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# Eco-friendly synthesis of 2-substituted benzimidazoles catalyzed by $FeCl_3$/Montmorillonite K-10

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## Abstract

2-substituted benzimidazoles have been synthesized in a single pot from aromatic aldehydes and *o*-phenylenediamine catalyzed by $FeCl_3$/Montmorillonite K-10 in DMF at room temperature. The prominent features of this method include mild conditions, short reaction times, high yields and simple procedure.

## Keywords

Benzimidazoles; *o*-phenylenediamine; Aromatic aldehydes; $FeCl_3$/Montmorillonite K-10.

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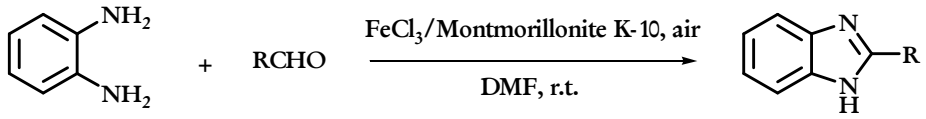
## INTRODUCTION

Benzimidazole derivatives have received much interest in the field of medicinal chemistry[1]. They exhibit significant activity against several viruses such as HIV[2], herpes (HSV-1)[3] and RNA influenza[4,5]. Therefore, the preparation of benzimidazoles has gained considerable attention in recent years. A variety of methods have been developed for the synthesis of benzimidazoles. Of these, one of the most traditional methods involves the condensation of an *o*-aryldiamines and carboxylic acids[6] or its derivatives[7] in the presence of strong acids and even sometimes combined with very high temperature[8]. Subsequently, because of the availability of a vast number of aldehydes, several improved protocols have been developed for the synthesis of benzimidazoles via the condensation of *o*-aryldiamine with aldehydes. Various oxidative reagents, such as nitrobenzene[9], $Mn(OAc)_3$[10], SDS[11], tetracyanoethylene[12], $NH_4OAc$[13], $MnO_2$[14], silica-supported thionyl chloride[15], air[16], sulfamic acid[17], sulfonic acid functionalized silica[18], $I_2$[19], $In(OTf)_3$[20], $Yb(OTf)_3$[21], $Sc(OTf)_3$[22], $KHSO_4$[23], IL[24], (bromodimethyl)sulfonium bromide[25], iodobenzene diacetate[26], $H_2O_2$/HCl[27], air[28], AlKIT-5[29], mono and bifunctional solid catalysts[30] and scolecite[31] etc have been employed in these procedures. However, a number of these methods suffer from certain drawbacks including long reaction times, unsatisfactory yields, harsh reaction condition, expensive reagents, tedious work up procedures and co-occurrence of several side reactions. Therefore, the introduction of new methods and/or further work on technical improvements to overcome the limitations is still an important experimental challenge.

The development of simple, efficient and environmentally friendly chemical processes for widely used organic compounds from readily available reagents is one of the major challenges for chemists in organic synthesis. Catalysts and reagents supported on inorganic substrates have received increasing attention in recent years as a means to develop more convenient or selective catalysts[32]. In particular, $FeCl_3$/Montmorillonite K-10 has been used as an efficient catalyst for a number of organic reactions and offered several advantages over classic acid, employing a reusable catalyst and minimally environmental

pollution. As reported in previous papers, ferric chloride adsorbed on Montmorillonite K-10 has been used as the catalyst in the preparation of 1,2-diaryl-1,2-ethanedione[33] to afford the desired products in higher yields. In continuation of a broad programme being pursued in our laboratory on supported reagent-induced organic reactions[34-38], herein we wish to report a new method for the condensation of *o*-phenylenediamine and aldehydes catalyzed by $FeCl_3$/Montmorillonite K-10 at room temperature (Scheme 1).




(1) 2(a-n) 3(a-n)

**Scheme 1 : Synthesis of 2-substituted benzimidazoles**

## EXPERIMENTAL

All chemicals were obtained from commercial suppliers and were used without further purification and melting points were uncorrected. IR spectra were recorded on a NICOLET 380 FT-IR spectrometer using KBr discs. $^1$H NMR spectra were recorded on a Bruker AVANCE 600 (600 MHz) spectrometer using TMS as internal standard and *d*-DMSO as solvent. Mass spectrometric data were determined on Agilent Technologies 6310 Lon Trap LC/MS.

