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ULTRASONIC ACCELERATED EFFICIENT & MILD CHEMO-SELECTIVE SYNTHESIS OF 2-ARYL-1-ARYLMETHYL-1*H*-1,3-BENZIMIDAZOLES PROMOTED BY AMMONIUM MOLYBDATE

Prathapa Reddy Madddiguda, Srinivas Angapalley, Shweta Sawner, & Arifuddin Mohammed*

**Department of Medicinal Chemistry,*
National Institute of Pharmaceutical Education and Research. (NIPER-Hyderabad)
Balanagar, Hyderabad-500 037. India;
Email:- arifabib@yahoo.com

Abstract: The reaction of 1, 2-phenylenediamine with aromatic aldehydes in the presence of ammonium molybdate and ultrasonically accelerated to produce selectively 2-aryl-1-(arylmethyl)-1-*H*-1.3-benzimidazoles in good yields. The reaction is very efficient and proceeds under mild reaction conditions giving rise to pure products without further purification.

Keywords: Ultrasonication, 2-Aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles, *O*-Phenylenediamine, Chemo-selective synthesis, Ammonium molybdate.

Introduction

Benzimidazoles are well known heterocyclic compounds known to posses significant pharmacological activities such as selective neuropeptide XY1 receptor antagonist,[1] 5-Lipoxygenase inhibitors for use as novel anti-allergic agents,[2] factor Xa (Fxa) inhibitors[3] etc. They are also known to exhibit prominent anticancer,[4] antiulcer,[5] antihypertensive,[6] non-nucleoside inhibitor activities against HIV-1 reverse transcriptase,[7] fungicidal [8] and antihelmintic properties.[9] Some of benzimidazole containing drugs are depicted in **Figure 1.** The most common protocol for the synthesis of 1, 2-disubstituted benzimidazoles involves of N-alkylation of 2-substituted benzimidazoles in the presence of a strong base,[10] direct one step condensation of *o*-phenylenediamines with aldehydes under the influence of different acid catalysts.[11-18] In addition, the synthesis of 2-arylbenzimidazoles is also reported under ultrasounication condition.[19] However, in spite of their potential utility most of these methods are not straight forward and have different disadvantages like low yield, prolonged reaction time, tedious work up and several side reactions. Moreover, all these methodologies fail to give good yields & selectivity in terms of N-1-substitution to form 1,2-disusbstitutted benzimidazoles extensively.[20-21] As a result, the introduction of an efficient and mild

chemoselective method is needed. Ultrasound waves have gradually been introduced in organic synthesis as a green synthetic approach over the last few decades.

