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An Efficient and Eco-Friendly Tungstate Promoted Zirconia (WO_x/ZrO_2) Solid Acid Catalyst for the Synthesis of 2-Aryl Benzimidazoles

Ramya V. Shingalapur · Kallappa M. Hosamani

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Abstract An eco-friendly catalytic amount (0.3 g) of tungstate-promoted zirconia (WO_x/ZrO_2) solid acid catalyst has been explored in the synthesis of 2-aryl benzimidazoles using aryl aldehydes and *o*-phenylenediamine. This is one of the fundamental aspects in green chemistry for simple experimental and product isolation protocol combined with easy recovery and reusability of the catalyst. It is expected to contribute in the development of clean and environment friendly strategy for synthetic protocols. The incorporated promoter showed strong influence on the surface and bulk properties of zirconia. The catalytic activity results suggest that the methodology adopted offers significant improvements for the synthesis of benzimidazole derivatives with respect to yields, simplicity and green aspects by avoiding toxic conventional catalysts and solvents. Henceforth, a good substrate conversion and excellent product selectivity were obtained over tungstate promoted zirconia solid acid catalyst.

Keywords Aryl aldehydes · *o*-Phenylenediamine · 2-Aryl benzimidazoles · Tungstate-promoted zirconia · WO_x/ZrO_2

1 Introduction

Solid green acid catalysts play an important role in the green synthesis and transformations in organic chemistry. Thus, a straightforward, efficient and environmentally acceptable synthetic protocol is an important aspect in green chemistry. Many organic reactions such as alkylation, acylation, isomerization, nitration, esterification and rearrangements like Pinacol, Meerwin, Beckmann, Ritter reactions etc., are accomplished by the homogeneous acid catalysts. All these acid-catalyzed reactions are almost carried out by employing conventional mineral acids like H_2SO_4, HNO_3 and HF or Lewis acids such as $AlCl_3$ and BF_3. Thus, these classical acid catalyzed organic reactions have been exploited as one of the most important basic reactions in organic chemistry for their use in polymer and pharmaceutical syntheses. However, all these procedures suffer from one or more of the following disadvantages such as low yields, use of expensive, lachrymatory or hygroscopic reagents, highly inflammable or potentially explosive solvents, high temperatures, a special oxidation process or long reaction times, tedious work-up procedures and co-occurrence of several side reactions.

Henceforth, number of methods has been developed for the synthesis of benzimidazole derivatives including the condensation of carboxylic acids [1, 2], acid chlorides [3], nitriles [4], orthoesters [5–7], amides [8], esters [9] or aldehydes [10–13] with *o*-phenylenediamine (OPD). In view of the environmental and economical reasons, there is an ongoing effort to replace such conventional homogeneous catalysts with newer solid green acid catalysts. This is mainly due to the distinct advantage of solid acid catalysts such as non-toxicity, non-corrosiveness, ease of handling, less expensive and easy to recover and reuse [14–21].

In this context, new avenues for various solid acid catalytical systems have been introduced including heteropolyacids, ion exchange resins (Amberlyst and Nafion-H), zeolites and clays. Amongst, zirconia supported oxoanions have been investigated [22], and the solid superacid catalyst, sulfated zirconia have also been gained much attention due to its high activity to catalyze many reactions even at

R. V. Shingalapur · K. M. Hosamani (✉)
P.G. Department of Studies in Chemistry, Karnatak University, Pavate Nagar, Dharwad 580003, India
e-mail: dr_hosamani@yahoo.com

low temperatures [23–25]. Thus, modified zirconia solid acid catalyst has been used for Mannich reaction, for the synthesis of α-amino nitriles, diphenylureas, coumarines, 1,5-benzodiazepines, and acylation of alcohols, phenols and amines and protection of carbonyl compounds [26–28].

Interest in the benzimidazole chemistry, there has been a exploration of biologically potent benzimidazole molecules for their significant physiological and pharmacological activities [29] and also encompasses a diverse range of pharmacological activities including anti-microbial, anti-inflammatory, analgesic, anti-histamine, anti-ulcerative, anti-oxidant, anti-proliferative, anti-allergic, anti-tumour, anti-kinase, epilepsy, diabetes, anti-fertility, anti-tubercular, anti-cancer, cytotoxicity and anti-HIV-1.

