# Ligand-Free Copper-Catalyzed Arylation of Imidazole and *N,N′*-Carbonyldiimidazole, and Microwave-Assisted Synthesis of *N*-Aryl-1*H*-imidazoles

by **Xiao-Dong Yang**, **Liang Li**, and **Hong-Bin Zhang***

Key Laboratory of Medicinal Chemistry for Natural Resource (Yunnan University), Ministry of Education, School of Chemical Science and Technology, Yunnan University, Kunming, Yunnan 650091, P. R. China

(phone: +86-871-5031119; fax: +86-871-5035538; e-mail: zhanghb@yun.edu.cn or zhanghbyd@gmail.com)

Microwave-assisted arylation of 1*H*-imidazoles and *N,N′*-carbonyldiimidazole under ligand-free copper-mediated conditions in tetraethyl orthosilicate is reported. Valuable evidence for understanding of the Cu-catalyzed mechanism of the *Ullmann* reaction is also presented.

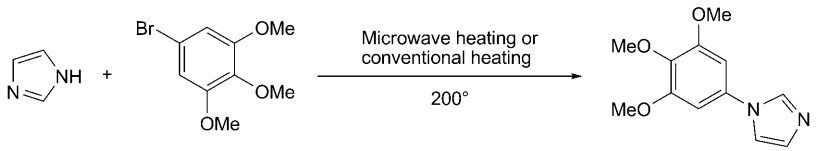
**Introduction.** – *N*-Arylimidazoles are important substructures present in natural products, synthetic materials, and pharmaceuticals [1]. They are also frequently used as building blocks for a broad array of imidazolium salts used as precursors to imidazolylidenes, a new family of ligands for homogeneous catalysis[1]). Traditionally, *N*-arylimidazoles have been obtained by nucleophilic aromatic substitution of a strongly electron-withdrawing activated aryl halide [3] or by conventional stoichiometric copper-promoted coupling of imidazole with an aryl iodide [4]. High temperatures and long periods of time are generally required for a better yield. Because catalyzed arylation of imidazoles with transition metals is an attractive way to access *N*-arylimidazoles, many new methods featured by addition of a promoting ligand, such as 4,7-dimethoxy-1,10-phenanthroline [5c] or L-proline [5i][5l], which is thought to increase catalyst solubility and stability, and to prevent aggregation of the metal [5q], have been developed, and the synthesis of *N*-arylimidazoles remains a focus of recent interests [5]. In most cases, however, considerable amount of ligands and long periods of time were required. In our previous work, we had developed a method for the synthesis of *N*-arylimidazoles [6]. Although this method provides a practical access to the highly sterically hindered *N*-arylimidazoles, unfortunately, it failed to afford acceptable yields for the highly electron-rich *N*-arylimidazoles, which are believed to be important building blocks for organic functional materials such as liquid crystals and fluorescent materials [7].

**Results and Discussion.** – In order to obtain highly electron-rich *N*-arylimidazoles, we recently initiated a research project towards the arylation of imidazoles. After a careful survey of the literature, microwave-assisted arylation of imidazoles has

[1]) For reviews of NHC-carbene, see [2].

attracted our attention, although only electron-deficient [3][8] or electron-neutral [9] arylbromides and aryliodides being used in the literature. We assumed that the microwave heating should reduce the reaction time and provide good access to the highly electron-rich *N*-arylimidazoles. The reaction conditions reported by *Wu et al.* [9] were thus tested for the synthesis of electron-rich 1-(3,4,5-trimethoxyphenyl)-1*H*-imidazole, as indicated in *Scheme 1*. Unfortunately, the reaction in *N*-methylpyrrolidine (NMP) under microwave irradiation provided an unacceptable low yield of the desired product, even in the presence of 20% of CuI (see *Scheme 1*, *Methods A* and *B*). Having failed to copy the literature procedure, we decided to carry out a copper(I)iodide catalyzed arylation of imidazole in tetraethyl orthosilicate, a solvent which has recently been identified by us as a beneficial medium for the high-temperature *Ullmann* aminations [10].

