Appendix

LIST OF PUBLICATIONS

- **Dutta, A.**, Saikia, R. A., and Thakur, A. J. A Mechanistic approach to Liquid assisted mechanochemical synthesis of 5-aryl/spiro-[1,2,4]-triazolidine-3-thiones. *European Journal of Organic Chemistry*, e202101472, 2022.
- Saikia, R. A., **Dutta, A**., Sarma, B., and Thakur, A. J. Metal-free regioselective *N2*-Arylation of 1*H*-Tetrazoles with Diaryliodonium Salts. *The Journal of Organic Chemistry*, 87(15):9782-9796, 2022.
- Baruah, M. J., **Dutta, A**., Biswas, S., Gogoi, G., Hoque, N., Bhattacharyya, P. K., and Bania, K. K. Fe_2O_3 Nanocatalysts supported on Zeolite-Y for the selective synthesis of *C2*-diindolyl indolones and isatins. *ACS Applied Nano Materials***,** 5(1):1446-1459, 2022.
- **Dutta, A**., Mahanta, A., Thakur, A. J., and Bora, U. Biocatalysis with Baker's yeast: A green and sustainable approach for C–B bond cleavage of aryl/heteroarylboronic acids and boronate esters at room temperature. *Sustainable Chemistry and Pharmacy*, 19:100363-, 2021.
- Abha Saikia, R., Barman, D., **Dutta, A**., and Thakur, A.J. *N1*-and *N3*-arylations of hydantoins employing diaryliodonium salts via copper (I) catalysis at room temperature. *European Journal of Organic Chemistry*, 2021(3):400-410, 2021.
- Bora, S. J., Paul, R., **Dutta, A**., Goswami, S., Guha, A. K., and Thakur, A. J. Trinuclear Mn^{2+}/Zn^{2+} based microporous coordination polymers as efficient catalysts for ipso-hydroxylation of boronic acids. *Dalton Transactions*, 49(17):5454-5462, 2020.
- Borah, R. K., Mahanta, A., **Dutta, A**., Bora, U., and Thakur, A. J. A green synthesis of palladium nanoparticles by *Sapindus mukorossi* seed extract and use in efficient room temperature Suzuki–Miyaura cross-coupling reaction. *Applied Organometallic Chemistry*, 31(11):e3784, 2017.

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- **Poster presentation**: “On-water synthesis of 5-aryl-1.2.4-triazolidine-3-thiones via domino Michael addition and ring contraction of benzylidene barbiturates and 4-hydroxycoumarins” at International Conference on Emerging Trends in Chemical Sciences, Department of Chemistry, Dibrugarh University, February 26-28, 2018.
- **Poster presentation**: “On-water, chromatography free synthesis of spiro-1,2,4-triazolidones/thiones via tandem Michael addition and ring contraction reaction” at International Conference on Advancement in Science and Technology (ICAST-(2018)) Visva Bharati- Shantiniketan, September 3-4, 2018.
- **Oral presentation**: “Benzylidene barbiturates: A precursor to unusual rearrangement and substitution reactions” at OrganiX-2018: an international conference in chemistry, Department of Chemical Sciences, Tezpur University, December 20-21, 2018.
- **Oral presentation**: “One-pot regio- and diastereoselective synthesis of spiro-[pyrimidine-5,2'-pyrrolizines] *via* multicomponent [3+2] cycloaddition reaction of azomethine ylides” at International Conference on Emerging Trends in chemical sciences (ETCS-2020), Department of Chemistry, Gauhati University, February 13-15, 2020

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A Mechanistic Approach to Liquid-Assisted Mechanochemical Synthesis of 5-Aryl/Spiro-[1,2,4]-triazolidine-3-thiones

Anurag Dutta,[a] Raktim Abha Saikia,[a] and Ashim Jyoti Thakur*[a]

1,3-dimethylbarbituric acid-H_2O mediated liquid assisted mechanochemical route has been developed for the synthesis of a wide array of 5-aryl/spiro-1,2,4-triazolidine-3-thiones, *via in situ* generation of benzylidene/alkylidene barbiturates, followed by tandem, base-driven Michael addition reaction and rearrangement of the pyrimido[4,5-e][1,2,4]triazepine intermediate. The method is an application of mechanochemistry in organic synthesis. It is efficient, easy to follow and avoids the tedious steps of catalyst preparation and chromatographic separation. Moreover, the protocol is compared to "on-water", room temperature approach and the reaction mechanism has been revisited with the aid of experiments.

