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MICROWAVE-ASSISTED SYNTHESIS OF 2-SUBSTITUTED 1*H*-BENZO[*d*]IMIDAZOLES AND THEIR ANTIFUNGAL ACTIVITIES *IN VITRO*

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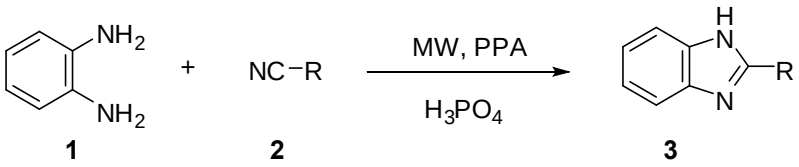
Abstract – An efficient and novel microwave-assisted synthesis of 1*H*-benzo[*d*]imidazole derivatives via nitriles and *o*-phenyldiamines in the presence of polyphosphoric acid (PPA) and phosphoric acid is described. This method provides several advantages such as commercially high availabilities of starting materials, short reaction times, high yields and a simple workup procedure. Systematically antifungal biological tests showed **3f** was most promising candidate against six phytopathogenic fungi.

Microwave-assisted organic synthesis (MAOS) is a hot topic in which a large number of papers have been published in last three decades.[1] MAOS has significantly affected synthetic chemistry by providing a new means of rapid, efficient, and scalable chemical operations. At the same time, MAOS can facilitate the discovery of new reactions and reduce cycle time in the optimization of reactions. 1*H*-Benzo[*d*]imidazoles,[2] which are also called benzimidazoles, play a key role in pharmacy and agrochemicals, as these compounds possess a variety of biological activities including antiarrhythmic, antiulcer, anthelmintic,[3] inotropic, antihistamine,[4] antifungal,[5] and antiviral. Recent pharmaceutical studies have revealed that some derivatives show promising biological activity as antiallergic agents, factor Xa inhibitors,[6] poly(ADP-ribose)polymerase inhibitors,[7] and human cytomegalovirus inhibitors.[8] Structurally, benzimidazole derivatives are isosteres of naturally occurring nucleotides, which allows them to interact easily with the biopolymers of living systems. Moreover, polybenimidazoles (PBI) have

been developed as a kind of polymers that have applications as high temperature matrix resins, non-flammable textile fibres, adhesives and foams.[9]

Generally, the synthesis of benzimidazoles is accomplished by utilizing the condensation reaction of arylenediamines with carboxylic acids, carboxylic acid esters, lactones, anhydrides, and aldehydes under different catalysts.[10] Especially, hein discolsed only one example of thermal cyclization of benzonitrile and *o*-phenyldiamine, however, it needed harsh condition such as high temperature 250-300 °C.[10f] To the best of our knowledge, there have been no reports on the condensation between nitriles and arylenediamines under the microwave irradiation. We envisioned that microwave irradiation could enhance the condensation of nitriles and arylenediamines and expand the scope this protocol. Compared with other carboxyl equivalents, nitriles are structurally labile and ready intermediates because they can be synthesized easily from alkyl halide and cyanide in large scale. Herein, we wish to report an efficient and novel microwave-assisted synthesis of 1*H*-benzo[*d*]imidazole from readily available starting materials and their antifungal activities to six phytopathogenic fungi *in vitro*.



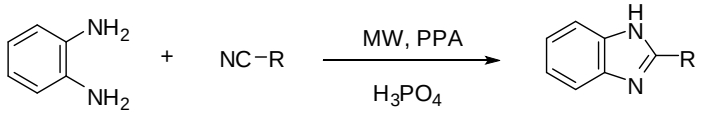
Scheme 1. Microwave-assisted synthesis of 1*H*-benzo[*d*]imidazole

