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Pyrrolidinium Acetate (PyrrIL) as a Green and Recyclable Catalyst: Synthesis of 2-Phenyl Benzimidazoles and 2-Phenyl Benzothiazoles under Solvent-Free Conditions at Room Temperature

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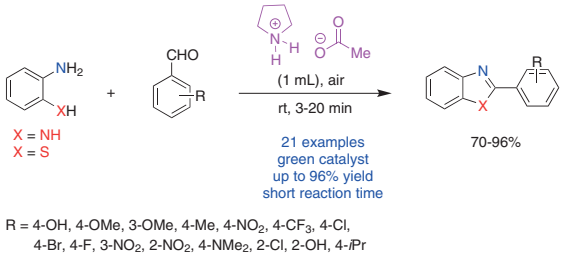

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Abstract Benzimidazoles and benzothiazoles are a class of pharmacologically potential compounds, which exhibited antimicrobial, anticancer, and anti-inflammatory activities. These can be obtained by simple condensation of *o*-phenylenediamine or *o*-aminothiophenol with aromatic aldehydes. The synthetic protocol can be accomplished/improved by varying reaction parameters such as temperature, solvents, and catalysts. To develop such condensation reactions in a sustainable way, nontoxic solvents and eco- friendly catalysts are presently used. In this study, we proposed a novel and interesting strategy for obtaining diversely substituted 2-phenyl benzimidazole and 2-phenyl benzothiazole derivatives *via* a one-pot protocol, employing pyrrolidinium ionic liquid as a green and environmentally benign catalyst under solvent-free conditions at room temperature in an open atmosphere. The resulting products were obtained in good to excellent yields within a short reaction time (3–20 min). A plausible mechanism was also discussed.

Key words ionic liquid, benzimidazoles, benzothiazoles, green chemistry, room temperature

The synthesis of heterocyclic compounds utilizing green chemistry principles is significantly important in modern organic chemistry. For example, reactions involving eco-friendly, recyclable catalysts, green solvents, and nontoxic reactants are essential in the production of pharmaceutically important compounds.

Ionic liquids (ILs) have shown potential properties as greener solvents or catalysts in the replacement of organic solvents and catalysts over the last decades. These are stable at high temperatures, low-volatile, environmentally benign, and recyclable, even though more expensive than other organic solvents.[1] In organic synthesis, it is crucial and desirable to employ affordable cations and anions.[2] Numerous studies have demonstrated that ionic liquids serve as solvents and catalysts in organic synthesis. These can be utilized as solvents in the presence of other catalysts or as catalysts in the presence of other solvents.[3–5]

Anouti and co-workers synthesized[6] and characterized the ionic liquids utilizing pyrrolidine as the cation source and formate, acetate, and trifluoroacetate as the anions. The pyrrolidinium-based ionic liquids are protic ionic liquids (PILs), which are often inexpensive and less hazardous than other ionic liquids. These ionic liquids are superionic with a broad spectrum of potential uses, in acid-catalyzed reactions, fuel cell devices, dye-sensitized solar cells, and thermal transfer fluids.[7–10]

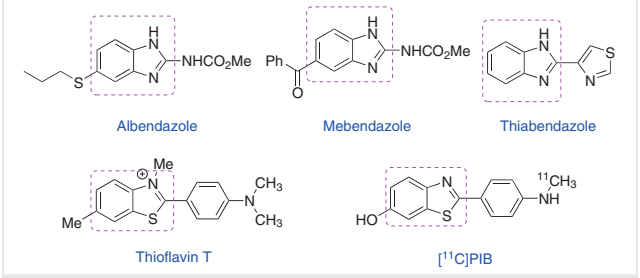


Figure 1 Bioactive motifs containing benzimidazole and benzothiazole skeletons

Benzimidazoles and benzothiazoles, which contain a five-membered ring fused to a six-membered ring, belong to fused heterocycles and are responsible for a broad spectrum of properties in domains like agrochemicals, pharmaceuticals, and natural products.[11–13] These fused heterocyclic scaffolds have been associated with numerous biologically active molecules (Figure 1).[14,15] Benzothiazole derivatives are present in a variety of terrestrial and marine natural products with a wide range of applications.[16,17] Ben-

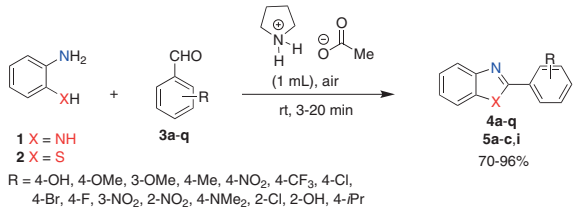
zimidazole analogues exhibit antifungal and antibacterial properties.[18–25] In addition, 2-phenyl or 2-alkyl benzimidazole derivatives have demonstrated antiviral activities against herpes (HVS-1),[26] human cytomegalovirus (HCMV),[27] influenza,[28,29] and HIV.[26] Moreover, 2-phenyl or 2-aryl benzothiazole derivatives are important organic functional materials and are utilized as radioactive amyloid-imaging agents. Some of them are employed as building blocks in the design and development of antidiabetic,[30] anticancer,[31] and anti-Alzheimer's molecular frameworks.[32] These also play a significant role as fluorescent dyes, chemosensors, and liquid crystals.[33,34]

Considering the significance of these molecules in divergent areas of chemistry with wider applications to human life, both benzothiazoles and benzimidazoles attracted the attention of researchers globally.

