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Regioselective *N*-Alkylation of 2-Aminoimidazoles with Alcohols to 2-(*N*-Alkylamino)imidazoles Catalyzed by the $[Cp^*IrCl_2]_2/K_2CO_3$ System

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Keywords: Synthetic methods / Homogeneous catalysis / Iridium / Regioselectivity / Hydrogen transfer / Nitrogen heterocycles

The direct *N*-alkylation of 2-aminoimidazoles to give the corresponding 2-(*N*-alkylamino)imidazoles was accomplished using alcohols as alkylating agents in the presence of a $[Cp^*IrCl_2]_2/K_2CO_3$ system. The iridium-catalyzed regioselective reaction is simple, efficient, general, and environmentally benign.

Introduction

2-Aminoimidazole derivatives are an important class of nitrogen-containing heterocyclic compounds. In particular, 2-(*N*-alkylamino)imidazoles display a wide range of biological activities.[1] Examples of the applications of this class of compounds include: as a human arginase 1 inhibitor (**A**),[1a] small conductance Ca^{2+}-activated K^+ (SK) channel inhibitors (NS8593 and NS11757; **B**),[1b] antiallergic antihistamines (Norastemizole and Astemizole; **C**),[1c] respiratory syncytial virus (RSV) inhibitors (JNJ-2408068; **D**),[1d–1e] metal-free artificial nucleases,[1f–1g] and nuclear Factor-kB activation inhibitors[1h] (Figure 1). The traditional method for the preparation of 2-(*N*-alkylamino)imidazoles was through S_NAr reactions of 2-haloimidazoles with alkylamines.[1–2]

This procedure requires the multistep synthesis of the starting materials, and suffers from harsh reaction conditions such as high temperature, high pressure, and microwave irradiation. Over the past few years, transition-metal-catalyzed methods have been developed for the preparation of 2-(*N*-alkylamino)imidazole derivatives. These include Pd-catalyzed amination of 2-halobenzimidazoles,[3] Pd- or Cu-catalyzed cyclization of *o*-halobenzoguanidines,[4] Cu-catalyzed coupling of dihalobenzenes with *N*-alkylguanidines,[5] and Cu-catalyzed cascade addition/cyclization of *o*-haloanilines and carbodiimides.[6] However, these procedures only allow the synthesis of benzo-fused 2-(*N*-alkylamino)imidazoles, so the scope of reaction was highly restricted. All of the procedures mentioned above produce a stoichiometric amount of the hydrogen halide as by-product, resulting in an environmental hazard.

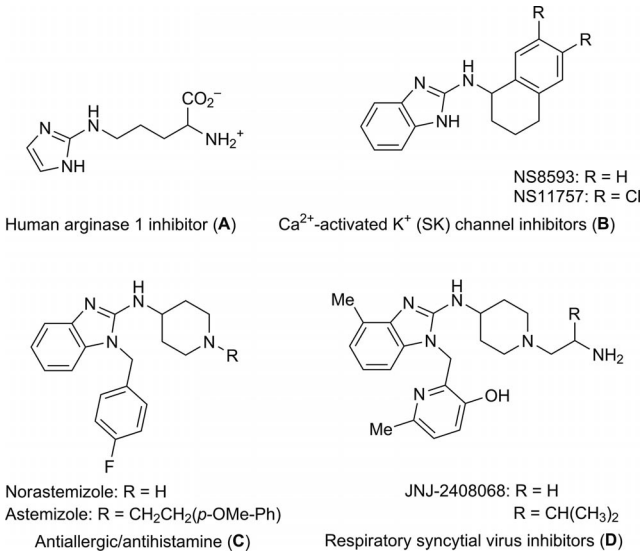

Figure 1. Biologically active 2-(*N*-alkylamino)imidazoles.

