Hindawi Publishing Corporation
Journal of Chemistry
Volume 2013, Article ID 108318, 7 pages
http://dx.doi.org/10.1155/2013/108318

Research Article

Zirconyl (IV) Nitrate as Efficient and Reusable Solid Lewis Acid Catalyst for the Synthesis of Benzimidazole Derivatives

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Received 27 April 2013; Accepted 24 May 2013

Academic Editor: Stojan Stavber

The present paper introduces a simple and efficient method for the synthesis of substituted benzimidazoles by heterocyclization of different *o*-phenylenediamines and substituted aromatic carboxylic acid/aldehyde in the presence of zirconyl nitrate as catalyst in ethanol under reflux, which produced excellent yield of corresponding benzimidazoles in a short reaction time with reusability of catalyst.

1. Introduction

Heteroaromatic compounds have awestruck significant attention in the design of biologically active molecules and advanced organic materials [1, 2]. Because of their pharmaceutical and biological significance, nitrogen-containing heterocyclic compounds have attracted considerable attention as an important class of organic molecules. In the continuation of our search for efficient synthetic methodologies for biologically important heterocyclic compounds, benzimidazoles have been chosen as target molecules; benzimidazole derivatives have several medicinal uses, such as antivirals, anticancer, antihypertensive, antihistamines, antiparasitics, and antiulcer [3–8].

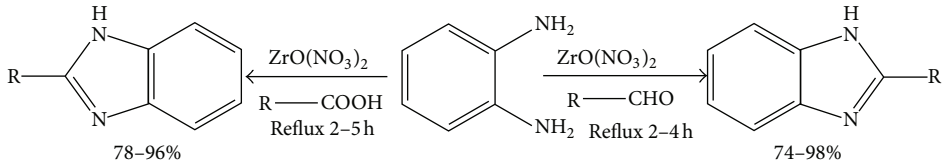
Diverse synthetic efforts for benzimidazoles have been reported, with the most common method being the heterocyclization of *o*-phenylenediamine and carboxylic acids [9, 10], aldehydes [11, 12], alcohols [13]; and nitriles [14, 15] which usually require strong acid, high temperature, and sometimes photoirradiation conditions, precious metal salts [16], molecular oxygen [17, 18]; or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone as oxidant [19]. Recently, a variety of catalysts such as homogeneous Lewis acids [20], pyridinium-*p*-toluenesulfonate [20], ultrasonic [21], $I_2/KI/K_2CO_3/H_2O$ [22], ionic liquids [23], (bromodimethyl) sulfonium bromide [24], and polyaniline-sulfate [25] and a tandem oxidation process [26] have been used for the synthesis of benzimidazole derivatives.

Lewis acid catalyst has attracted considerable attention in heterogeneous catalysis [27]. Although various kinds of Lewis acids have been developed, most of them are used only under strictly anhydrous conditions, in excess, and with hazardous organic solvents which are not environment friendly. The presence of even a small amount of water stops the reactions; and most Lewis acids immediately react with water rather than substrates [28].

In this context, in the present study, we report here the use of zirconyl nitrate as eco-friendly water-soluble Lewis acid catalyst for the synthesis of substituted benzimidazole. In recent years, Zr(IV) compounds have gained special attention as catalysts in organic synthesis, and some of these are stable in aqueous media [29–31]. In the continuation of our interest in synthesis of nitrogen-containing heterocyclic compounds [32], herein wefoundedthe application of $ZrO(NO_3)_2$ as a Lewis acid catalyst for the synthesis of substituted benzimidazoles viathe condensation reaction between *o*-phenylenediamine and aldehyde, carboxylic acid derivatives (Scheme 1).

2. Experimental Section

All chemicals and reagents were purchased from commercial suppliers and used without further purification. Column chromatography was carried out with silica gel (200–300 mesh) eluting with ethyl acetate and petroleum ether.



Scheme 1: Zirconyl nitrate-catalyzed synthesis of substituted benzimidazoles.

Thin layer chromatography was carried out using Merck silica gel GF254 plates. All products were characterized by NMR. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported in parts per million (ppm) downfield from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. HRMS was recorded on an ESI source.

