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Original article

A simple, rapid, expedient and sustainable green strategy for the synthesis of benz-/naphthimidazoles

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ABSTRACT

A versatile green chemical procedure for the highly selective construction of 2-aryl substituted benz-/naphthimidazoles starting from the reaction of aromatic 1,2-diamines with a series of substituted arylthioprolines with three to five drops of water under simple grinding at ambient temperature in good yields is described. The short reaction time, simplified experimental procedure, the absence of extraction and chromatographic purification steps in addition to the environment affability makes this green strategy highly attractive in view of green chemistry. The expected reaction to furnish the thiazole grafted benz-/naphthimidazole did not occur. Perhaps the arylthioprolines could be in zwitterionic form, which could react with 1,2-diamine giving dihyrobenzimidazole, which undergoes air oxidation to furnish the 2-aryl benzimidazole rather than the expected thiazole grafted imidazoles.

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1. Introduction

Fused imidazole analogues have acquired a protuberant place in medicinal chemistry due to their noteworthy properties as therapeutics. The benzimidazole structural motif, a renowned biologically interesting N-containing heterocyclic hybrid (Emery et al., 2002; Sondhi et al., 2002) is ubiquitous in diverse naturally occurring and synthetic organic compounds is a vital pharmacophore and is a 'privileged sub-structure' for drug design in medicinal chemistry (Evans et al., 1988; Mason et al., 1999). As these heterocyclic molecular scaffolds involves benzene and imidazole subunits, owing to their electron-rich scaffold and nitrogen atoms, these structural motifs can interact with diverse biological targets (Tahlan et al., 2019). The biological significance of benzimidazole tethered compounds have been highly recognized in the literature (Wright, 1951; Amari et al., 2002). Besides their biological significance, these molecular scaffolds are being employed as synthons for the construction of diverse building blocks and ligands (Samolova et al., 2019). Due to the huge importance as synthons and diverse bioactivities displayed by benzimidazole derivatives (Mederski et al., 2004; Kus et al., 2008) (Fig. 1), efforts have been made for the generation of libraries of these biologically important compounds (Breslin et al., 2003; Valdez et al., 2002). The augmented attention for these molecular scaffolds has also been due to their exceptional stability, bioavailability and noteworthy biological profiles (Yadav and Ganguly, 2015). A thorough retrospect over the reported routes for the synthesis of benzimidazoles reveals plenty of preparative methods (Katritzky and Boulton, 1980) amongst which the two momentous routes involves condensation of *o*-phenylenediamine with (i) aryl aldehydes (Moghaddam et al., 2006) and (ii) carboxylic acids (Dudd et al., 2003) or their analogues like nitriles, amidates and orthoesters (Chi and Sun, 2000; Huang and Scarborough, 1999) at high temperature in the presence of strong acids like polyphosphoric acid (Preston et al., 1981) or mineral acids (Kartritzky and Rees, 1984) and thermal or acid mediated cyclization of *N*-(*N*-arylbenzimidoyl)-1,4-benzo quinoneimines under harsh dehydrating conditions (Benincori and Sannicolo, 1988). Even though, some of these methods are acceptable for the construction of benzimidazoles, there are some disadvantages like the severe reaction conditions, luxurious reagents, usage of lethal organic solvents and prolong reaction times limit the usage of these methodology. Therefore, the research lasts for a better synthetic protocol, in terms of simple workup, economic feasibility, ecofriendly, and in specific with better selectivity as this would extend the scope in organic synthesis.