Initially, a model reaction of *o*-phenyldiamine **1** (10 mmol) and benzonitrile **2** (10 mmol) in presence of a kind of acid under microwave irradiation (275 W, 15 min) was planned (Scheme 1). When 6 M HCl, 12 M HCl, silica-supported sulfuric acids, and NH_4Cl were tested, unfortunately, the cyclization of benzo[*d*]imidazole did not occur and those acidic catalysts proved to be inappropriate. When the H_2SO_4/DMSO system was used, an oily residue without any product was obtained. At last, when PPA was used as the acid and solvent, 2-phenyl-1*H*-benzo[*d*]imidazole was provided in 75% yield. Because of the high viscidity of PPA, some H_3PO_4 was added to buffer the heat of the microwave. To our satisfactory, when 20 mL PPA and 10 mL H_3PO_4 were used, the yield of 2-phenyl-1*H*-benzo[*d*]imidazole increased to 92%. Therefore, we set up the optimized reaction conditions, 20 mL PPA and 10 mL H_3PO_4 used as the co-solvent for per 10 mmol *o*-phenyldiamine and benzonitrile.

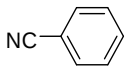
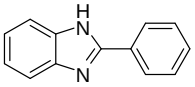
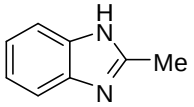
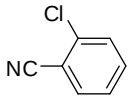
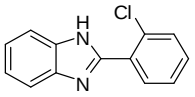
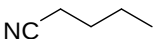
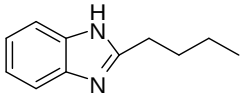
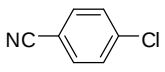
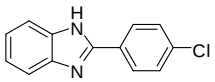
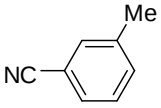
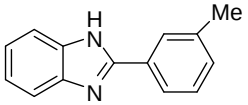
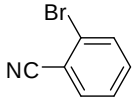
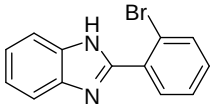
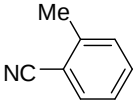
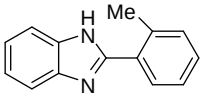
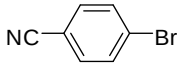
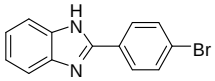
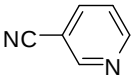
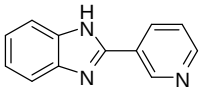
Under these optimized reaction conditions, we next examined the scope of PPA/H_3PO_4 catalyzed cyclization of *o*-phenyldiamine **1** and nitrile **2** for the synthesis of substituted 1*H*-benzo[*d*]imidazoles. The results are summarized in Table 1. A wide range of structurally diverse nitriles (Table 1), including aryl (Table 1, entries 1-8, entries 11-13), aliphatic (Table 1, entries 9-10) cyclization with

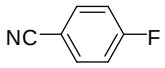
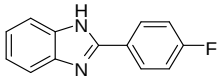
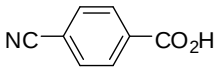
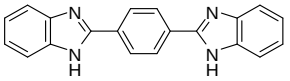
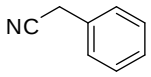
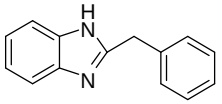
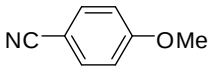
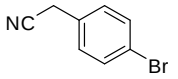
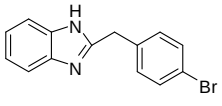
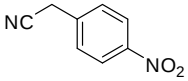
o-phenyldiamine under this protocol to give the corresponding substituted 1*H*-benzo[*d*]imidazoles in excellent yields. Among them, bromo (Table 1, entries 4-5), fluoro (Table 1, entry 6) and chloro (Table 1, entries 2-3) groups can be tolerated. The bromo and chloro moieties could be functionalized to boric acid or stannane easily, so our method effectively allows the preparation of halo 1*H*-benzo[*d*]imidazoles. It is worth notice that if the equivalent of carboxylic acid was included in starting materials, the cyclization occurred at both spots (Table entry 14). To our regret, the methoxy and nitro groups can not be tolerated in such conditions, complicated results was obtained (Table entries 15-16). We suspected that these two functional groups may react with PPA or H_3PO_4 under microwave irradiation. Thus, all the products in our reactions listed in Table 1 were easily characterized on the basis of physical and spectral data and also by comparison with authentic samples. All products (Table 1) were fully characterized by spectroscopic methods, as well as by the comparison of the spectral data with reported values.