3. A General Procedure for Synthesis of Substituted Benzimidazoles

0.5% (weight) of zirconyl nitrate was added to a solution of aldehyde/carboxylic acid (1 mmol) and *o*-phenylenediamine (1 mmol) in ethanol (10 mL). The reaction mixture was stirred under reflux for 2–6 h. The progress of reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature, 20 mL of ethanol was added, and resulting solution was filtered to remove the catalyst. The solvent was removed under reduced pressure by distillation, and residue was purified by column chromatography on silica gel using *n*-hexane-ethyl acetate or ethyl acetate-petroleum ether as an elutingagent The structures of the benzimidazole were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, and HRMS and were mostly known compounds.

Note. Excellent yield was obtained when 1% (weight) of zirconyl nitrate was used with carboxylic acids.

Characterization of selected compounds is as follows.

3.1. 2-Methyl-1H-benzimidazole (Table 2, Entry 1). Solid; mp 178–180°C (lit.[34] mp 175-176°C); IR (KBr) 3860, 3735, 3601, 2815, 2310, 1700, 1513, 735 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.82 (s, 1H), 7.3 (*d*, J = 8.0 Hz, 2H), 7.59 (d, 2H), 2.70 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 151.35, 138.60, 122.21, 114.48, 14.90. MS (EI, *m/z*): 132 [M$^+$].

3.2. 2-Phenyl-1H-benzimidazole (Table 2, Entry 2). Solid; mp 300–302°C (lit.[35] mp 301–303°C); IR (KBr) 3566, 2360, 1748, 1716, 1698, 1683, 1652, 1616 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.92 (s, 1H), 8.19 (*d*, J = 8.0 Hz, 2H), 7.61–7.55 (m, 4H), 7.52–7.48 (m, 1H), 7.23–7.19 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 151.7, 144.3, 135.5, 130.7, 130.3, 129.4, 126.9, 123.0, 122.1, 119.4, 111.8. MS (EI, *m/z*): 194 [M$^+$].

3.3. 2-(4-Nitrophenyl)-1H-benzimidazole (Table 2, Entry 3). Solid; mp 324–326°C (lit.[35] mp 326–327°C); IR (KBr) 3740, 3644, 3058, 1766, 1691, 1658, 1649, 1597, 1563, 1536, 1493, 1415, 722, 695 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.30 (s, 1H), 8.42 (s, 4H), 7.74 (s, 1H), 7.60 (s, 1H), 7.28 (s, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 162.7, 157.8, 149.4, 148.2, 136.5, 127.8, 127.4, 124.7, 123.3, 119.8, 112.4. MS (EI, *m/z*): 239 [M$^+$].

3.4. 5-Methyl-2-phenyl-1H-benzimidazole (Table 2, Entry 7). Solid; mp 245–247°C (lit.[36] mp 243-244°C); IR (KBr) 3109, 1511, 1463, 1354, 1176, 739, 701, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (s, 1H), 8.12–8.11 (m, 2H), 7.53 (*d*, J = 5.5 Hz, 1H), 7.40 (m, 2H), 7.28 (s, 2H), 7.08 (*d*, J = 5.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (DMSO, 100 MHz) δ 151.3, 131.8, 130.8, 130.1, 129.6, 129.4, 129.2, 126.8, 126.6, 126.4, 124.0, 21.8. MS (EI, *m/z*): 208 [M$^+$].

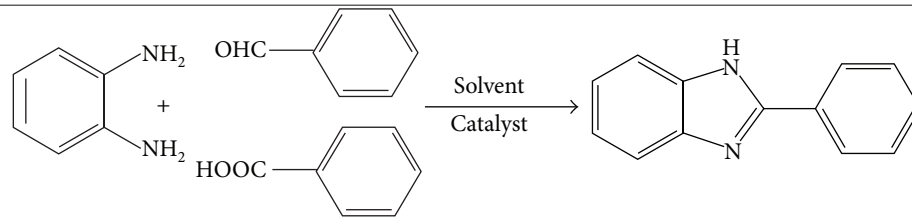
3.5. 2-(p-Tolyl)-1H-benzimidazole (Table 2, Entry 16). Solid; mp 264–266°C (lit.[35] mp 263–265°C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.83 (s, 1H), 8.08 (*d*, J = 7.8 Hz, 2H), 7.59 (s, 2H), 7.37 (*d*, J = 7.8 Hz, 2H), 7.21–7.19 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 151.9, 144.3, 140.0, 135.4, 130.0, 127.9, 126.9, 122.8, 122.0, 119.2, 111.7, 21.4. MS (EI, *m/z*): 208 [M$^+$].