Advancement of eco-friendly green synthetic protocols for the assembly of new chemical units is acquiring inordinate significance and in current years, organic transformations mediated by

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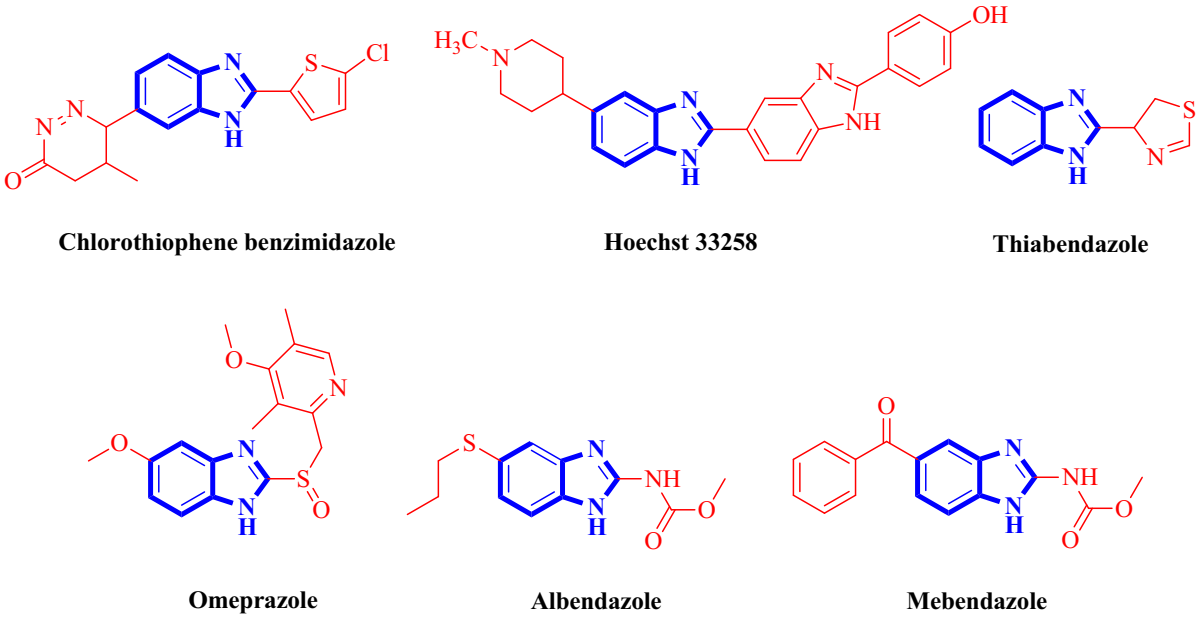


Fig. 1. Selected benzimidazole derivatives of pharmacological and biological interest.

water without employing conventional organic solvents has turn out to be one of the most significant features in synthetic organic chemistry as to meet the ecological demands. Performing organic reactions in water phase is very interesting both from the synthetic view point and also from the influence of the ecological pollution (Lindstrom, 2007). As the benzimidazole structural sub unit is the vital synthon for a variety of compounds of biological interest, there is a continuous and increasing attention over the years for an easy and convenient synthesis of compounds associated with imidazole derivatives. For these reasons and in extension of our earlier works towards the synthesis of novel biologically active hybrid heterocycles containing nitrogen and oxygen through tandem/multicomponent/green chemical transformations (Almansour et al., 2017, 2019; Kumar et al., 2011, 2013, 2018), in the present study, we report a facile, handy and green approach for the construction of benz-/naphthimidazoles under simple grinding with few drops of water. However, this would be the first report for the synthesis of benz-/naphthimidazole analogues employing 1,2-aryldiamine and arylthioprolines.

2. Experimental

*2.1. General procedure for the synthesis of benz-/naphthimidazoles (**3** and **8**)*

An equimolar mixture of mixture of 1,2-diamine **1/7** and substituted arylthioprolines **2** in 3-5 drops of water in a semi micro boiling tube were mixed thoroughly and ground well at ambient temperature. Progress of the reaction was indicated by the transformation of color of the reaction mixture, which became yellow/brown at the end when the reaction is complete. After completion of the reaction as evinced by the appearance of yellow/brown colour, the reaction mixture was dispensed into 50 mL of water. The solid settled down was filtered through a sintered glass crucible and washed repeatedly with water to furnish the benz-/naphthimidazoles as the only reaction product which was further purified by recrystallization from ethyl acetate.