The direct *N*-alkylation of 2-aminoimidazoles provides what is apparently one of the most simple routes to 2-(*N*-alkylamino)imidazoles. However, when alkyl halides are used as alkylating agents, such reactions give the isomeric 3-alkyl-2-iminoazolines as products rather than 2-(*N*-alkylamino)imidazoles, due to the fact that the endocyclic nitrogens are more basic than the exocyclic ones[7] (Scheme 1, top line). Recently, much effort has been put into research into the *N*-alkylation of amines using alcohols as alkylating agents, based on the "hydrogen autotransfer" (or "hydrogen-borrowing") process,[8] using iridium,[9] ruthenium,[10] or other transition metal catalysts.[11] The methodology is attractive because of its high atom efficiency and the formation of water as the only by-product, and it has also been applied to the *N*-alkylation of (hetero)aromatic amines.[12] Very recently, we reported the preparation of 2-(*N*-alkylamino)thiazoles and 2-(*N*-alkylamino)oxazoles by direct

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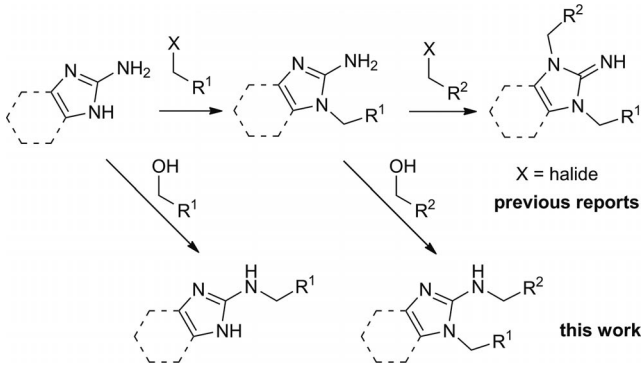
N-alkylation of the corresponding amines with primary alcohols, catalyzed by transition metal/base systems.[13,14]



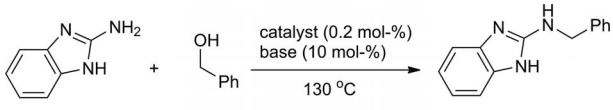
Scheme 1. Direct *N*-alkylation of 2-aminoimidazoles with alkyl halides and alcohols.

Realizing the unique potential influence on regioselectivities of alcohols as non-alkyl halide alkylating agents, and as part of our continuing interest in exploring regioselective *N*-alkylation reactions, in this paper, we wish to describe our efforts towards the iridium-catalyzed direct *N*-alkylation of 2-aminoimidazoles to give the corresponding 2-(*N*-alkylamino)imidazoles using alcohols as alkylating agents (Scheme 1, bottom line). A high reactivity was seen in the presence of a relatively weak base, and the reaction was effective not only for primary alcohols, but also for secondary alcohols.

Results and Discussion

In an initial experiment, the *N*-alkylation of 2-aminobenzimidazole (**1a**) with benzyl alcohol (**2a**) was chosen as a model reaction. The reaction was carried out in the presence of $[Cp^*IrCl_2]_2$ (Cp^* = pentamethylcyclopentadienyl) (0.2 mol-%) at 130 °C for 12 h to give the desired *N*-alkylated product (i.e., **3aa**) in 62% yield (Table 1, entry 1). As expected, the reaction was improved by the addition of a

Table 1. *N*-alkylation of 2-aminoimidazole (**1a**) with benzyl alcohol (**2a**) under various conditions.[a]

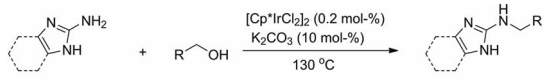


1a **2a** **3aa**

Entry	Catalyst	Base	Yield [%][b]
1	$[Cp^*IrCl_2]_2$	—	62
2	$[Cp^*IrCl_2]_2$	$NaHCO_3$	65
3	$[Cp^*IrCl_2]_2$	Li_2CO_3	72
4	$[Cp^*IrCl_2]_2$	Na_2CO_3	81
5	**$[Cp^*IrCl_2]_2$**	**K_2CO_3**	**96**
6	$[Cp^*IrCl_2]_2$	Cs_2CO_3	96
7	$[Ir(cod)Cl]_2$	K_2CO_3	91
8	$[Cp^*RhCl_2]_2$	K_2CO_3	93
9	—	K_2CO_3	0

[a] Reaction conditions: **1a** (1 mmol), **2a** (4 mmol), catalyst (0.2 mol-%), base (0.1 mmol), 130 °C, 12 h. [b] Isolated yields.