3.6. 2-(4-Methoxyphenyl)-1H-benzimidazole (Table 2, Entry 6). Solid; mp 235–237°C (lit.[35] mp 234-235°C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.44 (*d*, J = 7.2 Hz, 1H), 7.25–7.19 (m, 2H), 7.09 (*d*, J = 8.8 Hz, 2H), 6.95 (*d*, J = 8.4 Hz, 2H), 6.85 (*d*, J = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.8, 153.6, 143.2, 136.3, 129.3, 127.9, 122.5, 119.4, 114.7, 114.6, 111.5, 55.8. MS (EI, *m/z*): 224 [M$^+$].

3.7. 5-Nitro-2-(4-methylphenyl)-1H-benzimidazole (Table 2, Entry 12). Solid; mp 288°C (lit. mp 290–292°C); IR (KBr) 3858, 3747, 3672, 3059, 2349, 1805, 1691, 1649, 1641, 1597, 1493, 1135, 1025, 722, 695 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.50 (s, 1H), 8.10 (*d*, J = 7.7 Hz, 2H), 7.95 (*d*, J = 8.9 Hz, 1H), 7.39 (*d*, J = 7.8 Hz, 2H), 6.73 (s, 1H), 6.61 (*d*, J = 8.9 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 156.2, 136.1, 130.2, 129.1, 127.4, 126.8, 119.2, 118.6, 115.1, 112.8, 112.1, 21.5; MS (EI, *m/z*): 254 [M$^+$].

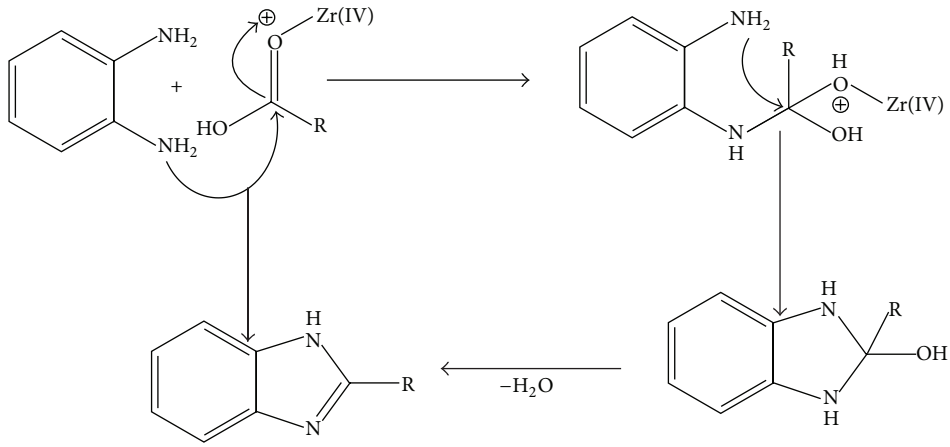
3.8. 2-(4-Chlorophenyl)-1H-benzimidazole (Table 2, Entries 4 and 15). Solid; mp 294–296°C (lit.[35] mp 290–292°C); IR (KBr) 3606, 3001, 2818, 2310, 1700, 1513, 735 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.00 (s, 1H), 8.20 (*d*, J = 8.4 Hz, 2H),

Table 1: Optimization of reaction conditions[a] for synthesis of substituted benzimidazoles from benzaldehyde/benzoic acid with *o*-phenylenediamine.



Entry	Solvents	Catalyst conc. (weight %)	Yield[b] (%)/reaction time (h)	
			Benzaldehyde	Benzoic acid
1	Ethanol	No catalyst	27/6	45/14
2	Ethanol	0.3	58/3	65/6
3	Ethanol	0.5	96/2	90/3
4	Ethanol	1	94/2.5	94/3
5	Dioxane	0.5	82/3	75/4.5
6	EtOAc	0.5	85/3.5	78/5
7	DCM	1	70/4	80/6

[a]Reflux the reaction mixture. [b]Isolated yield.



Scheme 2: Possible mechanism for the Zr(IV)-catalyzed synthesis of benzimidazoles form carboxylic acids.

7.64 (*d*, *J* = 8.4 Hz, 4H), 7.24–7.21 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 150.6, 144.3, 135.0, 134.8, 129.5, 128.6, 128.2, 122.9, 122.5, 119.4, 111.9. MS (EI, *m/z*): 228 [M^+].

