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RESEARCH ARTICLE

Natural Bio-surfactant for Pseudomulticomponent Synthesis of 2-Aryl-1-aryl Methyl-1*H*-benzimidazoles

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Abstract: Green chemistry emphasizes the development of environmentally benign chemical processes and technologies. Pseudo-multicomponent synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles using o-phenylenediamine and aromatic aldehydes is carried out by Brønsted acid type bio-surfactant as a catalyst. The green features of this method include the use of biodegradable catalyst obtained from renewable resource *i.e. Citrus Limonium* extract as bio-surfactant type Brønsted acid, which provides a micellar media for effective cyclocondensation. The critical micellar concentration (cmc) of biosurfactant was determined by conductivity method and visualized by light microscopy measurement. Identity of all pure compounds was ascertained on the basis of FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques.

Keywords: Aromatic aldehydes, bio-surfactant, Brønsted acid, biodegradable catalyst, *Citrus limonium*, benzimidazole.

1. INTRODUCTION

Heterocycles play important role for the design and discovery of new compounds of pharmaceutical applications [1]. Benzimidazoles are important structural motif exhibiting significant activity against several viruses such as HIV [2], herpes (HSV-1) [3], RNA [4]. Benzimidazoles act as DNA minor groove binding agents with antitumor activity [5], anticancer activity [6]. Their diverse applications comprise their role as potential angiotensin II inhibitors [7], 5-lipoxygenase inhibitors for use as novel anti-allergic agents [8], factor Xa (FXa) inhibitors [9], and ADP-ribose polymerase (PARP) inhibitors [10]. Some recently reported methods regarding benzimidazole synthesis are use of catalyst such as $VO(acac)_2$ [11], β-cyclodextrin (ZrO_2-β-CD) [12], KOB*u*t [13], Amberlite IR-120 [14], bnmim-HSO_4 [15], MoO_3/CeO_2-ZrO_2 [16], CAN [17], ([Hbim]BF_4) [18], L-Proline [19], $SnCl_2.2H_2O$ [20], Co-SBA~15 [21]. Although all these reactions can be efficient and selective but they often involve expensive reagents, drastic reaction conditions and tedious work up procedures. Therefore, it was thought that there is scope for improvement especially towards developing a green protocol for synthesis of benzimidazoles. Pseudomulticomponent reactions are multicomponent reactions in which at least one of the two reactants take part in two or more reaction steps. When two of the three or more components are identical, the reaction is better designated as pseudo-MCRs. Even though incorporation of two identical components in the product of a pseudo-MCR exhibits severe limitation in terms of scope and functional flexibility, these transformations follow advantage of being very time-efficient, allowing for the rapid, sometimes spectacular, generation of molecular complexity. Particularly valuable are pseudo-MCRs involving successive but distinct and complementary reactivity's of the same component [22].

Biosurfactants being natural and promising surfactants because have certain advantages over chemical surfactants, such as their lower toxicity, their biodegradable nature, and their ecological acceptability. Some surfactants are biologically produced by yeasts or bacteria and are grouped as glycolipids, lipopeptides, fatty acids, polymeric and particulate compounds [23, 24]. One of the fundamental properties of surfactants is there self-association into organized molecular structure such as micelles, vesicles, microemulsions, bilayers, membranes and liquid crystals [25]. The simplest class of association colloids is the micelle. Micellisation characteristics of surfactant are determined by micellization parameters such as critical micellar concentration(CMC), aggregation number *etc*. Combined Brønsted acid surfactant catalysts have also been employed in several organic reactions [26]. Considering the significance of surfactants, in this communication, *Citrus limonium* extract (CLE) was chosen as catalytic media without using any external promoters, external acids, ligands, biphasic media and ionic liquids. The catalytic medium is sourced from the direct extraction of

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Lemon fruit. A solution containing surfactants presents appreciable changes in physical and chemical properties at the critical micelle concentration (CMC). CMC is the concentration of surfactants above which micelles form spontaneously. Efficient surfactants have very low CMC values, *i.e.*, less surfactant is required to decrease surface tension [27, 28].

