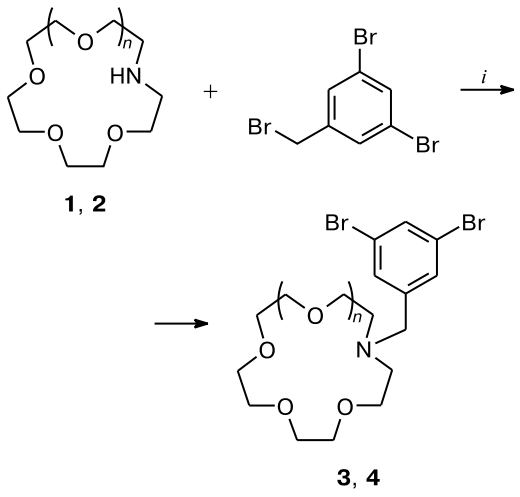
Reactions of the starting 1-aza-15-crown-5 (**1**) and 1-aza-18-crown-6 (**2**) with 3,5-dibromobenzylbromide (1 equiv.) in refluxing acetonitrile in the presence of K_2CO_3 as a base afforded *N*-(3,5-dibromobenzyl) derivatives **3** and **4** in yields of 95 and 90%, respectively (Scheme 1).

These compounds were subjected to the palladium-catalyzed amination reaction with several di- and polyamines **5a**—**h**, and the corresponding macrobicyclic compounds **6a**—**h** and **7a**—**h** with isolated macrocycles linked through a short and relatively flexible linker were obtained (Scheme 2). The reactions were carried out in refluxing

* Dedicated to the 60th anniversary of academician V. N. Charushin.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 968—979, May, 2011.

Scheme 1



n = 1 (**1**, **3**), 2 (**2, 4**)

i. K_2CO_3, MeCN, reflux, 24 h.

dioxane at the equimolar ratio of the reactants (concentration 0.02 mol L^{-1}) for 24 h using $Pd(dba)_2$ as a catalyst and Bu^tONa as a base. The experimental results are given in Table 1. It was found that the donor phosphine ligand DavePhos (2-dicyclohexylphosphino-2′-dimethylaminobiphenyl) is efficient in the reaction of the 1-aza-15-crown-5 derivative **3** with di- and triamines **5a—e** (see Table 1, Entries *1—5*). The highest yields of macrobicycles were obtained not only in the reaction with the "longest" diamines **5a**,**b**,**d** containing 12—15 atoms in the chain (see Table 1, Entries *1*, *2*, and *4*), but also with the shorter dioxadiamine **5c** (10 atoms in the chain), the yield being 41% (see Table 1, Entry *3*). The yields attained are in some cases higher than those of macrocyclization upon catalytic amination of 1,3-dibromobenzene.[1] The yield with triamine **5e** decreased to 29% (see Table 1, Entry *5*). In the case of tetramine **5f**, the ligand DavePhos was inefficient and we failed to obtain macrobicycle **6f** (see Table 1, Entry *6*). However, with BINAP as the phosphine ligand the corresponding macrobicycle was isolated in 18% yield (see Table 1, Entry *7*). The reaction with longer tetramine **5g** proceeded better, both phoshpine ligands providing the same yield (28%) of compound **6g** (see Table 1, Entries *8* and *9*). Tetramine **5h** was less reactive: the yield of macrobicycle **6h** was only 8% with DavePhos and 15% with BINAP (see Table 1, Entries *10* and *11*). It is important to note that BINAP was totally inefficient in the reactions with diamines where DavePhos resulted in high yields of macrobicycles (see Table 1, Entry *12*). The increase in the amount of the catalyst up to 16 mol.% did not lead to the increase in the yield of macrobicycles **6**. These facts suggest that in the case of the reactions with tetramines, which can form more stable chelate complexes than oxadiamines the use of BINAP is preferred due to its better ability to coordinate zerovalent palladium compared to DavePhos.

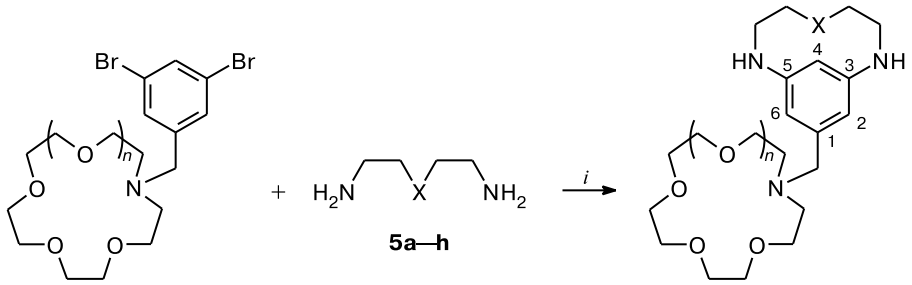
On the whole, the reactions of 1-aza-18-crown-6 derivative **4** with di- and polyamines **5a—h** furnished the corresponding macrobicycles **7a—h** in lower yields. For example, the reaction of **4** with trioxadiamine **5a** afforded macrobicycle **7a** in a yield of 30% with BINAP as a ligand (see Table 1, Entry *13*) and 32% with DavePhos (see Table 1, Entry *14*). Similar yield of the target macrobicycle **7d** (27%) was also obtained in the reaction of **4** with decanediamine **5d** (see Table 1, Entry *19*). The yields of the macrobicycles with the dioxadiamine linkers were considerably lower (see Table 1, Entries *15—18*), the use of BINAP being preferred. Finally, in the reactions of **4** with tri- and tetramines **5c—h**, only BINAP provided the formation of the desired products **7c—h** and DavePhos was totally ineffective. The lower yields of macrobicycles **7** compared to **6** can be explained by different abilities of 1-aza-15-crown-5 and 1-aza-18-crown-6 to coordinate the sodium cation, which results in different efficacy of sodium *tert*-butoxide in the catalytic amination cycle. Thus, we demonstrated for the first time the strong depen-

Table 1. Synthesis of macrobicycles **6a—h** and **7a—h**

Entry	Aza-crown ether derivative	Polyamine	Ligand[a]	Product	Yield[b] (%)
1	**3**	**5a**	DavePHOS	**6a**	53
2	**3**	**5b**	DavePHOS	**6b**	56
3	**3**	**5c**	DavePHOS	**6c**	41
4	**3**	**5d**	DavePHOS	**6d**	51
5	**3**	**5e**	DavePHOS	**6e**	29
6	**3**	**5f**	DavePHOS	**6f**	0
7	**3**	**5f**	BINAP	**6f**	18
8	**3**	**5g**	DavePHOS	**6g**	28
9	**3**	**5g**	BINAP	**6g**	28
10	**3**	**5h**	DavePHOS	**6h**	8
11	**3**	**5h**	BINAP	**6h**	15
12	**3**	**5a**	BINAP	**6a**	5
13	**4**	**5a**	BINAP	**7a**	30
14	**4**	**5a**	DavePHOS	**7a**	32
15	**4**	**5b**	BINAP	**7b**	15
16	**4**	**5b**	DavePHOS	**7b**	12
17	**4**	**5c**	BINAP	**7c**	14
18	**4**	**5c**	DavePHOS	**7c**	8
19	**4**	**5d**	BINAP	**7d**	27
20	**4**	**5e**	BINAP	**7e**	27
21	**4**	**5f**	BINAP	**7f**	28
22	**4**	**5f**	DavePHOS	**7f**	0
23	**4**	**5g**	BINAP	**7g**	20
24	**4**	**5g**	DavePHOS	**7g**	0
25	**4**	**5h**	BINAP	**7h**	16
26	**4**	**5h**	DavePHOS	**7h**	0

[a] 8 mol.% $Pd(dba)_2$ and 9 mol.% DavePhos or BINAP were used.
[b] The yields after chromatography on silica gel.

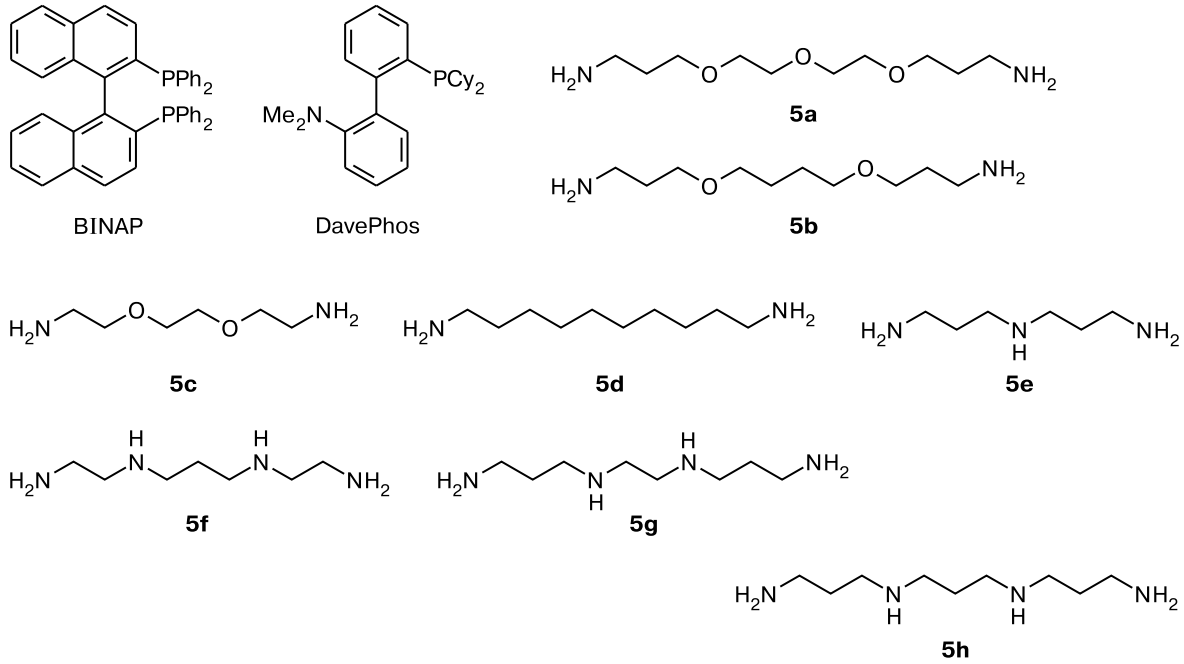
Scheme 2



3, **4** **6a—h**, **7a—h**

n = 1 (**3**, **6a—h**), 2 (**4, 7a—h**)

i. P(dba)$_2$, BINAP or DavePhos, Bu^{t}ONa, dioxane, reflux, 24 h.



dence of the result of catalytic amination on the nature of a phosphine ligand in reactions of structurally close starting compounds.