Scheme 1. *Attempts Towards the Synthesis of 1-(3,4,5-Trimethoxyphenyl)-1*H*-imidazole*



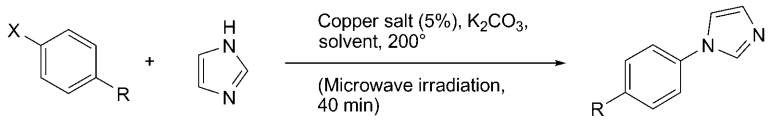

*Methods A* and *B*: Imidazole 2.0 mmol, arylbromide 1.0 mmol
*Method C*: Imidazole 1.0 mmol, arylbromide 1.0 mmol
*Method D*: Imidazole 10.0 mmol, arylbromide 10.0 mmol

*A*: CuI (0.1 mmol), $K_2CO_3$ (2.0 mmol), NMP (2 ml); Microwave irradiation, 40 min, Yield: 15%
*B*: CuI (0.2 mmol), $K_2CO_3$ (2.0 mmol), NMP (2 ml); Microwave irradiation, 40 min, Yield: 25%
*C*: CuI (0.2 mmol), $K_2CO_3$ (2.0 mmol), $(EtO)_4Si$ (2 ml); Microwave irradiation, 40 min, Yield: 50%
*D*: CuI (2.0 mmol), $K_2CO_3$ (20.0 mmol), $(EtO)_4Si$ (20 ml); High-pressure (1 MPa), 4 h, Yield: 24%

Initially, the reaction was conducted at a temperature of 145° under microwave irradiation conditions, but no desired product was detected. However, when the temperature was increased to 180°, the arylation of 1*H*-imidazole was observed. A good yield was obtained when the temperature was switched to 200° (*Scheme 1*, *Method C*). The same coupling could also be carried out in a high-pressure autoclave in the presence of CuI (*Scheme 1*, *Method D*). These results indicated that the temperature still plays a crucial role in this arylation, and the microwave heating can accelerate the coupling reaction. Next, we carried out a number of reactions in order to get further insight towards this arylation reaction (*Table 1*).

We found that the copper catalyzed arylation of 1*H*-imidazole with 4-bromoanisole under microwave conditions leads to the desired product in an excellent yield, even in the presence of only 5% CuI. Both, $Cu(OAc)_2$ and copper(II)acetylacetonate could also be used as active catalysts, however, they were less efficient than CuI. Tetraethyl orthosilicate remained the solvent of choice, not only for better yields, but also for its easy handling in product purifications. Although our method was the first reported procedure for ligand-free arylation of imidazole with aryl chlorides in the presence of CuI under microwave irradiation, the yields were lower than those with aryl bromides and aryl iodides (see *Table 1*). A number of arylimidazoles were then synthesized, and the results are shown in *Table 2*.

Table 1. *Studies on Copper Catalyzed Arylation of Imidazole*[a])




X = Cl, Br, I R = OMe, Acetyl

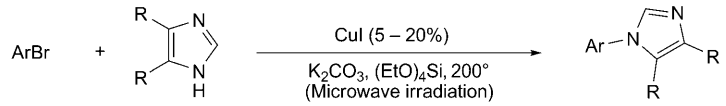
| *Entry* | Copper | Solvents | Aryl halides | R | X | Yield [%] |
|---|---|---|---|---|---|---|
| *1* | CuI | $(EtO)_4Si$ | 4-iodoanisole | MeO | I | 89 |
| *2* | CuI | $(EtO)_4Si$ | 4-bromoanisole | MeO | Br | 80 |
| *3* | CuI | $(EtO)_4Si$ | 4-chloroanisole | MeO | Cl | 15 |
| *4* | CuI | $(EtO)_4Si$ | 4-bromoacetophenone | MeCO | Br | 78 |
| *5* | CuI | $(EtO)_4Si$ | 4-chloroacetophenone | MeCO | Cl | 28 |
| *6* | $Cu(OAc)_2$ | $(EtO)_4Si$ | 4-bromoanisole | MeO | Br | 65[b]) |
| *7* | $Cu(Acac)_2$ | $(EtO)_4Si$ | 4-bromoanisole | MeO | Br | 72[b]) |
| *8* | CuI | *p*-xylene | 4-bromoanisole | MeO | Br | 70 |
| *9* | CuI | DMF | 4-bromoanisole | MeO | Br | 37 |
| *10* | CuI | DMSO | 4-bromoanisole | MeO | Br | 35 |

[a]) Reaction conditions: aryl halide (1.2 mmol), CuI (9.5 mg, 5 mol-%), imidazole (1 mmol), and $K_2CO_3$ (276 mg, 2 mmol) in commercially available organic solvent (2 ml) were subjected to microwave irradiation at 200° (CEM Discover) for 40 min. [b]) Reactions were carried out under identical conditions, but with $Cu(OAc)_2$ or $Cu(Acac)_2$ (5 mol-%).

