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CuI catalyzed C–N bond forming reactions between aryl/heteroaryl bromides and imidazoles in [Bmim]BF_4

Xin Lv, Zhiming Wang and Weiliang Bao*

Zhejiang University, Xi Xi Campus, Department of Chemistry, Hangzhou, Zhejiang 310028, P.R. China

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Abstract—By using CuI as the catalyst and L-Proline as the ligand, the Ullmann-type coupling reactions of aryl/heteroaryl bromides and imidazoles in [Bmim]BF_4 at 105–115 °C gave the corresponding *N*-arylimidazoles/*N*-heteroarylimidazoles in good yields. The system offers a convenient, recyclable, and environmentally benign method for these coupling reactions.

1. Introduction

N-Arylimidazoles and *N*-heteroarylimidazoles have been found useful for their biological effects and medicinal applications.[1] Recently, these arylimidazole derivatives show their important roles in the area of *N*-heterocyclic carbene chemistry.[2] Synthesis of these useful compounds becomes a meaningful work. One common strategy is the Ullmann-type C–N bond formations.[3] However, the reactions usually proceeds at high temperatures and their further applications would be limited. *N*-Arylimidazoles could be obtained by nucleophilic aromatic substitution,[4] but the method is suitable only for the substrates with electron withdrawing substituents. In 1998, Chan and Lam reported cupric acetate catalyzed coupling between aryl boronic acids and imidazoles.[5] The method could proceed at low temperatures, nevertheless the relatively expensive boronic reagents and the strict optimization of the condition limits its scope in synthetic areas.[6] Palladium catalyzed C–N bond forming coupling works effectively at mild temperatures, whereas the catalysts used is expensive and sensitive to air and moisture.[7]

Buchwald et al. firstly reported (CuOTf)·benzene/1,10-phenanthroline/*trans*,*trans*-dibenzylideneacetone catalyzed Ullmann-type reactions between aryl halides and imidazoles at low temperatures (110–125 °C),[8] and latterly found the diamines promoted CuI catalyzed coupling of aryl iodides and imidazoles.[9] However, Buchwald's method requires special catalysts or ligands. Recently, Ma and his co-workers developed the first amino acids promoted CuI catalyzed system in cross-coupling reactions, which were carried out in mild conditions.[10] Ma's protocol uses economical and readily available amino acids as promoters.

Room temperature ionic liquids (RTILs) are one class of non-molecular ionic solvents. They have special characteristics such as low vapor pressure, high polarity, and etc.[11] RTILs have been widely utilized in the area of organic chemistry as novel solvents.[11] In recent years, metal catalyzed coupling reactions have been studied in RTILs.[12] Ullmann-type reactions also have been tried in RTILs and many results revealed that they could proceed successfully in these special solvents.[13] Our laboratory reported a mild and efficient method for Ullmann-type coupling of vinyl bromides with imidazoles in ionic liquids, which was promoted by L-proline.[14]

On the other hand, although synthesis of *N*-arylimidazoles has been widely and intensively studied, researches on *N*-heteroarylation of imidazoles are still rare. Relating to this article, only two *N*-heteroarylimidazoles have been synthesized by Ullmann coupling methods.[15]

Herein we reported a copper (I) catalyzed cross-coupling reaction between aryl/heteroaryl bromides and imidazoles in RTIL, which would be a milder, economical, and recoverable way to obtain the *N*-arylimidazoles/*N*-heteroarylimidazoles. Considering the relatively rare reports on the latter and their important applications, our research mainly focused on the synthesis of *N*-heteroarylimidazoles.

