

Contribution of I. P. Beletskaya in the Twentieth Year Successful Russian–French Cooperation in Catalytic Syntheses

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The review covers the research conducted during last two decades and French collaborators in the field of application of the catalysis by transition metal complexes to organic synthesis. It includes the formation of C–N, C–C and C–P bonds, asymmetric catalysis, immobilization of the catalysts on solid supports. A special attention is paid to the application of the Pd-catalyzed amination reaction to the synthesis of versatile N- and O-containing macrocycles and polymacrocycles.

Keywords: Catalysis, macrocycles, amination, porphyrins, phosphonation.

Вклад И. П. Белецкой в двадцатилетнее успешное российско–французское сотрудничество в каталитических синтезах

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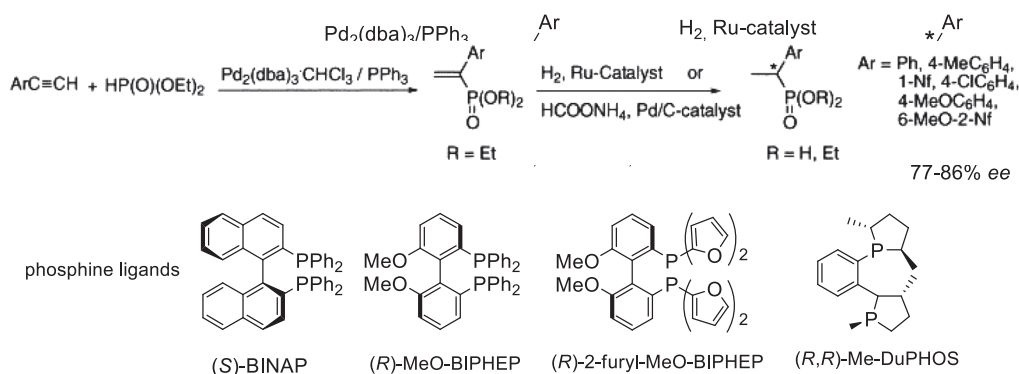
Обзор посвящен исследованиям, проводившимся в течение 20 последних лет совместными усилиями группы академика И. П. Белецкой и французскими коллегами в области использования катализа комплексами переходных металлов для органического синтеза. Рассмотрены реакции образования связей C–N, C–C и C–P, асимметрический катализ, иммобилизация катализатора на твердые подложки. Особое внимание уделено применению Pd-катализируемого аминирования в синтезе разнообразных азот- и кислородсодержащих макроциклов и полимакроциклов.

Ключевые слова: Катализ, макроциклы, аминирование, порфирины, фосфонирование.

Beginning from 1970s, since the origins of this prominent and extremely fruitful trend in organic chemistry, Professor I. P. Beletskaya has been always deeply interested in the studies of transition metal catalysis and its application to the synthesis of various organic compounds. This mini-review covers a restricted but nevertheless very important and interesting sphere of her investigations, namely, the research in catalysis carried out in a close cooperation with French partners. It is needless to say that international connections contribute much in enhancing efficiency

and versatility of the research, and the material present below will undoubtedly support this idea.

Prof. Beletskaya started her mutual investigations with the reactions of the catalytic C–P bonds formation. Together with Prof. Genet (that time working at Chimie Paris Tech) the conditions for the phosphonation of terminal alkynes were elaborated and it was found out that Pd(0) complex with the simplest phosphine ligand PPh₃ afforded corresponding alkenes, the products of α -phosphonylation of the triple bond in high yields (Scheme 1). These compounds were further

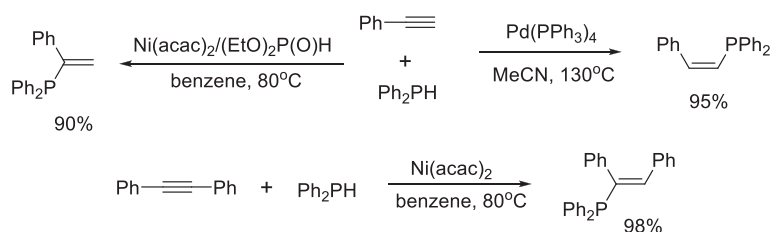


Scheme 1. Pd(0) catalysis in C–P bond formation; Ru(II) catalysis in asymmetric hydrogenation.

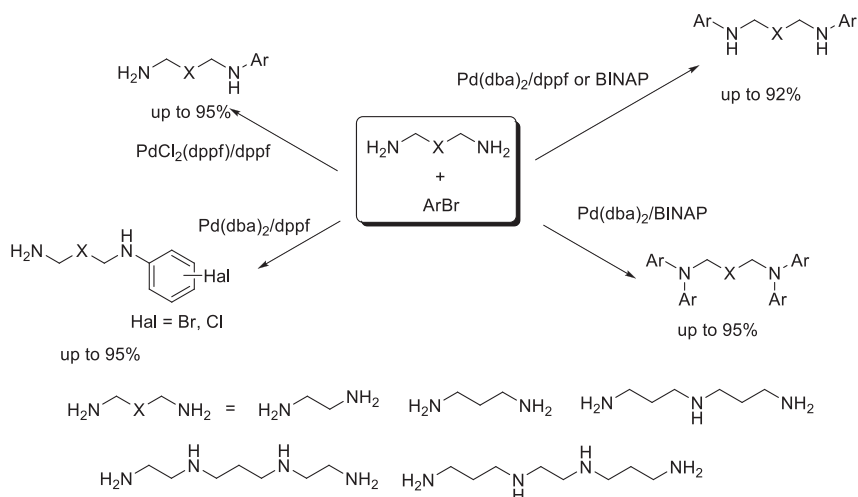
converted into highly demanded chiral α -arylphosphonates by hydrogenation in the presence of RuBr_2 complexes with various chiral diphosphines like BINAP, MeO-BIPHEP, 2-furyl-MeO-BIPHEP and Me-DuPHOS. Enantioselectivity of the process reached 86 % (Scheme 1).^[1,2]