*2.1.1. 2-(2,4-Dichlorophenyl)-5,6-dimethyl-1H-benzo[d]imidazole (**3d**)*

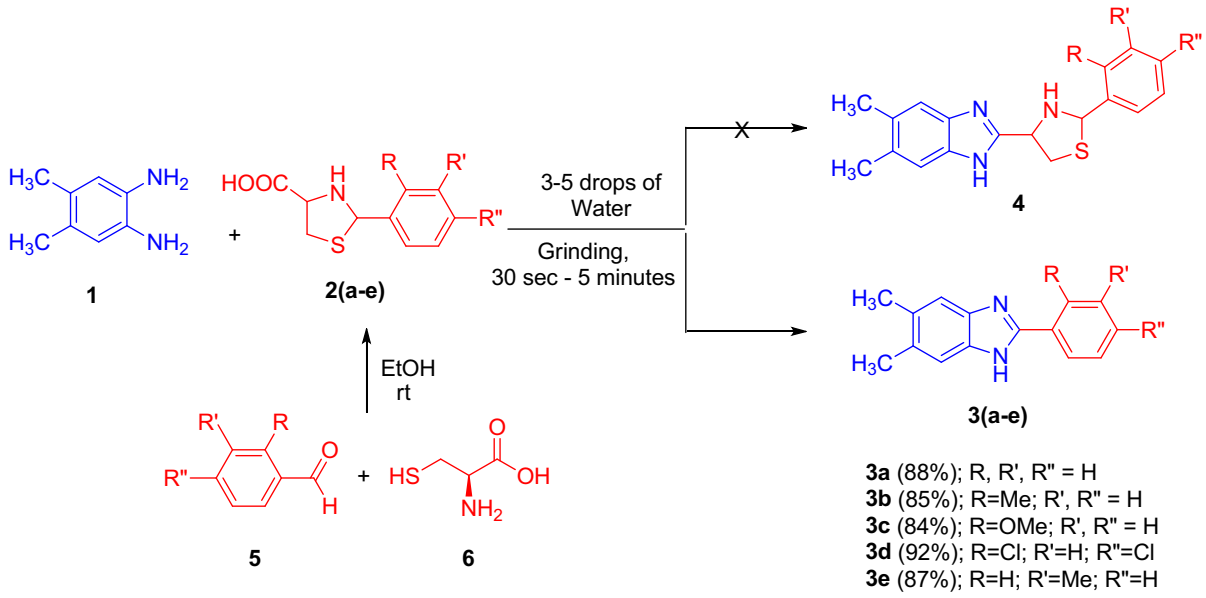
Yellow solid (92%); m.p. 226–227 °C; IR (KBr): 3402, 3029, 1648, 1582 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H2.20 (s, 6H, 2xCH_3), 4.09 (brs, 1H, NH), 6.60 (s, 1H, Ar-H), 6.91 (s, 1H, Ar-H), 7.30 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.43 (s, 1H, Ar-H), 8.18 (d, *J* = 8.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 19.1, 19.8, 117.4, 118.1, 126.6, 127.5, 129.2, 129.8, 132.5, 134.2, 136.1, 136.9, 137.4, 140.8, 150.7. Anal. calcd for $C_{15}H_{12}Cl_2N_2$: C, 61.87; H, 4.15; N, 9.62. Found: C, 61.70; H, 4.27; N, 9.73%.

*2.1.2. 2-(2,4-Dichlorophenyl)-3H-naphtho[2,1-d]imidazole (**8d**)*

Brown solid (85%); m.p. 231–232 °C; IR (KBr): 3408, 3035, 1652, 1596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.25–8.10 (m, 7H, Ar-H), 8.25 (d, *J* = 8.8 Hz, 1H, Ar-H), 9.05 (s, 1H, Ar-H), 10.40 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 116.5, 118.5, 121.6, 125.8, 126.0, 128.8, 129.7, 130.6, 131.2, 133.4, 134.7, 136.0, 136.7, 137.2, 138.9, 141.5, 150.9. Anal. calcd for $C_{17}H_{10}Cl_2N_2$: C, 65.20; H, 3.22; N, 8.94. Found: C, 65.41; H, 3.09; N, 8.85%.

