КАТАЛИЗ МЕТАЛЛАМИ В ПРЕВРАЩЕНИЯХ ПОРФИРИНОВ

И.П. Белецкая, А.Д. Аверин

Ирина Петровна Белецкая

Московский государственный университет им. М.В. Ломоносова, Химический факультет, Ленинские горы, 1-3, Москва, 11991
E-mail: beletska@org.chem.msu.ru

Алексей Дмитриевич Аверин

Институт физической химии и электрохимии им. А.Н. Фрумкина РАН, Ленинский пр., 31-4, Москва, 119991
E-mail: alexaveron@yandex.ru

Мини-обзор обобщает результаты, касающиеся различных превращений порфиринов и их комплексов, осуществленных в реакциях, катализируемых комплексами палладия, и приводящих к образованию связей C-C, C-N and C-P.

Ключевые слова: порфирин, комплекс, катализ, палладий

METAL CATALYSIS IN THE TRANSFORMATIONS OF PORPHYRINS

I.P. Beletskaya, A.D. Averin

Irina P. Beletskaya

Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory, 1-3, Moscow, 119991 Russia
E-mail: beletska@org.chem.msu.ru

Alexei D. Averin

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Leninskiy prosp., 31-4, Moscow, 119991, Russia
E-mail: alexaveron@yandex.ru

A mini-review outlines the results considering various transformations of porphyrins and their complexes achieved in the reactions catalyzed with Pd complexes leading to C-C, C-N and C-P bonds formation.

Ключевые слова: porphyrin, complex, catalysis, palladium

INTRODUCTION

Porphyrins constitute a very important class of organic compounds widely occurring in nature as a building block in living systems [1]. Bioporphyrins, like a magnesium-containing chlorophyll, are the pigments in plants, while hemoglobin in blood comprises gems containing iron. Porphyrin–related tetrapyrrolic macrocycles observed in nature as well as artificial porphyrinoids including phthalocyanine are given on Fig. 1. An important issue of the porphyrin chemistry is the formation of supramolecular assemblies potent of various useful applications [2].

It is well known that at the end of the XXth century principally new approaches to the construction of carbon-carbon and carbon-heteroatom bonds were widely developed. The reactions, named after their discoverers and pioneers like Heck, Suzuki, Miyaura, Sonogashira, began to be actively applied in various fields of organic chemistry. The porphyrin chemistry did not stay apart from this process and began to employ the catalytic reactions though it happened later than with more simple aromatic substrates. Examples of such reactions for the construction of the β-*meso* porphyrin dimer (*via* Suzuki-Miyaura reaction) [3],

mono- and divinyl substituted porphyrins (*via* Heck reaction) [4], β-alkynyl substituted porphyrin (*via* Sonogashira reaction) [5] are shown on Scheme 1. The same reactions were applied for the synthesis of porphyrin dyads and triads with phenylene and acetylene bridges (Scheme 2) [6]. It is to be stressed that carrying out such reactions with porphyrin compounds is usually more difficult than with simpler aromatics and to achieve good results one needs more catalyst and ligand loadings. The development of the catalytic transformations of porphyrins before 2010 was summarized in a review [7].

Pd-catalyzed amination of bromosubstituted porphyrins

Facile and efficient synthesis of *meso*-arylamino- and alkylamino-substituted porphyrins *via* Pd-catalyzed amination was proposed by Zhang in 2003 [8], while a convenient method for the preparation of a variety of amino substituted zinc porphyrins by Pd-catalyzed intermolecular carbon-nitrogen coupling reactions between haloporphyrins and amino substituted porphyrins was reported by van Lier even earlier [9]. The successes in the application of the Buchwald-Hartwig amination to the synthesis of porphyrin derivatives were outlined in [10].

Porphyrinoids occuring in nature

Porphyrin nucleus   Chlorin   Bacteriochlorin   Corrin

Chlorophyll   Heme b

Artificial prophyrinoids

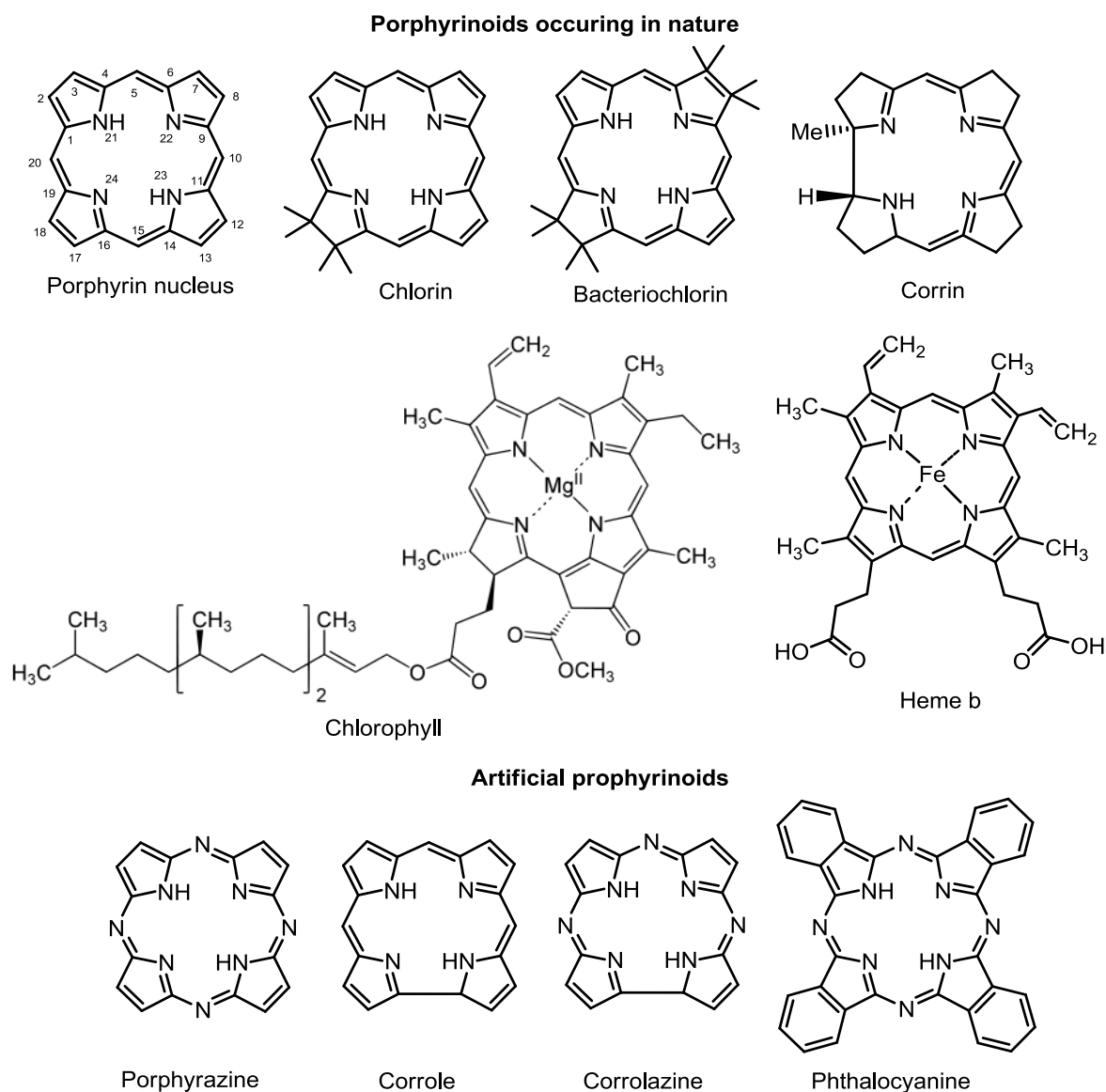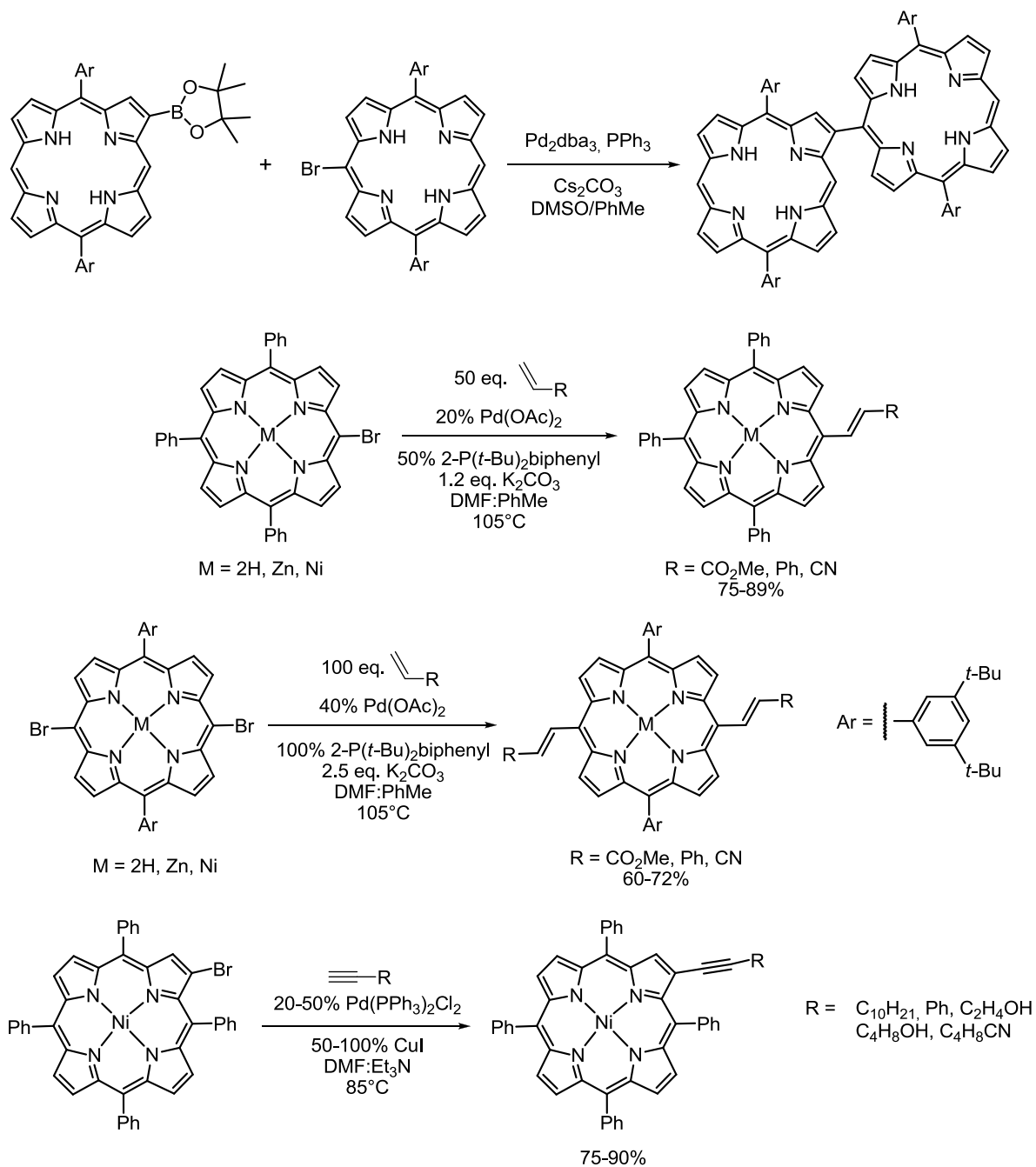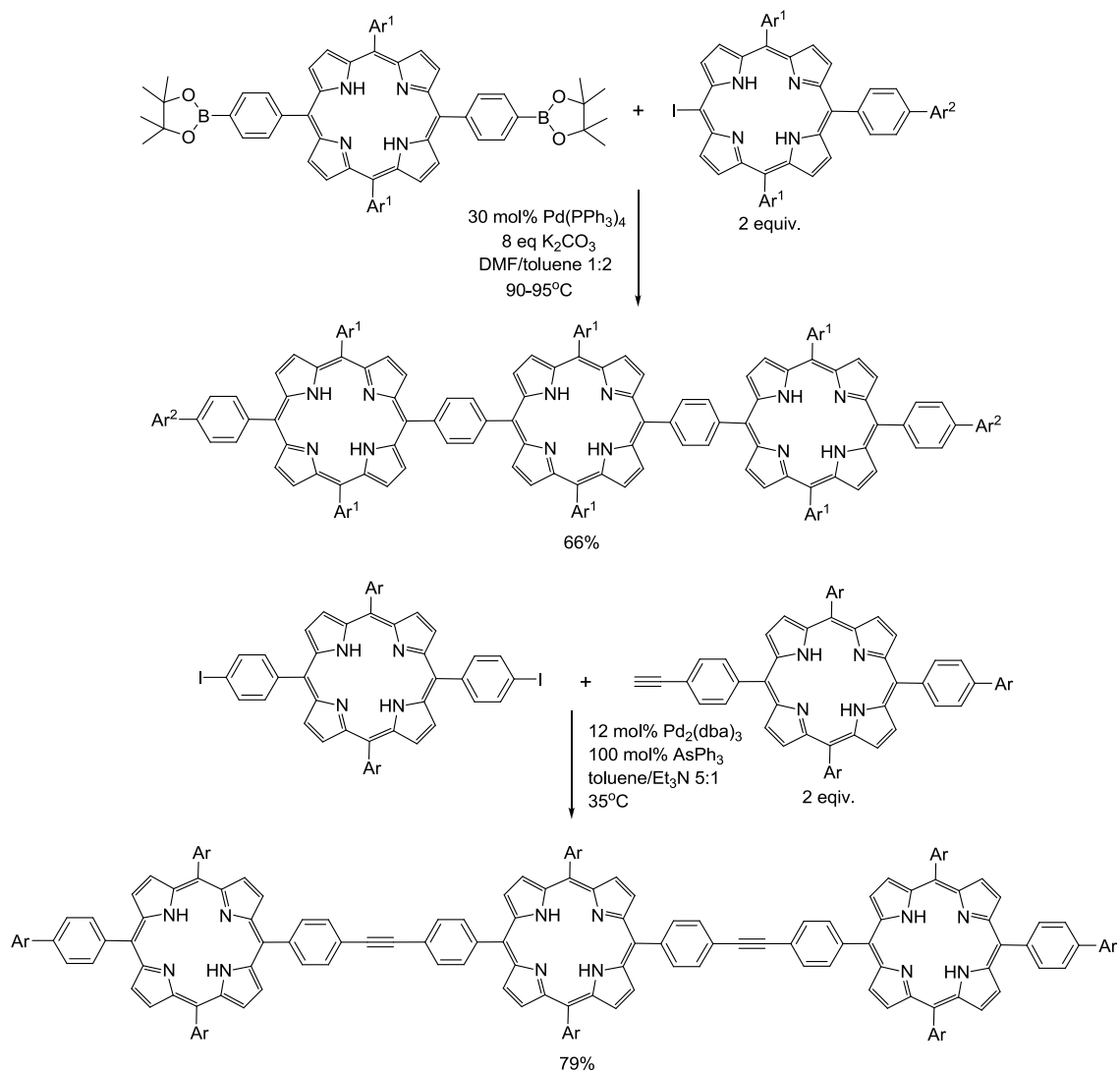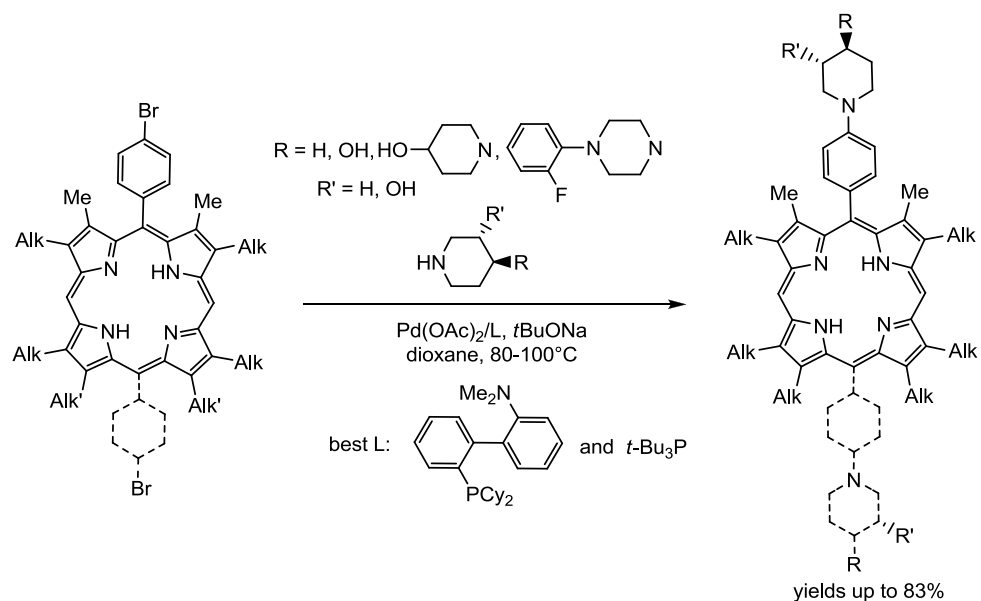Porphyrazine   Corrole   Corrolazine   Phthalocyanine