An intriguing line in the development of eco-friendly methodologies is being fueled by the basic paradigm shift from the use of traditional catalysts to natural catalyst. Different natural materials are used as solid support as well as catalysts in many reactions promoting the formation of final products. Natural materials such as clays, zeolites, enzymes, and different plant parts such as fruits, roots, leaves are used effectively in numerous chemical transformations. The applications of an aqueous extract of different parts of plants have witnessed a rapid development. In literature, a number of organic reactions are reported in which natural catalysts like clay [29-31], phosphates [32, 33], gold [33] and animal bone [34] are employed. In recent years, chemical reactions using plant cell cultures and part of plants as biocatalysts have received great attention [35-37]. The biocatalytical transformations using edible plants [38], plant root, [39, 40], plant tubers [41] and plant leave extract [42] can be applied in many organic reactions. Fruit extract is also naturally occurring source which was used as biocatalysts in organic synthesis [43].

The main objectives of this protocol are to develop an efficient synthetic process for the facile cyclocondensation of o-phenylenediamine and aldehydes under mild reaction conditions. The operational simplicity of the process without the need for special handling is also noteworthy. This new protocol for benzimidazoles can be accomplished with excellent yields for a broad range of aromatic aldehydes.

Phytochemical study showed the presence of limonoids, flavonoids and catechins [44] (Fig. **1**) present in lemon which may form micelles and help to forward the reactions in proper direction. In addition to this *Citrus Limonium* extract (CLE) exhibits acidic pH (2.3). In view of this data and in continuation of our ongoing research in the development of green synthetic methodologies [45, 46], we thought that, this amazing medium may serve as Bronsted acid-type biosurfactant, better alternative to chemical surfactants and to harmful corrosive acids for pseudomulticomponent synthesis of benzimidazoles.

2. RESULTS AND DISCUSSION

Fresh *Citrus Limonium* fruits were cut using knife and then pieces were pressed manually using domestic presser to obtain turbid extract. The turbid extract was then filtered through cotton/muslin cloth and then through filter paper to remove solid material to get clear extract. The pH of extract of every batch was measured using pH meter (ProLab 3000 laboratory pH meter) before use and it was found to be 2.1-2.3. The prepared catalyst was stored several days at 5°C and used for the synthesis of benzimidazole derivatives.

When o-phenylenediamine (1 mmol) 1 and various aromatic aldehydes (2 mmol) 2 were treated by employing CLE catalyst in ethanol at different temperatures (Scheme **1**), both expected products *viz*. 2-aryl-1H-benzimidazoles 3 and 2-aryl-1-arylmethyl-1H-benzimidazoles 4 were obtained depending on the reaction temperature and solvent employed. The best overall yields and selectivity's were obtained in ethanol at 80°C temperature, in which only N-substituted benzimidazoles 4 were produced.

Initially, to optimize the reaction conditions, we examined the condensation of *o*-phenylenediamine (1 mmol) **1** and benzaldehyde (2 mmol) **2** as a model reaction in the presence of CLE (0.5 mL) at room temperature in the absence of Co-surfactant. Surprisingly, contrary to our expectation, only 2-phenyl-1*H*-benzimidazole **3a** was obtained in 20

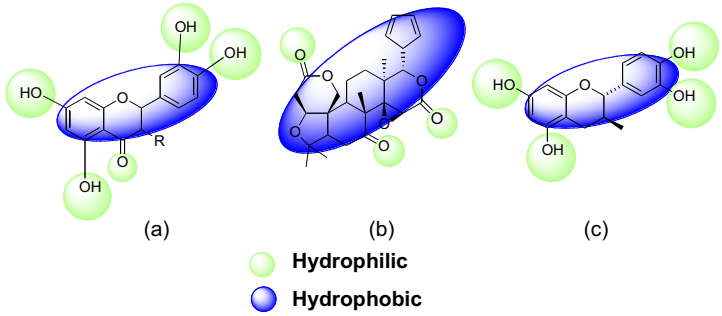
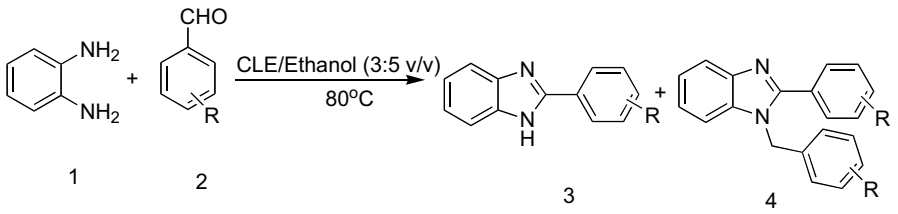


Fig. (1). Phytochemicals producing micelles (**a**) Flavonoids, (**b**) Limonoids and (**c**) Catechin.



Scheme (1). Synthesis of benzimidazoles.

