Synthesis of 2-Substituted Benzimidazoles Catalyzed by $FeCl_3/Al_2O_3$ Under Ultrasonic Irradiation

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Abstract: 2-substituted benzimidazoles have been synthesized in a single pot from aromatic aldehydes and *o*-phenylenediamine catalyzed by $FeCl_3/Al_2O_3$ in DMF under ultrasonic irradiation and afforded good yields in a short period of time.

Keywords: Aromatic aldehydes, benzimidazoles, $FeCl_3/Al_2O_3$, *o*-phenylenediamine, ultrasonic.

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]. Because of their importance, the synthesis of substituted benzimidazoles has become a focus of synthetic organic chemistry. A number of methods have been reported for the synthesis of benzimidazoles. These include the coupling of *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], 1,4-benzoquinone [10], DDQ [11], tetracyanoethylene [12], NH_4OAc [13], MnO_2 [14], silica-supported thionyl chloride [15], Oxone [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 have some drawbacks such as expensive reagents, drastic reaction conditions, low yields, tedious work up procedures and co-occurrence of several side reactions. As a consequence, the introduction of new methods to overcome the limitations is still an important experimental challenge.

In the last two decades, ultrasound has been widely used in organic synthesis [32]. Compared with traditional methods, this procedure is more convenient and easily controlled. A large number of organic reactions can be carried out in higher yields, shorter reaction times or using milder conditions under ultrasound than classical conditions [33-34].

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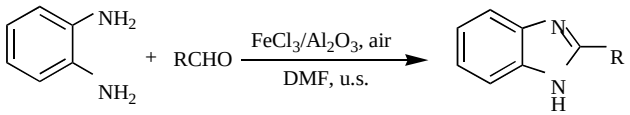
Catalysts and reagents supported on inorganic substrates have received increasing attention in recent years as a means to develop more convenient or selective catalysts or reagents [35]. In particular, $FeCl_3/Al_2O_3$ has been used as an efficient catalyst for a number of organic reactions and offered several advantages over classic acid, employing a reusable catalyst and minimally environmental pollution. As reported in previous papers, ferric chloride adsorbed on alumina has been used as the catalyst in the preparation of 2-amino-2-hydroxy-1,1'-binaphthyl [36], 1,1'-binaphthalene-2,2'-diol [37] and diphenylmethane [38] to afford the desired products in higher yields. In continuation of a broad programme being pursued in our laboratory on ultrasound-induced organic reactions, herein we wish to report a new method for the condensation of *o*-phenylenediamine and aldehydes catalyzed by $FeCl_3/Al_2O_3$ under ultrasonic irradiation (Scheme **1**).



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

Scheme 1. Synthesis of 2-substituted benzimidazoles.

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 $FeCl_3/Al_2O_3$ under ultrasonic irradiation 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, 1,4-dioxane, EtOH and CH_2Cl_2. The use of CH_2Cl_2, CH_3CN and MeOH as solvent gave poor yields (Table **1**, Entries 1-3). Solvents like 1,4-dioxane, ethanol gave moderate yields (Table **1**, Entries 4, 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.

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Table 1. The Effect of Solvent and Temperature on the Synthesis of 2-phenyl-1*H*-benzimidazole(3a)[A]

Entry	Solvent	T[°C]	Time[h]	Yield[B] [%]
1	CH_2Cl_2	38-41	8.0	21.3
2	CH_3CN	38-41	1.3	53.5
3	CH_3OH	38-41	1.0	42.1
4	1,4-Dioxane	38-41	3.0	77.2
5	CH_3CH_2OH	38-41	3.0	65.5
6	DMF	38-41	1.5	83.6
7	DMF	20-25	2.7	82.3
8	DMF	30-35	2.0	83.2
9[C]	DMF	38-41	1.5	47.9

[A]*o*-phenylenediamine (1.0 mmol) and benzaldehyde (1.0 mmol), $FeCl_3/Al_2O_3$ was 0.1 mmol (based on $FeCl_3$), the reactions were carried out in the presence of air. [B]Isolated yields. [C]Operated in nitrogen atmosphere.