Introduction

Establishing greener processes for the synthesis of functionalized heterocyclic moieties has become one of the most sought-after milestones in the research community.[1] It has come at the wake of demands for environmentally friendly procedures and obtaining desired targets with high yield and purity. The changes came in replacing organic solvents, energy sources, adding economic value to reaction routes and reducing the generation of chemical waste.[2] Also, turning to non-catalytic approaches, to eliminate the tedious processes of catalyst preparation and associated issues like availability, efficient disposal, extensive reusability and economic viability, is significantly gaining momentum.[3] In addition, the issues of high purity and yield are being addressed by the introduction of chromatography free product isolation techniques.[4] These advancements have led to development of reaction routes which are operationally simple, yet effective to meet the needs of organic and pharmaceutical chemists and therefore, are gaining significance in the promotion of the concept of clean synthesis.[5]

The growth of interests in discovering greener methodologies for organic transformation saw a considerable surge in the applicability of mechanochemical methods to serve the purpose.[6] A plethora of reactions that involved carbon-carbon[7] and carbon-heteroatom bond formation,[8] have been extensively explored. It has led to the application of mechanochemistry in multicomponent reactions and has been furthered by heterocycle synthesis,[9] which includes C–H Allylation and C-2 selective arylation of Indoles,[10,11] alkenylating and heteroarylating N1-protected 1H-Indazoles,[12] multicomponent synthesis of polysubstituted pyrroles and trans-2,3-Dihydropyrroles[13] and the preparation of hydantoins.[14] Another aspect of mechanochemical transformation includes Liquid-assisted grinding (LAG). As, on one hand, the solvent free processes enlist their own advantages, LAG, at many a times, have come up with its own set of merits in promoting chemo selectivity and improvement of yield.[15] The relationship was exemplified by Mack et al. showing dependence of the selectivity of diyne or enyne on the polarity of solvents[16] and by Halasz *et al.* showing the correlation of the rate of reaction with the donor number of solvents.[17] Although, ambiguity regarding the participation of solvent molecules, in the mechanism of both the reactions, is prominent, the mentioned effect cannot be disregarded. Falling in trend towards developing newer methodologies, particularly bearing greener prospects, the synthesis of 1,2,4-triazoles caught our attention. The reason being that ever since the incorporation of the 1,2,4-triazole ring, it has introduced an array of therapeutically important molecules, showing efficient bioactivities such as antimicrobial, antianxiety, antimigraine, antimycotic, anti-inflammatory, sedatives and CNS stimulants.[18,19] Commercially available drugs such as Triazolam, Rizatriptan (antimigraine), Estazolam (anticonvulsant) and Ribavirin (antiviral) also contains the 1,2,4-triazole nucleus.[20] This class of triazole is also the precursor to heteroatomic organic compounds like Mannich bases, thioethers and thioureas, triazolothia-diazoles, diazines azines and azepines and Schiff bases.[21] Furthermore, it is a well-known fact that heterocycles containing Sulphur have proven their efficacy in different arenas of practical applications. In combination with 1,2,4-triazoles, the mercapto and thione derivatives have been exclusively studied for their biological activities.[22] More specifically, the 5-aryl-1,2,4-triazolidine-3-thione derivatives have outperformed a number of over-the-counter anticonvulsant, antioxidant, anti-inflammatory, analgesic, antibacterial, antifungal, antiparasitic, antiurease and anticancer drugs (Figure 1).[23]

Despite the wide range applications of 5-aryl-1,2,4-triazolidine-3-thiones, reports on their synthesis are quite limited.

