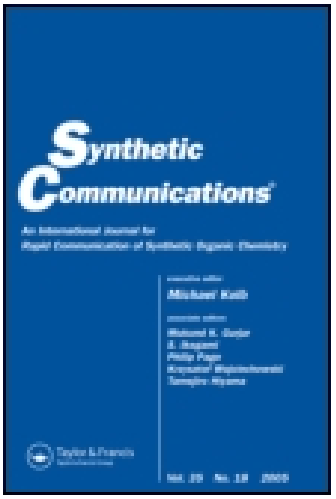

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SiO_2-NHC-Cu^I–CATALYZED *N*-ARYLATION OF IMIDAZOLES WITH ARYLBORONIC ACIDS UNDER BASE-FREE REACTION CONDITIONS

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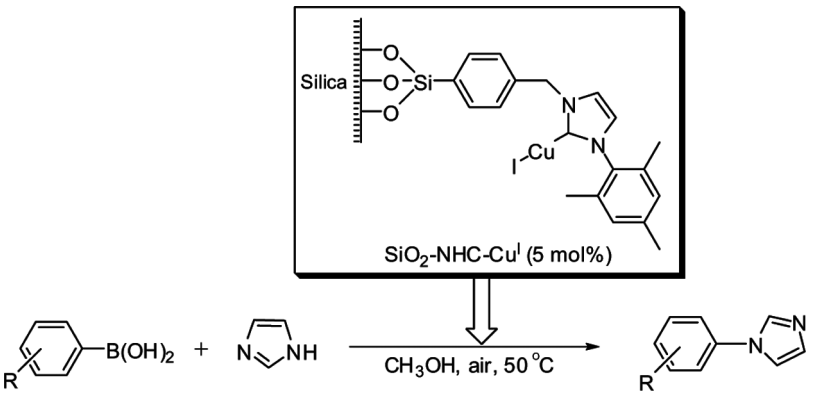
[2]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China*

GRAPHICAL ABSTRACT



Abstract N-*Arylation of imidazoles with arylboronic acids was efficiently carried out in the presence of a catalytic amount of SiO_2-NHC-Cu^I in methanol at room temperature under base-free reaction conditions. The reactions of a variety of arylboronic acids with imidazoles generated the corresponding products* N-*arylimidazoles in good to excellent yields. In addition, SiO_2-NHC-Cu^I could be recovered and recycled for six consecutive trials without significant loss of its reactivity.*

Keywords Arylboronic acid; copper(I); heterogeneous catalyst; imidazoles; *N*-arylation; NHC

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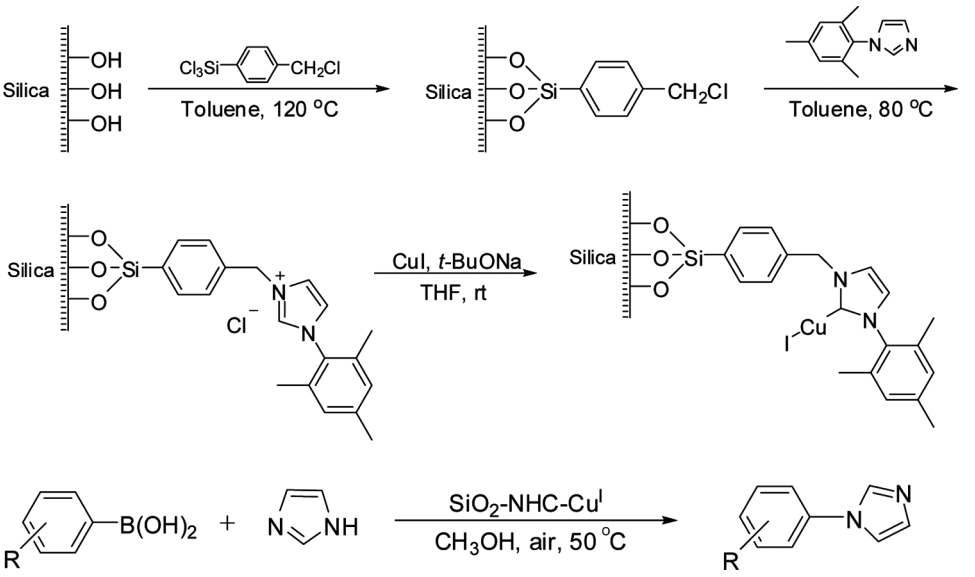
INTRODUCTION