Table 1. Optimization of reaction parameters for 2-aryl-1-aryl methyl-1H-benzimidazole 4a formation[a].

Entry	Amount of Catalyst (mL)	Co-surfactant 5 (mL)	Catalyst: Co-surfactant Ratio	Temp. (^{o}C)	Time (min)	Yield[b] (%)	
						3a	4a
1	0.5	--	--	RT	180	20	00
2	3.0	--	--	RT	180	27	00
3	5.0	-	-	RT	180	30	00
4	10.0	-	-	RT	180	33	00
5	5.0	--	--	80	180	31	60
6	5.0	Methanol	1:1	80	30	00	81
7	5.0	Ethanol	1:1	80	30	00	90
8	5.0	Iso-propanol	1:1	80	30	00	86
9	5.0	t-butanol	1:1	80	30	00	82
10	2.0	Ethanol	2:5	80	45	00	51
11	3.0	Ethanol	3:5	80	45	00	92
12	7.0	Ethanol	7:5	80	45	00	86
13	10.0	Ethanol	2:1	80	45	00	70
14	15.0	Ethanol	3:1	80	45	00	49
15	5.0	Ethanol	1:1	RT	180	36	00
16	--	Ethanol	-	80	180	00	00

[b]Reaction condition: Aromatic aldehyde (2 mmol), o-phenylelediamine (1 mmol) isolated yield.

% yield (Table **1**, entry 1). Expected N-substituted derivative 1-benzyl-2-phenyl-1*H*-benzo[*d*]imidazole **4a** was not obtained. On the increase in the catalytic amount from 0.5 to 10 mL, slight improvement was observed in the yield of **3a** without formation of any traces of **4a** (Table **1**, entry 2-4).

We continued our efforts for improvement in the result when model reactants were allowed to react at elevated temperature (80^{o}C) without co-surfactant, in the presence of 5 mL CLE, after 3 h, surprisingly both the products **3a** and **4a** were obtained (first observed on TLC) in 31 and 60 % yield respectively (Table **1**, entry 5). Since co-surfactnt properties play a crucial role in organic synthesis, the effect of co-surfactnt was studied for the synthesis of benzimidazoles. (Table **1**, entry 6-9). It was found that ethanol was a more efficient co-surfactant for the present transformation (Table **1**, entry 7). The results led us to examine co-surfactant effect for this condensation.

Ethanol at higher temperature worked as a co-surfactant leading to selective synthesis of **4a** along with enhanced product yield. It was also noticed that the condensation using co-surfactant proceeded rapidly and was superior to the reported procedures with respect to the reaction time and yield of product. We also optimized the surfactant:co-surfactant ratio for model reaction by changing amount CLE (Table **1**, entry 10-14). The result showed that CLE:Ethanol ratio at just above cmc (33 %) is a suitable medium for smooth conversion of reactant to the product with respect to time and yield (Table **1**, entry 11). At ambient temperature with same reaction conditions, 36 % yield of **3a** was obtained (Table **1**, entry 15). Moreover, the catalyst-free condition was also examined; the result observed was viscous reaction system and no product formation which indicates that the role of bio-surfactant is decisive for benzimidazoles formation (Table **1**, entry 16).

Initially on stirring, the reaction mixture turned to yellow turbid emulsion, (Fig. **2a**) which implies that there is the formation of micelles or micelle-like colloidal aggregates which was visualized through an optical microscope (Fig. **2b**). CMC is the narrow concentration range over which amphiplic or surfactant solution shows an abrupt change in physical property such as electrical conductivity, surface tension, osmotic pressure, density, light scattering, or refractive index [47]. The aggregation of organic ingredients from CLE during reaction condition results in the semi-ordered structure of micelles protruding into aqueous phase whereas the hydrophobic parts are brought to close proximity in the core of the aggregate excluding water. When organic compounds are introduced in an alcoholic micellar solution, hydrophobic interactions will cause binding of these compounds to the micelles and get collected in the core of micelle where the reaction occurs more easily. This further confirmed that, the catalyst does not simply provide the acidic medium to activate the substrate molecules but also helps to aggregate all the reactants into micelles.

Electrical conductivity method was employed to determine the critical micelle concentration (cmc) and it was found to be 33 % v/v (Fig. **3**). This helped us to maintain better surfactant:co-surfactant ratio for this cyclocondensation.