[a] *A. Dutta, R. Abha Saikia, Prof. A. Jyoti Thakur*
Department of Chemical Sciences
Tezpur University
Napaam, Tezpur, Assam, 784028, India
E-mail: ashim@tezu.ernet.in
https://nanocathetero.wixsite.com/website

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Biocatalysis with Baker's yeast: A green and sustainable approach for C–B bond cleavage of aryl/heteroarylboronic acids and boronate esters at room temperature

Abhijit Mahanta [a,b,1], Anurag Dutta [a,1], Ashim Jyoti Thakur [a,**], Utpal Bora [a,*]

[a] Department of Chemical Sciences, Tezpur University, Tezpur, Napaam, 784028, Assam, India
[b] Department of Chemistry, Digboi College, Tinsukia, 786171, Assam, India

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ABSTRACT

This work shows the application of a cheap biocatalyst, Baker's Yeast, towards quick, water mediated, chemoselective, oxidative hydroxylation of aryl/heteroarylboronic acids and arylboronate esters at room temperature, in a metal and ligand free condition, without the addition of external base or acid. A total of eighteen (18) different types of aryl/heteroaryl boronic acids and arylboronate esters were studied for the applicability of this protocol and the resultant phenols were formed in excellent yields (85–97% isolated). The reaction procedure is easy to follow and takes place at room temperature (25-28 °C) and under weakly acidic conditions (pH ~ 6). Baker's Yeast is a fairly stable substrate, bearing considerably good shelf life. Commercially available Baker's Yeast is very cheap and is required in very less amount (5 mg per mmol of arylboronic acid). Thus, economic viability, easy availability of catalyst and ease of handling the reaction, make this an efficient and facile methodology for the synthesis of diversified phenols.

1. Introduction

Consciousness towards environmental safeguarding has drawn the attention of scientific communities to develop sustainable routes for the synthesis of fine chemicals; thereby, instigating a search for naturally abundant and environmentally benign biochemicals to fulfil the purpose. Thus, application of biocatalysts, especially enzymes, in organic transformations has nowadays turned out to be a popular choice. Their display of versatility and efficient regio-as well as chemoselectivity under mild reaction conditions, fall in the lines of green chemistry and therefore, have prompted to their utility in diverse fields (Mane et al., 2016, Sheldon and Woodley, 2018). However, the enzyme based biocatalysis has not yet seen its full potential, as their laboratory isolation has been only marginally explored. Another aspect of enzymatic catalysis is immobilisation. It is a known fact that the properties of the biocatalyst can be altered by this method but in many a case, it has only led to impoverished catalytic activity due to the distortions in the structure of the enzyme upon interaction with the surface on which it is immobilised (Silva et al., 2013; Hanefeld et al., 2009, Rodrigues et al., 2013; Reis et al., 2019; Sheldon and Pelt, 2013). In addition to this, enzyme catalysis can also demand functional group protection. This only makes the process more tedious (Mateo et al., 2007; Galvao et al., 2018; Pinheiro et al., 2018; Lima et al., 2017). Again, isolated enzymes require the addition of cofactors. Therefore, the processes of biocatalysis has shifted its attention towards employing whole cells instead of isolated enzymes (Silva et al., 2013). Whole cells already contain all of the cofactors and under given conditions, they can continue with the metabolic pathways required for the regeneration of the cell, thereby aiding the process of reusability of the catalyst. The elimination of the process of addition of cofactors eventually eliminates the potential for generating products due to side reactions. Baker's Yeast (*Saccharomyces cerevisiae*), which had been at the centre stage of the bakery industry for centuries, is one such biocatalyst, which generates metabolites *in situ* and these metabolites catalyse various chemical transformations. Despite being a microorganism, it is nontoxic in nature and has been known to catalyse various functional group conversions (Singh et al., 2014; Avalani et al., 2013). Organic transformations such as reduction of ketones to optically active alcohols, particularly, is abundantly found in literature (Sih and

* Corresponding author. Tezpur University Napaam Tezpur, Assam, 784028, India.
** Corresponding author.
E-mail addresses: ashim@tezu.ernet.in (A.J. Thakur), utbora@yahoo.co.in (U. Bora).
[1] Equal contributions.