As in recent times more emphasis has been given to develop clean process, it is essential to find a suitable alternate catalyst to meet the requirements. In continuation to our quest in organic synthesis employing inexpensive catalysts [2, 30] use of bifunctional solid acid catalysts seems to be the right solution. To the best of our knowledge, there has been no report for the utilization of solid acid catalyst such as mixed metal oxides consisting of WO_x/ZrO_2 for the green synthesis of benzimidazole derivatives. Hence, it is a right time to explore such solid green acid catalysts in organic reactions to synthesize clean and green compounds.

Therefore, the use of eco-friendly green solid acid catalysts for the organic synthesis and transformation reactions in the liquid phase under hazardous free solvents or environmentally benign solvents has represented the ideal green chemical technology protocols from both environmental and economical point of view. Thus, combining the potent pharmacological activities and green compounds would re-inforce greening of such eco-friendly organic reactions. To the best of our knowledge, this will be one of the promising approaches for the green synthesis of benzimidazole derivatives.

With reference to the research work on green catalysts [31, 32] and in order to explore the expertise in green chemistry, we are currently exploiting tungstate promoted zirconia solid catalyst for the green synthesis. In the present research investigation, we are reporting such green solid acid catalyzed synthetic protocol for the synthesis of benzimidazole derivatives [33–35]. However, efforts are still ongoing to develop clean and eco-friendly strategy for the synthesis of novel organic compounds.

2 Experimental

2.1 Instrumentation

The melting points of the products were determined by open capillaries on a Buchi apparatus and are uncorrected. The IR spectra were recorded on a Nicolet Impact-410 FT-IR Spectrophotometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300F 300 MHz spectrometer in $CDCl_3$/DMSO solvents using TMS as an internal standard with ^{1}H resonant frequency of 300 MHz and ^{13}C resonant frequency of 75 MHz. D_2O exchange was applied to confirm the assignment of the signals of NH protons. The mass spectra were recorded on Shimadzu GCMS-QP2010S at 70 eV. The elemental analysis was carried out by using Heraus CHN rapid analyzer. All the compounds gave C, H and N analysis within ±0.4% of the theoretical values. The homogeneity of the compounds was described by TLC on aluminum silica gel 60 F_{254} (Merck) detected by UV light (254 nm) and iodine vapours.

2.2 Catalyst Preparation

Zirconium hydroxide was prepared from zirconium oxychloride by hydrolysis with dilute aqueous ammonia solution. For this purpose, the requisite quantity of $ZrOCl_2{\cdot}8H_2O$ (Aldrich, GR grade) was dissolved in doubly distilled water and to this clear solution, aqueous NH_3 was added drop-wise with vigorous stirring until the pH of the solution reached 8. The obtained precipitate was washed with hot distilled water several times until free from chloride ions and dried at 393 K for 24 h. On the obtained $Zr(OH)_4$, a nominal 10 wt% WO_x was deposited by adopting a wet impregnation method. To achieve this, the requisite quantity of ammonium metatungstate (Aldrich, AR grade) was dissolved in doubly distilled water and to this clear solution the desired quantity of oven dried $Zr(OH)_4$ was added and excess of water was evaporated on a water-bath. The resulting cake was oven dried at 393 K for 24 h and calcined at 923 K for 6 h in a flow of oxygen. A small portion of the hydrous zirconia was calcined at 923 K for 6 h to make unpromoted ZrO_2. Depending on the calcination temperatures, WO_x/ZrO_2 catalysts were designated as WZ-temp (temp means the calcination temperature). WZ-amorphous catalyst represents the amorphous WO_x/ZrO_2 catalyst.

2.3 Materials and Methods

A mixture of *o*-phenylenediamine (1.0 mmol), different aromatic aldehydes (1.0 mmol), and a pinch of WZ catalyst (0.3 g) in 10 ml 1,4-dioxane were stirred for 10 min and refluxed further at 100 °C for an appropriate time (Table 3) which was monitored by TLC. After completion of the reaction, catalyst was recovered by simple filtration and reused. The products were recovered from the filtrate, concentrated on a rotatory evaporator and chromatographed on a silica gel column to offer pure products. All

the compounds were characterized by comparing their physical and spectral data with those of reported compounds. The m.p., IR, ^{1}H NMR, ^{13}C NMR and EIMS data of all synthesized compounds are given below-