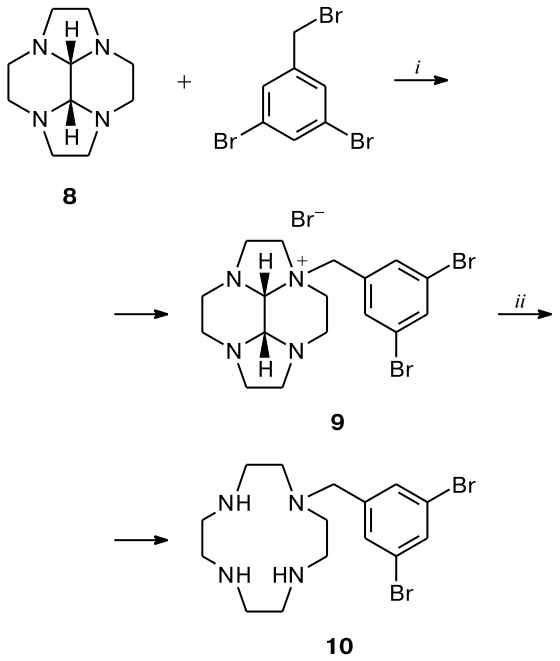
In the NMR spectra of compounds **6a—e** and **7a—e**, many signals are noticeably broadened (the half-height line width $\Delta\nu_{1/2}$ is up to 100 Hz in the ^{1}H NMR spectra and up to 200 Hz in the ^{13}C NMR spectra). This fact can be explained by the hindered rotation of the benzyl group due to the increase in the steric hindrance.

Having studied the possibilities of the synthesis of macrobicyclic compounds with isolated rings based on *N*-(3,5-dibromobenzyl)aza-crown ethers, we used this reaction to prepare macrobicycles containing the monosubstituted cyclene. Thus, the reaction of *cis*-glyoxal-cyclene **8** (see Ref. 18) with 3,5-dibromobenzylbromide (1 equiv.) in toluene at room temperature afforded the corresponding salt **9** in 67% yield. This compound was refluxed with ethanolic KOH for 72 h resulting in *N*-(3,5-dibromobenzyl)cyclene (**10**) in 65% yield (over two steps) (Scheme 3).

The cyclene derivative **10** reacted with oxadiamines **5a—c** in the presence of the catalytic system Pd(dba)$_2$/DavePhos (8 or 16 mol.%); however, in this case, the yields of the target products **11a—c** were low (BINAP was totally ineffective). For example, the reaction of **10** with trioxadiamines **5a** and **5b** afforded macrobicycles **11a** and **11b** in yields of 13% and 10%, respectively, and compound **11c** was isolated in only 2% yield (Scheme 4). The attempts to perform reactions with tetramines failed; however, total conversion of the starting cyclene derivative **10** was observed in all cases.

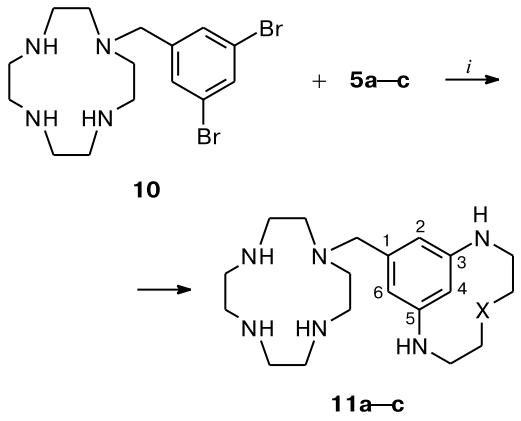
Low reactivity of this compound in the amination reactions can be explained by remarkable coordination of ze-

Scheme 3



i. PhMe, 20 °C, 24 h; *ii.* KOH, EtOH, reflux, 72 h.

Scheme 4



i. $Pd(dba)_2$, DavePhos, Bu^tONa, dioxane, reflux, 24 h.
X = $(CH_2OCH_2)_3$ (**a**), $CH_2O(CH_2)_4OCH_2$ (**b**), $O(CH_2)_2O$ (**c**)

rovalent palladium to tetraazamacrocycle, whereby it is removed from the catalytic amination cycle, other reactions, where the starting dibromoderivative **10** is consumed, beginning to play a leading role.

We performed preliminary studies of the coordination properties of macrobicycles **6a** and **7a** by NMR titration (^1H) with zinc and cadmium nitrates in CD_3OD. In order to compare the coordination properties of the starting aza-crown ether and macrobicyclic ligands prepared by us and to reveal the influence of the second attached macrocycle on the course of complexation, we first titrated the starting aza-crown ethers **1** and **2** with these metal salts. The signals for the CH_2N groups in both the starting aza-crown ethers **1** and **2** and their macrobicyclic derivatives **6a** and **7a** were most convenient for monitoring the complexation process, since these signals do not overlap with the signals for other groups and their chemical shifts depend strongly on the amount of the metal salt added.

Titration of 1-aza-15-crown-5 (**1**) showed that a regular downfield shift of the signal for the CH_2N groups from δ 2.73 to δ 3.00 and 3.18, respectively, occured upon addition of 0.25 and 0.5 equiv. of zinc nitrate, which was accompanied by broadening of the muliplet (Fig. 1, *a*, *b*), and the signal was split into three broadened singlets of unequal intensities at δ 2.81, 3.12, and 3.24 upon addition of 0.75 equiv. of zinc nitrate (Fig. 1, *c*). Upon subsequent addition of the metal salt, the chemical shifts of these signals did not change (Fig. 1, *d*); however, the intensity ratio changed slightly: the signal at δ 3.24 became less intensive and the intensities of the signals at δ 2.82 and 3.12 increased, the latter having always equal intensities. Upon heating the solution to 55 °C, these signals coalesced into a broadened singlet at δ 3.19 (Fig. 1, *e*). The above-mentioned changes are represented graphically in Fig. 2, *a*. The results obtained allow one to assume that two different complexes are in equilibrium in a solution, which is sufficiently slow on the NMR time scale at room temperature, since both forms of the ligand in these complexes are observed simultaneously, but the signals are noticeably broadened, and, with the increase in the temperature, the exchange rate increases and only one averaged form is observed. The stoichiometry of these two complexes must be different, since the average ligand : metal ratio, at which the signals achieve plateau, is about 1 : 0.75, which suggests the presence of the ligand—metal complexes of the composition 1 : 1 and 2 : 1. The chemical shifts for two CH_2N protons in one of the complexes, presumably of the composition 1 : 1, differ strongly (by 0.3 ppm), which can be explained by the staggered conformation of the OCH_2CH_2N fragment due to the coordination of the zinc ion to one aza-crown ether.

In the second complex, presumably of the composition 2 : 1, such an effect is not pronounced clearly, which is apparently due to a less rigid fixation of the macrocycle conformation in the sandwich-like complex.

Another pattern was observed during titration of aza-crown ether **1** with cadmium nitrate: the signal for the CH_2N group was downfield shifted (from δ 2.73 to δ 2.98, Fig. 3, *a*, *b*) upon slow addition of the metal salt up to 0.75 equiv. and split into two broadened singlets of equal intensities at δ 2.90 and 3.11 upon addition of 1 equiv. of cadmium nitrate (Fig. 3, *c*). The spectral pattern did not change upon increase in the amount of cadmium nitrate added and these signals coalesced into one broadened singlet at δ 3.03 upon heating to 55 °C (Fig. 3, *d*).

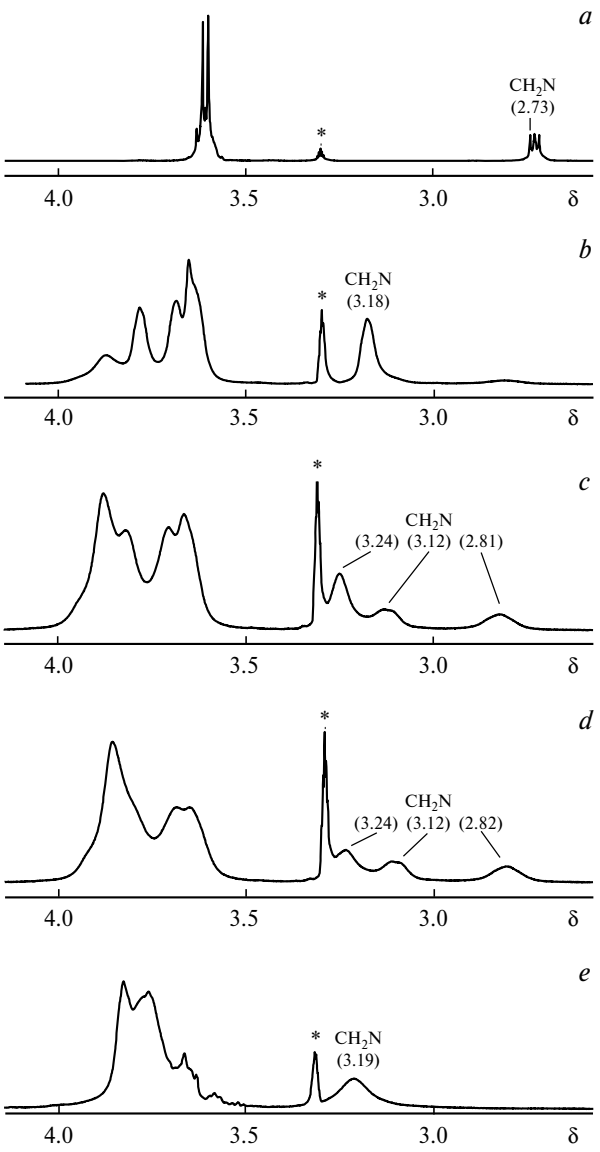


Fig. 1. The ^{1}H NMR spectra of 1-aza-15-crown-5 (**1**) in CD_3OD before (*a*) and after addition of 0.5 (*b*), 0.75 (*c*) and 1 equiv. of $Zn(NO_3)_2$ (*d*) at 20 °C, as well as after heating with $Zn(NO_3)_2$ (1 equiv.) to 55 °C (*e*). Here and in Figs 3 and 6, the signal for the residual proton of the solvent is marked with an asterisk.

