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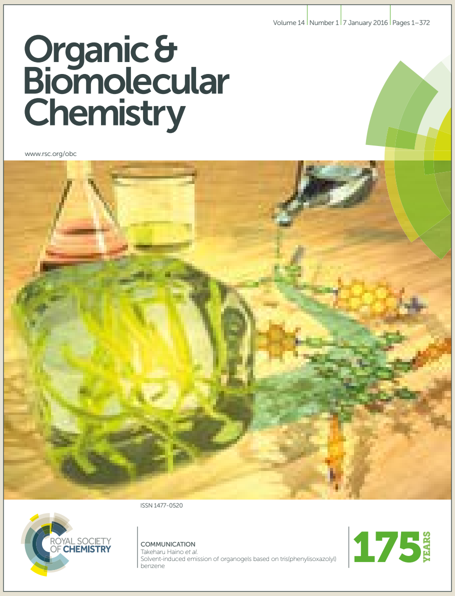

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General method of Suzuki-Miyaura cross-coupling of 4- and 5-halo-1,2,3-triazoles in water

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General method of synthesis of 1,4,5-trisubstituted-1,2,3-triazoles by Suzuki-Miyaura cross-coupling from 4- and 5-halo-1,2,3-triazoles is reported. The reaction is mediated by expanded-ring N-heterocyclic carbene palladium complex in water. The developed reaction protocol meets the requirements of "green chemistry". Cross-coupling of 4- and 5-chlorotriazoles is reported for the first time.

1,2,3-triazoles is a very important class of heterocyclic compounds widely used as fragments in biologically active molecules and drugs[1] due to broad spectrum of biological activity, such as antitumor, antiviral and antiparasitic.[2] These heterocycles have found numerous applications in polymer science,[3] as ligands in homogeneous catalysis,[4] directing groups in transition metal catalyzed C-H activations,[5] and in organic synthesis.[6] The main approach for synthesis of this class of heterocycles is a copper catalyzed azide alkyne cycloaddition.[7] This approach is extensively used in biochemistry and material science.[3a, 8]

The key intermediate in copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) reaction that governs high reaction rate and selectivity is the copper(I) acetylide formed from the copper catalyst and a terminal alkyne.[9] Due to this, CuAAC is mainly applied in cycloaddition of terminal alkynes. Internal alkynes are several orders less reactive and there are difficulties in regio-controlled preparation of fully substituted 1,2,3-triazoles. To date, formation of 1,4,5-trisubstituted 1,2,3-triazoles via CuAAC remains problematic.[10]

1,4,5-Trisubstituted 1,2,3-triazoles can be obtained via CuAAC reaction followed by transition metal catalyzed C-H activation/arylation.[11] In 2008, the Ackermann group reported a copper-catalyzed, one-pot two-step coupling reaction of an alkyne, azide, and an aryl iodide.[11c] However, to conduct the reaction of low-reactive 1,2,3-triazole, harsh conditions were used: 140 °C, 20h using conventional or microwave heating.

Xu et al. proposed a modular method of synthesis of 1,4,5-trisubstituted 1,2,3-triazoles from accessible reagents using Cu/Pd transmetallation relay catalyst. This method enables to obtain triazoles bearing three different substituents relatively easy in one reaction step.[12] However, this method has several disadvantages: 50% excess of organic azide, 50% excess of aryl halide and from 2 to 10 mol% of palladium precatalyst $Pd_2(dba)_3$, taking into accounts it's high molecular weight, the mass of the catalyst is comparable to the mass of organic substrates. Moreover, one equivalent of copper(I) salt (CuCl), up to 20 mol% of phosphine ligand, and hazardous teratogenic DMF solvent are used. Thus, this procedure is far from atom economy and dangerous for the environment.

One of the mostly used approaches for the formation of C-C bonds is palladium-catalyzed cross-coupling reactions that became a golden standard in organic chemistry and metal mediated catalysis.[13] Among others, Suzuki-Miyaura cross-coupling is the most preferable. Due to the growing tendency to avoid hazardous substances in synthesis,[14] many variations of Suzuki-Miyaura methodology using "green" solvents, were developed.[15] Water as solvent is especially attractive since it is nontoxic, non-flammable, inexpensive, and can be easily separated from organic products.

