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HIGHLY CHEMOSELECTIVE SYNTHESIS OF BENZIMIDAZOLES IN SC(OTF)$_3$-CATALYZED SYSTEM

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Abstract – The present researches elicit a simple, green and efficient method for the synthesis of substituted benzimidazoles through the coupling of *o*-phenylenediames with aldehydes catalyzed by Sc(OTf)$_3$ in ethanol, which obtains high chemoselectivity and excellent yield of many biologically active 1,2-disubstitued and 2-substituted benzimidazoles respectively and are also environment friendly.

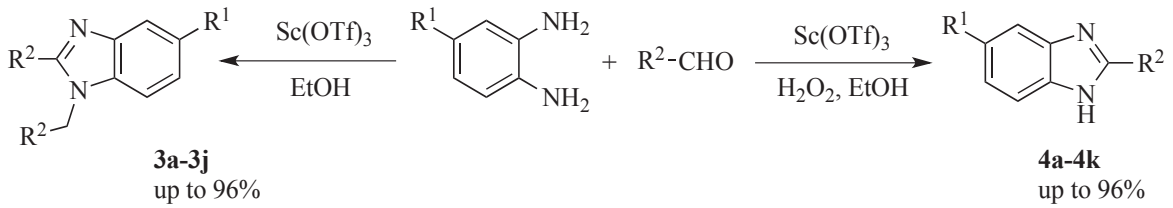
INTRODUCTION

Nitrogen-containing heterocyclic compounds have attracted considerable attention[1] owing to their potential involvement as key component for various pharmacological activities.[2] Among the various heteroaromatic compounds, benzimidazoles exhibit antiviral, antiseptic, antihypertensive and anticancer properties.[3] They are important intermediates in many pharmaceutical synthesis cases, such as drugs for the treatment of obesity[4] and hypertension.[5]

Diverse synthetic methodologies available for the synthesis of benzimidazoles have been developed,[6] with the most common method involving the treatment of *o*-phenylenediamines with either carboxylic acids[7] or their derivatives (nitriles,[8] aldehydes[9] or alcohols[10]) catalyzed by Lewis acids,[11] ionic liquids,[12] nanosized material[13] and Zeolite.[14] Although the reaction was efficiently promoted by the above conditions, some of these methods suffer from some degree of disadvantages. One of the major limitation to benzimidazoles is that some show poor selectivity, which results in the formation of two compounds (the mixture of 2-substituted and 1,2-disubstituted benzimidazoles).[15] In view of this drawback, Sasaki and his group attempted the use of Co(OH)$_2$ and CoO[16] as catalyst to form 1,2-disubstitued benzimidazoles. In 2013, Boroujeni developed PS-PyCl-xACl$_3$[17] a heterogeneous catalyst to obtain relatively high chemoselective 2-substitued benzimidazoles. To a certain extent, these methodologies have made significant improvement in the formation of benzimidazoles with good chemoselectivity. At present, a better reaction system to gain different substituted benzimidazoles with high chemoselectivity

respectively in mild reaction conditions has not yet founded.

Herein, we report the $Sc(OTf)_3$-catalyzed condensation of *o*-phenylenediamine with aldehydes in EtOH, furnishing a practicable approaches for the formation of 1,2-disubstitued benzimidazoles with high chemoselectivity and excellent yields in the presence of H_2O_2. Furthermore, the absence of H_2O_2 obtained high reaction selectivity and productivity for the synthesis of 2-substitued benzimidazoles (Scheme 1).

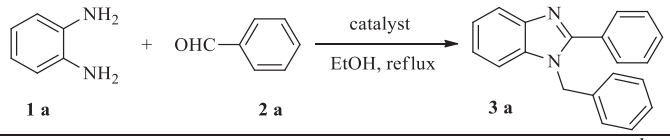


Scheme 1. The process to 1,2-sustituted and 2-substituted benzimidazoles

RESULTS AND DISCUSSION

Reactions were started by examing the reaction of benzaldehyde (2 mmol) and 1, 2-phenylenediamines (1.2 mmol) as model reaction. As is shown in Table 1, the use of $Sc(OTf)_3$ allowed the direct conversion of mixture into corresponding 1,2-disubstituted benzimidazole in a yield of 95% in EtOH (Table 1, Entry 1). Conversely, the use of other rare earth catalyst did not obviously enhance yields (Table 1, Entry 2-4).

