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A Facile KOH Catalyzed One-Pot Synthesis of Benzofused Heteroaromatic Compounds

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Abstract

A series of 2-substituted benzimidazoles were efficiently prepared by combining o-diaminoarene with aryl, heteroaryl aldehydes in EtOH/H₂O mixture at ambient temperature, employing KOH as promoter and atmospheric air as an efficient oxidant. The procedure afforded the products from good to excellent yields. The method is very simple mild and applicable to aryl as well as heteroaryl aldehydes without significant difference. These commercially available cheap catalysts are more active than many reported expensive heterogeneous catalysts.

Key words: o-Diaminoarene, Aldehydes, Benzimidazoles, EtOH/H₂O, KOH

1. INTRODUCTION

Benzofused heteroaromatic compounds display an array of applications in pharmaceutical and medicinal chemistry. This class of heterocycles also showed wide range of biological activities including anti-hypertensive, anti-ulcer, antiviral, antifungal, anticancer, antihistamine, anti-helminthic, anti-parasitic, anticoagulant, anti-allergic, analgesic, anti-inflammatory, antimicrobial, and immunosuppressant. A few representative compounds having benzofuran core is shown in Figure 1.¹

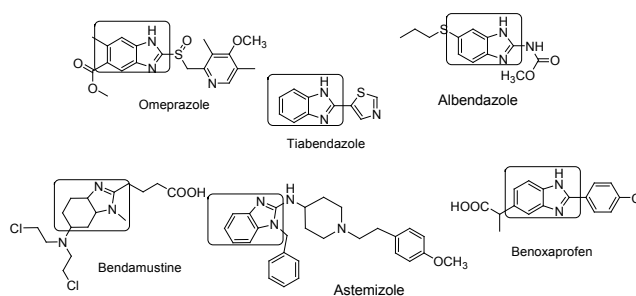


Figure 1: Biologically important benzimidazole

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Moreover, benzimidazole derivatives are an integral part of various clinical medicines against several viruses such as herpes (HSV-1), [1-2] HIV, [3] RNA [4] and influenza. [5] The traditional methods for the synthesis of 2-substituted benzimidazoles involve the treatment of 1,2-phenylenediamines with a carboxylic acid or their derivatives. [6] The reported procedures for the synthesis of benzimidazole derivatives from *o*-diaminoarene and aldehydes involved a wide spectrum of reagents such as PhI(OAc)₂, [7] DDQ, [8] heteropoly acids, [9] Zn-proline, [10] MnO₂, [11] H₂O₂/HCl, [12] H₂O₂/CAN, [13] oxone, [14] NaHSO₃, [15] Na₂S₂O₅, [16] sulfamic acid, [17] FeCl₃·6H₂O [18] KHSO₄, [19] ZrCl₄, [20] In(OTf)₃, [21] Yb(OTf)₃, [22] Sc(OTf)₃, [23] Cu(OTf)₂, [24] p-TSA, [25] polymer-supported hypervalent iodine, [26] cobalt(II) chloride hexahydrate, [27] Sm(OTf)₃, [28] thiamine hydrochloride, [29] FeCl₃-doped polyaniline nanoparticles, [30] mixture of Ti(IV) isopropoxide and cumene hydroperoxide, [31] animal bone meal, [32] nano ceria, [33] cobalt (II) hydroxide and oxide, [34] Zn²⁺-K10-clay, [35] laccase, [36] 4-methoxy TEMPO, [37] CuO nano-particles supported silica, [38] sodium perborate. [39-44] However, the reported methods suffer from one or the other drawbacks such as drastic reaction conditions, longer reaction time with poor yield, formation of side products, and use of toxic reagents and hazardous solvents, expensive and excessive oxidative catalysts, which makes them undesirable under the aspect of green chemistry, sustainable development and industrial applications.

However, a greener route for the synthesis of benzimidazole, from *o*-diaminoarene and aldehydes are still in demand. Furthermore, there is a need for an efficient and eco-friendly synthetic protocol to obtain these compounds in high yields. Hence, this present work involves the detailed study on the synthesis, and characterization of various benzofused heterocyclic derivatives by multicomponent method in the presence of KOH as a catalyst.

2. EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. FT-IR spectra were recorded on a Thermo Mattson Satellite Fourier Transform-IR 3000 spectrophotometer using KBr tablets for solids and absorbencies are reported in cm⁻¹. NMR spectra were recorded at Bruker NMR spectrometer (400.13 and 100.47 MHz) or a Jeol-500 MHz spectrometer (500.13 and 125.77 MHz). Chemical shifts are reported in δ (ppm) relative to TMS (¹H) or CDCl₃ (¹³C) as internal standards. Integrals are in accordance with assignments; coupling constants (*J*) are reported as values in Hz. Data for ¹H

NMR are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br s = broad singlet. All ¹³C NMR spectra were recorded with complete proton decoupling. Yields refer to quantities obtained after chromatography.