The effect of the temperature on the reaction was also observed. As shown in Table **1**, the reactions were carried out using $FeCl_3/Al_2O_3$ in the temperature range of 20~41 °C under ultrasonic irradiation. The temperature had a significant effect on the reaction time of **3a** (Table **1**, Entries 6-8). It was found that the reaction time became longer at lower temperature. Increasing the temperature from 20~25 °C to 38~41 °C, the reaction time for formation **3a** decreased from 2.7 h to 1.5 h as expected. When the reaction was run in nitrogen atmosphere, 2-phenyl-1*H*-benzimidazole (**3a**) was obtained in 47.9% yield (Table **1**, Entry 9). These results suggest that aerial oxygen played an oxidant role in this reaction. Using the optimized reaction conditions, a range of 2-substituted benzimidazoles **3**(**a**–**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 $FeCl_3/Al_2O_3$ in DMF under ultrasonic irradiation. However, the most dramatic changes observed were with regard to reaction time. In the reaction catalyzed by $Sc(OTf)_3$ [22b], **3l** was obtained in 55% yield under O_2 after stirring for 44 h at room temperature, whereas the present procedure resulted in 97.5% yield of **3l** at 38-41 °C within 1.7 h. In the reaction catalyzed by activated carbon (Darco KB) in xylene under an oxygen atmosphere [39], **3a** was obtained in 64% yield at 120 °C for 26 h, whereas the present procedure afforded **3a** in 83.6% yield within 1.5 h. It is worth noting that increasing the amount of benzaldehyde (**2a**) did not give better yield (Table **2**, Entry 5).

In order to verify the effect of ultrasonic irradiation, we also did the experiments under silent conditions at 38-41 °C. As shown in Table **2**, **3a, 3j** and **3l** were obtained in 51.5%, 64.0% and 51.8% yields within 1.5 h, 1.2 h and 1.7 h respectively. Whereas under ultrasonic irradiation, **3a, 3j** and **3l** were obtained in 83.6%, 87.3% and 97.5% yields within 1.5 h, 1.2 h and 1.7 h respectively. It is obvious that the condensation can be finished in good yeild within short reaction time under ultrasonic irradiation. The reason may be the phenomenon of cavitation produced by ultrasound [32].

The same scale reaction using only $FeCl_3$ without any neutral Al_2O_3 being present yielded 63.3% of **3a** after 1.5 h under ultrasound (Table **2**, Entry 2), The alumina support itself showed very little activity (34.2%) in the synthesis of **3a** after 1.5 h under ultrasound (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 alumina-supported $FeCl_3$ is higher than without any support. These data showed that both $FeCl_3$ alone and neutral Al_2O_3 alone were anything but satisfactory for the synthesis of 2-substituted benzimidazoles. Encouraged by these results, the condensation of furfuraldehyde (**2n**) and *o*-phenylenediamine (**1**) was also examined to extend the scope of this method, 2-(2'-furanylphenyl)benzimidazole (**3n**) was obtained in moderate yields (76.8%) within 1.4 h. 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 25, 26).

At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with ethyl acetate and reused under similar conditions. As shown by the formation of 2-(3'-bromo phenyl)benzimidazole (**3g**), there was an appreciable loss in the activity in the reuse of these catalysts (79.8% on the second run for 3 h and 77.3% on the third run for 5 h, Table **2**, Entries 12, 13). This is because of the leaching of the active catalyst component (i.e. iron) in the entire treatment process [38], which is in our expectation. Further work is necessary to strongly bind the active component on the support.

In summary, we have found a practical procedure for the preparation of 2-substituted benzimidazoles catalyzed by $FeCl_3/Al_2O_3$ under ultrasonic irradiation. Our procedure is characterized by milder conditions, shorter reaction time, higher yield and involvement of non toxic and expensive catalyst.

Table 2. The Synthesis of 2-substituted Benzimidazole Derivatives Catalyzed by $FeCl_3/Al_2O_3$ Under Ultrasound