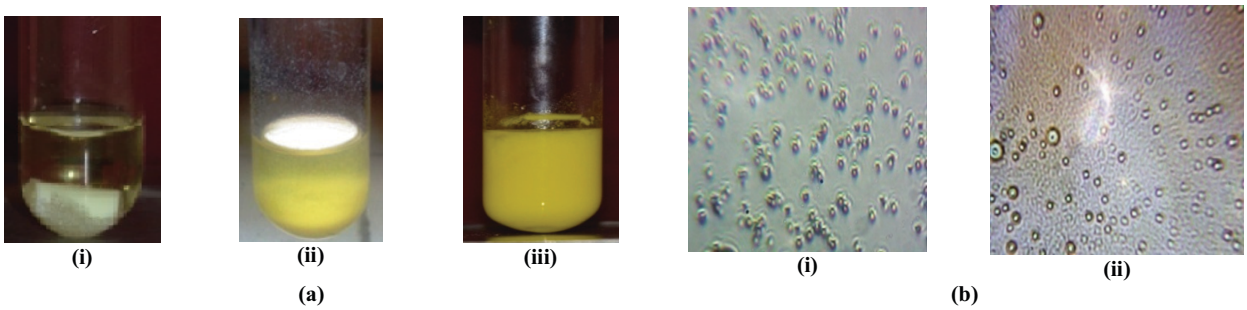


Fig. (2). (**a**) Reaction mixtures at different stages, (i) at starting: 0 min, (ii) after: 10 min, (iii) after completion of reaction: 30 min; (**b**) Optical micrograph of reaction mixture, (i) normal view [40x magnification], (ii) magnified view [100x magnification].

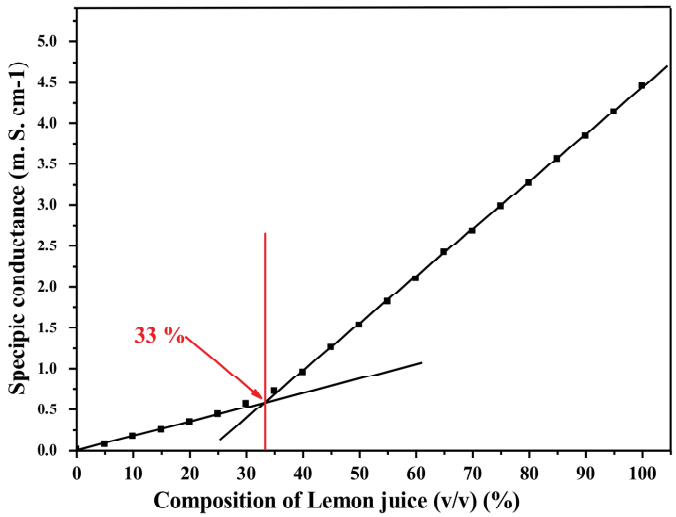


Fig. (3). Critical micelle concentration (cmc) obtained from plot of specific conductance against percentage composition of bio-surfactant in ethanol.

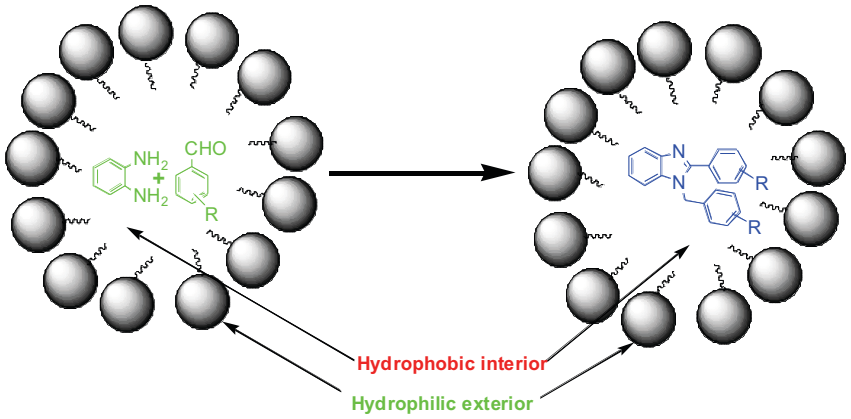


Fig. (4). Mechanistic picture of role of micellae for Benzimidazole formation.

The micelle formation occurs above CMC at which the monomers undergo self-assembly to form aggregate in the solution. This caused the solution converted from true solution to become a colloidal system. The micellar solution is known as a colloidal dispersion (association colloid) of organized surfactant molecules. The micelle formed in the solution is spherical structure which the hydrophilic head group was exposed to the solution while the hydrophobic tails were faced toward the interior of the micelle structure (Fig. **4**).