3. Results and discussion

With an aim of developing a sustainable reaction protocol for the construction of imidazoles, we reported in the current study, the reaction of a mixture of 4,5-dimethyl-1,2-phenylenediamine **1** (1 mmol) and substituted arylthioprolines **2**(**a-e**) (1 mmol) with two to three drops of water under simple grinding at ambient temperature for 1–5 min (Scheme 1) furnishing a series of 2-arylbenzimidazoles **3**(**a-e**) in good yields (84–92%). The expected reaction to furnish the thiazole grafted benzimidazole **4** has not been favored (Scheme 1). The aryl substituted thioprolines **2**(**a-e**) required for the present study was synthesized by following the literature reported procedure (Liu et al., 2011), by the reaction of an equimolar mixture of L-cysteine hydrochloride hydrate, $NaHCO_3$ in water (200 mL) with benzaldehyde in ethanol (200 mL). The reaction mixture was stirred for 6 h and the precipitate obtained was filtered using a sintered glass crucible, washed with ethanol, and dried to afford **2**(**a-e**) as white solids.



Scheme 1. Synthesis of 2-aryl substituted benzimidazoles **3**(**a-e**).

For optimizing the reaction conditions and yield of **3**, we started our investigation by considering the model reaction of an equimolar ratio of 4,5-dimethyl-1,2-phenylenediamine (**1**) and 2-(2,4-dichlorophenyl)thiazolidine-4-carboxylic acid (**2d**) under different conditions (Table 1). Initially an equimolar ratio of the aforesaid reactants, **1** and **2d** in 5 mL of water were stirred at room temperature. The reaction progress being evidenced through change of colour of the reaction mixture and also monitored with thin layer chromatographic (TLC) analysis. The reaction progress was monitored at one-minute time intervals. In about two minutes the reaction mixture became yellow, the TLC analysis of the reaction mixture revealed the formation of a sole product without any side products. After completion, the reaction mixture was kept aside for 15 min. The precipitate settled down was then filtered carefully, washed with 50 mL of water and dried in vacuum, the yield of **3d** obtained by this method was found to be 83% (Entry 1). In order to enhance the yield and to further reduce the reaction time, in a separate experiment the same reactants in 5 mL of water was heated under reflux, as expected the reaction time has considerably been reduced. The reaction was completed in 1 min, affording a gummy solid, TLC analysis revealed the formation of the product along with minor impurities. The reaction mixture was extracted and recrystallized from ethyl acetate to furnish the benzimidazole **3d** in 78% yield (Entry 2). In a different attempt, the above model reaction was performed under neat conditions in the absence of solvent. The two reactants were simply mixed and ground thoroughly in a semi micro boiling tube, the reaction progression was monitored after each one-minute time interval. The reaction was completed in about 5 min, affording the product **3d** in 81% yield (Entry 3). Furthermore, to ensure thorough mixing of aryldiamine **1** and substituted arylthioproline **2d**, the reaction mixture was ground well in a semi micro boiling tube at ambient temperature with three drops of water. Progress of the reaction is being revealed by the weakening color of the reaction mixture, which became yellow at completion of the reaction. To our surprise, the reaction was completed in just 1 min and afforded solely the benzimidazole without the formation of any side products and therefore neither crystallization nor column chromatography was required for purification. Then 50 mL of water was added to the reaction mixture and the precipitate obtained was filtered to afford pure 2-(2,4-dichlorophenyl)-5,6-dimethyl-1H-benzo[*d*]imidazole in an excellent yield (92%). The results obtained were consolidated in Table 1, it is clearly evident from the above experiments that the best results were obtained by entry 4, in terms of yield and reaction time. Continuous monitoring of the reaction progress was not required in the optimized method as the reaction is completed in just 1 min and the reaction scale up does not envisage any decrease in either the yield or purity of the product, since the reaction necessitates only an in-depth mixing of the reactants at ambient temperature. The reactions with other substituted thioprolines **2**(**a-c**) and **2e** were performed under the optimized conditions, all these reactions afforded good yields of the product as expected in short reaction time. Among the five benzimidazoles synthesized, compounds **3a**, **3c** and **3e** with phenyl, 2-OMe phenyl and 3-Me phenyl rings respectively has already been reported in the literature. There are plenty of literature reports available for the synthesis of **3a** employing different reagents and conditions both by conventional and green chemistry approaches. Nguyen et al. Synthesized compound **3a** by a cobalt- or iron-catalyzed redox condensation of 2-nitroanilines and benzylamines under a solvent-free conditions. The reaction was carried out at 120 °C for 24 h affording a reasonable yield (80%) of the product (Nguyen et al., 2013). Rostamizadeh et al. performed the reaction of o-phenylenediamine and benzaldehyde in 1 M solution of glucose at 60 °C. Although the reaction for the synthesis of **3a** has been carried under green chemical approach, a quite long time of 7 h has been consumed for its completion (Shahnaz et al., 2011). Mukhopadhyay and Tapaswi (Mukhopadhyay and Tapasw, 2008) reported PEG-mediated synthesis of **3c** under solvent free condi-