Fig. 1. Naturally occurring and artificial porphyrinoids
Рис. 1. Природные и синтетические порфириноиды
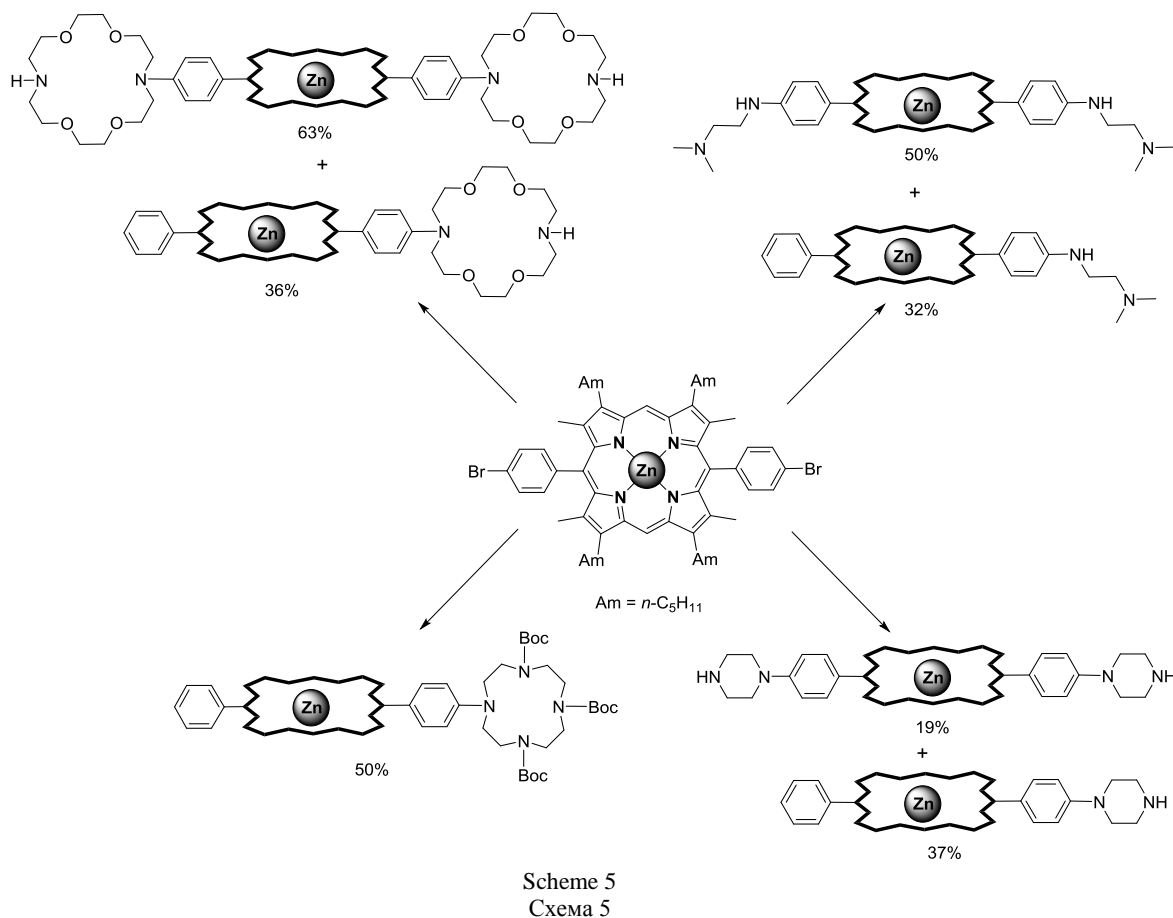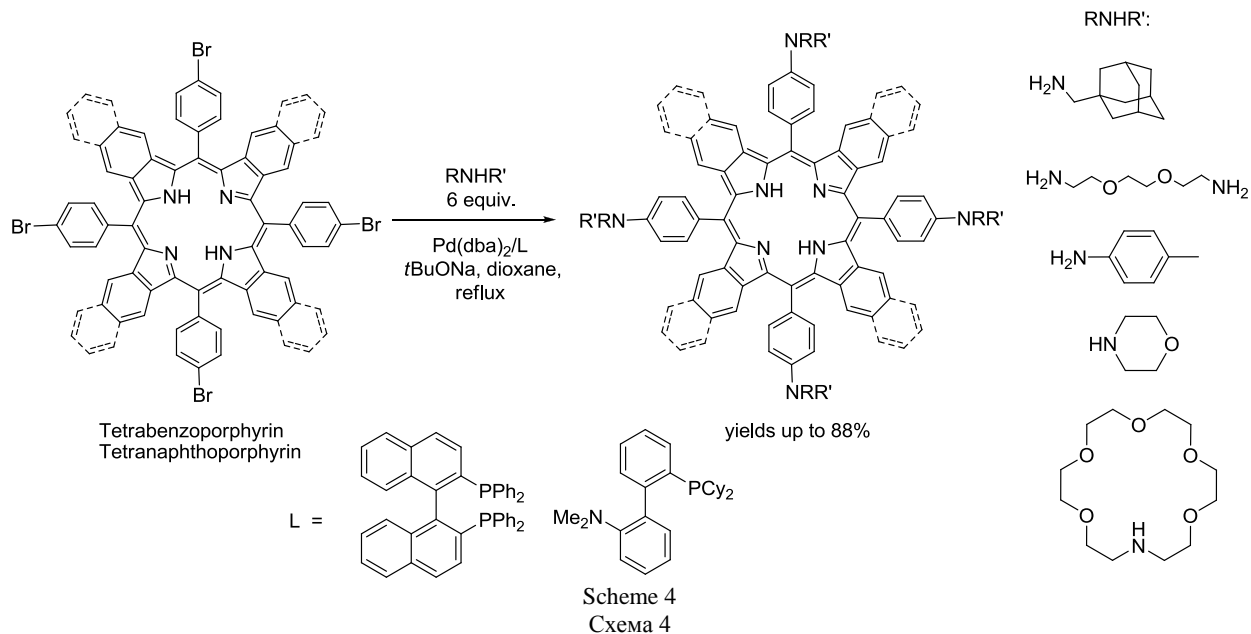
Scheme 1
Схема 1

The investigations conducted in the Laboratory of Organoelement Compounds of the Department of Chemistry of the Lomonosov MSU were at first focused at the application of the Pd(0)-catalyzed amination of meso-(bromophenyl)substituted porphyrins due to our vast experience in the application of this method to the chemistry of macrocyclic compounds. 5-(4-Bromophenyl)- and 5,15-di(4-bromophenyl)porphyrins were involved in the catalytic amination and compounds containing chiral hydroxypiperidine fragments were thus obtained (Scheme 3) [11, 12]. This was one of the first rare examples of the Pd-catalyzed amination reactions in porphyrin series using Buchwald (2-(dicyclohexylphosphino)-2'-(dimethylamino)biphenyl, DavePhos) and Fu (tris(tert-butyl)phosphine) ligands.

30 mol% Pd(PPh₃)₄
8 eq K₂CO₃
DMF/toluene 1:2
90-95°C

2 equiv.

66%

12 mol% Pd₂(dba)₃
100 mol% AsPh₃
toluene/Et₃N 5:1
35°C

2 eqiv.

79%

Scheme 2
Схема 2

R = H, OH, HO—⟨N⟩, ⟨N⟩—F
R' = H, OH

Pd(OAc)₂/L, tBuONa
dioxane, 80-100°C

best L: PCy₂ / Me₂N   and t-Bu₃P

yields up to 83%

Scheme 3
Схема 3

Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 2018. V. 61. N 12

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Previously unknown 5,10,15,20-tetrakis(4-bromophenyl) substituted tetrabenzo- and tetranaphthoporphyrins with extended π-system were successfully obtained in our laboratory and their Pd-catalyzed polyamination was carried out using BINAP or DavePhos ligands (Scheme 4) [13]. The same approach was applied for the synthesis of polymacrocyclic compounds featuring one central porphyrin and several surrounding azacrown moieties.