Table 2. Recyclable properties of CLE catalyst.

Run	1	2	3	4	5
% Yield	92	92	90	85	82

Table 3. CLE catalyzed synthesis of 2-aryl-1-aryl methyl-1H-benzimidazole derivatives[a].

Sr. No.	Aldehydes	Product	Time (min)	Yield[b] (%)
1	C_6H_5	4a	30	92
2	4-ClC_6H_4	4b	25	92
3	4-OHC_6H_4	4c	35	88
4	4-$CH_3C_6H_4$	4d	40	84
5	4-$OCH_3C_6H_4$	4e	35	89
6	4-$NO_2C_6H_4$	4f	20	94
7	2-ClC_6H_4	4g	30	90
8	2-$NO_2C_6H_4$	4h	25	92
9	2-OHC_6H_4	4i	40	86
10	4-$(Me)_2NC_6H_4$	4j	45	86
11	2-OH,5-NO_2 C_6H_3	4k	40	90
12	4-FC_6H_4	4l	40	90
13	5-OC_2H_5,4-OHC_6H_3	4m	45	84
14	2, 5-$OCH_3C_6H_3$	4n	45	81
15	4-OH,5-$OCH_3C_6H_3$	4o	45	84
16	3-Br,4-FC_6H_3	4p	20	92
17	2-F,4-BrC_6H_3	4q	25	91
18		4r	50	83
19		4s	45	86

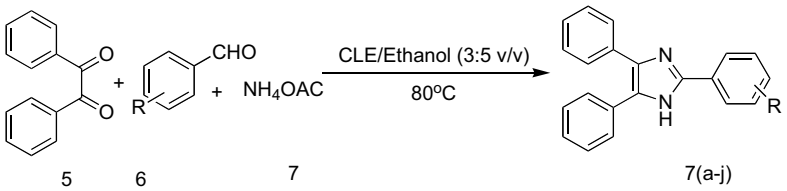
[a]Reaction conditions: *o*-phenylenediamine (1 mmol), aromatic aldehyde (2mmol), bio-surfactant (3 mL), ethanol (5 mL), 80°C temperature.

[b]Isolated yield based on *o*-phenylenediamine.

Co-surfactants are weakly amphiphilic molecules, which are assumed to concentrate in the surfactant layer of the aggregates formed by the primary surfactant. Due to their weak amphiphilic character, co-surfactants alone do not form aggregates, but they strongly support aggregation of the primary surfactant [48]. Alcohols being a good co-surfactant when used with surfactants, it can lower the surface tension and reduce the emulsion size. Alcoholic -OH head group can fit into the gap between the surfactant molecules providing bonus steric repulsion. Due to reduction in micellar size, there is more aggregation of substrate molecules, enhancing the solublisation effect for better conversion of reactants into products. Short chain co-surfactant molecules like ethanol can more easily accommodate themselves among the surfactant molecules at the droplet interface thereby releasing this bending stress [49]. Both the surfactant property and strong Bronsted acidity of CLE are essential to promote the reaction efficiency.

In order to investigate the recyclability and reusability of lemon extract, we synthesized compound 4a, after appropriate work-up (see experimental), lemon extract was treated with activated charcoal and, after filtration, was used for re-synthesis of 4a. Synthesis was performed five times and the influence of recycling lemon extract on yields of 4a is shown (Table **2**). As can be seen, lemon extract can be reused five times without any appreciable loss in catalytic activity, clearly proving its recyclability and reusability.

In order to evaluate the generality of the process, scope and limitation of the catalysts, several diversified examples illustrating the present method for the 2-aryl-1-aryl methyl-1*H*-benzimidazoles **4** were examined. The reaction of o-phenylenediamine with various aromatic aldehydes bearing electron withdrawing groups or electron releasing groups was carried out in optimized reaction conditions. The product obtained were good to excellent yield, which are normally observed under the influence of strong acids. The results obtained in the current method are illustrated in Table **3**. From results, it was revealed that aldehydes having electron withdrawing groups reacted very well at faster rate compared with aromatic aldehydes substituted with electron releasing



Scheme (2). Synthesis of 2, 4, 5-trisubstituted imidazole derivatives 7.

Table 4. CLE catalyzed synthesis of 2, 4, 5-trisubstituted imidazole derivatives[a].