3.9. 5-Methyl-2-(4-nitrophenyl)-1H-benzimidazole (Table 2, Entries 9 and 18). Solid; mp 278–280°C (lit. mp 280–282°C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.39 (s, 5H), 7.54 (*d*, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.09 (*d*, *J* = 8.3 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 159.0, 153.6, 143.2, 136.3, 131.0, 129.3, 127.9, 119.4, 114.7, 114.6, 111.5, 31.1. MS (EI, *m/z*): 254 [M^+].

3.10. 2-(3-Methylphenyl)-1H-benzimidazole (Table 2, Entries 5 and 19). Solid; mp 285–287°C (lit. mp 286–288°C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.88 (s, 1H), 8.03 (s, 1H), 7.98 (*d*, *J* = 7.8 Hz, 1H), 7.60 (s, 2H), 7.44 (*t*, *J* = 7.6 Hz, 1H), 7.31 (*d*, *J* = 7.6 Hz, 1H), 7.23–7.19 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 156.2, 143.1, 141.4, 136.1, 130.1, 127.4, 126.8, 126.7, 118.3, 112.8, 21.5. MS (EI, *m/z*): 208 [M^+].

4. Results and Discussion

We examined the cyclocondensation of *o*-phenylenediamine with different substituted aromatic carboxylic acid/aldehydes using zirconyl nitrate/Zr(IV) as a Lewis acid catalyst for the synthesis of substituted benzimidazoles. While establishing a new synthetic route, solvent and catalyst play an important role in organic synthesis. We studied the effect of solvent and molecular percent weight of catalyst on the synthesis of benzimidazoles using $ZrO(NO_3)_2$. Among various solvents,

Table 2: Synthesis of substituted benzimidazoles by $ZrO(NO_3)_2$-catalyzed reaction between aromatic aldehydes and carboxylic acids with *o*-phenylenediamines.