The diphenyl phosphine addition to the triple bond was investigated in the partnership with Prof. Dixneuf (University of Rennes). It was demonstrated that the catalytic addition of Ph_2PH to phenylacetylene regioselectively led to the $\text{Ph}_2\text{P}-\text{CH}=\text{CHPh}$ isomer in the presence of $\text{Pd}(\text{PPh}_3)_4$ in acetonitrile and to the $\text{Ph}_2\text{P}-\text{C}(\text{Ph})=\text{CH}_2$ isomer when using $\text{Ni}(\text{acac})_2/(\text{EtO})_2\text{P(O)H}$ in benzene. Very high regioselectivity was also observed in the catalytic addition of Ph_2PH to *tert*-butylacetylene and toluene (Scheme 2).^[3] In all cases near to quantitative yields of the addition products were obtained.

Next step in the application of transition metal catalyzed reactions was a thorough investigation of the C–N bond formation *via* Pd-catalyzed amination of aryl halides. The process found independently in mid 1990s by Buchwald, Hartwig and Beletskaya,^[4-6] was applied to the arylation of diamines and polyamines. This aspect of the catalytic amination became the domain of Prof. Beletskaya for two decades to come. A fruitful and long-run cooperation with Prof. Guillard (University of Burgundy, Dijon) began from the investigation of the conditions for selective mono-, di- and exhaustive arylation of di- and polyamines (Scheme 3). It was established that the application of $\text{PdCl}_2(\text{dppf})$ complex with additional amount of dppf in boiling dioxane was helpful for selective monoarylation of diamines and polyamines with various aryl bromides provided polyamines



Scheme 2. Pd(0) vs Ni(II) catalysis in the triple bond phosphorylation.



Scheme 3. Studies of the Pd(0)-catalyzed amination of linear di- and polyamines.

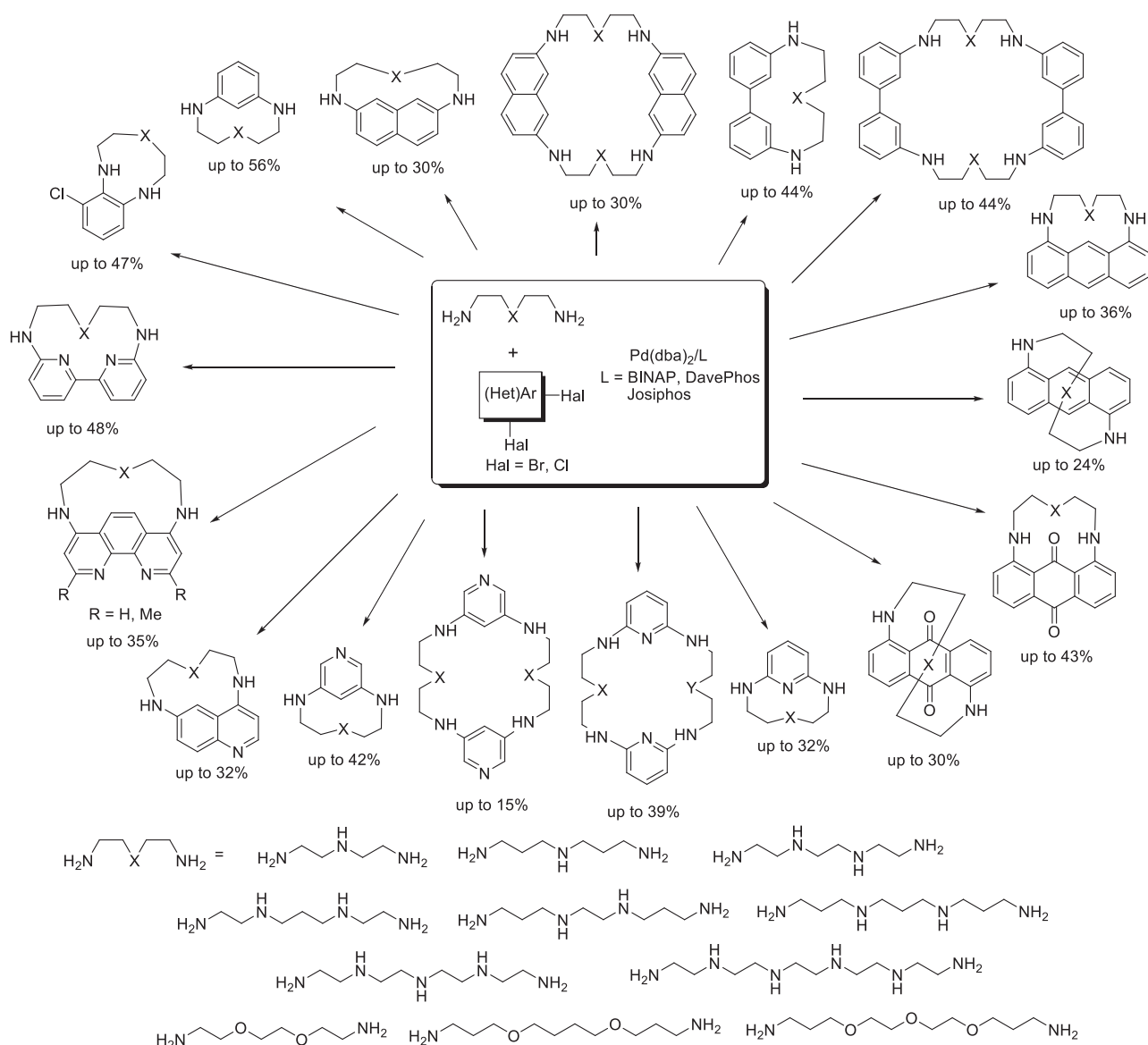
were taken in excess. In all reactions sodium *tert*-butoxide was used as a base. This protocol allowed up to 95 % yields of the target products.^[7] The main feature of this approach was selective arylation of only primary amino group in the presence of secondary amino groups. This exciting finding was further successfully applied in numerous reactions employing different polyamines. In the case of active aryl bromides Pd(dba)₂/dppf catalytic system could be used for the *N,N'*-diarylation while in other reactions Pd(dba)₂ with a more efficient BINAP ligand should have been used. The same catalyst but in greater amounts was shown to be efficient for polyarylation of diamines also providing excellent yields of the desired products.^[8]