Scheme 4
Схема 4

Scheme 5
Схема 5

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The diamination reactions of Zn(II) 5,15-bis(4-bromophenyl)porphyrinate with various nitrogen-containing compounds (Scheme 5) was carried out in order to obtain polydentate ligands which possess three coordination sites: one electrophilic site where Zn can coordinate nucleophiles, and two nucleophilic sites to form complexes with metal cations [14, 15].


Ln = La, Eu, Gd   yields up to 88%
M = Zn, Cu

Scheme 6
Схема 6

30%
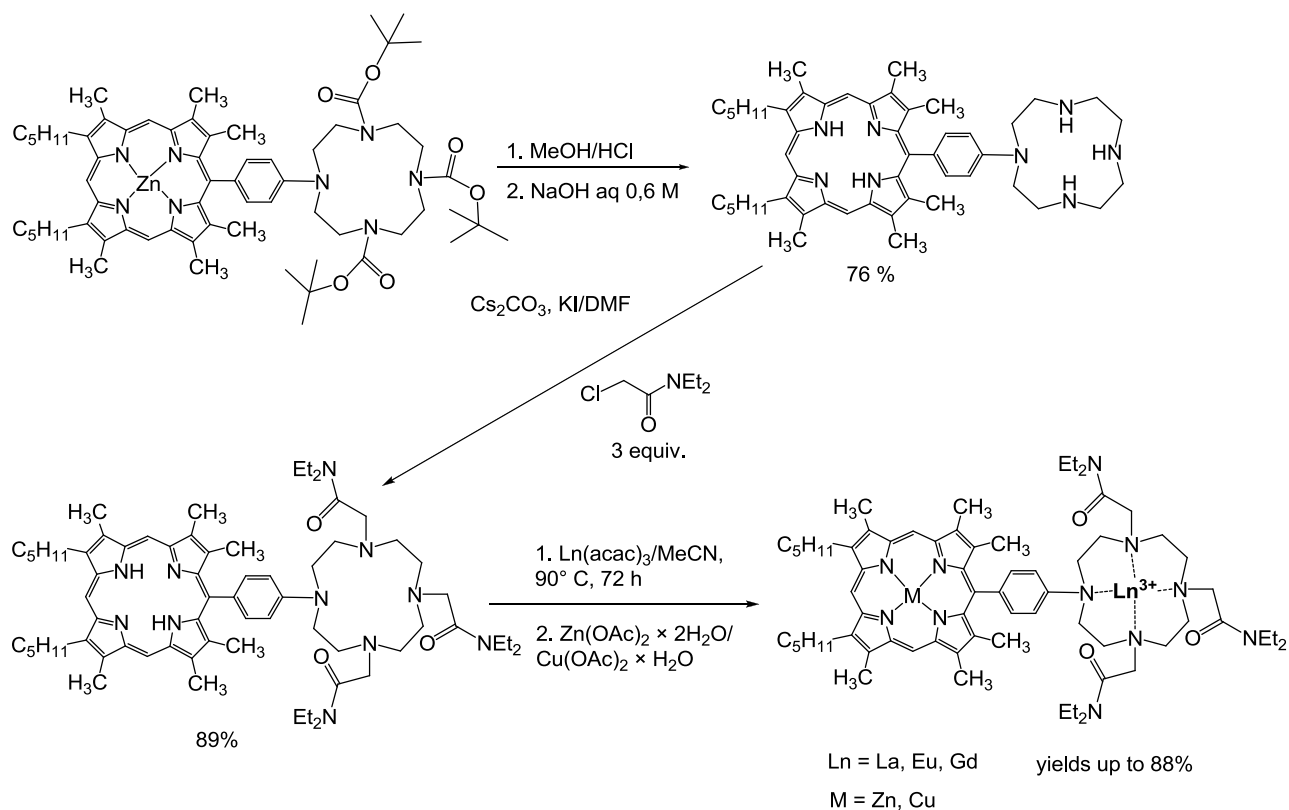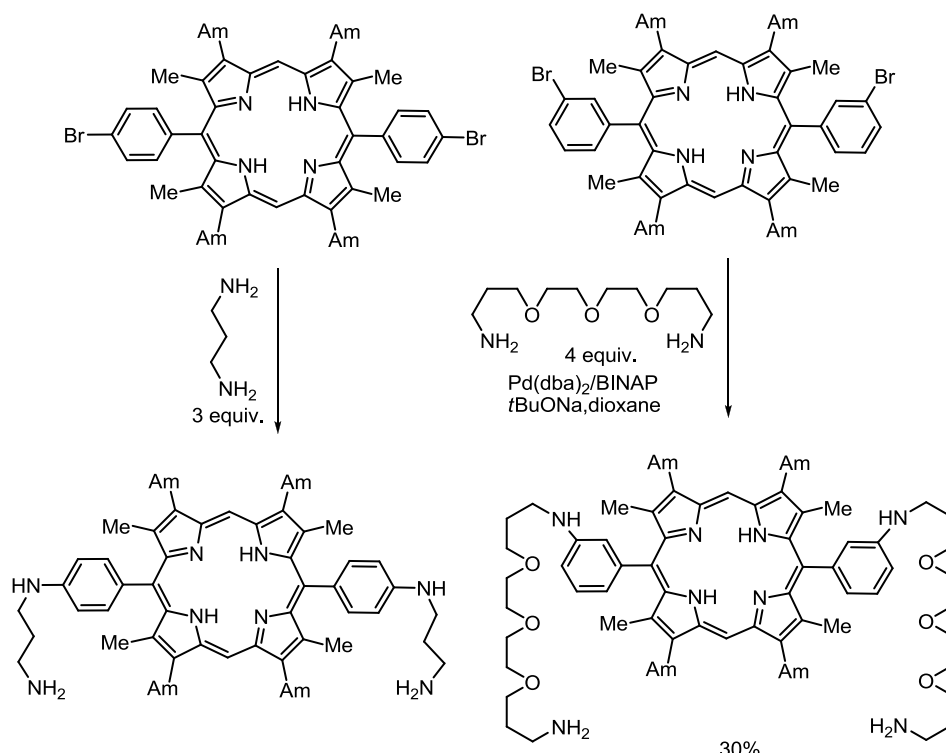
Scheme 7
Схема 7

The diamination of this porphyrinate with diazacrown ether or DMEDA (*N,N'*-dimethyl-1,2-ethanediamine) proceeded with good yields of the desired products (50-63%) though it was complicated with a usual hydrodebromination side process which led to corresponding products of monoamination in 32-36% yields. In the case of the amination with piperazine monoamination with the reduction of the second C-Br bond became the predominant process, and with N,N',N''-triBOCcyclen only monoaminated product was formed in 50% yield. Interesting conjugates of metalloporphyrins with the lanthanide complexes of triamidocyclen were synthesized according to a three-step procedure starting from triBoccyclen derivative of Zn(II) porphyrinate (Scheme 6).

Catalytic diamination of 5,15-bis(3- or 4-bromophenyl)porphyrins taken as free bases with excess

1,3-propanediamine and trioxadiamine gave corresponding bis(dimaino) derivatives of porphyrins (Scheme 7). More sophisticated conjugates possessing several coordination sites were obtained *via* the reactions of diamino derivatives of *N*-benzylazacrown ethers [16].

The synthesis of the porphyrin dimers linked by various diamines like 1,2-ethanediamine, DMEDA, piperazine, diazacrown ether can be carried out either in a stepwise mode, *via* intermediate diamino derivatives of corresponding metal porphyrinates, or directly from the diamines and prophyrinates taken in 1:2 ratio [17]. A similar approach using bis(diamino) derivatives of Zn(II) porphyrinates and 5-(4-bromophenyl)-porphyrinate taken in 1:2 ratio allows to create more sophisticated porphyrin trimers in which three porphyrin units are linked with two diamine moieties (Scheme 8).
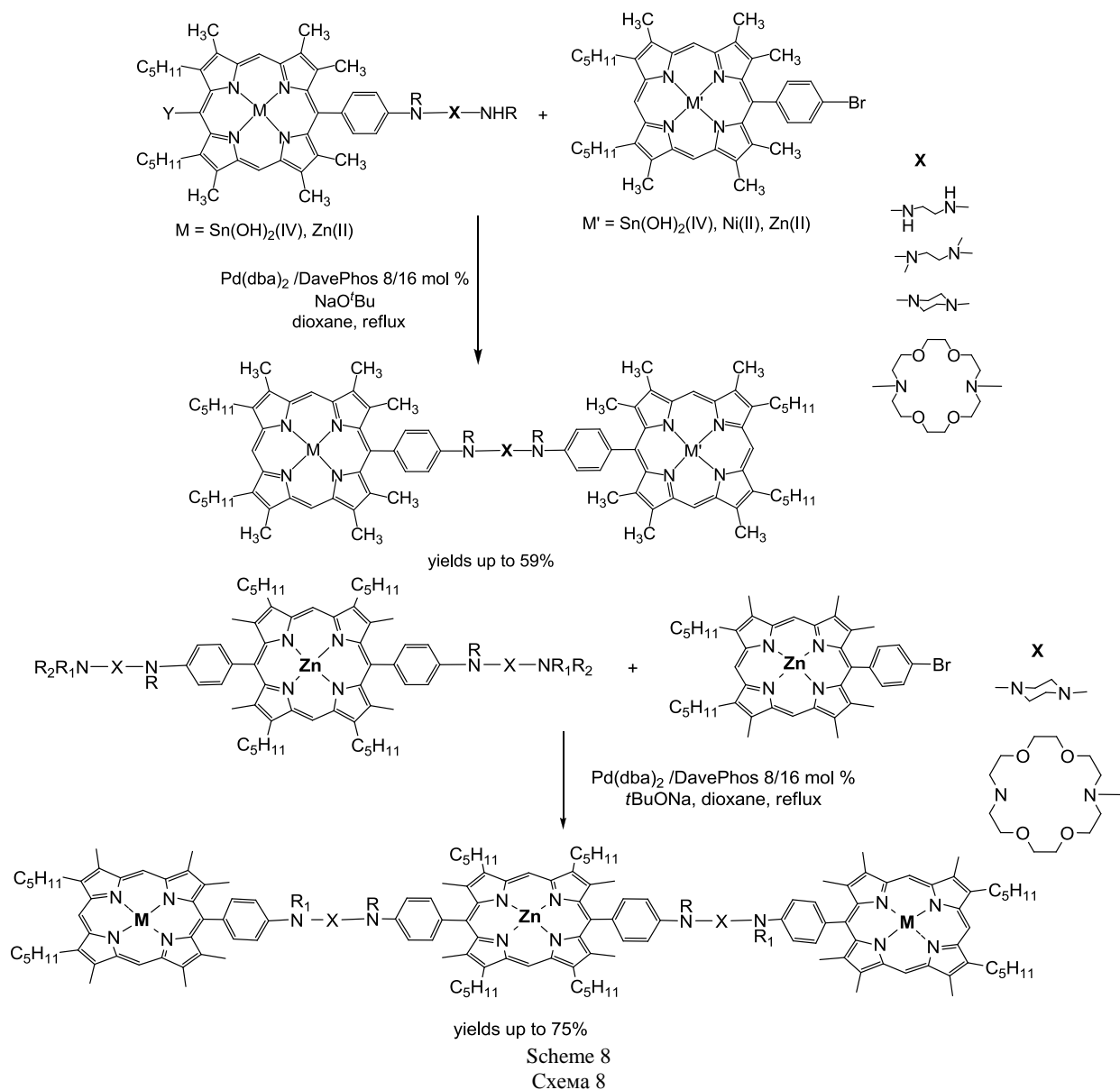
Scheme 8
Схема 8

We demonstrated the possibility to create another porphyrin trimer in which macrocycles are linked *via* simple NH units (Scheme 9), for this purpose 2 equiv. of Zn(II) 5-(4-bromophenyl)porphyrinate were reacted with 1 equiv. of Zn(II) 5,15-(4-aminophenyl)porphyrinate [17].

Using previously developed naphthalene- and biphenyl-based diazacrown ethers, we successfully applied Pd(0)-catalyzed amination to the synthesis of interesting trimacrocyclic compounds comprising either two porphyrin and one diazacrown or two diazacrown and one porphyrin moieties (Scheme 10) [18, 19].