Numerous methodologies have been developed to generate these compounds. Condensation reactions employing *o*-phenylenediamine (**1**) or *o*-amino thiophenol (**2**) and alkyl/aryl/heteroaryl aldehydes **3** have shown promising results in synthesizing these compounds (**4**, **5**). The cyclization of benzene-1,2-diamines with aryl isothiocyanates,[35] the cyclization of benzene-1,2-diamine with aldehydes,[36] a simple condensation between 2-amino thiophenols with aryl aldehydes,[37,38] acyl chlorides,[39,40] nitriles,[41] carboxylic acids,[42] or alcohols[43] are some of the approaches presented in the literature.

The above-mentioned reports contain drawbacks, such as the use of hazardous reagents, solvents, expensive catalysts, prolonged reaction times, high temperatures, and harsh reaction conditions, as well as the formation of unwanted products. The methodologies employing green catalysts, such as nonmetal salts, heterogeneous recyclable catalysts, or ionic liquids, [44–51] and green solvents, or solvent-free or microwave or ultrasonic conditions,[52–54] are desirable to promote sustainable eco-friendly research.[55–57] In this regard, ionic liquids have shown promising results in a variety of synthetic processes because of their great selectivity and catalytic efficiency.[58–61]

Due to the significance of these classes of compounds, it is important to develop more sustainable methods. In the present study, various experiments were carried out to evaluate different reaction conditions to obtain 2-phenyl benzimidazole and 2-phenyl benzothiazole compounds in the absence of metal salts as catalysts, as well as under solvent-free conditions or in the presence of nontoxic solvents. The investigations described in this study are aimed to utilize ionic liquid as a catalytic alternative, which made it easier to perform several experiments and provided the desired products in excellent yields within a short reaction time (Scheme 1).



Scheme 1 Synthesis of 2-phenyl benzimidazoles and 2-phenylbenzothiazoles using pyrrolidinium acetate [Pyrr][CH_3COO]

Initially, various ionic liquids are prepared by combining different carboxylic acids, such as formic acid, acetic acid, or trifluoracetic acid, with pyrrolidine by following the literature methods (Figure 2).[2,6]

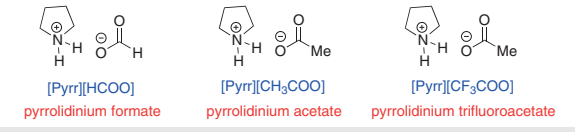


Figure 2 Pyrrolidinium ionic liquids

The ionic liquids were used as catalysts to obtain benzimidazole and benzothiazole derivatives through a simple condensation reaction involving *o*-phenylenediamine (**1**) or o-amino thiophenol (**2**) with aromatic aldehydes **3a–q** containing variable substituents on the ring affording a series of desired products with excellent yields (**4a–q**). These reactions were conducted under solvent-free conditions and at ambient temperature, providing diversely functionalized compounds as shown in Scheme 1.

To establish the scope of this methodology, a number of experiments were conducted employing different solvents, catalysts, temperatures, and reaction times (Table 1). The reaction between *o*-phenylenediamine (**1**) and salicylaldehyde (**3o**) was conducted as a model reaction in the absence of a catalyst and a solvent, resulting in a trace amount of the product (Table 1, entry 1). Several solvents such as EtOH, MeOH, DCM, $CHCl_3$, H_2O, acetic acid, and sodium acetate were employed to examine the suitability, and the products were obtained in the range of 28–53% (Table 1, entries 4–8, 11, and 12). Further, the reaction was performed under reflux conditions also resulting in the product in 56% (Table 1, entry 9).

To improve the yields, the model reaction was carried out in the presence of the catalyst pyrrolidinium acetate, in the absence of solvent, and the yield was encouraging (Table 1, entry 10). The optimization experiments revealed that the product was obtained in maximum yield when the reaction was conducted in the presence of the catalyst pyrrolidinium acetate under solvent-free conditions (Table 1, entry 10).

Table 1 Optimization of the Reaction Conditions for the Synthesis of 2-(1*H*-Benzo[*d*]imidazol-2-yl)phenol[a]

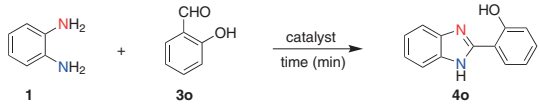
Entry	Catalyst	Solvent	T (min)	Yield (%)[b]
1	–	–	20	–[c]
2	–	EtOH	20	51[d]
3	–	EtOH	50	55[d]
4	[Pyrr][OAc]	EtOH	3	53[d]
5	[Pyrr][OAc]	MeOH	3	49[d]
6	[Pyrr][OAc]	DCM	3	37[d]
7	[Pyrr][OAc]	$CHCl_3$	3	28[d]
8	[Pyrr][OAc]	H_2O	3	44[d]
9	[Pyrr][OAc]	EtOH	3	56[e]
10	[Pyrr][OAc]	–	3	96[d]
11	–	acetic acid	3	45[d]
12	–	sodium acetate	3	35[d]

[a] Reaction conditions: 2-hydroxy benzaldehyde (1 mmol), *o*-phenylenediamine (1 mmol).
[b] Isolated yields.
[c] Absence of the catalyst and solvent.
[d] Reaction carried out at room temperature.
[e] Reaction carried out under reflux conditions.