2. Results and discussion

2.1. Synthesis of *N*-arylimidazoles/*N*-heteroarylimidazoles by Ullmann-type method in RTIL

Initially, CuI catalyzed coupling reactions between aromatic heterocyclic bromides and imidazoles in ([Bmim]BF_4) were studied. It was found that in the presence of some weak bases

* Corresponding author. Tel./fax: +86 571 88911554; e-mail: wbao@hzcnc.com

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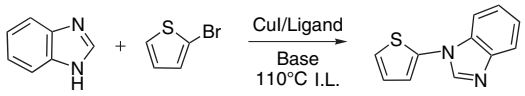
(such as K_2CO_3 and K_3PO_4), together with some α-amino acids as ligands, CuI could facilitate this type of coupling reactions in [Bmim]BF_4 under mild conditions. The coupling between aryl (including substituted phenyl and naphthyl) bromides and imidazoles under the similar conditions was also tested, as a supplement for the arylation of the imidazoles.

By using a moderate base (K_2CO_3), we firstly altered the ligand α-amino acids to search the most suitable promoter. It was found that the type of ligands affected this reaction significantly and L-proline seemed to be the best ligand (Table 1, entries 1–4).

Table 1. Effect of ligands and bases in one coupling reaction[a]



Entry	Ligand	Base	Yield (%)[b]
1	L-Alanine	K_2CO_3	73
2	L-Arginine	K_2CO_3	51
3	L-Serine	K_2CO_3	65
4	L-Proline	K_2CO_3	76
5	L-Proline	KOH	52
6	L-Proline	K_3PO_4	71
7	L-Proline	AcONa	26

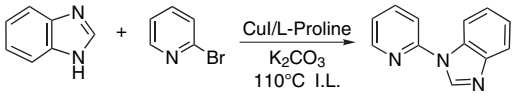
[a] Reaction conditions: CuI (0.9 mmol), base (5.4 mmol), amino acid (1.8 mmol), and benzimidazole (3 mmol), 2-bromothiophene (5.4 mmol), at 110 °C in [Bmim]BF_4 (3 ml), 24 h.
[b] Isolated yields.

After the favorable ligand has been sought out, several different bases were tried (Table 1, entries 4–7). By comparing the yields of these reactions, both K_2CO_3 and K_3PO_4 could facilitate this coupling reaction and K_2CO_3 was the best one. Although KOH was much stronger than the others, the yield was lower, and more complex mixture was obtained when the reaction was finished. In our opinion, when KOH was used as a base, the reagents or solvent might decompose and side reactions might exist. In contrast, AcONa was too weak to facilitate the metal exchange process and so the reactivity was lower.

The reactions also seem to be sensitive to the amount of catalyst and ligand. Different amount of the catalyst and ligand were added into the reaction systems. The yield was significantly improved when the amount of CuI was increased from 10 to 30 mol % gradually (Table 2). However, no obvious improvement was observed when the amount of CuI was raised from 30 to 40 mol %. This results show that the reaction might have been saturated when more than 40 mol % CuI was used. In our opinion, 30 mol % CuI is sufficient and optimum.

After optimizing the reaction conditions, we explored the scope of the coupling reactions between heteroaryl bromides and imidazoles. The results are listed in Table 3, entries 1–13. The coupling reactions between aryl (including substituted phenyl and naphthyl) bromides and imidazole were also carried out under the above-mentioned conditions. The reactions proceeded successfully and the yields were satisfactory (Table 3, entries 14–19).

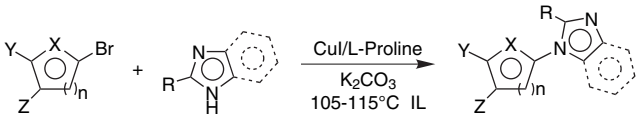
Table 2. Effect of the amount of CuI and ligand[a]