C–N bond formation via transition-metal catalysis is currently a subject of great interest, and intensive research is being carried out to ensure useful organic transformations.[1] *N*-Arylimidazoles are common motifs in pharmaceutical research, and the synthesis of *N*-arylimidazoles has attracted significant interest because of the frequent occurrence of these structural units in biologically active inhibitors.[2,3] After the initial reports of Chan and Lam, Cu-catalyzed cross-coupling between *N*-heterocycles and arylboronic acids has become an important synthetic methodology in modern organic synthesis.[4a–c] The discovery and development of the catalytic pathway for *N*-arylation of *N*-heterocycles by Buchwald with bromoarenes and iodoarenes by using copper as catalyst in the presence of a ligand generated greater interest in industry.[4d,e] Later, Collman and coworkers reported that Cu(II) complexes with nitrogen-chelating bidentate ligands have been successful used in the coupling of imidazoles.[5] Very recently, Lan and coworkers developed the simple copper salt CuI-catalyzed cross-coupling of imidazoles with arylboronic acids in protic solvent without any base.[6] Thus, the development of mild and cost-effective catalytic procedures for the *N*-arylation of imidazoles still remains an active research area.[7]

Silica modified with different functionalities such as $-NH_2$, –SH, diamines, and amino acids was reported to be an excellent inorganic support for various transition metals such as Pd, Cu, Sc, Ru, Pt, and V, etc. and was used in different organic transformations.[8] *N*-Heterocyclic carbenes (NHCs) have been widely used as effective ligands in inorganic and organometallic chemistry since Arduengo and coworkers isolated the first stable *N*-heterocyclic carbene in 1991.[9] NHCs were first considered as simple phosphane mimics in organometallic chemistry.[10] However, increasing experimental data clearly showed that NHC–metal catalysts can surpass their phosphane-based counterparts in both activity and scope.[11] NHCs are stronger σ donors and weaker π acceptors, causing the properties of NHC–metal complexes to be notably different from those of a corresponding phosphane complex. Because of their specific coordination chemistry, NHCs can both stabilize and activate metal centers in quite different key catalytic steps of organic syntheses, for example, C–C, C–H, C–O, and C–N bond formation reactions.[12] To avoid catalyst leaching, polymer-, PEG, or silica-supported NHC–metal complexes were synthesized and applied successfully in a variety of organic reactions.[13]

Because new types of silica-supported catalysts have theoretical and practical significance, currently the preparation of 3-[(2-aminoethyl)amino]propyl-functionalized silica-anchored copper and subsequently its uses as highly efficient and recyclable catalysts for the Sonogashira reaction and 1,3-dipolar cycloaddition reaction were reported.[14] In this article, we report the synthesis of NHC functionalized silica immobilized Cu(I) catalyst, SiO_2-NHC-Cu^I (Scheme 1), which was found to be the effective catalysts for the *N*-arylation of imidazoles with arylboronic acids. *N*-Arylation of imidazoles with arylboronic acids was efficiently carried out in the presence of a catalytic amount of SiO_2-NHC-Cu^I in methanol under base-free reaction conditions. The reactions of a variety of arylboronic acids with imidazoles generated the corresponding products *N*-arylimidazoles in good to excellent yields. In addition, SiO_2-NHC-Cu^I could be recovered and recycled for six consecutive trials without significant loss of its reactivity.

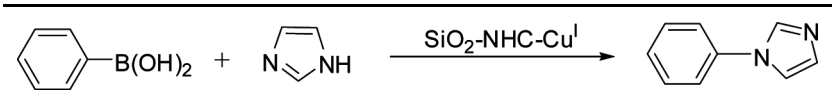


Scheme 1.