Table 2. *N*-alkylation of 2-aminoimidazoles **1** with various alcohols **2**.[a]

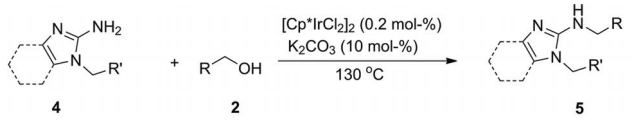


1 **2** **3**

Entry	2-Aminoimidazole	Alcohol	Product	Yield [%][b]
1	**1a**	**2b**	**3ab**	87
2	**1a**	**2c**	**3ac**	84
3	**1a**	**2d**	**3ad**	92
4	**1a**	**2e**	**3ae**	90
5	**1a**	**2f**	**3af**	87
6	**1a**	**2g**	**3ag**	95
7	**1a**	**2h**	**3ah**	81
8	**1a**	**2i**	**3ai**	78
9	**1a**	**2j**	**3aj**	84
10	**1a**	**2k**	**3ak**	87
11	**1a**	**2l**	**3al**	71[c]
12	**1b**	**2a**	**3ba**	95
13	**1b**	**2g**	**3bg**	85
14	**1c**	**2a**	**3ca**	84
15	**1d**	**2a**	**3da**	89

[a] Reaction conditions: amine (1 mmol), alcohol (4 mmol), $[Cp^*IrCl_2]_2$ (0.2 mol-%), K_2CO_3 (0.1 mmol), 130 °C, 12 h. [b] Isolated yields. [c] 150 °C.

Table 3. *N*-alkylation of 1-alkyl-2-aminoimidazoles **4** with various alcohols **2**.[a]



4 **2** **5**

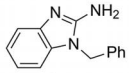
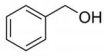
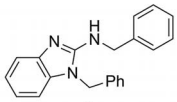
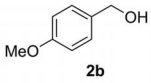
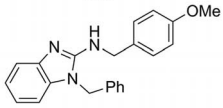
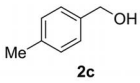
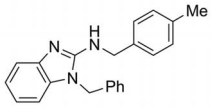
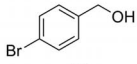
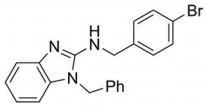
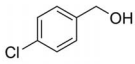
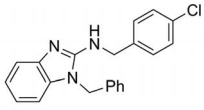
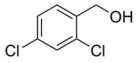
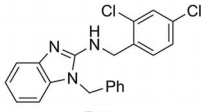
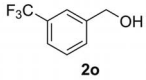
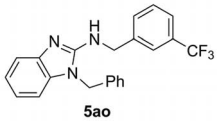
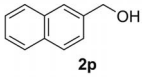
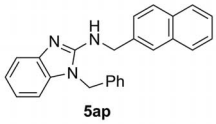
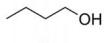
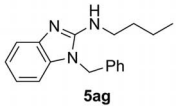
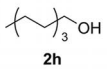
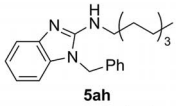
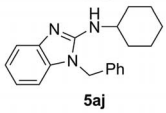
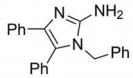
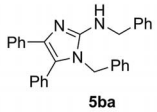
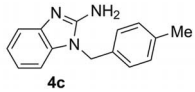
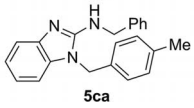
Entry	1-Alkyl-2-aminoimidazole	Alcohol	Product	Yield [%][b]
1	 **4a**	 **2a**	 **5aa**	87
2	**4a**	 **2b**	 **5ab**	82
3	**4a**	 **2c**	 **5ac**	84
4	**4a**	 **2e**	 **5ae**	88
5	**4a**	 **2m**	 **5am**	91
6	**4a**	 **2n**	 **5an**	82
7	**4a**	 **2o**	 **5ao**	83
8	4a	 **2p**	 **5ap**	78
9	**4a**	 **2g**	 **5ag**	87[c]
10	**4a**	 **2h**	 **5ah**	71[c]
11	**4a**	 **2j**	 **5aj**	68[c]
12	 **4b**	**2a**	 **5ba**	75[d]
13	 **4c**	**2a**	 **5ca**	86