The possibility to selectively substitute one halogen atom in the presence of another in dihalobenzenes was shown also using Pd(dba)₂/dppf catalytic system, and the priority of the substitution in the range I>Br>Cl was firmly established.^[9,10] Key role of Dr. A. Bessmertnykh-Lemeune in the elaboration of this fruitful approach to versatile polyamines modifications leading to linear and macrocyclic derivatives as well as in their further use in the chemistry

of chemosensors and organo-inorganic materials is to be underlined.

The scope of Pd(0)-catalyzed arylation of di- and polyamines was elucidated and appropriate catalytic systems were selected for further proliferation of this method which was applied in the synthesis of novel series of *N*- and *O*-containing macrocycles in the course of a close cooperation between the group of Prof. Beletskaya and French colleagues from Dijon (Scheme 4).

The protocol for Pd(0)-catalyzed macrocyclization implies the reaction of dihaloarenes or dihaloheteroarenes (preferably dibromides) with polyamines taken in equimolar amounts. Enough diluted solutions (0.01–0.04 M) in dioxane should be used to suppress competing formation of cyclic and linear oligomers. The most universal catalytic system Pd(dba)₂/BINAP was shown to be appropriate in the majority of cases. The first attempts to introduce the simplest 1,2-dibromobenzene in the macrocyclization failed, however, 2-bromo-1,3-dichlorobenzene successfully reacted with a variety of polyamines and oxadiazines to give corresponding macrocycles in yields up to 47 %.^[11]



Scheme 4. Pd(0)-Catalyzed amination in the synthesis of polyazamacrocycles.

This approach was extended to the derivatives of 1,3-disubstituted benzene and in this case the highest yield was 56 % what can be regarded as a big success.^[12] Further investigations were carried out by exploiting different aryl dihalides as building blocks for the new macrocycles. It was shown that 2,7-dibromonaphthalene could be successfully transformed into naphthalene-containing macrocycles by (1+1) cycloaddition reactions.^[13] The possibility to form so-called cyclic dimers comprising two naphthalene and two polyamine fragments was investigated *via* two alternative two-step processes.^[14] In the reactions with 2,7-dibromonaphthalene another catalytic system, Pd(dba)₂/DavePhos, in some cases demonstrated its utility. Similar protocols were applied to the synthesis of biphenyl-containing macrocycles which were synthesized in yields up to 44 %.^[15-17] It should be noted that in every case the dependence of the reaction outcome on the structure of polyamines was investigated.

An interesting investigation was conducted with 1,8- and 1,5-dichloroanthracenes and anthraquinones.^[18-20] The macrocyclization was quite successful with dichlorides, moreover, in the case of dichloroanthraquinones cesium carbonate instead of sodium *tert*-butoxide was employed as starting compounds did not tolerate this stronger base. Further development of this approach led to the application of chiral phosphine ligands like (*R*)-BINAP or ferrocene-based ligands of Josiphos series for enantioselective synthesis of planar-chiral macrocycles based on 1,5-disubstituted anthracene and anthraquinone. The best enantiomeric excess reached 60 %.^[21] Another research direction was the synthesis of colorimetric detectors for metal cations using cyclic and non-cyclic polyamino derivatives of anthraquinone, this became possible due to intensive absorption of such compounds in visible region (*ca* 520–530 nm). The decoration of the compounds with amidophosphonate arms in order to provide solubility in water resulted in the creation of several selective molecular sensors for Cu(II) and Pb(II) cations (Figure 1).^[22,23]