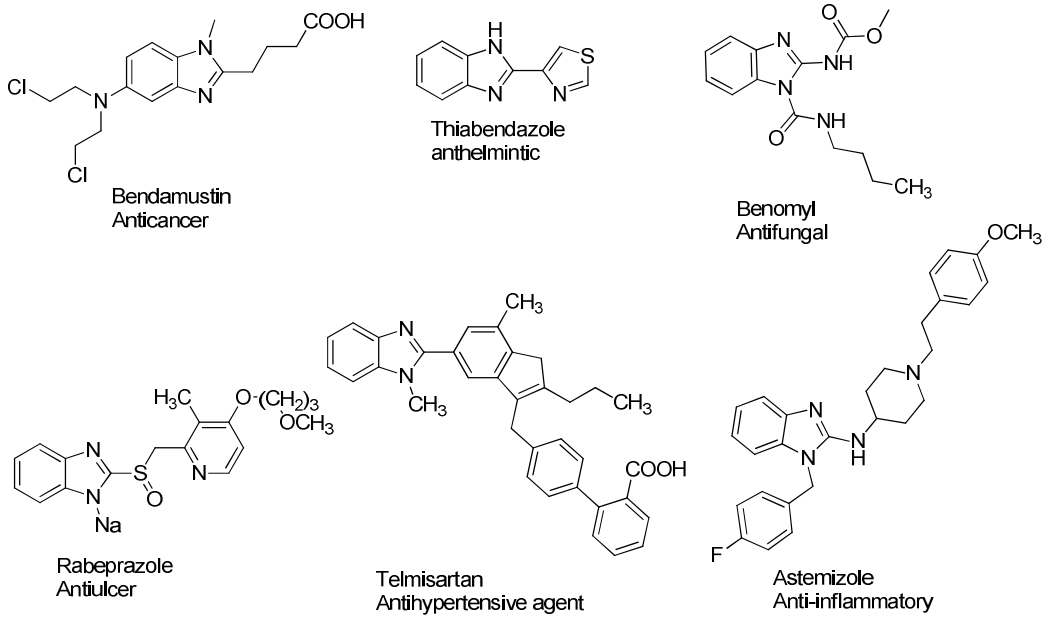
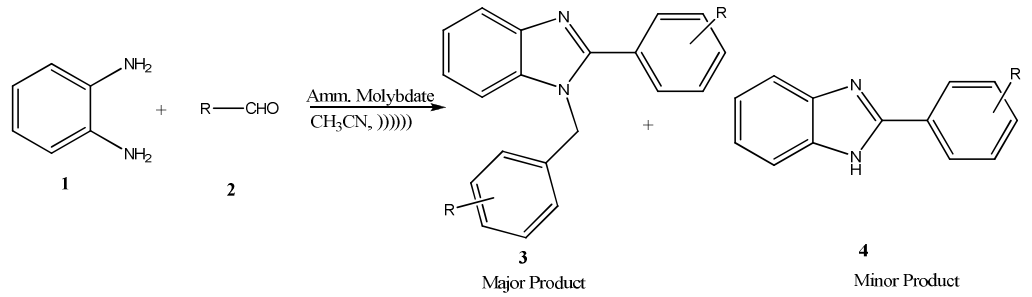


Figure 1. Structure of various drugs containing Benzimidazole moiety

Due to the unique biological properties of 1,2-disubstituted benzimidazoles and our interest in ultrasound mediated green chemistry, we report herein ammonium molybdate mediated, an efficient and facile synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles under ultrasonication. (**Scheme 1**)



Scheme 1. Synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1.3-benzimidazoles

Experimental

General remarks

Melting points were determined in open capillaries in a sulphuric acid bath and are uncorrected. All chemicals and solvents were of analytical grade and were used without further purification as received from the suppliers. Infrared spectra were recorded on Perkin-Elmer infrared spectrometer with NaCl optics; samples were scanned as neat, or as KBr thin films. IR values are expressed as cm^{-1}. ^{1}H-NMR spectra were recorded on Bruckner Avance 300MHz spectrometer. The samples were made in $CDCl_3$/DMSO-d_6 and TMS was used as the internal standard with values chemical shift given in δ scale. The progress of the reaction

was monitored by TLC on pre-coated silica gel 60-GF 254 (0.5mm) TLC plates. Mass spectra were recorded on ESI mass spectrometer. Powersonic 405 of Hwashin Technology, Seoul, Korea (with frequency of 50 Hz and a power 350 w) ultrasonic bath was used for ultra sonication.

General Procedure for the synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles (3a-3k)

A mixture of *o*-Phynelenediamine (1) (1 mmol) aromatic aldehyde (2) (2 mmol) and ammonium molybdate heptahydrate (1 mmol) and acetonitrile was taken in a round bottomed flask and subjected to sonication at RT for 1 hr. After completion of the reaction as indicated by the TLC, the solid was filtered off and the filtrate was evaporated under reduced pressure in rotary evaporator. The residue was diluted with water and extracted with ethyl acetate. The organic layer was washed with water followed by brine. The organic layer was separated out, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue obtained was purified by column chromatography over silica gel by using 10% ethyl acetate: hexane as eluent to give the product in quantitative yield.