Table 3. *(Continued)*

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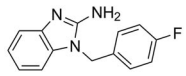
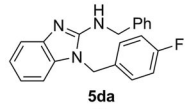
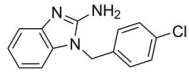
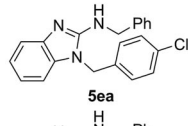
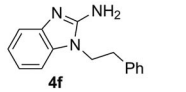
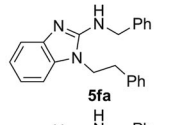
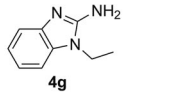
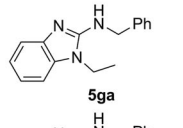
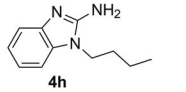
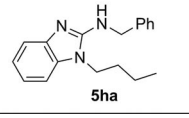
14	 **4d**	**2a**	 **5da**	82
15	 **4e**	**2a**	 **5ea**	85
16	 **4f**	**2a**	 **5fa**	90
17	 **4g**	**2a**	 **5ga**	81
18	 **4h**	**2a**	 **5ha**	80

[a] Reaction conditions: amine (1 mmol), alcohol (4 mmol), $[Cp^*IrCl_2]_2$ (0.2 mol-%), K_2CO_3 (0.1 mmol), 130 °C, 12 h. [b] Isolated yields. [c] K_2CO_3 (1 mmol). [d] 150 °C.

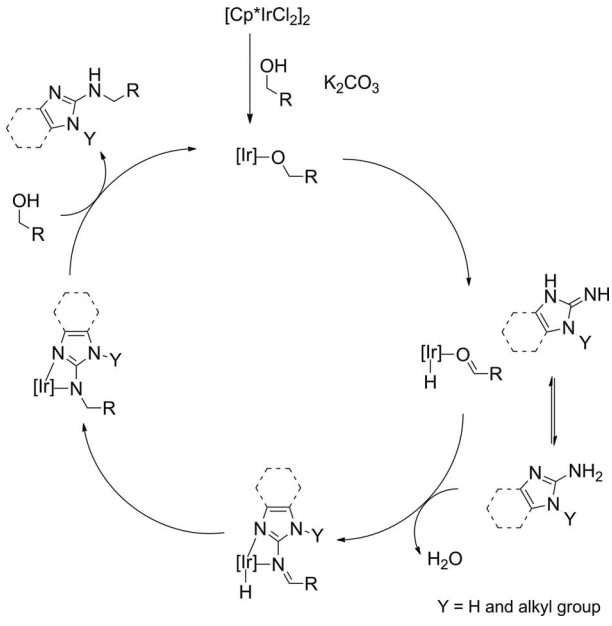
base (10 mol-%) (Table 1, entries 2–6). Product **3aa** could be obtained in 96% yield when K_2CO_3 or Cs_2CO_3 was used as a base (Table 1, entries 5–6). When $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadienyl) or $[Cp^*RhCl_2]_2$ were used as alternative catalysts in the presence of K_2CO_3, the reactions gave **3aa** in 91 and 93% yields, respectively (Table 1, entries 7–8). We also found that no reaction occurred in the presence of K_2CO_3 alone (Table 1, entry 9).