The importance of the introduction of heteroaromatic moieties as endocyclic fragments is obvious as they can profoundly modify binding properties of macrocycles and contribute useful optical and physicochemical properties. Thus the elaboration of the synthesis of pyridine-based macrocycles was conducted using 2,6- and 3,5-dihalopyridines and a wide range of polyamines.^[24-27] Corresponding macrocycles were obtained in yields ranging from near trace to 42 % depending on the polyamine used, and cyclic dimers with larger cavity sizes were also synthesized. This

investigation was helpful for the further synthesis of valuable macrocycles based on 6,6'-diamino-2,2'-bipyridine.^[28] One of the products, the macrocycle with trioxadiazine chain, was tested as a colorimetric and fluorescent detector of some metal cations. Later on the synthetic procedures leading to 1,10-phenanthroline-based and quinoline-based macrocycles were worked out, in these reactions the standard Pd(dba)₂/BINAP was found to be less efficient, thus the ligands DavePhos and Josiphos were applied in order to increase the yields up to 32–35 %.^[29,30] In the case of phenanthroline-based macrocycle with trioxadiazine chain its Ru(II) complex with additional bipyridyl ligands was synthesized which was tested as an efficient fluorimetric sensor for Cu(II) cations. Quinoline-based macrocycles were equally shown to be applicable as fluorimetric detectors of the same metal. Thus the Pd(0)-catalyzed amination for macrocycles construction contributes to the solution of the problem of heavy and toxic metals detection.

The methodology of Pd(0)-catalyzed macrocyclization was tried in the synthesis of *bis*macrocyclic compounds in view of producing polytopic macrocyclic receptors for metal cations. In order to achieve this goal the arylation of the secondary amino groups should have been carried out. In this connection the formation of *bis*(cyclen) and *bis*(cyclam) derivatives with *m*-phenylene spacer was thoroughly investigated,^[31] and a meticulous adjustment of the reaction conditions allowed to synthesize target molecules in yields up to 32 % overcoming almost inevitable catalytic reduction of the second bromine atom (Scheme 5). For this purpose the application of *N,N,N'*-trimethylsubstituted tetraazamacrocycles was important. The introduction of two tetraazamacrocycles or two azacrown ethers to positions 1 and 8 of the anthracene moiety helped to synthesize compounds with face-to-face arranged macrocycles. However, the amination process was accompanied by the reduction of the second chlorine atom and the yields of the target *bis*macrocycles were enough humble.^[32]

The difficulty of the diamination of dihaloarenes with compounds bearing secondary amino groups was partially overcome in the syntheses of trimacrocycles when *N,N'*-*bis*(bromobenzyl) derivatives of cyclen, cyclam and diazacrown ethers were employed in the reactions with azacrown ethers (Scheme 4). The catalytic system Pd(dba)₂/DavePhos was helpful and corresponding trimacrocycles were isolated in better yields reaching 45–46 %.^[33,34]

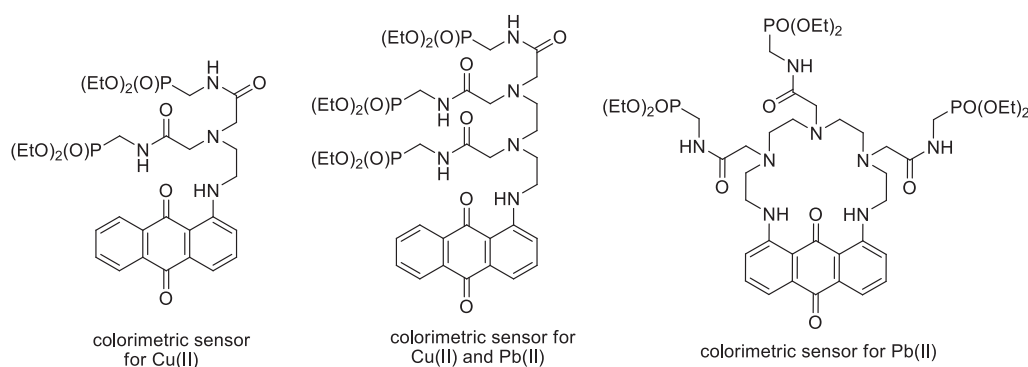
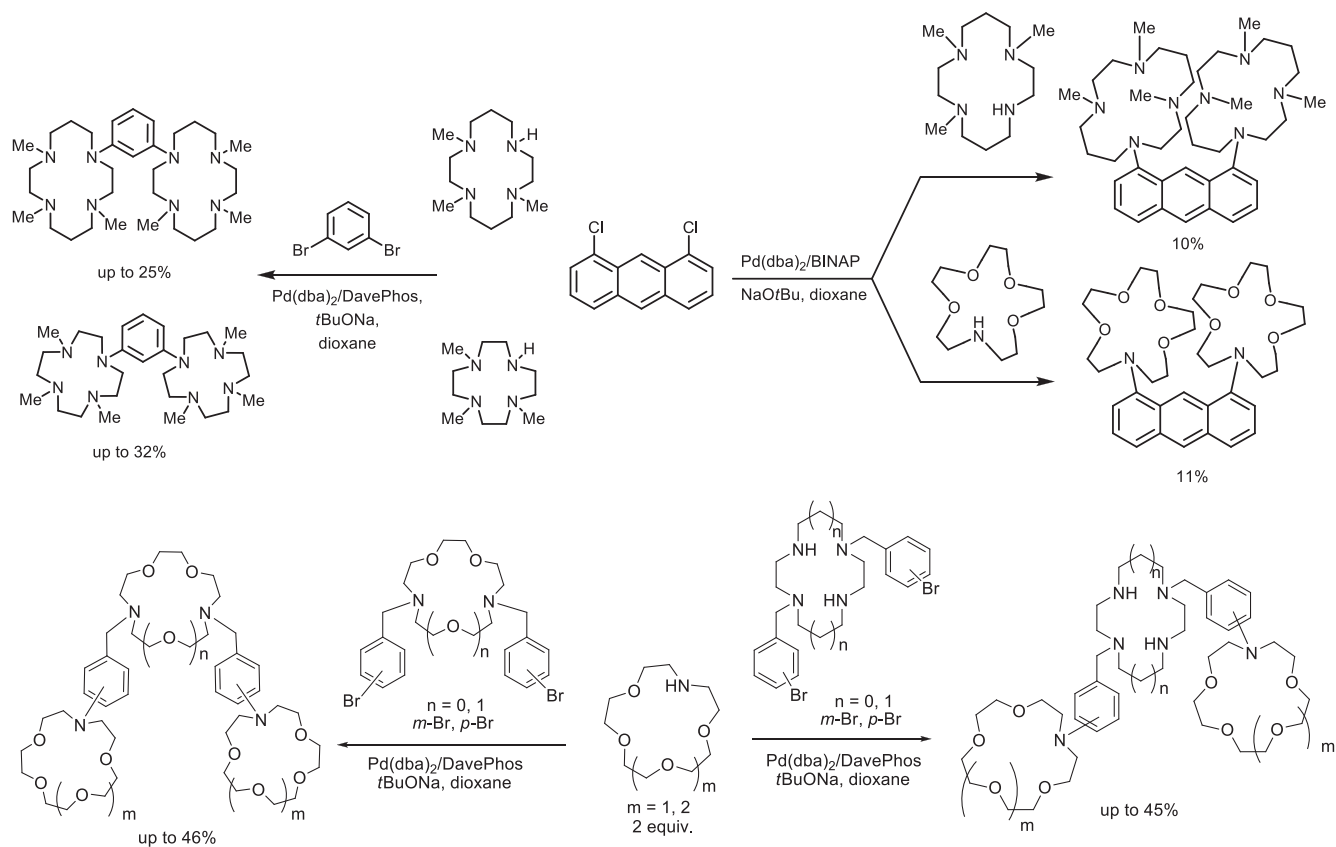