Sr. No.	Aldehydes	Product[a]	Time (min)	Yield[b](%)
1	C_6H_5	7a	40	90
2	4-ClC_6H_4	7b	25	92
3	4-OHC_6H_4	7c	40	84
4	4-MeC_6H_4	7d	40	82
5	4-$NO_2C_6H_4$	7e	25	90
6	4-$MeOC_6H_4$	7f	30	86
7	4-$(Me)_2NC_6H_4$	7g	30	83
8	2-OH,3-OMe C_6H_3	7h	40	84
9	2,5-$(OMe)_2$ C_6H_3	7i	45	81
10	4-FC_6H_4	7j	50	84

[a]Reaction conditions: Benzil (1 mmol), aromatic aldehyde (1 mmol), ammonium acetate (2 mmol) bio-surfactant (3 mL), ethanol (5 mL), 80°C temperature.

[b]Isolated yield based on benzil.

groups. A heterocyclic aromatic aldehyde such as 2-furaldehyde and 2-thiophine aldehyde could also react efficiently to afford the corresponding benzimidazole derivatives with a good yield (Table **3**, entry 18, 19).

Based on recently reported method for the synthesis of trisubstituted imidazoles from simple and easily available starting materials under much milder reaction conditions [50], we extended present protocol for the synthesis of highly substituted imidazoles by performing one-pot condensation (Scheme **2**) in CLE:EtOH (3:5, v/v) at 80°C. The feasibility of the reaction is tested on various aromatic aldehydes with 1,2-dicarbonyl compound (benzil) and ammonium acetate. The results obtained are in good yield and are summarized in Table **4**. In all cases, the products are isolated in stipulated time and are characterized by their IR, ^{1}H NMR,^{13}C NMR spectroscopy.

3. EXPERIMENTAL

3.1. General Procedure for the Synthesis of 2-aryl-1-arylmethyl-1H-benzimidazoles 4(a-s)

To the reaction mixture containing *o*-phenylenediamine (1 mmol) **1**, aromatic aldehyde (2 mmol) **2**, freshly prepared CLE (3 mL) and ethanol (5 mL) was added. Then the reaction mixture was stirred at 80°C on preheated oil bath for appropriate time mentioned in Table **2**. The progress of reaction was monitored by TLC (n-hexane:ethyl acetate, 3:1). The crude product **4** obtained after cooling at room temperature were separated by filtration and washed with 10 mL of cold water by twice to remove the catalyst and dried in vacuum. The pure product was obtained by recrystallization from 96% ethyl alcohol and their identity was ascertained on the basis of FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. The physical and spectroscopic data are in consistent with the proposed structure and is in harmony with the literature values. Similar procedure was applied for the synthesis of 2, 4, 5-trisubstituted imidazole derivatives in which aromatic aldehydes, benzil and ammonium acetate were employed as a substrate in 1:1:2 proportion respectively.

CONCLUSION

To the best of our knowledge, this is the first report of an environmental-friendly protocol for benzimidazole cyclocondensation reaction carried out in CLE as bio-surfactant type Brønsted acid. In the present scheme, we project biosurfactant nature of catalyst obtained from renewable resource which provides green, efficient and eco-compatible process for the selective pseudomulticomponentsynthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles by one-pot reaction. The use of readily available and biodegradable catalyst in replacement to hazardous acids and toxic chemical surfactants is a promising alternative for the organic reactions. This method also offers to overcome the problem of obtaining two possible products in reaction mixture for benzimidazole synthesis by varying the temperature conditions.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's website along with the published article.

REFERENCES

[1] (a) Couladourous, E.A.; Strongilos, A.T. *Angew. Chem. Int.*, **2002**, *41*, 3677-3680. (b) Gan, Z.; Reddy, P.T.; Quevillon, S.; Couve-Bonnaire, S.; Arya, P. *Angew. Chem. Int.*, **2005**, *44*, 1366-1368.

[2] Porcari, A.R.; Devivar, R.V.; Kucera, L.S.; Drachand, J.C.; Townsend, L.B. *J. Med. Chem.*, **1998**, *41*(B), 1252-1262.

[3] Migawa, M.T.; Girardet, J.L.; Walker, J.A.; Koszalka, G.W.; Chamberlain, S.D.; Drach, J.C.; Townsend, L.B. *J. Med. Chem.*, **1998**, *41*(B), 1242-1251.

[4] Hirashima, S.; Suzuki, T.; Ishida, T.; Noji, S.; Ando, I.; Komatsu, M.; Ikede, S.; Hashimoto, H. *J. Med. Chem.*, **2006**, *49*, 4721-4736.