### Preparation of $FeCl_3$/Montmorillonite K-10

The $FeCl_3$/Montmorillonite K-10 (10% w/w) was prepared by following process. Hydrated ferric chloride ($FeCl_3 \cdot 6H_2O$) 8 g was mixed with 72 mL methanol and 43.2 g Montmorillonite K-10. The mixture was stirred at room temperature for 1 h. The methanol was removed under reduced pressure. The resulting yellow-green powder was dried at 120 °C for 4 h. The content of $FeCl_3$ was determined to be about 10%.

$FeCl_3$/Montmorillonite K-10 (5% w/w) and $FeCl_3$/Montmorillonite K-10 (15% w/w) were prepared in accordance with the above-described method. All the catalysts were stored in desiccators.

### General procedure for synthesis of 2-substituted benzimidazoles

Aromatic aldehydes (2, 1.0 mmol), *o*-phenylenediamine (1, 1.0 mmol) and $FeCl_3$/Montmorillonite K-10 (160 mg) were added to DMF (5 mL) and the reaction stirred at room temperature in a 25 mL round bottomed flask for the appropriate time (see TABLE 1-2). The reaction mixture was then concentrated in vacuo, and the residue was dissolved in ethyl acetate. The catalyst was removed by filtration and washed with ethyl acetate. The solvent was evaporated under reduced pressure. The crude product was subjected to chromatography on silica gel (200–300 mesh) eluted with petroleum ether or the mixture of petroleum ether and ethyl acetate. The authenticity of the products was established by spectroscopic data and by comparing their melting points with literature values.

### 2-phenyl-1H-benzimidazole (3a)

Isolated as white crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3049, 2965, 2921, 2848, 2718, 2671, 1589, 1542, 1446, 1313, 1275, 1224, 1115, 969, 928, 743; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.91 (s, 1H, N-H), 8.19 (d, 2H, $J$ = 6.0 Hz, Ar-H), 7.68 (d, 1H, $J$ = 6.0 Hz, Ar-H), 7.54 (m, 4H, Ar-H), 7.21 (m, 2H, Ar-H); *m/z* (ESI): 195 $[M+H]^+$.

### 2-(2'-chlorophenyl)benzimidazole (3b)

Isolated as white crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3054, 2919, 1621, 1441, 1386, 1317, 1274, 1229, 1221, 1052, 974, 878, 746; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.73 (s, 1H, N-H), 7.90 (dd, 1H, $J_1$ = 7.4 Hz, $J_2$ = 1.9 Hz, Ar-H), 7.71 (d, 1H, $J$ = 7.8 Hz, Ar-H), 7.65-7.67 (m, 1H, Ar-H), 7.51-7.58 (m, 3H, Ar-H), 7.21-7.27 (m, 2H, Ar-H); *m/z* (ESI): 229 $[M+H]^+$.

### 2-(3'-chlorophenyl)benzimidazole (3c)

Isolated as white crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3043, 2964, 2920, 2786, 1599, 1441, 1389, 1275, 1121, 1081, 892, 744; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 13.05 (s, 1H, N-H), 8.23 (d, 1H, $J$ = 1.0 Hz, Ar-H), 8.15 (dd, 1H, $J_1$ = 7.5 Hz, $J_2$ = 0.9 Hz, Ar-H), 7.69 (s, 1H, Ar-H), 7.56-7.61 (m, 3H, Ar-H), 7.24 (s, 2H, Ar-H); *m/z* (ESI): 229 $[M+H]^+$.

### 2-(4'-chlorophenyl)benzimidazole (3d)

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3053, 2924, 2850, 1593, 1427, 1385, 1316, 1270, 1222, 1088, 1011, 961, 828, 741; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 13.01 (s, 1H, N-H), 8.19-8.21 (m, 2H, Ar-H), 7.68 (s, 1H, Ar-H), 7.63-7.65 (m, 2H, Ar-H), 7.52-7.58 (m, 1H, Ar-H), 7.23 (s, 2H, Ar-H); *m/z* (ESI): 229 $[M+H]^+$.