Furthermore, the influence of several ionic liquids (Figure 2) as catalysts on the synthesis of compound **4o** was investigated (Table 2, entries 1–3). Among these catalysts, pyrrolidinium acetate [Pyrr][OAc] afforded the product in excellent yield (96%, Table 2, entry 2). The influence of different catalyst concentrations of pyrrolidinium acetate was assessed at 0.5, 1.0, and 2.0 mL, obtaining the desired product in 76% and 96% yield, respectively (Table 2, entries 2, 4, 5). There was no significant improvement even when that catalyst quantity was doubled from 1.0 to 2.0 mL (Table 2, entry 5).

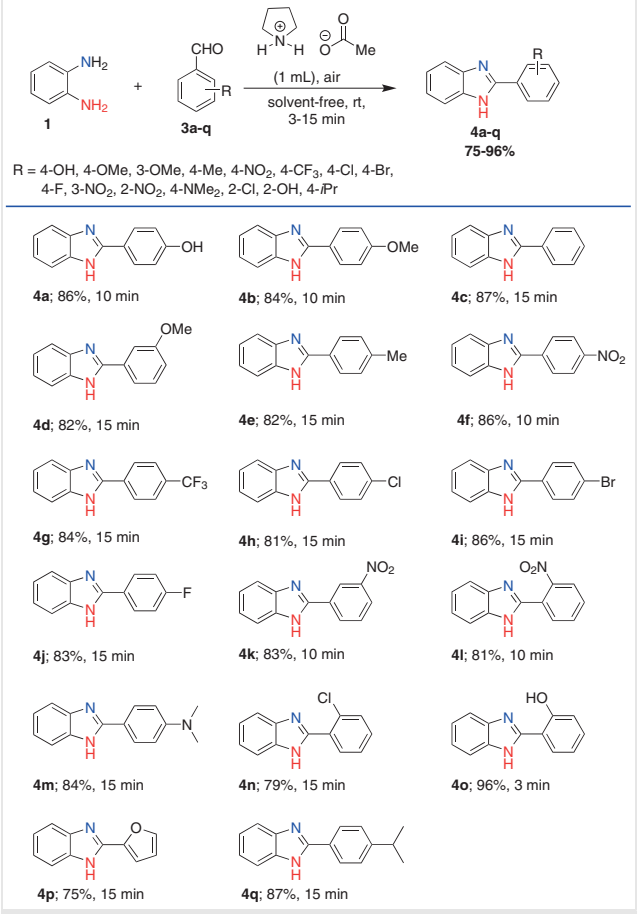
After standardizing the reaction parameters, the scope of the protocol was extended employing several aromatic/heteroaromatic aldehydes as reactants affording the desired products (Scheme 2). Aromatic aldehydes bearing electron-donating groups at the *para*, *meta*, and *ortho* positions provided better yields (Scheme 2, 4a, 4b, 4e, 4m, 4q, 4d, 4o). Aldehydes with electron-withdrawing groups, such as 4-NO_2-benzaldehyde, 4-CF_3-benzaldehyde, 4-Cl-benzaldehyde, 4-Br-benzaldehyde, 4-F-benzaldehyde, 3-NO_2-benzaldehyde, 2-NO_2-benzaldehyde, and 2-Cl-benzaldehyde also produced the compounds in encouraging yields (Scheme 2, entries **4f**, **4g**, **4h**, **4i**, **4j**, **4k**, **4l**, **4n**). Heteroaromatic aldehyde, such as 2-furfural, reacted readily with *o*-phenylenediamine, affording 75% of the product. Simple benzaldehyde (**4c**) generated. A total of 17, 2-phenyl benzimidazole derivatives were synthesized (Scheme 2).

Table 2 Optimization of the Reaction Conditions for the Synthesis of **4o** Compound[a]



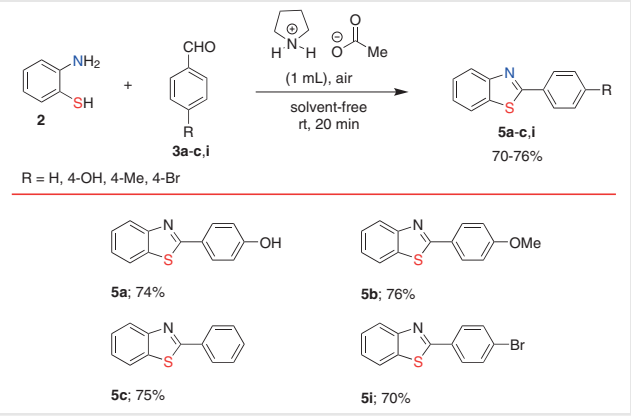
Entry	Catalyst	Time (min)	Catalyst (mL)	Yield (%)[b]
1	[Pyrr][HCOO]	3	1.0	71
2	[Pyrr][OAc]	3	1.0	96
3	[Pyrr][CF_3COO]	3	1.0	60
4	[Pyrr][OAc]	3	0.5	76
5	[Pyrr][OAc]	3	2.0	96

[a] Reaction conditions: 2-hydroxy benzaldehyde (**3o**, 1 mmol), *o*-phenylenediamine (**1**, 1 mmol).
[b] Isolated yields.