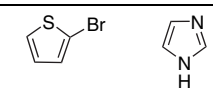
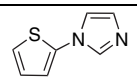
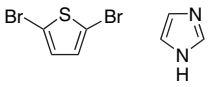
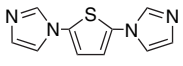
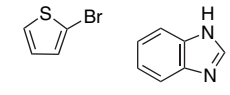
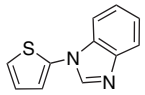
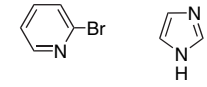
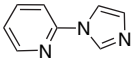
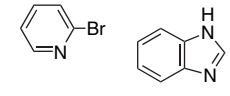
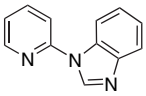
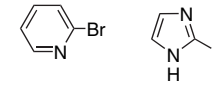
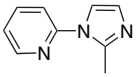
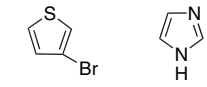
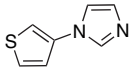
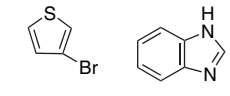
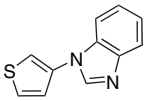
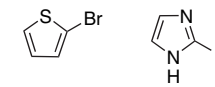
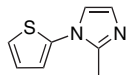
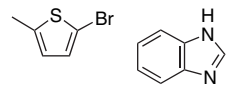
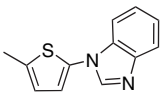
Entry	CuI (L-Proline) (mol %)	Yield (%)[b]
1	10 (20)	56
2	20 (40)	78
3	30 (60)	87
4	40 (80)	89

[a] Reaction conditions: CuI (0.3–1.2 mmol), base (5.4 mmol), amino acid (0.6–2.4 mmol), benzimidazole (3 mmol), 2-bromopyridine (5.4 mmol), at about 110 °C in [Bmim]BF_4 (3 ml), 10 h.
[b] Isolated yields.

Table 3. CuI/α-amino acid catalyzed coupling reactions of heteroaryl/aryl bromides with imidazoles in RTIL[a]



X=CH, S, N; n=1, 2; Y=H, CH_3, Br; Z=H, CH_3, Cl, NO_2; R=H, CH_3

Entry	Substrates	Product	Time (h)	Yield[b] (%)
1			26	74
2			50	77[c]
3			24	76
4			18	81
5			10	87
6			48	71
7			36	72
8			36	75
9			48	62
10			36	73

(continued)

Table 3. (*continued*)

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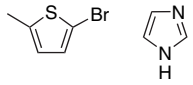
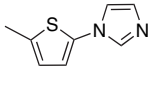
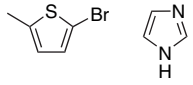
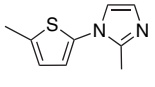
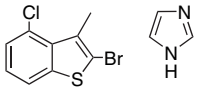
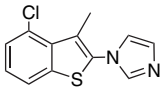
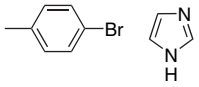
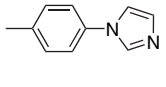
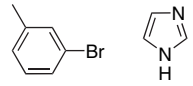
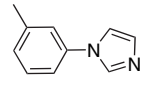
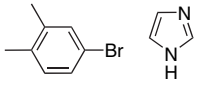
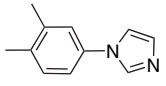
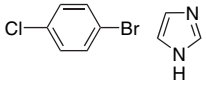
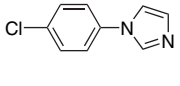
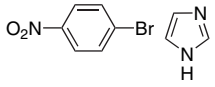
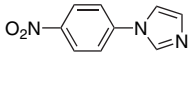
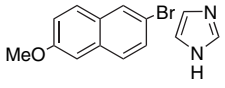
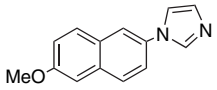
11			48	68
12			48	46
13			48	19
14			24	82
15			24	75
16			24	70
17			24	80
18			24	62
19			24	85

[a] Reaction conditions: CuI (0.9 mmol), base (5.4 mmol), amino acid (1.8 mmol), imidazole (3 mmol), heteroaryl/aryl bromide (5.4 mmol), at 110 °C in [Bmim]BF_4 (3 ml).
[b] Isolated yields.
[c] CuI (1.8 mmol), base (10.8 mmol), amino acid (3.6 mmol), imidazole (6 mmol), 2,5-dibromothiophene (2 mmol), at 115 °C in [Bmim]BF_4 (5 ml).