Spectral Data for Representative Compounds:

1-Benzyl-2-phenyl-1-*H*-1,3-benzimidazole (3a) : M.P. = 133^0C; ^{1}H-NMR (300MHz, $CDCl_3$); δ 5.36 (s, 2H, CH_2-Ph); 7.03 (t, 2H, Ar), 7.11 (t, 2H, Ar), 7.22-7.25 (m, 4H, Ar), 7.36 (m, 3H, Ar), 7.57 (dd, 2H, Ar), 7.77 (d, 1H, Ar); IR= cm^{-1} (KBr) 3056, 1597, 696; MS: m/z: 285.13 (M^+ +1).

1-(Thiophen-2-ylmethyl)-2-(thiophen-2-yl)-1-*H*-benzimidazole (3b): M.P. = 151^0C; ^{1}H-NMR (300MHz, $CDCl_3$); 5.46 (s, 2H, CH_2-Ph), 6.62 (d, 2H, Ar), 6.91 (t, 1H, Ar), 7.05 (m, 3H, Ar), 7.28 (dd, 2H, Ar), 7.61 (d, 2H, Ar); IR= cm^{-1} (KBr) 3063, 1589,1568; MS: m/z: 297.05 (M^+ +1).

1-(2-Naphthylmethyl)-2-(2-Naphthyl)- 1-*H*-benzimidazole (3c) : M.P. = 223-225^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); 5.54 (s, 2H, CH_2-Ph), 7.13 (t, 2H, Ar), 7.20 (m, 2H, Ar), 7.36-7.45 (m, 5H, Ar), 7.57 (d, 2H, Ar), 7.751 (t, 25H, Ar), 7.83 (dd, 1H, Ar), 8.06 (t, 1H, Ar); IR= cm^{-1} (KBr) 3128, 1560,1412; MS: m/z: 385.25 (M^+ +1).

1-(2-hydroxybenzyl)-2-(2-hydroxyphenyl)-1-*H*-1,3-benzimidazole (3d): M.P. = 226-228^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); 5.51 (s, 2H, CH_2-Ph), 6.8-7.10 (m, 3H, Ar), 7.15-7.50 (m, 5H, Ar), 7.62-7.65 (m, 2H, Ar), 8.01 (d, 2H, Ar), 7.751 (t, 2H, Ar), 10.96 (br, 2H, OH); IR= cm^{-1} (KBr) 3410, 1620; MS: m/z: 317.12 (M^+ +1).

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1-*H*-1,3-benzimidazole (3e): M.P. = 135-136^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); δ 5.45 (s, 2H, CH_2-Ph), 7.11 (d, 2H, Ar), 7.21-7.25 (m, 2H, Ar), 7.35 (d, 2H, Ar), 7.48 (d, 1H, Ar), 7.79 (d, 2H, Ar), 7.70 (d, 3H, Ar); IR= cm^{-1} (KBr) 3110, 1610; MS/ m/z= 353.06 (M^+ +1).

1-(4-Bromobenzyl)-2-(4-bromophenyl)-1-*H*-1,3-benzimidazole (3f): M.P. = 157-158^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); δ 5.48 (s, 2H, CH_2-Ph), 7.08 (d, 2H, Ar), 7.25-7.28 (m, 2H, Ar), 7.36 (d, 2H, Ar), 7.50 (d, 1H, Ar), 7.82 (d, 2H, Ar), 7.75 (d, 3H, Ar); IR= cm^{-1} (KBr) 3120, 1620; MS: m/z: 443.13 (M^+ +1).

1-(3,4,5-trimethoxybenzyl)-2-(3,4,5-trimethoxyphenyl)-1-*H*-1,3-benzimidazole (3g):
M.P. 260^{0}C, ^{1}H-NMR (300 MHz, $CDCl_3$); δ 3.83 (s, 6H, OCH_3), 3.95 (s, 6H, OCH_3), 4.02 (s, 6H, OCH_3), 5.42 (s, 2H, CH_2-Ph), 6.35 (s, 2H, Ar), 7.28-7.32 (m, 5H, Ar), 7.92 (d, 1H, Ar); IR = cm^{-1} (KBr) 3020, 1620, 1440,1230; MS: m/z: 465.41 (M^+ +1).