The SiO_2-NHC-Cu^I catalyst was readily prepared in a three-step procedure (Scheme 1). Activated silica was treated with trichloro[4-(chloromethyl)phenyl]silane in dry toluene at 120 °C under nitrogen for 24 h to afford the benzyl chloride–functionalized silica. The obtained functionalized silica material was then treated with *N*-mesitylimidazole in toluene at 80 °C for 24 h to generate the corresponding silica-supported ionic liquid. The silica-supported ionic liquid was then treated with freshly prepared CuI in the presence of *t*-BuONa in dry tetrahydrofuran (THF) at room temperature under an inert gas for 6 h. Then, the SiO_2-NHC-Cu^I catalyst was obtained as a gray-green powder, and the copper content of the catalyst was found to be 0.86 $mmol \cdot g^{-1}$.

In our preliminarily investigation on the model reaction of phenylboronic acid with imidazole, it was found that the reaction could be finished under very simple reaction conditions in the presence of a catalytic amount of SiO_2-NHC-Cu^I (5 mol%) in the absence of any additive, which gives the desired 1-phenyl-1*H*-imidazole in 90% yield (Table 1, entry 1). The effects of solvent, catalyst, reaction temperature, and time on the reaction were investigated. It was found that CH_3OH is the best solvent among the solvents tested, and the reaction proceeded smoothly in CH_3OH and generated the desired product in 90% yield, while dimethylformamide (DMF) or C_2H_5OH afforded trace amounts of the desired product (entries 1, 4, and 5). Moreover, the use of toluene, THF, and CH_3CN as solvents led to no occurrence of positive reactions (entries 2, 3, and 6). Fortunately, the reaction also generated the desired product in 80% yield when the reaction was carried out in ethanol/H_2O (9/1). A reaction temperature of 50 °C for 3 h was found to be optimal. Thus, the optimized reaction conditions for the reaction were found to be SiO_2-NHC-Cu^I (5 mol%) in CH_3OH at 50 °C for 3 h.

Table 1. Effect of solvent on the *N*-arylation of imidazole with phenylboronic acid[a]



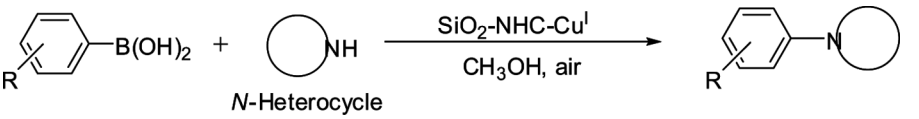
Entry	Solvent	Yield[b](%)
1	CH_3OH	90
2	Toluene	NR
3	THF	NR
4	DMF	Trace
5	C_2H_5OH	Trace
6	CH_3CN	NR
7	C_2H_5OH/H_2O (9/1)	80

[a]SiO_2-NHC-Cu^I(containing Cu 0.05 mmol, 5 mol%), imidazole (1.1 mmol), and phenylboronic acid (1.0 mmol) was carried out in solvent (3.0 mL) at 50 °C for 3 h under air.
[b]Isolated yields.

We chose a variety of structurally divergent arylboronic acids possessing a wide range of functional groups to understand scope and generality of the SiO_2-NHC-Cu^I–catalyzed *N*-arylation of imidazoles, which affords the corresponding *N*-arylated imidazoles. The results are summarized in Table 2. An arylboronic acid with an electron-withdrawing group such as 4-trifluoromethphenylboronic acid greater yield than that of the arylboronic acid with an electron-donating group, such as 4-methoxyphenylboronic acid or 4-*tert*-butylphenylboronic acid (Table 2, entry 7 vs entries 2 and 4). 2-Methyl, 3-methyl, and 4-methylphenylboronic acid reacted similarly with phenylboronic acid to generate the corresponding *N*-arylated imidazoles, which showed that there is not much more *ortho*-, *meta*-, and *para*-substitution effect on the substituted phenylboronic acid (Table 2, entries 3, 8, and 9). The results listed in Table 2 also indicated that the reactions of imidazole with other aromatic boronic acids, such as naphthalen-1-ylboronic acid, naphthalen-2-ylboronic acid, and biphenyl-4-ylboronic acid, gave good yields of the desired coupling products under the optimized reaction conditions (Table 2, entries 12–14). Meanwhile, an *ortho*-substitution effect on CHO- substituted phenylboronic acid was observed (Table 2, entry 15). It is important to note that no side product, such as deboronation of organoboronic acid, was observed in *N*-arylation of imidazole with phenylboronic acid, and the selectivity of 1-phenyl-1*H*-imidazole is $> 99\%$. Other *N*-heterocycles, such as 1*H*-pyrazole, benzimidazole, and phthalimide, also coupled smoothly with phenylboronic acid to produce the desired products in good yields (83–90%) under the present reaction conditions (Table 2, entries 16–18). It is noteworthy to point out that when the reaction was conducted in the absence of air, there was no any desired coupling product observed, which clearly emphasizes that the process is redox. Further investigation on the reaction mechanism is under way in our laboratory.