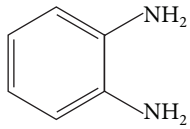
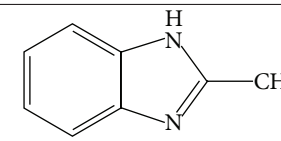
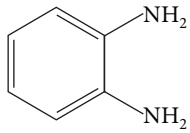
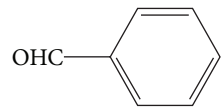
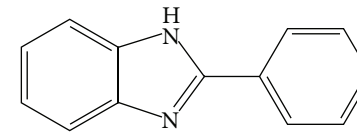
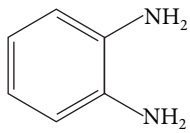
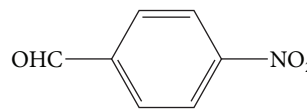
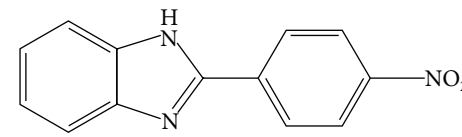
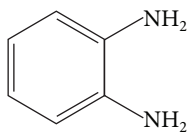
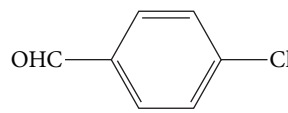
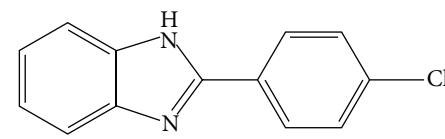
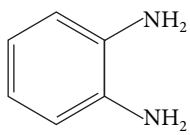
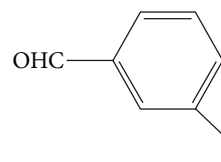
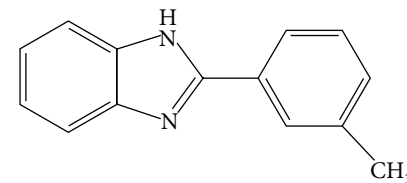
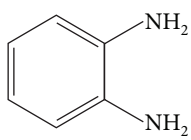
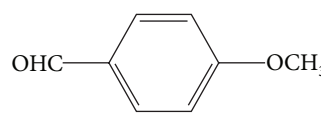
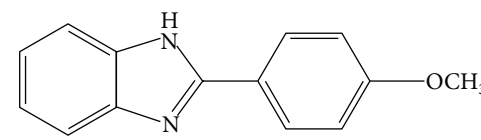
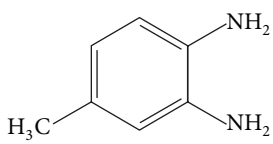
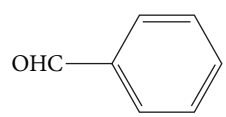
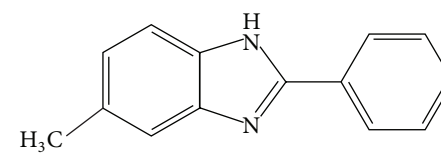
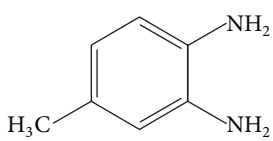
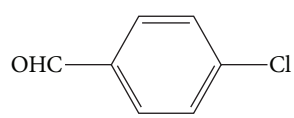
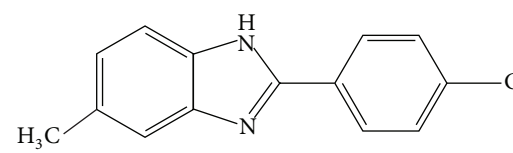
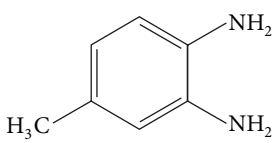
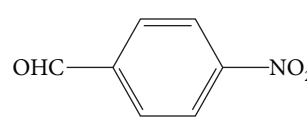
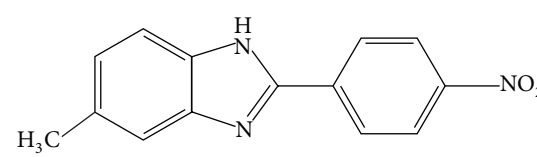
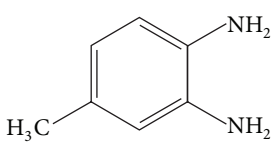
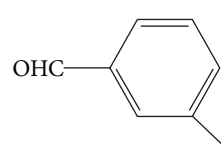
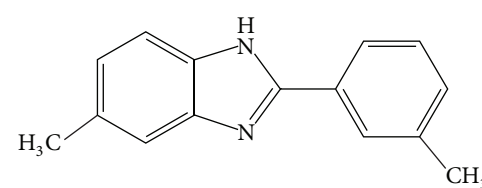
Entry	Amine	Reactant	Product	Yield (%)	Time (h)
1				85	3.9
2				96	2
3				98	3.2
4				97	3.1
5				94	3.5
6				78	4.3
7				86	3.5
8				94	2.3
9				95	2.5
10				78	3.5

Table 2: Continued.