Although the *Ullmann* reaction has been studied for more than one century, its mechanism has not been well-established [11]. To get some insight into the mechanism, we decided to use *N,N′*-carbonyldiimidazole (CDI; 0.5 mmol, 0.5 equiv.), which is not nucleophilic, as a source of imidazole to see whether an arylation could take place. To our surprise, the arylation with 4-bromoanisole (1.2 mmol, 1.2 equiv.) under the conditions described above occurred and led to arylimidazole in excellent yield (85% yield after isolation, see *Table 3*). This coupling, to the best of our knowledge, represents the first example of copper catalyzed arylation of *N,N′*-carbonyldiimidazole with both imidazole subunits in CDI (0.5 mmol amount of CDI equals to 1.0 mmol amount of imidazole) being utilized.

In the absence of Cu salts, however, identical microwave irradiation provided mainly 4-bromoanisole and CDI, no significant hydrolysis of CDI was observed by TLC analysis. When the reaction was carried out with stoichiometric amounts of CuI (1 mmol), CDI (0.5 mmol), and $K_2CO_3$ (2 mmol) in the absence of 4-bromoanisole, a grey-blue colored mixture was obtained. This mixture was subjected to TLC analysis, and only a trace of CDI was detected. Addition of 4-bromoanisole to this blue-colored mixture followed by heating under microwave irradiation (200°) led to 1-(4-methoxyphenyl)-1*H*-imidazole, although in relatively low yield (30–45%). We also carried out a control reaction with a stoichiometric amount of CuI (1 mmol), imidazole (1 mmol), and $K_2CO_3$ (2 mmol) in the absence of 4-bromoanisole. A grey-blue colored mixture was also formed after heating under microwave irradiation (200°) for 20 min, and only a trace of imidazole was detected by TLC analysis. Addition of 4-

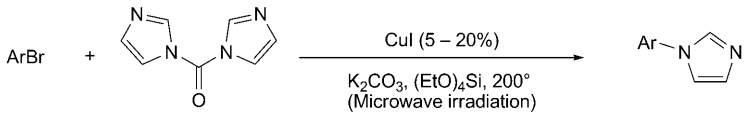
Table 2. *CuI-Catalyzed Synthesis of Arylimidazoles in Tetraethyl Orthosilicate Assisted by Microwave Irradiation*[a])




| *Entry* | Ar | R | Yield [%] |
|---|---|---|---|
| *1* | 3,4,5-trimethoxyphenyl | H | 53[b]) |
| *2* | 4-phenylphenyl | H | 94 |
| *3* | 4-*tert*-butylphenyl | H | 36; 71[b]) |
| *4* | pyridin-2-yl | H | 83 |
| *5* | 4-nitrophenyl | H | 85 |
| *6* | 2,4-dimethoxyphenyl | H | 57[b])[c]) |
| *7* | 4-methoxy-2-methylphenyl | H | 48[b])[c]) |
| *8* | 4-(*N*,*N*-dimethylamino)phenyl | H | 90 |
| *9* | phenanthren-9-yl | H | 40[b])[c]) |
| *10* | anthracen-9-yl | H | 18[b])[c]) |
| *11* | phenyl | H | 88 |
| *12* | 4-phenylphenyl | Ph | 91 |
| *13* | 4-acetylphenyl | H | 78[b]) |

[a]) Reagents and conditions: Aryl bromides (1.2 mmol), CuI (9.5 mg, 0.05 mmol), imidazole (1 mmol), and $K_2CO_3$ (276 mg, 2 mmol) in commercially available tetraethyl orthosilicate (2 ml) were subjected to microwave irradiation at 200° (CEM Discover) for 40 min. [b]) Reactions were carried out under identical conditions, but with 20% of CuI (38 mg, 0.2 mmol). The indicated yields represent the yields of isolated products. [c]) The low yields were due to steric hindrance.

