**Conference paper**

Irina P. Beletskaya* and Alexei D. Averin

# New trends in the cross-coupling and other catalytic reactions

## Catalytic cross-coupling

DOI 10.1515/pac-2016-1110

**Abstract:** A mini-review covers the latest achievements in the field of metal-mediated cross-coupling reactions among which are palladium-catalyzed Heck, Suzuki, cyanation and amination reactions. The aspects of the application of Pd nanoparticles (PdNPs) are discussed. The possibilities of the applications of Cu(I)-catalyzed reactions are described. Special emphasis is made on the synthesis of polymacrocyclic compounds like porphyrin dyads and triads, polyazacryptands bearing fluorophore groups using catalytic methods. The application of Pd-catalyzed CH-activation reactions for porphyrin modifications is described, the use of Lewis acids catalysis and organocatalysis for enantioselective C–C bond formation is considered with the emphasis on the application of immobilized organocatalyst.

**Keywords:** carbon–heteroatom bonds formation; catalysis; copper; cross-coupling reactions; Mendeleev XX; nanoparticles; palladium.

## Introduction

In the second part of the XX$^{th}$ century a real revolution occurred in organic chemistry due to invention and rapid proliferation of the catalytic methods in organic synthesis. Chemists got extremely powerful and at the same time rather simple approaches to many types of organic compounds. This outstanding discovery resulted in three Nobel Prizes during 10 years period. This mini-review highlights the contribution to the field of the catalytic cross-coupling reactions made by the Laboratory of Organoelement Compounds of the Lomonosov Moscow State University.

The cross-coupling process reminds a well-known ancient Wurtz reaction which is yet of limited use as only alkyl halides and very reactive organometallic compounds normally participate in it [1]. However, this notorious reaction was very important for understanding the mechanism of metal-mediated processes. The reaction of C($sp^2$)–Hal bonds with organometallic compounds was discovered independently by Corriu (France) [2] and Tamao et al. (Japan) [3] in 1972. The first was the reaction of vinyl halides with organolithium compounds catalyzed by Ni complexes, and 2 years later Murahashi used Pd complexes in the reactions of aryl halides with Grignard reagents [4, 5]. The development of the palladium-catalyzed reactions in this field became very rapid, and Milstein and Stille [6], Mizoroki-Heck [7, 8], Sonogashira et al. [9], Suzuki-Miyaura [10, 11] couplings, catalytic carbonylation [12–14] began to flourish and became wide-spread tools even on industrial scale for the drug synthesis [15].

**Article note:** A collection of invited papers based on presentations at the XX Mendeleev Congress on General and Applied Chemistry (Mendeleev XX), held in Ekaterinburg, Russia, September 25–30, 2016.

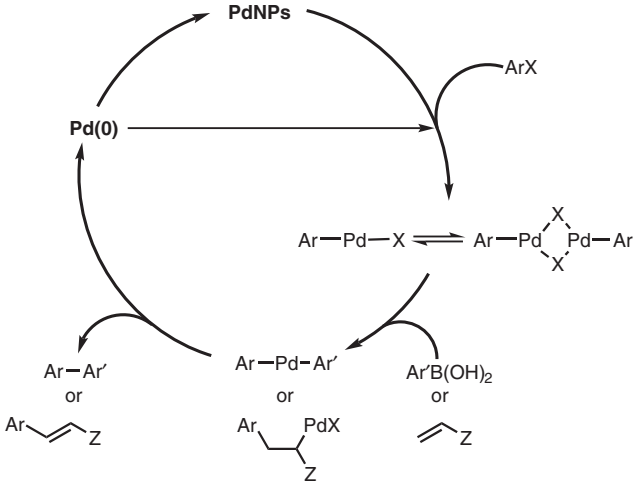
***Corresponding author: Irina P. Beletskaya,** Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119991, Russian Federation, e-mail: beletska@org.chem.msu.ru
**Alexei D. Averin:** Lomonosov Moscow State University – Chemistry, Moscow, Russian Federation

Our background in this field dealt with so-called "ligandless" processes. Various cross-coupling reactions involving organotin, organoaluminium and organomercury compounds were studied by us [16] as well as Heck and carbonylation reactions [17], and the main goal was to elaborate catalytic processes without additional ligands using water as a reaction medium [18–20]. It was amazing that it was possible to carry out these reactions without formation of Pd black from $Pd(OAc)_2$. Aryl boronic acids were found to be the best acting organoelement compounds in water due to a good solubility of the salts formed in the presence of a base. As a result, various substituted biphenyls were produced in high yields. The same was true for Heck, carbonylation and hydrogenation reactions catalyzed by palladium (II) chloride or acetate. In the case when both components were soluble in water even Pd black demonstrated good catalytic activity. It was possible to use very low concentration of Pd and enormous TONs (up to 250 000 for that time) in ligandless processes were achieved. To solve the problem of solubility, the processes were run in microemulsion media with simple surfactants, and the Heck reaction yielded 90 % of the product with 0.01 % Pd [21]. Block-copolymer micelles were also successfully used for this purpose [22].

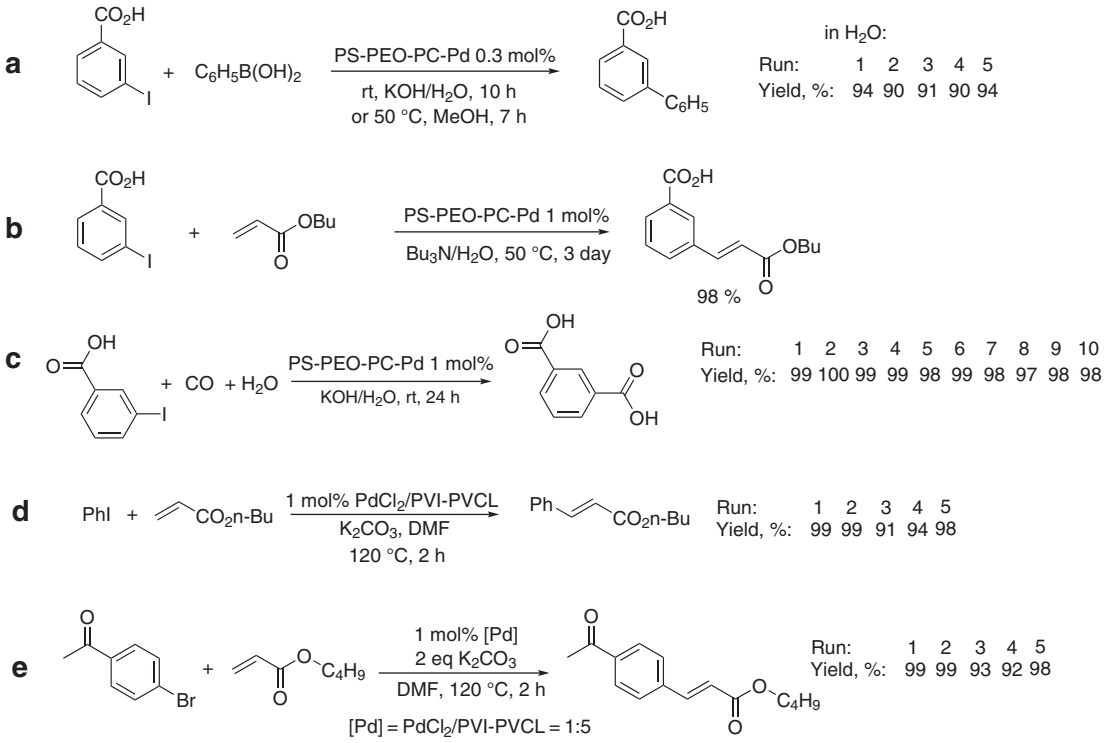
## Pd catalysis in cross-coupling reactions

During our first experiments employing ligandless conditions, no idea was yet circulating in the scientific community about nanoparticles and their exciting properties. When the concept of nanosized particles emerged, the average size of palladium nanoparticles (PdNPs) which were formed in the above mentioned reactions was measured to give 10 nm. Considering the mechanism of this reaction presented on Scheme 1 [23], the first step is certainly a heterogeneous oxidative addition. Thus formed ArPdX exists in the equilibrium with dimer which is inactive, but the monomer is more active than ligated Pd species. It might be the explanation of the fact that PdNPs are often as reactive or even more than homogeneous Pd complexes.

Another way was to use an amphiphilic water-soluble copolymer poly(styrene-co-ethyleneoxide) (PS-PEO). The Suzuki coupling was found to proceed at room temperature or at 50 °C in MeOH giving high yields of the products and with good recyclability (five cycles with retention of the yield Scheme 2a) [24]. The same result was observed for Heck reaction (Scheme 2b), and in the case of carbonylation reaction [25] we carried out 10 cycles with simple filtration or centrifugation of the catalyst (Scheme 2c). For the cases which need higher temperature we used poly(N-vinylimidazole-co-N-vinylcaprolactam) (PVI-PVCL) copolymer and DMF as a solvent and carried out Heck reactions with different aryl iodides and aryl bromides (Scheme 2d) [26]. With an active 4-bromoacetophenone the reutilization of the catalyst after five cycles was possible. TEM disclosed that that metal nanoparticles were active species in these reactions (Scheme 2e).