Table 1. Microwave-Assisted Synthesis of 1*H*-benzo[*d*]imidazoles



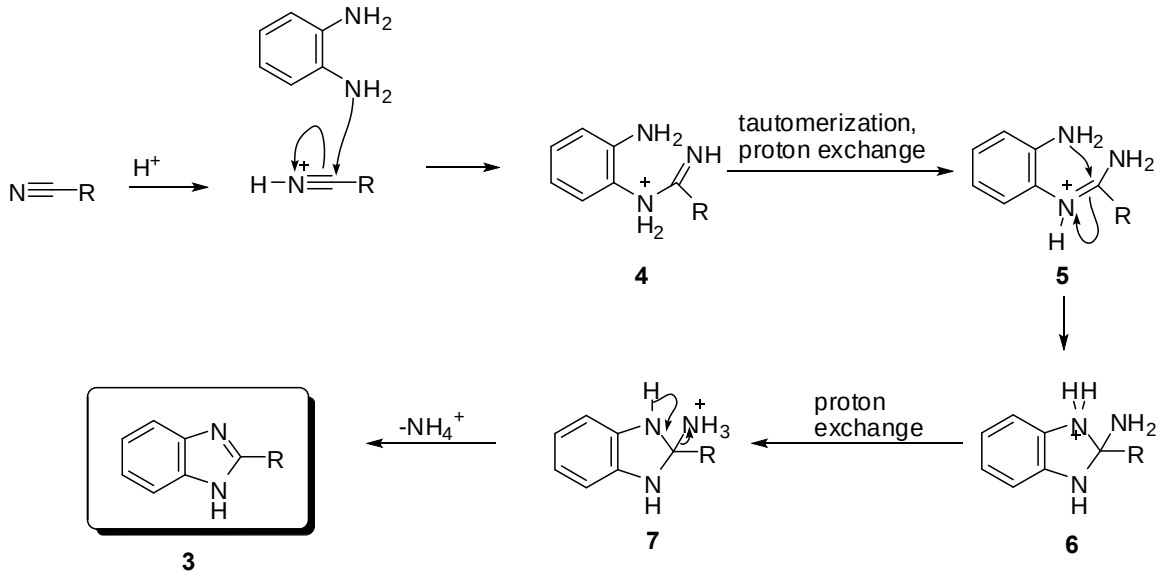
1 **2** **3**

Entry	**Compd 2**	Product **3**	Yield (%)[a]	Entry	**Compd 2**	Product **3**	Yield (%)[a]
1		 **3a**	92	9	NC−Me	 **3i**	85
2		 **3b**	84	10		 **3j**	95
3		 **3c**	86	11		 **3k**	90
4		 **3d**	75	12		 **3l**	89
5		 **3e**	86	13		 **3m**	86

6		 **3f**	96	14		 **3n**	78[b]
7		 **3g**	72	15		complicated results	-
8		 **3h**	77	16		complicated results	-

[a] isolated yield. [b] 2 equiv. of **1** are used.

The reaction presumably proceeds in four steps: nucleophilic addition of one amino group to *o*-phenyldiamine **1** to acidified nitrile **2** to give the adduct **4**. Then, **4** tautomerized to intermediate **5** via proton exchange. Because of the high electrophilicity of the protonated imine, another amino group in *o*-phenyldiamine would attack the carbon center to form intermediate **6**. This could be transformed into the final product 1*H*-benzo[*d*]imidazole after another proton exchange and deamination.