Under the optimal conditions (Table 1, entry 5), the *N*-alkylation of a series of 2-aminoimidazoles **1** with various alcohols **2** was examined, and the results are summarized in Table 2. The *N*-alkylation of 2-aminobenzimidazole (**1a**) with benzylic alcohols bearing an electron-donating group (i.e., **2b** and **2c**) or electron-withdrawing group (i.e., **2d**) gave the corresponding products (i.e., **3ab**–**3ad**) in 84–92% yields. Similarly, the reactions of **1a** with benzylic alcohols bearing a halogen atom (i.e., **2e** and **2f**) gave the desired products (i.e., **3ae** and **3af**) in 90 and 87% yields, respectively. Aliphatic primary alcohols, such as 1-butanol (**2g**) and 1-octanol (**2h**), were also converted into the corresponding products (i.e., **3ag** and **3ah**) in high yields. Surprisingly, cyclic secondary alcohols with a high degree of steric hindrance, such as cyclopentanol (**2i**) and cyclohexanol (**2j**), were successfully used, and the desired products (i.e., **3ai** and **3aj**) were obtained in 78 and 84% yields, respectively. *N*-Alkylation with functionalized alcohols **2k** and **2l** gave the corresponding products (i.e., **3ak** and **3al**) in 87 and 71% yields, respectively. Furthermore, the reactions of substituted 2-aminobenzimidazole **1b** with **2a** and **2g** gave the desired products (i.e., **3ba** and **3bg**) in 95 and 85% yields, respectively. For non-benzo-fused 2-aminoimidazoles **1c** and **1d**, *N*-alkylation with **1a** gave the corresponding products (i.e., **3ca** and **3da**) in 84 and 89% yields, respectively.

To further expand the scope of the reaction, the *N*-alkylation of 1-alkyl-2-aminoimidazoles **4** with various alcohols **2** was investigated. As shown in Table 3, the reactions of 1-benzyl-2-aminobenzimidazole (**4a**) with various benzylic alcohols gave the desired products (i.e., **5aa**–**5ap**) in 78–91% yields. The alkylation of **4a** with aliphatic alcohols **2g**–**j** gave the corresponding products (i.e., **5ag**–**5aj**) in 68–87% yields. Furthermore, the reaction of non-benzo-fused substrate **4b** with **2a** gave the corresponding product (i.e., **5ba**) in 75% yield, although an elevated reaction temperature was required. 2-Aminoimidazoles bearing other substituents at the 1*N* position were also shown to be suitable substrates. The reactions of **4c**–**h** with **2a** gave the desired products (i.e., **5ca**–**5ha**) in 80–90% yields.

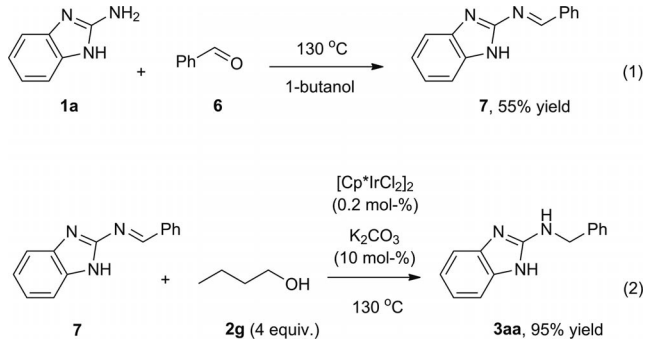
It should be noted that no isomeric 1-alkyl-2-iminoazolines or over-alkylated 1,3-dialkyl-2-iminoazolines or 2-(*N*-dialkylamino)imidazoles were observed in any reactions. Only the desired 2-(*N*-alkylamino)imidazole products were seen.

