Annexure I

List of paper published in referred journals:

1. "Biosynthesis of Poly (ethylene glycol)- supported Palladium nanoparticles using Colocasia esculenta leaf extract and their catalytic activity for Suzuki -Miyaura cross- coupling reaction." **Raju Kumar Borah**, Hirok Jyoti Saikia, Abhijit Mahanta, Utpal Bora and Ashim Jyoti Thakur*, *RSC Advances*, **2015**, 5, 72453-72457.

2. "A green synthesis of palladium nanoparticles by Sapindus mukorossi seed extract and use in efficient room temperature Suzuki–Miyaura cross-coupling reaction." **Raju Kumar Borah**, Abhijit Mahanta, Anurag Dutta, Utpal Bora and Ashim Jyoti Thakur*, *Applied Organometallic Chemistry*, **2017**, e3784.

3. "Copper Oxide nanoparticles as a mild and efficient Catalyst for N-Arylation of imidazole and aniline with boronic Acids at room temperature." **Raju Kumar Borah**, Prasanta Kumar Raul, Abhijit Mahanta, Andrey Shchukarev, Jyri-Pekka Mikkolac, Ashim Jyoti Thakur* *Synlett*, **2017**, 28, 1177-1182.

4. "A convenient room temperature *ipso*-nitration of arylboronic acid catalyzed by molecular iodine using zirconium oxynitrate as nitrating species: An experimental and theoretical investigation." Abhijit Mahanta, Nanda Kishor Gour, Plaban Jyoti Sarma, **Raju Kumar Borah**, Prasanta Kumar Raul, Ramesh Chandra Deka, Ashim Jyoti Thakur*, Utpal Bora*, Applied Organometallic Chemistry, **2019**, e4951.

Annexure II

Lists of Seminar/Workshop attended and paper presented.

1. Poster presentation on "Synthesis of palladium nanoparticles using Sapindus mukorossi seed extract as reducing agent and its use in efficient room temperature Suzuki-Miyaura cross-coupling reaction" at International conference on "Sophisticated Instruments in Modern Research" held on Central Instruments Facility, IIT Guwahati, July, 2017.

2. Poster presentation on "Poly (ethylene glycol)-supported palladium nanoparticles synthesized using Colocasia esculanta leaf extract as bioreducing agent and their catalytic activity in Suzuki-Miyaura cross coupling reactions" at the national seminar on Emerging Trends in Chemical Sciences, 2015, held at Gauhati University, November, 2015.

3. Poster presentation on "Copper oxide nanoparticles as an efficient catalyst for Chan-Lam reactions of aryl boronic acid and aniline derivatives under mild conditions" at the national seminar on Contemporary Developments in Chemical Sciences-2015, held at Tezpur University, November, 2015.

4. Attended the "Science Academics Lecture Workshop on Modern Trends in Chemistry", held at Tezpur University, Assam, November, 2036.

5. Attended the 20th National Magnetic Resonance Society (NMRS) Symposium cum Annual Meeting, held at Tezpur University, Assam, February, 2014.

6. Attended National Workshop on Crystallography Education, held at Gauhati University, Assam, November, 2014.

7. Attended the Science academies lecture workshop on "Emerging Trends in Chemical Sciences", held at Tezpur University, Assam, November, 2016.

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FULL PAPER

WILEY Applied Organometallic Chemistry

A convenient room temperature *ipso*-nitration of arylboronic acid catalysed by molecular iodine using zirconium oxynitrate as nitrating species: An experimental and theoretical investigation

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A simple and convenient protocol has been developed for *ipso*-nitration of arylboronic acid catalysed by molecular iodine at room temperature, using zirconium oxynitrate as the nitrating species. The protocol is applicable to electronically diverse aryl- and heteroarylboronic acid moieties under mild reaction conditions with good to excellent isolated yields. Furthermore, a theoretical investigation has been performed for the same reaction, and reaction profiles are modelled using modern density functional theory (DFT). DFT-based results support the experimentally observed results.