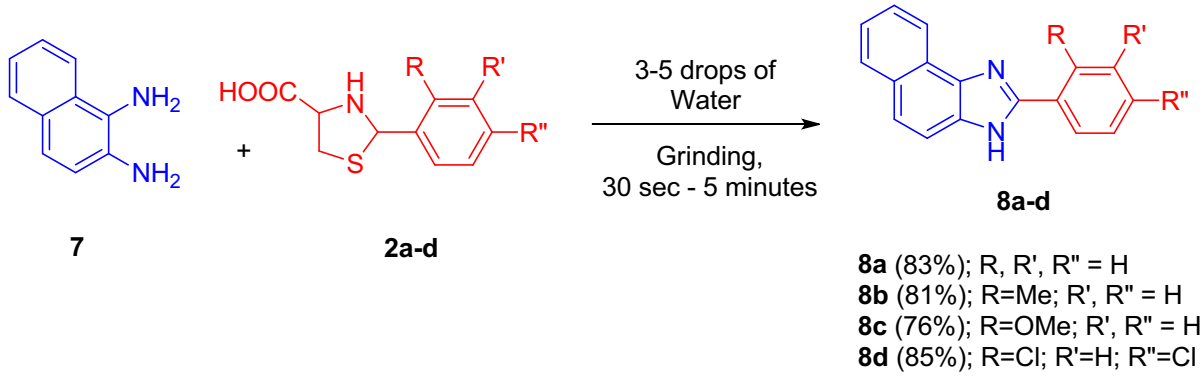
Table 1
Optimization of the reaction conditions for the synthesis of **3d**.

Entry	Reaction condition	Reaction time	Yield (%) of 3d[a]
1	Stirring at ambient temperature with 5 mL of water	2 min	83
2	Heating under reflux with 5 mL of water	1 min	78
3	Simple grinding at ambient temperature under solvent free condition	5 min	81
4	Simple grinding at ambient temperature with 3 drops of water	30 s	92