**Scheme 1:** The mechanism for the PdNPs–mediated cross-coupling reactions.

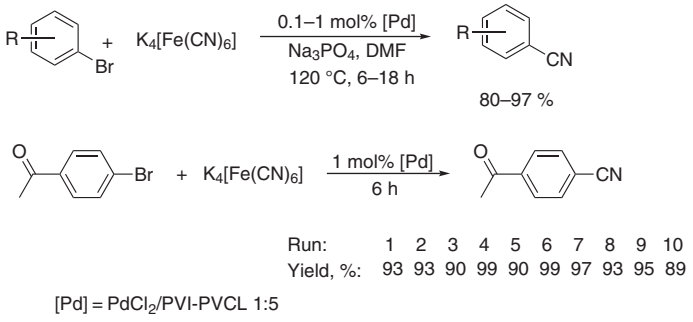



**Scheme 2:** Pd-catalyzed reactions with polymer-supported PdNPs.

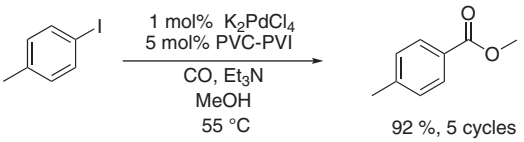
Cyanation which is a more reluctant process proceeded smoothly with aryl bromides in the presence of immobilized Pd nanoparticles in DMF at 120 °C, and only at the tenth cycle a slight decrease in the product yield was observed [27] (Scheme 3).

Alkoxycarbonylation needs adjustment of conditions (source of PdNPs, temperature, base), and after proper optimization we obtained good yields of the products and demonstrated that after five cycles the catalyst was still working [25] (Scheme 4).

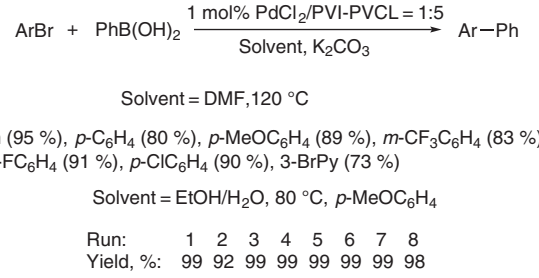
The Suzukli coupling catalyzed by PdNPs afforded very good results for a great variety of aryl bromides even in water, but the catalyst could not be recycled in all cases studied. For example, in water with NaOH as a base the yield in the first cycle attained 85 % and only 15 % in the second, while in EtOH-$H_2O$ (80 °C) or DMF (120 °C) with $K_2CO_3$ as a base the yield did not diminish after eight cycles (Scheme 5). The studies of the kinetics and PdNPs size after several runs disclosed that *ca* 60 % of conversion took part in 1–2 min and after that the process got much slower and it took 4 h for its completion. After the first cycle the average size of nanoparticle was 2.41 nm and after the eighth cycle it equaled 2.5 nm, however, the smallest particles




**Scheme 3:** Pd-catalyzed cyanation using immobilized catalyst.




**Scheme 4:** Pd-catalyzed alkoxycarbonylation reaction.




**Scheme 5:** PVI-PVCL supported Pd catalyst in Suzuki coupling.

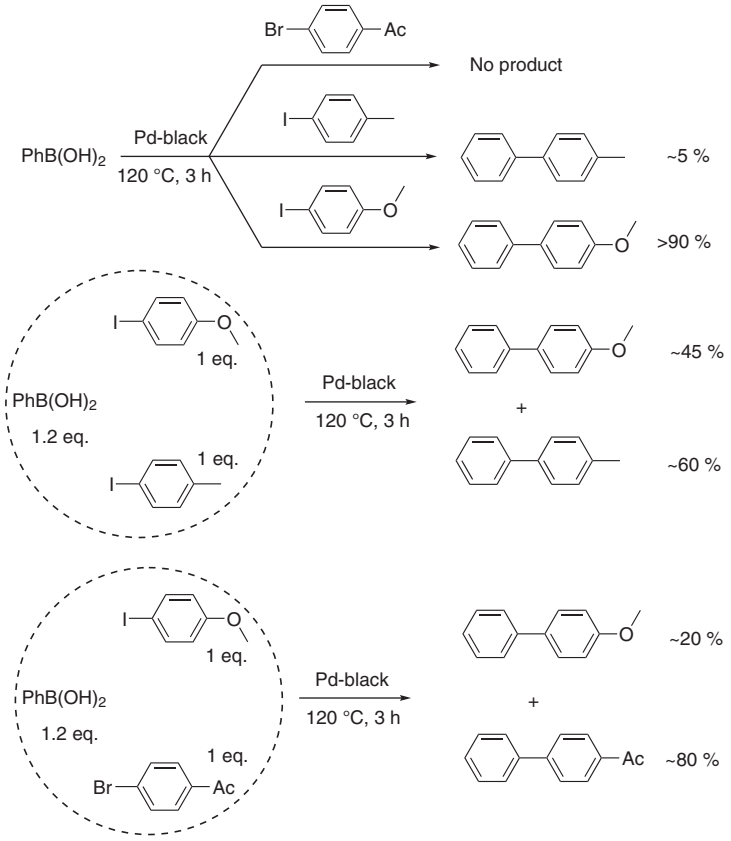
(smaller than 1.7 nm) were totally absent. Nevertheless the reaction after longer run provided the same good result [28]. These observations favor the mechanism of leaching ("release and capture"), thus the leaching can be not a negative phenomenon but rather useful. On this basis one can draw out the following conclusion: if the catalyst can be recycled several times without loss of its efficiency, it does not mean that the process is purely heterogeneous.

The Pd black with a clearly observed nanostructure was synthesized by the vacuum evaporation of palladium on polyvinyl alcohol followed by the elimination of support in hot water. This catalyst turned to be inactive for the reactions of either electron rich aryl iodides or aryl bromides but it catalyzed the coupling of *p*-methoxyiodobenzene which is a special case due to a good interaction of methoxy group with palladium surface. The idea was that the Pd(0), which was released after the reductive elimination in the catalytic cycle with the participation of this compound, could be more active than the initial catalyst and further promoted the reactions of less active aryl halides. It was exactly the case as *p*-iodotoulene or bromobenzene, which were initially inactive, readily participated in the Suzuki coupling after the addition of *p*-methoxyiodobenzene in the reaction mixture [29] (Scheme 6). The same was true when the reaction was catalyzed by Pd deposited on multiwall carbon tubes. Thus it was undoubtedly established that leaching helped the reaction to proceed.

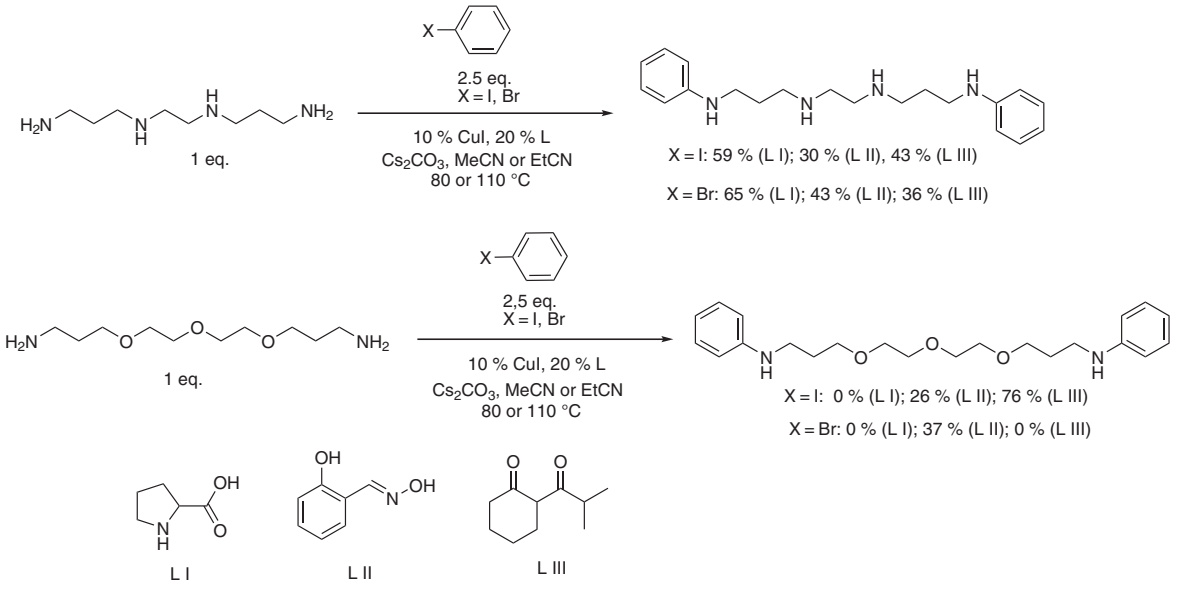
## Copper-catalyzed cross-coupling reactions

Another modern tendency in the transition metal catalysis is the replacement of expensive palladium with a cheaper copper (in the form of oxides, salts and complexes). In many cases, particularly in the formation of C-heteroatom bonds via substitution reactions (but not addition) copper catalysis demonstrated excellent results, though there are still problems with the choice of ligands as it is difficult to predict which one would be better for a certain pair of reagents. Also there is a need for greater catalyst loadings, higher temperatures and concentrations for Cu-mediated reactions. For example, when we carried the arylation of diamines, diketone ligand was successful, but the arylation of polyamines could be run successfully only with the proline ligand [30] (Scheme 7).