KEYWORDS
iodine, *ipso*-nitration, zirconium oxynitrate

1 | INTRODUCTION

In the challenging domain of synthetic organic chemistry, nitration of arenes has emerged as one of the most fundamental and important organic transformation reactions, both for academic interest and industrial applications. In real terms, over the decades, nitroarenes have shown their potentialities by contributing to varieties of important areas like pharmaceuticals, dyes and plastics.[1–4] They have also been used as explosives and precursors for azo dyes.[5] This indispensable significance in organic synthesis may be attributed to their easy availability, ease of transformation to other functional groups and the ability of nitroaryl moieties to impart tunable physical and chemical properties to many structurally targeted organic molecules. In general, the traditional method for synthesis of nitroarenes involves electrophilic nitration of arenes in the presence of excess amount of conc. sulfuric acid and nitric acid under harsh reaction conditions which are problematic, primarily due to the involvement of strong acid and secondly to the requirement of high temperature. Another common reagent for nitration of arenes is dinitrogen pentoxide, which is a hazardous oxidizer and an important reservoir[6,7] for NOx that are responsible for ozone layer depletion and acid rain. Additionally, regioselectivity is a major issue in traditional methods as the reaction is often associated with other oxidation products and mixtures of isomers.[8] Therefore, looking for some efficient alternative strategies eliminating the drawbacks of existing methodologies has significance which has attracted considerable attention among researchers and has become a long-standing challenge for synthetic organic chemists. In contemporary organic synthesis, as far as nitration of arenes is concerned, *ipso*-nitration occupies a much superior position. In 2009, Fors and Buchwald reported[9] the nitration of aryl chlorides, triflates and nonaflates to nitroaromatics catalysed by Pd. It is a fascinating protocol, but use of expensive ligand-based Pd catalyst limits its practical application. An efficient Cu-catalysed protocol for the

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Biosynthesis of poly(ethylene glycol)-supported palladium nanoparticles using *Colocasia esculenta* leaf extract and their catalytic activity for Suzuki–Miyaura cross-coupling reactions†

Raju Kumar Borah, Hirak Jyoti Saikia, Abhijit Mahanta, Vijay Kumar Das, Utpal Bora and Ashim Jyoti Thakur*

A simple and green protocol for the synthesis of poly(ethylene glycol) stabilized palladium nanoparticles under ambient conditions from the aqueous extracts of *Colocasia esculenta* leaves has been reported. The nanoparticles are characterized using UV-visible spectroscopy, FTIR spectroscopy, XRD and SEM analysis. The prepared Pd NPs showed excellent catalytic activity towards Suzuki–Miyaura cross coupling reactions for a wide variety of aryl halides and phenyl boronic acid substrates. The catalytic system was found to be recyclable and could be reused in subsequent catalytic runs without significant loss of activity.

From their inception, the palladium-catalyzed carbon–carbon bond forming reactions developed by Heck, Negishi and Suzuki have had a vital impact in the development of modern synthetic organic chemistry.[1,2] Such coupling reactions have wide applications in the production of polymers, agrochemicals, and pharmaceutical intermediates.[3,4] Their widespread use is mainly due to the mild conditions associated with these reactions and also with their compatibility to a wide variety of functional groups. Nowadays, metal nanoparticles (NPs) are considered to be very attractive and efficient catalysts compared to their bulk counterparts since they have high surface to volume ratios and also their surface atoms are very active. In recent years, much attention had been focused by the researchers on palladium nanoparticle (Pd NP) synthesis because of their remarkable physical, chemical, optical and thermodynamic properties.[21] Because of these unique properties, Pd NPs find many applications in the field of catalysis[5] and drug delivery.[6] Nowadays, Pd NPs of various sizes and shapes are synthesized by different wet synthetic processes such as chemical,[7] sonochemical[8] and polyols reduction.[9] These types of synthetic processes are generally simple, provide high growth rate and high yield. However, these methods are not environment friendly and therefore some alternative methods are in continuous search for the synthesis of NPs. Biological materials such as plant extracts, microorganisms *etc.* can be used as nanofactories for the synthesis of NPs as they have the reduction potential required for the synthesis and also in addition, they act as stabilizers.[10,11] The use of biological materials such as plant extract for the synthesis of NPs offer several advantages of eco-friendliness and are compatible for pharmaceutical and other biomedical applications as they do not use any toxic chemical for their synthetic protocols.[22] Also, the processes are cost effective, environment friendly and can easily be scaled up for large scale synthesis. Hence, there is a huge demand for these types of simple, inexpensive and easily accessible catalysts which can be generated through green procedure for these coupling reactions. As far as biosynthesis of Pd NPs is concerned; very few reports are available for their synthesis. Few recently reported biological synthesis for Pd NPs are peel extract of *Annona squamosa* (sugar-apple),[12] leaf extract of *Anacardium occidentale* (cashew nut),[13] *Cinnamom zeylanicum* (cinnamon) bark extract,[14] and *Musa paradisiaca* (banana) peal extracts.[15] The biologically synthesized Pd NPs have been used for various applications in recent years such as in azo dye decolorization[16] and as a catalyst for Heck reaction.[17] Therefore, immense opportunities are available for synthesizing Pd NPs using biological materials which can be used for various environmental and biological applications. The present work deals with biosynthesis of Pd NPs using *Colocasia esculenta* Linn. (*C. esculenta*) leaf extract as reducing agent followed by evaluation of catalytic activity of biosynthesized Pd NPs in Suzuki cross coupling reactions. *C. esculenta*, locally known as 'kochu' (Fig. 1) in Assam, a North Eastern State of India is widely available and used by folks in traditional system of medicine in north-eastern India.