Table 3. *Arylation of N,N′-Carbonyldiimidazole* (CDI)[a])



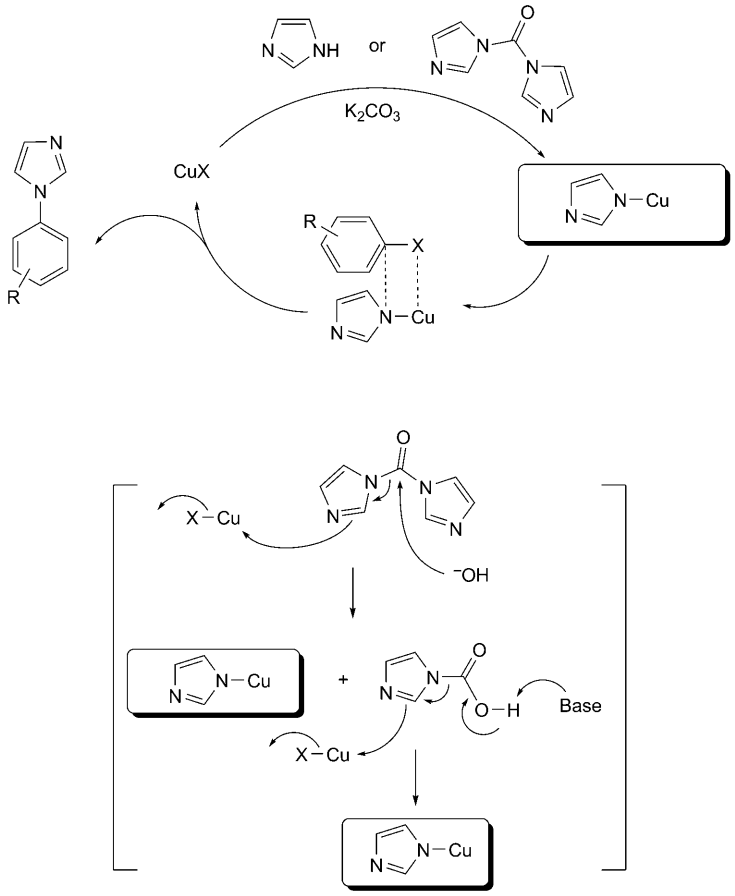

| *Entry* | Ar | Yield [%] |
|---|---|---|
| *1* | 4-methoxyphenyl | 85 |
| *2* | 3,4,5-trimethoxyphenyl | 51[b]) |
| *3* | 4-phenylphenyl | 90 |
| *4* | pyridin-2-yl | 87 |
| *5* | 2,4-dimethoxyphenyl | 59 |
| *6* | phenanthren-9-yl | 41[b])[c]) |
| *7* | anthracen-9-yl | 18[b])[c]) |

[a]) Reagents and conditions: Aryl bromides (1.2 mmol), CuI (9.5 mg, 0.05 mmol), CDI (0.5 mmol), and $K_2CO_3$ (276 mg, 2 mmol) in commercially available tetraethyl orthosilicate (2 ml) were subjected to microwave irradiation at 200° (CEM Discover) for 40 min. [b]) Reactions were conducted under identical reaction conditions, but with 20% of CuI (38 mg, 0.2 mmol). The indicated yields represent the yields of isolated products. [c]) The low yields were due to steric hindrance.

bromoanisole to this blue-colored mixture followed by heating under microwave irradiation (200°) also led to 1-(4-methoxyphenyl)-1*H*-imidazole in fair yield (65%).

To date, four main mechanisms for *Ullmann*-type coupling reactions have been described in the literature: *1*) oxidative addition/reductive elimination of ArX on copper(I) proposed by *Cohen* in 1974 [12]; *2*) $\pi$-complexation of ArX on copper(I) proposed by *Paine* in 1987 [13]; *3*) *Lewis*-type complexation of ArX on copper(I) [11]; and *4*) aryl-radical intermediates [4][14]. The results observed in this work are in favor of *Paine*'s proposal. The initial step in the catalytic cycle might be the formation of a copper-imidazole complex (a grey-blue colored mixture). It would be less likely that an oxidative addition of an arylbromide towards the copper(I)iodide occurred first. The possible pathway is shown in *Scheme 2*.