Table 1. Catalyst-screen for the synthesis of **3a**[a]

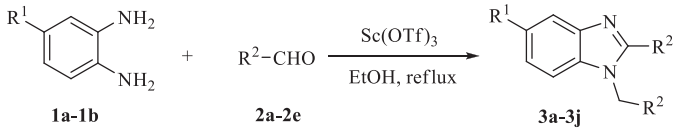


Entry	Catalyst (10 mol %)	Yield[b] (%)
1	none	22
2	$Sc(OTf)_3$	95
3	$ScCl_3$	86
4	$Y(OTf)_3$	79
5	YCl_3	78

[a] 1, 2-phenylenediamine (**1a**, 1.2 mmol.), benzaldehyde (**2a**, 2.0 mmol.), $Sc(OTf)_3$ (0.2 mmol.), 80 °C in EtOH, reflux. [b] Isolated yield

To generalize the reagent system, the applicability of $Sc(OTf)_3$-catalyzed system was then examined for the reactions of series of aromatic aldehydes with 1,2-phenylenediamines under the optimized reaction conditions (Table 2). As shown, a variety of benzaldehydes bearing electron-donating (Table 1, Entries 3, 4) or electron-withdrawing (Table 1, Entries 2, 5) were successfully employed to the corresponding benzimidazole derivatives in good yields. And the formation of the corresponding benzimidazoles could be realized with other diamines under the same conditions (Table 2, Entries 6–10).

Table 2. $Sc(OTf)_3$-catalyzed synthesis of 1,2- benzimidazole **3**[a]



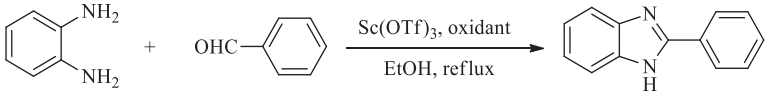
1a-1b 2a-2e 3a-3j

Entry	R^1	R^2	Product	Yield[b](%)
1	H **1a**	Ph **2a**	**3a**	90
2	H **1a**	4-ClC_6H_4 **2b**	**3b**	92
3	H **1a**	4-$MeOC_6H_4$ **2c**	**3c**	95
4	H **1a**	4-MeC_6H_4 **2d**	**3d**	93
5	H **1a**	4-FC_6H_4 **2e**	**3e**	96
6	NO_2 **1b**	Ph **2a**	**3f**	84
7	NO_2 **1b**	4-ClC_6H_4 **2b**	**3g**	91
8	NO_2 **1b**	4-$MeOC_6H_4$ **2c**	**3h**	88
9	NO_2 **1b**	4-MeC_6H_4 **2d**	**3i**	85
10	NO_2 **1b**	4-FC_6H_4 **2e**	**3j**	88

[a] 1, 2-phenylenediamines (**1a-1b**, 1.2 mmol.), benzaldehydes (**2a-2e**, 2.0 mmol.), $Sc(OTf)_3$ (0.2 mmol.), 80 °C in EtOH, reflux. [b] Isolated yield

Furthermore, the scope of this system has been successfully extended to the synthesis of 2-substituted benzimidazoles, which represents the first synthesis of these compounds through adding the oxidant.[18]During the research, we found that $Sc(OTf)_3$ could catalyze the synthesis of 2-substituted benzimidazoles in presence of H_2O_2 (Table 3, Entry 2). However, the yield was not satisfactory. The direct reflux condensing of *o*-pheylenediamines and aldehydes was a competitive formation of the 1, 2-disubstituted and the 2-substituted benzimidazoles. So we change the reaction process, diluting the aldehydes into EtOH and dropping them into the reaction mixture, the yield was improved. This reaction also proceeded smoothly with morpholine, AATEMPO-BF_4 and $PhI(OAc)_2$, but with relatively lower yields. With decreasing amounts of H_2O_2, the yield decreased.