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Fe_2O_3 Nanocatalysts Supported on Zeolite-Y for the Selective Synthesis of C2 Di-Indolyl Indolones and Isatins

Manash J. Baruah, Anurag Dutta, Subir Biswas, Gautam Gogoi, Nazimul Hoque, Pradip K. Bhattacharyya, and Kusum K. Bania*

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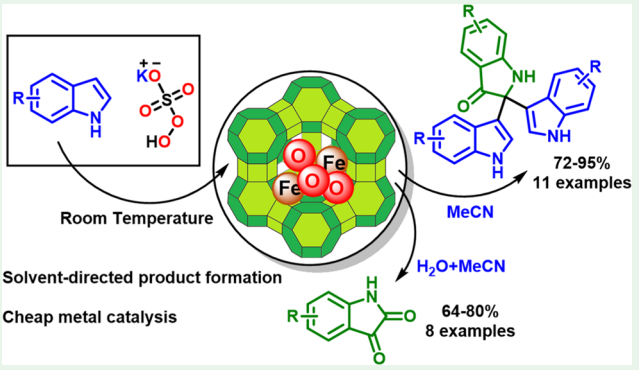
ABSTRACT: Iron-oxide (Fe_2O_3) nanoparticles in the dimension of ~2.3 nm supported on zeolite-Y appeared as an excellent, reusable heterogeneous catalyst for the chromatography-free selective synthesis of 2,2-di(3-indolyl)-3-indolones, a C2-trimerized product. The zeolite-Y-supported Fe-oxide nanocatalyst showed the catalytic activity better than the Pd- and Au-based catalysts in the synthesis of C2 di-indolyl indolones under the prevailing reaction conditions. Besides, this low-cost catalyst displayed the ability to synthesize the pharmaceutically significant isatin molecules with high selectivity. The nature of the solvent and oxidant played a crucial role in the regioselective trimerization of indoles. The selective formation of the C2-trimerized product was accomplished in acetonitrile with peroxymonosulfate (oxone) as the oxidant, while in a water/acetonitrile mixture, it led to the formation of isatin. Compared to many other high-cost catalysts, the cheaper zeolite-Y-supported iron oxide catalyst promoted the reaction at room temperature with high selectivity. The products were obtained within 15−30 min with ≤95% yield. Different pieces of spectroscopic and electrochemical evidence supported by density functional theory (DFT) studies provided strong evidence for the proposed reaction mechanism. The kinetics of the reaction was studied through UV−vis spectroscopy and found to follow first-order kinetics. The UV−vis spectrum of the C2-trimerized product was further evaluated through time-dependent DFT calculations. The CO_2-temperature programmed desorption study indicated the presence of strong basic sites in the Fe_2O_3-Y catalyst, favoring the interaction of the acidic indole molecule with the catalyst surface.



KEYWORDS: *Fe_2O_3-Y, C2 trimerization reaction, C2 trimer, isatin, peroxymonosulfate*