To screen the recyclability of SiO_2-NHC-Cu^I catalyst, a more practical method was applied to the reaction of imidazole and phenylboronic acid under the present reaction conditions. After separation of the product and the recovery of the SiO_2-NHC-Cu^I, fresh starting materials and CH_3OH were charged into the reaction

Table 2. SiO_2-NHC-Cu^I–catalyzed *N*-arylation of imidazoles with arylboronic acids[a]



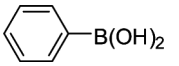
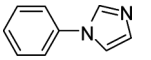
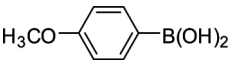
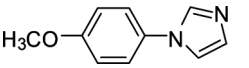
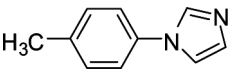
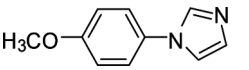
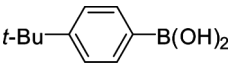
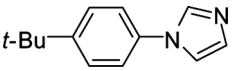
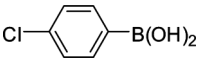
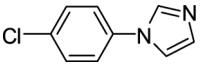
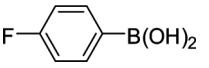
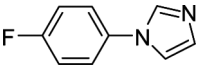
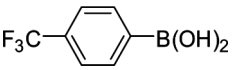
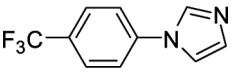
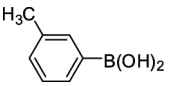
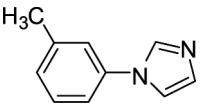
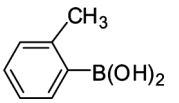
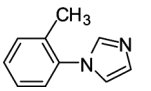
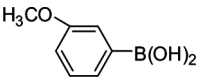
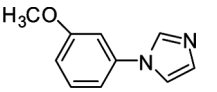
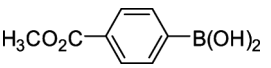
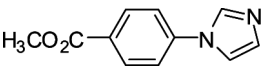
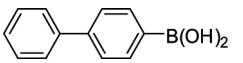
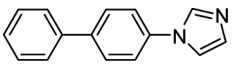
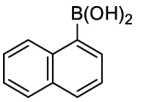
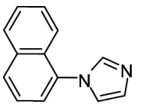
Entry	Azole	Arylboronic acid	Product	Yield[b] (%)
1				90
2				72
3				82
4				76
5				86
6				88
7				96
8				80
9				77
10				89
11				83
12				70
13				72