Table 3. Effect of additives in the formation of **4a**[a]



1a 2 b 4 a

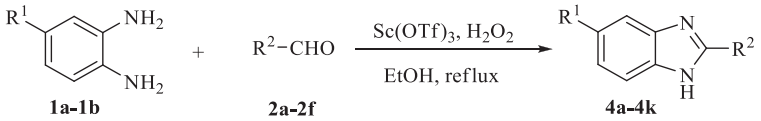
Entry	Oxidant (200 mol %)	Yield[b] (%)
1	none	Trace
2	H_2O_2	60[c]
3	H_2O_2	88
4	H_2O_2 (100 mol%)	71
5	$PhI(OAc)_2$	80
6	AATMPO·BF_4^-	41
7	morpholine	70

[a] 1, 2-phenylenediamine (**1a**, 1.2 mmol), benzaldehyde (**2b**, 1.0 mmol.), $Sc(OTf)_3$ (0.15 mmol.), H_2O_2 (2mmol.) was added into the mixture dropwise, 80 °C in EtOH, reflux. [b] Isolated yield.[c] benzaldehyde was added into the mixture in one batch.

Aromatic aldehydes with electron-donating and electron-withdrawing groups both participated in this

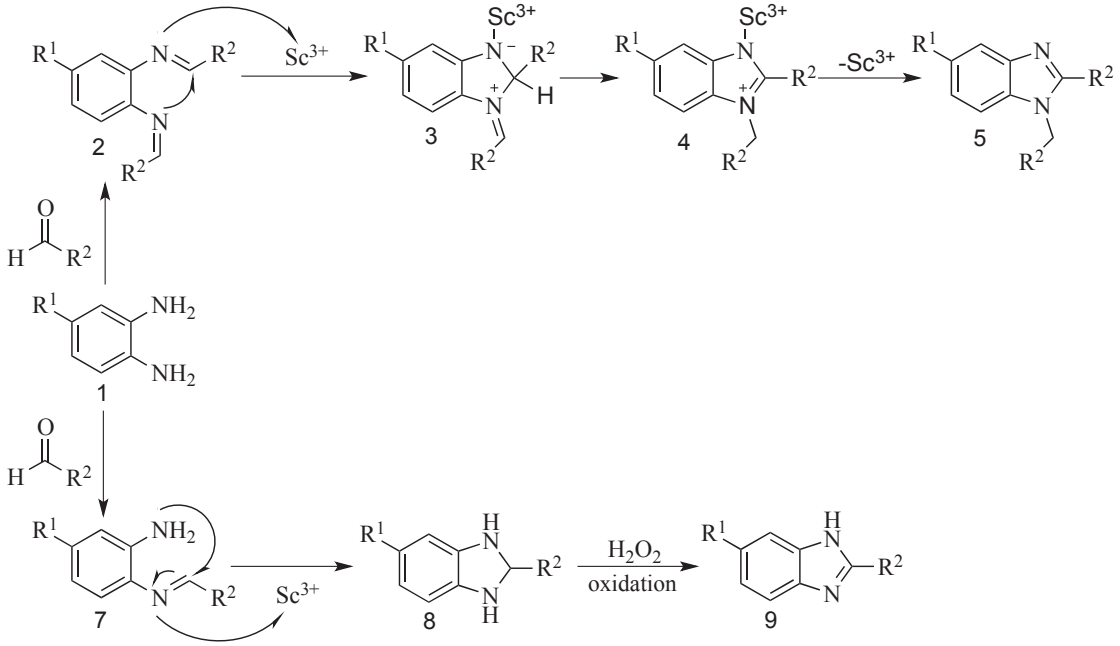
reaction equally well- apparently, the nature of substitution on the aryl ring does not make much difference (Table 4, Entry 2-5). This procedure is also applicable to substituted 1, 2-phenylendiamines, which produce the corresponding 2-arylbenzimidazoles smoothly in excellent yields (Table 4, Entry 6-10). It is worthy to notice that the catalyst is also found to be active in the synthesis of benzidazoles using furfuraldehyde (**4k**). And it is the main component of Fuberidazoles.[19] Two reasonable mechanisms for the condensation reaction of 1, 2-phenylenediamine and aldehydes are shown in Scheme 2.