21%
Scheme 9
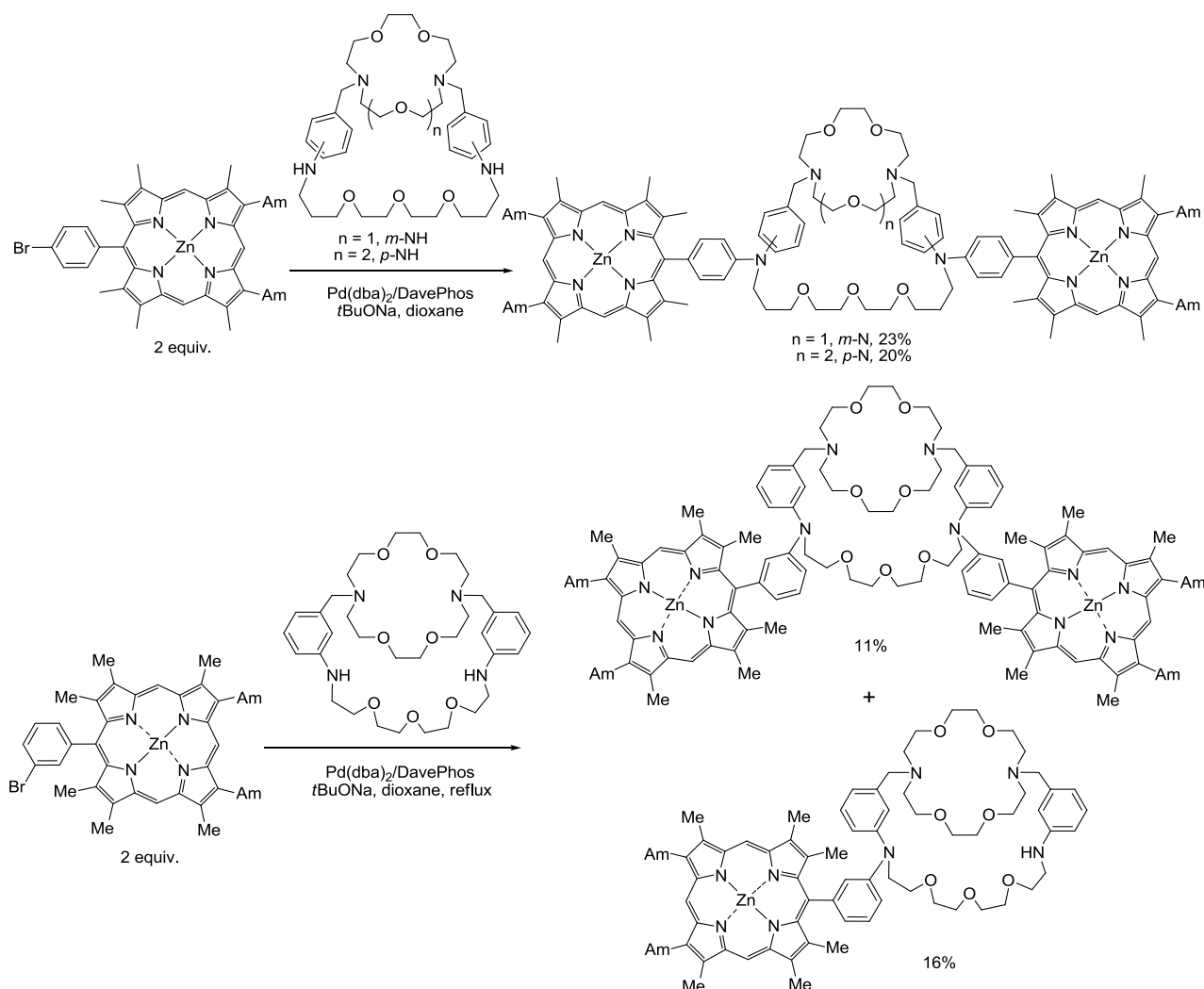Схема 9

27% 18%

9%
Scheme 10
Схема 10
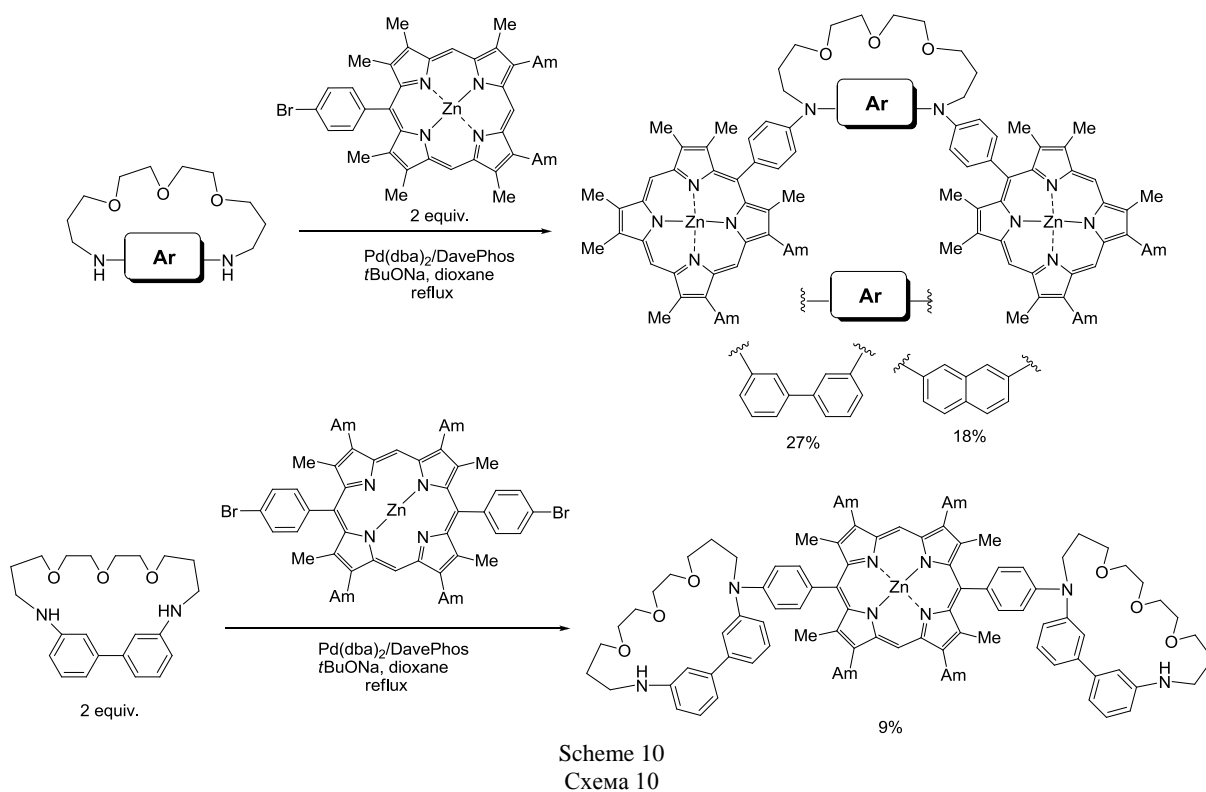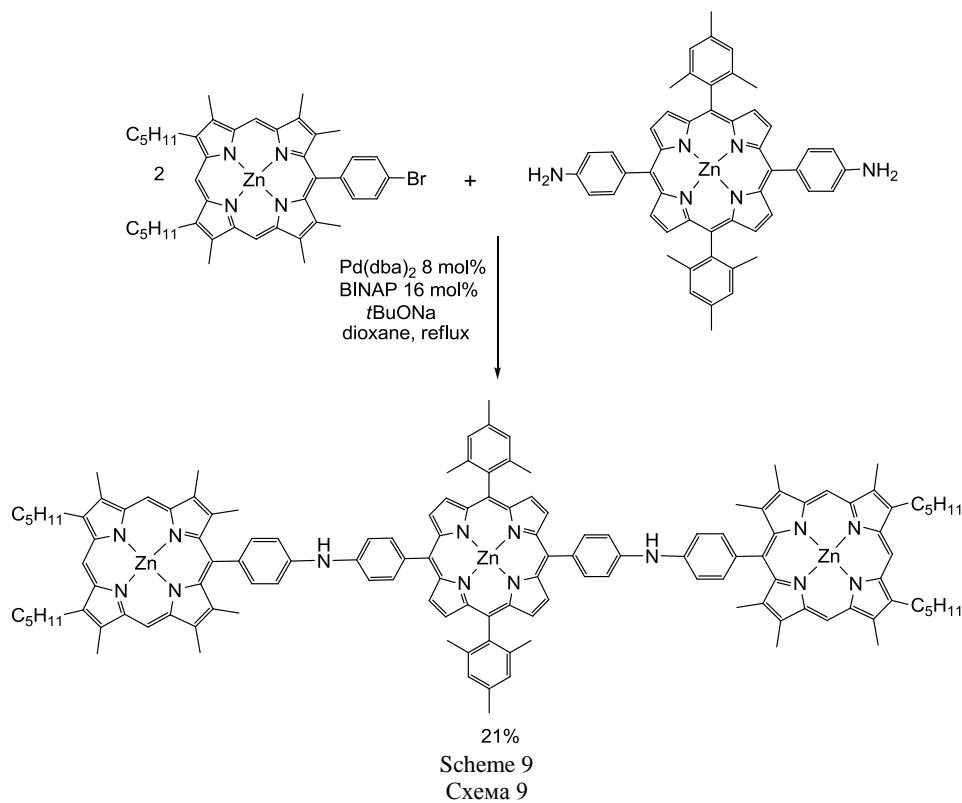
Important conjugates of macrobicyclic compounds based on diazacrown ethers with porphyrins were synthesized *via* Pd-catalyzed amination using 2 equiv. of Zn(II) 5-(4-bromophenyl)porphyrinate (Scheme 11) [20, 21]. The aim of the synthesis of such molecules was to obtain fluorescent sensors for metal cations employing receptor abilities of macrobicyclic cryptands and fluorescent properties of the attached porphyrin units.

Another type of the conjugates with porphyrins as fluorophore groups are those based on diaminocalix[4]arenes taken in cone and 1,3-alternate forms (Scheme 12). The dependence of the yields of the target trimacrocyclic derivatives on the structure

of the starting diaminocalix[4]arene was clearly demonstrated.

Coordination studies of porphyrin-derived polymacrocycles

Many polymacrocyclic compounds containing porphyrin moieties were studied in the complexation with metal cations. For example, spectrophotometric titration of the bis(azacrown) derivative of Zn(II) porphyrinate at $\lambda = 419$ nm with NaBr in CHCl$_3$/MeOH showed the formation of the complex with two sodium cations (Fig. 2). On the other hand the titration of the same trimacrocyclic compounds with KI resulted in the formation of the complex with 2:2 stoichiometry due to a larger ionic radius of K(I) cation (Fig. 3) [15].