1-(3-hydroxybenzyl)-2-(3-hydroxyphenyl)-1-*H*-1,3-benzimidazole (3h): M.P. = 251-253^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); δ 5.35 (s, 2H, CH_2-Ph), 6.80-6.91 (m, 4H, Ar), 7.11-

7.46 (m, 6H, Ar), 7.91 (d, 2H, Ar), 10.86 (br, 2H, OH)); IR= cm^{-1} (KBr) 3410, 1620; MS: m/z: 317.12 (M^+ +1).

1-(4-Dimethylaminobenzyl)-2-(4-dimethylaminophenyl)-1-*H*-1,3-benzimidazole (3i): M.P. = 252-254^{0}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.84 (d, 6 H, $N(CH_3)_2$), 5.25 (s, 2 H, CH_2-Ph), 6.56 (M, 6 H, Ar), 7.89 (dd, 2 H, Ar), 7.47 (d, 2 H, Ar); IR = cm^{-1} (KBr) 3310, 1620, 1430; MS/ m/z = 371.22 (M^+ +1)

1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1-*H*-1,3-benzimidazole (3j): M.P. = 185-186^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); δ 5.50 (s, 2H, CH_2-Ph); 6.52 (m, 6H, Ar), 6.85 (dd, 2H, Ar), 7.12 (m, 2H, Ar), 7.50 (d, 2H, Ar); IR= cm^{-1} (KBr) 3330, 1580; MS: m/z: 375.24 (M^+ +1).

1-(4-Cyanobenzyl)-2-(4-cyanophenyl)-1-*H*-1,3-benzimidazole (3k): M.P. = 190-191^{0}C; ^{1}H-NMR (300MHz, $CDCl_3$); δ 5.32 (s, 2H, CH_2-Ph); 6.61 (m, 2H, Ar), 6.92 (dd, 2H, Ar), 7.14 (m, 2H, Ar), 7.51 (d, 2H, Ar); IR= cm^{-1} (KBr) 33430, 2100, 1560; MS: m/z: 335.31 (M^+ +1).

Results and discussion

To optimized, Firstly, the reaction was carried out in solvent free condition and found to be sluggish. Subsequently, the effect of solvents, stochiometry & recyclability of the ammonium molybdate under ultrasonic condition were investigated. The reaction of benzaldehyde with 1,2-phenylenediamine was carried out in different solvents such as ethanol, methanol, toluene, DCM, THF and acetonitrile using ammonium molybdate under ultrasonic condition. The reaction does not proceed to give the desired product when toluene or THF were used as solvents and reactants were recovered unchanged. The reaction with protic solvents such as ethanol or methanol gave a mixture of 2-substituted product & 1, 2-disubstituted product in 40:60 ratios, whereas, the aprotic solvents such as DCM resulted in low yield of desired product with lesser chemo-selectivity. On the other hand, acetonitrile gave remarkable chemo-selectivity of 1,2-disubstituted benzimidazole in 90% overall yield. Therefore, acetonitrile was selected as solvent for chemo-selective synthesis of 1,2-disubstituted benzimidazoles in the present protocol. (**Table-1**)

The reaction is been carried out in the presence of ultrasound to check the affect of ultrasound on the reaction and the results are found to be overwhelming when the condensation of 1,2-phenylenediamine (1) with benzaldehyde (2a) is carried out in the presence of ammonium molybdate under ultrasonic irradiation. The product 2-phenyl-1-(benzylmethyl)-1-*H*-1,3-benzimidazole (**3a**) obtained in 90% yield. Finally, the effect of ammonium molybdate was tested on the progress of the reaction. The reaction does not proceed in the absence of the ammonium molybdate. The reaction was performed using various equivalents of ammonium molybdate and it is found that 1 equivalent of ammonium molybdate gives good yield with maximum chemo-selectivity (**Table 2**). With this observation it is concluded that ammonium molybdate only promoting the reaction and not acting as catalyst.