Scheme 2. *Proposed Pathway for the Arylation of Imidazole and CDI*




**Conclusions.** – In summary, a microwave-assisted synthesis of *N*-arylimidazoles by a ligand-free copper-catalyzed *Ullmann* reaction was disclosed. Although trends have been directed toward the discovery of efficient ligands (in most cases, a 10–20%

amount of ligand is required [5], in an extreme case, a 60% amount of ligand is used to ensure a good yield [5i]) for palladium or copper catalyzed arylation of imidazoles, the ligand-free copper catalyzed *Ullmann* process is still attractive in view of industrial application. The arylation results obtained with CDI, as well as imidazole in this research also reveal some interesting evidence towards the mechanism of the copper catalyzed *Ullmann* reaction.

This work was supported by a grant (706052) from the *Foundation of the Chinese Ministry of Education for Fostering Important Scientific Program* and a grant (2007B0006Z) from the *Natural Science Foundation of Yunnan Province*, which are gratefully acknowledged.

## Experimental Part

*General.* Starting materials and reagents used in the reactions were obtained commercially from *Acros*, *Aldrich*, and *Fluka*, and were used without purification, unless otherwise indicated. M.p.: *XT-4* melting-point apparatus, uncorrected. NMR Spectra: *Bruker-Avance-300* instrument; TMS as internal reference, $\delta$ in ppm, $J$ in Hz. EI-MS: *VG Autospec-3000* mass spectrometer; in $m/z$ (rel. %).

*General Procedure for the Synthesis of* N-*Aryl-1*H-*imidazoles.* A mixture of CuI (9.5–38 mg, 0.05–0.2 mmol), $K_2CO_3$ (276 mg, 2 mmol, 2.0 equiv.), *N,N′*-carbonyldiimidazole or imidazoles (0.5 mmol or 1 mmol), and aryl halides (1.2 mmol) in tetraethyl orthosilicate (2 ml) was put in a vial (*CEM Discover*). The sealed vial was then heated at 200° under microwave irradiation (*CEM Discover*) for 40 min. After cooling to r.t., the residue was diluted with AcOEt (3 ml) and 95% EtOH (3 ml). $NH_4F/H_2O$ on $SiO_2$ (2 g, pre-prepared by addition of $NH_4F$ (10 g) in $H_2O$ (150 ml) to $SiO_2$ (50 g, 100–200 mesh)) was added, and the resulting mixture was kept at r.t. for 3–5 h. The solidified materials were filtered and washed with AcOEt. After removal of the solvents, the residue was chromatographed on $SiO_2$ (AcOEt/petroleum ether) to afford the products.

*1-(3,4,5-Trimethoxyphenyl)-1*H-*imidazole* [7]. Colorless oil. $^1$H-NMR (300 MHz, $CDCl_3$): 7.72 (*s*, 1 H); 7.16 (*s*, 1 H); 7.10 (*s*, 1 H); 6.51 (*s*, 2 H); 3.83 (*s*, 6 H); 3.79 (*s*, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 153.52; 137.12; 135.39; 132.88; 129.62; 118.29; 99.42; 60.47; 55.88.

*1-(Biphenyl-4-yl)-1*H-*imidazole* [5l]. White solid. M.p. 150–152°. $^1$H-NMR: 7.93 (*s*, 1 H); 7.71 (*d*, $J$ = 8.5, 2 H); 7.63 (*dd*, $J$ = 7.8, 1.3, 2 H); 7.47–7.52 (*m*, 4 H); 7.42 (*d*, $J$ = 7.4, 1 H); 7.34 (*s*, 1 H); 7.26 (*s*, 1 H). $^{13}$C-NMR: 139.62; 138.75; 135.50; 134.63; 129.47; 127.96; 127.51; 126.80; 126.01; 120.77; 117.24.

*1-[4-*tert-*Butylphenyl]-1*H-*imidazole* [15]. White solid. M.p. 78–80°. $^1$H-NMR: 7.76 (*s*, 1 H); 7.42 (*d*, $J$ = 8.7, 2 H); 7.24 (*d*, $J$ = 8.7, 2 H); 7.19 (*s*, 1 H); 7.12 (*s*, 1 H); 1.28 (*s*, 9 H). $^{13}$C-NMR: (75 MHz, $CDCl_3$): 150.76; 135.65; 134.94; 130.23; 126.70; 121.24; 118.33; 34.63; 33.28.