2.4 Product Characterization Data

2.4.1 2-Phenyl-1H-benzimidazole ***3a***

White solid: m.p. = 287–288 °C [33]; IR (KBr): 3334, 3198, 1625, 1510, 1287 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.93 (1H, s, –NH), 7.92 (2H, d, J = 1.3 Hz), 7.47 (m, 1H), 7.22 (4H, m), 6.95 (2H, s); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 142.8, 136.1, 135.2, 129.4, 120.2, 114.9; EIMS: *m/z* 194.0 $(M + H)^{+}$; Anal. Calcd. for $C_{13}H_{10}N_2$ (194): C, 80.39; H, 5.19; N, 14.42. Found: C, 80.35; H, 5.21; N, 14.39.

2.4.2 2-(2-Chlorophenyl)-1H-benzimidazoles ***3b***

White solid: m.p. = 231–233 °C [34]; IR (KBr): 3421, 3068, 2886, 1637, 1464, 1245 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.21 (br, 1H, s, –NH), 7.25–7.95 (8H, m); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 145.0, 132.5, 138.2, 120.8, 119.5, 114.1; EIMS: *m/z* 219.0 (^{35}Cl $[M + H]^{+}$); Anal. Calcd. for $C_{13}H_9N_2Cl$ (229): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.25; H, 3.99; N, 12.22.

2.4.3 2-(4-Chlorophenyl)-1H-benzimidazoles ***3c***

Light yellow solid: m.p. = 291–293 °C [34]; IR (KBr): 3338, 2923, 1624, 1448, 1487 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.55 (br, 1H, s, –NH), 8.14 (2H, d, J = 1.52 Hz), 7.61 (1H, s), 7.23–7.28 (3H, s), 7.12–7.04 (2H, s); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 142.5, 137.1, 133.9, 129.8, 120.5, 114.1; EIMS: *m/z* 219.0 (^{35}Cl $[M + H]^{+}$); Anal. Calcd. for $C_{13}H_9N_2Cl$ (229): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.29; H, 3.94; N, 12.27.

2.4.4 2-(1H-Benzimidazole-2-yl)-phenol ***3d***

White solid: m.p. = 235–237 °C [33]; IR (KBr): 3378, 3459, 2859, 1614, 1495 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.48 (br, 1H, s, –NH), 7.18–7.93 (8H, m); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 21.4, 140.8, 138.0, 126.3, 122.5, 116.8; EIMS: *m/z* 208 $(M + H)^{+}$; Anal. Calcd. for $C_{13}H_{10}N_2O$ (210): C, 74.27; H, 4.79; N, 13.33 Found: C, 74.30; H, 4.75; N, 13.35.

2.4.5 4-(1H-Benzimidazole-2-yl)-phenol ***3e***

Yellow solid: m.p. = 218–220 °C [33]; IR (KBr): 3357, 1609, 1510, 1444, 1247 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.30 (br, 1H, s, –NH), 7.21–8.05 (8H, m); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 141.8, 130.2, 138.0, 125.1, 120.5, 115.1; EIMS: *m/z* 210 $(M + H)^{+}$; Anal. Calcd. for $C_{13}H_{10}N_2O$ (210): C, 74.27; H, 4.79; N, 13.33. Found: C, 74.26; H, 4.78; N, 13.32.

2.4.6 2-(4-Methylphenyl)-1H-benzimidazole ***3f***

Light yellow solid: m.p. = 261–263 °C [34]; IR (KBr): 3340, 3016, 2854, 1625, 1439, 1288 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.24 (3H, s), 12.21 (br, 1H, s, –NH), 7.12–7.90 (m, 8H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 21.4, 116.8, 122.5, 126.3, 138.0,140.8; EIMS: *m/z* 208 $(M + H)^{+}$; Anal. Calcd. for $C_{14}H_{12}N_2$ (208): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.82; H, 5.78; N, 13.41.