Scheme 11
Схема 11

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Изв. вузов. Химия и хим. технология. 2018. Т. 61. Вып. 12
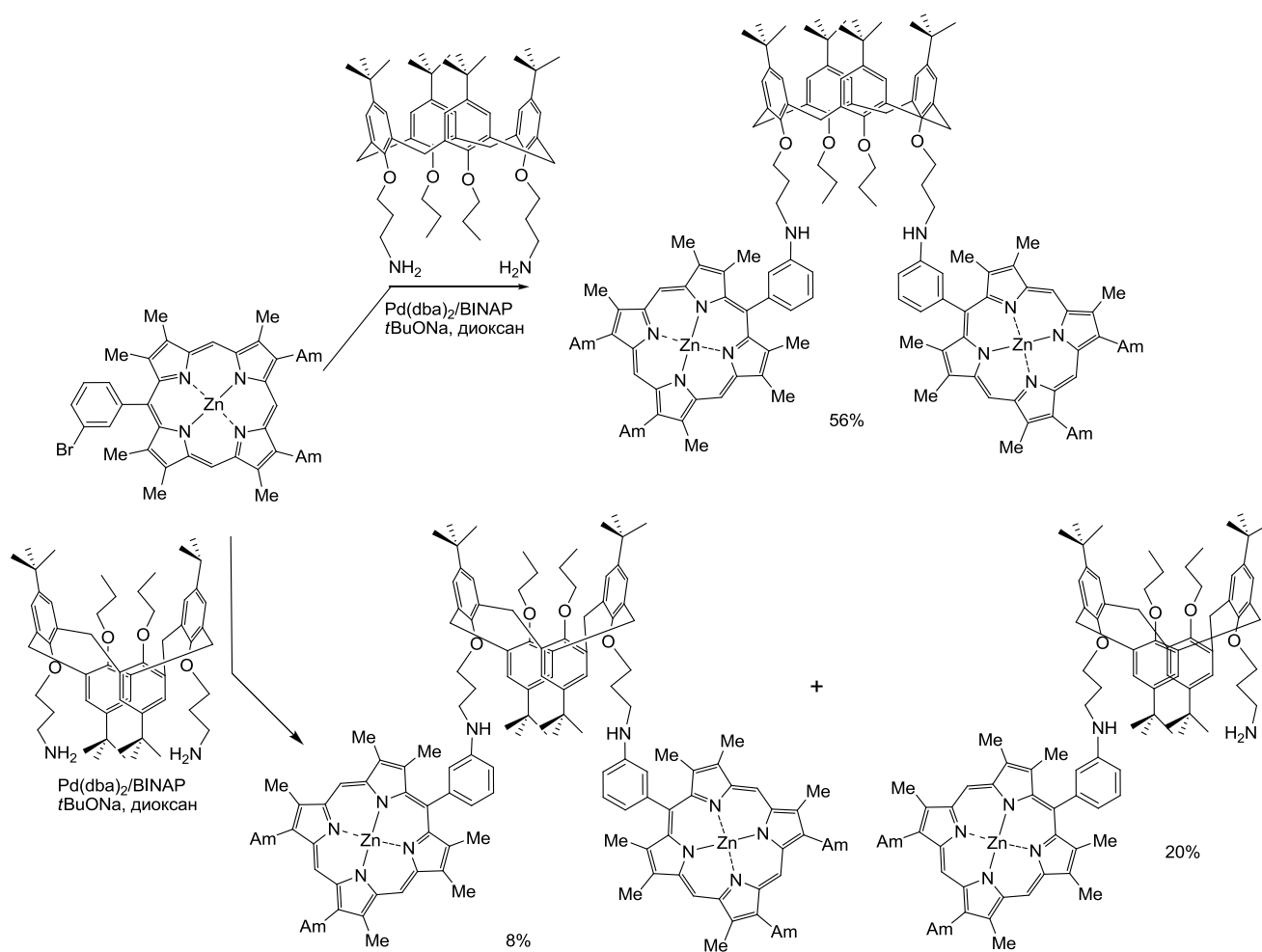
Scheme 12
Схема 12
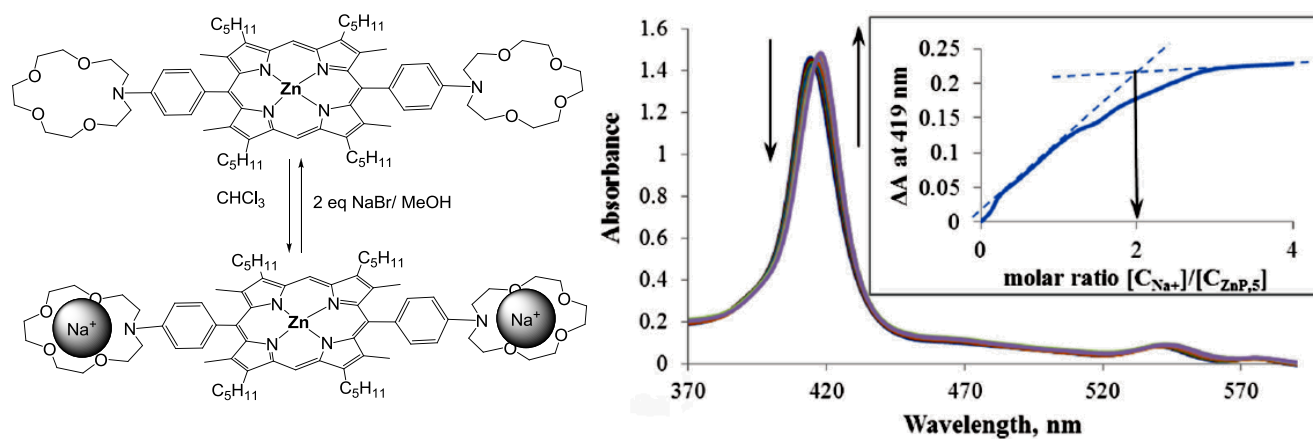
Fig. 2. Coordination of bis(azacrown) derivative of Zn(II) porphyrinate with Na(I) cations
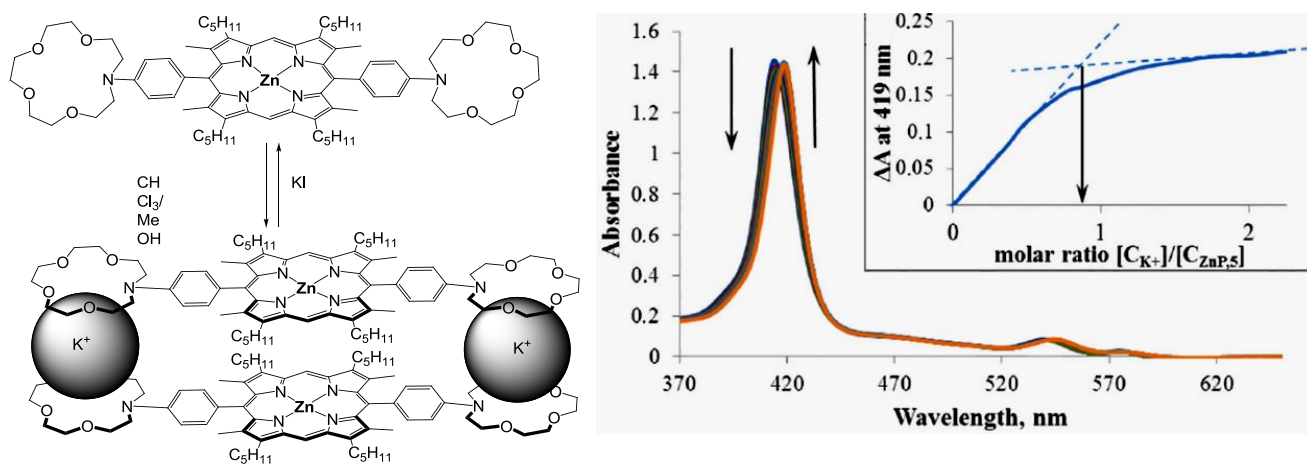Рис. 2. Координация бис (азакраун) производного порфирината Zn (II) с катионами Na (I)

Fig. 3. Coordination of bis(azacrown) derivative of Zn(II) porphyrinate with K(I) cations

Рис. 3. Координация производного бис (азакраун) порфирината Zn (II) с катионами K (I)

Interesting coordination between a porphyrin dyad in which two Zn(II) porphyrinates are linked *via* ethylenediamine bridge and a molecule of DABCO was studied. Spectrophotometric titration at $\lambda = 406$ nm revealed the formation of the 1:1 complex with co-facial arrangement of the porphyrin macrocycles at the first stage after the addition of 0.5 equiv. of the organic base. More DABCO led to the formation of the complex with two DABCO molecules (Fig. 4).
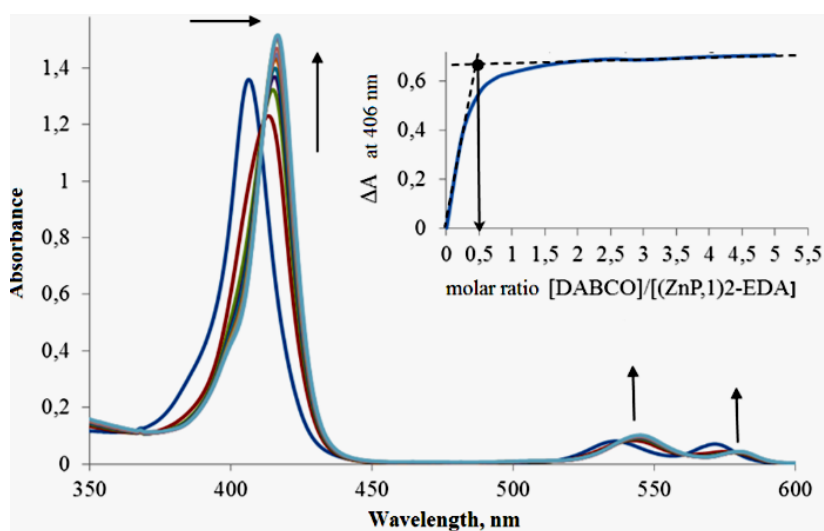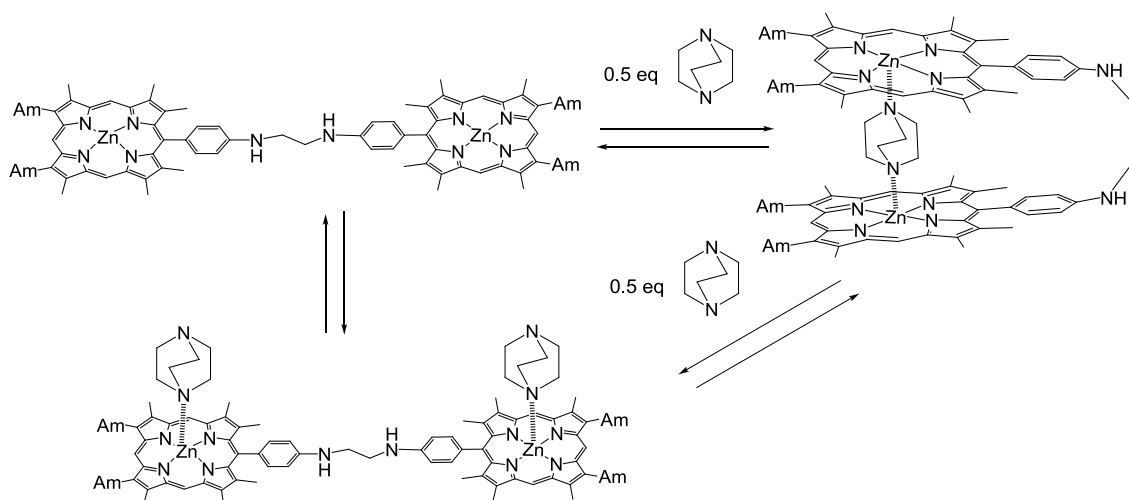

Fig. 4. Coordination of Zn(II) bisporphyrinate with DABCO

Рис. 4. Координация биспорфирината Zn (II) с DABCO

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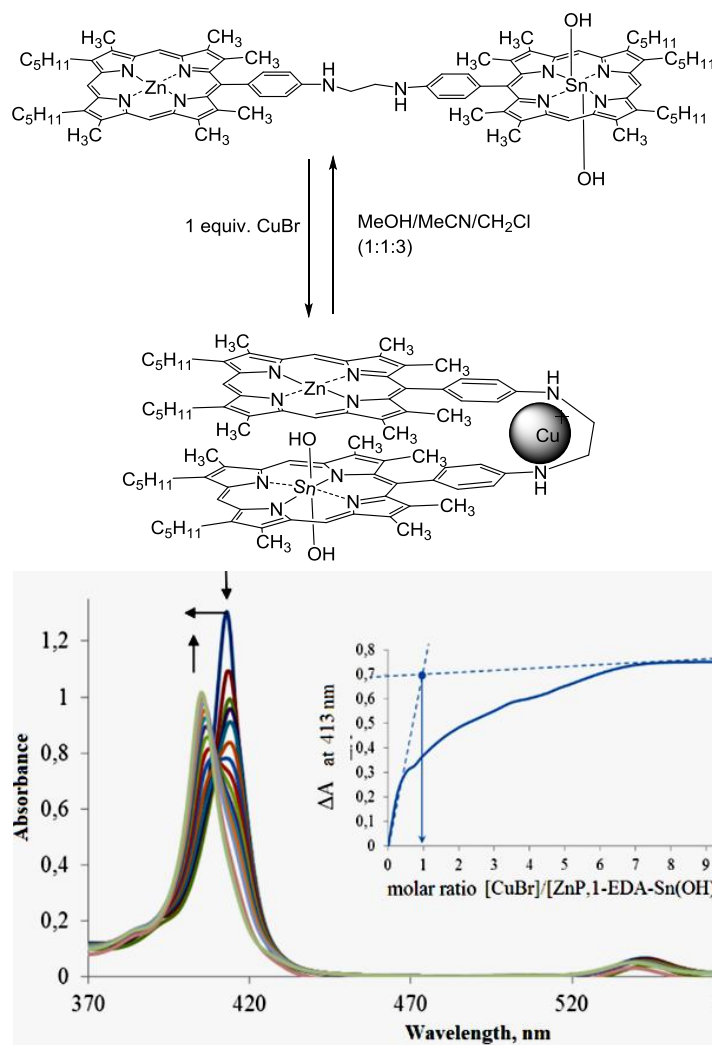Изв. вузов. Химия и хим. технология. 2018. Т. 61. Вып. 12

Fig. 5. Coordination of Zn(II)-Sn(II) bisporphyrinate with Cu(I)
Рис. 5. Координация биспорфирината Zn (II) -Sn(II) с DABCO

Similar coordination mode was established in the case of titration of the Zn(II)-Sn(II) bisporphyrinate with CuBr (Fig. 5). The porphyrin dyad acts as a tweezer forming a 1:1 complex with Cu(I) [22]. The driving force of this process is the formation of the chelate complex involving ethylenediamine and copper as well as the axial coordination of Zn cation with the hydroxyl group of the Sn(II) porphyrinate unit of the dyad. After the addition of either a more strong ligand (phenanthroline) or acid (HCl), which protonates two nitrogen atoms in the ethylenediamine fragment, a linear structure of the porphyrin dyad is recovered.