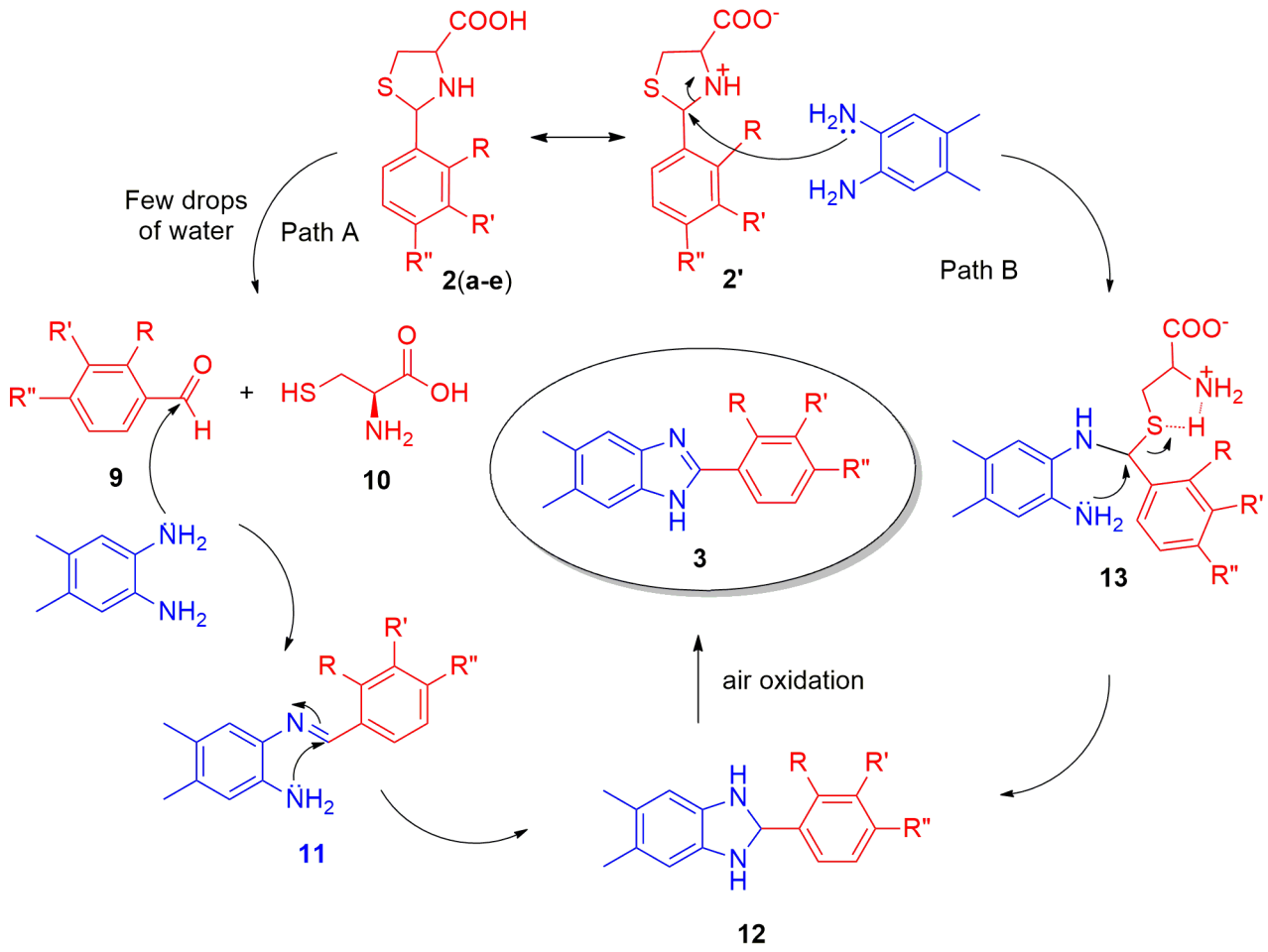
[a] Isolated yield.

tions. Even though a good yield of the product has been achieved, the reaction was performed at a quite high temperature, 110 °C. Singh and his co-workers (Singh et al., 2013) reported the two-step synthesis of **3e** starting from benzoylisothiocyanates and *ortho*-phenylenediamines. The bisthioureas obtained undergoes cyclization on refluxing in pyridine furnishing **3e** in 87% yield. The synthetic methodology described by us in the present study is advantageous than the above reported procedures for the synthesis of benzimidazoles of this kind with respect to short reaction time, operational simplicity and eco-friendliness. So far, no method has been reported for the synthesis of benzimidazoles (**3**) employing arylthioprolines and aromatic diamines.

A careful structural elucidation of benzimidazoles **3** was accomplished with the help of NMR spectroscopic and elemental analysis data. As a distinguishing case, structural explanation of compound **3d** is discussed here. In the ^{1}H NMR, the singlet at 2.20 ppm can be ascribable to two $-CH_3$ groups while the other singlets in the downfield region at 6.60, 6.91 and 7.43 ppm are due to the aromatic ring protons. A doublet at 7.30 ppm (J = 8.0 Hz) is attributed to one of the aromatic ring protons of 2,4-dichloro phenyl ring. The other doublet at 8.18 ppm with J = 8.8 Hz related by a H,H-COSY correlation is due to the remaining aromatic ring protons. In ^{13}C NMR spectrum (vide supplementary data), the two methyl carbons resonated at 19.07 and 19.77 ppm whereas the aromatic carbons



Scheme 2. Synthesis of 2-aryl naphthimidazoles (**8**).