Scheme 2 Synthesis of 2-aryl benzimidazoles **4a–q** using pyrrolidinium acetate [Pyrr][CH_3COO]

Inspired by the above results, the same procedure was applied to produce 2-phenyl benzothiazole derivatives using *o*-amino thiophenol and aromatic aldehydes (Scheme 3). A total of four benzothiazole derivatives **5a–c,i** were synthesized in this series. A wide range of aromatic aldehydes were subjected to condensation with *o*-amino benzenethiol employing [Pyrr][OAc] as a catalyst at ambient temperature, resulting in the desired products in the range of 70–76% (Scheme 3).

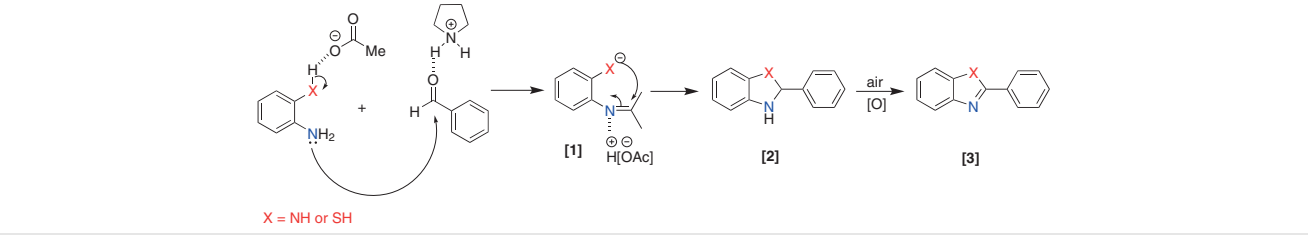


Scheme 3 Synthesis of 2-aryl benzothiazoles **5a–c,i** using pyrrolidinium acetate [Pyrr][CH_3COO]

The plausible mechanistic pathway involving [Pyrr][OAc] as an efficient and green catalyst was explained (Scheme 4). The carbonyl oxygen in aldehyde was first activated by the [Pyrr] cation, and the [OAc] anion formed a hydrogen bond with either *o*-phenylenediamine/*o*-amino benzothiazole. Simultaneously, nucleophilic addition occurs, leading to the formation of an intermediate **[1]** that facilitates ring closure **[2]**, followed by oxidative aromatization leads to the formation of the desired product **[3]**.

The comparative evaluation of the catalytic activity of pyrrolidinium acetate with other recently reported catalysts from the literature,[62–68] which produced 2-phenyl benzimidazoles and 2-phenyl benzothiazoles, is given in Table 3. It can be seen from Table 3 that the pyrrolidinium acetate catalyst is more efficient than others.

Moreover, the catalytic efficiency of pyrrolidinium acetate was assessed in the model reaction employing *o*-phenylenediamine and salicylaldehyde under solvent-free conditions at room temperature (Figure 3). The ionic liquid was recycled and reused up to four consecutive cycles without significant loss of activity (Figure 3). A facile, robust, and efficient approach for 2-aryl benzimidazole and benzothiazole derivatives catalyzed by [Pyrr][CH_3COO] under solvent-free conditions was established in high yields (Schemes 2 and 3).



Scheme 4 A plausible mechanistic pathway for the synthesis of 2-aryl benzimidazoles and 2-aryl benzothiazoles involving [Pyrr][CH_3COO]

Table 3 Comparison of Pyrrolidinium Acetate Catalytic Activity vs some other Recently Reported Methods

Catalyst	Amount of catalyst/reaction conditions	Time	Yield (%)
pyrrolidinium acetate (our work)	1 mL (7.62 mmol), solvent-free, air, rt	3–20 min	70–96
Fe(III)–Schiff base/SBA-15[62]	0.01 g, water, reflux	3 h	79–92
$ZnBr_2$/ABM[63]	100 mg, 5 mL, toluene, 111 °C	10–25 min	83–96
Indion 190 resin[64]	10%/weight, 5 mL EtOH, 70 °C	4 h	78–92
nano-ZnO[65]	10 mol%, 10 mL EtOH, reflux	80–100 min	64–88
CuO-NPs/SiO_2[66]	10 mol%, 10 mL, MeOH, rt	4–14 h	68–93
Cu NPs/SiO_2[66]	10 mol%, methanol, rt	4–8 h	72–86
CeO_2 NPs[67]	10 mol%, H_2O, rt	20–40 min	58–97
$FeCl_3$/montmorilonite K-10[68]	10%w/w, MeOH, condensation, ultrasonic irradiation	0.7–5 h	33–95
β-CD[15]	10 mol%, 10 mL, H_2O, 60–65 °C	4–10 h	76–81
Zn(L-Pro)$_2$[14]	5 mol%, 4 mL, EtOH, air, rt	4–30 min	65–94