Several porphyrin-azacrown conjugates were tested as fluorescent chemosensors for metal cations [18]. The investigations revealed that bisporphyrinate derivative of the biphenyl-based diazacrown ether could be regarded as a fluorescent molecular probe for Cu(II), Al(III) and Cr(III) as only these cations quenched emission (Fig. 6a). Interestingly, a quite similar trimacrocycle, the derivative of the naphthalene-based diazacrown ether containing the same prophyrinate units, was found to be much more selective towards Cu(II) as only the addition of this cation led to full quenching of the emission (Fig. 6b).
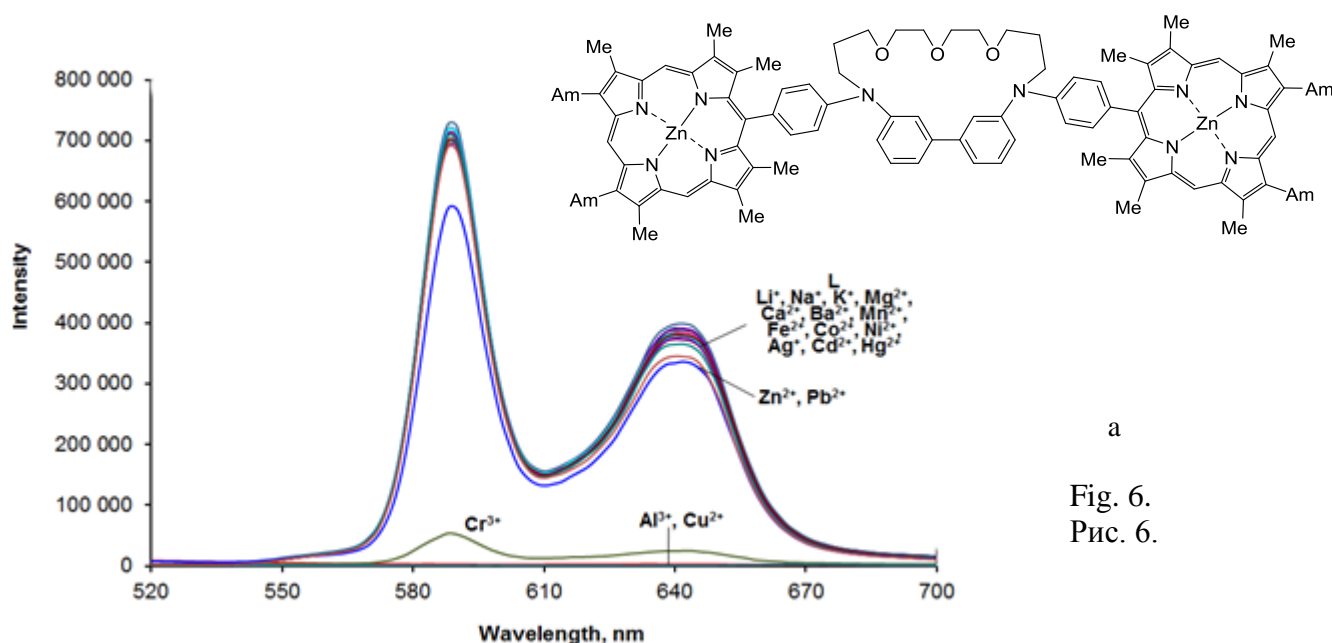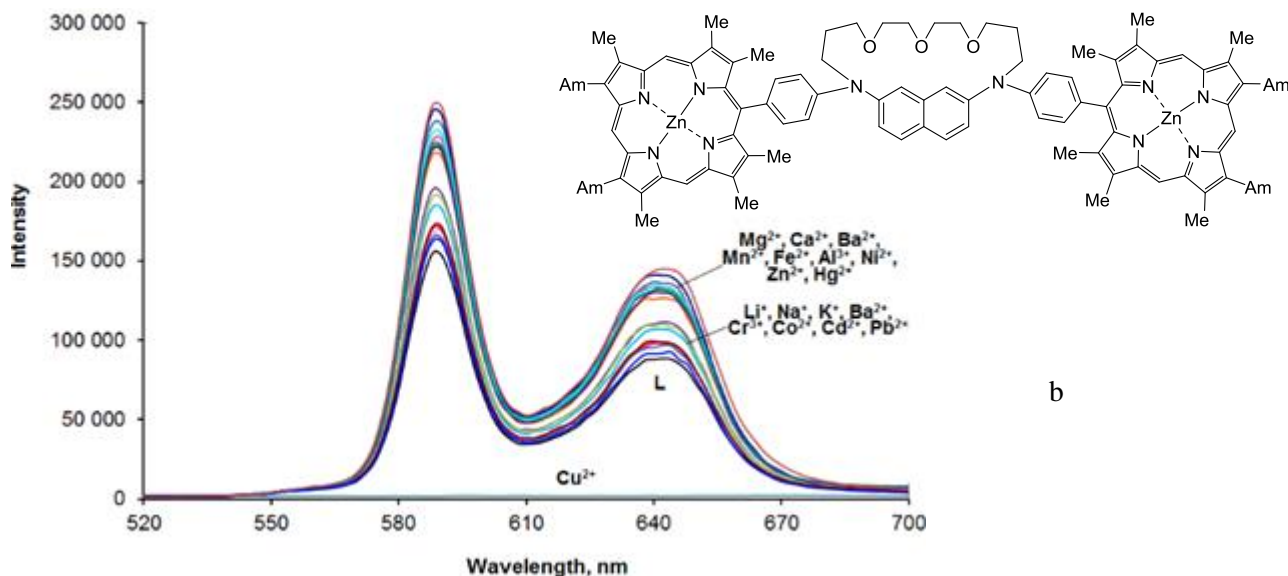

a

Fig. 6.
Рис. 6.

Fig. 6. Fluorescent spectra of the bisporphyrin-diazacrown conjugate with biphenyl-containing diazacrown ether (a) and naphthalene-based diazacrown ether (b) in the presence of 5 equiv. of different metal cations

Рис. 6. Флуоресцентные спектры диазакраун-биспорфиринового конъюгата с бифенилсодержащим диазакраун-эфиром (a) и нафталинсодержащим диазакраун-эфиром (b) в присутствии 5 экв. различных катионов металлов
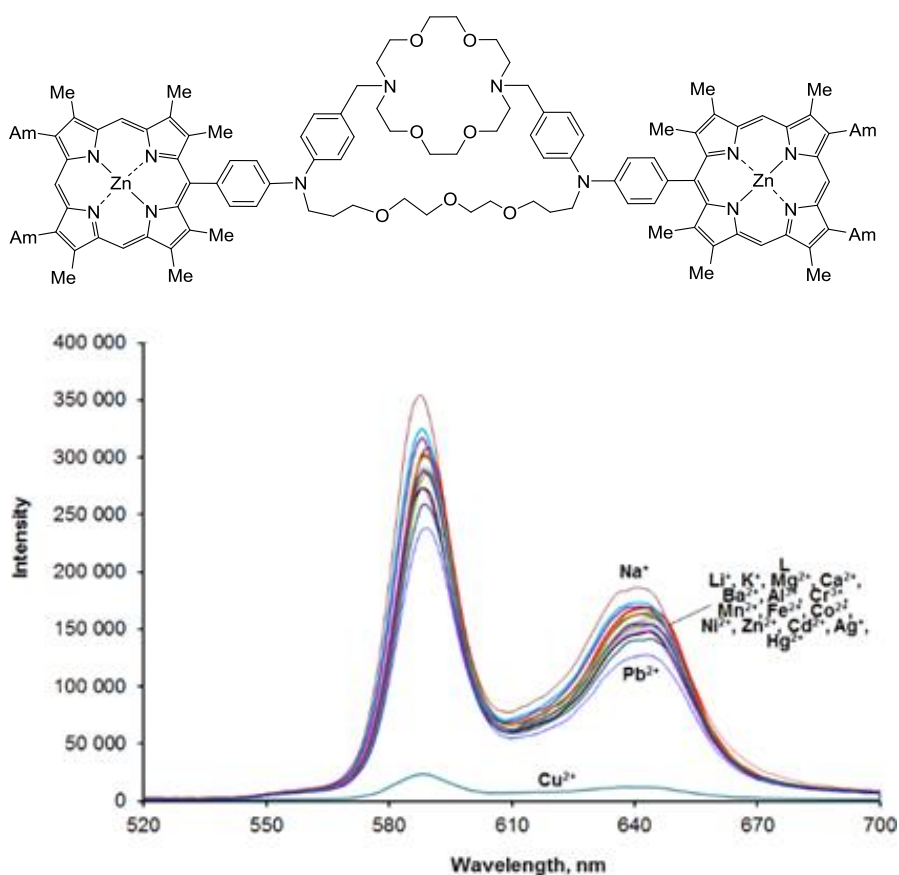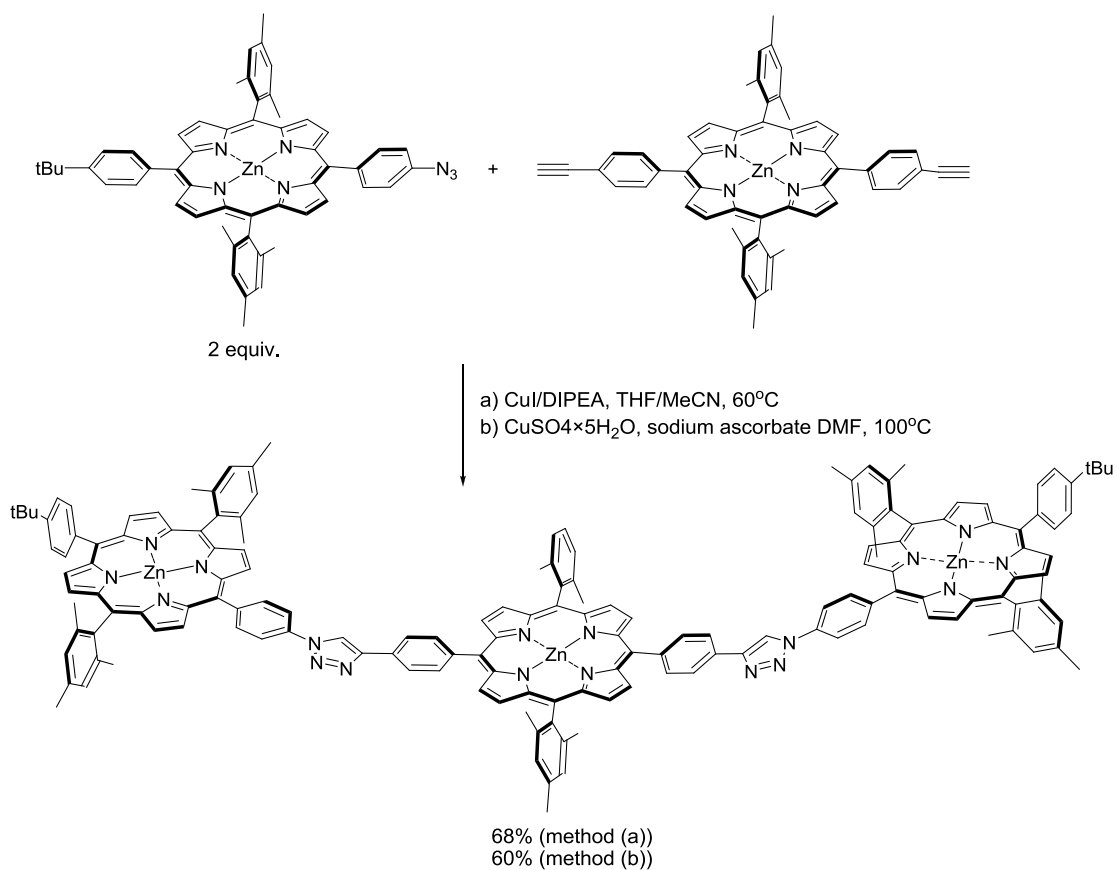