Entry	R	Time[h]	Product	Yield[A] [%]	Mp[°C] (lit)
1	C_6H_5	1.5	**3a**	83.6	298(298)[19b]
2	C_6H_5	1.5		63.3[B]	
3	C_6H_5	1.5		34.2[C]	
4	C_6H_5	1.5		51.5[D]	
5	C_6H_5	2.0		66.9[E]	
6	2-ClC_6H_4	6.5	**3b**	86.5	233-235(233-234)[13]
7	3-ClC_6H_4	1.4	**3c**	99.5	237-238(238)[6c]
8	4-ClC_6H_4	1.4	**3d**	82.5	300-301 (302-303)[13]
9	2,4-$Cl_2C_6H_3$	1.0	**3e**	86.6	237-238(230-232)[18]
10	4-$CH_3OC_6H_4$	2.2	**3f**	99.5	227-228(226)[13]
11	3-BrC_6H_4	0.9	**3g**	85.7	250-252(252)[6c]
12	3-BrC_6H_4	3.0		79.8[F]	
13	3-BrC_6H_4	5.0		77.3[G]	
14	3-BrC_6H_4	0.9		70.4[H]	
15	3-BrC_6H_4	0.9		80.2[I]	
16	4-BrC_6H_4	1.0	**3h**	81.4	300-301(299)[6c]
17	3-$NO_2C_6H_4$	1.2	**3i**	83.7	205-207(201)[13]
18	4-$NO_2C_6H_4$	1.2	**3j**	87.3	300-301(298-300)[19b]
19	4-$NO_2C_6H_4$	1.2		64.0[D]	
20	2-OHC_6H_4	4.5	**3k**	91.7	239-240(236-237)[19b]
21	4-$CH_3C_6H_4$	1.7	**3l**	97.5	268-269(270)[15]
22	4-$CH_3C_6H_4$	1.7		51.8[D]	
23	4-$(Me)_2NC_6H_4$	2.7	**3m**	80.7	242-243 (233-236)[17]
24	2-Furyl	1.4	**3n**	76.8	310-312(310-312)[19b]
25	$CH_3CH_2CH_2$	3.0		trace	
26	$CH_3(CH_2)_5$	3.0		trace	

[A]Isolated yield. [B]$FeCl_3$ as catalyst. [C]Al_2O_3 as catalyst. [D]Stirred without ultrasound. [E]*o*-phenylenediamine (1.0 mmol) and benzaldehyde (2.0 mmol). [F]First recycled $FeCl_3/Al_2O_3$ was used. [G]Second recycled $FeCl_3/Al_2O_3$ was used. [H]Ultrasonic cleaner with a frequency of 25 KHz. [I]Ultrasonic cleaner with a frequency of 59 KHz.

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. ^1H 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. Sonication was performed in Shanghai Branson-CQX ultrasonic cleaner (with a frequency of 25, 40 and 59 kHz and a nominal power 250 W). The reaction flask was located in the ultrasonic bath, where the surface of reactants is slightly lower than the level of the water. The reaction temperature was controlled by addition or removal of water from ultrasonic bath.

Preparation of the Catalyst ($FeCl_3/Al_2O_3$)

The $FeCl_3/Al_2O_3$ was prepared by mixing with ~10% its weight of hydrated ferric chloride ($FeCl_3{\cdot}6H_2O$) 4.8 g in acetone (72 mL) and adding 26 g neutral Al_2O_3. The mixture was stirred at room temperature for 1 h. The acetone was removed under reduced pressure. The resulting yellow-brown powder was dried at 120 °C for 4 h.

General Procedure for Synthesis of 2-Substituted Benzimidazole Derivatives

Aromatic aldehydes (**2**, 1.0 mmol) and *o*-phenylenediamine (**1**, 1.0 mmol) were dissolved in DMF (2 mL) in a 25 mL conical flask. The $FeCl_3/Al_2O_3$ (160 mg, 0.1 mmol, based on $FeCl_3$) was then added and the mixture was irradiated in the water bath of an ultrasonic cleaner at 38-41 °C (bath temperature, the temperature inside the reactor was also 38-41 °C) for a period time as indicated in Table **1-2** (sonication was continued until aromatic aldehydes disappeared as indicated by TLC). The mixture 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.

Compound 3a

2-phenyl-1*H*-benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3049, 2965, 2921, 2848, 2718, 2671, 1589, 1542, 1446, 1313, 1275, 1224, 1115, 969, 928, 743; *m/z* (ESI): 195 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3b

2-(2'-chlorophenyl)benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3054, 2919, 1621, 1441, 1386, 1317, 1274, 1229, 1221, 1052, 974, 878, 746; *m/z* (ESI): 229 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3c

2-(3'-chlorophenyl)benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3043, 2964, 2920, 2786, 1599, 1441, 1389, 1275, 1121, 1081, 892, 744; *m/z* (ESI): 229 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3d

2-(4'-chlorophenyl)benzimidazole, Isolated as light yellow crystal. IR (KBr, cm^{-1}): 3053, 2924, 2850, 1593, 1427, 1385, 1316, 1270, 1222, 1088, 1011, 961, 828, 741; *m/z* (ESI): 229 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3e

2-(2,4-dichlorophenyl)-1H-benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3052, 2841, 1929, 1892, 1775, 1622, 1590, 1427, 1362, 1386, 1348, 1316, 1268, 1139, 1008, 978, 882, 820; *m/z* (ESI): 263 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 13.08 (s, 1H, N-H), 8.40 (d, 1H, *J* = 2.0 Hz, Ar-H), 8.15 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.1 Hz, Ar-H), 7.84 (d, 1H, *J* = 2.1 Hz, Ar-H), 7.54-7.69 (m, 2H, Ar-H), 7.25 (s, 2H, Ar-H).