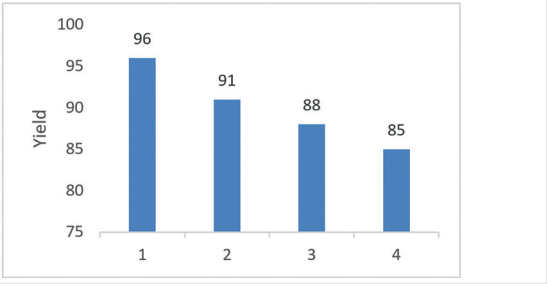


Figure 3 Recyclability of pyrrolidinium acetate

All the chemicals were purchased from Sigma Aldrich with purity not less than 99.9%. Analytical thin-layer chromatography (TLC) was carried out by using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp of I_2 stain. All the products were characterized by their NMR and mass spectra. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 or 200 MHz, in DMSO and $CDCl_3$, and the chemical shifts were reported in parts per million (ppm, δ) downfield from the tetramethyl silane.

Synthesis of Ionic Liquids

Pyrrolidinium Acetate Catalyst

Pyrrolidine (1.0 mmol, 10 g) is placed in a three-neck round-bottom flask immersed in an ice bath and equipped with a reflux condenser, a dropping funnel to add acetic acid, and a thermometer to monitor the temperature. Under vigorous stirring, acetic acid (2.47 mmol, 20.85 g) is added dropwise to pyrrolidine (60 min). The temperature is maintained less than 25 °C during the addition of the acid by use of the ice bath. Stirring is maintained for 4 h at ambient temperature, and a low-viscous liquid is obtained. This new phase is yellow-pale colored. The residual pyrrolidine or acid is evaporated under reduced pressure and the remaining liquid is further dried at 80 °C under reduced pressure (1–5 mmHg) to obtain pyrrolidinium acetate catalyst (18.05 g; yield 98%).[6] The same procedure was applied to synthesize other ionic liquids, such as a pyrrolidium format [Pyrr][HCOO] and pyrrolidium trifluoroacetate [Pyrr][CF_3COO].[6]

Pyrrolidinium Acetate

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.24 (s, 2 H, br), 3.22–3.19 (m, 4 H), 1.98 (s, 3 H), 1.97–1.94 (m, 4 H).

2-Phenyl Benzimidazoles Mediated by Ionic Liquid

o-Phenylenediamine (1.0 mmol), benzaldehydes (1.0 mmol), and pyrrolidinium acetate (7.62 mmol (1 mL) with respect to the *o*-phenylenediamine) were taken in a 25 mL round-bottom flask. Then, the reaction mixture was stirred at room temperature for 3–15 min. After completion of the reaction as indicated by TLC, the crude residue was extracted with diethyl ether (3 × 10 mL) and water. The organic layer was washed with brine solution and dried over $MgSO_4$. The combined organic layers were evaporated under reduced pressure, and the resulting crude product was purified by column chromatography using ethyl acetate and hexane (1:9) as eluents. Some of them (solids) were recrystallized using appropriate solvents. Further, the residual ionic liquid catalyst was dried under vacuum at 80 °C for 4 h, which could be reused for further cycles without loss of its catalytic activity. The identity and purity of the products were confirmed by comparing with the authentic samples and also confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectra.[14,15]

2-Phenyl Benzothiazoles Mediated by Ionic Liquid

o-Aminothiophenol (1.0 mmol), benzaldehydes (1.0 mmol), and pyrrolidinium acetate (7.62 mmol, 1 mL) with respect to the *o*-aminothiophenol) were taken in a 25 mL round-bottom flask. Then, the reaction mixture was stirred at room temperature for 20 min. After completion of the reaction as indicated by TLC, the crude residue was extracted with diethyl ether (3 × 10 mL) and water. The organic layer was washed with brine solution and dried over $MgSO_4$. The combined organic layers were evaporated under reduced pressure, and the resulting crude product was purified by column chromatography using ethyl acetate and hexane (1:9) as eluents. Some of them (solids) were recrystallized using appropriate solvents. Further, the residual ionic liquid catalyst was dried under vacuum at 80 °C for 4 h, which could be reused for further cycles without loss of its catalytic activity. The identity and purity of the products were confirmed by comparing with the authentic samples and also confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectra.[14,15]

4-(1*H*-Benzo[*d*]imidazol-2-yl)phenol (4a)[14]

Yield 180.6 mg (86%); white solid; mp 132–134 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.07 (s, 1 H), 8.66 (s, 1 H), 7.42–7.35 (m, 3 H), 7.28–7.24 (m, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 6.98–6.92 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.85, 161.47, 142.68, 133.49, 132.46, 127.82, 119.85, 119.36, 119.09, 117.67.

IR: 2926, 2855, 1747, 1370, 1220, 1072, 1043, 752 cm^{-1}.

MS (ESI): *m/z* = 211 [M + H]$^+$.

2-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (4b)[14]

Yield 188 mg (84%); white solid; mp 226–228 °C.