Due to the compositional abundance of ascorbic acid, thiamine, riboflavin, niacin, carbohydrates, fats *etc.* in its leaves may be responsible for its reductive potency.[18] In this context, one of our laboratory groups has recently reported the utilization of *C. esculenta* leave extract for the preparation of

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FULL PAPER

WILEY Applied Organometallic Chemistry

A green synthesis of palladium nanoparticles by *Sapindus mukorossi* seed extract and use in efficient room temperature Suzuki–Miyaura cross-coupling reaction

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A simple and green method for the synthesis of palladium nanoparticles using an aqueous extract of *Sapindus mukorossi* seed has been demonstrated. The synthesized nanoparticles were characterized using UV–visible spectroscopy, powxder X-ray diffraction, energy-dispersive X-ray analysis and transmission electron microscopy. The nanocatalyst was successfully utilized in an efficient Suzuki–Miyaura cross-coupling reaction at room temperature.

KEYWORDS
boronic acid, palladium nanoparticles, *Sapindus mukorossi*, Suzuki–Miyaura

1 | INTRODUCTION

The Suzuki–Miyaura cross-coupling reaction is considered to be one of the most elegant and powerful tools for constructing C─C bonds, particularly in the formation of biaryls – a structural motif found in many products of commercial importance.[1,2] Since the first report of palladium-catalysed Suzuki coupling of aryl halides and arylboronic acids,[3] the reaction has undergone tremendous developments as far as the catalyst, reaction conditions and substrate scope are concerned. Now, it has reached a status of respect in modern chemistry. The credit can be attributed to the mild reaction conditions involved and also due to the tolerance to wide varieties of functional groups. The catalytic system used for such coupling reaction is generally either Pd(0) or Pd(II) species, in some cases together with suitable phosphine- or nitrogen-based ligands.[4] Owing to the sensitivity of the catalytic species to oxygen and moisture, the palladium-catalysed Suzuki reaction is generally performed under inert atmosphere or involving hazardous organic solvents. On the other hand, availability, stability and cost of the palladium species are the main drawbacks of this reaction. However, from the green chemistry perspective, environmentally friendly solvents such as water,[5] ionic liquids[6] or supercritical carbon dioxide[7] are considered to be more favourable alternatives compared to organic solvents.

This is an era of emergence and applications of nanocatalysis due to the peculiar size-dependent properties of nanoparticles (NPs).[8] Often, this high catalytic activity is attributed to high surface area of NPs compared to the bulk counterparts. Pd NPs of various shapes and sizes are generally prepared using a variety of chemical and physical methods. In wet chemical methods, Pd NPs are synthesized via the reduction of Pd(II) species in the presence of stabilizing agents,[9] capping agents or solid supports, which can control both their size and morphology.[10] Though the synthesized Pd NPs show excellent catalytic activity, there are some demerits associated with these methods. Examples are the requirement of high temperature, ultrasonication, etc., thereby making the process tedious and time-consuming, contamination from precursor chemicals, use of toxic solvents and formation of by-products which are environmentally not benign. Common physical methods for their synthesis include attrition and pyrolysis involving large energy input.[11] Consequently, there are continuing demands for the development of green and eco-friendly routes for the synthesis of NPs in a single synthetic step with minimum loss of chemicals in environmentally friendly solvents.