[5] Tanious, F.A.; Hamelberg, D.; Bailly, C.; Czarny, A.; Boykin, D.W.; Wilson, W.D. *J. Am. Chem. Soc.,* **2004**, *126*, 143-153.

[6] Hong, S.Y.; Kwak, K.W.; Ryu, C.K.; Kang, S.J.; Chung, K.H. *Bioorg. Med. Chem.*, **2008**, *16*, 644-649.

[7] Kohara, Y.; Kubo, K.; Imamiya, E.; Wada, T.; Inada, Y.; Naka, T. *J. Med. Chem.*, **1996**, *39*, 5228-5235.

[8] Nakano, H.; Inoue, T.; Kawasaki, N.; Miyataka, H.; Matsumoto, H.; Taguchi, T.; Nagai, H.; Satoh, T. *Bioorg. Med. Chem.*, **2000**, *8*, 373-380.

[9] Zhao, Z.S.; Arnaiz, D.O.; Griedel, B.; Sakata, S.; Dallas, J.L.; Whitlow, M.; Trinh, L.; Post, J.; Liang, A.; Morrissey, M.M.; Shaw, K. *J. Bioorg. Med. Chem. Lett.*, **2000**, *10*, 963-966.

[10] White, A.W.; Almassy, R.; Calvert, A.H.; Curtin, N.J.; Griffin, R.J.; Hostomsky, Z.; Maegley, K.; Newell, D.R.; Srinivasan, S.; Golding, B.T. *J. Med. Chem.*, **2000**, *43*, 4084-4097.

[11] Dhar, S.S.; Dey, M.; Deb, K. *Chem. Lett.*, **2011**, *22*(3), 296-299.

[12] Girish, Y.R.; SharathKothanahally, K.S.; kumar, S.S.; Thimmaiah, K.N.; Rangappa, K.S.; Shashikanth, S. *RSC Adv.*, **2015**, *5*, 75533-75546.

[13] Xiang, S.K.; Tan, W.; Zhang, D.X.; Tian, X.L.; Feng, C.; Wang, B.Q.; Zhao, K.Q.; Hu, P.; Yang, H. *Org. Biomol. Chem.*, **2013**, *11*, 7271-7275.

[14] Nile, S.H.; Kumar, B.; Park, S.W. *Arabian J Chem.*, **2015**, *8*(5), 685-691.

[15] Sapkal, S.B.; Shelke, K.F.; Sonar, S.S.; Shingate, B.B.; Shingare. M.S. *Bull. Korean Chem. Soc.*, **2009**, *30*(5), 1057-1060.

[16] Rathod, S.B.; Lande, M.K.; Arbad, B.R. *Bull. Korean Chem. Soc.*, **2010**, *31*(10), 2835-2840.

[17] Kidwai, M.; Jahan, A.; Bhatnagar, D. *J. Chem. Sci.*, **2010**, *122*(4), 607-612.

[18] Nadaf, R.N.; Siddiqui, S.A.; Daniel, T.; Lahoti, R.J.; Srinivasan, K.V. *J. Mol. Catal. A Chem.*, **2004**, *214*, 155-160.

[19] Adapa, S.R.; Varala, R.; Nasreen, A.; Enugula, R. *Tetrahedron Lett.*, **2007**, *48*(1), 69-72.

[20] Duan, L.P.; Li, Q.; Wu, N.B.; Xu, D.F.; Zhang, H.B. *Chin. Chem. Lett.*, **2014**, *25*, 155-158.

[21] Rajabi, F.; De, S.; Luque, R. *Catal Lett.*, **2015**, *145*(8), 1566-1570.

[22] Castillo, J.C.; Quiroga, J.; Abonia, R.; Rodriguez, J.; Coquerel, Y. *J. Org. Chem.*, **2015**, *80*(19), 9767-9773.

[23] Sarubbo, L.A.; Farias, C.B.B. *Curr. Microbiol.*, **2007**, *54*, 68-73.

[24] Khopade, A.; Biao, R.; Liu, X.; Mahadik, K.; Zhang, L.; Kokare, C. *Desalin.*, **2012**, *285*, 198-204.

[25] Shah, S.S.; Shah, S.W.H.; Naeem, K.; Somasundaran, P.; Hubbard, A. *Surfactant dye aggregate*, *Encyclopedia of surface and colloid science*, Marcel Dekker, Inc, **2006**, 6082.