General Procedure for the Synthesis of Benzimidazoles (3)

A mixture of *o*-phenylenediamine **2** and aldehyde **1** in 1:1 molar ratios was taken in a 50 mL round bottom flask. To this water-ethanol (1:1) 5mL and 100 mg KOH was stirred for the appropriate period of time. After the completion of the reaction (TLC monitoring), it was then filtered; the solid reaction mixture was dissolved with dichloromethane (25 mL) and evaporated under vacuum. The crude product was then recrystallized from ethanol or subjected to silica gel column chromatography to get the pure product.

2-(4-Chlorophenyl)-1*H*-benzimidazole (3a) [43]

White crystalline solid, Mp 290 °C; FT-IR (KBr) ν_{\max} : 3449, 1606, 1455 cm⁻¹; ¹H NMR (400.13 MHz, DMSO-d₆): δ 13.05 (s, 1H, NH), 8.23 (s, 1H), 8.13-8.16 (m, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.55-7.62 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (100.61 MHz, DMSO-d₆): δ 149.6, 133.7, 132.1, 130.9, 129.5, 125.9, 124.9, 122.9, 121.9, 119.0, 111.4

2-(3-Chlorophenyl)-1*H*-benzimidazole (3b) [40]

White crystalline solid, Mp 228–230 °C; FT-IR (KBr) ν_{\max} : 3445, 1623, 1456 cm⁻¹; ¹H NMR (400.13 MHz, DMSO-d₆): δ 12.99 (s, 1H, NH), 8.18 (d, *J* = 8.4 Hz, 2H), 7.56-7.64 (m, 4H), 7.21 (d, *J* = 4.4 Hz, 2H); ¹³C NMR (100.61 MHz, DMSO-d₆): δ 150.1, 134.4, 129.0, 128.1, 124.9, 122.9, 122.0, 119.0, 111.5.

2-(4-Bromophenyl)-1*H*-benzimidazole (3c) [43]

White crystalline solid, Mp 300 °C; FT-IR (KBr) ν_{\max} : 3438, 1635, 1434 cm⁻¹; ¹H NMR (400.13 MHz, DMSO-d₆): δ 12.99 (s, 1H, NH), 8.12 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.18-7.26 (m, 2H); ¹³C NMR (100.61 MHz, DMSO-d₆): δ 150.1, 143.7, 134.9, 131.9, 129.3, 128.3, 123.2, 122.7, 121.8, 118.9, 111.3.

2-(4-Nitrophenyl)-1*H*-benzimidazole (3d) [43]

Yellow crystalline solid, Mp 308–310 °C; FT-IR (KBr) ν_{\max} : 3448, 1626, 1587, 1529, 1356 cm⁻¹; ¹H NMR (400.13 MHz, DMSO-d₆): δ 8.62 (s, 1H, NH), 8.31 (d,

$J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H), 7.11-7.15 (m, 2H), 6.75-6.81 (m, 2H); ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 153.7, 143.1, 141.9, 129.2, 129.1, 124.0, 118.4, 116.9, 115.8.

2-Phenyl-1H-benzimidazole (3e) [43]

White crystalline solid, Mp 288-290 °C; FT-IR (KBr) ν_{max} : 3452, 1618, 1460 cm^{-1} ; ^1H NMR (400.13 MHz, DMSO- d_6): δ 12.94 (s, 1H, NH), 8.20 (d, $J = 7.6$ Hz, 2H), 7.44-7.61 (m, 5H), 7.14-7.25 (m, 2H); ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 151.2, 130.1, 129.8, 128.9, 128.4, 126.4, 122.4.

2-(4-Methylphenyl)-1H-benzimidazole (3f) [43]

White crystalline solid, Mp 224-226 °C; FT-IR (KBr) ν_{max} : 3429, 1573, 1442 cm^{-1} ; ^1H NMR (400.13 MHz, DMSO- d_6): δ 12.82 (s, 1H, NH), 8.07 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 7.2$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.16-7.22 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 151.3, 143.7, 139.5, 134.9, 129.4, 127.4, 126.3, 122.2, 121.5, 118.6, 111.1, 20.9.

2-(3-Methylphenyl)-1H-benzimidazole (3g) [42]

White crystalline solid, Mp 256 °C; FT-IR (KBr) ν_{max} : 3354, 1621, 1552 cm^{-1} ; ^1H NMR (400.13 MHz, DMSO- d_6): δ 12.90 (s, 1H, NH), 7.75-7.77 (m, 2H), 7.66 (br, s, 1H), 7.545 (br, s, 1H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.21 (d, $J = 3.6$ Hz, 2H), 7.05-7.08 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 159.6, 151.0, 131.4, 130.0, 122.5, 121.6, 118.7, 115.8, 111.3, 55.2.