### 2-(3,4-dichlorophenyl)benzimidazole (3e)

Isolated as white crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3052, 2840, 1891, 1619, 1590, 1434, 1394, 1284, 1268, 1228, 1139, 1029, 979, 883, 825; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ:

13.06 (s, 1H, N-H), 8.39 (d, 1H, $J$ = 1.3 Hz, Ar-H), 8.15 (dd, 1H, $J_1$ = 8.3 Hz, $J_2$ = 1.4 Hz, Ar-H), 7.80 (d, 1H, $J$ = 8.3 Hz, Ar-H), 7.65-7.69 (s, 1H, Ar-H), 7.56 (s, 1H, Ar-H), 7.24 (s, 2H, Ar-H); *m/z* (ESI): 263 $[M+H]^+$.

**2-(4'-methylphenyl)benzimidazole (3f)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 2920, 2850, 1552, 1500, 1431, 1385, 1316, 1273, 963, 821, 744; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.83 (s, 1H, N-H), 8.07 (d, 2H, $J$ = 8.1 Hz, Ar-H), 7.64 (s, 1H, Ar-H), 7.52 (s, 1H, Ar-H), 7.36 (d, 2H, $J$ = 7.9 Hz, Ar-H), 7.20 (s, 2H, Ar-H), 2.38 (s, 3H, $CH_3$); *m/z* (ESI): 209 $[M+H]^+$.

**2-(4'-methoxyphenyl)benzimidazole (3g)**

Isolated as white crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3055, 2919, 2850, 1739, 1609, 1500, 1438, 1386, 1293, 1253, 1178, 1121, 1032, 964, 847, 742; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.75 (s, 1H, N-H), 8.11-8.13 (m, 2H, Ar-H), 7.62 (d, 1H, $J$ = 5.2 Hz, Ar-H), 7.49 (d, 1H, $J$ 5.2 = Hz, Ar-H), 7.18 (s, 2H, Ar-H), 7.11-7.13 (m, 2H, Ar-H), 3.85 (s, 3H, $CH_3$); *m/z* (ESI): 225 $[M+H]^+$.

**2-(2'-hydroxyphenyl)benzimidazole (3h)**

Isolated as white crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3325, 3055, 1596, 1518, 1490, 1449, 1422, 1321, 1262, 1132, 1038, 840, 727; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 13.17 (s, 2H, N-H, OH), 8.06 (dd, 1H, $J_1$ = 7.9 Hz, $J_2$ = 1.5 Hz, Ar-H) 7.62-7.72 (m, 2H, Ar-H), 7.38-7.40 (m, 1H, Ar-H), 7.29 (s, 2H, Ar-H), 7.01-7.05 (m, 2H, Ar-H); *m/z* (ESI): 211 $[M+H]^+$.

**2-(4'-nitrophenyl)benzimidazole (3i)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 2920, 2850, 1600, 1514, 1435, 1384, 1341, 1101, 965, 852, 744, 709; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 13.31 (s, 1H, N-H), 8.41-8.44 (m, 4H, Ar-H), 7.74 (d, 1H, $J$ = 7.9 Hz, Ar-H), 7.60 (d, 1H, $J$ = 7.9 Hz, Ar-H), 7.24-7.31(m, 2H, Ar-H); *m/z* (ESI): 240 $[M+H]^+$.

**2-(2'-hydroxy-3'-methoxyphenyl)benzimidazole (3j)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 2923, 2853, 1592, 1530, 1457, 1422, 1385, 1253, 1056, 977, 827, 782, 742; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 13.27 (s, 1H, N-H), 13.20 (s, 1H, O-H), 7.73 (s, 1H, Ar-H), 7.60-7.65 (m, 2H, Ar-H), 7.29-7.30 (m, 2H, Ar-H), 7.09 (d, 1H, $J$ = 7.2 Hz, Ar-H), 6.95-6.97 (m, 1H, Ar-H), 3.82 (s, 3H, $CH_3$); m/z (ESI): 241 $[M+H]^+$.