A plausible mechanism for this regioselective reaction based on the "hydrogen autotransfer" (or "hydrogen-borrowing") process[8,9] is outlined in Scheme 2. The alcoholate is first dehydrogenated to form the aldehyde and the metal hydride species. Then condensation occurs between the aldehyde and 2-aminoimidazole to give the imine intermediate. Finally, the unsaturated intermediate is hydrogenated, which consumes the hydride species and gives the desired product. The exocyclic nitrogen of 2-aminoimidazole is favored over the endocyclic one in the condensation with the aldehyde, and this results in the regioselectivity of the reaction.



Scheme 2. Plausible mechanism.

To confirm the proposed mechanism, the condensation of 2-aminoimidazole with an aldehyde was first examined. Treatment of 2-aminobenzimidazole (**1a**) with benzaldehyde (**6**) at 130 °C for 12 h gave imine **7** in 55% yield as the only product; see Equation (1). Furthermore, the reaction of **7** with **2g** was carried out for 12 h in the presence of $[Cp^*IrCl_2]_2$ (0.2 mol-%) and K_2CO_3 (10 mol-%), and gave an almost quantitative yield of **3aa**, supporting the hydrogen-transfer mechanism; see Equation (2).



Conclusions

We have demonstrated the first example of the preparation of 2-(*N*-alkylamino)imidazoles by direct *N*-alkylation of the corresponding 2-aminoimidazoles with alcohols. This iridium-catalyzed regioselective reaction has advantages over existing methods, such as the ready availability of starting materials, high atom efficiency, and environmental friendliness. Efforts to extend the potential of alcohols as electrophiles are currently underway in our laboratory.

Experimental Section

General Methods: Infra-red spectra were recorded with a Nicolet iS10 FTIR spectrometer. High-resolution mass spectra (HRMS) were obtained with a HPLC-Q-Tof MS (Micro) spectrometer and are reported as *m*/*z* values. Melting points were measured with a X-6 micro-melting apparatus (Beijing Tech Instrument Co., Ltd). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported on the δ scale in parts per million (ppm) relative to tetramethylsilane, using residual solvent peaks (δ = 7.26 ppm for $CDCl_3$; 2.50 ppm for $[D_6]$DMSO; 4.78 and 3.31 ppm for CD_3OD) as internal standards. Coupling constants (*J* values) are reported in Hertz (Hz), and splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported on the δ scale in ppm relative to tetramethylsilane, using solvent peaks (δ = 77.0 ppm for $CDCl_3$; 39.5 ppm for $[D_6]$DMSO; 49.0 ppm for CD_3OD) as internal standards.

$[Cp^*IrCl_2]_2$,[15] $[Ir(cod)Cl]_2$,[16] and $[Cp^*RhCl_2]_2$[17] were prepared according to literature methods. All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Anhydrous solvents were transferred by oven-dried syringe. Reaction tubes were oven-dried and cooled under a stream of nitrogen. Reaction tubes were purchased from Beijing Synthware Glass Inc. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercially available silica gel plates. Solvents for chromatography are listed as volume/volume ratios.

General Procedure for Iridium-Catalyzed *N*-Alkylation of 2-Aminoimidazoles Using Alcohols as Alkylating Agents: 2-Aminoimidazole derivative (1 mmol), alcohol (4 mmol), base (0.1 mmol, 10 mol-%) and iridium complex (0.002 mmol, 0.2 mol-%) were added to an oven-dried, nitrogen-purged 20 mL Schlenk tube. The reaction mixture was heated at 130 °C for 12 h, and was then allowed to cool to ambient temperature. The mixture was concentrated in vacuo and purified by flash column chromatography with hexane/ethyl acetate to give the corresponding product.