Table 4. $Sc(OTf)_3$-catalyzed synthesis of 2- benzimidazole **4**[a]



Entry	R^1	R^2	Product	Yield[b] (%)
1	H **1a**	Ph **2a**	**4a**	90
2	H **1a**	4-ClC_6H_4 **2b**	**4b**	92
3	H **1a**	4-$MeOC_6H_4$ **2c**	**4c**	95
4	H **1a**	4-MeC_6H_4 **2d**	**4d**	93
5	H **1a**	4-FC_6H_4 **2e**	**4e**	96
6	NO_2 **1b**	Ph **2a**	**4f**	84
7	NO_2 **1b**	4-ClC_6H_4 **2b**	**4g**	91
8	NO_2 **1b**	4-$MeOC_6H_4$ **2c**	**4h**	88
9	NO_2 **1b**	4-MeC_6H_4 **2d**	**4i**	85
10	NO_2 **1b**	4-FC_6H_4 **2e**	**4j**	88
11	H **1a**	2-Furyl **2f**	**4k**	70

[a] 1, 2-phenylenediamine (**1a-1b**, 1.2 mmol.), benzaldehyde (**2a-2f**, 1.0 mmol.), $Sc(OTf)_3$ (0.15 mmol.), H_2O_2 (2 mmol.), 80 °C in EtOH, reflux. [b] Isolated yield



Scheme 2. Proposed mechanism for the synthesis of 1,2-sustituted and 2-substituted benzimidazoles catalyzed by $Sc(OTf)_3$

EXPERIMENTAL

^{1}H and ^{13}C NMR spectrums were recored on Bruker ARX 400 for proton. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.36 ppm), DMSO-d_6 (δ: 40.45) and $(CD_3)_2CO$ (δ: 30.60, 205.87) used as an internal reference. And ^{1}H NMR were reported downfield from $CDCl_3$ (δ: 7.27 ppm), DMSO-d_6 (δ: 2.49), and $(CD_3)_2CO$ (δ: 2.09) Column chromatographies were performed with silica gel (200-300 mesh ASTM).

Starting Materials. All chemicals used in this study were commmercially available.

Typical experimental procedure of the preparation of products 3a, 3b, 3c, 3d, 3e, 3f, 3g, 3h, 3i, and 3j.

1-Benzyl-2-phenyl-1*H*-benzo(*d*)imidazole (3a): A mixture of $Sc(OTf)_3$ (98.4 mg, 0.2 mmol) and EtOH (5 mL) were well stirred until the solid dissolved completely at reflux condition; then *o*-phenylenediamine **1a** (129.8 mg, 1.2 mmol) and benzaldehyde **2a** (202 μL, 2.0 mmol) was added into the above mixture. The reaction was monitored by TLC. The reaction mixture was cooled to rt, and then evaporated in vacuum. The product purified by column chromatography (PE-EtOAc= 5:1) to give **3a** (269.6 mg, 95%); Light yellow solid; mp 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 1 H), 7.48-7.45 (m, 3 H), 7.34-7.30 (m, 4 H), 7.25-7.21 (m, 2 H), 7.11 (d, J = 7.2 Hz, 2 H), 5.47 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.22, 143.23, 136.44, 136.11, 130.12, 129.97, 129.30, 129.11, 128.81, 127.83, 126.01, 123.10, 122.74, 120.03, 110.61, 48.41.