We carried out multiple cross-coupling reactions forming C–N (arylation) [31] and C–C (via Sonogashira reaction) [32] bonds in steroids which produced azole-substituted derivatives or steroids with indole moieties (Scheme 8).

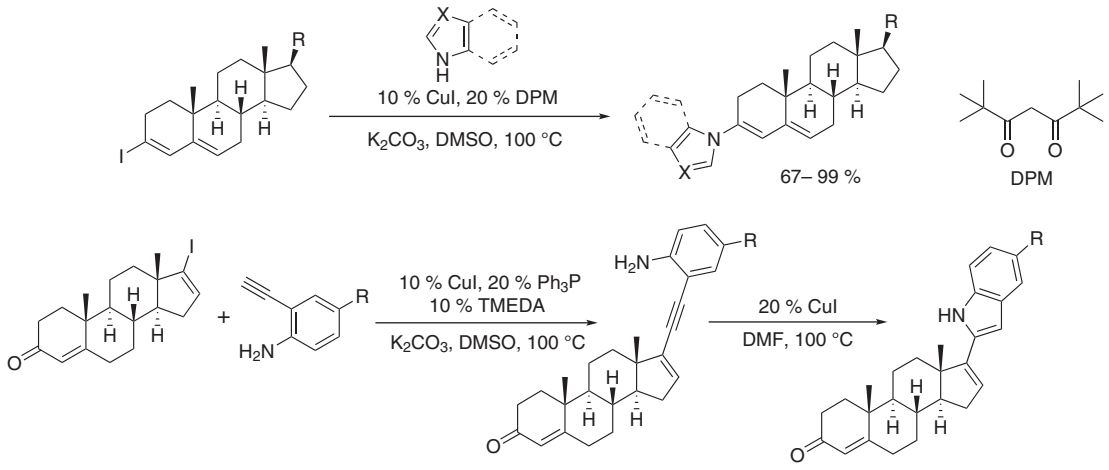



**Scheme 6:** Suzuki coupling catalyzed with Pd black.

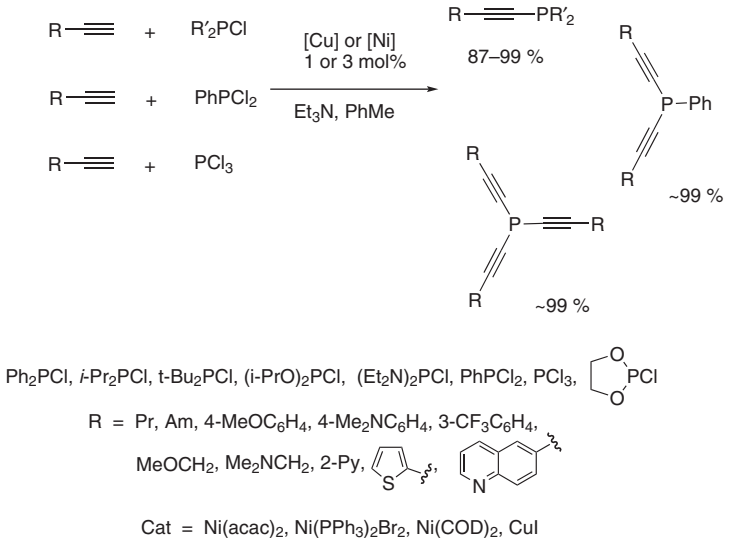



**Scheme 7:** Cu(I)-catalyzed amination of di- and polyamines.

In some cases copper catalyst works better than palladium, e.g. in the reactions of terminal acetylenes with P–Cl bond. Also nickel catalysis gave better results than palladium in the formation of various alkynyl phosphines (mono-, di- and trisubstituted), and it was indispensable in the case of the compounds possessing P–O and P–N bonds [33, 34] (Scheme 9).




**Scheme 8:** Cu(I)-catalyzed modifications of steroids.




**Scheme 9:** Cu(I)- and Ni(II)-catalyzed alkynylation of phosphines.

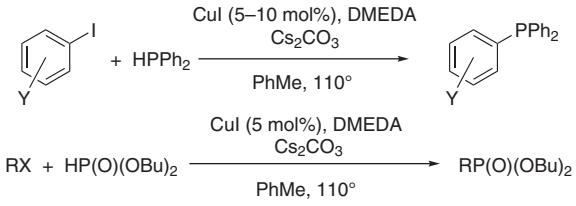
Cross-coupling reactions of aryl halides and vinyl halides with diphenyl phosphine or dibutyl phosphite were also catalyzed by CuI very efficiently, with diphenyl phosphine even without any additional ligand [35] (Scheme 10).

Copper catalysis is widely and successfully employed in "click" reactions and this methodology was applied to the synthesis of macrocycles including those with steroidal scaffold [36, 37] (Scheme 11).

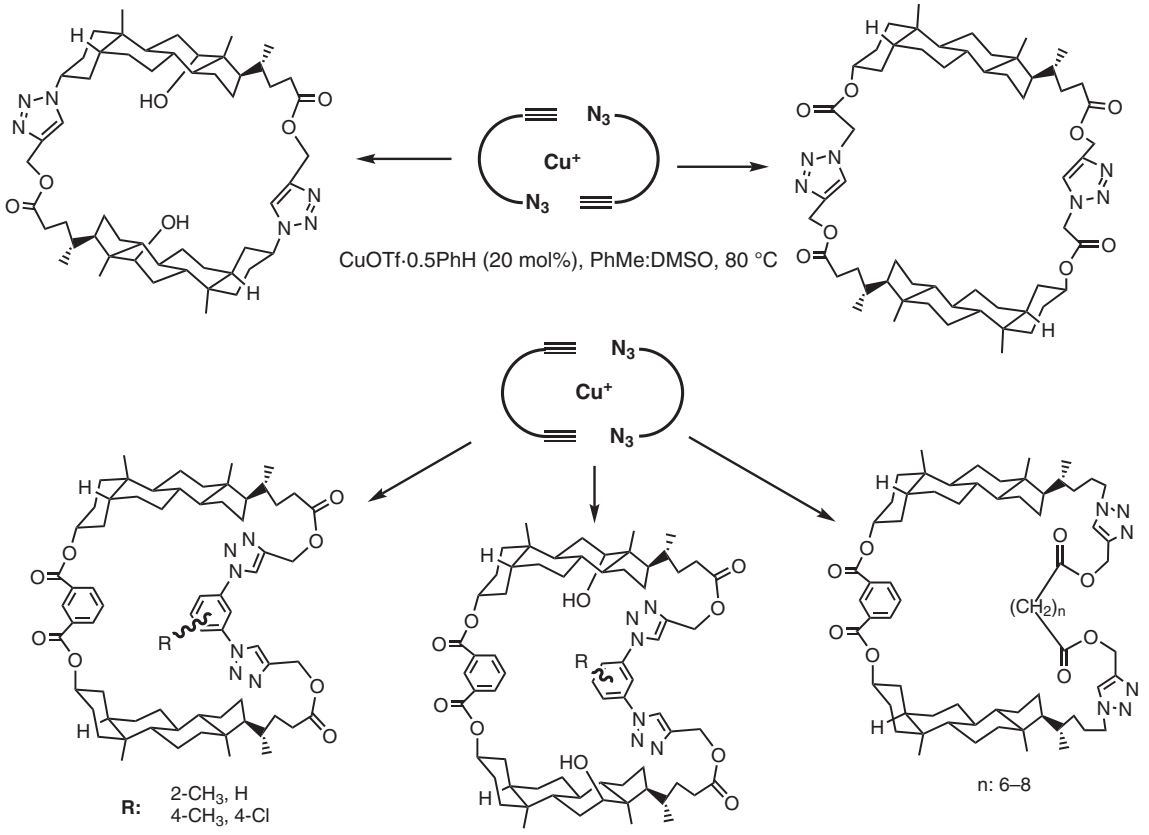
The formation of linked polyporphyrin compounds (dyads and triads, including a star-shaped trimer), which possess interesting photophysical properties, was achieved using "click" methodology [38, 39] (Scheme 12).