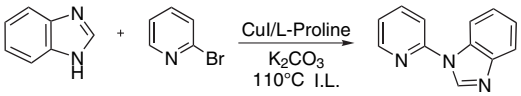
2-Bromopyridine is found to be the most reactive heteroaryl bromide in our experiment and benzimidazole seems to be a little more reactive than imidazole and alkyl-substituted imidazoles (Table 3, entries 4–6 and entries 7–9). We think both electrophilicity of heteroaryl bromides and the nucleophilicity of imidazoles might affect these reactions.

As shown in Table 3, the reaction is hypersensitive to the steric environment of the heteroaryl/aryl bromides and imidazoles, i.e., steric hindrance of the substrates obviously affects these coupling reactions. As indicated in Table 3 (entries 1, 4, 11 and entries 6, 9, 12), the conversion declined when imidazole is replaced by 2-methylimidazole. The effect of the 2-position steric hindrance on the bromides seems to be much stronger than on the imidazoles. As a result, the *o*-substituted heterocycle bromides such as 2-bromo-4-chloro-3-methylbenzo[*b*]thiophene are much more difficult to react with imidazole (Table 3, entry 13) probably because the methyl group on 3-position hinder the co-planarity of the imidazole and the thiophene moieties, which gives a negative effect on the product formation. Prolonging the reaction time from 48 to 72 h did not substantially improve the yield. The reactions between aryl bromides and imidazole could proceed successfully in the similar catalytic system (Table 3, entries 14–17) in relatively short reaction time (24 h). It is observed that these reactions tolerate both electron withdrawing and electron donating substituents on the bromides (Table 3, entries 14–19, yields 62–85%). The electron donating groups on the bromides are found to be more favorable for these reactions than the electron withdrawing ones (Table 3, entries 14 and 18). 2-Bromo-6-methoxy-naphthalene is found more reactive than phenyl bromides and the yield of the corresponding product obtained is also better.

2.2. Reusability and solvent effects of the coupling reactions in RTIL

One of the most attractive properties of ionic liquids is that the catalyst system could be recycled. The recovery possibility of the reaction has also been investigated. To our satisfaction, the results are rather good. After fourth runs, the system still gave good yield (Table 4). The catalyst system, including the solvent ionic liquids, the catalyst CuI and the ligand could be favorably recycled. Because of the high polarity of ionic liquid, the reaction mixture can be extracted directly by lower polar solvents. Therefore the workup of these reactions is simple. The recovered ionic liquid can be recycled after proper treatment.

Table 4. Reuse of CuI/L-proline/IL reaction system[a]

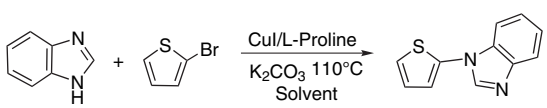


Cycle	Yield (%)	Cycle	Yield (%)[b]
1	87	3	80
2	82	4	76

[a] Reaction conditions: CuI (0.9 mmol), K_2CO_3 (5.4 mmol), L-proline (1.8 mmol), benzimidazole (3 mmol), 2-bromopyridine (5.4 mmol), at 110 °C in [Bmim]BF_4 (3 ml), 10 h. After reaction, the product was extracted with ether/ethyl acetate (v/v=4/1, 3×5 ml). The remaining ionic liquid was concentrated in vacuo (6.0 torr for 1 h at 110 °C), further amounts of base (5.4 mmol) and reactants were added and next turn began.
[b] Isolated yields.

Lastly, we have tried the reactions in traditional organic solvents such as DMF and DMSO. The yields obtained in these two solvents were also good but not as good as in the ionic liquid (Table 5).