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1. INTRODUCTION

Iron (Fe) being abundant, environment friendly, and an inexpensive metal appears as a suitable candidate for its application in the field of catalysis.[1−3] Different types of organic transformation reactions are known to be catalyzed using a Fe-based catalyst with high selectivity.[4,5] With the advancement in nanoscience and nanotechnology, Fe-based nanocatalysts due to their high abundancy and low cost are gaining importance for different applications including catalysis.[6−8] However, manifesting the loss of activity under certain conditions and the recyclability of the Fe-oxide nanocatalysts remains a challenging area. In this respect, the supported iron catalysts are found to be advantageous due to their controlled growth, easy recoverability, or magnetic separability without hampering the catalytic activity.[9,10] Aluminosilicate supports such as zeolites, halloysite nanotubes (HNTs), and MCM-41 appeared as a suitable support for maintaining the true heterogeneity of the various metal nanocatalysts.[11−13] Iron-oxide nanocatalyst supported on such an inorganic matrix has recently been applied for various catalytic reactions and other applications.[9,12] Very recently, we found halloysite-supported Fe_2O_3 nanocatalyst as an efficient photocatalyst for various alcohol oxidation reactions.[14] Among the different types of aluminosilicates, zeolite-Y with a pore opening of ~0.74 nm and having a super-cage of ~1.3 nm is used as a suitable host for metal catalysts.[15] They are also known as "zeozymes" as zeolite-Y can provide a similar steric and confinement effect similar to that of metalloenzymes.[16] So far, different types of metal complexes and metal nanocatalysts are synthesized within the super-cage of zeolite-Y or on the zeolite support.[15,17,18] Zeolite-Y having both external and internal surface hydroxyl groups favor a good metal-to-surface interaction.[19] Zeolite-Y is known to be an excellent hard

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Metal-Free Regioselective N^2-Arylation of 1*H*-Tetrazoles with Diaryliodonium Salts

Raktim Abha Saikia, Anurag Dutta, Bipul Sarma, and Ashim Jyoti Thakur*

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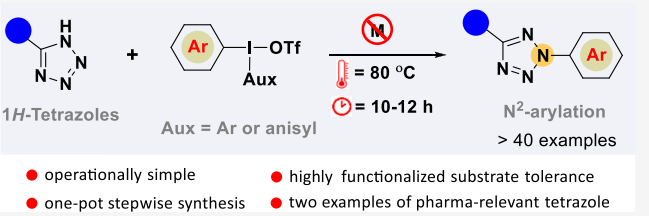
ABSTRACT: We describe a simple, metal-free regioselective N^2-arylation strategy for 5-substituted-1*H*-tetrazoles with diaryliodonium salts to access 2-aryl-5-substituted-tetrazoles. Diaryliodonium salts with a wide range of both electron-rich and previously challenged electron-deficient aryl groups are applicable in this method. Diversely functionalized tetrazoles are tolerable also. We have devised a one-pot system to synthesize 2,5-diaryltetrazoles directly from nitriles. The synthetic utility of this method is furthered extended to late-stage arylation of two biologically active molecules.



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Tetrazoles (Tzs) and their N-substituted compounds are highly privileged nitrogen-rich heterocycles owing to their occurrence in several important bio-active compounds (Figure 1).[1] In addition to this, the Tz moiety has been found in compounds having applications in material science (photography and military)[2] and agriculture as herbicides.[3] Owing to the presence of a large number of nitrogen atoms in the Tz moiety, it is useful as an environmentally friendly gas generator.[4] Since 1*H*-Tz can be formulated as a bio-isostere of carboxylic acids, drugs possessing 1*H*-5-substituted tetrazoles (1*H*-Tzs) are widely useful as antibacterial agents, antihypertensive agents, and so forth.[5] For example, valsartan (**II**), a drug containing 1*H*-Tz, is a multibillion-dollar angiotensin-II receptor antagonist used for the treatment of high blood pressure and heart failure.[6] Likewise, both 1,5-disubstituted tetrazoles (1,5-Tzs)[7] and 2,5-disubstituted tetrazoles (2,5-Tzs)[8] have been studied in a few biologically active compounds, and they reveal a bio-isosteric nature with an amide bond (**I**). 2-Aryl-5-substituted Tzs display interesting biological activities. HM30181 derivatives (**III**) are remarkable inhibitors of breast cancer resistance proteins (BCRP/ABCG2).[9]