^{1}H NMR (400 MHz, DMSO): δ = 12.90 (s, 1 H), 7.77 (t, *J* = 4.2 Hz, 2 H), 7.61 (s, 2 H), 7.47 (d, *J* = 8.3 Hz, 1 H), 7.21 (dd, *J* = 6.0, 3.1 Hz, 2 H), 7.07–7.04 (m, 1 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, DMSO): δ = 159.65, 151.09, 131.48, 130.09, 122.14, 118.75, 115.86, 111.40, 55.28.

IR (KBr): 3440, 3060, 2950, 1610, 1500, 1480, 1450, 1435, 1400, 1255, 1180, 740 cm^{-1}.

MS (ESI): *m/z* = 225 [M + H]$^+$.

2-Phenyl-1*H*-benzo[*d*]imidazole (4c)[14]

Yield 168 mg (87%); white crystals; mp 295–296 °C.

^{1}H NMR (400 MHz, DMSO): δ = 12.93 (s, 1 H), 8.19 (d, *J* = 7.3 Hz, 2 H), 7.69–7.48 (m, 5 H), 7.21 (dd, *J* = 10.1, 7.2 Hz, 2 H).

^{13}C NMR (101 MHz, DMSO): δ = 151.24, 130.18, 129.84, 129.41, 128.69, 126.44.

IR (KBr): 3440, 1620, 1591, 1450, 1412, 1315, 1277, 1113, 742 cm^{-1}.

MS (ESI): *m/z* = 195 [M + H]$^+$.

2-(3-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (4d)[14]

Yield 183 mg (82%); white solid; mp 201–204 °C.

^{1}H NMR (400 MHz, DMSO): δ = 12.89 (s, 1 H), 7.77 (d, *J* = 7.7 Hz, 2 H), 7.67 (d, *J* = 7.0 Hz, 1 H), 7.54 (d, *J* = 7.0 Hz, 1 H), 7.46 (t, *J* = 7.9 Hz, 1 H), 7.21 (s, 2 H), 7.06 (d, *J* = 8.7 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (101 MHz, DMSO): δ = 159.65, 151.08, 143.72, 134.94, 131.47, 130.10, 122.60, 121.70, 118.82, 115.87, 111.35, 55.29.

IR (KBr): 3192, 2985, 1629 cm^{-1}.

MS (ESI): *m/z* = 225 [M + H]$^+$.

2-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole (4e)[14]

Yield 170 mg (82%); white solid; mp 276–278 °C.

^{1}H NMR (400 MHz, DMSO): δ = 8.07 (d, *J* = 8.1 Hz, 2 H), 7.59 (dd, *J* = 5.8, 3.1 Hz, 2 H), 7.37 (d, *J* = 7.9 Hz, 2 H), 7.20 (dd, *J* = 5.9, 3.1 Hz, 2 H), 2.38 (s, 3 H).

^{13}C NMR (101 MHz, DMSO): δ = 151.26, 139.76, 129.54, 127.11, 126.45, 122.12, 20.98.

IR (KBr): 3450, 3095, 2980, 2920, 1550, 1500, 1460, 1430, 1390, 1270, 965, 822 cm^{-1}.

MS (ESI): *m/z* = 209 [M + H]$^+$.

2-(4-nitrophenyl)-1*H*-benzo[d]imidazole (4f)[15]

Yield 205 mg (86%); brown solid; mp 292–294 °C.

^{1}H NMR (400 MHz, $CDCl_3$ + DMSO): δ = 8.71 (s, 1 H), 8.27–8.22 (m, 2 H), 8.15 (dd, *J* = 8.8, 1.6 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.56 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$ + DMSO): δ = 152.87, 148.16, 144.24, 141.95, 133.97, 128.91, 128.52, 123.41, 116.50, 116.22, 114.94.

IR (KBr): 3065, 3010, 1610, 1485, 1420, 1285, 1240, 1210, 1180, 820 cm^{-1}.

MS (ESI): *m/z* = 240 [M + H]$^+$.

2-[4-(Trifluoromethyl)phenyl]-1*H*-benzo[*d*]imidazole (4g)[15]

Yield 220 mg (84%); pale yellow solid; mp 265–267 °C.

^{1}H NMR (400 MHz, DMSO): δ = 8.23 (d, *J* = 7.8 Hz, 1 H), 8.18 (s, 1 H), 7.98 (d, *J* = 7.8 Hz, 1 H), 7.75 (t, *J* = 7.8 Hz, 1 H), 6.52–6.47 (m, 2 H), 6.39–6.34 (m, 2 H), 4.86 (s, 1 H).

^{13}C NMR (101 MHz, DMSO): δ = 166.31, 134.90, 133.22, 132.49, 130.01, 129.50, 129.16, 125.51, 125.21, 117.32, 114.58.

IR (KBr): 3055, 2955, 1612, 1426, 1278, 726 cm^{-1}.

MS (ESI): *m/z* = 263 [M + H]$^+$.

2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole (4h)[15]

Yield 184 mg (81%); white solid; mp 301–302 °C.

^{1}H NMR (400 MHz, DMSO): δ = 12.98 (s, 1 H), 8.19 (d, *J* = 8.6 Hz, 2 H), 7.62 (d, *J* = 8.5 Hz, 4 H), 7.22 (t, *J* = 7.8 Hz, 2 H).