2-(2-Thienyl)-1H-benzimidazole (3h)[40]

Yellow crystalline solid, Mp >330 °C; FT-IR (KBr) ν_{max} : 3447, 1620, 1452 cm^{-1} ; ^1H NMR (400.13 MHz, DMSO- d_6): δ 12.91 (s, 1H, NH), 7.80 (d, $J = 3.6$ Hz, 1H), 7.72 (d, $J = 4.8$ Hz, 1H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.15-7.27 (m, 3H); ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 146.9, 143.5, 134.6, 133.6, 128.7, 128.2, 127.0, 126.6, 122.5, 121.7, 118.5, 111.0.

2-(2-Ferrocenyl)-1H-benzimidazole (3i) [41]

Yellow crystalline solid, Mp 230 °C; FT-IR (KBr) ν_{max} : 3423, 3072, 1602, 1444 cm^{-1} ; ^1H NMR (400.13 MHz, DMSO- d_6): δ 12.36 (s, 1H, NH), 7.54 (d, $J = 7.2$ Hz, 1H), 7.43-7.45 (m, 1H), 7.09-7.17 (m, 2H), 5.03-5.04

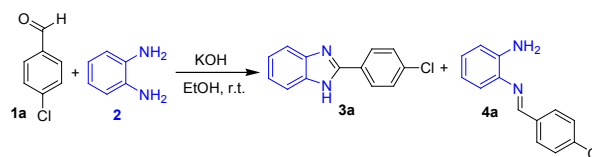
(m, 2H), 4.47-4.48 (m, 2H), 4.10 (s, 5H); ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 152.9, 143.8, 121.4, 121.0, 117.9, 110.5, 74.3, 69.6, 69.3, 67.2.

2-((Z)-(2-aminophenylimino) methyl) 4-chlorobenzene (4a) [44]

Yellow crystalline solid, Mp 167 °C; ^1H NMR (400.13 MHz, CDCl_3): δ 8.42 (s, 1H, ArH), 7.61 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.17-7.13 (m, 2H), 6.82-6.74 (m, 2H), 5.02 (br, 2H, NH_2); ^{13}C NMR (100.61 MHz, CDCl_3): δ 160.1, 143.2, 141.6, 135.6, 129.7, 129.2, 124.3, 119.46 116.9, 115.9.

3. RESULTS AND DISCUSSION

Initially, for the synthesis of benzimidazole **3a**, a 1:1 mixture of o-phenylenediamine **2** and 4-chlorobenzaldehyde **1a** was treated with KOH (0.1 g) in EtOH at ambient temperature. The reaction resulted in the product **3a** and imine **4a**, in 75% and 15% yields (Scheme 1, Table 1, entry 1), respectively. The structure of compounds **3a** and **4a** was thoroughly characterized by spectroscopic data. Since initial reaction afforded lower yield of the desired cyclized product **3a** and to improve the yield, the same reaction was carried out in MeOH as solvent to afford **3a** in 65% yield (Table 1, entry 2) and imine derivative in 25% yield. To study the influence of solvent, the reaction was carried out with various solvents, however, a considerable amount of desired product **3a** was formed in CH_3CN and H_2O (Table 1, entries 3 and 4). To increase the yield of the 2-(4-Chlorophenyl)-1H-benzimidazole **3a**, the reaction was carried out with KOH (0.1 g), in H_2O : EtOH (1:1) the yield of the product **3a** is substantially improved to 95% and the reaction also completed in a shorter time (Table 1, entry 6). We then compared the influences of different ratio of the aqueous ethanol and found the 1:1 ratio of water and ethanol seemed to be the best solvent combination for this reaction (Table 1, entry 6). It is also noted that the best catalytic activity of KOH was optimized to be 0.1 g (Table 1, entry 6) and any beyond this proportion (0.05 g), did not show any increase in the conversion and the product yield (Table 1, entry 8).