## Catalytic amination reactions

The most difficult cross-coupling reactions is C–N formation which is now known as Buchwald–Hartwig amination [40, 41]. Amination of aryl halides with N,N-diethylaminotributyltin was carried out by Kosugi and




**Scheme 10:** Cu(I)-catalyzed formation of C($sp^2$)–P bond.

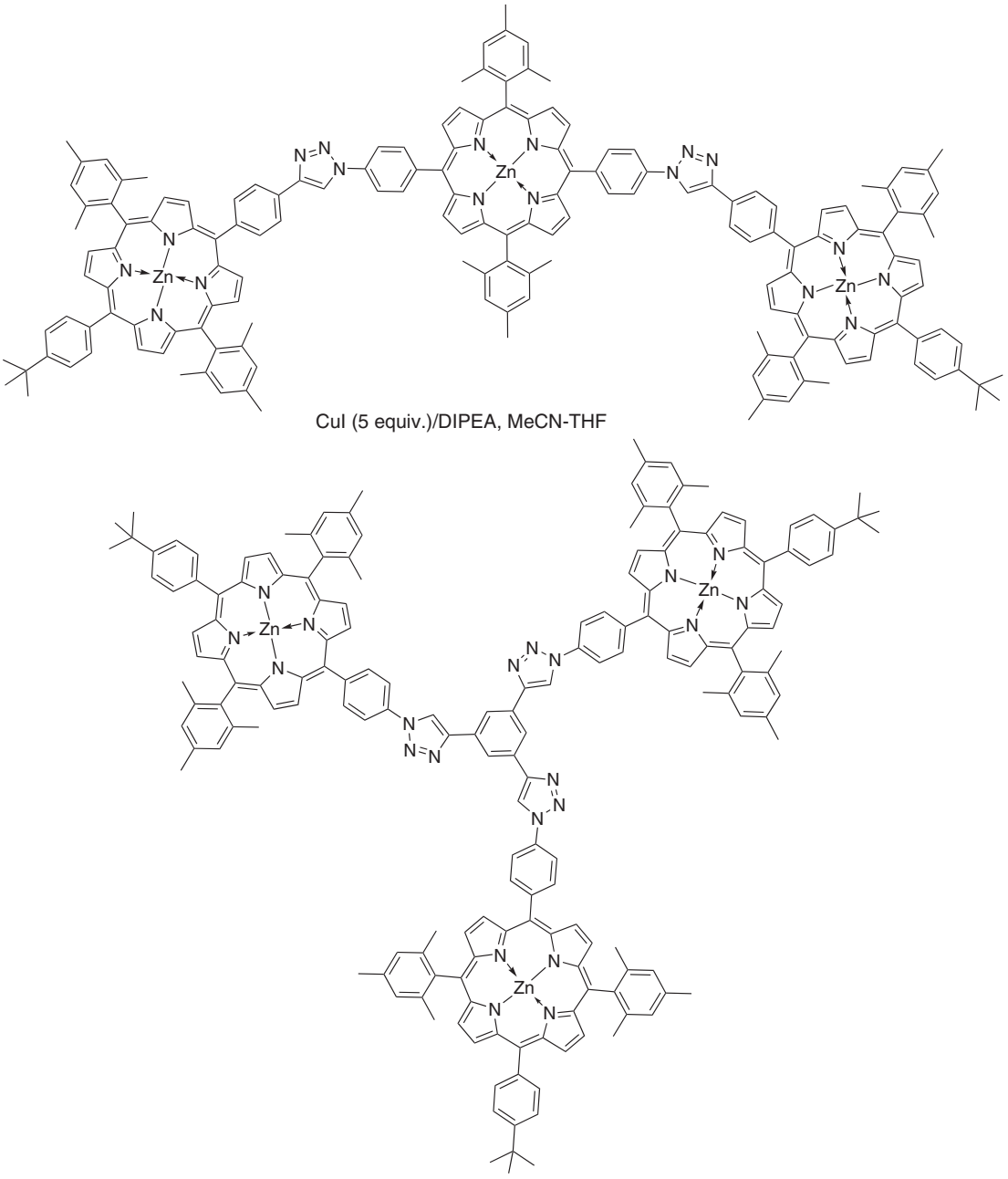



**Scheme 11:** Cu(I)-catalyzed cycloaddition reactions leading to steroidal macrocycles.

Migita in 1983 [42], and our contribution to this field was the first palladium-catalyzed arylation of diphenylamine in water under ligandless conditions [43]. We concentrated our efforts on the arylation of polyamines and found conditions to obtain mono-, di- and polyarylated derivatives [44], and with dibromobenzene we studied the diamination process [45]. Sometimes it is possible to use Cu(I) with a proper ligand, but in the majority of cases palladium is preferable [46]. We used Pd(0)-catalyzed amination in the synthesis of porphyrin dyads and triads using diamine linkers [47] (Scheme 13).

These compounds can coordinate both electrophiles and nucleophiles at the same time and can be used in supramolecular chemistry. For example, the porphyrin dyad with ethylenediamine linker changed linear structure upon coordination with CuBr forming a tweezer, and on the addition of HCl or a stronger ligand like phenanthroline it resumed the initial structure [48] (Scheme 14). Analogous tweezer structure was obtained after the coordination of the same dyad with DABCO.

Macrocycles with two porphyrin moieties or conjugates of calyx[4]crown ether with two porphyrins possess three centers of coordination; some of them were found to be efficient fluorescent chemosensors for Cu(II) [49, 50] (Scheme 15).

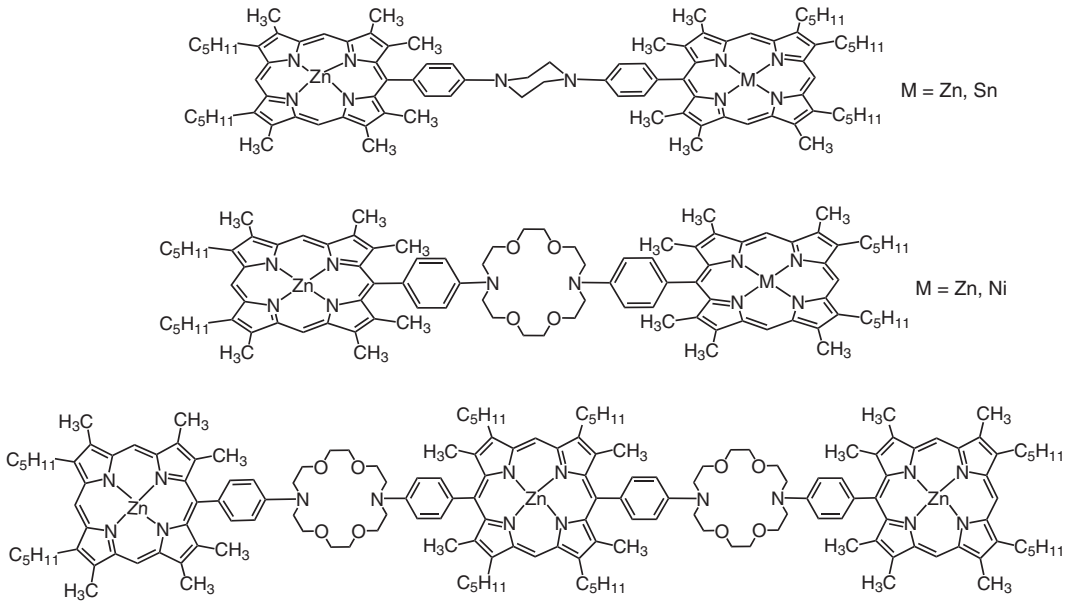



**Scheme 12:** Cu(I)-mediated "click" reactions in the synthesis of porphyrin trimers of different architectures.

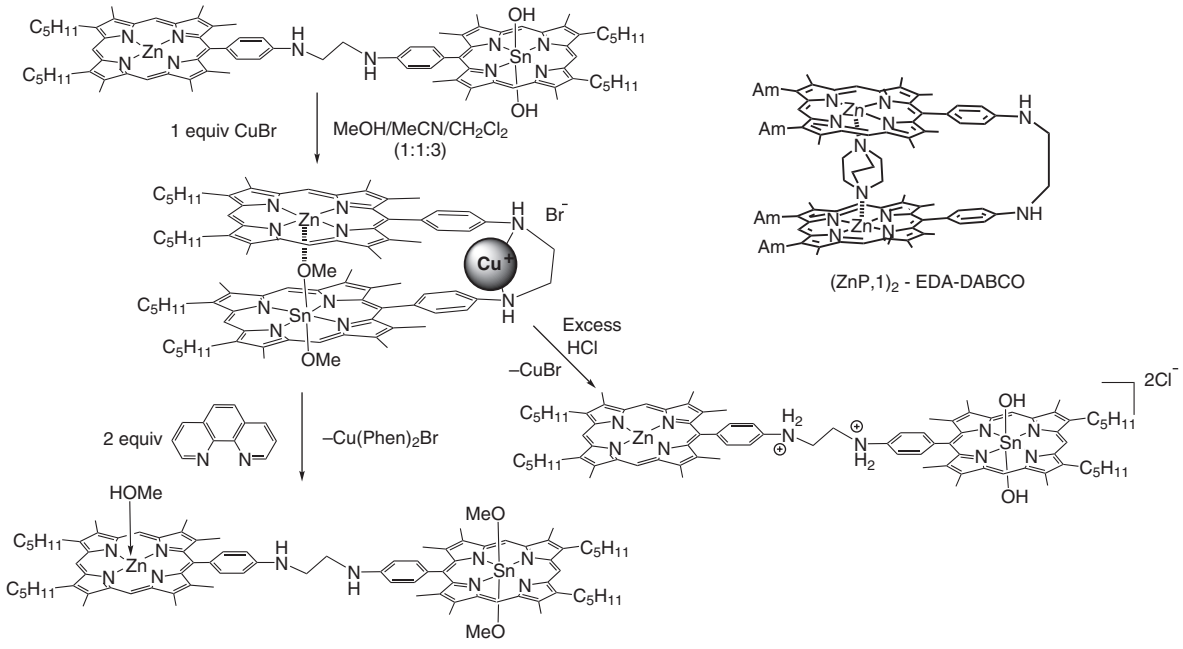
Using Pd(0)-catalyzed amination we obtained a great variety of polyazamacrocycles, for example, those possessing chromophore and fluorophore endocyclic moieties which were found to be chemosensors for Pb(II) and Cu(II) cations [51, 52] (Scheme 16).