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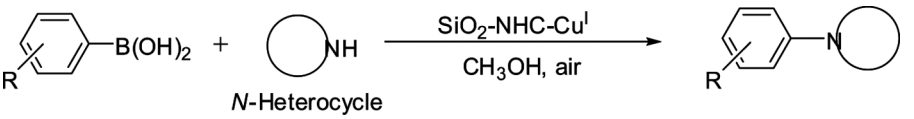
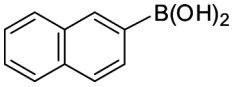
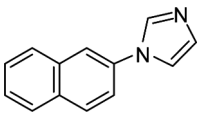
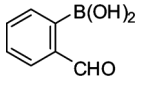
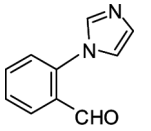
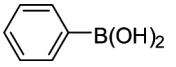
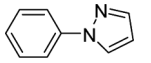
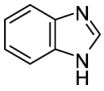
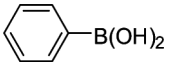
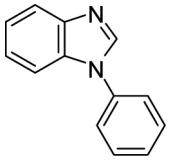
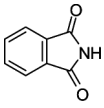
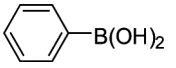
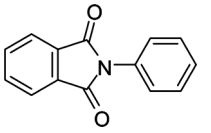
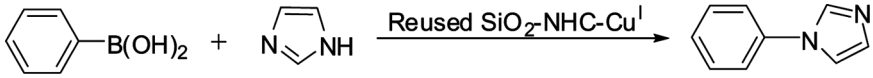
Table 2. Continued



Entry	Azole	Arylboronic acid	Product	Yield[b] (%)
14				77
15				40
16				88
17				90
18				83

[a]SiO_2-NHC-Cu^I(containing Cu 0.05 mmol, 5 mol%), azole (1.1 mmol), and arylboronic acid (1.0 mmol) was carried out in CH_3OH (3.0 mL) at 50 °C for 3 h under air.
[b]Isolated yields.

Table 3. Successive trials by using recoverable SiO_2-NHC-Cu^I catalyst[a]



Entry	Reused SiO_2-NHC-Cu^I	Yield[b] (%)
1	Fresh	90
2	First reuse	90
3	Second reuse	88
4	Third reuse	89
5	Forth reuse	87
6	Fifth reuse	86

[a]Reused SiO_2-NHC-Cu^I (containing Cu 0.05 mmol, 5 mol%), imidazole (1.1 mmol), and phenylboronic acid (1.0 mmol) was carried out in CH_3OH (3.0 mL) at 50 °C for 3 h under air.
[b]Isolated yields.

system. The reactions still proceeded well, and no unreacted substrates were detected at the end of the reaction. The SiO_2-NHC-Cu^I catalyst was recovered and recycled for six consecutive trials without any decrease in its activity.

CONCLUSION

In conclusion, SiO_2-NHC-Cu^I has been demonstrated to be a highly selective and efficient catalyst for the *N*-arylation of imidazoles with arylboronic acids. The reactions were performed smoothly to generate the desired products *N*-arylimidazoles in good yields under base-free and simple reaction conditions. The notable advantages of this methodology are mild conditions, short reaction times, and good yields free from any side reaction products. This method offers one of the important motifs for synthesis of *N*-arylimidazoles as natural products, biologically active compounds, and pharmaceutical agents.

EXPERIMENTAL

All ^1H NMR and ^{13}C NMR spectra were recorded on a 400-MHz Bruker FT-NMR spectrometer. All chemical shifts are given as δ values (ppm) with reference to tetramethylsilane (TMS) as an internal standard. Products were purified by flash chromatography on 230- to 400-mesh silica gel, SiO_2.

The chemicals and solvents were purchased from commercial suppliers either from Aldrich, Fluka, USA, or Shanghai Chemical Company, China, and were used without purification prior to use.

Preparation of Benzyl Chloride–Functionalized Silica

Anhydrous toluene (30 mL), activated silica (Qingdao Haiyang Chemical Company, China, specific surface area 300–400 m^2/g, pore size 280–600 μm, and pore volume 0.7 mL/g, 5.0 g), and trichloro[4-(chloromethyl)phenyl]silane (2.0 g) were introduced successively in a 100-mL, round-bottom flask. The mixture was refluxed at 120 °C under nitrogen for 24 h. Then the solution was filtered, and the solid was washed subsequently with toluene, dichloromethane, and methanol and dried under reduced pressure at 80 °C for 10 h to yield benzyl chloride functionalized silica (5.81 g). The loading of the modified silica was readily quantified by CHN microanalysis and found to be 1.12 mmol g^{-1} based on nitrogen content. The surface area and pore volume of the modified silica were found to be 433 $m^2\,g^{-1}$ and 0.53 $cm^3\,g^{-1}$, respectively.