^{13}C NMR (101 MHz, DMSO): δ = 150.15, 143.75, 135.02, 134.48, 129.05, 128.13, 122.76, 121.83, 118.96, 111.41.

IR (KBr): 3050, 1650, 1490, 1470, 1430, 1320, 1275, 1090, 1015, 965, 830 cm^{-1}.

MS (ESI): *m/z* = 229 [M + H]$^+$.

2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole (4i)[15]

Yield 234 mg (86%); white solid; mp 241–244 °C.

^{1}H NMR (400 MHz, DMSO): δ = 8.16 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.10–8.01 (m, 3 H), 7.80–7.75 (m, 2 H), 7.59–7.54 (m, 1 H), 7.51–7.46 (m, 1 H).

^{13}C NMR (101 MHz, DMSO): δ = 148.22, 130.93, 129.68, 129.16, 128.82, 125.98, 121.22.

IR (KBr): 3040, 1645, 1495, 1465, 1420, 1310, 1265, 1080, 1025, 830 cm^{-1}.

MS (ESI): *m/z* = 274 [M + H]$^+$.

2-(4-Fluorophenyl)-1*H*-benzo[*d*]imidazole (4j)[15]

Yield 189 mg (83%); pale yellow solid; mp 247–249 °C.

^{1}H NMR (400 MHz, DMSO): δ = 12.48 (s, 1 H), 7.98–7.88 (m, 1 H), 7.74–7.49 (m, 3 H), 7.48–7.38 (m, 2 H), 7.22–7.14 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.20, 130.92, 128.96, 127.52, 126.25, 125.13, 123.17, 121.56.

IR (KBr): 3050, 2952, 1610, 1425, 1275, 721 cm^{-1}.

MS (ESI): *m/z* = 229 [M + H]+.

2-(3-Nitrophenyl)-1*H*-benzo[*d*]imidazole (4k)[15]

Yield 198 mg (83%); light brown solid; mp 198–200 °C.

^{1}H NMR (400 MHz, DMSO): δ = 8.72 (d, *J* = 24.8 Hz, 4 H), 8.34 (dd, *J* = 17.9, 7.9 Hz, 3 H), 7.80 (s, 2 H), 7.35 (s, 4 H).

^{13}C NMR (101 MHz, DMSO): δ = 160.27, 148.23, 143.36, 137.76, 134.41, 130.58, 127.01, 125.64, 122.69, 120.96.

IR (KBr): 3060, 3000, 1600, 1480, 1430, 1280, 1250, 1220, 1170, 830 cm^{-1}.

MS (ESI): *m/z* = 240 [M + H]$^+$.

2-(2-Nitrophenyl)-1*H*-benzo[*d*]imidazole (4l)[15]

Yield 193 mg (81%); yellow solid; mp 278–280 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (s, 1 H), 8.31–8.25 (m, 1 H), 8.01 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.70 (dd, *J* = 11.3, 3.9 Hz, 1 H), 7.61–7.56 (m, 1 H), 7.15–7.09 (m, 2 H), 6.80–6.74 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.08, 143.06, 136.06, 133.28, 131.08, 129.85, 129.07, 124.60, 118.67, 117.58, 115.88.

IR (KBr): 3070, 3010, 1620, 1485, 1420, 1290, 1250, 1205, 1150, 810 cm^{-1}.

MS (ESI): *m/z* = 240 [M + H]$^+$.

4-{1*H*-Benzo[*d*]imidazol-2-yl}-*N*,*N*-dimethylaniline (4m)[14]

Yield 198 mg (84%); white solid; mp 228–230 °C.

^{1}H NMR (400 MHz, DMSO): δ = 8.44 (s, 1 H), 7.78 (d, *J* = 8.9 Hz, 2 H), 7.01 (dd, *J* = 7.8, 1.2 Hz, 1 H), 6.93–6.88 (m, 1 H), 6.77 (d, *J* = 8.9 Hz, 2 H), 6.69 (dd, *J* = 7.9, 1.2 Hz, 1 H), 6.54 (td, *J* = 7.7, 1.3 Hz, 1 H), 3.00 (s, 6 H).

^{13}C NMR (101 MHz, DMSO): δ = 156.41, 152.12, 143.27, 136.53, 130.05, 126.25, 124.46, 116.68, 116.30, 114.29, 111.48.

IR (KBr): 3420, 3050, 2941, 1610, 1429, 1263, 780 cm^{-1}.

MS (ESI): *m/z* = 238 [M + H]$^+$.

2-(2-Chlorophenyl)-1*H*-benzo[d]imidazole (4n)[14]

Yield 180 mg (79%); white solid; mp 233–235 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.34 (s, 1 H), 8.45–8.42 (m, 1 H), 7.50 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.41 (td, *J* = 7.3, 1.9 Hz, 3 H), 7.31 (dd, *J* = 6.0, 3.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.14, 132.39, 131.12, 130.85, 128.45, 127.73.

IR (KBr): 3445, 3050, 1440, 1400, 1050, 740 cm^{-1}.

MS (ESI): *m/z* = 229 [M + H]$^+$.