Catalytic amination became a powerful tool for the synthesis of macrobicyclic compounds possessing central diazacrown moieties, tri- and tetraazamacrocycles with exocyclic fluorophore groups like dansyl, and were found to be efficient fluorescent molecular probes for Al(III) and Cu(II) cations causing total emission quenching (Scheme 17).

Macrotricycles of different architecture containing cyclen and cyclam central moieties which were obtained via Pd(0)-mediated amination possess spherical or cylindrical shape and these compounds can also serve as hosts for cations [53] (Scheme 18).




**Scheme 13:** Examples of various di- and triporphyrin structures obtained using Pd(0)-catalzyed amination reactions.

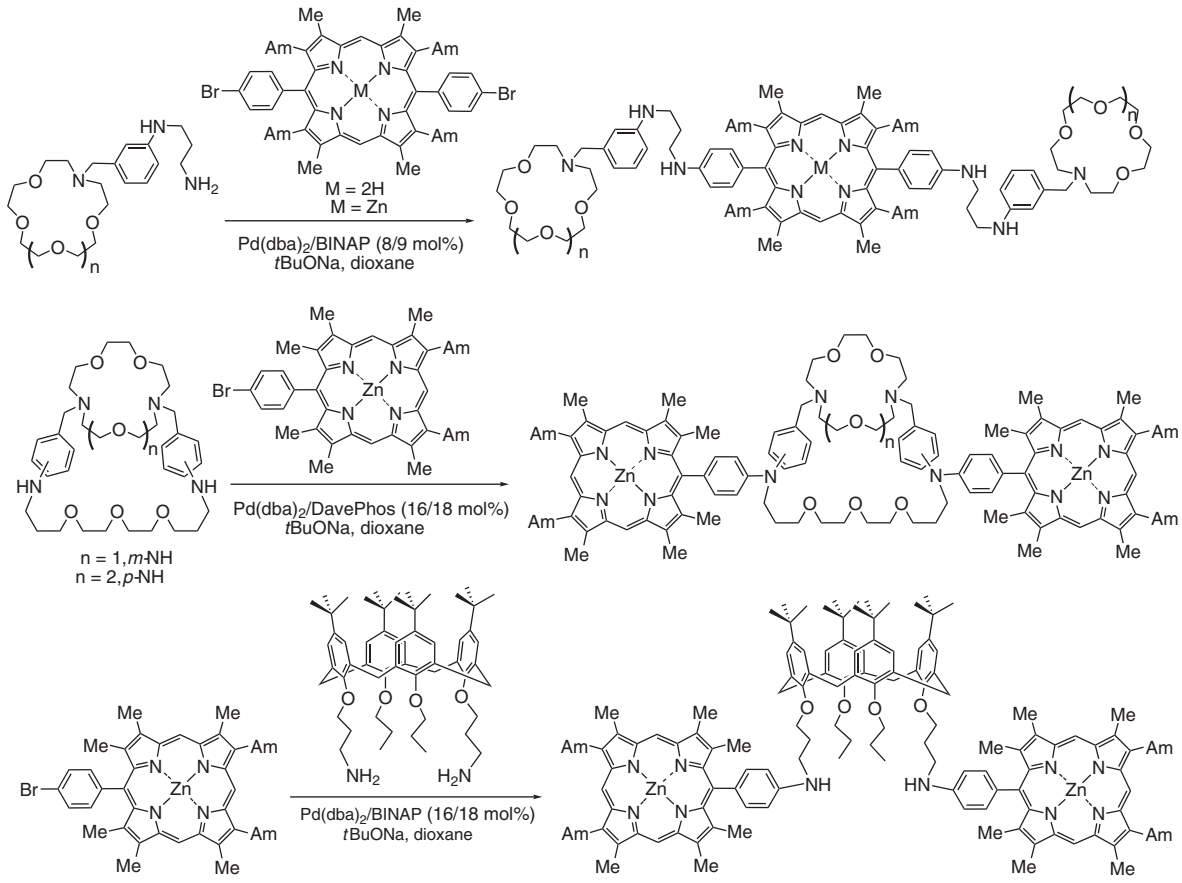



**Scheme 14:** Porphyrin dyad with a flexible linker as a tweezer.

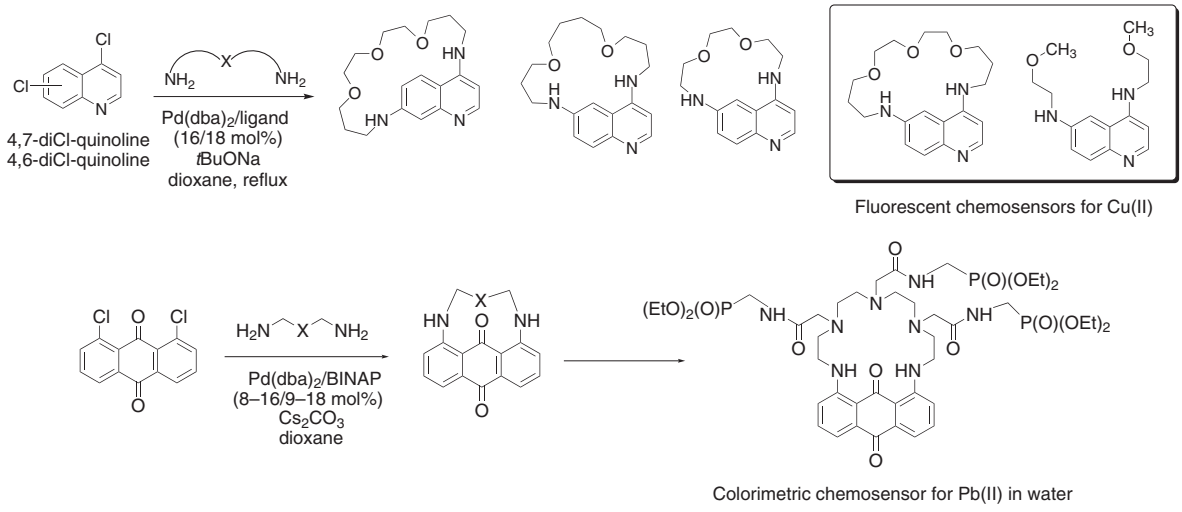
We also introduced the chiral elements in macrocycles and obtained planar-chiral macrocycles based on 1,5-disubstituted anthraquinone using a chiral phosphine ligand (Scheme 19). Enantiomeric excess exceeded 60 % and after one crystallization it was possible to obtain pure enantiomer [54].

Also the attempts to synthesize planar-chiral macrobicycles on the basis of cyclam were undertaken [55] (Scheme 20).

Chiral macrocycles organized around BINAM scaffold possessing different aryl spacers and oxadiamine linkers, provided with fluorophore groups like dansyl or aminoquinoline, were synthesized using