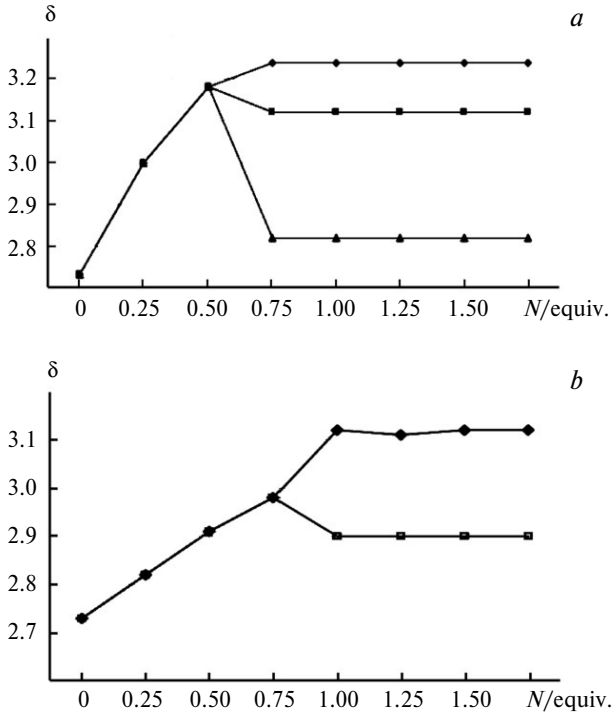


Fig. 2. Changes in the chemical shifts of the CH_2N protons in the ^{1}H NMR spectrum of 1-aza-15-crown-5 (**1**) during titration with zinc nitrate (*a*) and cadmium nitrate (*b*). Here and in Figs 4, 5, and 7, *N* is the number of equivalents of the corresponding salt added during NMR titration.

The above-mentioned changes are graphically presented in Fig. 2, *b*. From the titrimetric data, one can conclude that in this case the ligand—metal complex of the composition 1 : 1 formed, wherein, as in the case of one of the complexes of aza-crown ether **1** with zinc nitrate, the conformation mobility of the OCH_2CH_2N fragment is restricted due to room-temperature coordination of the zinc ion and, for this reason, the chemical shifts of two CH_2N protons differ by 0.21 ppm.

Titration of 1-aza-18-crown-6 (**2**) with zinc nitrate resulted in the downfield shift of the signals for the CH_2N group upon addition of 0.5 equiv. of the salt and, with subsequent addition of zinc nitrate, there were no changes in the spectrum, which suggests the formation of the ligand—metal complex of the composition 2 : 1 (Fig. 4, *a*). One can assume that not all the oxygen atoms of aza-crown ether are involved in coordiation of the zinc ion due to unfavorable geometric factors; therefore, the remaining coordination vacancies are occupied by the nitrogen and oxygen atoms from the second macrocycle thereby creating the sandwich-like structure.

Upon addition of cadmium nitrate to a solution of aza-crown ether **2**, the downfield shift of the signal for the CH_2N group was observed up to the addition of 1 equiv. of the salt, whereafter no shift was observed, which suggests the formation of the 1 : 1 complex (Fig. 4, *b*). The absence of splitting of the signal for the methylene protons in this case can indicate the conformation of the macrocycle in the complex that is less rigidly fixed by the metal. Thus, both aza-crown ethers **1** and **2** afford the 1 : 1 complexes with cadmium nitrate, while the formation of more complex structures is observed in both cases upon coordination of the zinc ion.

Titration of macrobicycle **6a** with zinc nitrate is also characterized by the downfield shift of the signal for the CH_2N group of the aza-crown ether ring (Fig. 5), altough the dependence of the chemical shift on the amount of the salt added is not so much pronounced in this case as in the

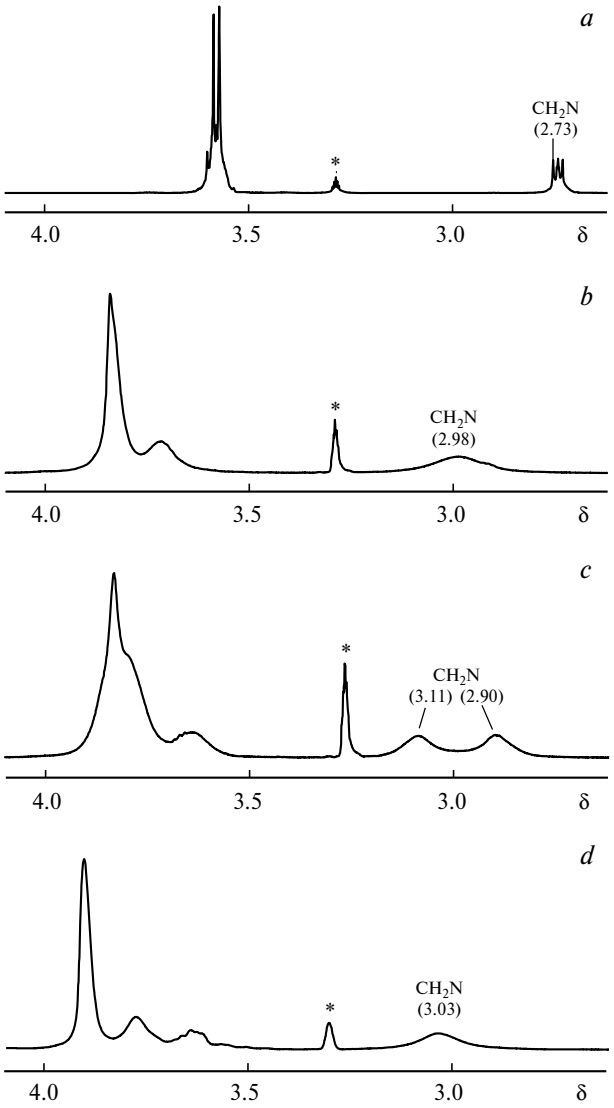


Fig. 3. The ^{1}H NMR spectra of 1-aza-15-crown-5 (**1**) in CD_3OD before (*a*) and after addition of 0.75 (*b*) and 1 equiv. of $Cd(NO_3)_2$ (*c*) at 20 °C, as well as after heating with $Cd(NO_3)_2$ (1 equiv.) to 55 °C (*d*).

case of the starting aza-crown ether **1**. We observed also the downfield shift of the NH protons, which evidences in favor of involvement of the second macrocycle in coordination to the zinc ion. Most likely, the second macrocycle coordinates the zinc ion through the oxygen atoms of the trioxadiamine chain, and through these atoms the effect of coordination is transferred to the NH protons. The data obtained evidence the formation of the 1 : 1 complex, although the values of chemical shifts do not achieve the plateau, which is evidently due to a lower stability of the complex compared to that of aza-crown ether **1**. Thus, with regard to the coordination properties towards the zinc ions, macrobicycle **6a** differs considerably from 1-aza-15-crown-5 (**1**) due to the involvement of the second mac-

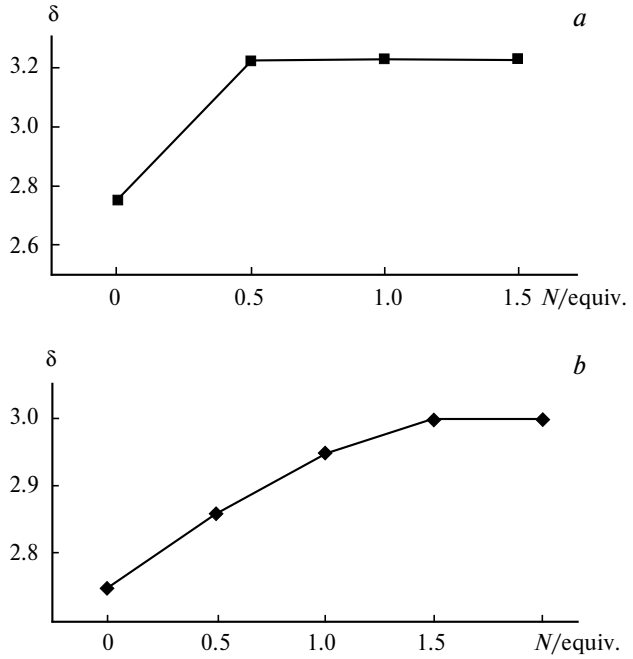


Fig. 4. Changes in the chemical shifts of the CH_2N protons in the ^{1}H NMR spectrum of 1-aza-18-crown-6 (**2**) during titration with zinc nitrate (*a*) and cadmium nitrate (*b*).

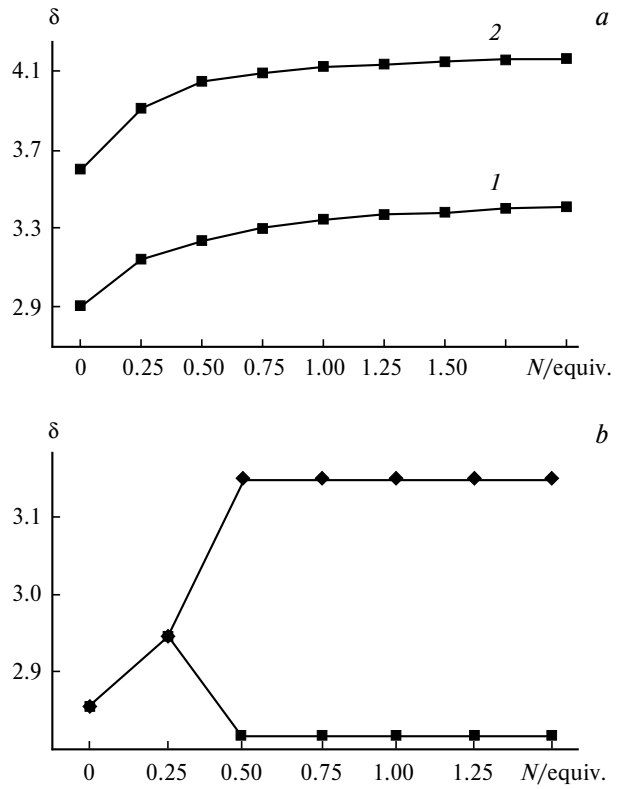


Fig. 5. Changes in the chemical shifts of the CH_2N (*1*) and NH (*2*) protons in the ^{1}H NMR spectrum during titration of macrobicycle **6a** with zinc nitrate (*a*) and the CH_2N protons during titration with cadmium nitrate (*b*).

rocycle in coordination, which results in the formation of only one complex in a solution.