Recently, 4- and 5-halo-1,2,3-triazoles became more synthetically accessible.[16] Arguably, functionalization of such substrates via Suzuki-Miyaura cross-coupling might became a convenient tool for preparation of 1,4,5-trisubstituted 1,2,3-triazoles. However, there are less than 20 reports in the literature devoted to cross-coupling of bromo- and iodo-1,2,3-triazoles (9 references for bromides,[17] and 10 for iodides)[10b, 17b-d, 18] Most of the reported protocols suffer from a number of disadvantages: in all cases high loadings of palladium catalysts (from 4 up to even 20 mol%) are used; utilization of "non-green" solvents such as DMF, THF, 1,4-dioxane, acetonitrile; in some cases, harsh reaction conditions should be applied (intensive microwave heating). Finally, most of the methods give moderate yields and the scope of substrates is narrow.

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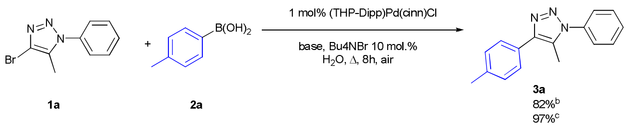
Thus, it can be stated that there is no general approach for Suzuki-Miyaura cross-coupling of bromo- and iodo-1,2,3-triazoles to date. Importantly, there are no reports on Suzuki-Miyaura cross-coupling of chloro-1,2,3-triazoles.

The development of the convenient general approach for synthesis of 1,4,5-trisubstituted 1,2,3-triazoles is a challenging task. Thus, we performed a systematic study of the Suzuki-Miyaura reactions of 4- and 5-halo-1,2,3-triazoles with special emphasis on coupling of low-reactive challenging chloro-1,2,3-triazoles. Where possible, aryl chlorides are employed as the least expensive of the aryl halides. [19]

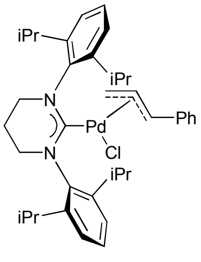
Previously, our group reported on the development of the reaction protocol for Suzuki-Miyaura cross-coupling in water.[15k] It is of high interest to develop analogous synthetic procedure for coupling of 4- and 5-halo-1,2,3-triazoles with arylboronic acids. We used 4-bromo-5-methyl-1,2,3-triazole (**1a**) and 4-methylphenylboronic acid (**2a**) as a test system for optimization of reaction conditions.

Scheme 1 Optimization of reaction conditions [a]



[a] Reaction conditions: 4-bromo-5-methyl-1-phenyl-1H-1,2,3-triazole (0.5 mmol), $ArB(OH)_2$ (1.2 eq., 0.6 mmol), (THP-Dipp)Pd(cinn)Cl (0.005 mmol), KOH (1.7 eq., 0.85 mmol), Bu_4NBr (0.05 mmol), H_2O (0.8 ml), Δ, 8h. [b] $NaHCO_3$ as a base (3.06 eq.). [c] KOH as a base (1.7 eq.).