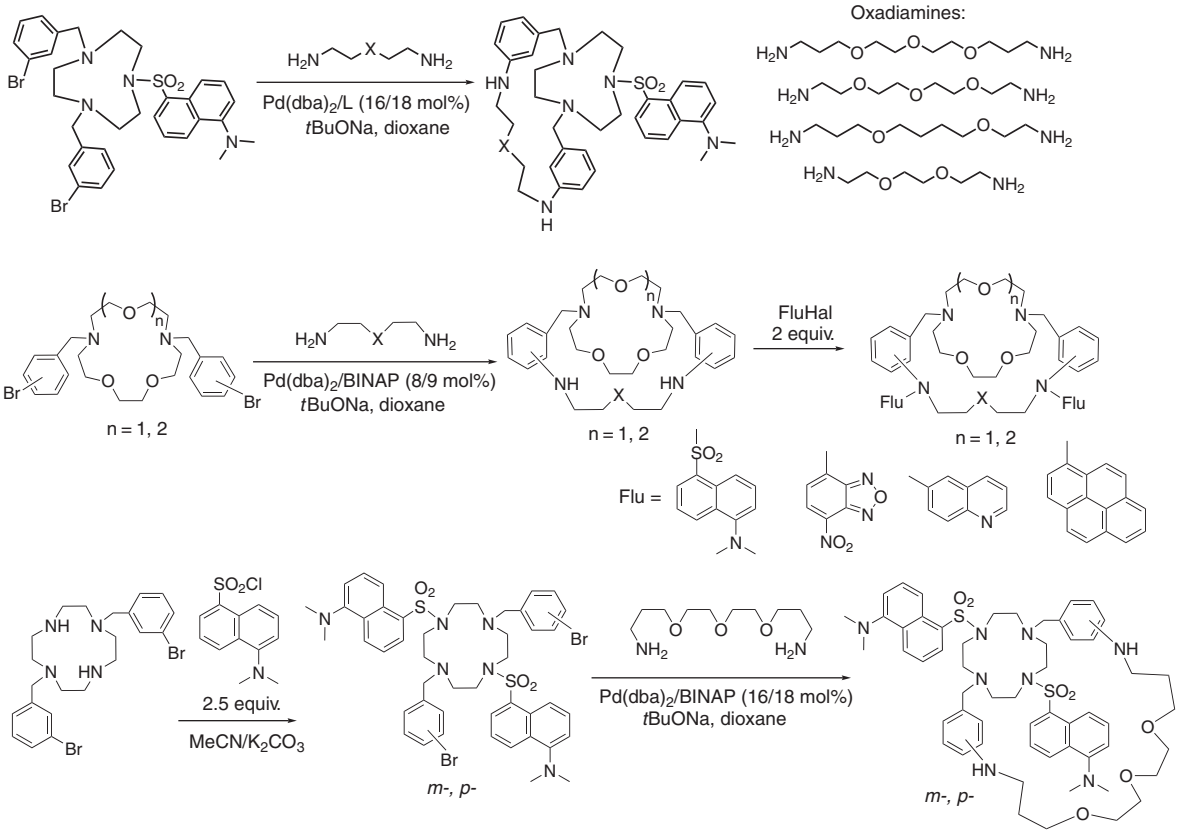



**Scheme 15:** Pd(0)-catalyzed amination in the synthesis of porphyrin conjugates with macrocycles and calix[4]arenes.

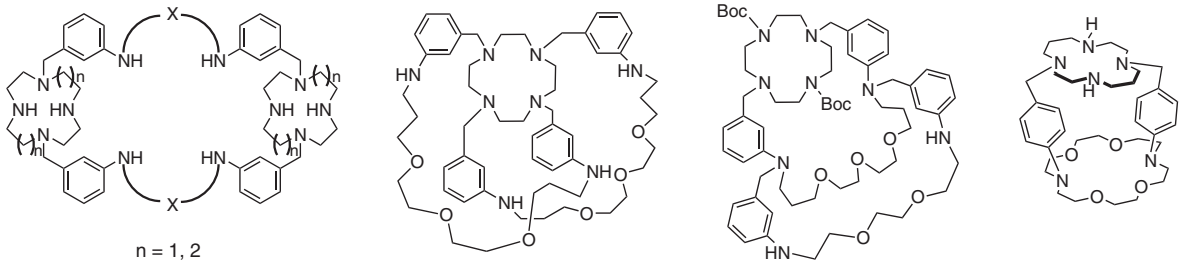



**Scheme 16:** Pd(0)-catalyzed amination in the synthesis of chemosensors with endocyclic chromophore or fluorophore moieties.

Pd(0)-catalyzed macrocyclization (Scheme 21) and are being studied now as fluorescent chemosensors for small chiral molecules like aminoalcohols by changing their fluorescence on binding with certain enantiomer [56].




**Scheme 17:** Pd(0)-catalyzed amination in the synthesis of chemosensors with exocyclic fluorophore moieties.



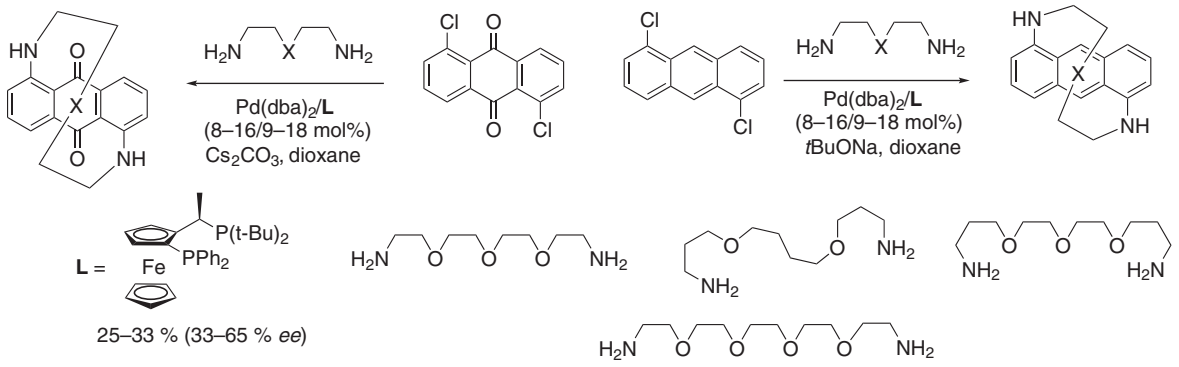

**Scheme 18:** Macropolycyclic compounds synthesized via Pd-catalyzed amination reactions.

## CH-activation, organocatalysis and catalysis by Lewis acids in C–C bonds formation

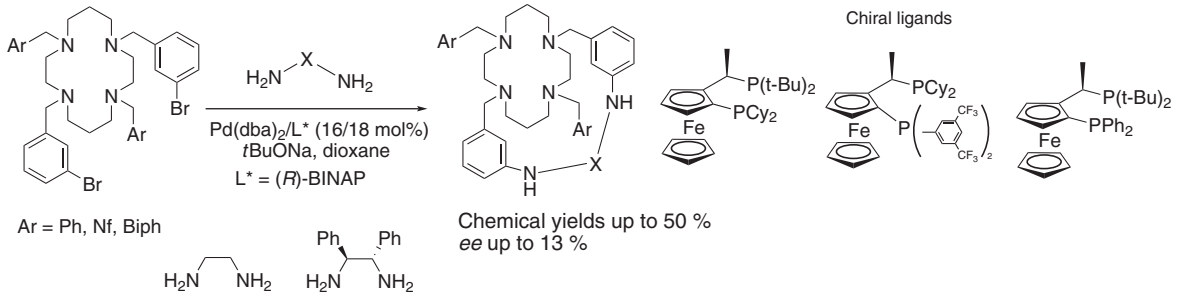
Our recent studies are also dedicated to C–H activation reactions which allow to use aromatic compounds without halogen or without metal in cross-coupling reactions. The introduction of the phosphoryl group in porphyrins was carried out successfully via palladium-catalyzed oxidative coupling of *meso*-CH of the porphyrin dialkyl phosphine or dihenylphosphonous acid (Scheme 22).

In the another approach to substituted porphyrins we exploited the Pd-mediated coupling of mono- and di(bromophenyl) derivatives with so-called “acidic” heteroaromatic compounds like thiazole, benzoxazole, imidazole (Scheme 23).

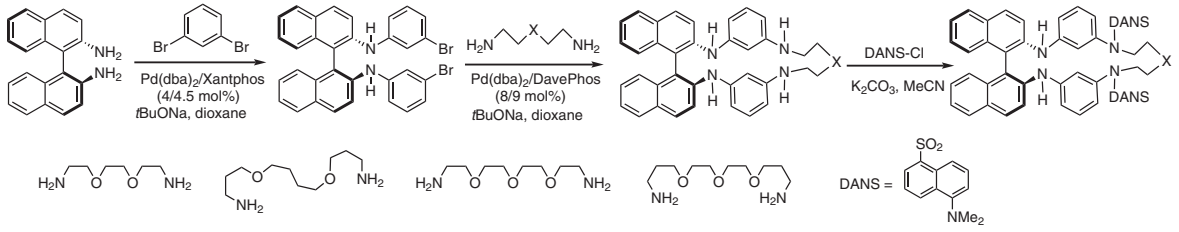
Another very important trend in the organic synthesis of the XXI century is a strong interest to asymmetric catalysis to produce optically pure compounds. Such reactions are mediated by either organocatalysts or by



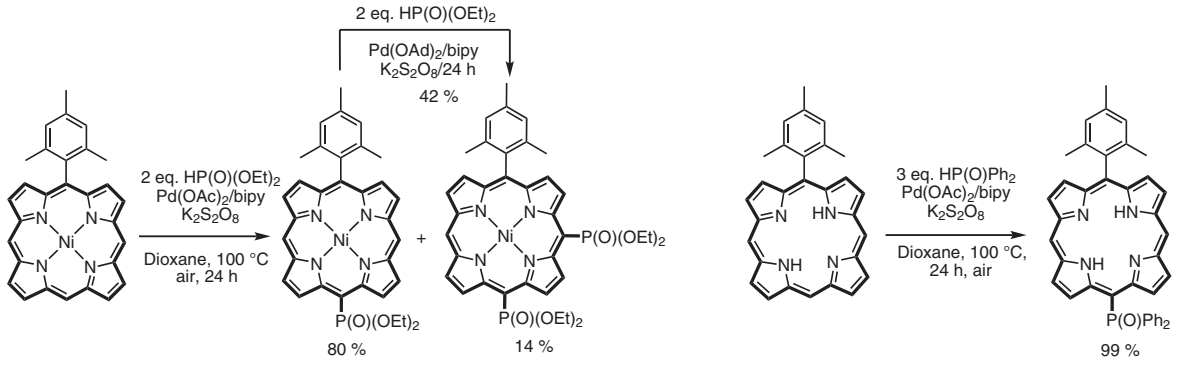

**Scheme 19:** Pd(0)-catalyzed amination in the synthesis of planar-chiral macrocycles.




**Scheme 20:** Pd(0)-catalyzed amination in the synthesis of planar-chiral macrobicycles.

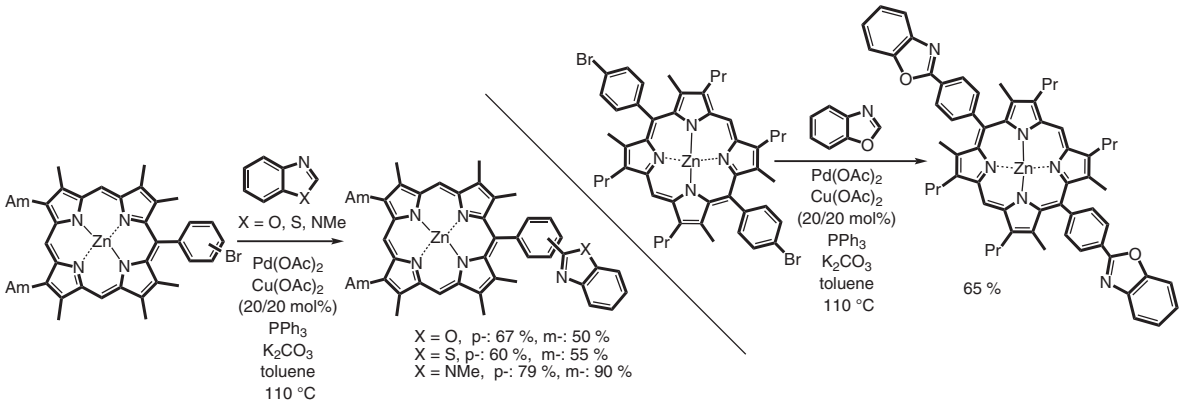



**Scheme 21:** Pd(0)-catalyzed amination in the synthesis of the macrocycles with chiral BINAM and fluorescent dansyl moieties.