Table 5. Effect of different solvents[a]



Entry	Solvent	Yield (%)[b]
1	[Bmim]BF_4	76
2	DMF	66
3	DMSO	71

[a] Reaction conditions: CuI (0.9 mmol), K_2CO_3 (5.4 mmol), L-proline (1.8 mmol), benzimidazole (3 mmol), 2-bromothiophene (5.4 mmol), at 110 °C, Solvent (3 ml), 24 h.
[b] Isolated yields.

3. Conclusions

In summary, we have developed an efficient and mild method to synthesize *N*-arylimidazoles/*N*-heteroarylimidazoles by Ullmann coupling strategy, in which ionic liquid was used as a favorable solvent. The procedure is simple and can be carried out under mild conditions, using comparatively cheap CuI as the catalyst and natural amino acid as the ligand. The conveniently recoverable and reusable catalytic system makes the methodology environmentally benign and economical.

4. Experimental

4.1. General information

All reagents and solvents used were analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. All the NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 (400 MHz) instrument with TMS as internal standard. IR spectra were taken as liquid film or KBr plates. TLC was carried out with 0.2 mm silica gel plates (GF254). Visualization was accomplished by UV light or I_2 staining. The columns were hand packed with silica gel 60 (200–300 mesh). All reactions were carried out under atmosphere, if not stated otherwise. The ionic liquid, $[Bmim]BF_4$, was dehumidified in vacuo by heating at about 110 °C for 30 min prior to use. All products were confirmed by ^1H NMR, ^{13}C NMR, IR, and elemental/HRMS analysis (excepting the known compounds and the *N*-arylimidazoles).

4.2. General procedure for *N*-heteroarylation/*N*-arylation of imidazoles under the catalysis of CuI and α-amino acid in RTIL

4.2.1. Synthesis of 1-(thiophen-2-yl)-1*H*-imidazole in $[Bmim]BF_4$. Table 3, entry 1. CuI (1.71 g, 0.9 mmol), L-proline (0.207 g, 1.8 mmol), K_2CO_3 (0.745 g, 5.4 mmol) and dry $[Bmim]BF_4$ (3.00 ml) were added to a 10 ml flask. Stirred and humidified in vacuo by heating in an oil bath at 110 °C for 0.5 h. Imidazole (0.204 g, 3 mmol) was add to the stirred mixture, then bromothiophene (0.880 g, 5.4 mmol, 1.8 equiv) was added by a syringe into the flask (sealed). The reaction was monitored by TLC. After the reaction was completed, the resulting mixture was cooled to room temperature and was extracted by Et_2O/EtOAc (v/v=4/1, 3×5 ml). The extracts were combined and washed by water (2×10 ml), brine (15 ml), and dried ($MgSO_4$). Evaporating the solvent under reduced pressure gave a dark brown oil, which was further purified by column chromatography (v/v=4/1, Et_2O/EtOAc) to afford an viscous oil (0.316 g, 74%). The ^1H NMR is in accordance with literature.[15,16] ^1H NMR (400 MHz, $CDCl_3$) δ 6.92–6.95 (m, 2H), 7.07–7.10 (m, 1H), 7.11 (s, 1H), 7.14 (s, 1H), 7.72 (s, 1H); IR: 3079, 2920, 2858, 1611, 1565, 1502, 1450, 1331, 1228, 1197, 1046, 800, 743 cm^{-1}.

4.2.2. 2,5-Di(1*H*-imidazol-1-yl)thiophene. Table 3, entry 2, yield 77%. Mp 71–72 °C (lit.[16] mp 71–72 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 7.18–7.19 (m, 4H), 7.75 (s, 2H); IR (KBr): 3103, 2925, 2870, 1649, 1575, 1481, 1310, 1251, 1047, 844, 808, 749 cm^{-1}.