Scheme 2. Proposed mechanism of PPA/H_3PO_4 catalysed cyclization of *o*-phenyldiamines **1** and nitriles **2**

Meanwhile, 13 products of 2-substituted 1*H*-benzo[*d*]imidazoles (**3a-3m**) against six phytopathogenic fungi (*Cytospora mandshurica, Colletotrichum* gloeosporioides*, Botrytis cinerea, Alternaria solani, Fusarium solani* and *Pyricularia oryzae*) were investigated at the concentration of 100 μg/mL *in vitro* by poisoned food technique. While thiophanate-methyl, a commercially available agricultural fungicide, was used as a positive control at 100 μg/mL. As shown in the Table 2, we can see most of the 2-substituted

1*H*-benzo[*d*]imidazoles showed good to excellent antifungal activities. It should be note that the compound **3f** gave almost equal potential to thiophanate-methyl, but compound **3i** and **3m** give poor antifungal activities, relatively. With regard to **3f**, we suspected high penetrability of the fluoro atom contributed to excellent activities as well as less aromatic moiety gave rise to low activities of **3i**.

Table 2. Antifungal activities of **3a-3m** to six phytopathogenic fungi

	Antifungal activities (inhibition %)					
Compound	*Cytospora mandshurica*	*Colletotrichum gloeosporioide*	*Botrytis cinerea*	*Alternaria solani*	*Fusarium solani*	*Pyricularia grisea*
3a	86.85	85.16	64.31	79.08	75.73	65.17
3b	69.09	84.42	59.22	78.43	64.08	52.92
3c	84.87	74.04	57.67	71.24	53.89	68.40
3d	78.95	81.44	58.48	69.93	59.23	38.73
3e	44.09	61.06	60.12	49.02	44.67	45.82
3f	90.79	92.21	100.00	88.24	92.23	89.68
3g	61.19	55.87	35.76	64.71	47.10	54.85
3h	44.09	32.50	14.35	41.18	40.79	28.41
3i	30.28	14.33	7.21	23.53	15.07	12.93
3j	27.65	76.64	32.19	76.47	58.75	45.18
3k	85.53	92.21	57.17	81.70	82.04	76.78
3l	68.43	74.04	78.59	83.01	62.14	79.36
3m	2.66	27.31	10.78	42.48	24.77	14.86
thiophanate-methyl	86.85	76.99	78.59	54.25	94.18	30.99

In conclusion, a novel PPA/H_3PO_4 catalyzed cyclization of *o*-phenyldiamine and nitriles for the synthesis of substituted 1*H*-benzo[*d*]imidazoles under microwave irradiation has been developed. This method offers several advantages, such as high yields, short reaction times, clean reaction profiles, and simple experimental and easy work-up procedures. 13 products of 2-substituted 1*H*-benzo[*d*]imidazoles were tested again six phytopathogenic fungi.

EXPERIMENTAL

A mixture of nitrile (10 mmol), *o*-phenyldiamines (10 mmol) and PPA (20 mL) and H_3PO_4 (10 mL) was vigorously stirred and irradiated in microwave reactor (Sineo MAS-II, Shanghai, China) at internal 150 °C for 15 min (Table 1). Then the reaction mixture was poured into ice water and netrualized by 5 M NaOH to pH = 8. The mixture was extracted by DCM (3×30 mL) and the combined organic layers were

washed with saturated aqueous $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuum and the residue was purified through column chromatography to give **3** (Table 1). The ^{1}H-NMR and ^{13}C-NMR data were recorded in DMSO solution with Bruker-NMR spectrometers (DRX 500, AM 400) if not noted otherwise. The chemical shifts are measured relative to TMS ($\delta = 0$) or chloroform ($\delta = 7.26$) and the coupling *J* is expressed in Hertz.

2-Phenyl-1*H*-benzo[*d*]imidazole (3a)

Mp 290-292 °C (lit.,[11] 292 °C). ^{1}H-NMR: 7.27 (dd, 2H, *J* = 3.0, *J* = 6.0), 7.49 (d, 1H, *J* = 7.4), 7.57 (d, 2H, *J* = 7.7), 7.73 (d, 2H, *J* =7.3), 8.34 (dd, 2H, *J* =1.1, *J* =7.9), 13.11 (s, 1H). ^{13}C-NMR: 111.9, 119.4, 122.4, 122.9, 127.0, 129.4, 130.3, 130.8, 135.6, 144.5, 151.9.