2.4.7 2-(4-Methoxyphenyl)-1H-benzimidazole ***3g***

Light yellow solid: m.p. = 225–227 °C [33]; IR (KBr): 3339, 3000, 2928, 1609, 1440, 1292 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.70 (1H, s), 8.15 (2H, d, J = 1.75 Hz), 7.66 (1H, s), 7.42 (1H, s), 7.18 (4H, m), 3.76 (3H, s); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 56.3, 115.6, 119.1, 121.9, 122.6, 126.7, 127.8, 129.8, 135.3, 139.9, 144.1, 151.7; EIMS: *m/z* 225 $(M + 1)^{+}$; Anal. Calcd. for $C_{14}H_{12}N_2O$ (224): C, 74.98; H, 5.39; N, 12.49. Found: C, 75.00; H, 5.38; N, 12.45.

2.4.8 2-(1H-Benzimdazole-2-yl)-6-methoxy-phenol ***3h*** *(Unknown)*

White solid: m.p. = 185–187 °C; IR (KBr): 3360, 2923, 2843, 1612, 1495, 1272 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.70 (s, 1H), 7.12–7.98 (8H, d, J = 1.54 Hz), 3.62 (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 55.2, 115.1, 120.6, 122.8, 125.4, 137.2, 141.2, 149.1; EIMS: *m/z* 235 $(M + 1)^{+}$; Anal. Calcd. for $C_{14}H_{12}N_2O_2$ (240): C, 69.99; H, 5.03; N, 11.66. Found: C, 69.95; H, 5.05; N, 11.62.

2.4.9 4-(1H-Benzimidazole-2-yl)-phenylamine ***3i***

Yellowish white crystals: m.p. = 246–248 °C, lit m.p. = 248 °C [35]; IR (KBr): 3351, 3062, 2923, 1610, 1491, 1281 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.42 (s, 1H), 6.92–7.75 (d, 8H, J = 1.50 Hz), 4.55 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 115.7, 122.1, 126.0, 138.3, 140.9; EIMS: *m/z* 209 $(M + 1)^{+}$; Anal. Calcd. for $C_{13}H_{11}N_3$ (209): C, 74.62; H, 5.30; N, 20.08. Found: C, 74.60; H, 5.29; N, 20.10.

2.4.10 2-(3-Nitrophenyl)-1H-benzimidazole **3j**

Pale yellow solid: m.p. = 210–212 °C [33]; IR (KBr): 3350, 2924, 1609, 1491, 1281 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 12.51 (s, 1H), 6.98–7.80 (d, 8H, J = 1.47 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 115.7, 122.1, 126.0, 137.9, 141.9, 142.9, 146.9; EIMS: *m/z* 235 $(M + 1)^+$; Anal. Calcd. for $C_{13}H_9N_3O_2$ (239): C, 65.27; H, 3.79; N, 17.56. Found: C, 65.29; H, 3.80; N, 17.54.

2.4.11 2-(4-Nitrophenyl)-1H-benzimidazole **3k**

Pale red solid: m.p. = 308–310 °C [33]; IR (KBr): 3353, 3050, 2924, 1609, 1491, 1280 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 12.38 (br, 1H, s, –NH), 7.27–7.85 (m, 8H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 149.2, 141.9, 140.8, 136.3, 124.5, 115.9; EIMS: *m/z* 238 $(M + 1)^+$; Anal. Calcd. for $C_{13}H_9N_3O_2$ (239): C, 65.27; H, 3.79; N, 17.56. Found: C, 65.29; H, 3.75; N, 17.52.

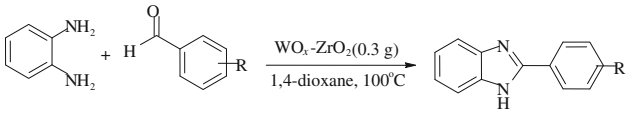
2.4.12 2-Fural-1H-benzimidazole **3l**

White solid: m.p. = 284–286 °C [33]; IR (KBr): 3352, 3017, 2923, 1625, 1441, 1288 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 12.47 (br, 1H, s, –NH), 6.54 (s, 2H, –CH), 7.2 (s, 1H, –CH), 7.5–7.82 (m, 4H); ^{13}C-NMR (DMSO-d_6, 75 MHz): δ 152.0, 142.7, 105, 110.4, 136.2, 120.3; EIMS: *m/z* 182 $(M + 1)^+$; Anal. Calcd. for $C_{11}H_8N_2O$ (184): C, 71.73; H, 4.38; N, 15.21. Found: C, 71.70; H, 4.35; N, 15.19.