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1*H*-benzo(*d*)imidazole (3b): a light yellow solid (324.2 mg, 95%); mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 1 H), 7.60-7.58 (m, 2 H), 7.45-7.43 (m, 2 H), 7.36-7.27 (m, 4 H), 7.20 (d, J = 8 Hz, 1 H), 7.02 (d, J = 8.4 Hz, 2 H), 5.40 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.90, 143.14, 136.36, 135.96, 134.68, 133.87, 130.47, 129.41, 129.12, 128.41, 127.29, 123.50, 123.07, 120.22, 110.34, 47.82.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-benzo(*d*)imidazole (3c)： a yellow solid (326.9 mg, 95%); mp 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8 Hz, 1 H), 7.65-7.63 (m, 2 H), 7.31-7.27 (m, 1 H), 7.24-7.21 (m, 2 H), 7.03 (d, J = 8.8 Hz, 2 H), 7.00-6.96 (m, 2 H), 6.86-6.84 (m, 2 H), 5.38 (s, 2 H), 3.85 (s, 3 H), 3.70(s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.90, 159.12, 154.14, 143.22, 136.13, 130.72, 128.51, 127.23, 122.74, 122.53, 122.49, 119.74, 114.44, 114.20, 110.45, 55.40, 55.32, 47.90.

1-(4-Methylbenzyl)-2-*p*-tolyl-1*H*-benzo(*d*)imidazole (3d): a yellow solid (290.3 mg, 93%); mp 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=8 Hz, 1 H), 7.59 (d, J = 8 Hz, 2 H), 7.31-7.27 (m, 1 H), 7.25-7.24 (m, 2 H), 7.21-7.16 (m, 2 H), 7.13(d, J = 8 Hz, 2 H), 6.99 (d, J = 8 Hz, 2 H), 5.40 (s, 1 H),

2.40 (s, 3 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 154.38, 143.22, 140.05, 137.46, 136.14, 133.50, 129.73, 129.48, 129.19, 127.22, 125.93, 122.86, 122.58, 119.85 (s), 110.55 (s), 48.22, 21.48, 21.14.

1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-1*H*-benzo(*d*)imidazole (3e): a yellow solid (307.1 mg, 96%); mp 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1 H), 7.66-7.63 (m, 2 H), 7.34-7.28 (m, 2 H), 7.24-7.20 (m, 1 H), 7.17-7.13 (m, 2 H), 7.07-6.99 (m, 4 H), 5.40 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.54, 161.08, 153.11, 143.07, 135.90, 131.95, 131.24, 127.64, 126.17, 123.33, 122.96, 120.11, 116.22 116.01 , 110.36, 47.74.

1-Benzyl-5-nitro-2-phenyl-1*H*-benzo(*d*)imidazole (3f): a yellow solid (277.4 mg, 84%); mp 163-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1 H), 8.18 (d, *J* = 2 Hz, 2 H), 7.90 (d, *J* = 8.8 Hz, 1 H), 7.73-7.70 (m, 2 H), 7.55-7.48 (m, 3 H), 7.39-7.32 (m, 3 H), 7.10-7.07 (m, 2 H), 5.55 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$,): δ = 158.87, 147.65, 143.70, 135.45, 135.19, 130.94, 129.42, 129.36, 129.30, 129.09, 125.88, 120.03, 118.73, 107.47, 48.84.

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-5-nitro-1*H*-benzo(*d*)imidazole (3g): a yellow solid (362.4 mg,91%); mp 144-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 9.0 Hz, *J* = 2 Hz, 1 H), 8.17 (d, *J* = 1.6 Hz, 2 H), 7.65-7.60 (m, 2 H), 7.51-7.49 (m ,2 H), 7.37-7.34 (m, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 5.49 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.26, 140.50, 137.54, 134.42, 130.50, 129.74, 129.52, 129.15, 128.96, 127.15, 118.81, 103.82, 98.95, 82.60, 48.18.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-5-nitro-1*H*-benzo(*d*)imidazole (3h): a yellow solid (342.6 mg, 88%); mp 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.8 Hz, *J* = 2 Hz, 1 H), 8.17 (d, *J* = 2 Hz, 1 H), 7.86 (d, *J* = 8.8 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.02 (dd, *J* = 8.8 Hz, *J* = 4 Hz, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 5.48 (s, 2 H), 3.87 (s, 3 H), 3.80 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.87, 159.10, 158.97, 146.54, 140.74, 139.71, 129.77, 129.11, 128.91, 128.13, 127.59, 119.00, 114.25, 114.14, 114.06, 55.32, 47.93, 47.26.