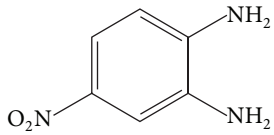
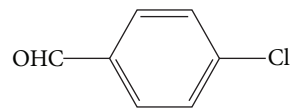
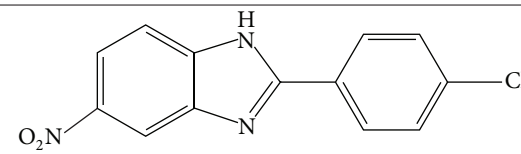
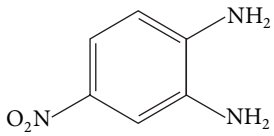
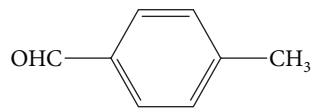
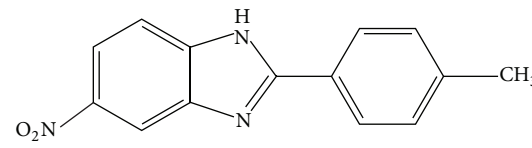
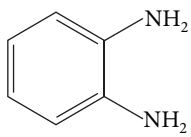
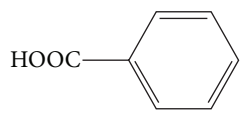
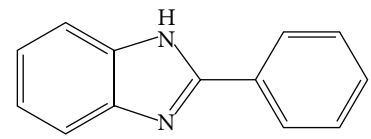
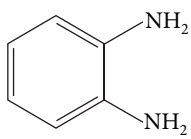
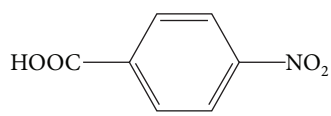
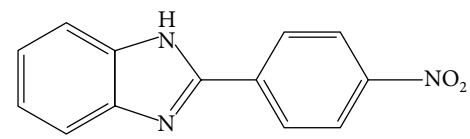
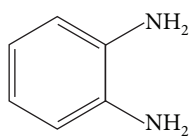
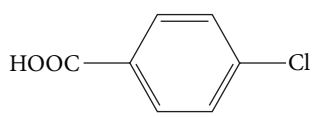
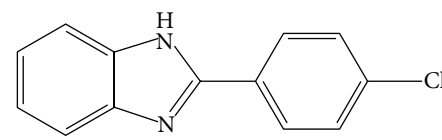
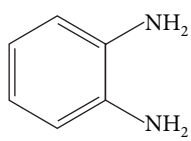
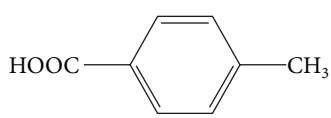
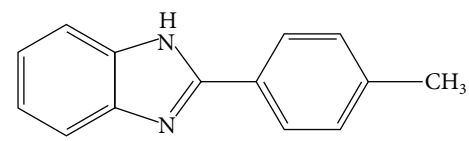
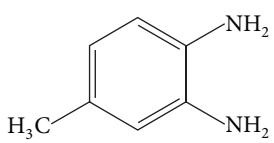
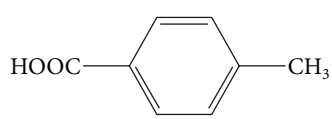
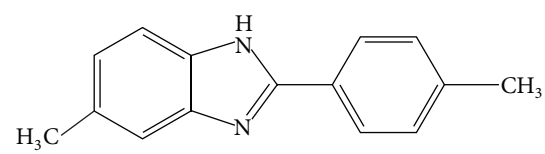
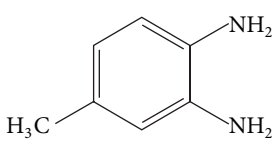
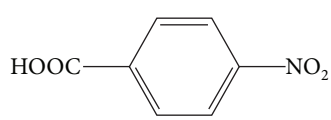
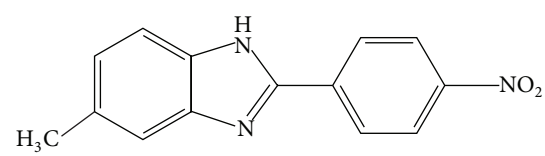
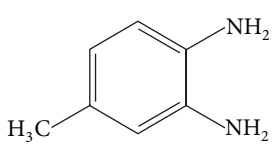
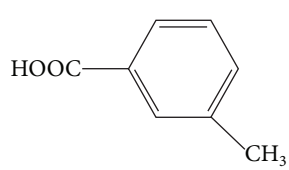
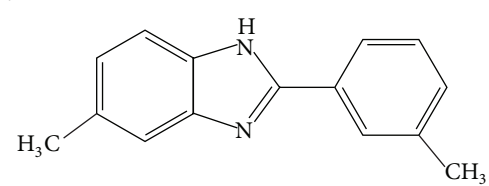
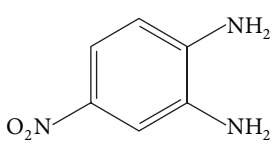
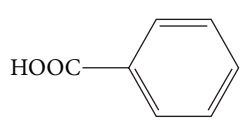
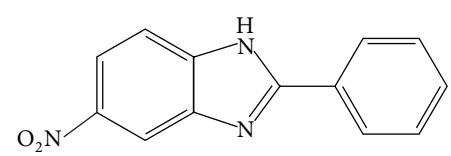
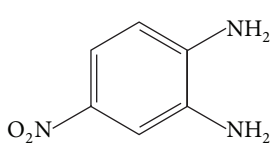
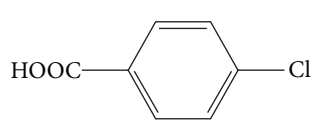
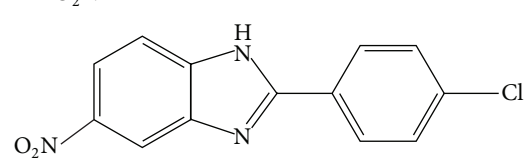
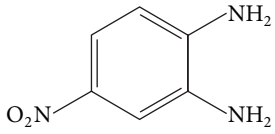
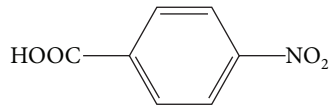
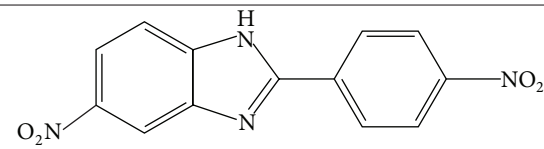
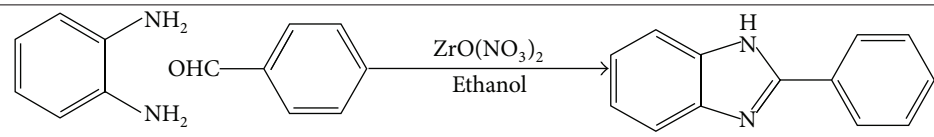
Entry	Amine	Reactant	Product	Yield (%)	Time (h)
11				92	3
12				76	4.5
13				96	3
14				97	2.5
15				95	3.5
16				80	4.5
17				82	3.8
18				96	2.7
19				78	4
20				82	4.1
21				85	3.1