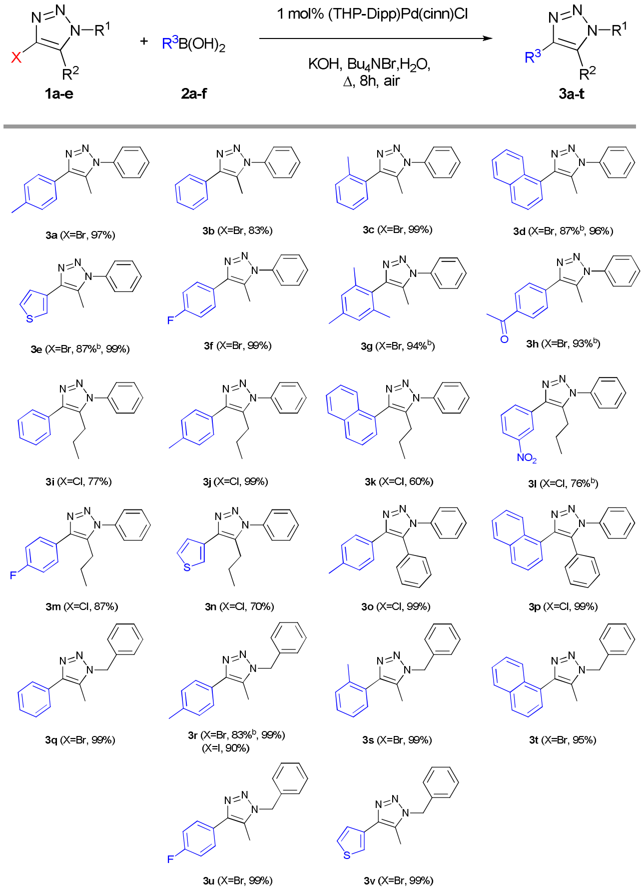
Catalytic tests were performed in distilled water as solvent. $NaHCO_3$ was used as a base, and Bu_4NBr as a phase transfer agent. We tested (THP-Dipp)Pd(cinn)Cl (THP-Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) complex bearing expanded-ring carbene[15k, 15l, 20] and bulky Dipp groups as precatalyst.[15k] Reaction mixtures were refluxed in air for 8h. The product was isolated using flash-chromatography to give 82% yield. Upon substitution of 3 eq. of $NaHCO_3$ with 1.7 eq. of KOH the yield raised up to 97% (Scheme 1).



(THP-Dipp)Pd(cinn)Cl

In order to determine the substrate scope of Suzuki-Miyaura cross-coupling of a variety of 4- and 5-bromotriazoles we further applied the developed conditions to obtain 1,4,5-trisubstituted 1,2,3-triazoles (Tables 1 and 2). Target 1,4,5-tisubstituted 1,2,3-triazoles were obtained in yields varying from good to virtually quantitative from 4-bromo-1,2,3-triazoles bearing aromatic (**3a**-**3h**), as well as benzylic (**3q**-**3v**) substituents at the nitrogen atom (Table 1). We then tested a variety of boronic acids for coupling: donor substituted (phenyl-, **3b**, **3q**, *para*-, **3a**, **3r** and *ortho*-tolyl, **3c**, **3s**), acceptor substituted (4-fluorophenyl-, **3f**, **3u**; 3-nitrophenyl-, **3l**; 4-acetylphenyl-, **3h**), sterically hindered (1-naphthyl-, **3d**, **3t;** mesityl-, **3g**) aryl- and heteroaryl boronic acids (3-thienyl-, **3e**, **3v**) can be suitable substrates.

Table 1 Suzuki-Miyaura cross-coupling of 4-halotriazoles in water[a]



[a] *Reaction conditions*: 4-halo-1,2,3-triazole (0.5 mmol), $ArB(OH)_2$ (1.2 eq., 0.6 mmol), (THP-Dipp)Pd(cinn)Cl (0.005 mmol), KOH (1.7 eq., 0.85 mmol), Bu_4NBr (0.05 mmol), H_2O (0.8 ml), Δ, 8h. [b] $NaHCO_3$ as a base (3.06 eq.)

5-Bromo-1,2,3-triazoles can be efficiently coupled under the developed conditions (Table 2). Thus, 5-aryl-1,2,3-triazoles, such as N-benzyl (**5a**) and N-phenylethyl (**5e**, **5f**) 1,2,3-triazoles were obtained in virtually quantitative yields. It is worth mentioning that **5a** can be obtained in virtually quantitative yield even in presence of a mild base, $NaHCO_3$. Importantly, the melting temperature of the starting N-substituted 5-bromo-1,2,3-triazole influence the yield of the reaction. Thus, **5d** and **5g** were obtained in 20% and 67% yields, respectively. Most probably, this is due to incomplete melting of the substrate at 100 °C, leading to incomplete homogeneity of the

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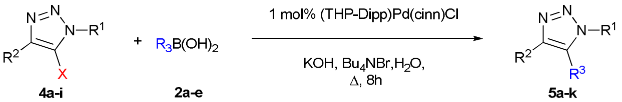
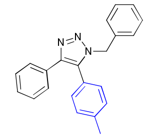
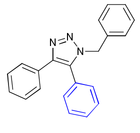
reaction mixture. In these two cases, significant amounts of starting materials were recovered.