2-(2-Chlorophenyl)-1*H*-benzo[*d*]imidazole (3b)

Mp 234-236 °C (lit.,[11] 233-236 °C). ^{1}H-NMR: 7.26 (s, 2H), 7.51-7.56 (m, 2H), 7.60-7.72 (m, 3H), 7.93 (dd, 1H, *J* = 1.8, *J* = 7.1), 12.76 (s, 1H). ^{13}C-NMR: 111.8, 119.2, 121.8, 122.9, 127.5, 130.1, 130.5, 131.3, 131.8, 132.2, 134.8, 143.4, 149.2.

2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole (3c)

Mp 292-294 °C (lit.,[11] 292-293 °C). ^{1}H-NMR: 7.23 (s, 2H), 7.55-7.67 (m, 4H), 8.19 (d, 2H, *J* = 8.4), 13.01 (s, 1H). ^{13}C-NMR: 111.9, 119.4, 122.4, 123.3, 128.6, 129.4, 129.6, 135.0, 144.1, 150.5.

2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole (3d)

Mp 242-244 °C (lit.,[12] 242 °C). ^{1}H-NMR: 7.23-7.28 (m, 2H), 7.48 (t, 1H, *J* = 7.7), 7.56 (t, 2H, *J* = 7.6), 7.70 (d, 1H, *J* = 7.7), 7.76 (d, 1H, *J* = 7.6), 7.83 (d, 1H, *J* = 8.0), 12.74 (s, 1H). ^{13}C-NMR: 112.0, 119.6, 122.0, 122.1, 123.2, 128.3, 131.9, 132.7, 132.8, 133.9, 134.8, 143.6,150.8.

2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole (3e)

Mp 298-300 °C (lit.,[12] 298 °C). ^{1}H-NMR: 7.24 (dd, 2H, *J* = 2.6, *J* = 5.4), 7.48-7.66 (m, 4H), 8.27(d, 2H, *J* = 7.7), 13.01 (s, 1H).^{13}C-NMR: 111.6, 119.1, 122.1, 122.8, 123.4, 128.5, 129.5, 132.1, 135.2, 143.8, 150.4.

2-(4-Fluorophenyl)-1*H*-benzo[*d*]imidazole (3f)

Mp 251-252 °C (lit.,[12] 250-251 °C). ^{1}H-NMR: 7.22 (dd, 2H, *J* = 3.0, *J* = 5.8), 7.41 (t, 2H, *J* = 8.8), 7.63 (s, 2H), 8.27 (dt, 2H, *J* = 3.9, *J* = 7.0), 12.97 (s, 1H). ^{13}C-NMR: 111.2, 116.0, 116.2, 122.3, 126.9, 127.0, 128.9, 129.0, 150.6, 162.3, 164.2.

2-Benzyl-1*H*-benzo[*d*]imidazole (3g)

Mp 195-196 °C (lit.,[13] 195-196 °C). ^{1}H-NMR: 4.17 (s, 2H), 7.11-7.15 (m, 2H), 7.23 (t, 1H, *J* = 6.3), 7.30-7.34 (m, 4H), 7.41 (d, 1H, *J* = 7.3), 7.53 (d, 1H, *J* = 7.3), 12.29 (s, 1H). ^{13}C-NMR: 35.4, 111.4, 118.7, 121.5, 122.2, 127.0, 129.0, 129.2, 134.7, 138.1, 143.8, 153.9.

2-(4-Bromobenzyl)-1*H*-benzo[*d*]imidazole (3h)

Mp 210-212-196 °C (lit.,[14] 212-213 °C). ^{1}H-NMR: 4.16 (s, 2H), 7.13 (t, 2H, J = 6.8), 7.29 (d, 2H, J = 8.1), 7.42 (d, 1H, J = 7.4), 7.52 (t, 3H, J = 7.9), 12.29 (s, 1H). ^{13}C-NMR: 34.6, 111.4, 118.8, 120.2, 121.5, 122.3, 131.5, 131.8, 134.7, 137.5, 143.7, 153.4.