Titration of macrobicycle **6a** with cadmium nitrate (see Fig. 5, *b*) suggests the formation of the ligand—metal complex of the composition 2 : 1. The downfield shift of the CH_2N protons from δ 2.87 to δ 2.94 was observed upon addition of 0.25 equiv. of the salt (Fig. 6, *a*, *b*) and the signal was split into two broadened singlets of equlal intensities at δ 3.16 and 2.82 upon addition of 0.5 equiv. of cadmium nitrate (Fig. 6, *c*). Subsequent addition of the salt (Fig. 6, *d*) caused no changes in the spectrum, which allows conclusion on the formation of the ligand—metal complex of the composition 2 : 1. In addition, the absence of the shift of the signals for the NH protons evidences that the second attached macrocycle is not involved in complexation with the cadmium ion. This is quite unexpected, since the starting 1-aza-15-crown-5 (**1**) formed the 1 : 1 complex with cadmium nitrate. In this case, probably due to the changes in the conformation of aza-crown ether induced by the macrocyclic substituent at the nitrogen atom, the cadmium ion is coordinated by not all the donor atoms of aza-crown ether, which results in the formation of the sandwich-like structure involving the second aza-crown ether fragment. However, splitting of the signal for the methylene protons suggests the rigidly fixed conformation of the macrocycle in the complex as it was upon coordination of the starting aza-crown ether **1** to cadmium nitrate.

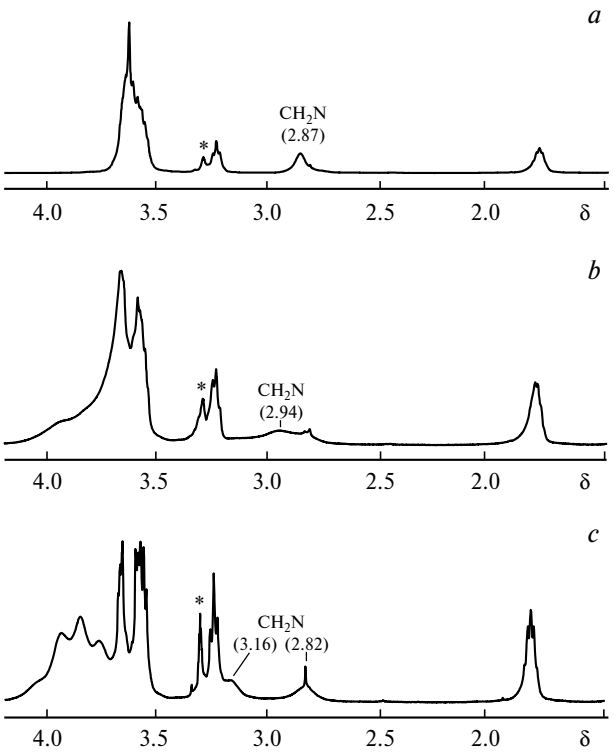


Fig. 6. The ^{1}H NMR spectra of macrobicycle **6a** in CD_3OD before (*a*) and after addition of 0.25 (*b*) and 0.5 equiv. of $Cd(NO_3)_2$ (*c*) at 20 °C.

In the case of macrobicycle **7a**, titration with zinc nitrate (Fig. 7, *a*) occured in a similar way as titration of macrobicycle **6a** and resulted in the formation of the 1 : 1 complex. In this case, owing to the fact that the signals for the NH protons are considerably shifted downfield, one may also conclude that the second attached macrocycle is involved in complexation through the oxygen atoms. Since the chemical shifts of the CH_2N and NH protons do not achieve completely the plateau at the ratio metal : ligand = 1 : 1, the complex that formed is less stable than the complex of the starting 1-aza-18-crown-6 (**2**).

The result of titration of macrobicycle **7a** with cadmium nitrate (Fig. 7, *b*) differed from that for macrobicycle **6a**, since, in the case of **7a**, there was a distinct inflexion point corresponding to addition of 1 equiv. of $Cd(NO_3)_2$, although the value of $\Delta\delta_H$ (0.04) was much smaller than in all other experiments, where it changed from 0.30 to 0.51. There were also no changes in the chemical shifts of the NH protons, which is evidence of the fact that in this case the cadmium ion is coordinated only by the 1-aza-18-crown-6 fragment and the second attached macrocycle is not involved in coordination to the metal. Finally, the absence of splitting of the signals for the methylene protons in this case is very similar to the effect observed upon

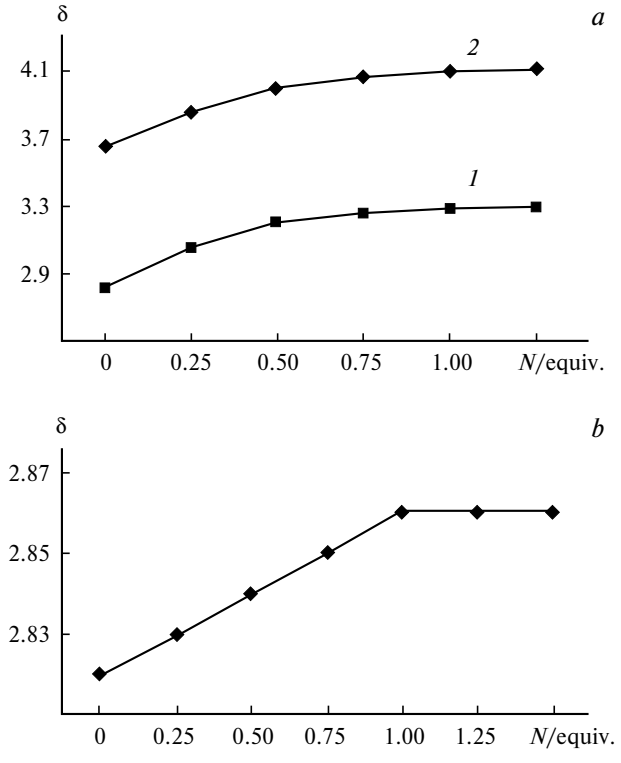


Fig. 7. Changes in the chemical shifts of the CH_2N (*1*) and NH (*2*) protons in the ^{1}H NMR spectrum of macrobicycle **7a** during titration with zinc nitrate (*a*) and the CH_2N protons during titration with cadmium nitrate (*b*).

complexation of the starting aza-crown ether **2** with cadmium nitrate.

Thus, in the present study, we developed an efficient method for the synthesis of macrobicyclic compounds containing two structurally different fragments of aza-crown ethers using palladium-catalyzed amination. We also showed the possibility of variation in the size of the second attached macrocycle and the amount of the nitrogen and oxygen atoms therein and established the dependence of the yields of the target macrobicycles on the nature of the starting compounds. It was shown that this approach has restrictions with regard to the use of analogous derivatives of tetraazamacrocycles. The coordination properties of the starting aza-crown ethers and two representatives of novel macrobicycles were studied by NMR titration, which showed that 1-aza-15-crown-5 (**1**) forms the ligand—metal complexes of the composition 1 : 1 and 2 : 1 with zinc nitrate and the 1 : 1 complex with cadmium nitrate and 1-aza-18-crown-6 (**2**) affords the 2 : 1 complex with the zinc ion and the 1 : 1 complex with the cadmium ion. Macrobicycles **6a** and **7a** form the 1 : 1 ligand—metal complexes with the zinc ions, macrobicycle **6a** forms the 2 : 1 ligand-metal complex with the cadmium ion, and compound **7a** forms the 1 : 1 complex with the cadmium ion, two macrocycles being involved in complexation upon coordination to the zinc ions and only the fragments of the starting aza-crown ethers being involved in complexation upon coordination to the cadmium ions.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Bruker Avance-400 (400 and 100 MHz, respectively) spectrometer. The chemical shifts in the ^{1}H and ^{13}C NMR spectra are given in the δ scale relative to Me_4Si (internal standard). MALDI—TOF mass spectra were obtained on a Bruker Ultraflex instrument in the positive ion mode using 1,8,9-trihydroxyanthracene as a matrix and poly(ethylene glycols) as the internal standards. The starting aza-crown ethers **1** and **2**, 3,5-dibromobenzyl bromide, di- and polyamines **5a**—**h**, the phosphine ligands BINAP and DavePhos (Aldrich or Acros) were used without additional purification. *cis*-Glyoxal-cyclene **8** was synthesized from cyclene according to the known procedure;[18] $Pd(dba)_2$ was synthesized accoding to the published procedure.[19] Dioxane was distilled over alkali and metallic sodium, acetonitrile was distilled over calcium hydride, dichloromethane and methanol were distilled.

NMR titration was performed as follows: a solution of aza-crown ether **1**, **2** or macrobicycles **6a**, **7a** (50 μmol) in CD_3OD (0.5 mL, $c = 0.1$ mol L^{-1}) was placed in an NMR tube, a solution of hexaqua zinc nitrate or tetraaqua cadmium nitrate in CD_3OD ($c = 0.2$ mol L^{-1}) was added at the interval of 12.5 μmol (63 μL of a solution), the mixture was thoroughly stirred, and then ^{1}H NMR spectra were recorded.