Table 2: Continued.

Entry	Amine	Reactant	Product	Yield (%)	Time (h)
22				87	4

[a]Isolated yield.

Table 3: Catalyst reusability study for the reaction of benzaldehyde with *o*-phenylenediamine[a].



Entry	Yield [b] (%)	Catalyst recovery (%)
1	96	97
2	93	94
3	90	92
4	88	91

[a]Reaction condition: benzaldehyde (1 mmol), *o*-phenylenediamine (1 mmol), $ZrO(NO_3)_2$ (0.5 wt.%), ethanol, reflux. [b]Isolated yield.

dichloromethane, dioxane, ethyl acetate, and ethanol were used and their results are shown in Table 1.

Initially, the reaction between *o*-phenylenediamine (1 mmol) and benzaldehyde (1 mmol) was selected for the synthesis of benzimidazoles as a model reaction for optimization. It was found that ethanol gave the highest yield (96%) when using 0.5% zirconyl nitrate for 2 h, compared to other solvents and different molecular percent weight of catalyst used in the reaction (Table 1, entry 3).

In the continuation of our scheme, to search for better alternative route by using the same catalyst, we also carried out the reaction between substituted benzoic acids with *o*-phenylenediamine. To optimize this reaction we used benzoic acid (1 mmol) as a model; it also produced good yield of 2-phenyl-1H-benzimidazole in ethanol, but excellent yield was obtained when 1% of zirconyl nitrate was used with carboxylic acid (Table 1, entry 4). As per a possible mechanism the reaction proceeds via the activation of carboxylic acid by Zr(IV) which is shown in Scheme 2.

After the optimization of the reaction condition, we extended the study with different *o*-phenylenediamine against different aromatic and aliphatic aldehydes, aromatic carboxylic acids. In general, most of the reactions proceeded very smoothly to give corresponding substituted benzimidazoles in moderate to excellent yields, and the results are summarized in Table 2 (entries 1–22).

Then, we examined the general applicability of this synthetic route by using a variety of substituted benzaldehydes and carboxylic acids for the study of electronic factors. It is clearly seen from the Table 2 that the electron-deficient analogues give good yield in a short reaction time as compared to electron-rich ones. Another advantage of the present methodology is the reusability of the catalyst. After the completion of the reaction, the catalyst is removed by the simple filtration and it is treated with dichloromethane. The catalyst is dried at 80°C for 2 h and can be reused for another reaction. The recycled catalyst is used for four consecutive reactions without any appreciable change in its catalytic activity; the results are shown in Table 3.

5. Conclusion

In conclusion, a facile methodology for synthesis of substituted benzimidazoles in good to excellent yield is provided by zirconyl-nitrate-catalyzed condensation reaction of substituted *o*-phenylenediamines and aldehyde/carboxylic acid. The zirconyl-nitrate-catalyzed system reduced the reaction time and increased the yields. The environmental compatibility, excellent reusability of the catalyst, and ease for isolation of product are among the other added advantages that made this approach a good alternative way for the synthesis of benzimidazole derivatives.

Acknowledgment

Pratapsinha B. Gorepatil is thankful to the CSIR, New Delhi, for Junior Research Fellowship (JRF).

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