Figure 1. Colorimetric chemosensors derived from polyamine-substituted anthraquinones.



Scheme 5. Pd(0)-Catalyzed amination in the synthesis of polymacrocyclic compounds.

The approach to cryptand-type macrobicycles implies the introduction of two bromobenzyl moieties in the structure of the first macrocycle followed by the Pd(0)-catalyzed macrocyclization. Above mentioned macrocycles based on 2,7-disubstituted naphthalene and 3,3'-disubstituted biphenyl moieties were modified with two bromobenzyl fragments followed by macrocyclization with various polyamines and oxdiamines to provide corresponding cryptands in yields up to 30–35%.^[35,36] Much more versatile cryptands were synthesized on the basis of *trans*-*N,N'*-di(bromobenzyl) substituted cyclen and cyclam. At first the scope and limitations of this approach were determined to demonstrate the possibility of the synthesis of the cryptands in yields up to 45%, the formation of interesting by-products, cylindrically shaped macrotricycles, was noted in many cases.^[37] The possibility to synthesize macrobicycles with pyridine-containing spacers was also shown though the maximal yields were lower.^[38] Important cryptands bearing two naphthalene spacers were obtained by the similar approach,^[14] and later on the family of macrobicycles and macrotricycles was extended to compounds with tetrabenzyl- and dibenzylpyrimidinyl substituted cyclen or cyclam central moieties.^[39,40] Unusual bicyclic conjugates of tetraazamacrocycles with 1,3-disubstituted adamantane were described,^[41] and the investigation of the synthesis of planar-chiral macrobicycles derived from tetrasubstituted cyclam with short diamine linkers unable to rotate around the cyclam moiety was carried out using a panel of chiral diphosphine ligands.^[42] Quite different architecture of macrotricyclic compounds, *i.e.* spherically shaped cryptands, was developed by a stepwise accomplishment of the catalytic macrocyclization reactions.^[43] The possibility

to obtain another representatives of heteroditopic cylindrical cryptands was achieved by the combination of tetraazamacrocycles with end-capping diazacrown ether moieties.^[33]

Thus, a great variety of various macropolycycles differing by the number of nitrogen and oxygen atoms and cavity sizes can be obtained using the described general approach. Now these compounds are being further modified to create fluorescent chemosensors for metal cations and small organic molecules. More detailed information on the Pd(0)-catalyzed amination aimed at the synthesis of linear (hetero)aryl derivatives of polyamines can be found in ref.^[44] while the syntheses of macrocycles and polymacrocycles are collected in the following reviews.^[45–47]

The interests of Prof. Beletskaya cover the chemistry of porphyrins as well. During last decade she boosted the research of the catalytic transformations of these important molecules. As the porphyrins have been always very important research domain at the University of Burgundy, two joint reviews were published. One is a chapter in a profound Handbook of Porphyrin Science dedicated to catalytic transformations of porphyrins^[48] while another one is a deep review of the supramolecular chemistry of metalloporphyrins in Chemical Reviews.^[49]