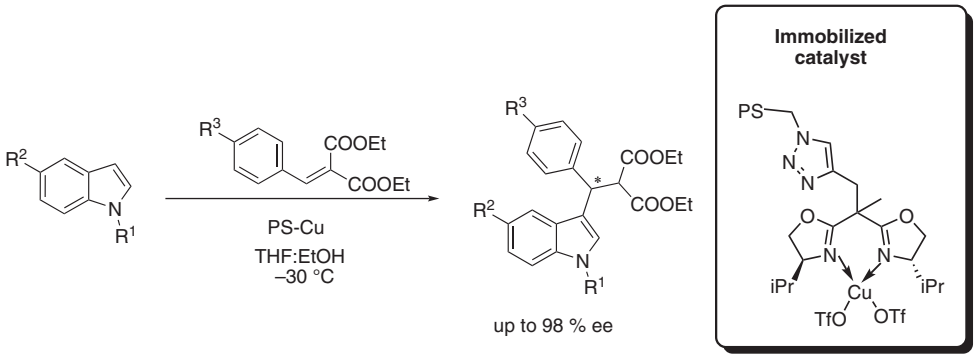



**Scheme 22:** CH-activation in the synthesis of *meso*-phosphorylated porphyrins.

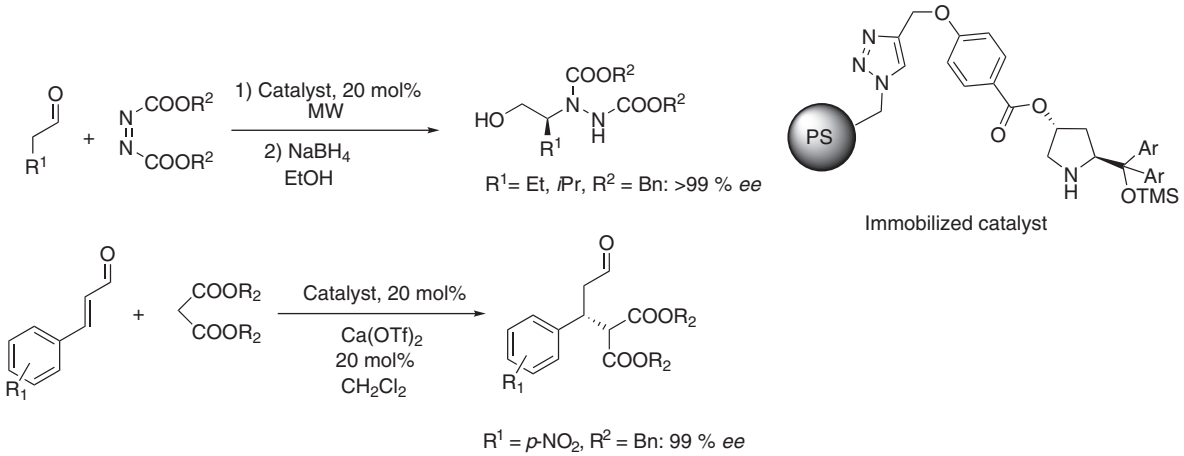
Lewis or Broensted acids, and among them are such important processes as aldol condensation, Michael addition, Friedel–Crafts and Diels–Alder reactions, cyclopropanation which form compounds with one or several chiral centers. Our contribution to this field is the use of the $Cu(OTf)_2$ complex with a chiral bisoxazoline ligand immobilized on the Merrifield resin in Michael addition reactions of indole and its derivatives with benzylydene malonate [57]. We achieved 96 % *ee* and showed the possibility of recycling the catalyst (Scheme 24). The same catalyst was demonstrated to be used also in the addition reactions to the carbonyl group.



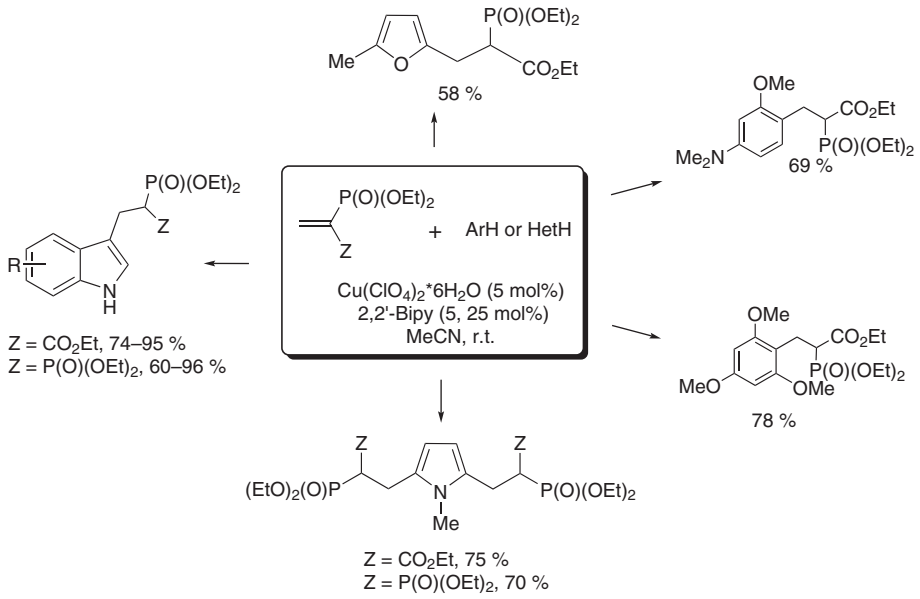

**Scheme 23:** CH-activation in the synthesis of porphyrins substituted with heterocyles.



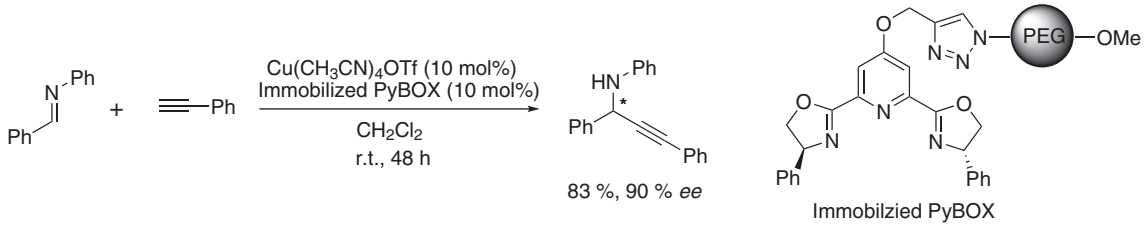

**Scheme 24:** Asymmetric addition to benzylydene malonates using immobilized catalyst.




**Scheme 25:** Asymmetric α-amination and addition to α,β-unsaturated aldehydes using immobilized organocatalyst.




**Scheme 26:** Lewis acid catalyzed addition to vinyl phosphonates.




**Scheme 27:** Asymmetric alkynylation of imine using immobilized reusable PyBOX ligand.

Polystyrene-supported derivative of proline was found to be an efficient organocatalyst for the asymmetric α-amination of aldehydes using diazadicarboxylates [58], and a careful choice of substituents in the aminating agent resulted in excellent enantioselectivity (>99 % *ee*) (Scheme 25). The same immobilized oraganocatalyst was equally applicable to the asymmetric Michael addition of malonates to unsaturated aldehydes in the presence of Lewis acid $Ca(OTf)_2$ acting as a cocatalyst [59] (Scheme 25).

Rather simple Lewis acid $Cu(ClO_4)_2$ with 2,2′-bipyridyl as a ligand served for the Michael addition of aromatic and heteroaroamtic compounds to vinyl phosphonates under mild conditions [60] (Scheme 26).

Another immobilized catalyst – PEG-supported PyBOX was successfully applied in the asymmetric alkynylation of the Schiff base by phenylacetylene (Scheme 27). The reaction produced the target product in 83 % yield with 90 % enantioselectivity, and the catalyst was shown to be recycled at least three times without loss of efficiency [61].

**Acknowledgement:** The research was financially supported by the Russian Science Foundation (RSF grant N 14-23-00186).

# References

[1] A. Wurtz. *Ann. Chem.* **96**, 364 (1855).
[2] R. J. P. Corriu, J. P. Masse. *J. Chem. Soc. Chem. Commun.* 144a (1972).