The traditional and practical approach to access 2-aryl-5-substituted Tzs is via the Kakehi methodology, where potentially explosive aryl diazonium salts and phenyltosylhydrazones are used (Scheme 1a).[10] Another route to avail 2,5-Tzs is N^2-arylation of tetrazolic N−H under transition-metal-catalyzed[11] or metal-free conditions.[12] Lam and co-workers back in 1998 mentioned one example of N-arylation between 5-phenyltetrazole and *p*-tolylboronic acid, but a stoichiometric amount of $Cu(OAc)_2$ was used.[13] Another methodology for N^2-arylation was achieved with $Ph_3Bi(OAc)_2$ under copper catalysis.[14] Despite the rationalization of diaryliodonium salts in this N-arylation, it was a metal-catalyzed method, and limited substrates scopes were described.[15] Interestingly, in 2012, Han and co-workers accomplished this task with aryl boronic acids, where Cu_2O was used as a catalyst and high temperature was applied (Scheme 1b).[16] Later, Maegawa et al. improvised this protocol with another catalyst, $[Cu(OH)(TMEDA)]_2Cl_2$, and accomplished the reaction at room temperature (Scheme 1b).[17] These protocols were highly regioselective, and various functionalized Tzs were exemplified; however, electron-withdrawing aryl groups were not discussed. Transition metal catalysts do come with their own set of benefits but pose challenges to the methodologies for the synthesis of marketed drugs, from the perspective of pharmaceutical prospects. In a metal-free arylation approach, Patel and co-workers reported an efficient and robust protocol for regioselective N^2-alkylation or arylation where they rationalized N^2-selectivity via a nitrogen-centered radical (NCR).[12] In their work, they used aryl diacyl peroxides or aryl peroxyanhydrides as the arylating source, and the mechanism was suitably evidenced with both experimental optimizations and density functional theory calculations. Moreover, in the light of the NCR mechanism of N^2 functionalization of Tzs, the Patel group further reported remote functionalization of unactivated C_{sp^3}−H alkyl groups possessing a traceless directing group with Tzs,[18] and Ruan et al. developed benzylic C−H amination of Tzs via electrooxidation including late-stage modification pharmaceutically relevant drugs.[19] Considering the significance of this privileged moiety, 2-aryl-5-substituted tetrazoles, developing a metal-free technique to access these moieties would be beneficial from the perspective of sustainability.

Amidst the advancement of metal-free arylation, diaryliodonium salts have been recognized as a robust and versatile arylating source facilitated with diverse carbon and heter-

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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

Raju Kumar Borah | Abhijit Mahanta | Anurag Dutta | Utpal Bora | Ashim J. Thakur

Department of Chemical Sciences, Tezpur University, Napaam 784028Assam, India

Correspondence
Ashim J. Thakur, Department of Chemical Sciences, Tezpur University, Napaam 784028, Assam, India.
Email: ashim@tezu.ernet.in

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

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N^1- and N^3-Arylations of Hydantoins Employing Diaryliodonium Salts *via* Copper(I) Catalysis at Room Temperature

Raktim Abha Saikia,[a] Dhiraj Barman,[a, b] Anurag Dutta,[a] and Ashim Jyoti Thakur*[a]

Dedicated to Prof. Viktor V. Zhdankin for his outstanding contribution to Hypervalent Iodine Chemistry.

Copper(I)-catalyzed *N*-arylation (both N^1- and N^3-) of hydantoins with diaryliodonium salts as aryl partners at room temperature is reported. The transformation allows diverse scopes on both hydantoins and diaryliodonium salts delivering functionalized N^3-arylated products under mild reaction conditions. The presence of hydrogens at C^5- and N^1- position of the hydantoin does not lead to other side products. Chiral hydantoins can also be synthesized via this methodology. Sterically complicated *ortho*-substituted diaryliodonium salts are tolerated and delivered challenging *ortho*-arylated products. In addition, this strategy can also be effectively extended to N^1-arylation of hydantoins.