Biological feedstocks such as plant extracts, microorganisms, etc., can be used for the synthesis of NPs[12] as they have the required potential for the reduction of Pd(II) to Pd(0).[13] The advantages of biological methods over

Copper Oxide Nanoparticles as a Mild and Efficient Catalyst for N-Arylation of Imidazole and Aniline with Boronic Acids at Room Temperature

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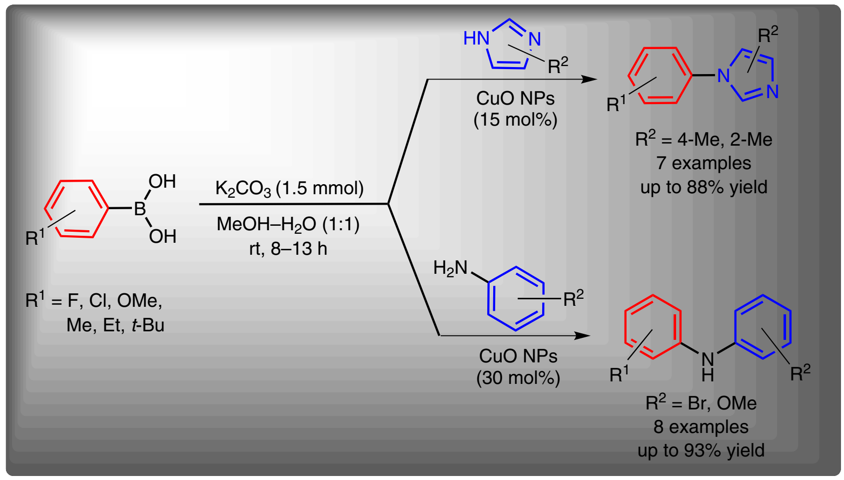

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Abstract The present work describes the excellent catalytic activity of copper(II) oxide nanoparticles (NPs) towards N-arylation of aniline and imidazole at room temperature. The copper(II)oxide NPs were synthesized by a thermal refluxing technique and characterized by FT-IR spectroscopy; powder XRD, SEM, EDX, TEM, TGA, XPS, BET surface area analysis, and particle size analysis. The size of the NPs was found to be around 12 nm having a surface area of 164.180 $m^2\ g^{-1}$.The catalytic system was also found to be recyclable and could be reused in subsequent catalytic runs without a significant loss of activity.

Key words nanoparticles, base, N-arylation, aniline, imidazole, reusability

In the domain of organic synthesis, transition-metal-mediated carbon–heteroatom bond-forming reactions have made a significant contribution to the recent growth. Nitrogen-containing compounds can now be easily generated by transition-metal-catalyzed protocols that find diverse applications in the field of advanced organic synthesis. Among them diarylamines and *N*-arylimidazoles attract particular interest due to their widespread presence in natural products, agrochemicals, materials, dyes, pharmaceuticals,[1] and biologically active inhibitors.[2]

Buchwald and Hartwig developed a method for palladium-catalyzed cross-coupling of aryl halides and triflates with amines.[3] Though the process is credited with milder reaction conditions than Ullmann reaction,[4] there are some limitations, such as difficulties associated with aryl halides having free N–H groups[5] and the use of expensive palladium sources and ligands.

Considering the above facts, in 1998 Chan, Evan, and Lam[6] developed a mild and efficient protocol for copper-mediated oxidative amination, where arylboronic acids were used as arylating agents instead of aryl halides. Arylboronic acids are organometallic moieties possessing wide applicability in contemporary organic synthesis owing to their stability, structural diversity, and low toxicity.[7] However, the requirement of 1–2 equivalents of $Cu(OAc)_2$ and large excess of arylboronic acid[8] are drawbacks associated with this cross-coupling methodology. Further work on the Chan–Lam coupling reaction resulted in its catalytic version[9] along with its application to other nucleophiles for cross-coupling reactions such as amides,[10] oximes,[11] and sulfoximines.[12] Subsequently, a large number of modifications has been made using different copper salts in the presence of various ligands to improve the efficiency of the reaction.[10–12] However, the long reaction times and high reaction temperatures are disadvantages associated with these protocols and thus, a further optimization is desirable in the case of this reaction.

Additionally, in line with recent trends, nanoparticles (NPs) are considered as very efficient and attractive catalysts compared to their macroscopic counterparts due to their high surface-to-volume ratio as well as very active surface atoms. Although many methods are available for the synthesis of NPs, routes that are based on solution-based processes are more effective leading to well-controlled shapes, sizes, and structures. Amongst the metal NPs, copper-based NPs hold a superior position due to their versatil-