2-(1*H*-Benzo[*d*]imidazol-2-yl)phenol (4o)[14]

Yield 201 mg (96%); white solid; mp 270–273 °C.

^{1}H NMR (400 MHz, $CDCl_3$ + DMSO): δ = 12.95 (s, 1 H), 8.78 (s, 1 H), 7.54 (dd, *J* = 4.9, 2.8 Hz, 1 H), 7.33 (d, *J* = 6.1 Hz, 4 H), 6.90 (t, *J* = 6.0 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$ + DMSO): δ = 163.91, 160.61, 142.18, 133.26, 132.55, 127.75, 123.27, 119.61, 119.26, 118.98, 116.70.

IR (KBr): 3185, 2989, 1620 cm^{-1}.

MS (ESI): *m*/*z* = 211 $[M + H]^+$.

2-(Furan-2-yl)-1*H*-benzo[*d*]imidazole (4p)[14]

Yield 138 mg (75%); white solid; mp 285–287 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.72 (m, 1 H), 7.59 (dd, *J* = 1.7, 0.7 Hz, 1 H), 7.45 (dd, *J* = 6.1, 2.7 Hz, 1 H), 7.26–7.23 (m, 2 H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1 H), 6.21 (ddd, *J* = 3.9, 3.3, 1.2 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.36, 144.98, 143.88, 143.61, 142.44, 135.14, 123.16, 122.87, 119.45, 113.28, 112.01, 110.36, 109.90, 108.28.

IR (KBr): 3450, 3045, 1430, 1410, 1040, 755 cm^{-1}.

MS (ESI): *m*/*z* = 185 $[M + H]^+$.

2-(4-Isopropylphenyl)-1*H*-benzo[*d*]imidazole (4q)[14]

Yield 205 mg (87%); white solid; mp 249–251 °C.

^{1}H NMR (400 MHz, DMSO): δ = 12.81 (s, 1 H), 8.11 (d, *J* = 8.2 Hz, 2 H), 7.66–7.52 (m, 2 H), 7.42 (d, *J* = 8.2 Hz, 2 H), 7.19 (dd, *J* = 6.0, 3.1 Hz, 2 H), 2.96 (dt, *J* = 13.8, 6.9 Hz, 1 H), 1.24 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, DMSO): δ = 151.36, 150.33, 127.84, 126.87, 126.49, 33.34, 23.67.

IR (KBr): 3417, 3055, 2951, 1620, 1439, 1273 cm^{-1}.

MS (ESI): *m*/*z* = 237 $[M + H]^+$.

4-(Benzo[*d*]thiazol-2-yl)phenol (5a)[14]

Yield 167 mg (74%); white solid; mp 230–232 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11–8.03 (m, 3 H), 7.89 (d, 1 H, *J* = 7.6 Hz), 7.49 (t, 1 H, *J* = 6.5 Hz), 7.38 (t, 1 H, *J* = 6.2 Hz), 7.20–7.14 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.16, 159.71, 153.28, 133.79, 128.31, 125.34, 123.97, 123.87, 121.66, 120.75, 115.32.

IR (KBr): 2918, 1604, 1526, 821, 732 cm^{-1}.

MS (ESI): *m*/*z* = 228 $[M + H]^+$.

2-(4-Methoxyphenyl)benzo[*d*]thiazole (5b)[14]

Yield 183 mg (76%); white solid; mp 120–122 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, 2 H, *J* = 8.1 Hz), 7.89 (d, 2 H, *J* = 7.6 Hz), 7.51–7.48 (m, 1 H), 7.33 (s, 3 H), 3.99 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 157.15, 152.09, 131.72, 129.45, 125.82, 124.51, 122.71, 121.13, 111.59.

IR (KBr): 2995, 1604, 1482, 1256, 968, 832 cm^{-1}.

MS (ESI): *m*/*z* = 242 $[M + H]^+$.

2-Phenylbenzo[*d*]thiazole (5c)[14]

Yield 158 mg (75%); Yellow solid; mp 111-113 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11–8.07 (m, 3 H), 7.90 (d, 1 H, *J* = 7.9 Hz), 7.52–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 130.93, 128.98, 127.50, 126.27, 125.14, 123.18, 121.57.

IR (KBr): 3065, 1479, 1454, 1226, 964, 765 cm^{-1}.

MS (ESI): *m*/*z* = 212 $[M + H]^+$.

2-(4-Bromophenyl)benzo[*d*]thiazole (5i)[14]

Yield 203 mg (70%); white solid; mp 130–132 °C.

^{1}H NMR (400 MHz, DMSO): δ = 8.15 (dd, *J* = 7.9, 0.6 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 8.04–8.01 (m, 2 H), 7.78–7.75 (m, 2 H), 7.58–7.54 (m, 1 H), 7.50–7.45 (m, 1 H).

^{13}C NMR (101 MHz, DMSO): δ = 166.07, 153.47, 134.54, 132.37, 132.01, 129.02, 126.79, 125.75, 124.86, 122.97, 122.43.

IR (KBr): 3057, 1591, 1394, 973, 758 cm^{-1}.

MS (ESI): *m*/*z* = 291 $[M + H]^+$.

Conflict of Interest

The authors declare no conflict of interest.

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