Introduction

Biologically active arylated hydantoin (imidazolidine-2,4-dione) derivatives[1] have marked skeletal appearances in a wide array of natural products[2] and synthetic products.[3] This motif is purposely and effectively used in medicinal chemistry,[4] coordination chemistry,[5] agrochemistry,[6] and polymer sciences.[7] Though, structurally simple and first synthesized[8] in 1861, intense research efforts have been devoted to synthetic developments and studies of this class of five-membered compound.[1a] Hydantoin based drugs such as Nilutamide (**1**) and Enzalutamide (**3**) (Figure 1) have been used as *anti*-androgen and *anti*-prostate cancer agents respectively. GLGP-0492 (**2**), BMS-587101 (**4**), and BMS-564929 (**5**) are candidates under clinical development (Figure 1).

In the traditional approach, condensation of aryl isocyanates with amino acid derivatives afforded N^3-arylated hydantoins (Scheme 1a).[9] This strategy required strong acidic or basic conditions during the cyclization of ureido derivatives. Moreover, substituted aryl isocyanates needed extra steps for their syntheses. Moreover, isocyanates are often toxic and unstable under ambient conditions.[10]

Menendez *et al.* pioneered Cu-mediated N^3-arylation of hydantoins (only one example) with *p*-tolyllead triacetate[11] as an arylating source. Thereafter, triarylbismuthane,[12] aryl boronic acid,[12] and aryl iodide[13] were also employed as aryl

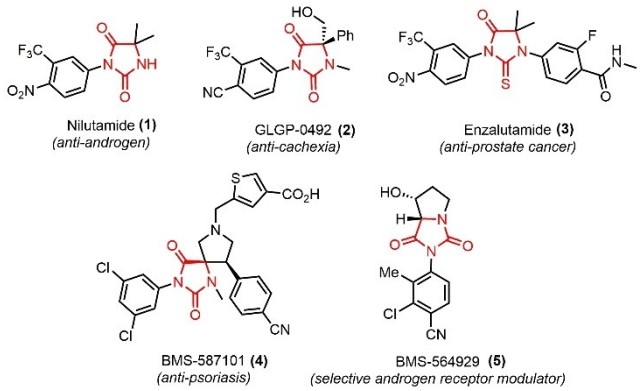

Figure 1. Important hydantoin based drugs.

partners in Cu-mediated protocols (Scheme 1b). Recently, Petit's group re-established the Cu-mediated N^3-arylation and subsequently Cu-catalysed N^1-arylation of N^3-aryl hydantoins using aryl halides (Scheme 1c).[14] Although the method highlighted broad substrate scopes, *ortho*-substituted aryl groups failed to tolerate the reaction condition. Also, N^3-arylation of hydantoins containing both acidic C^5–H and N^1–H exhibited poor selectivity and hence limited hydantoins were studied.

Diaryliodonium salts have emerged as a versatile arylating partner over the past decades because of their ease of synthesis, less environmental impact, affordability, and reactivity within a wide range of nucleophiles.[15] Owing to the presence of an excellent leaving group (aryl iodide), diaryliodonium salts have encompassed their importance in metal-free and transition-metal catalyzed arylation chemistry.[16] Arylation of lactams and primary amides with diaryliodonium salts with the aid of Cu-catalysis has been achieved.[17] Pioneering works on metal-free arylation of a wide range of secondary amides have been reported by Olofsson's group.[18] But, hydantoins (containing imide and amide functional groups)

[a] *R. Abha Saikia, D. Barman, A. Dutta, Prof. A. Jyoti Thakur*
Department of Chemical Sciences
Tezpur University
Napaam-784028, Assam, India
E-mail: ashim@tezu.ernet.in
http://www.tezu.ernet.in/dcs/personal_profile_ajt.html
[b] *D. Barman*
Department of Chemistry
Shiv Nadar University
Greater Noida-201314, Uttar Pradesh, India

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Trinuclear Mn^{2+}/Zn^{2+} based microporous coordination polymers as efficient catalysts for *ipso*-hydroxylation of boronic acids†