**2-(3',4'-methylenedioxyphenyl)benzimidazole (3k)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3053, 2905, 2761, 1618, 1548, 1470, 1449, 1388, 1334, 1255, 1230, 1113, 1081, 1039, 974, 930, 882, 849, 813, 743; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.77 (s, 1H, N-H), 7.73 (dd, 1H, $J_1$ = 8.1 Hz, $J_2$ = 1.6 Hz, Ar-H), 7.70 (d, 1H, $J$ = 1.6 Hz, Ar-H), 7.57 (s, 2H, Ar-H), 7.17-7.20 (m, 2H, Ar-H), 7.10 (d, 1H, $J$ = 8.0 Hz, Ar-H), 6.13 (s, 2H, $CH_2$); m/z (ESI): 239 $[M+H]^+$.

**2-[4'-(N,N-dimethylaminophenyl)]benzimidazole (3l)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 2922, 1609, 1566, 1500, 1440, 1380, 1273, 1200, 1110, 946, 823, 746; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.54 (s, 1H, N-H), 7.99-8.01 (m, 2H, Ar-H), 7.50 (s, 2H, Ar-H), 7.12-7.14 (m, 2H, Ar-H), 6.80-6.88 (m, 2H, Ar-H), 2.97 (s, 6H, $CH_3$); *m/z* (ESI): 238 $[M+H]^+$.

**2-(2'-furyl)benzimidazole (3m)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3060, 2823, 2774, 2664, 1628, 1588, 1524, 1415, 1317, 1276, 1231, 1168, 1116, 1075, 1014, 977, 907, 738; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.93 (s, 1H, N-H), 7.95 (d, 1H, $J$ = 1.2 Hz, Furanyl), 7.57 (s, 2H, Ar-H), 7.19-7.22 (m, 3H, Ar-H, Furanyl), 6.73-6.74 (m, 1H, Furanyl); *m/z* (ESI): 185 $[M+H]^+$.

**2-styryl-1H-benzimidazole (3n)**

Isolated as light yellow crystal. IR (KBr), $\tilde{\nu}$ /cm$^{-1}$: 3061, 2739, 1636, 1422, 1380, 1314, 1274, 1024, 960, 749; $^1$H NMR (DMSO-$d_6$, 600 MHz) δ: 12.67 (s, 1H, N-H), 7.67-7.69 (m, 3H, Ar-H), 7.56 (s, 2H, Ar-H), 7.45 (t, 2H, $J$ = 7.6 Hz, Ar-H), 7.37 (t, 1H, $J$ = 7.3 Hz, Ar-H), 7.24 (d, 1H, $J$ = 16.6 Hz, Ar-H), 7.19 (m, 2H, -CH=CH-); m/z (ESI): 221 $[M+H]^+$.

## RESULTS AND DISCUSSION

In order to get the best experimental condition, we have considered the reaction of *o*-phenylenediamine (1) and benzaldehyde (2a) in the presence of $FeCl_3$/Montmorillonite K-10 stirring at room temperature as a standard model reaction. To evaluate the effect of the solvent, we carried out the model reaction in different solvents including DMF, $CH_3CN$, MeOH, $CHCl_3$, EtOH and $CH_2Cl_2$. The use of EtOH and $CHCl_3$ as solvent gave poor yields (TABLE 1, Entries 1, 4). Solvents like MeOH, $CH_2Cl_2$ and $CH_3CN$ gave moderate yields (TABLE 1, Entries 2, 3, 5). When the reaction was run in DMF, the yield of 2-phenyl-1*H*-benzimidazole (3a) was relatively better (TABLE 1, Entry 6). Therefore, DMF was selected as the best solvent for this reaction.