Different aspects of catalysis were also the ground for the collaboration with F. Lamaty (University of Montpellier). One was the studies of the amination reactions run in poly(ethylene) glycols under microwave irradiation catalyzed by copper and amino acids as ligands. The best results were achieved with CuO/*L*-histidine in PEG-400. Also the *N*-arylation of amino acids without additional ligands in PEGs catalyzed by Cu₂O was studied (Scheme 6).^[50]

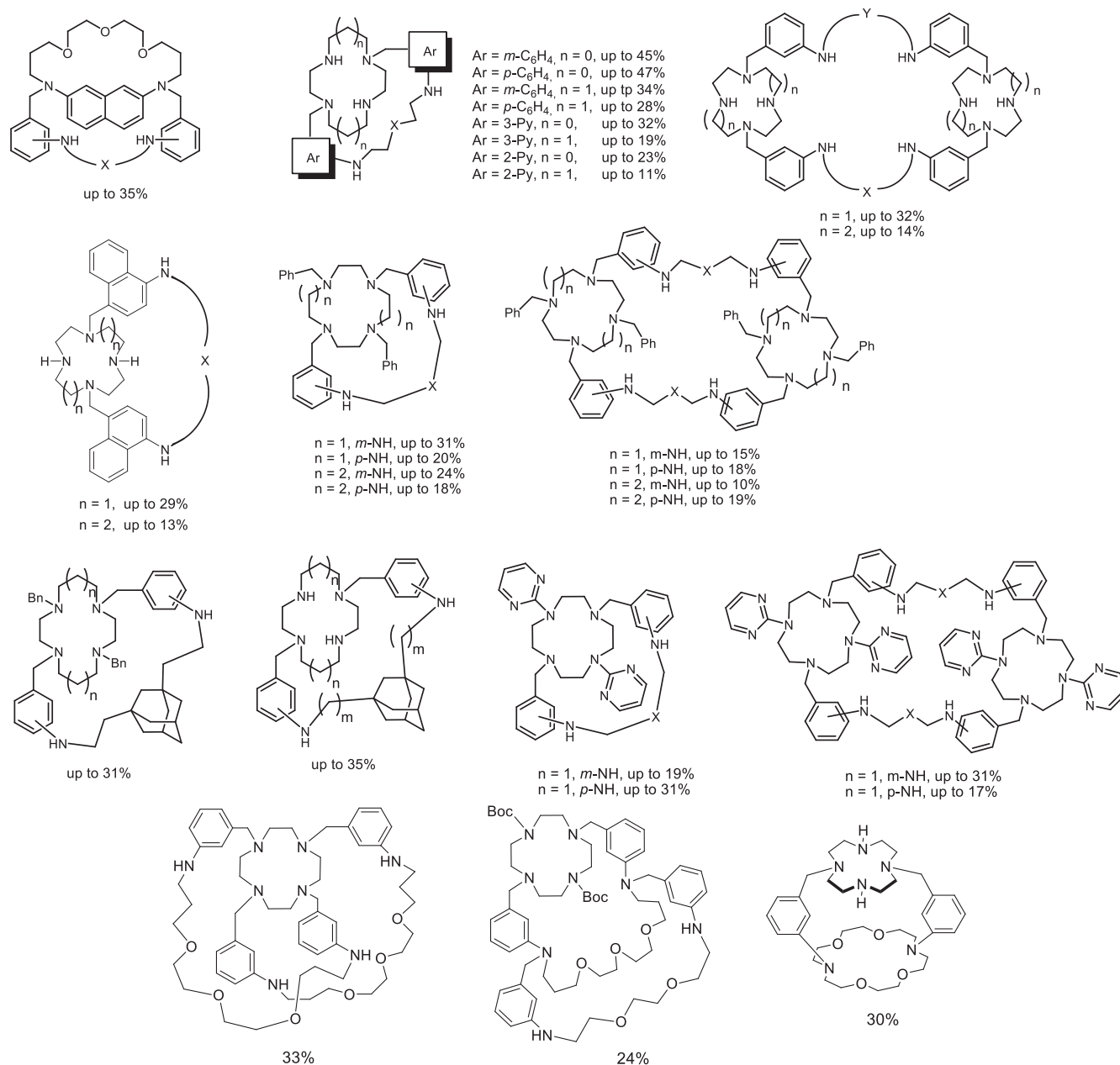


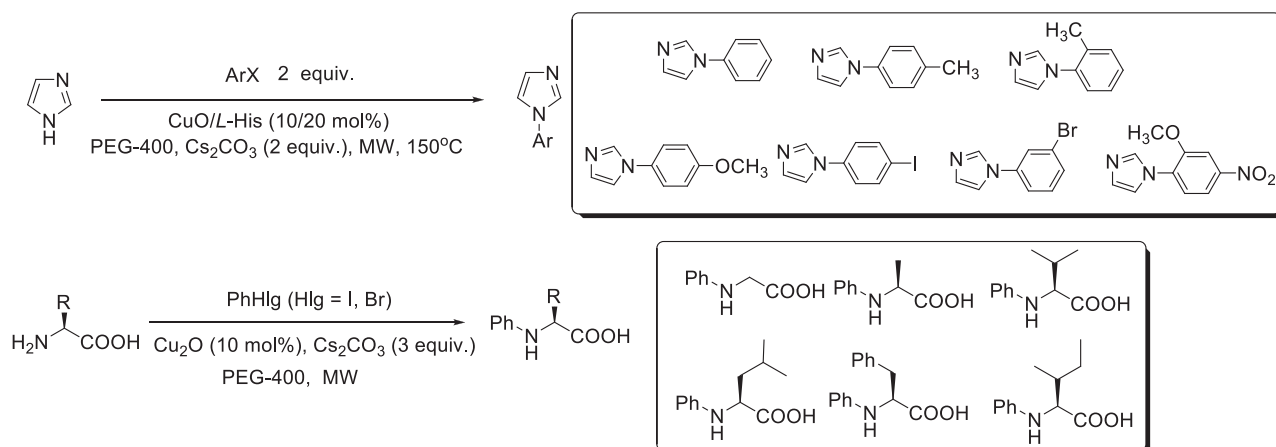
Figure 2. Versatile architecture of polymacrocyclic compounds obtained by Pd(0)-catalyzed amination.