Finally when the reaction is carried out in the absence of ultrasound the reaction is very sluggish as even after 24 hr only 20% conversion of the product is observed. Thus it is been concluded that the ultrasound is accelerating the reaction enormously.

Table 1. Solvent effect on the reaction of benzaldehyde with O-phenylenediamine under ultrasonic irradiation for 1 hr

Entry	Solvent	Product 3a (Yield %)	4a (Yield %)	Conversion (%)
1	Ethanol	40	60	80
2	Methanol	50	50	80
3	Toulene	No reaction	No reaction	No reaction

4	Dichloromethane	50	50	40
5	THF	No reaction	No reaction	No reaction
6	Acetonitrile	90	10	90

Table 2. Effect of catalyst on the reaction of benzaldehyde with O-phenylenediamine under ultrasonic irradiation for 1 hr

Entry	**Catalyst (in equiv.)**	**Conversion (%)**
1	Without catalyst	Sluggish reaction
2	0.10 eq	20%
3	0.25 eq	30%
4	0.50 eq	40%
5	0.75 eq	60%
6	1 eq	90%

Thus, after optimizing the reaction conditions, the generality of this method was examined by the reaction of several substituted arylaldehydes with 1,2-phenylenediamine. The results obtained encouraged us to do the detailed study on the chemo-selectivity of the product. The results are summarised in the **Table 3**. It is observed from the **Table 3** that aromatic aldehydes with electron donating groups (entries **2a-h**) gave high yields of the corresponding 1,2-disubstituted benzimidazoles (**3a-h**) when compared to aromatic aldehydes with electron withdrawing groups (entries **2i-k**). All products were characterized by ^{1}H-NMR, Mass and/ or comparison of their properties with those of authentic samples.

Table 3. Amonium molybdate promoted synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles under ultrasonic conditions

Entry	**Aldehyde (2)**	**Product 3 (% Yield) 4 (%Yield)**		**Time (in hr)**
1	Benzaldehyde (2a)	3a (90)	4a (10)	1
2	Thiophene-2-carboxaldehyde (2b)	3b (80)	4b (20)	1
3	2-Napahthaldehyde (2c)	3c (80)	4c (20)	1
4	Salicyladehyde (2d)	3d (75)	4d (25)	1
5	4-chlorobenzaldehyde (2e)	3e (80)	4e (20)	1
6	4-bromobenzaldehyde (2f)	3f (80)	4f (20)	1
7	3,4,5-Trimethoxy-benzaldehyde (2g)	3g (80)	4g (20)	1
8	3-Hydroxybenzaldehyde (2h)	3h (75)	4h (25)	1
9	*P*-Dimethylamino-benzaldehyde (2i)	3i (75)	4i (25)	1
10	*P*-Nitrobenzaldehyde (2j)	3j (70)	4j (30)	1
11	4-cyanobenzaldehyde (2k)	3k (70)	4k (30)	1

The recyclability of the ammonium molybdate was checked by repeating the reaction with recycled ammonium molybdate. The result shows that ammonium molybdate can easily be recovered by filtration and reused after simple washing and drying. The reagent is found to be active up to 3 runs and gives products in good yield (**Table 4**).

The proposed mechanism for this reaction is shown in **Figure 2**. In the path-1, ammonium molybdate is believed to chelate with the nitrogen of imino intermediate **5**. This chelation facilitates the intra-molecular cyclisation of **6** to **7** followed by 1,3-hydride shift to give 2-aryl-1-(arylmethyl)-1-H-1,3-benzimidazole (**3**). In the path-2, the monobenzylidene-*o*-phenylenediamine (**8**) is formed which undergoes ring closure to form the 2,3-dihydrointermediate **9**. This 2,3-dihydrointermdiate then undergoes oxidation to give the product **4**. The formation of **3** is confirmed by ^{1}H-NMR spectra of the product which gives the characteristic benzylic peak between 5.2-5.5 ppm as a singlet.