As shown in TABLE 1, with changing the reaction temperature from 25 °C to 55 °C (TABLE 1, Entries 6, 8), the

**TABLE 1 : The effect of solvent and temperature on the synthesis of 2-phenyl-1*H*-benzimidazole (3a)[A]**

| Entry | Solvent | t/h | (3a)Yield[B](%) |
|---|---|---|---|
| 1 | $C_2H_5OH$ | 0.3 | 58.8 |
| 2 | $CH_3OH$ | 0.6 | 68.6 |
| 3 | $CH_2Cl_2$ | 9.0 | 65.1 |
| 4 | $CHCl_3$ | 10 | 53.5 |
| 5 | $CH_3CN$ | 0.5 | 66.6 |
| 6 | DMF | 2.0 | 86.8 |
| 7[C] | DMF | 2.0 | 52.1 |
| 8[D] | DMF | 0.7 | 65.8 |
| 9[E] | DMF | 0.4 | 70.6 |
| 10[F] | DMF | 2.2 | 79.1 |
| 11[G] | DMF | 1.5 | 69.4 |

[A] *o*-phenylenediamine (1.0 mmol), benzaldehyde (1.0 mmol), $FeCl_3$/Montmorillonite K-10 was 160 mg (10% w/w), the reactions were carried out in the presence of air at r.t. [B] Isolated yields. [C] Operated in nitrogen atmosphere. [D] Stirred at 55 °C. [E] Ultrasound irradiation at 40 °C. [F] $FeCl_3$/Montmorillonite K-10 was 160 mg (5% w/w). [G] $FeCl_3$/Montmorillonite K-10 was 160 mg (15% w/w).

yield of 3a decreased from 86.8% to 65.8%. When the reaction was run in nitrogen atmosphere, 3a was obtained in 52.1% yield (TABLE 1, Entry 7). These results suggest that aerial oxygen played an oxidant role in this reaction. We also observed the effect of ultrasound irradiation on the reaction. 3a was obtained in 70.6% yield under ultrasound irradiation at 40 °C (TABLE 1, Entry 9).

The effect of the amount of $FeCl_3$ supported on Montmorillonite K-10 on the reaction was observed in DMF. When the content of $FeCl_3$ was 5%, 10% and 15%, the yield of 3a was 79.1% (TABLE 1, Entry 10), 86.8% (TABLE 1, Entry 6) and 69.4% (TABLE 1, Entry 11) respectively. It seems that changing the amount of $FeCl_3$/Montmorillonite K-10 (TABLE 1, Entries 6, 10, 11) had a remarkable effect on the yield of 3a, the more or less of the amount is both unfavorable for the reaction. So we chose 10% w/w $FeCl_3$/Montmorillonite K-10 as the optimum amount. Using the optimized reaction conditions, a range of 2-substituted benzimidazoles 3a–n were synthesized (TABLE 2).

Most products described herein were previously reported in the literature. As shown in TABLE 2, the condensation of *o*-phenylenediamine with a series of aromatic aldehydes afforded 2-substituted benzimidazoles in excellent yields catalyzed by $FeCl_3$/Montmorillonite K-10 in DMF at room temperature. However, the most dramatic changes observed were with regard to reaction time. In the reaction catalyzed by $Sc(OTf)_3$[22], 3f was obtained in 55% yield under $O_2$ after stirring for 44 h at room temperature, whereas the present procedure resulted in 84.9% yield of 3f at room temperature within 2.0 h. In the reaction catalyzed by activated carbon (Darco KB) in xylene under an oxygen atmosphere[34], 3a was obtained in 64% yield at 120 °C for 26 h, whereas the present procedure afforded 3a in 86.8% yield within 2.0 h.

The same scale reaction using only $FeCl_3$ without any Montmorillonite K-10 being present yielded 60.8% of 3a after 2.0 h at room temperature (TABLE 2, Entry 2), The Montmorillonite K-10 support itself showed very little activity (38.1%) in the synthesis of 3a after 2.0 h (TABLE 2, Entry 3), however, the catalytic activity was increased drastically because of the impregnation of $FeCl_3$ (TABLE 2, Entry 1). The conversion which was catalyzed by the Montmorillonite K-10-supported $FeCl_3$ is higher than without any support. These data showed that both $FeCl_3$ alone and Montmorillonite K-10 alone were anything but satisfactory for the synthesis of 2-substituted benzimidazoles.