Mutual investigations also dealt with the Cu(I)-catalyzed amination of diamines and oxadiazines for the synthesis of polyoxadiazino derivatives of azacrown ethers, this research was essential for establishing the scope and limitations of the copper catalysis in the modifications of macrocycles in order to replace much more expensive palladium.^[51]

Prof. Beletskaya has been deeply interested in the synthesis of immobilized catalysts for their repeated use. The synthetic approach to chiral Brønsted acids like 3,3'- or 6,6'-disubstituted (*R*)-BINOL phosphoric acids (BINOL=1,1'-binaphthyl-2,2'-diol) bearing either triple bonds or azide groups was developed. Their immobilization using Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC, "click"-reaction) with azide or propargyl derivative of PEG-5000 was carried out. In the first case the synthetic procedure included 6 steps, in the second

case – 5 steps. As a result, two immobilized (*R*)-BINOL phosphoric acids with triazolyl cycles in positions 3 and 3' were obtained (Figure 3). The substituents in *ortho*-position to the acid catalytic center are necessary to achieve higher enantiomeric excess compared to unsubstituted (*R*)-BINOL phosphoric acids. Both immobilized acids showed catalytic activity in the Pudovik reaction and in the imines reductions using Hantzsch ester. Products yields were good and did not decrease in 3 cycles, however, enantioselectivity was 23 % *ee* in the Pudovik reaction and 26 % *ee* in the reduction reaction. To note, the introduction of the substituents in positions 3 and 3' led to a twofold increase in enantioselectivity.^[52]

Another aspect is the preparation of hybrid organo-inorganic materials for catalysis and detection. The approach to the precursors of interesting building blocks, cyclopropane-based diphosphonic esters, was elaborated, a key step



Scheme 6. Copper-catalyzed amination conducted in PEGs.

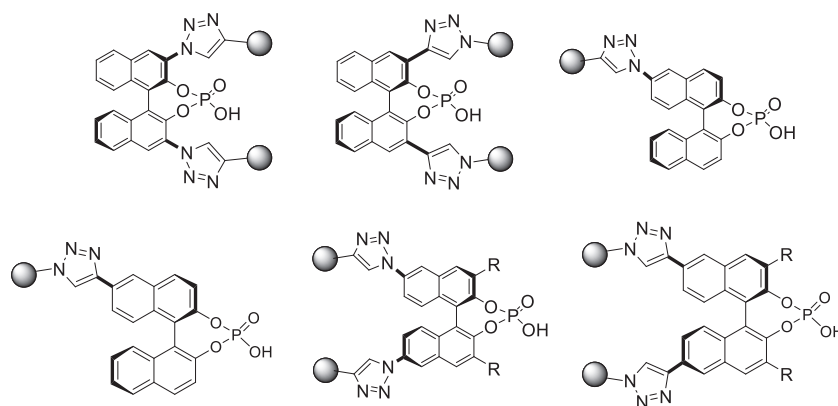
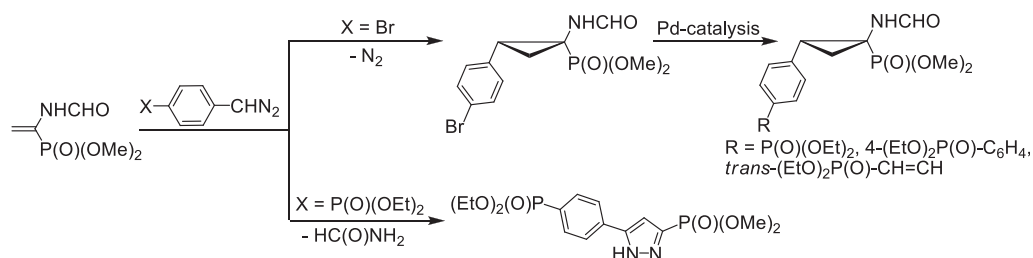


Figure 3. PEG-supported chiral BINOL-phosphoric acids.