13-(3,5-Dibromobenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (3). Anhydrous acetonitrile (10 mL), 1-aza-15-crown-5 (**1**) (657 mg, 3 mmol), 3,5-dibromobenzyl bromide (1 g, 3.04 mmol), and potassium carbonate (1.06 г, 7.68 mmol) were placed in a flask equipped with a reflux condenser and the reaction mixture was magnetically stirred under reflux for 24 h. After cooling to room temperature, the precipitate that formed was filtered off, the solvent was evaporated *in vacuo*, and the oily residue was dissolved in dichloromethane (10 mL), washed with water (10 mL), the organic phase was dried with magnesium sulfate, and the solvent was evaporated *in vacuo* to yield product **3** as an oily pale yellow substance. The yield was 1.33 g (95%). ^{1}H NMR ($CDCl_3$), δ: 2.75 (t, 4 H, $CH_2C\underline{H}_2N$, $J = 5.9$ Hz); 3.61 (t, 4 H, CH_2O, $J = 6.5$ Hz); 3.61—3.64 (m, 6 H, CH_2O, $ArCH_2N$); 3.67 (s, 4 H, CH_2O); 3.66—3.69 (m, 4 H, CH_2O); 7.44 (d, 2 H, H(2), H(6), $J = 1.4$ Hz); 7.50 (t, 1 H, H(4), $J = 1.4$). ^{13}C NMR ($CDCl_3$), δ: 54.4 (2 C, $CH_2\underline{C}H_2N$); 59.6 (1 C, $ArCH_2N$); 69.8 (2 C, CH_2O); 70.2 (2 C, CH_2O); 70.5 (2 C, CH_2O); 71.0 (2 C, CH_2O); 122.7 (2 C, C(3), C(5)); 130.3 (2 C, C(2), C(6)); 132.4 (1 C, C(4)); 144.3 (1 C, C(1)). MS (MALDI), *m/z*: $[M]^+$, found 465.0146, calculated 465.0150. $C_{17}H_{25}Br_2NO_4$.

16-(3,5-Dibromobenzyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (4). Anhydrous acetonitrile (10 mL), 1-aza-18-crown-6 (**2**) (1 g, 3.8 mmol), 3,5-dibromobenzyl bromide (1.44 g, 3.8 mmol), and potassium carbonate (1.44 g, 10.4 mmol) were placed in a flask equipped with a reflux condenser and the reaction mixture was magnetically stirred under reflux for 24 h. After cooling to room temperature, the precipitate that formed was filtered off, the solvent was evaporated *in vacuo*, and the oily residue was dissolved in dichloromethane (10 mL), washed with water (10 mL), the organic phase was dried with magnesium sulfate, and the solvent was evaporated *in vacuo* to yield product **4** as an oily pale yellow substance. The yield was 1.75 g (90%). ^{1}H NMR ($CDCl_3$), δ: 2.73 (t, 4 H, $CH_2C\underline{H}_2N$, $J = 5.2$ Hz); 3.50—3.60 (m, 16 H, CH_2O); 3.61 (s, 4 H, CH_2O); 3.63 (s, 2 H, $ArCH_2N$); 7.30 (br.s, 2 H, H(2), H(6)); 7.46 (t, 1 H, H(4), $J = 1.5$ Hz). ^{13}C NMR ($CDCl_3$), δ: 54.4 (2 C, $CH_2\underline{C}H_2N$); 56.5 (1 C, $ArCH_2N$, $\Delta\nu_{1/2} = 15$ Hz); 68.3 (2 C, CH_2O, $\Delta\nu_{1/2} = 10$ Hz); 69.9 (2 C, CH_2O); 70.0 (2 C, CH_2O); 70.1 (2 C, CH_2O); 70.2 (2 C, CH_2O); 122.6 (2 C, C(3), C(5)); 130.4 (2 C, C(2), C(6)); 132.3 (1 C, C(4)); 143.1 (1 C, C(1)). MS (MALDI), *m/z*: $[M]^+$, found 509.0429, calculated 509.0412. $C_{19}H_{29}Br_2NO_5$.

Synthesis of macrobicycles 6 and 7 (general procedure). Aza-crown ether derivative **3** or **4** (0.25 mmol, 116 mg or 128 mg, respectively), dry dioxane (12 mL), $Pd(dba)_2$ (12 mg, 8 mol.%), and BINAP or DavePhos (14 mg or 9 mg, respectively, 9 mol.%) were placed in a two-necked flask flushed with dry argon and equipped with a reflux condenser. The reaction mixture was magnetically stirred for 2 min, the corresponding polyamine **5a**—**h** (0.25 mmol) and sodium *tert*-butoxide (72 mg, 0.75 mmol) were added, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature, the precipitate that formed was filtered off, and dioxane was evaporated *in vacuo*. The residue was chromatographed on silica gel using the following elution with CH_2Cl_2, CH_2Cl_2—MeOH (from 50 : 1 to 3 : 1), CH_2Cl_2—MeOH—NH_3 (from 100 : 20 : 1 to 10 : 4 : 1). The target macrobicycles were obtained as viscous oily pale yellow or pale beige compounds vitrifying on standing. Numbering of the atoms of the benzene ring in the ^{1}H and ^{13}C NMR spectra of compounds **6** and **7** is shown in Scheme 2.

19-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-6,9,12-trioxa-2,16-diazabicyclo[15.3.1]enicosa-1(21),17,19-triene (6a) was synthesized from trioxadiamine **5a** (55 mg) in the presence of DavePhos (9 mg, 9 mol.% or 18 mg, 18 mol.%). Since the spectra of both reaction mixtures were identical, the

latter were combined and chromatographed (CH_2Cl_2—MeOH, 10 : 1). The total yield was 140 mg (53%). ^{1}H NMR ($CDCl_3$), δ: 1.77 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 5.6 Hz); 2.93 (br.s, 4 H, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 30 Hz); 3.24 (t, 4 H, CH_2NAr, J = 6.3 Hz); 3.53 (t, 4 H, CH_2O, J = 5.2 Hz); 3.55—3.67 (m, 26 H, CH_2O, $ArCH_2N$); 5.97 (br.s, 2 H, H(2), H(6)); 6.05 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 29.5 (2 C, $CH_2\underline{C}H_2CH_2$); 41.7 (2 C, CH_2NAr); 54.1 (2 C, $CH_2\underline{C}H_2N$); 60.1 (1 C, $ArCH_2N$); 67.2 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 10 Hz); 69.3 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 10 Hz); 69.4 (2 C, CH_2O); 69.5 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 10 Hz); 69.6 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 10 Hz); 69.9 (2 C, CH_2O); 70.7 (2 C, CH_2O); 95.9 (1 C, C(4)); 103.6 (2 C, C(2), C(6)); 128.1 (1 C, C(1), $\Delta\nu_{1/2}$ = 20 Hz); 150.4 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M]^+$, found 525.3334, calculated 525.3414. $C_{27}H_{47}N_3O_7$.

18-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-6,11-dioxa-2,15-diazabicyclo[14.3.1]icosa-1(20),16,18-triene (6b) was synthesized from dioxadiamine **5b** (51 mg). The eluent was CH_2Cl_2—MeOH (10 : 1). The yield was 71 mg (56%). ^{1}H NMR ($CDCl_3$), δ: 1.73—1.77 (m, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.80 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 5.3 Hz); 2.74 (br.s, 4 H, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 50 Hz); 3.23 (t, 4 H, CH_2NAr, J = 6.1 Hz); 3.38—3.43 (m, 4 H, CH_2O); 3.50 (t, 4 H, CH_2O, J = 5.0 Hz); 3.56—3.62 (m, 6 H, CH_2O, $ArCH_2N$); 3.64—3.74 (m, 12 H, CH_2O); 6.01 (br.s, 2 H, H(2), H(6)); 6.05 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 26.5 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 30.0 (2 C, $CH_2\underline{C}H_2CH_2$); 42.3 (2 C, CH_2NAr); 54.5 (2 C, $CH_2\underline{C}H_2N$, $\Delta\nu_{1/2}$ = 30 Hz); 60.2 (1 C, $ArCH_2N$, $\Delta\nu_{1/2}$ = 40 Hz); 67.2 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 20 Hz); 69.1 (6 C, CH_2O, $\Delta\nu_{1/2}$ = 60 Hz); 69.9 (4 C, CH_2O); 95.4 (1 C, C(4), $\Delta\nu_{1/2}$ = 30 Hz); 103.4 (2 C, C(2), C(6)); 130.3 (1 C, C(1), $\Delta\nu_{1/2}$ = 20 Hz); 150.6 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M]^+$, found 509.3440, calculated 509.3465. $C_{27}H_{47}N_3O_6$.

14-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-5,8-dioxa-2,11-diazabicyclo[10.3.1]hexadeca-1(16),12,14-triene (6c) was synthesized from dioxadiamine **5c** (37 mg). The eluent was CH_2Cl_2—MeOH (3 : 1). The yield was 47 mg (41%). ^{1}H NMR ($CDCl_3$), δ: 2.73 (br.s, 4 H, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 60 Hz); 3.37 (t, 4 H, CH_2NAr, J = 4.9 Hz); 3.56—3.63 (m, 14 H, CH_2O, $ArCH_2N$); 3.65—3.75 (m, 12 H, CH_2O); 6.15 (br.s, 2 H, H(2), H(6)); 6.86 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 45.1 (2 C, CH_2NAr); 54.7 (2 C, $CH_2\underline{C}H_2N$, $\Delta\nu_{1/2}$ = 30 Hz); 60.5 (1 C, $ArCH_2N$, $\Delta\nu_{1/2}$ = = 200 Hz); 67.1 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 30 Hz); 68.8—69.6 (m, 6 C, CH_2O); 70.2 (2 C, CH_2O); 72.0 (2 C, CH_2O); 98.8 (1 C, C(4)); 106.2 (2 C, C(2), C(6)); 149.7 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M]^+$, found 453.2827, calculated 453.2839. $C_{23}H_{39}N_3O_6$.

16-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-2,13-diazabicyclo[12.3.1]octadeca-1(18),14,16-triene (6d) was synthesized from diamine **5d** (43 mg). Elution was carried out with CH_2Cl_2—MeOH (3 : 1) and CH_2Cl_2—MeOH—NH_3 (100 : 20 : 1). The yield was 61 mg (51%). ^{1}H NMR ($CDCl_3$), δ: 1.33 (br.s, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.38 (br.s, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.60 (qu, 4 H, $C\underline{H}_2CH_2NHAr$, J = 7.0 Hz); 2.88 (br.s, 4 H, $CH_2C\underline{H}_2N$), 3.14 (t, 4 H, CH_2NHAr, J = 7.6 Hz); 3.61—3.67 (m, 18 H, CH_2O, $ArCH_2N$); 4.54 (br.s, 2 H, NH); 5.91 (br.s, 1 H, H(4)); 5.97 (br.s, 2 H, H(2), H(6)). ^{13}C NMR ($CDCl_3$), δ: 24.5 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 26.5 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 26.6 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 28.0 (2 C, $\underline{C}H_2CH_2NHAr$); 44.1 (2 C, CH_2NHAr); 54.3 (2 C, $CH_2\underline{C}H_2N$); 60.5 (1 C, $ArCH_2N$); 69.0 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 25 Hz); 70.1 (2 C, CH_2O); 70.2 (2 C, CH_2O); 70.6 (2 C, CH_2O); 93.5 (1 C, C(4)); 105.3 (2 C, C(2), C(6)); 145.1 (1 C, C(1)); 150.0 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 478.25, calculated 478.36. $C_{27}H_{48}N_3O_4$.