**TABLE 2 : The synthesis of 2-substituted benzimidazole derivatives catalyzed by $FeCl_3$/Montmorillonite K-10**

| Entry | Ar | t/h | Product | Yield (%) | m.p./°C [lit] |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | 2.0 | 3a | 86.8 | 292-294(292)[15] |
| 2 | | 2.0 | 3a | 60.8[A] | |
| 3 | | 2.0 | 3a | 38.1[B] | |
| 4 | | 10 | 3a | 60.3[C] | |
| 5 | | 10 | 3a | 35.6[D] | |
| 6 | 2-$ClC_6H_4$ | 2.8 | 3b | 94.5 | 230-232(233-234)[13] |
| 7 | 3-$ClC_6H_4$ | 1.8 | 3c | 73.1 | 237-238(238)[6b] |
| 8 | 4-$ClC_6H_4$ | 1.5 | 3d | 85.3 | 282-284(288-291)[23] |
| 9 | 3,4-$Cl_2C_6H_3$ | 1.0 | 3e | 80.6 | 236 ~238(233-235)[16] |
| 10 | 4-$CH_3C_6H_4$ | 2.0 | 3f | 84.9 | 270-272(270)[15] |
| 11 | 4-$CH_3OC_6H_4$ | 1.3 | 3g | 71.4 | 233-235(228-230)[23] |
| 12 | 2-$OHC_6H_4$ | 6.0 | 3h | 79.1 | 248(240-242)[23] |
| 13 | 4-$NO_2C_6H_4$ | 1.3 | 3i | 95.0 | 294-297(298-300)[19b] |
| 14 | 2-OH-3-$MeOC_6H_3$ | 2 | 3j | 95.4 | 272-274(270-271)[10] |
| 15 | 3,4-$OCH_2OC_6H_3$ | 2.0 | 3k | 91.6 | 239 ~241(246)[17] |
| 16 | 4-$Me_2NC_6H_4$ | 2.5 | 3l | 91.7 | 231 ~232(233-236)[17] |
| 17 | 2-Furyl | 1.5 | 3m | 61.7 | 283-285(286)[11] |
| 18 | $C_6H_5CH$=CH | 2.0 | 3n | 63.6 | 185 ~187(199-201)[23] |
| 19 | 2,4-$(NO_2)_2C_6H_3$ | 6.0 | | nr | |
| 20 | $CH_3$ | 7.0 | | nr | |
| 21 | $C_3H_7$ | 7.0 | | nr | |

[A] Only $FeCl_3$ as catalyst. [B] Only montmorillonite K-10 as catalyst. [C] Catalyzed by first recycled $FeCl_3$/ montmorillonite K-10 as catalyst. [D] Catalyzed by second recycled $FeCl_3$/ montmorillonit K-10 as catalyst.

Encouraged by these results, the condensation of furfuraldehyde (2m) and *o*-phenylenediamine (1) was also examined to extend the scope of this method, 2-(2'-furyl)benzimidazole (3m) was obtained in moderate yields (61.7%) within 1.5 h. It was noteworthy that no corresponding product was obtained when the substrate was 2,4-dinitrobenzaldehyde (TABLE 2, Entry 19) in this experiment. Aliphatic aldehyde was less reactive than arylaldehyde in this reaction, no product was obtained when aliphatic aldehyde was used. The results were summarized in TABLE 2 (Entries 20, 21).

At the end of the reaction, the catalyst was separated by ?ltration, thoroughly washed with ethyl acetate and reused under similar conditions. As shown by the formation of 3a, there was an appreciable loss in the activity in the reuse of these catalysts (60.3% on the second run for 10 h and 35.6% on the third run for 10 h, TABLE 2, Entries 4, 5). This is because of the leaching of the active catalyst component (i.e. iron) in the entire treatment process[40], which is in our expectation. Further work is necessary to strongly bind the active component on the support.

## CONCLUSIONS

In summary, we have found a practical procedure for the preparation of 2-substituted benzimidazoles catalyzed by $FeCl_3$/Montmorillonite K-10 at room temperature. Our procedure is characterized by milder conditions, shorter reaction time, higher yield and involvement of non toxic and expensive catalyst.

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