Preparation of Silica-Supported Ionic Liquid

Under nitrogen, 1-mesityl-1H-imidazole (0.41 g, 5.0 mmol) and benzyl chloride functionalized silica (2.0 g) were mixed in toluene (15 mL) in a round-bottom flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered, and the solid was washed with chloroform, methanol, and ethyl acetate and dried under vacuum at 60 °C to yield a silica-supported ionic liquid (pale powder, 2.08 g). The loading of the silica-supported ionic liquid was quantified by CHN microanalysis

and found to be 0.96 mmol g^{-1} based on nitrogen content. The surface area and pore volume of the silica-supported ionic liquid were found to be 308 m^2 g^{-1} and 0.43 cm^3 g^{-1}, respectively. ^{29}Si NMR (solid): $\delta = -79.4$ (br., SiC), -111.5 (br., SiO_2) ppm.

Preparation of SiO_2-NHC-Cu^I Catalyst

In an oven-dried Schlenk flask, freshly prepared CuI (0.190 g, 1.0 mmol), *t*-BuONa (0.096 g, 1.0 mmol), silica-supported ionic liquid (1.0 g), and THF (5 mL) were added. The resulting suspension was stirred at room temperature under nitrogen for 6 h. Then the solution was filtered, and the solid was washed with water, methanol, and acetone and dried under vacuum at 60 °C for 12 h. The SiO_2-NHC-Cu^I catalyst was obtained as a gray-green powder (1.14 g). The copper content of the catalyst was found to be 0.86 mmol g^{-1} based on AAS analysis. The surface area and pore volume of SiO_2-NHC-Cu^I were found to be 275 m^2 g^{-1} and 0.38 cm^3 g^{-1}, respectively. ^{29}Si NMR (solid): $\delta = -78.7$ (br., SiC), -111.5 (br., SiO_2) ppm.

General Procedure for *N*-Arylation of Imidazoles with Arylboronic Acid

An oven-dried, round-bottomed flask was charged with SiO_2-NHC-Cu^I (0.05 mmol), imidazole (1.1 mmol), arylboronic acid (1.0 mmol), and CH_3OH (3 mL). The mixture was stirred at 50 °C for 3 h under an atmosphere of air. The progress of the reaction was monitored by TLC. On completion of the reaction, the mixture was filtered. The solution was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane–EtOAc, 70:30) to afford the corresponding pure *N*-arylated imidazole.

Selected Data

1-Phenyl-1*H*-imidazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.45–7.41 (m, 2H), 7.34–7.30 (m, 3H), 7.23 (br s, 1H), 7.17 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 135.3, 130.1, 129.7, 127.3, 121.3, 118.1.

1-(4-Methoxyphenyl)-1*H*-imidazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (s, 1H), 7.28–7.24 (m, 2H), 7.19–7.15 (m, 2H), 6.97–6.92 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 135.5, 130.5, 129.9, 122.9, 118.6, 114.6, 55.3.

1-(4-Methylphenyl)-1*H*-imidazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (s, 1H), 7.25–7.24 (m, 5H), 7.18 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 135.4, 134.8, 131.9, 130.1, 121.2, 118.1, 20.7.

1-(4-*tert*-Buthylphenyl)-1*H*-imidazole[16]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 7.19 (s, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 135.4, 134.6, 130.0, 126.5, 120.9, 118.0, 34.4, 31.0.

1-(4-Chlorophenyl)-1*H*-imidazole[17]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.65 (s, 1H), 7.42 (s, 1H), 7.34 (s, 1H), 7.31 (s, 1H), 7.25 (s, 1H), 7.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.7, 135.3, 132.9, 130.5, 129.8, 122.4, 117.9.

1-(4-Fluorophenyl)-1*H*-imidazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 1H), 7.31– 7.27 (m, 2H), 7.16 (s, 1H), 7.12–7.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.7, 160.2, 135.5, 133.4, 130.2, 123.3, 123.2, 118.4, 116.6, 116.4.