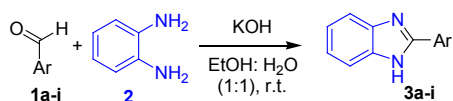
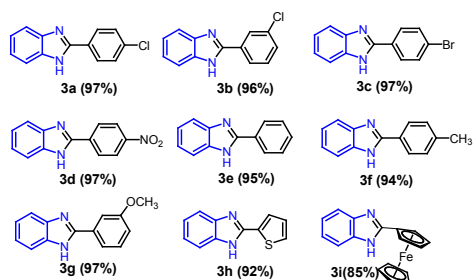
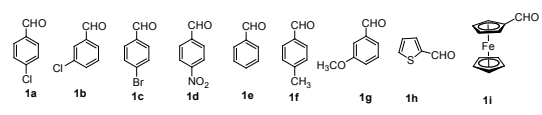
Scheme 1

Table - 1: Optimization of reaction for the synthesis of compound 3a^a

Entry	Solvent	KOH (mg)	Time (min)	Yield ^[b] 3a (%)	Yield ^[b] 4a (%)
1	EtOH	100	60	75	15
2	MeOH	100	90	65	25
3	CH ₃ CN	100	90	70	20
4	H ₂ O	100	120	15	78
5	EtOH/H ₂ O (3:1)	100	20	90	8
6	EtOH/H ₂ O (1:1)	100	20	95	< 4
7	EtOH/H ₂ O (1:3)	100	20	88	10
8	EtOH/H ₂ O (1:1)	50	20	78	8

[a] Reaction condition: 4-Chloro benzaldehyde (**1a**), *o*-Phenylenediamine (**2**), were taken in a 1:1 ratio at r.t. [b] Isolated yield.

Encouraged by these results, the methodology was extended with various aryl aldehydes **1a-i** were reacted with *o*-phenylenediamine **2** and the reactions preceded well to afford benzimidazoles **3a-i** (Scheme 2) in excellent yields (Chart 1, Table 2).

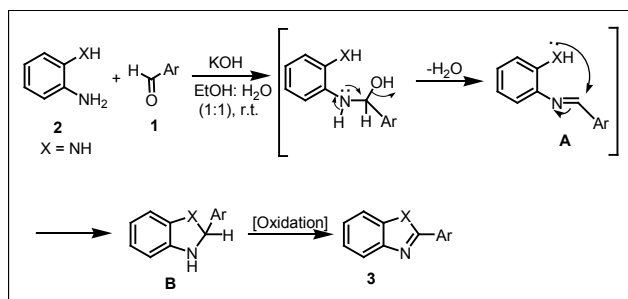
**Scheme 2****Table - 3: Synthesis of benzimidazoles catalyzed by KOH^a**

Entry	Aldehydes	Diamine	Time (min)	Product	Yield (%) ^[b]	Mp (°C)
1	1a	2	20	3a	97	290 ^[43]
2	1b	2	20	3b	96	228-230 ^[40]
3	1c	2	20	3c	97	300 ^[43]
4	1d	2	20	3d	97	308-310 ^[43]
5	1e	2	25	3e	95	288-290 ^[43]
6	1f	2	30	3f	94	224-226 ^[43]
7	1g	2	20	3g	97	256 ^[42]
8	1h	2	30	3h	92	> 300 ^[40]
9	1i	2	40	3i	85	230 ^[41]

[a] Reaction conditions: aldehydes (**1**), *o*-Phenylenediamine (**2**), were taken in a 1:1 ratio in the presence of 0.1 g of KOH in 5 mL of H₂O:EtOH (1:1) under r.t.; [b] Isolated yield.

From the results, it has been observed that both electrons withdrawing (4-chloro **1a**, 3-chloro **1b**, 4-bromo **1c** and 4-nitro) and donating substituents (4-methyl **1f**, 3-methoxy **1g**) in the aryl aldehyde caused slightly lower yields. It is noteworthy that heteroaryl and organometallic aldehydes such as 2-thiophenealdehyde **1h** and ferrocenealdehyde **1i** also took part in the reaction to provide benzimidazole products **3h** and **3i**, respectively (Table 2, entries 8 and 9). The isolated compounds were characterized using spectroscopic and physical methods and compared with those data in literature.

A plausible mechanism for the formation of benzimidazoles **3** derivatives is shown in scheme 3. Accordingly, the intermediate Schiff bases **A** (generated by condensation from aldehyde **1** and aromatic amine **2** under the catalytic influence of KOH) from which the cyclic adduct **B** (dihydrobenzimidazole) is produced by intramolecular participation of the *o*-amino group, which subsequently undergoes aerial oxidation to give the corresponding compounds **3**.

**Scheme 3.**

Plausible mechanism for the formation of compound 3

4. CONCLUSION

In conclusion, 2-substituted benzimidazoles were synthesized by combining *o*-phenylenediamine with various aldehydes in H₂O: EtOH (1:1) as solvent at room temperature using commercially available KOH as an efficient catalyst under atmospheric air as an efficient oxidant. The method is of great value because of its environmentally benign, efficient, and easy handling method. In addition, low cost and ready availability of reagents are the added advantages of this protocol.

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