1-(4-Methylbenzyl)-5-nitro-2-(*p*-tolyl)-1*H*-benzo(*d*)imidazole (3i): a yellow solid (303.7 mg, 85%); mp 154-156 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.8 Hz, *J* = 2 Hz, 1 H), 8.15 (d, *J* = 2 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 5.50 (s, 2 H), 2.43 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.07, 147.73, 143.53, 141.31, 138.14, 135.49, 132.22, 130.04, 129.77, 129.22, 125.81, 119.79, 118.65, 107.45, 48.67, 27.38, 21.55, 21.14.

1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-5-nitro-1*H*-benzo(*d*)imidazole (3j): a yellow solid (321.9 mg, 88%); mp 186-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.8 Hz, *J* = 2 Hz, 1 H), 8.18 (d, *J* = 2.0 Hz, 1 H), 7.90 (d, *J* = 9.2 Hz, 2 H), 7.70 (dd, *J* = 8.6 Hz, *J* = 5.6 Hz, 2 H), 7.24-7.19 (m, 2 H), 7.09-7.05 (m, 4 H), 5.50 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.57, 163.05, 157.75, 147.42 –

147.29, 143.83 – 143.71, 135.32, 131.4, 130.76, 127.59, 125.03, 120.17, 118.92, 116.73 – 116.53, 116.50 – 116.30, 107.25, 48.19.

Typical experimental procedure of the preparation of products 4a, 4b, 4c, 4d, 4e, 4f, 4g, 4h, 4i, 4j, and 4k.

2-Phenyl-1*H*-benzo(*d*)imidazole (4a): A mixture of *o*-phenylenediamine **1a** (129.8 mg, 1.2 mmol), $Sc(OTf)_3$ (73.8 mg, 0.15 mmol) and EtOH (15 mL) wre well stirred until the solid dissolved completely at reflux condition. Benzaldehyde **2b** (101 μL, 1.0 mmol) and H_2O_2 (61 μL, 30 wt%, 2 mmol) was diluted to 20 mL EtOH, and dropwised into the preprocessed mixture. After TLC showed the reaction to be complete, the reaction mixture was cooled to rt, and then evaporated in vacuum. The product purified by column chromatography (PE-EtOAc= 4:1) to give **4a** (160.6 mg, 90%); Light yellow solid; mp 289-291 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.91(s, 1 H), 8.19-8.17(m, 2 H), 7.67-7.49 (m, 5 H), 7.21(s, br, 2H); ^{13}C NMR (100 MHz, DMSO-d_6,) δ 151.58, 143.38,135.50, 130.73, 130.29, 129.11, 126.87, 122.89, 121.20, 118.89, 111.84.

2-(4-Chlorophenyl)-1*H*-benzo(*d*)imidazole (4b): a yellow solid (208.8 mg, 92%); mp 289-291 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.90 (s, 1H), 8.21 (d, J =8.4Hz, 2H), 7.64 (d, J = 8.4Hz, 4H), 7.23–7.20 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.56, 144.31, 135.02, 134.81, 129.50, 128.66, 128.22, 122.91, 122.50, 119.34, 111.69.

2-(4-Methoxyphenyl)-1*H*-benzo(*d*)imidazole (4c): a yellow solid (213.0 mg, 95%); mp 222-224 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, J = 7.2Hz, 1H), 7.24–7.20 (m, 2H), 7.08 (d, J = 8.8Hz, 2H), 6.96 (d, J = 8.4Hz, 2H), 6.83 (d, J = 8.8Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.80, 153.56, 143.27, 136.30, 129.27, 127.85, 122.47, 119.37, 114.68, 114.59, 111.48, 55.80.

2-(*p*-Tolyl)-1*H*-benzo(*d*)imidazole (4d): a yellow solid (193.7 mg, 93%); mp 274-276 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.81 (s, 1H), 8.06 (d, J = 7.8Hz, 2H), 7.55 (s, 2H), 7.34 (d, J = 7.8Hz, 2H), 7.21–7.18 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 151.78, 144.28, 140.00, 135.36, 129.88, 127.86, 126.85, 122.69, 121.99, 119.12, 111.66, 21.33.