4.2.3. 1-(Thiophen-2-yl)-1*H*-benz[*d*]imidazole. Table 3, entry 3, yield 76%. Viscous oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.07–7.09 (dd, J=3.9, 5.5 Hz, 1H), 7.12–7.14 (dd, J=1.4, 3.9 Hz, 1H), 7.26–7.28 (dd, J=1.4, 5.5 Hz, 1H), 7.32–7.36 (m, 2H), 7.53–7.56 (m, 1H), 7.83–7.87 (m, 1H), 8.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.75, 120.76, 122.06, 123.40, 123.61, 124.33, 126.63, 143.87, 137.23, 143.36, 143.75; IR: 3077, 2925, 2860, 1611, 1550, 1488, 1327, 1231, 1196, 743, 699 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_8N_2SNa$ $(M+Na)^+$, 223.0306; found: $(M+Na)^+$, 223.0305.

4.2.4. 2-(1*H*-Imidazol-1-yl) pyridine.[15c,17] Table 3, entry 4, yield 81%. Mp 38–40 °C (lit.[17] mp 38–40 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.29–7.32 (dd, J=5.0, 7.4 Hz, 1H), 7.76–7.78 (d, J=8.0 Hz, 1H), 7.92–7.96 (m, 2H), 8.44–8.46 (m, 1H), 8.54 (s, 1H); IR (KBr): 3078, 2926, 2865, 1611, 1601, 1488, 1328, 1231, 1196, 770, 650 cm^{-1}.

4.2.5. 1-(Pyridin-2-yl)-1*H*-benz[*d*]imidazole.[15a,b] Table 3, entry 5, yield 87%. Mp 59–60 °C (lit.[18] mp 59–60 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.24 (m, 1H), 7.31–7.37 (m, 2H), 7.46–7.51 (m, 1H), 7.77–7.86 (m, 2H), 8.02–8.04 (m, 1H), 8.55 (s, 2H); IR (KBr): 3060, 3028, 2927, 2850, 1588, 1478, 1462, 1327, 1235, 1204, 773, 742 cm^{-1}.

4.2.6. 2-(2-Methyl-1*H*-imidazol-1-yl) pyridine. Table 3, entry 6, yield 71%. Viscous oil. ^1H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H), 6.98 (d, J=1.0 Hz, 1H), 7.24 (d, J=1.0 Hz, 1H), 7.25–7.27 (m, 2H), 7.78–7.83 (td, J=2.0, 8.0 Hz, 1H), 8.50–8.52 (d, J=4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.16, 117.13, 118.86, 122.26, 127.74, 138.58, 144.83, 149.06, 150.58; IR: 3101, 2931, 2860, 1588, 1499, 1475, 1442, 1312, 1283, 787, 741, 677 cm^{-1}; HRMS (ESI) calcd for $C_9H_{10}N_3$ $(M+H)^+$, 160.0875; found: $(M+H)^+$, 160.0869.

4.2.7. 1-(Thiophen-3-yl)-1*H*-imidazole. Table 3, entry 7, yield 72%. Mp 82–83 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J=1.2 Hz, 1H), 7.16 (d, J=1.6 Hz, 1H), 7.18–7.19 (dd, J=1.2, 2.8 Hz, 1H), 7.21 (s, 1H), 7.39–7.41 (dd, J=2.8, 5.4 Hz, 1H), 7.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.19, 116.50, 121.37, 127.12, 129.87, 135.81, 136.14; IR (KBr): 3110, 2928, 2858, 1555, 1494, 1337, 1247, 856, 777, 736, 658 cm^{-1}; Anal. Calcd for $C_7H_6N_2S$: C 55.97, H 4.03, N 18.65; found: C 56.08, H 4.03, N 18.68.