Scheme 3. Plausible mechanism for the formation of 2-aryl benzimidazoles **3.**

appeared between 117.36 and 150.71 ppm. The structure of other compounds was also arrived through similar considerations and all new compounds were in agreement with their analytical and NMR spectroscopic data.

The versatility of this green protocol was further investigated by performing the reaction with a different diamine viz. 1,2-diaminonaphthelene **7**. The reaction with this aromatic bicyclic diamine was performed adopting the optimized synthetic procedure. As in the previous cases, the naphthimidazoles **8**(**a-d**) were also obtained in good yields (76–85%) (Scheme 2). Among the naphthimidazoles **8**(**a-d**) synthesized, compound **8a** has already been reported in literature by different research groups employing different synthetic methodologies. In one of the reports by Reddy et al. (Reddy et al., 1994), the synthesis of compound **8a** involved a three-step reaction sequence starting from acetylnaphthelene in the presence of polyphosphoric acid at high temperatures. The yield obtained in this three-step reaction is low when compared to the yield obtained in the present study. Naphthoimidazole **8a** has also been synthesized using different reagents and conditions. Our methodology for the synthesis of naphthoimidazole **8a** is more advantageous that the reported methods in terms of reaction time, yield and safety. The structure of other compounds is in agreement with their NMR spectroscopic and analytical data, whilst the spectroscopic and physical data of the known compound correlate well with the reported results. The position and electronic or steric properties of the substituent at the aromatic ring of arylthioprolines **2**(**a-e**) does not have any major influence on the yield or rate of the reaction. All the reactions (Scheme 1 and 2) proceeded well and afforded the benz-/naphthimidazoles in good yields. To the best of our knowledge the method developed in the present study is more advantageous than the literature reported methods.

A probable mechanism for the formation of benz-/naphthimidazoles (**3**/**8**) is shown in scheme 3. There are two plausible mechanistic routes, in the first pathway (Path A), the arylthioprolines **2**(**a-e**) in the presence of few drops of water may dissociate into benzaldehyde (**9**) and 2-amino-3-mercaptopropanoic acid (**10**). The sp3 carbon of amino acid **2** was attacked by a hydroxyl group of water molecule furnishing the benzaldehyde **9** and 2-amino-3-mercaptopropanoic acid. The benzaldehyde obtained may react with 1,2-diamine (**1**) to give the imine intermediate **11** which upon intramolecular cyclization, i.e., the amine group attacks the electrophilic iminocarbon affording the dihydrobenzimidazole (**12**). The dihydrobenzimidazole (**12**) upon air oxidation may furnish the final 2-aryl benzimidazoles (**3**). In a separate experiment, the arylthioproline in presence of few drops of water was stirred/ground well, we didn't observe the dissociation of arylthioproline in to benzaldehyde as postulated. Therefore, the possibility of this pathway was ruled out. In the second pathway (Path B), perhaps the arylthioprolines could be in zwitterionic form, which could react with 1,2-diamine giving dihyrobenzimidazole, which undergoes air oxidation to furnish the 2-aryl benzimidazole (**3**).

4. Conclusions

In conclusion, the present work describes a versatile, handy and environment friendly protocol for the synthesis of 2-substitued benz-/naphthimidazoles by the reaction of substituted 1,2-pheny lene-/naphthalenediamines with arylthioprolines under simple grinding at ambient temperature. The synthetic methodology described in the present study is advantageous than the synthetic procedures reported in the literature for the synthesis of benz-/naphthimidazoles of this kind with respect to selectivity, short reaction time, operational simplicity and eco-friendliness. Further, studies on the synthesis of a wide range of heterocyclic hybrids employing green chemical transformations are under progress in our research group.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jksus.2020.09.001.

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