3 Results and Discussion

In continuation of our interest in the application of heterogeneous acids on the development of useful synthetic methodologies [2, 30] for biologically important heterocycles, we have observed that benzimidazoles can be synthesized efficiently by the treatment of *o*-phenylenediamine with aromatic aldehydes using tungstate-promoted zirconia (WO_x/ZrO_2) catalyst.

The reaction proceeded as per Scheme 1. Initially, to optimize the reaction conditions, the effect of solvent and catalyst was carried out with benzaldehyde, *o*-phenylenediamine as a model. It was observed that this reaction goes well in 1,4-dioxane among the commonly used organic solvents such as *N*,*N*-dimethyl formamide, acetonitrile, toluene, tetrahydrofuran (Table 1, entries 1–5). From these results we concluded that 1,4-dioxane takes less time and the comparative yield was high. To evaluate the quantity of WZ catalyst, 0.1–0.5 g of WZ was used and the products were obtained in 70–95% yields. To verify the efficiency of catalyst loading we have investigated the amount of WZ on



R = a) -H, b) 2-Cl, c) 4-Cl, d) 2-OH, e) 4-OH, f) 4-CH_3, g) 4-OCH_3, h) 2-OH,3-OCH_3 , i) 4-NH_2, j) 3-NO_2, k) 4-NO_2, l) Furfural

Scheme 1 Synthesis of 2-aryl substituted benzimidazoles using tungstate-promoted zirconia (WO_x/ZrO_2) catalyst

Table 1 Search for optimal solvent for the synthesis of 2-aryl-1H-benzimidazoles **3(a–l)**

Entry	Solvent	Time (h)[a]	Yield (%)[b]	Temp. in °C
1	1,4-Dioxane	4.5	95	100
2	*N*,*N*-Dimethyl formamide	10	69	100
3	Toluene	8	65	100
4	Acetonitrile	6	70	80
5	Tetrahydrofuran	8	73	65

The mixture of *o*-phenylenediamine (0.01 mol) and aromatic aldehydes (0.01 mol) with WZ catalyst (0.3 g)

[a] All the reactions monitored by TLC

[b] Isolated yields

Table 2 Effect of WZ catalyst concentration for the synthesis of 2-aryl-1H-benzimidazoles **3(a–l)**

Entry	Catalyst concentration (g)	Time (h)[a]	Yield (%)[b]
1	0.1	4.0	70
2	0.2	3.5	80
3	0.3	3.5	95
4	0.4	4.0	79
5	0.5	5.0	80

The mixture of the *o*-phenylenediamines (0.01 mol) and aromatic aldehydes (0.01 mol) with different weights of WZ catalyst in 1,4-dioxane at 100 °C

[a] All the reactions were monitored by TLC

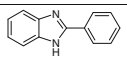
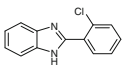
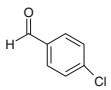
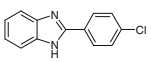
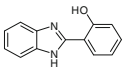
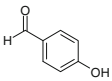
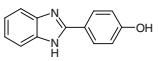
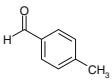
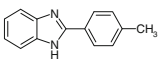
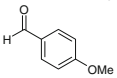
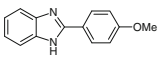
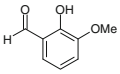
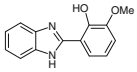
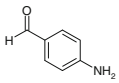
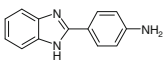
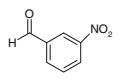
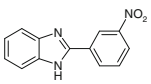
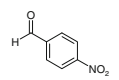
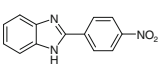
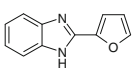
[b] Isolated yields

the reaction. At mild temperature no product was formed in the absence of WZ. Therefore, decreasing the quantity of catalyst from 0.2 to 0.1 g drastically reduced the yield from 95 to 70%. However, increase in the quantity of catalyst from 0.4 to 0.5 g reduced the yield from 95 to 79% (Table 2, entries 1–5). From this, we concluded that 0.3 g of catalyst as optimum amount of the catalyst for this reaction. Lower catalytic activities were observed when typical organic solvents such as *N*,*N*-DMF, Toluene, CH_3CN and THF were employed which is probably interfering with the active sites of the catalyst.