2-Methyl-1*H*-benzo[*d*]imidazole (3i)

Mp 184-185 °C (lit.,[13] 184-185 °C). ^{1}H-NMR: 2.55 (s, 3H), 7.14 (dd, 2H, J = 3.2, J = 9.2), 7.52 (dd, 2H, J = 3.3, J = 5.8). ^{13}C-NMR: 15.1, 114.6, 121.6, 139.5, 151.9.

2-Butyl-1*H*-benzo[*d*]imidazole (3j)

Mp 184-185 °C (lit.,[15] 184-185 °C). ^{1}H-NMR: 0.91 (t, 3H, J = 7.4), 1.31-1.40 (m, 2H), 1.73-1.81 (m, 2H), 2.84 (t, 2H, J = 15.1), 7.10-7.14 (m, 2H), 7.49 (s, 2H), 12.29 (s, 1H). ^{13}C-NMR: 14.1, 22.3, 28.7, 30.2, 114.6, 121.5, 138.6, 155.6.

2-(3-Methylphenyl)-1*H*-benzo[*d*]imidazole (3k)

Mp 221-222 °C (lit.,[13] 222-223 °C). ^{1}H-NMR: 2.42 (s, 3H), 7.21 (dd, 2H, J = 2.8, J = 6.0), 7.31 (d, 1H, J = 7.5), 7.44 (t, 1H, J = 7.6), 7.59-7.64 (m, 2H), 7.99 (d, 1H, J = 7.8), 8.05 (s, 1H), 12.90 (s, 1H). ^{13}C-NMR: 21.5, 111.8, 119.2, 122.3, 122.9, 124.1, 127.5, 129.3, 130.6, 131.0, 133.9, 138.6, 144.3, 151.8.

2-(2-Methylphenyl)-1*H*-benzo[*d*]imidazole (3l)

Mp 239-240 °C (lit.,[13] 239-240 °C). ^{1}H-NMR: 2.62 (s, 3H), 7.22 (t, 2H, J = 8.1), 7.35-7.41 (m, 3H), 7.54 (d, 1H, J = 7.4), 7.69 (d, 1H, J = 7.4), 7.75 (d, 1H, J = 7.0), 12.64 (s, 1H). ^{13}C-NMR (125 M, DMSO): 21.5, 111.7, 119.4, 121.9, 122.8, 126.4, 129.8, 129.9, 130.5, 131.7, 134.9, 137.5, 144.2, 152.4.

2-(Pyridin-3-yl)-1*H*-benzo[*d*]imidazole (3m)

Mp 218-219 °C (lit.,[11] 218 °C). ^{1}H-NMR: 7.24-7.28 (m, 2H), 7.59-7.63 (m, 1H), 7.67 (s, 2H), 8.53 (dt, 1H, J = 2.2, J = 8.1), 8.70 (dd, 1H, J = 1.6, J = 4.8), 9.39 (dd, 1H, J = 0.6, J = 2.2), 13.15 (s, 1H). ^{13}C-NMR: 111.7, 119.3, 122.3, 123.0, 124.5, 126.6, 134.2, 135.0, 143.9, 148.0, 149.3, 151.0.

1,4-Bis(1*H*-benzo[*d*]imidazol-2-yl)benzene (3n)

Mp >300 °C (dec., lit.,[16] >300 °C). ^{1}H-NMR (400 MHz, DMSO-d_6): 7.19-7.26 (m, 4 H), 7.57 (d, J = 7.6 Hz, 2 H), 7.70 (d, J = 7.6 Hz, 2 H), 8.35 (s, 4 H), 13.05 (s, 2 H). ^{13}C NMR (100MHz, DMSO-d_6): 119.0, 121.9, 122.9, 126.9, 131.2, 143.9, 150.6.

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