4.2.8. 1-(Thiophen-3-yl)-1*H*-benz[*d*]imidazole.[19] Table 3, entry 8, yield 75%. Mp 90–91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.25 (dd, J=1.6, 5.2 Hz, 1H), 7.28–7.32 (m, 2H), 7.33–7.35 (dd, J=1.6, 2.8 Hz, 1H), 7.46–7.48 (dd, J=3.2, 5.2 Hz, 1H), 7.49–7.53 (m, 1H), 8.07 (s, 1H), 7.83–7.88 (m, 1H); IR (KBr): 3106, 2963, 2858, 1548, 1491, 1226, 1194, 855, 789, 744, 642 cm^{-1}.

4.2.9. 2-Methyl-1-(thiophen-2-yl)-1*H*-imidazole. Table 3, entry 9, yield 62%. Viscous oil. ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.95–6.96 (dd, J=1.6, 4.0 Hz, 1H), 6.98–6.99 (d, J=1.6 Hz, 1H), 7.00–7.02 (m, 2H), 7.23–7.26 (dd, J=1.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.32, 121.92, 123.16, 123.76, 125.84, 127.68, 138.60, 145.94; IR: 3107, 2927, 2850, 1553, 1496, 1451,

1289, 984, 845, 703 cm^{-1}; HRMS (ESI) calcd for $C_8H_9N_2S$ $(M+H)^+$ 165.0486; found: $(M+H)^+$, 165.0481.

4.2.10. 1-(5-Methylthiophen-2-yl)-1*H*-benz[*d*]imidazole. Table 3, entry 10, yield 73%. Viscous oil. ^1H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 6.72–6.73 (d, J=3.6 Hz, 1H), 6.91–6.92 (d, J=3.6 Hz, 1H), 7.31–7.36 (m, 2H), 7.51–7.55 (m, 1H), 7.82–7.87 (m, 1H), 8.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.40, 110.37, 120.27, 121.96, 122.84, 123.78, 123.94, 133.80, 134.62, 138.06, 143.05, 143.27; IR: 3079, 2921, 2857, 1651, 1612, 1503, 1451, 1283, 919, 882, 800, 743, 676 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{11}N_2S$ $(M+H)^+$ 215.0643; found: $(M+H)^+$, 215.0637.

4.2.11. 1-(5-Methylthiophen-2-yl)-1*H*-imidazole. Table 3, entry 11, yield 68%. Viscous oil. ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 6.64–6.65 (m, 1H), 6.79–6.80 (d, J=3.6 Hz, 1H), 7.16 (s, 2H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.30, 119.00, 120.21, 123.87, 129.80, 136.00, 136.54, 136.97; IR: 3112, 2921, 2859, 1644, 1568, 1510, 1474, 1302, 1215, 1038, 909, 801, 733, 657 cm^{-1}; HRMS (ESI) calcd for $C_8H_9N_2S$ $(M+H)^+$ 165.0486; found: $(M+H)^+$, 165.0481.

4.2.12. 2-Methyl-1-(5-methylthiophen-2-yl)-1*H*-imidazole. Table 3, entry 12, yield 46%. Mp 40–41 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.45 (s, 3H), 6.61–6.62 (d, J=3.6 Hz, 1H), 6.70–6.71 (d, J=4.0 Hz, 1H), 6.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.33, 15.46, 122.08, 123.44, 123.72, 127.48, 135.72, 138.62, 146.25; IR: 3110, 2923, 2858, 1566, 1531, 1502, 1446, 1408, 1291, 1221, 1168, 1134, 985, 931, 802, 731, 671 cm^{-1}; Anal. Calcd for $C_9H_{10}N_2S$: C 60.64, H 5.65, N 15.72; found: C 60.74, H 5.80, N 15.70.