Table 4. Catalyst Recyclability on the reaction of benzaldehyde with O-phenylene-diamine under Ultrasound

Entry	**Catalyst**	**Product**		**Recovery of Catalyst**
		3a Yield (%)	**4a Yield (%)**	
1	Run 1	90	10	90%
2	Run 2	85	15	90%
3	Run3	80	20	80%

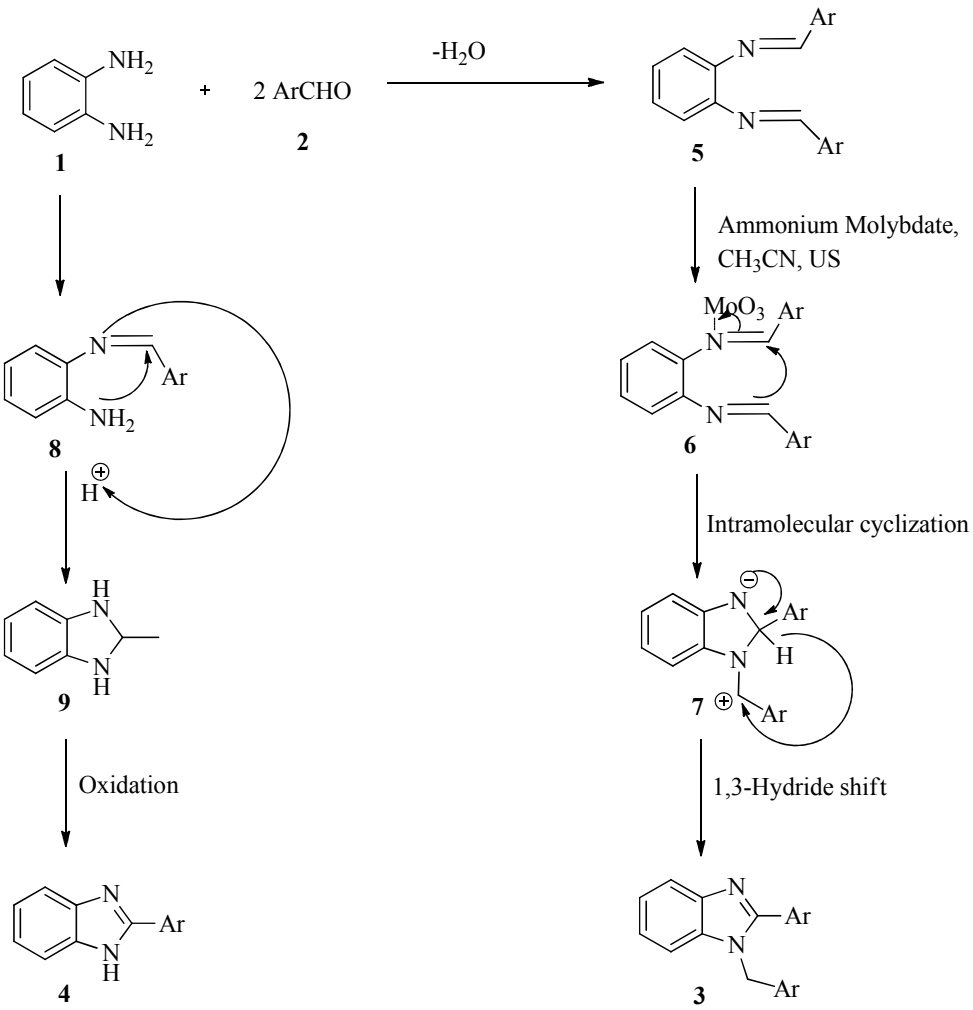


Figure 2. Proposed mechanism for ammonium molybdate promoted synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles under ultrasonic conditions

Conclusions

In conclusion, it is demonstrated that ultrasound accelerated & ammonium molybdate promotes the efficient and mild chemo-selective synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles. The simple experimental procedure and fast reaction rates make this procedure very useful and environmental friendly. In addition, the present method doesn't require expensive reagents and high temperature for the synthesis of 2-aryl-1-(arylmethyl)-1-*H*-1,3-benzimidazoles compared to the traditional protocols and it also has broad substrate applicability.

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