Compound 3f

2-(4'-methoxyphenyl)benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3055, 2919, 2850, 1739, 1609, 1500, 1438, 1386, 1293, 1253, 1178, 1121, 1032, 964, 847, 742; *m/z* (ESI): 225 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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);

Compound 3g

2-(3'-bromophenyl)benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3043, 2917, 2784, 2662, 1564, 1401, 1360, 1264, 1228, 1120, 1072, 1009, 973, 893; *m/z* (ESI): 273 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 13.01 (s, 1H, N-H), 8.37 (t, 1H, *J* = 1.7 Hz, Ar-H), 8.19 (d, 1H, *J* = 7.9 Hz, Ar-H), 7.69 (t, 2H, *J* = 7.8 Hz, Ar-H), 7.52-7.56 (m, 2H, Ar-H), 7.21-7.27 (m, 2H, Ar-H).

Compound 3h

2-(4'-bromophenyl)benzimidazole, Isolated as light yellow crystal. IR (KBr, cm^{-1}): 3164, 3087, 3050, 2992, 2948, 2908, 1598, 1587, 1491, 1427, 1394, 1384, 1367, 1273, 1069, 1011, 827; *m/z* (ESI): 273 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 12.98 (s, 1H, N-H), 8.11-8.14 (m, 2H, Ar-H), 7.76-7.78 (m, 2H, Ar-H), 7.68 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.54 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.20-7.24 (m, 2H, Ar-H).

Compound 3i

2-(3'-nitrophenyl)benzimidazole, Isolated as yellow crystal.IR (KBr, cm^{-1}): 3333, 1620, 1517, 1434, 1385, 1349, 1279, 886, 807, 740; *m/z* (ESI): 240 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 13.29 (s, 1H, N-H), 9.00 (t, 1H, *J* = 1.8 Hz, Ar-H), 8.60 (d, 1H, *J* = 7.9 Hz, Ar-H), 8.31 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz, Ar-H), 7.84 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.72 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.58 (d, 1H, *J* = 7.7 Hz, Ar-H), 7.22-7.29 (m, 2H, Ar-H);

Compound 3j

2-(4'-nitrophenyl)benzimidazole, Isolated as light yellow crystal. IR (KBr, cm^{-1}): 2920, 2850, 1600, 1514, 1435, 1384, 1341, 1101, 965, 852, 744, 709; *m/z* (ESI): 240 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: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).

Compound 3k

2-(2'-hydroxyphenyl)benzimidazole, Isolated as white crystal. IR (KBr, cm^{-1}): 3325, 3055, 1596, 1518, 1490, 1449, 1422, 1321, 1262, 1132, 1038, 840, 727; *m/z* (ESI): 211 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3l

2-(4'-methylphenyl)benzimidazole, Isolated as light yellow crystal.IR (KBr, cm^{-1}): 2920, 2850, 1552, 1500, 1431, 1385, 1316, 1273, 963, 821, 744; *m/z* (ESI): 209 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3m

2-[4'-(N,N-dimethylaminophenyl)]benzimidazole, Isolated as light yellow crystal. IR (KBr, cm^{-1}): 2922, 1609, 1566, 1500, 1440, 1380, 1273, 1200, 1110, 946, 823, 746; *m/z* (ESI): 238 $[M+H]^+$; ^1H NMR (600 MHz, DMSO-d_6) δ_H: 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).

Compound 3n

2-(2'-furanylphenyl)benzimidazole, Isolated as light yellow crystal. IR (KBr, cm^{-1}): 3060, 2823, 2774, 2664, 1628,

1588, 1524, 1415, 1317, 1276, 1231, 1168, 1116, 1075, 1014, 977, 907, 738; *m/z* (ESI): 185 $[M+H]^+$; ^{1}H NMR (600 MHz, DMSO-d_6) δ_H: 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).

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