2-(4-Fluorophenyl)-1*H*-benzo(*d*)imidazole (4e): a brown solid (203.2 mg, 96%); mp 246-247 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ12.92 (s, 1H), 8.25-8.21 (m, 2 H), 7.66-7.54 (m, 2 H), 7.43-7.38 (m, 2 H), 7.21-7.16 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.78, 162.23, 150.91, 129.72, 129.60, 129.22, 129.10, 127.33, 122.58,118.13, 116.88.

5-Nitro-2-phenyl-1*H*-benzo(*d*)imidazole (4f): a yellow solid (193.7 mg , 84%); mp 207-209 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.55 (s, 1H), 8.40 (s, 1H), 8.14–8.1 (m, 2H), 8.09–8.04 (m, 1H), 7.70 (d, 1H), 7.54 (s, 1H), 7.52 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ 155.12, 143.10, 137.62, 131.37, 129.55, 129.42, 128.75, 127.37, 118.37, 110.71, 104.93.

2-(4-Chlorophenyl)-5-nitro-1*H*-benzo(*d*)imidazole (4g): a yellow solid (249.6 mg , 91%); mp 305-306 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.72 (s, 1 H), 8.51(s, br, 1 H), 8.24 (d, J = 8.8 Hz, 2 H), 8.16 (dd, J = 8.8 Hz, J = 2.0 Hz, 1 H), 7.80 (s, br, 1 H), 7.71 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-*d6*) δ 155.13, 150.53, 143.50, 136.36, 131.46, 129.88, 129.32, 128.55, 118.92, 115.64, 112.65.

2-(4-Methoxyphenyl)-5-nitro-1*H*-benzo(*d*)imidazole (4h): a yellow solid (235.6 mg, 88%); mp 237-238 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 12.50 (s, 1H), 8.48 (s, 1H), 8.21 (t, J = 13.9 Hz, 2H), 8.16 (dd, J = 8.8, 2.1 Hz, 1H), 7.76 (t, J = 17.8 Hz, 1H), 7.15 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 162.06, 143.71, 142.35, 128.70, 121.81, 117.76, 116.38, 114.35, 113.37, 100.35, 99.67 54.99.

5-Nitro-2-(*p*-tolyl)-1*H*-benzo(*d*)imidazole (4i): a yellow solid (216.3 mg, 85%); mp 209-211 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.45 (s, 1H), 8.10 (s, br, 1 H), 8.09 (dd, J_1 = 8.8 Hz, J_2 = 1 Hz, 1 H), 7.98 (d, J = 8.4 Hz, 2 H), 7.67 (s, br, 1 H), 7.36 (d, J = 8.4 Hz, 2 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.32, 136.37,130.12, 129.15, 127.77, 126.02, 118.67, 115.02, 112.81, 112.39, 109.91, 21.11.

2-(4-Fluorophenyl)-5-nitro-1*H*-benzo(*d*)imidazole (4j): a yellow solid (226.3 mg, 88%); mp 221-223 ^{o}C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 12.64 (s, 1H), 8.51 (s, 1H), 8.37 – 8.28 (m, 2H), 8.18 (dt, J = 8.9, 2.0 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.39 (td, J = 8.7, 1.7 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 165.55, 163.07, 154.84, 143.52, 139.38, 129.43,129.40, 125.98, 118.05, 116.09, 116.03.

2-(Furan-2-yl)-1*H*-benzo(*d*)imidazole (4k): a yellow solid (129.4 mg, 70%); mp 285-286 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.91 (brs, 1H), 7.94 (s, 1 H), 7.62 (d, J = 8.4 Hz, 1 H), 7.50 (d, 1H, J = 8.0 Hz), 7.25-7.18 (m, 3H), 6.77-6.74 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.00, 143.45, 143.45, 137.12, 134.16, 122.43, 121.56, 118.66, 112.33, 111.23, 110.34.

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