Fig. 7. Fluorescent spectra of the bisporphyrin-macrobicycle conjugate in the presence of 5 equiv. of different metal cations

Рис. 7. Флуоресцентные спектры макробицикл-биспорфиринового конъюгата в присутствии 5 экв. различных катионов металлов
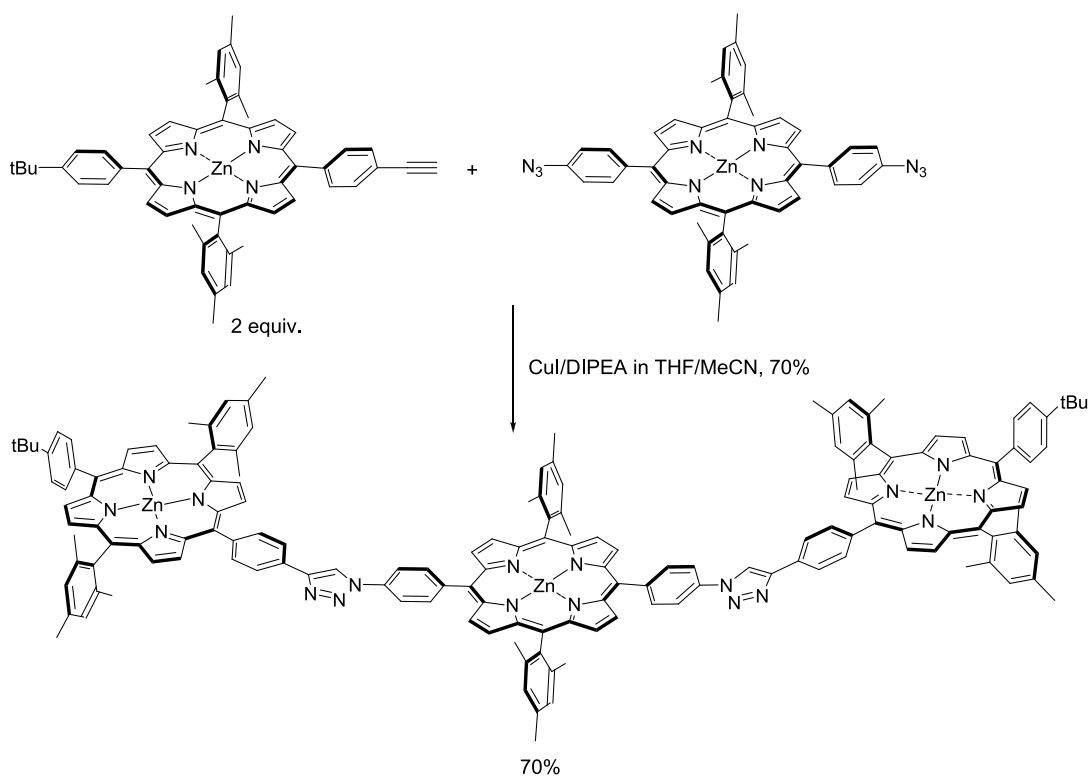
More sophisticated tetra-macrocyclic conjugate containing two Zn(II) porphyrinate units and a central macrobicyclic cryptand was also efficient in the fluorescent detection of Cu(II) [19] as only this cation among other 17 led to almost full quenching of fluorescence (Fig 7).

Copper-catalyzed synthesis of porphyrin dyads and triads

Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions were successfully used for the synthesis of non-linear porphyrin triads containing 1,2,3-triazole linkers. Two alternative approaches were developed for this purpose, the first employing the reaction of 5,15-bis-(ethynylphenyl) derivative of porphyrin with 2 equiv. of *meso*-(4-azidophenyl)substituted porphyrinate (Scheme 13) [23]. The application of CuI/DIPEA in THF-MeCN was advantageous over a classical system (CuSO$_4$/sodium ascorbate in DMF). The second approach involved Zn(II) 5,15-bis-(4-azidophenyl) substituted porphyrinate with 2 equiv. of *meso*-(4-ethynylphenyl)porphyrinate in the presence of CuI/DIPEA in THF-MeCN (Scheme 14) and it produced an isomeric porphyrin triad also in a high 70% yield.

a) CuI/DIPEA, THF/MeCN, 60°C
b) CuSO4×5H2O, sodium ascorbate DMF, 100°C

68% (method (a))
60% (method (b))

Scheme 13
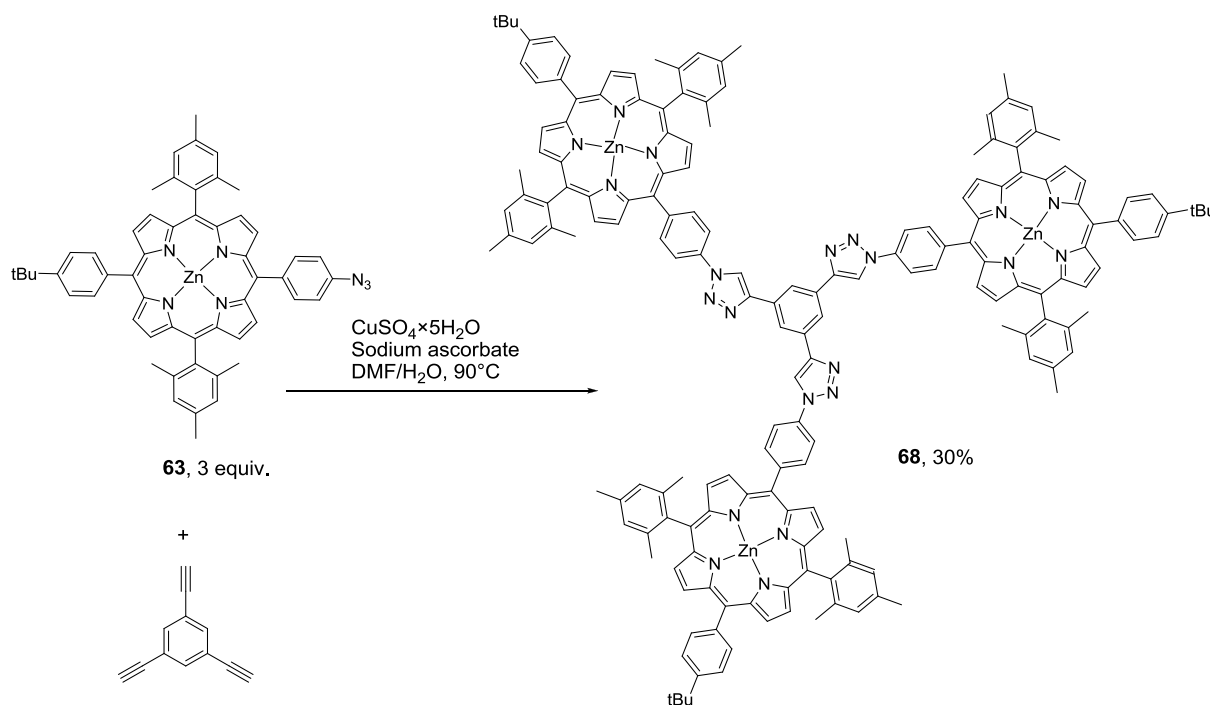Схема 13

CuI/DIPEA in THF/MeCN, 70%

70%

Scheme 14
Схема 14

Porphyrin triad of a star shape [24] was obtained using the similar approach in which 1,3,5-tri-(ethynyl)benzene was reacted with 3 equiv. of *meso*-(4-azidophenyl) substituted porphyrinate. The target star-shaped triad was isolated in 30% yield (Scheme 15).

All these porphyrin trimers possess very interesting photophysical properties important for studying femtosecond processes occurring in nature [25].
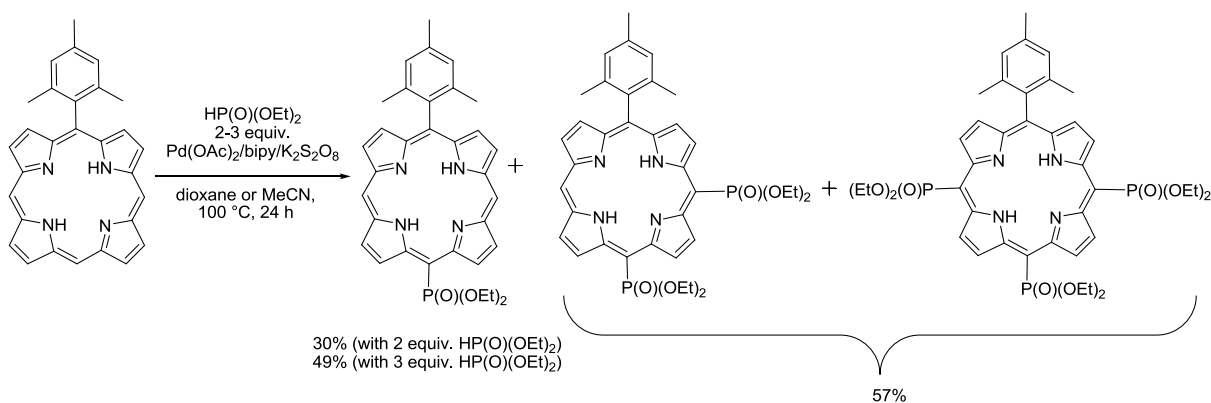

Scheme 15
Схема 15

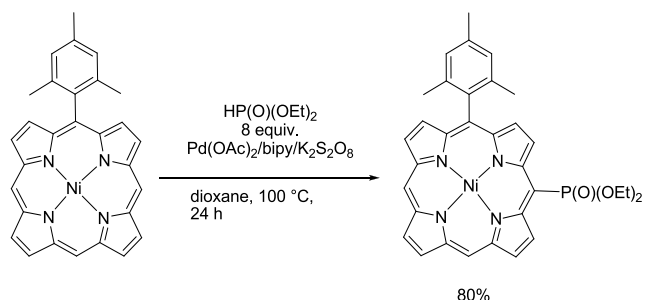## CH-activation reactions for porphyrins transformations

Application of palladium catalysis to the synthesis of phosphorylated porphyrins in view of their coordination and versatile physico-chemical studies is much addressed in the works by Bessmertnykh-Lemeune and Gorbunova [26-32]. Another approach to P-containing porphyrins, namely, Pd(II)-catalyzed oxidative phosphonation of the *meso*-position of porphyrins and their metal complexes was studied using 5-me-sityl-, 5,15-dimesityl- and 5,10,15-trimesitylsubstit-tued porphyrins in the reactions with diethyl phosphite in the presence of $K_2S_2O_8$ and bipyridyl [33]. It was disclosed that an accurate adjustment of the amount of catalyst, base and oxidant was important to obtain good yields of the desired compounds. Also, the dependence of the nature of starting porphyrins was crucial for a success of the synthesis. Thus, monophosphonation of 5-mesitylporphyrin taken as a free base gave only a moderate yield of the *trans*-monophosphonated product (Scheme 16).
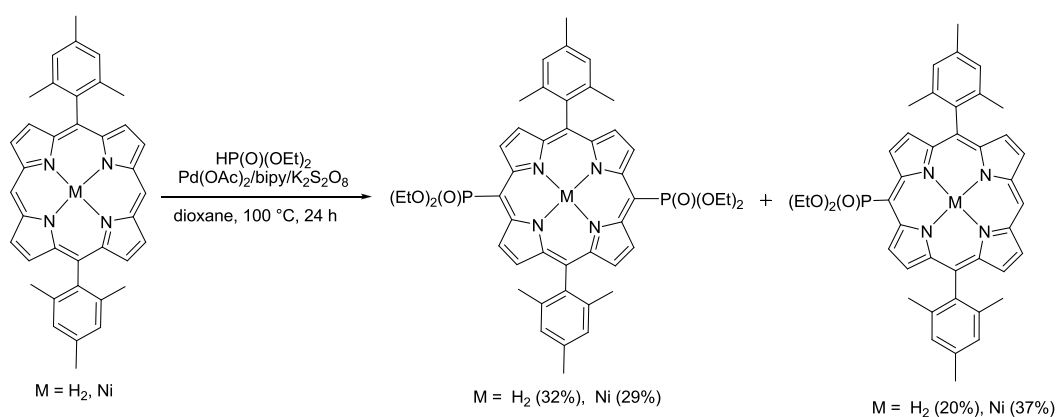

Scheme 16
Схема 16

The application of Ni(II) 5-mesitylporphyrinate produced the product of *cis*-phosphonation in a high yield (Scheme 17).