13-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-2,6,10-triazabicyclo[9.3.1]pentadeca-1(15),11,13-triene (6e) was synthesized from triamine **5e** (33 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 20 : 3). The yield was 32 mg (29%). ^{1}H NMR ($CDCl_3$), δ: 1.62 (br.s, 4 H, $CH_2C\underline{H}_2CH_2$, $\Delta\nu_{1/2}$ = 15 Hz); 2.67 (br.s, 4 H, $CH_2CH_2C\underline{H}_2$, $\Delta\nu_{1/2}$ = 15 Hz); 2.79 (br.s, 4 H, $CH_2C\underline{H}_2N$ $\Delta\nu_{1/2}$ = 50 Hz); 3.42 (br.s, 4 H, CH_2NAr, $\Delta\nu_{1/2}$ = 50 Hz); 3.50—3.70 (m, 18 H, CH_2O, $ArCH_2N$); 5.98 (br.s, 2 H, H(2), H(6)); 7.05 (br.s, 1 H, H(4), $\Delta\nu_{1/2}$ = 30 Hz) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 30.1 (2 C, $CH_2\underline{C}H_2CH_2$, $\Delta\nu_{1/2}$ = 10 Hz); 39.6 (2 C, CH_2NAr, $\Delta\nu_{1/2}$ = 10 Hz); 45.9 (2 C, $CH_2CH_2\underline{C}H_2$); 54.0 (2 C, $CH_2\underline{C}H_2N$, $\Delta\nu_{1/2}$ = 15 Hz); 60.7 (1 C, $ArCH_2N$); 69.2 (2 C, CH_2O); 70.1 (6 C, CH_2O $\Delta\nu_{1/2}$ = 90 Hz); 94.8 (1 C, C(4), $\Delta\nu_{1/2}$ = 20 Hz); 103.6 (2 C, C(2), C(6)); 149.9 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + H]^+$, found 437.30, calculated 437.31. $C_{23}H_{40}N_4O_4$.

15-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-2,5,9,12-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (6f) was synthesized from tetramine **5f** (40 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 25 : 3). The yield was 21 mg (18%). ^{1}H NMR ($CDCl_3$), δ: 1.70 (br.s, 2 H, $CH_2C\underline{H}_2CH_2$); 2.72 (t, 4 H, $CH_2C\underline{H}_2N$, J = 5.2 Hz); 2.78—2.87 (m, 8 H, $CH_2C\underline{H}_2N$); 3.46 (t, 4 H, CH_2NAr, J = 4.6 Hz); 3.55—3.67 (m, 18 H, CH_2O, $ArCH_2N$); 6.02 (br.s, 2 H, H(2), H(6)); 6.15 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 24.9 (1 C, $CH_2\underline{C}H_2CH_2$); 42.2 (2 C, CH_2NAr); 48.8 (2 C, $CH_2\underline{C}H_2NH$); 49.9 (2 C, $CH_2\underline{C}H_2NH$); 54.7 (2 C, $CH_2\underline{C}H_2N$); 60.6 (1 C, $ArCH_2N$); 69.4 (2 C, CH_2O); 69.8 (2 C, CH_2O); 70.1 (2 C, CH_2O); 70.6 (2 C, CH_2O); 94.3 (1 C, C(4)); 105.0 (2 C, C(2), C(6)); 148.8 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + H]^+$, found 466.3445, calculated 466.3393. $C_{24}H_{44}N_5O_4$.

17-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-2,6,10,14-tetraazabicyclo[13.3.1]nonadeca-1(19),15,17-triene (6g) was synthesized from tetramine **5g** (44 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 25 : 5). The yield was 33 mg (28%). ^{1}H NMR ($CDCl_3$), δ: 1.68 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 5.4 Hz); 2.67 (t, 4 H, $CH_2CH_2C\underline{H}_2NH$, J = 5.6 Hz); 2.68 (s, 4 H, $NHC\underline{H}_2C\underline{H}_2NH$); 2.74 (t, 4 H, $CH_2C\underline{H}_2N$, J = 5.5 Hz); 3.32 (t, 4 H, CH_2NAr, J = 6.2 Hz); 3.58—3.67 (m, 14 H, CH_2O, $ArCH_2N$); 3.65 (s, 4 H, CH_2O); 4.88 (br.s, 2 H, NHAr); 5.93 (br.s, 2 H, H(2), H(6)); 6.13 (br.s, 1 H, H(4)) (the signals for two NH protons were not observed). ^{13}C NMR ($CDCl_3$), δ: 31.5 (2 C, $CH_2\underline{C}H_2CH_2$); 41.3 (2 C, CH_2NAr); 46.0 (2 C, CH_2NH); 49.1 (2 C, CH_2NH); 54.5 (2 C, $CH_2\underline{C}H_2N$); 60.8 (1 C, $ArCH_2N$); 69.7 (2 C, CH_2O); 70.0 (2 C, CH_2O); 70.2 (2 C, CH_2O); 70.7 (2 C, CH_2O); 93.0 (1 C, C(4)); 104.5 (2 C, C(2), C(6)); 141.1 (1 C, C(1)); 150.4 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 479.3407, calculated 479.3472. $C_{23}H_{40}N_4O_4$.

17-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-ylmethyl)-2,6,10,14-tetraazabicyclo[13.3.1]nonadeca-1(19),15,17-triene (6h) was synthesized from tetramine **5h** (47 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (10 : 4 : 1). The yield was 19 mg (15%).

^{1}H NMR ($CDCl_3$), δ: 1.75 (br.s, 6 H, $CH_2C\underline{H}_2CH_2$); 2.73 (t, 4 H, $CH_2C\underline{H}_2N$, J = 5.5 Hz); 2.75 (t, 4 H, $CH_2C\underline{H}_2N$, J = 6.0 Hz); 2.78 (t, 4 H, $CH_2C\underline{H}_2N$, J = 5.6 Hz); 3.28 (t, 4 H, CH_2NAr, J = 7.2 Hz); 3.57—3.66 (m, 18 H, CH_2O, $ArCH_2N$); 5.94 (br.s, 3 H, H(2), H(4), H(6)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 27.7 (1 C, $CH_2\underline{C}H_2CH_2$); 29.0 (2 C, $CH_2\underline{C}H_2CH_2$); 42.2 (2 C, CH_2NAr); 47.2 (2 C, $CH_2\underline{C}H_2NH$); 49.5 (2 C, $CH_2\underline{C}H_2NH$); 54.5 (2 C, $CH_2\underline{C}H_2N$); 60.9 (1 C, $ArCH_2N$); 69.7 (2 C, CH_2O); 70.0 (2 C, CH_2O); 70.3 (2 C, CH_2O); 70.8 (2 C, CH_2O); 93.9 (1 C, C(4)); 104.2 (2 C, C(2), C(6)); 141.2 (1 C, C(1)); 149.2 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 494.3681, calculated 494.3706. $C_{26}H_{48}N_5O_4$.

19-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-6,9,12-trioxa-2,16-diazabicyclo[15.3.1]enicosa-1(21),17,19-triene (7a) was synthesized from trioxadiamine **5a** (55 mg) in the presence of DavePhos (9 mg, 9 mol.% or 18 mg, 18 mol.%). Since the spectra of the reaction mixtures were identical, the latter were combined and chromatographed. The eluent was CH_2Cl_2—MeOH (10 : 1). The total yield was 90 mg (32%). ^{1}H NMR ($CDCl_3$), δ: 1.77 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 5.2 Hz); 2.70 (br.s, 4 H, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 60 Hz); 3.24 (t, 4 H, CH_2NAr, J = 6.2 Hz); 3.53 (t, 4 H, CH_2O, J = 5.1 Hz); 3.55—3.70 (m, 30 H, CH_2O, $ArCH_2N$); 5.90 (br.s, 2 H, H(2), H(6)); 6.04 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 29.6 (2 C, $CH_2\underline{C}H_2CH_2$); 41.7 (2 C, CH_2NAr); 53.6 (2 C, $CH_2\underline{C}H_2N$); 59.1 (1 C, $ArCH_2N$, $\Delta\nu_{1/2}$ = = 30 Hz); 67.3 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 50 Hz); 69.2 (2 C, CH_2O); 69.3 (4 C, CH_2O); 69.4 (4 C, CH_2O); 70.0 (2 C, CH_2O); 70.8 (2 C, CH_2O); 95.6 (1 C, C(4), $\Delta\nu_{1/2}$ = 15 Hz); 103.4 (2 C, C(2), C(6)); 150.5 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + K]^+$, found 608.3331, calculated 608.3313. $C_{29}H_{51}KN_3O_8$.

18-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-6,11-dioxa-2,15-diazabicyclo[14.3.1]icosa-1(20),16,18-triene (7b) was synthesized from dioxadiamine **5b** (51 mg). The eluent was CH_2Cl_2—MeOH (5 : 1). The yield was 21 mg (15%). ^{1}H NMR ($CDCl_3$), δ: 1.73—1.77 (m, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.79 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 4.7 Hz); 2.70 (br.s, 4 H $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 100 Hz); 3.22 (t, 4 H, CH_2NAr, J = 5.7 Hz); 3.37—3.42 (m, 4 H, $C\underline{H}_2CH_2CH_2C\underline{H}_2$); 3.50 (t, 4 H, CH_2O, J = 4.4 Hz); 3.55—3.68 (m, 26 H, CH_2O, $ArCH_2N$); 5.99 (br.s, 2 H, H(2), H(6)); 6.06 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 26.4 (2 C, $CH_2\underline{C}H_2C\underline{H}_2CH_2$); 30.0 (2 C, $CH_2\underline{C}H_2CH_2$); 42.3 (2 C, CH_2NAr); 53.9 (2 C, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 15 Hz); 58.3 (1 C, $ArCH_2N$, $\Delta\nu_{1/2}$ = 90 Hz); 69.5 (4 C, CH_2O, $\Delta\nu_{1/2}$ = 25 Hz); 69.8 (10 C, CH_2O); 95.5 (1 C, C(4), $\Delta\nu_{1/2}$ = 90 Hz); 103.5 (2 C, C(2), C(6), $\Delta\nu_{1/2}$ = 20 Hz); 150.6 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + Na]^+$, found 553.3691, calculated 553.3727. $C_{29}H_{51}N_3NaO_7$.