*2-(1*H-*Imidazol-1-yl)pyridine* [5l]. Colorless solid. M.p. 38–40°. $^1$H-NMR: 8.33 (*d*, $J$ = 4.0, 1 H); 8.25 (*s*, 1 H); 7.64–7.70 (*m*, 1 H); 7.53 (*s*, 1 H); 7.22 (*d*, $J$ = 8.2, 1 H); 7.07–7.11 (*m*, 2 H). $^{13}$C-NMR: (75 MHz, $CDCl_3$): 148.49; 138.43; 134.37; 130.03; 121.42; 115.58; 111.71.

*1-(4-Nitrophenyl)-1*H-*imidazole* [7]. Yellow solid. M.p. 177–178°. $^1$H-NMR: 8.38 (*d*, $J$ = 9.1, 2 H); 8.00 (*s*, 1 H); 7.60 (*d*, $J$ = 9.1, 2 H); 7.40 (*s*, 1 H); 7.29 (*s*, 1 H). $^{13}$C-NMR: 146.30; 142.00; 135.41; 131.75; 125.75; 121.05; 117.63.

*1-(2,4-Dimethoxyphenyl)-1*H-*imidazole* [5l]. Pale yellow oil. $^1$H-NMR: 7.66 (*s*, 1 H); 7.17 (*s*, 1 H); 7.15 (*s*, 1 H); 7.11 (*d*, $J$ = 8.5, 1 H); 6.57 (*d*, $J$ = 2.5, 1 H); 6.51 (*dd*, $J$ = 8.5, 2.5, 1 H); 3.83 (*s*, 3 H); 3.79 (*s*, 3 H). $^{13}$C-NMR: 160.39; 153.97; 138.00; 128.64; 126.48; 120.64; 120.06; 104.45; 99.83; 55.79; 55.63.

*1-(4-Methoxy-2-methylphenyl)-1*H-*imidazole.* Colorless oil. $^1$H-NMR: 7.52 (*s*, 1 H); 7.16 (*s*, 1 H); 7.13 (*d*, $J$ = 8.5, 1 H); 6.99 (*s*, 1 H); 6.82 (*d*, $J$ = 2.5, 1 H); 6.78 (*dd*, $J$ = 8.5, 2.5, 1 H); 3.82 (*s*, 3 H); 2.11 (*s*, 3 H). $^{13}$C-NMR: 159.64; 137.83; 135.55; 129.71; 129.19; 127.71; 120.84; 116.21; 111.83; 55.50; 17.72. ESI-MS: 189 (12, $[M+1]^+$), 188 (100, $M^+$), 187 (7), 174 (70), 161 (36), 147 (37), 146 (60), 134 (10), 118 (12), 91 (11), 77 (10). HR-ESI-MS: 189.1032 ($[M+1]^+$, $C_{11}H_{13}N_2O^+$; calc. 189.1027).

*4-(1*H-*Imidazol-1-yl)-*N,N-*dimethylaniline* [16]. Colorless solid. M.p. 109–110°. $^1$H-NMR: 7.32 (*s*, 1 H); 7.22 (*d*, $J$ = 8.9, 2 H); 7.17 (*s*, 2 H); 6.75 (*d*, $J$ = 8.9, 2 H); 2.99 (*s*, 6 H). $^{13}$C-NMR: (75 MHz, $CDCl_3$): 149.96; 135.98; 129.69; 127.03; 123.05; 118.92; 112.78; 40.54.