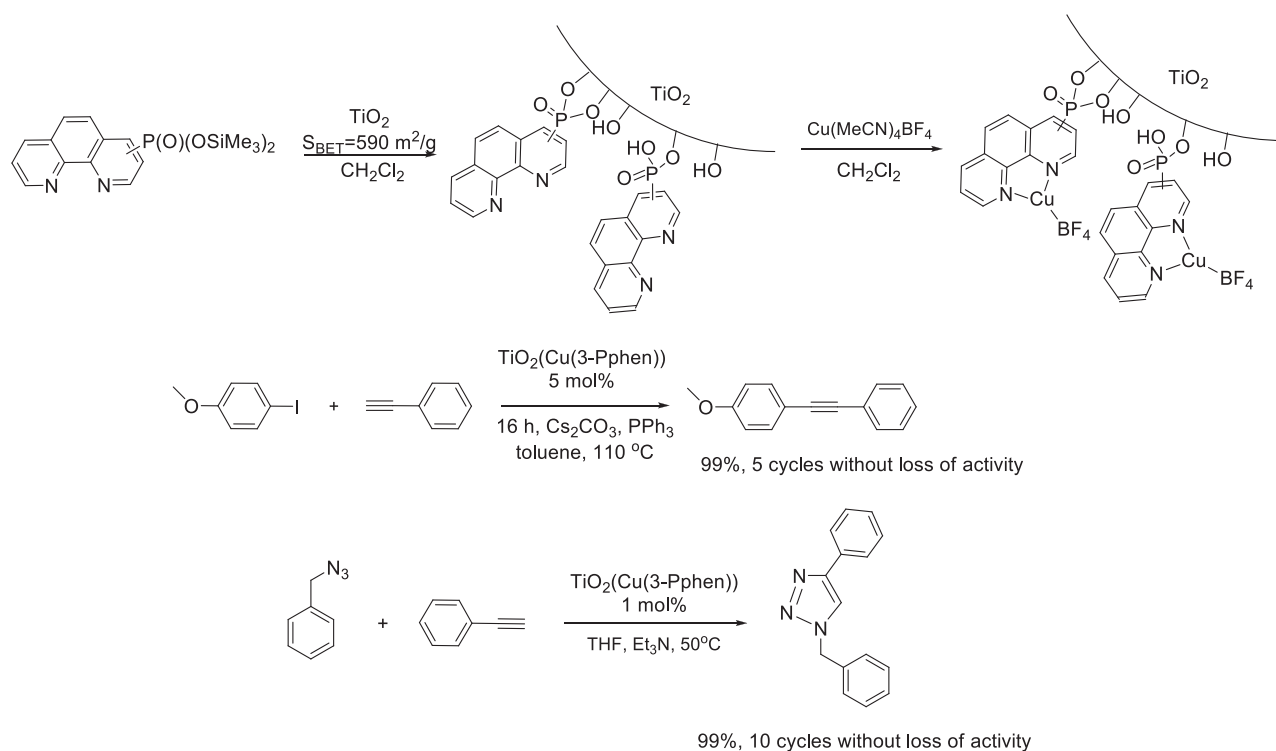
Scheme 7. Formation of cyclopropane-based diphosphonic esters.

being the introduction of the second phosphorus in the molecules by means of Pd catalysis (Scheme 7).^[53]

The first step of the research dealing with immobilized copper catalysts was the synthesis of mono- and diphosphorylated 1,10-phenanthrolines. For this purpose a general protocol for the coupling of mono- and dihalo-1,10-phenanthrolines with diethyl phosphite was elaborated featuring the Pd(OAc)₂/dppf catalytic system and triethylamine taken as a base.^[54] Further on two series of copper(I) complexes with diethoxyphosphoryl substituted 1,10-phenanthroline ligands were synthesized and characterized in the solid state and in solution. The first comprised mixed-ligand CuI complexes with phenanthroline and triphenylphosphine,

the second series included *bis*chelates with two phenanthroline ligands, both were studied using NMR and X-Ray technique.^[55] Diethoxyphosphoryl substituted 1,10-phenanthroline copper(I) complexes were tested as catalysts in the Sonogashira-type reaction, α -arylation of phosphoryl-stabilized C–H acids, C–N, C–P bond forming reactions (substitution reactions) and in the reaction of phenylacetylene and *bis*(pinacolato)diboron (addition reaction). The complexes demonstrated fairly high catalytic activity and in some cases their efficiency was superior to that of the parent Cu(phen)(PPh₃)Br (phen = phenanthroline).^[56]

Such fruitful collaboration with the chemists from Dijon resulted in the synthesis of the immobilized copper



Scheme 8. Grafted copper complexes with phenanthroline and their use in the catalysis.

catalyst. Different strategies for the immobilization of copper complexes with 1,10-phenanthroline (phen) using the phosphonate anchoring group were investigated to prepare robust and porous heterogeneous catalysts. Homoleptic and heteroleptic copper(I) complexes with phenanthroline bearing the *bis*(trimethylsiloxy)phosphoryl anchoring group (Pphen-Si) at different positions of the phenanthroline backbone were prepared and covalently incorporated into titania (TiO_2) xerogels by using the sol-gel process or grafted onto the surface of mesoporous TiO_2 ($S_{\text{BET}} = 590 \text{ m}^2/\text{g}$). Copper(I) *bis*(Pphen-Si) complexes were the only complexes that were successfully anchored onto the TiO_2 surface because the heterogenization was often accompanied by the undesirable dissociation of copper complexes. Hybrid materials based on copper(I) chelates with one phenanthroline ligand were obtained following a two-step procedure involving the immobilization of Pphen-Si chelators and their successive complexation with copper(I) ions. Porous material was synthesized according to this approach and excellent catalytic performance of this reusable immobilized complex in the Sonogashira-type coupling and the Huisgen 1,3-dipolar cycloaddition was also demonstrated (Scheme 8).^[57] The catalyst can be recycled 5 times without loss of activity.

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