4.2.13. 1-(4-Chloro-3-methylbenzo[*b*]thiophen-2-yl)-1*H*-imidazole. Table 3, entry 13, yield 19%. Yellow needles. Mp 111–112 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.19 (s, 1H), 7.25 (s, 1H), 7.37–7.40 (dd, J=2.0, 8.4 Hz, 1H), 7.68–7.71 (m, 2H), 7.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.11, 121.26, 122.26, 123.43, 125.75, 126.06, 130.12, 131.37, 133.64, 134.23, 138.30, 139.64; IR (KBr): 3088, 3044, 2920, 2861, 1649, 1581, 1541, 1476, 1443, 1283, 1234, 1151, 1103, 910, 853, 809, 734, 657 cm^{-1}; Anal. Calcd for $C_{12}H_9ClN_2S$: C 57.95, H 3.65, N 11.26; found: C 57.71, H 3.82, N 11.19.

4.2.14. 1-*p*-Tolyl-1*H*-imidazole.[20,21] Table 3, entry 14, yield 82%. Mp 45–47 °C (lit.[20] mp 45–48 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.16–7.22 (m, 1H), 7.24 (s, 5H), 7.80 (s, 1H); IR (KBr): 3112, 2922, 2855, 1651, 1522, 815 cm^{-1}.

4.2.15. 1-*m*-Tolyl-1*H*-imidazole.[22] Table 3, entry 15, yield 75%. ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.15–7.18 (m, 4H), 7.25 (s, 1H), 7.31–7.35 (m, 1H), 7.82 (s, 1H); IR: 3113, 2920, 2860, 1611, 1504, 1365, 785.13, 734.6, 691.2 cm^{-1}.

4.2.16. 1-(3,4-Dimethylphenyl)-1*H*-imidazole. Table 3, entry 16, yield 70%. ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.31 (s, 3H), 7.09–7.11 (d, J=8.0 Hz, 1H), 7.15 (m, 1H), 7.18 (s, 1H), 7.19–7.21 (d, J=8.0 Hz, 1H), 7.23 (s, 1H), 7.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.25, 19.84, 118.33, 118.75, 122.61, 129.71, 130.66, 135.02, 135.48, 136.11, 138.33; IR: 3113, 2922, 2850, 2363, 1623, 1513, 1310, 814, 734 cm^{-1}.

4.2.17. 1-(4-Chlorophenyl)-1*H*-imidazole.[23] Table 3, entry 17, yield 80%. Mp 84–86 °C (lit.[23a] mp 85–87 °C). ^1H NMR (400 MHz, d_6-DMSO) δ 7.13 (s, 1H), 7.58–7.60 (td, J=2.0, 8.0 Hz, 2H), 7.70–7.72 (td, J=2.0, 8.0 Hz, 2H), 7.78 (s, 1H), 8.30 (s, 1H). IR (KBr): 3110, 2926, 2854, 1635, 1508, 1303, 830 cm^{-1}.

4.2.18. 1-(4-Nitrophenyl)-1*H*-imidazole.[15c,20] Table 3, entry 18, yield 62%. Mp 203–205 °C (lit.[20] mp 204.4–205.2 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.32 (m, 1H), 7.43 (s, 1H), 7.73–7.78 (t, J=8.0 Hz, 1H), 7.81–7.83 (d, J=8.0 Hz, 1H), 8.04 (s, 1H), 8.28–8.30 (d, J=8.0 Hz, 1H), 8.33 (s, 1H); IR (KBr): 3100, 2924, 2853, 2363, 1621, 1529, 1358, 812 cm^{-1}.

4.2.19. 1-(6-Methoxynaphthalen-2-yl)-1*H*-imidazole.[24] Table 3, entry 19, yield 85%. Mp 84–85 °C (lit.[24] mp 85 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.17 (d, J=2.0 Hz, 1H), 7.22–7.25 (m, 2H), 7.36 (s, 1H), 7.46–7.48 (dd, J=2.0, 8.5 Hz, 1H), 7.73–7.74 (m, 1H), 7.75–7.77 (m, 1H), 7.82–7.84 (d, J=8.5 Hz, 1H), 7.93 (s, 1H); IR (KBr): 3110, 2931, 2849, 2361, 1606, 1513, 1246, 852 cm^{-1}.

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