*1-(Phenanthren-9-yl)-1*H-*imidazole*. Pale yellow solid. M.p. 97–99°. $^1$H-NMR: 8.78 (*d*, *J* = 8.4, 1 H); 8.73 (*d*, *J* = 8.4, 1 H); 7.92 (*d*, *J* = 7.8, 1 H); 7.82 (*s*, 1 H); 7.67–7.77 (*m*, 4 H); 7.59–7.62 (*m*, 2 H); 7.32 (*d*, *J* = 9.6, 2 H). $^{13}$C-NMR: 138.54; 132.75; 131.20; 130.71; 130.31; 129.65; 128.93; 128.71; 127.88; 127.75; 127.66; 127.54; 124.59; 123.22; 123.13; 122.81; 121.75. ESI-MS: 245 (19, $[M+1]^+$), 244 (100, $M^+$), 243 (37), 217 (38), 204 (20), 189 (26), 176 (29), 165 (5), 151 (8), 135 (5), 122 (12), 107 (8), 94 (13), 88 (9). HR-ESI-MS: 245.1074 ($[M+1]^+$, $C_{17}H_{13}N_2^+$; calc. 245.1078).

*1-(Anthracen-9-yl)-1*H-*imidazole*. Yellow solid. M.p. 154–156°. $^1$H-NMR: 8.60 (*s*, 1 H); 8.08 (*d*, *J* = 8.2, 2 H); 7.79 (*s*, 1 H); 7.47–7.54 (*m*, 7 H); 7.26 (*dd*, *J* = 6.2, 1.2, 1 H). $^{13}$C-NMR: 139.66; 131.27; 129.73; 128.83; 128.47; 128.36; 127.58; 125.90; 122.76; 122.43. ESI-MS: 245 (19, $[M+1]^+$), 244 (100, $M^+$), 243 (44), 216 (48), 204 (15), 189 (17), 176 (25), 163 (3), 149 (6), 122 (14), 107 (18), 94 (12), 88 (9). HR-ESI-MS: 245.1085 ($[M+1]^+$, $C_{17}H_{13}N_2^+$; calc. 245.1078).

*1-Phenyl-1*H-*imidazole* [15]. Colorless solid. M.p. 53–55°. $^1$H-NMR: 7.79 (*s*, 1 H); 7.40 (*t*, *J* = 8.5, 2 H); 7.26–7.32 (*m*, 3 H); 7.21 (*s*, 1 H); 7.14 (*s*, 1 H). $^{13}$C-NMR: 137.33; 135.52; 130.35; 129.82; 127.41; 121.39; 118.16.

*1-(Biphenyl-4-yl)-1*H-*benzimidazole* [17]. Colorless solid. M.p. 188–190°. $^1$H-NMR: 8.16 (*s*, 1 H); 7.89–7.92 (*m*, 1 H); 7.79 (*d*, *J* = 8.5, 2 H); 7.65 (*d*, *J* = 7.9, 2 H); 7.58–7.61 (*m*, 3 H); 7.48–7.53 (*m*, 2 H); 7.42–7.44 (*m*, 1 H); 7.35–7.38 (*m*, 2 H). $^{13}$C-NMR: 144.18; 14.24; 141.11; 139.82; 129.01; 128.68; 127.89; 127.12; 124.31; 123.74; 122.83; 120.70; 110.50. ESI-MS: 271 (25, $[M+1]^+$), 270 (100, $M^+$), 269 (32), 241 (4), 165 (5), 152 (10), 135 (5), 121 (8), 109 (3), 77 (2). ESI-HR-MS: 271.1240 ($[M+1]^+$, $C_{19}H_{15}N_2^+$; calc. 271.1235).

*1-[4-(1*H-*Imidazol-1-yl)phenyl]ethanone* [7]. White solid. M.p. 110–111°. $^1$H-NMR: 8.07 (*d*, *J* = 8.7, 2 H); 7.93 (*s*, 1 H); 7.48 (*d*, *J* = 8.7, 2 H); 7.34 (*s*, 1 H); 7.23 (*s*, 1 H); 2.62 (*s*, 3 H). $^{13}$C-NMR: 196.43; 140.74; 135.81; 135.37; 131.17; 130.30; 120.70; 117.68; 26.55.

*1-(4-Methoxyphenyl)-1*H-*imidazole* [7]. White solid. M.p. 60–61°. $^1$H-NMR: 7.68 (*s*, 1 H); 7.21 (*d*, *J* = 8.8, 2 H); 7.12 (*s*, 1 H); 7.10 (*s*, 1 H); 6.90 (*d*, *J* = 8.8, 2 H); 3.75 (*s*, 3 H). $^{13}$C-NMR: 158.87; 135.76; 130.65; 130.00; 123.07; 118.66; 114.86; 55.52.

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*Received January 29, 2008*