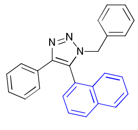
Table 2 Suzuki-Miyaura cross-coupling of 5-halotriazoles in water[a]

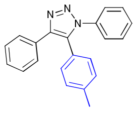


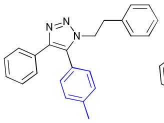
4a-i **2a-e** **5a-k**

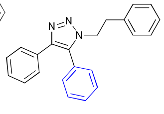

5a (X=Cl, 71%[b], 99%)
(X=Br, 93%)
(X=I, 99%)

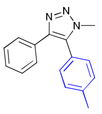

5b (X=Cl, 87%)

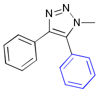

5c (X=Cl, 60%)

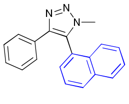

5d (X=Cl, 99%)
(X=Br, 20%)

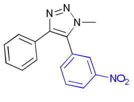

5e (X=Cl, 95%)
(X=Br, 93%)

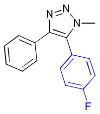

5f (X=Br, 98%)

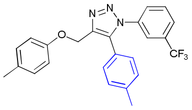

5g (X=Cl, 99%[b], 83%)
(X=Br, 67%)


5h (X=Cl, 99%)


5i (X=Cl, 99%)


5j (X=Cl, 86%[b])


5k (X=Cl, 94%)


5l (X=Cl, 82%)

[a] *Reaction conditions*: 5-halo-1,2,3-triazole (0.5 mmol), $ArB(OH)_2$ (1.2 eq., 0.6 mmol), (THP-Dipp)Pd(cinn)Cl (0.005 mmol), KOH (1.7 eq., 0.85 mmol), Bu_4NBr (0.05 mmol), H_2O (0.8 ml), Δ, 8h. [b] $NaHCO_3$ as a base (3.06 eq.)

To the best of our knowledge, no examples of the Suzuki-Miyaura cross-coupling of chloro-substituted 1,2,3-triazoles were reported to date. A variety of boronic acids can be efficiently coupled with low-melting 4-chloro-1,2,3-triazoles (Table 1, **3i**-**3p**) and 5-chloro-1,2,3-triazoles (Table 2, **5a**-**5e**, **5g**-**5k**) under aqueous conditions in presence of KOH or $NaHCO_3$ as a base. Reactions with donor substituted (**3i**, **5b**, **5h**, **3j**, **3o**, **5a**, **5d**, **5e**, **5g**), acceptor substituted (**3l**, **5k**, **3m**, **5j**), and heterocyclic substituted (**3n**) boronic acids give products with yields from high to virtually quantitative. Sterically hindered 1,4,5-trisubstituted 1,2,3-triazoles were obtained in lower yields (60% for **5c**). Notably, to avoid hydrolysis of the 3-nitrophenylboronic acid in alkali solution, cross-coupling reactions were performed in presence of $NaHCO_3$ as a mild base. Despite that, **3l** and **5j** were obtained in high yields.

In conclusion, we have developed a highly efficient method of the Suzuki-Miyaura cross-coupling of 4- and 5-halo-1,2,3-triazoles in water as a solvent. The reaction is mediated by palladium complex (THP-Dipp)Pd(cinn)Cl bearing expanded-ring carbene and bulky Dipp substituents. Catalytic reaction conditions were optimized to meet the requirements of "green chemistry".[21] The developed cross-coupling protocol has several prominent features: a) the reaction takes place in water with no addition of organic solvents; b) the reaction is carried out under air, no degasation of water is needed; c) mild, cheap, environmentally benign KOH is used as a base; d) low loadings of a phase transfer agent Bu_4NBr. Thus, we developed a versatile, robust, highly active catalytic system for coupling of bromo- and chloro-1,2,3-triazoles. Arylboronic acids bearing donor, acceptor as well as sterically bulky substituents can be efficiently used as coupling partners. To our knowledge, this work is the first systematic study of the Suzuki-Miyaura cross-coupling of 4- and 5-bromo-1,2,3-triazoles as well as the first report on the Suzuki-Miyaura cross-coupling of 4- and 5-chloro-1,2,3-triazoles.

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