The diphosphonation of 5,15-dimesityl porphyrin was shown to proceed with the free base and Ni(II) porphyrinate, the formation of the monophosphonated products in comparable yields was observed in all cases (Scheme 18).

The phosphonation of the isomeric 5,10-dimesityl porphyrin and 5,10,15-trimesitylporphyrin was a more difficult task and only Ni complexes could be successfully involved in this process (Scheme 19). It is interesting that if Zn(II) porphyrinate was employed, full demetallation was observed and a free phosphonated porphyrin was obtained in a rather good yield.
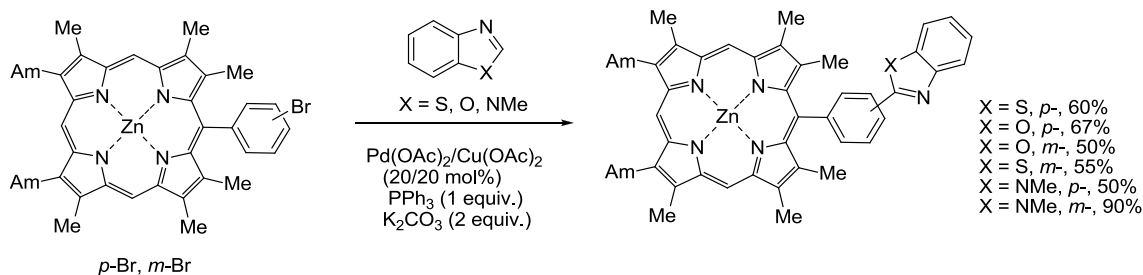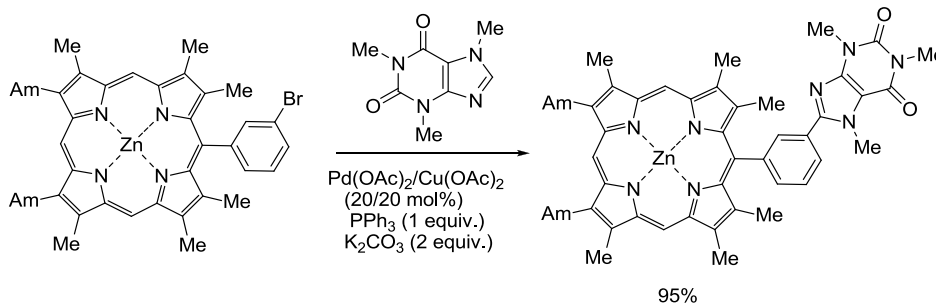

Scheme 17
Схема 17

Scheme 18
Схема 18

Scheme 19
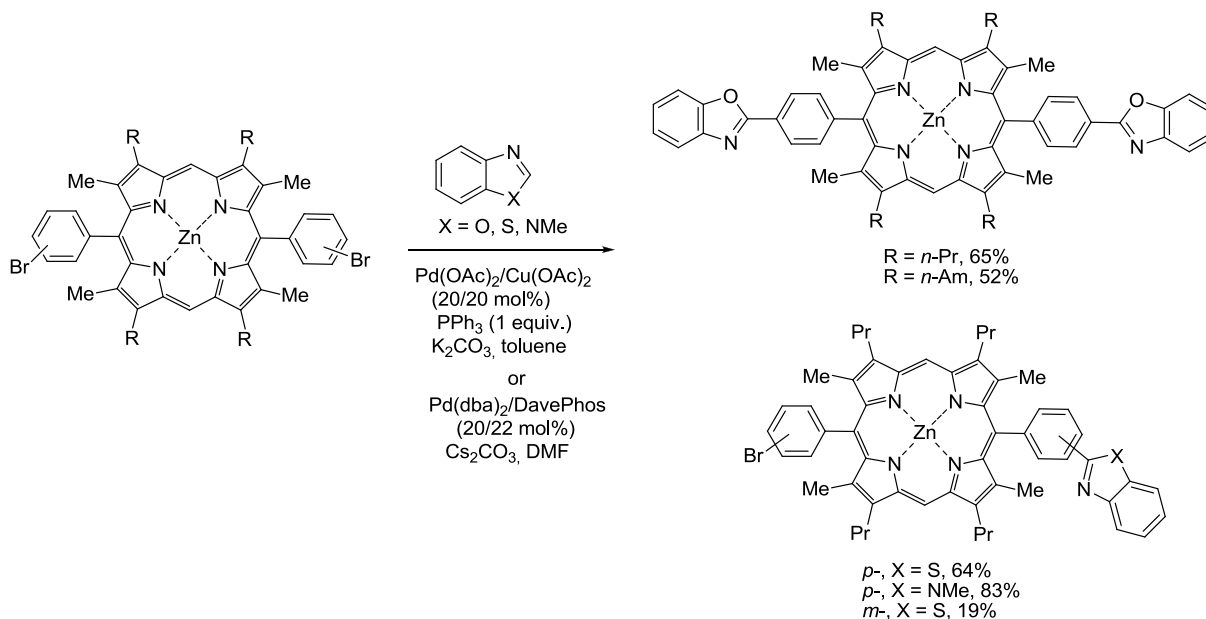Схема 19

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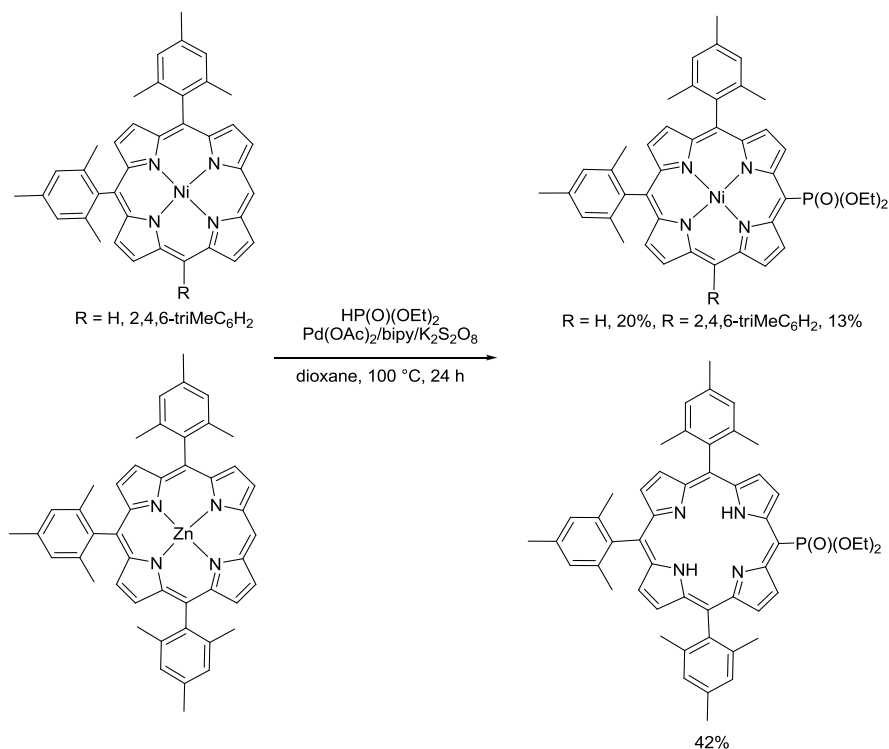
Heteroarylation of Zn(II) 5-(bromophenyl)-porphyrinates with the heterocycles possessing an "acidic" C-H bond (benzoxazole, benzothiazole and *N*-methylbenzimidazole) was carried out in the presence of Pd(II)/Cu(II) catalytic system. Corresponding heterocyclic derivatives were obtained in yields from good to high, up to 95% (Scheme 20) [34].

In the case of Zn(II) 5,15-di(bromophenyl)porphyrinate the possibility of diheteroarylation was shown with benzoxazole while other heterocycles could produce only monoheterocyclic derivatives (Scheme 21).

Benzoxazole was also the sole heterocycle helpful in the formation of tri- and tetraheteroaryl derivatives in the reaction with Zn(II) 5,10,15,20-tetrakis-(4-bromophenyl)porphyrinate (Scheme 22).

Scheme 20
Схема 20

Scheme 21
Схема 21

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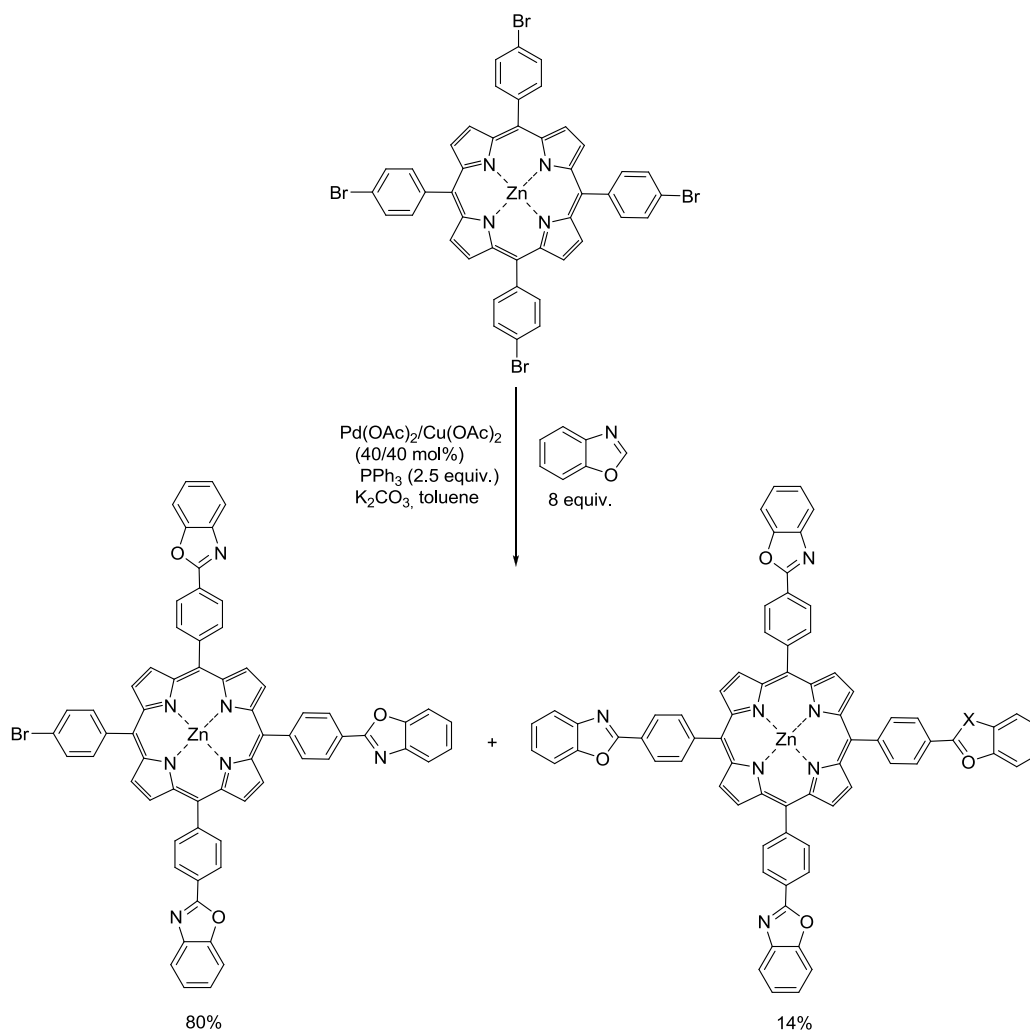
Scheme 22
Схема 22

CONCLUSIONS

We demonstrated wide possibilities of the Pd(0)-catalyzed amination for various modifications of *meso*-(bromophenyl)substituted porphyrins using monoamines, linear di- and polyamines, azacrown ethers, more sophisticated nitrogen-containing macrocycles and macrobicycles and diaminocalix[4]arenes. It was shown that porphyrins taken as free bases as well as their metal complexes could participate in such reactions. As a result novel polytopic ligands were elaborated and their coordination studies were done. Some of them were shown to be suitable as potential fluorescent chemosensors for Cu(II) cations. Cu-catalyzed synthesis of the porphyrin triads was elaborated. Novel approaches to phosphonated porphyrins and heterocyclic derivatives *via* CH-activation reactions catalyzed by Pd(II) or Pd(II)/Cu(II) were worked out.

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