14-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-5,8-dioxa-2,11-diazabicyclo[10.3.1]hexadeca-1(16),12,14-triene (7c) was synthesized from dioxadiamine **5c** (37 mg). The eluent was CH_2Cl_2—MeOH (from 5 : 1 to 2.5 : 1). The yield was 13 mg (14%). ^{1}H NMR ($CDCl_3$), δ: 2.75 (br.s, 4 H, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 90 Hz); 3.38 (t, 4 H, CH_2NAr, J = 4.6 Hz); 3.55—3.71 (m, 30 H, CH_2O, $ArCH_2N$); 6.08 (br.s, 2 H, H(2), H(6)); 6.87 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 45.0 (2 C, CH_2NAr); 53.6 (2 C, $CH_2\underline{C}H_2N$, $\Delta\nu_{1/2}$ = 12 Hz); 61.2 (1 C, $ArCH_2N$); 67.4 (2 C, CH_2O, $\Delta\nu_{1/2}$ = = 80 Hz); 69.4—69.8 (m, 8 C, CH_2O); 70.2 (2 C, CH_2O); 72.0 (2 C, CH_2O); 98.5 (1 C, C(4)); 106.2 (2 C, C(2), C(6)); 149.7 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + Na]^+$, found 520.3077, calculated 520.2999. $C_{25}H_{43}N_3NaO_7$.

16-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-2,13-diazabicyclo[12.3.1]octadeca-1(18),14,16-triene (7d) was synthesized from diamine **5d** (44 mg). The eluent was CH_2Cl_2—MeOH (5 : 1). The yield was 35 mg (27%). ^{1}H NMR ($CDCl_3$), δ: 1.28 (br.s, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.33 (br.s, 8 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.54 (br.s, 4 H, $C\underline{H}_2CH_2NHAr$); 2.73 (br.s, $CH_2C\underline{H}_2N$); 3.09 (t, 4 H, $C\underline{H}_2NAr$, J = 7.6 Hz); 3.50—3.65 (m, 22 H, CH_2O, $ArCH_2N$); 5.86 (br.s, 1 H, H(4)); 5.91 (br.s, 2 H, H(2), H(6)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 24.3 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 26.3 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 26.4 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 27.7 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 43.7 (2 C, CH_2NAr); 54.3 (2 C, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 50 Hz); 57.2 (1 C, $ArCH_2N$, $\Delta\nu_{1/2}$ = 50 Hz); 67.2 (2 C, CH_2O, $\Delta\nu_{1/2}$ = 100 Hz); 69.4 (2 C, CH_2O); 69.5 (2 C, CH_2O); 69.6 (2 C, CH_2O); 69.7 (2 C, CH_2O); 93.3 (1 C, C(4)); 105.3 (2 C, C(2), C(6)); 138.9 (1 C, C(1)); 150.3 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 522.3997, calculated 522.3907. $C_{29}H_{52}N_3O_5$.

13-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-2,6,10-triazabicyclo[9.3.1]pentadeca-1(15),11,13-triene (7e) was synthesized from triamine **5e** (33 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 20 : 3). The yield was 32 mg (27%). ^{1}H NMR ($CDCl_3$), δ: 1.65 (br.s, 4 H, $CH_2C\underline{H}_2CH_2$, $\Delta\nu_{1/2}$ = 15 Hz); 2.69 (br.s, 4 H, $C\underline{H}_2NHC\underline{H}_2$, $\Delta\nu_{1/2}$ = 15 Hz); 3.25 (br.s, 4 H, $CH_2C\underline{H}_2N$, $\Delta\nu_{1/2}$ = 35 Hz); 3.44 (br.s, 4 H, CH_2NAr, $\Delta\nu_{1/2}$ = 30 Hz); 3.55—3.62 (m, 14 H, CH_2O, $ArCH_2N$); 3.64 (s, 4 H, CH_2O); 3.71 (br.s, 4 H, CH_2O, $\Delta\nu_{1/2}$ = 15 Hz); 6.03 (br.s, 2 H, H(2), H(6)); 6.95 (br.s, 1 H, H(4), $\Delta\nu_{1/2}$ = 15 Hz) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 29.6 (2 C, $CH_2\underline{C}H_2CH_2$, $\Delta\nu_{1/2}$ = 10 Hz); 39.3 (2 C, CH_2NAr); 45.7 (2 C, CH_2NHCH_2); 54.1 (2 C, $CH_2\underline{C}H_2N$, $\Delta\nu_{1/2}$ = 15 Hz); 60.0 (1 C, $ArCH_2N$); 69.6 (2 C, CH_2O); 69.7 (2 C, CH_2O); 70.1 (2 C, CH_2O); 70.4 (2 C, CH_2O); 70.5 (2 C, CH_2O); 95.5 (1 C, C(4), $\Delta\nu_{1/2}$ = 25 Hz); 104.3 (2 C, C(2), C(6)); 150.3 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + H]^+$, found 481.28, calculated 481.34. $C_{25}H_{44}N_4O_5$.

15-(1,4,7,10,13-Pentaoxa-16-azacyclooct-16-ylmethyl)-2,5,9,12-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (7f) was synthesized from tetramine **5f** (40 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (10 : 4 : 1). The yield was 36 mg (28%). ^{1}H NMR ($CDCl_3$), δ: 1.57 (br.s, 2 H, $CH_2C\underline{H}_2CH_2$); 2.67—2.77 (m, 12 H, $C\underline{H}_2NHC\underline{H}_2$, $CH_2C\underline{H}_2N$); 3.33 (t, 4 H, CH_2NAr, J = 4.7 Hz); 3.55—3.69 (m, 22 H, CH_2O, $ArCH_2N$); 5.98 (br.s, 2 H, H(2), H(6)); 6.19 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 26.6 (1 C, $CH_2\underline{C}H_2CH_2$); 43.7 (2 C, CH_2NAr); 49.2 (2 C, $\underline{C}H_2NH\underline{C}H_2$); 49.6 (2 C, $\underline{C}H_2NH\underline{C}H_2$); 54.3 (2 C, $CH_2\underline{C}H_2N$); 60.0 (1 C, $ArCH_2N$); 69.7 (2 C, CH_2O); 70.2 (2 C, CH_2O); 70.5 (4 C, CH_2O); 70.7 (2 C, CH_2O); 94.5 (1 C, C(4)); 104.6 (2 C, C(2), C(6)); 141.4 (1 C, C(1)); 149.1 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 510.3626, calculated 510.3655. $C_{26}H_{48}N_5O_5$.

17-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-2,6,10,14-tetraazabicyclo[13.3.1]nonadeca-1(19),15,17-triene (7g) was synthesized from tetramine **5g** (33 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (10 : 4 : 1). The yield was 26 mg

(20%). ^{1}H NMR ($CDCl_3$), δ: 1.67 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 5.2 Hz); 2.68 (t, 4 H, $CH_2CH_2C\underline{H}_2NH$, J = 5.4 Hz); 2.69 (s, 4 H, $NHC\underline{H}_2C\underline{H}_2NH$); 2.73 (t, 4 H, $CH_2C\underline{H}_2N$, J = 5.5 Hz); 3.32 (t, 4 H, CH_2NAr, J = 6.2 Hz); 3.55—3.59 (m, 8 H, CH_2O); 3.61—3.66 (m, 14 H, CH_2O, $ArCH_2N$); 5.90 (br.s, 2 H, H(2), H(6)); 6.13 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 31.4 (2 C, $CH_2\underline{C}H_2CH_2$); 41.3 (2 C, CH_2NAr); 46.0 (2 C, $CH_2NH\underline{C}H_2$); 48.9 (2 C, $\underline{C}H_2NHCH_2$); 54.2 (2 C, $CH_2\underline{C}H_2N$); 59.8 (1 C, $ArCH_2N$); 69.6 (2 C, CH_2O); 70.1 (2 C, CH_2O); 70.5 (4 C, CH_2O); 70.7 (2 C, CH_2O); 92.9 (1 C, C(4)); 104.3 (2 C, C(2), C(6)); 141.2 (1 C, C(1)); 150.4 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 524.3797, calculated 524.3812. $C_{27}H_{50}N_5O_7$.

17-(1,4,7,10,13-Pentaoxa-16-azacyclooctadec-16-ylmethyl)-2,6,10,14-tetraazabicyclo[13.3.1]nonadeca-1(19),15,17-triene (7h) was synthesized from tetramine **5h** (47 mg). The eluent was CH_2Cl_2—MeOH—NH_3 (10 : 4 : 1). The yield was 21 mg (16%). ^{1}H NMR ($CDCl_3$), δ: 1.74 (br.s, 6 H, $CH_2C\underline{H}_2CH_2$); 2.70 (t, 4 H, $CH_2C\underline{H}_2N$, J = 4.9 Hz); 2.72—2.80 (m, 8 H, $CH_2C\underline{H}_2N$); 3.28 (t, 4 H, CH_2NAr, J = 7.1 Hz); 3.55—3.69 (m, 22 H, CH_2O, $ArCH_2N$); 5.92 (br.s, 2 H, H(2), H(6)); 5.95 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 28.3 (1 C, $CH_2\underline{C}H_2CH_2$); 29.3 (2 C, $CH_2\underline{C}H_2CH_2$); 42.2 (2 C, CH_2NAr); 47.3 (2 C, $\underline{C}H_2NH\underline{C}H_2$); 49.5 (2 C, $\underline{C}H_2NH\underline{C}H_2$); 54.1 (2 C, $CH_2\underline{C}H_2N$); 60.0 (1 C, $ArCH_2N$); 69.7 (2 C, CH_2O); 70.2 (2 C, CH_2O); 70.6 (4 C, CH_2O); 70.7 (2 C, CH_2O); 93.7 (1 C, C(4)); 103.9 (2 C, C(2), C(6)); 149.4 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + H]^+$, found 538.4001, calculated 538.3968. $C_{28}H_{52}N_5O_5$.