[26] Firouzabadi, H.; Iranpoorand, N.; Garzan, A. *Adv. Synth. Catal.*, **2005**, *347*,1925-1928.

[27] Sarubbo, L.A.; Luna, J.M.; Campos-Takaki, G.M. *Electron. J. Biotechnol.,* **2006**, *9*, 400-406.

[28] George, S.; Jayachandran, K. *Appl. Biochem. Biotechnol.*, **2009**, *158*, 694-705.

[29] Ramesh, E.; Raghunathan, R. *Synth. Commun.*, **2009**, *39*, 613-625.

[30] Habibi, D.; Marvi, O. *Arkivoc*, **2006**, xii, 8-15.

[31] Zahouily, M.; Mounir, B.; Charki, H.; Mezdar, A.; Bahlaouan, B.; Ouammou, M. *Arkivoc*, **2006**, xiii, 178-186.

[32] Zahouily, M.; Bahlaouan, B.; Rayadh, A.; Sebti, S. *Tetrahedron Lett.*, **2004**, *45*, 4135-4137.

[33] Genin, E.; Toullec, P.Y.; Marie, P.; Antoniotti, S.; Brancour, C.; Genet, J.P.; Michelet, V. Gold catalysis in organic synthesis: efficient intramolecular cyclization of γ-acetylenic carboxylic acids to 5-exo-alkylidene-butyrolactones *Arkivoc*, **2007**, *67*, 68.

[34] Riadi, R.; Mamouni, Y.; Azzalou, R.; Boulahjar, R.; Abrouki, Y.; Haddad, M.E.; Routier, S.; Guillaumet, G.; Lazar, S. *Tetrahedron Lett.*, **2010**, *51*, 6715-6717.

[35] Giri, A.; Dhinga, V.; Giri, C.C.; Singh, A.; Ward, O.P.; Narasu, M.L. *Biotechnol. Adv.*, **2001**, *19*, 175-199.

[36] Villa, R.; Molinari, F.; Levati, M.; Aragozzini, F. *Biotechnol. Lett.*, **1998**, *20*, 1105-1108.

[37] Bruni, R.; Fantin, G.; Medici, A.; Pedrini, P.; Sacchetti, G. *Tetrahedron Lett.*, **2002**, *43*, 3377-3379.

[38] Andrade, L.H.; Utsunomiya, S.; Omori, A.T.; Porto, A.L.M.; Comasseto, J.V. *J. Mol. Catal. B: Enzyme.*, **2006**, *38*, 84-87.

[39] Comasseto, J.V.; Omori, A.T.; Porto, A.L.M.; Andrade, L.H. *Tetrahedron Lett.*, **2004**, *45*, 473-476.

[40] Yadav, J.S.; Reddy, T.; Nanda, S.; Rao, A.B. *Tetrahedron: Asymmetry*, **2001**, *12*, 3381-3385.

[41] Mironowicz, A. *Phytochemistry*, **1998**, *47*, 1531-1534.

[42] Silver G.M.; Fall, R. *Plant Physiol.*, **1991**, *97*, 1588-1591.

[43] Pal, R. *Open J. Org. Chem.,* **2013**, *1*(4), 47-56.

[44] Manabe, K.; Mori, Y.; Wakabayashi, T.; Nagayamaand, S.; Kobayashi, S. *J. Am. Chem. Soc.*, **2000**, *122*, 7202-7207.

[45] Deshmukh, M.B.; Patil, S.S.; Jadhav, S.D.; Pawar, P.B. *Synth. Commun.*, **2012**, *42*(8),1177-1183.

[46] Morbale, S.T.; Jadhav, S.D.; Deshmukh, M.B.; Patil, S.S. *RSC Adv.*, **2015**, *5*, 84610-84620.

[47] Shah, S.S.; Zamroz, N.U.; Sharif, Q.M. *Colloids Surf. A,* **2001**, *178*, 199-206.

[48] Chennamsetty, N.; Bock, H.; Scanu, L.F.; Siperstein, F.R.; Gubbins, K.E. *J. Chem. Phys.*, **2005**, *122*, 094710.

[49] Porter, C.J.H.; Pouton, C.W.; Cuine, J.F. *Adv. Drug Deliv. Rev.*, **2008**, *60*, 673-691.

[50] Esmaeilpour, M.; Javidi, J.; Dehghani, F.; Zahmatkesh, S. *Res. Chem. Intermed.*, **2017**, *43*, 163-185.