Sanchay J. Bora, *[a] Rima Paul,[a] Anurag Dutta,[b] Shyam Goswami,[a] Ankur K. Guha [c] and Ashim J. Thakur [b]

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Two microporous coordination polymers based on hourglass trinuclear building units, $[Mn_3(bpdc)_3(bpy)]\cdot 2DMF$ and $[Zn_3(bpdc)_3(bpy)]\cdot 2DMF\cdot 4H_2O$ (bpdc = 4,4′-biphenyl dicarboxylic acid, bpy = 4,4′-bipyridine), have been synthesized under solvothermal conditions employing DMF as the solvent. Each structure consists of two crystallographically distinct M^{2+} (M1 and M2) centers that are connected *via* carboxylate bridges from six bpdc ligands, generating a trinuclear metal cluster, $[M_3(bpdc)_3(bpy)]$. Cluster representation of the structure resulted in an interpenetrated net of rare **hex** topological type. Catalytic activities of the CPs have been assessed for the oxidative hydroxylation of phenylboronic acids (PBAs) using aqueous hydrogen peroxide (H_2O_2). Various substituted aryl/hetero-arylboronic acids RB$(OH)_2$ [R = phenyl, 2,4-difluorophenyl, 4-aminophenyl, 2-thiophene *etc.*] underwent *ipso*-hydroxylation smoothly at room temperature to generate the corresponding phenols in excellent yields. The main advantages of this protocol are the aqueous medium reaction, heterogeneous catalytic system, and short reaction time with excellent yield.

Introduction

In addition to their widespread application in the field of gas storage and separation,[1–3] Metal–Organic Frameworks (MOFs) or porous coordination polymers (PCPs) have been widely known to be worthy catalysts for a number of organic transformations.[4–11] They belong to a fascinating class of porous crystalline materials built from metal ions/nodes and poly-functional organic linkers.[12–15] The uniform pore sizes/environments and high surface area possessed by these materials provide an edge over traditional microporous and mesoporous materials, including zeolites, mesoporous silica and activated carbon. Although rapid progress has been witnessed in the construction of functional MOFs, it is also a great challenge to rationally prepare and control the structures and compositions of the target molecules with desired properties.[16–19] The most effective and facile method for MOF construction involves intelligent selection of metal ions and multifunctional organic linkers. Dicarboxylate ligands spanning network nodes to link metal centers have proved to be good candidates for the construction of new MOFs.[20–23] Unlike other neutral linker molecules, these anionic dicarboxylate linkers generate infinite coordination networks in which it is not necessary to accommodate other counter ions to achieve electroneutrality. A linear dicarboxylate linker 4,4′-biphenyldicarboxylate has been used extensively in the synthesis of new porous framework materials.[24–27]

Phenols are considered as versatile precursors of a large assemblage of polymers, drugs, herbicides and antioxidants in simple and polyphenolic forms.[28–30] The general procedures for their synthesis involve the nucleophilic substitution of activated aryl halides or Cu-catalyzed conversion of diazoarenes[31] and Pd-catalyzed conversion of aryl halides[32] to the desired products. It is to be noted that the involvement of fairly inactive starting materials in the concerned existing methodologies leads to routes that are either economically not viable for large-scale synthesis or that require harsher conditions such as high temperature, high pressure, handling hazardous chemicals *etc.* Adding to this list is the requirement of additives, solvent issues, lower yields and longer reaction times. The continuing quest for an efficient alternative methodology reveals that arylboronic acids have emerged as excellent starting materials for the synthesis of phenols. The recognition of

[a]*Department of Chemistry, Pandu College, Guwahati-781012, Assam, India. E-mail: sanchay.bora@gmail.com; Tel: +91-361-2570450*
[b]*Department of Chemistry, Tezpur University, Napaam, Tezpur-784028, Assam, India*
[c]*Department of Chemistry, Cotton University, Guwahati-781001, Assam, India*

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