1-(3,5-Dibromobenzyl)-1,4,7,10-tetraazacyclododecane (10). 3,5-Dibromobenzyl bromide (5.32 g, 16.2 mmol) was added to a solution of *cis*-glyoxal-cyclene (**8**) (3.14 g, 16.2 mmol) in anhydrous toluene (30 mL) and the mixture was stirred for 24 h at room temperature. The white crystalline precipitate that formed was filtered off, washed with toluene (25 mL), then with acetone (25 mL), and dried *in vacuo* to yield 2a-(3,5-dibromobenzyl)-decahydro-4a,6a,8a-triaza-2a-azoniacyclopenta[*fg*]acenaphthylene bromide (**9**) (5.71 g, 67%). ^{1}H NMR (D_2O), δ: 2.45—2.55 (m, 4 H, CH_2N); 2.73—2.85 (m, 3 H, CH_2N); 2.87—2.91 (m, 1 H, CH_2N); 3.02—3.10 (m, 1 H, CH_2N); 3.15 (d, 1 H, CH_2N, J = 12.3 Hz); 3.20—3.34 (m, 3 H, CH_2N); 3.47 (td, 1 H, CH_2N, J = 8.5 Hz, J = 2.9 Hz); 3.52—3.62 (m, 3 H, CH_2N); 3.71 (d, 1 H, CHN_2, J = 2.3 Hz); 4.01 (d, 1 H, CHN_2, J = 2.3 Hz); 4.15 (td, 1 H, CH_2N, J = 11.1 Hz, J = 3.4 Hz); 4.64 (d, 1 H, $ArCH_2N$, J = 13.6 Hz); 4.83 (d, 1 H, $ArCH_2N$, J = 13.6 Hz); 7.73 (br.s, 2 H, H(2), H(6)); 7.98 (br.s, 1 H, H(4)). ^{13}C NMR (D_2O), δ: 43.7 (1 C, CH_2N); 47.4 (1 C, CH_2N); 47.6 (1 C, CH_2N); 48.1 (1 C, CH_2N); 48.2 (1 C, CH_2N); 51.2 (1 C, CH_2N); 57.2 (1 C, CH_2N); 59.9 (1 C, CH_2N); 61.4 (1 C, CH_2N); 71.6 (1 C, CHN_2); 83.0 (1 C, CHN_2); 123.4 (2 C, C(3), C(5)); 130.4 (1 C, C(1)); 133.9 (2 C, C(2), C(6)); 136.6 (1 C, C(4)). Compound **9** was dissolved in ethanol (60 mL), KOH (8.9 g, 0.159 mol) was added, and the mixture was refluxed for 72 h. Upon completion of the reaction, the solvent was evaporated *in vacuo*, the solid residue was extracted with dichloromethane (3×25 mL), dried with magnesium sulfate, and the solvent was evaporated *in vacuo* to yield compound **10** as a pale yellow crystalline powder. The yield was 4.45 g (98%, 65% over two steps), m.p. 119—121 °C. ^{1}H NMR ($CDCl_3$), δ: 2.55—2.60 (m, 8 H, CH_2N); 2.67 (t, 4 H, CH_2N, J = 4.9 Hz); 2.83 (t, 4 H, CH_2N, J = 4.9 Hz); 3.56 (s, 2 H, NCH_2Ar); 7.42 (br.s, 2 H, H(2), H(6)); 7.51 (br.s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 45.6 (2 C, CH_2N); 46.6 (2 C, CH_2N); 47.6 (2 C, CH_2N); 51.7 (2 C, CH_2N); 58.5 (1 C, NCH_2Ar); 122.8 (2 C, C(3), C(5)); 130.6 (2 C, C(2), C(6)); 132.7 (1 C, C(4)); 143.4 (1 C, C(1)). MS (MALDI), m/z: $[M + H]^+$, found 419.0470, calculated 419.0446. $C_{15}H_{25}Br_2N_4$.

The general procedure for the synthesis of macrobicycles **11a—c** is identical with that for macrobicycles **6** and **7**. Numbering of the atoms of the benzene ring in the ^{1}H and ^{13}C NMR spectra of compounds **11** is shown in Scheme 4.

19-(1,4,7,10-Tetraazacyclododec-1-ylmethyl)-6,9,12-trioxa-2,16-diazabicyclo[15.3.1]enicosa-1(21),17,19-triene (11a). According to the first method, compound **11a** was synthesized from compound **10** (104 mg, 0.25 mmol) and trioxadiamine **2a** (55 mg, 0.25 mmol) in the presence of $Pd(dba)_2$ (12 mg, 8 mol.%), DavePhos (9 mg, 9 mol.%), and sodium *tert*-butoxide (72 mg, 0.375 mmol) in dioxane (12 mL). According to the second method, compound **11a** was synthesized from compound **10** (104 mg, 0.25 mmol) and trioxadiamine **2a** (55 mg, 0.25 mmol) in the presence of $Pd(dba)_2$ (24 mg, 16 mol.%), DavePhos (18 mg, 18 mol.%), and sodium *tert*-butoxide (72 mg, 0.375 mmol) in dioxane (12 mL). The combined reaction mixtures were chromatographed on silica gel. The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 25 : 5). The total yield was 32 mg (13%). ^{1}H NMR ($CDCl_3$), δ: 1.78 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 5.7 Hz); 2.52—2.92 (m, 16 H, CH_2N); 3.23 (t, 4 H, CH_2NAr, J = 5.9 Hz); 3.44—3.63 (m, 14 H, CH_2O, $ArCH_2N$); 5.86 (s, 2 H, H(2), H(6)); 6.02 (s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 29.5 (2 C, $CH_2\underline{C}H_2CH_2$); 41.8 (2 C, CH_2NHAr); 45.5 (2 C, CH_2N); 45.8 (2 C, CH_2N); 47.6 (2 C, CH_2N); 51.2 (2 C, CH_2N); 60.3 (1 C, $ArCH_2N$); 69.4 (2 C, CH_2O); 69.9 (2 C, CH_2O); 70.7 (2 C, CH_2O); 95.7 (1 C, C(4)); 102.9 (2 C, C(2), C(6)); 140.3 (1 C, C(1)); 150.2 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 479.3675, calculated 479.3709. $C_{25}H_{47}N_6O_3$.

18-(1,4,7,10-Tetrpazacyclododec-1-ylmethyl)-6,11-dioxa-2,15-diazabicyclo[14.3.1]icosa-1(20),16,18-triene (11b) was synthesized from compound **10** (104 mg, 0.25 mmol) and dioxadiamine **2b** (51 mg, 0.25 mmol) in the presence of $Pd(dba)_2$ (12 mg, 8 mol.%), DavePhos (9 mg, 9 mol.%), and sodium *tert*-butoxide (72 mg, 0.375 mmol) in dioxane (12 mL). The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 20 : 3). The yield was 11 mg (10%). ^{1}H NMR ($CDCl_3$), δ: 1.76 (br.s, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$); 1.81 (qu, 4 H, $CH_2C\underline{H}_2CH_2$, J = 4.7 Hz); 2.72—2.82 (m, 12 H, $C\underline{H}_2NHC\underline{H}_2$); 2.93—2.97 (m, 4 H, CH_2N); 3.24 (t, 4 H, CH_2NAr, J = 5.6 Hz); 3.38—3.45 (m, 6 H, $C\underline{H}_2CH_2CH_2C\underline{H}_2$, $ArCH_2N$); 3.52 (t, 4 H, CH_2O, J = 4.6 Hz); 5.89 (s, 2 H, H(2), H(6)); 6.05 (s, 1 H, H(4)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 26.5 (2 C, $CH_2\underline{C}H_2\underline{C}H_2CH_2$); 30.0 (2 C, $CH_2\underline{C}H_2CH_2$); 42.5 (2 C, CH_2NAr); 45.8 (2 C, CH_2N); 46.9 (2 C, CH_2N); 48.4 (2 C, CH_2N); 51.5 (2 C, CH_2N); 61.1 (1 C, $ArCH_2N$); 69.9 (4 C, CH_2O); 95.3 (1 C, C(4)); 102.4 (2 C, C(2), C(6)); 150.4 (2 C, C(3), C(5)) (the signal for one quarternary aromatic carbon atom was not observed). MS (MALDI), m/z: $[M + H]^+$, found 463.39, calculated 463.38. $C_{25}H_{47}N_6O_2$.

15-(1,4,7,10-Tetrpazacyclododec-1-ylmethyl)-5,9-dioxa-2,12-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (11c) was synthesized from compound **10** (104 mg, 0.25 mmol) and dioxadiamine **2c** (37 mg, 0.25 mmol) in the presence of $Pd(dba)_2$ (12 mg, 8 mol.%), DavePhos (9 mg, 9 mol.%), and sodium

tert-butoxide (72 mg, 0.375 mmol) in dioxane (12 mL). The eluent was CH_2Cl_2—MeOH—NH_3 (100 : 25 : 5). The yield was 2 mg (2%). ^{1}H NMR ($CDCl_3$), δ: 2.64—2.76 (m, 12 H, $C\underline{H}_2NHC\underline{H}_2$); 2.86 (t, 4 H, CH_2N, J = 4.9 Hz); 3.25 (t, 4 H, CH_2NAr, J = 5.2 Hz); 3.61—3.65 (m, 10 H, CH_2O, $ArCH_2N$); 5.82 (s, 1 H, H(4)); 6.02 (s, 2 H, H(2), H(6)) (no signals for the NH protons were observed). ^{13}C NMR ($CDCl_3$), δ: 43.5 (2 C, CH_2NAr); 45.9 (2 C, CH_2N); 46.3 (2 C, CH_2N); 48.1 (2 C, CH_2N); 51.6 (2 C, CH_2N); 60.5 (1 C, $ArCH_2N$); 69.8 (2 C, CH_2O); 70.1 (2 C, CH_2O); 96.3 (1 C, C(4)); 103.7 (2 C, C(2), C(6)); 141.3 (1 C, C(1)); 149.6 (2 C, C(3), C(5)). MS (MALDI), m/z: $[M + H]^+$, found 407.3179, calculated 407.3134. $C_{21}H_{39}N_6O_2$.

This work was financially supported by the Russian Academy of Sciences (Program "Development of the methodology of organic synthesis and design of compounds with valuable applied properties") and the Russian Foundation for Basic Research (Project No. 09-03-00735).

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Received March 1, 2011;
in revised form April 13, 2011