1-(4-(Trifluoromethyl)phenyl)-1*H*-imidazole[18]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.75–7.71 (m, 2H), 7.54–7.50 (m, 2H), 7.36 (s, 1H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 135.1, 130.7, 129.4, 129.1, 128.8, 128.4, 127.4, 126.9, 126.8, 124.7, 122.0, 120.8, 119.3, 117.5.

1-(3-Methylphenyl)-1*H*-imidazole[19]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.35–7.31 (m, 1H), 7.25 (s, 1H), 7.18–7.17 (m, 3H), 7.15 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8, 137.1, 135.3, 130.0, 129.4, 128.0, 121.9, 118.3, 118.0, 21.2.

1-(2-Methylphenyl)-1*H*-imidazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.55–7.32 (m, 2H), 7.30–7.26 (m, 1H), 7.21–7.19 (m, 2H), 7.04 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 136.3, 133.5, 131.0, 129.0, 128.5, 126.6, 120.2, 17.3.

1-(3-Methoxyphenyl)-1*H*-imidazole[19]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.36–7.34 (m, 1H), 7.26 (s, 1H), 7.18 (s, 1H), 6.96–6.93 (m, 1H), 6.91–6.87 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5, 138.2, 135.4, 130.5, 130.1, 118.0, 113.4, 112.4, 107.5, 55.3.

1-(4-Methoxycarbonylphenyl)-1*H*-imidazole[20]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17–8.13 (m, 2H), 7.97 (s, 1H), 7.49–7.46 (m, 2H), 7.37 (s, 1H), 7.24 (s, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 140.5, 135.2, 131.3, 130.8, 128.8, 120.3, 117.6, 52.1.

1-Biphenyl-1*H*-imidazole[21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (s, 1H), 7.62–7.60 (m, 2H), 7.56–7.53 (m, 2H), 7.43–7.39 (m, 2H), 7.38–7.35 (m, 3H), 7.26 (s, 1H), 7.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.0, 139.4, 136.1, 135.2, 130.2, 128.7, 128.2, 127.5, 126.7, 121.3, 117.8.

1-(Naphthalen-1-yl)-1*H*-imidazole[22]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.92–7.87 (m, 1H), 7.85–7.82 (m, 2H), 7.78–7.77 (m, 1H), 7.57–7.47 (m, 3H), 7.38 (s, 1H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.6, 133.4, 132.1, 130.5, 129.9, 127.8, 127.7, 127.3, 126.4, 120.1, 118.9, 118.3.

1-(Naphthalen-2-yl)-1*H*-imidazole[22]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.85–7.82 (m, 1H), 7.83–7.78 (m, 2H), 7.71 (s, 1H), 7.53–7.45 (m, 2H), 7.43–7.40 (m, 1H), 7.33 (s, 1H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.5, 134.3, 133.2, 131.8, 130.2, 129.7, 127.6, 127.5, 127.1, 126.2, 119.8, 118.6, 118.1.

2-(1*H*-Imidazol-1-yl)benzaldehyde[23]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 8.01–7.99 (m, 1H), 7.72–7.68 (m, 2H), 7.59–7.55 (m, 1H), 7.40–7.38 (m, 1H), 7.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.3, 139.2, 138.2, 134.9, 130.8, 130.2, 129.1, 128.9, 126.8, 121.8.

1-Phenyl-1*H*-pyrazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90–7.88 (m, 1H), 7.72–7.67 (m, 3H), 7.43–7.40 (m, 2H), 7.27–7.23 (m, 1H), 6.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 139.4, 129.3, 126.7, 126.4, 119.2, 107.5.

1-Phenyl-1*H*-benzimidazole[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22–8.19 (m, 4H), 7.56–7.55 (m, 2H), 7.50–7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.8, 142.0, 135.6, 132.6, 130, 127.9, 124, 123.5, 122.8, 120.6, 110.5.

2-Phenyl-iso-indoline-1,3-dione[24]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88–7.85 (m, 4H), 7.43–7.41 (m, 4H), 7.17–7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 132.5, 132.0, 131.8, 128.7, 127.9, 127.8, 123.5.

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