[3] K. Tamao, K. Sumitani, M. Kumada. *J. Am. Chem. Soc.* **94**, 4374 (1972).
[4] M. Yamamura, I. Moritani, S.-I. Murahashi. *J. Organomet. Chem.* **91**, C39 (1975).
[5] S.-I. Murahashi, M. Yamamoto, K. Yanagisawa, N. Mita, K. Kondo. *J. Org. Chem.* **44**, 2408 (1979).
[6] D. Milstein, J. K. Stille. *J. Am. Chem. Soc.* **100**, 3636 (1978).
[7] N. Mizoroki, K. Mori, A. Ozaki. *Bull. Chem. Soc. Jpn.* **44**, 581 (1971).
[8] R. F. Heck, J. P. Nolley. *J. Org. Chem.* **37**, 2320 (1972).
[9] K. Sonogashira, Y. Tohda, N. Hagihara. *Tetrahedron Lett.* **16**, 4467 (1975).
[10] N. Miyaura, K. Yamada, A. Suzuki. *Tetrahedron Lett.* **20**, 3437 (1979).
[11] N. Miyaura, A. Suzuki. *Chem. Rev.* **95**, 2457 (1995).
[12] A. Schoenberg, I. Bartoletti, R. F. Heck. *J. Org. Chem.* **39**, 3318 (1974).
[13] M. Hidai, T. Hikita, Y. Wada, Y. Fujikura, Y. Uchida. *Bull. Chem. Soc. Jpn.* **48**, 2075 (1975).
[14] T. Ito, K. Mori, T. Mizoroki, A. Ozaki. *Bull. Chem. Soc. Jpn.* **48**, 2091 (1975).
[15] A. O. King, N. Yasuda. *Top. Organomet. Chem.* **6**, 205 (2004).
[16] I. P. Beletskaya. *J. Organomet. Chem.* **250**, 551 (1983).
[17] N. A. Bumagin, K. V. Nikitin, I. P. Beletskaya. *J. Organomet. Chem.* **358**, 563 (1988).
[18] I. P. Beletskaya, A. V. Cheprakov. "Aqueous transition-metal catalysis", in *Organic Synthesis in Water*, P. A. Grieco (Ed.), p. 141, Blackie Academic and Professional, London (1998).
[19] I. P. Beletskaya, A. V. Cheprakov. "Palladium-catalyzed reactions: from the art of today to a common tool of tomorrow", in *Transition Metal Catalyzed Reactions*, S.-I. Murahashi, S. G. Davies (Eds.), p. 29, Blackwell Science, Oxford (1999).
[20] I. P. Beletskaya, A. V. Cheprakov. "Aqueous palladium catalysis", in *Handbook of Organopalladium Chemistry* vol. 2, E. I. Negishi (Ed.), p.2957, Wiley Int., New York (2002).
[21] A. V. Cheprakov, N. V. Ponomareva, I. P. Beletskaya. *J. Organomet. Chem.* **486**, 297 (1995).
[22] I. P. Beletskaya, A. N. Kashin, A. E. Litvinov, V. S. Tyurin, P. M. Valetsky, G. van Koten. *Organometallics* **25**, 154 (2006).
[23] A. S. Sigeev, A. S. Peregudiv, A. V. Cheprakov, I. P. Beletskaya. *Adv. Synth. Catal.* **357**, 417 (2015).
[24] I. P. Beletskaya, A. N. Kashin, I. A. Khotina, A. R. Khokhlov. *Synlett* **2008**, 1547 (2008).
[25] I. P. Beletskaya, O. G. Ganina. *React. Kinet. Mech. Cat.* **99**, 1547 (2010).
[26] I. P. Beletskaya, A. R. Khokhlov, E. A Tarasenko, V. S. Tyrin. *J. Organomet. Chem.* **692**, 4402 (2007).
[27] A. V. Selivanova, V. S. Tyurin, V. V. Matveev, A. R. Khokhlov. *Russ. J. Org. Chem.* **46**, 157 (2010).
[28] A. V. Selivanova, V. S. Tyrin, I. P. Beletskaya. *ChemPlusChem* **79**, 1278 (2014).
[29] A. N. Kashin, O. G. Ganina, A. V. Cheprakov, I. P. Beletskaya. *ChemCatChem* **7**, 2113 (2015).
[30] M. V. Anokhin, A. D. Averin, I. P. Beletskaya. *Eur. J. Org. Chem.* **2011**, 6240 (2011).
[31] Y. N. Kotovshchikov, G. V. Latyshev, N. V. Lukashev, I. P. Beletskaya. *Eur. J. Org. Chem.* **2013**, 7823 (2013).
[32] Y. N. Kotovshchikov, G. V. Latyshev, N. V. Lukashev, I. P. Beletskaya. *Org. Biomol. Chem.* **13**, 5542 (2015).
[33] I. P. Beletskaya, V. V. Afanasiev, M. A. Kazankova, I. V. Efimova. *Org. Lett.* **5**, 4309 (2003).
[34] V. V. Afanasiev, I. P. Beletskaya, M. A. Kazankova, I. V. Efimova, M. U. Antipin. *Synthesis* **295**, 2835 (2003).
[35] D. Gelman, L. Jiang, S. L. Buchwald. *Org. Lett.* **5**, 2315 (2003).
[36] G. V Latyshev, M. S. Baranov, A. V. Kazantsev, A. D. Averin, N. V. Lukashev, I. P. Beletskaya. *Synthesis* **35**, 2605 (2009).
[37] D. A. Erzunov, G. V. Latyshev, A. D. Averin, I. P. Beletskaya, N. V. Lukashev. *Eur. J. Org. Chem.* **2015**, 6289 (2015).
[38] Y. P. Polevaya, V. S. Tyurin, I. P. Beletskaya. *J. Porphyrins Phthalocyanines* **18**, 20 (2014).
[39] Y. P. Yashchuk, V. S. Tyurin, I. P. Beletskaya. *Macroheterocycles* **5**, 302 (2012).
[40] B. H. Yang, S. L. Buchwald. *J. Organomet. Chem.* **576**, 125 (1999).
[41] J. F. Hartwig. *Angew. Chem. Int. Ed.* **37**, 2046 (1998).
[42] M. Kosugi, M. Kameyama, T. Migita. *Chem. Lett.* **12**, 927 (1983).
[43] D. V. Davydov, I. P. Beletskaya. *Russ. Chem. Bull.* **44**, 1141 (1995).
[44] R. Guilard, A. G. Bessmertnykh, I. P. Beletskaya. *Tetrahedron Lett.* **38**, 2287 (1997).
[45] I. P. Beletskaya, A. G. Bessmertnykh, R. G. Guilard. *Synlett* **1999**, 1459 (1999).
[46] I. P. Beletskaya, A. G. Bessmertnykh, A. D. Averin, F. Denat, R. Guilard. *Eur. J. Org. Chem.* **234**, 261 (2005).
[47] V. S. Tyurin, E. A. Mikhalitsyna, A. S. Semeikin, I. P. Beletskaya. *Macroheterocycles* **8**, 358 (2015).
[48] E. A. Mikhalitsyna, V. S. Tyurin, I. P. Beletskaya. *J. Porphyrins Phthalocyanines* **19**, 874 (2015).
[49] A. A. Yakushev, A. D. Averin, O. A. Maloshitskaya, S. A. Syrbu, O. I. Koifman, I. P. Beletskaya. *Mendeleev Commun.* **26**, 199 (2016).
[50] A. A. Yakushev, A. D. Averin, O. A. Maloshitskaya, S. A. Syrbu, O. I. Koifman, I. P. Beletskaya. *Macroheterocycles* **9**, 65 (2016).
[51] A. S. Abel, A. D. Averin I. P. Beletskaya. *New J. Chem.* **40**, 5818 (2016).
[52] E. Ranyuk, C. Morkos-Douaihy, A. Bessmertnykh, F. Denat, A. Averin, I. Beletskaya, R. Guilard. *Org. Lett.* **11**, 987 (2009).
[53] S. M. Kobelev, A. D. Averin, A. K. Buryak, F. Denat, R. Guilard, I. P. Beletskaya. *Tetrahedron Lett.* **53**, 210 (2012).
[54] E. R. Ranyuk, A. D. Averin, I. P. Beletskaya. *Adv. Synth. Catal.* **352**, 2299 (2010).
[55] S. M. Kobelev, A. D. Averin, O. A. Maloshitskaya, F. Denat, R. Guilard, I. P. Beletskaya. *Macroheterocycles* **5**, 389 (2012).
[56] O. K. Grigorova, A. D. Averin, O. A. Maloshitskaya, I. P. Beletslaya. *Macroheterocycles* **9**, 425 (2016).
[57] V. G. Desyatkin, M. V. Anokhin, I. P. Beletskaya. *Russ. J. Org. Chem.* **52**, 1727 (2016).

[58] A. A. Guryev, M. V. Anokhin, A. D. Averin, I. P. Beletskaya. *Mendeleev Commun.* **25**, 410 (2015).
[59] A. A. Guryev. M. V. Anokhin, A. D. Averin, I. P. Beletskaya. *Mendeleev Commun.* **26**, 469 (2016).
[60] E. A. Tarasenko, I. P. Beletskaya. *Synthesis* **49**, 1689 (2017).
[61] E. A. Tarasenko, I. P. Beletskaya. *Mendeleev Commun.* **26**, 477 (2016).