Under identical conditions, the unpromoted ZrO_2 catalyst exhibited insignificant product yields. Using optimized reaction parameters, a number of 2-substituted aryl benzimidazoles (**3a–l**) were synthesized. The time required and the yields of the compounds are given in Table 3. Aromatic aldehydes possessing both electron-donating and electron-withdrawing groups were employed for benzimidazole formation and in all the cases, the yields were excellent (Table 3). The method is suitable for the preparation of benzimidazoles from an acid sensitive aldehyde such as furfuraldehyde (Table 3, entry 3l).

Reactions were carried out under same reaction conditions for a comparative evaluation of the efficacy of WZ with those of other catalysts reported recently for the synthesis of

Table 3 Synthesis of 2-substituted benzimidazoles **3(a–l)** using a WZ (WO_x/ZrO_2) catalyst

Entry	Aryl aldehydes	Product	Time (hr)[b]	Yield (%)[c]
3a			5.0	92
3b			5.0	92
3c			4.5	95
3d			5.0	90
3e			4.5	96
3f			5.5	92
3g			5.0	95
3h			5.5	90
3i			5.0	92
3j			5.5	90
3k			5.0	93
3l			5.5	90

The mixture of the *o*-phenylenediamines (0.01 mol) and aromatic aldehydes (0.01 mol) with 0.3 g of WZ catalyst in 1,4-dioxane at 100 °C

[a] All the reaction monitored by TLC

[b] Isolated yields

Table 4 Comparison of catalytic activity of WZ (WO_x/ZrO_0) catalyst with several other catalysts for the synthesis of 2-aryl-1H-benzimidazoles **3a**[a]

Entry	Catalysts	Quantity of catalyst	Yield (%)
1	6 N HCl	10 ml	70
2	Phosphotungstic acid	0.01 mol	75
3	*p*-Toluenesulfonic acid	0.01 mol	88
4	Wells-Dawson heteropolyacid	0.01 mol	80
5	Glyoxalic acid	0.01 mol	72
6	WZ	0.3 g	95

[a] Reaction condition: The mixture of the *o*-phenylenediamine (0.01 mol) and aryl aldehydes (0.01 mol) with WZ catalyst (0.3 g) in 1,4-dioxane at 100 °C for about 5 h

biologically active potent 2-substituted benzimidazoles via this route (Table 4). The table shows that the yield of the desired product in the presence of WZ was comparably higher than other catalysts used. Additionally, the present method is indeed more expeditious than the rest of the methods. Consequently, our method can certainly be considered as a convenient alternative to the other eco-friendly catalysts used for one-pot synthesis of substituted benzimidazoles via this route. The biological activities of synthesized substituted benzimidazole derivatives are under progress.

In summary, WO_x/ZrO_2 was found to function as mild and effective catalyst for the synthesis of 2-arylbenzimidazoles under mild conditions by the rapid condensation of various aryl aldehydes with *o*-phenylenediamine. In this, the solvents were selected based on the solubility of reactants and dispersion of catalyst. It is observed that the best results are obtained in the least polar solvent (1,4-dioxane). Hence, we have attributed lower yields and higher reaction time due to the inference with active sites of catalyst which is more likely with more polar solvents. To verify the role of air as an oxidant in this reaction, the experiment was also carried out under nitrogen atmosphere. The yields and reaction time are almost same and identical. Hence, the role of catalyst is very important in its optimum condition with 1,4-dioxane. Thus, this method has advantages over other reported methods in terms of product with better yields, selectivity, operational simplicity (easy work up of reactions), and eco-friendly (non-corrosive reagent).

4 Conclusions

The incorporation of tungsten into zirconia is favourable in the formation of the tetragonal phase, which inhibits the sintering of the support and enhances the acid strength of these solids by slight reduction of the WO_x species. The WO_x/ZrO_2 catalyst having the tetragonal structure of zirconia is one of the best catalysts for the synthesis of

benzimidazole derivatives in medicinal chemistry as well as in green chemistry. More than the acidic properties, the mesoporous structure of tungstated zirconia favours the dispersion of the tungsten species, which improves the transport of reactants and products in the solid and avoids the secondary reactions promoted by the diffusion constraints that slow down the removal of initial isomerization of the products from the catalyst. Henceforth, this methodology works well and is environmentally benign ecofriendly procedure, which would prove beneficial to both academia and industry for the socio-economic change.

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