***N*-Benzyl-1*H*-benzo[*d*]imidazol-2-amine (3aa):**[1b] M.p. 164–166 °C (ref.[1b] m.p. 165–166 °C). ^{1}H NMR (500 MHz, CD_3OD): δ = 7.38 (br. s, 2 H, ArH), 7.31 (br. s, 2 H, ArH), 7.23–7.18 (m, 3 H, ArH), 6.96 (br. s, 2 H, ArH), 4.57 (s, 2 H, CH_2N) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.9, 140.6, 139.2, 129.5, 128.3, 128.2, 121.3, 112.8, 47.4 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{14}H_{14}N_3$ $[M + H]^+$ 224.1188; found 224.1184.

***N*-(4-Methoxybenzyl)-1*H*-benzo[*d*]imidazol-2-amine (3ab):**[18] M.p. 193–195 °C (ref.[18] m.p. 207–208 °C). ^{1}H NMR (500 MHz, CD_3OD): δ = 7.30 (d, J = 7.9 Hz, 2 H), 7.18 (br. s, 2 H), 6.96 (br. s, 2 H), 6.87 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 160.4, 156.9, 139.1, 132.5, 129.7, 121.3, 114.9, 112.8 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{15}H_{16}N_3O$ $[M + H]^+$ 254.1293; found 254.1300.

***N*-(4-Methylbenzyl)-1*H*-benzo[*d*]imidazol-2-amine (3ac):**[19] M.p. 172–173 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 7.26 (d, J = 7.9 Hz, 2 H, ArH), 7.19–7.17 (m, 2 H, ArH), 7.13 (d, J = 7.7 Hz, 2 H, ArH), 6.96–6.94 (m, 2 H, ArH), 4.51 (s, 2 H, CH_2N), 2.29 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.9, 139.1, 137.9, 137.4, 130.1, 128.3, 121.3, 112.8, 47.3, 21.1 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{15}H_{16}N_3$ $[M + H]^+$ 238.1344; found 238.1343.

***N*-[4-(Trifluoromethyl)benzyl]-1*H*-benzo[*d*]imidazol-2-amine (3ad):**[18] M.p. 222–223 °C (ref.[18] m.p. 222–223 °C). ^{1}H NMR (500 MHz, CD_3OD): δ = 7.62 (d, J = 8.3 Hz, 2 H, ArH), 7.57 (d, J = 8.1 Hz, 2 H, ArH), 7.20–7.18 (m, 2 H, ArH), 6.97–6.96 (m, 2 H, ArH), 4.67 (s, 2 H, CH_2N) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.7, 145.5, 139.1, 130.3 (q, $J_{C,F}$ = 31.2 Hz), 125.8 (q, $J_{C,F}$ = 269.4 Hz), 126.3, 121.4, 112.9, 46.8 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{15}H_{13}N_3F_3$ $[M + H]^+$ 292.1062; found 292.1070.

***N*-(4-Bromobenzyl)-1*H*-benzo[*d*]imidazol-2-amine (3ae):**[19] M.p. 162–163 °C (ref.[19] m.p. 195–197 °C). ^{1}H NMR (500 MHz, CD_3OD): δ = 7.46 (d, J = 8.1 Hz, 2 H, ArH), 7.30 (d, J = 8.1 Hz, 2 H, ArH), 7.19–7.17 (m, 2 H, ArH), 6.97–6.95 (m, 2 H, ArH) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.7, 140.1, 139.1, 132.5, 130.2, 121.8, 121.4, 112.9, 46.7 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{14}H_{13}N_3Br$ $[M + H]^+$ 302.0293; found 302.0298.

***N*-(2-Chlorobenzyl)-1*H*-benzo[*d*]imidazol-2-amine (3af):**[18] M.p. 182–184 °C (ref.[18] m.p. 212–214 °C). ^{1}H NMR (500 MHz, CD_3OD): δ = 7.46–7.45 (m, 1 H, ArH), 7.41–7.39 (m, 1 H, ArH), 7.26–7.24 (m, 2 H, ArH), 7.19–7.18 (m, 2 H, ArH), 6.97–6.95 (m, 2 H, ArH), 4.67 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.7, 139.2, 137.8, 134.3, 130.4, 129.6, 128.1, 121.3, 112.9, 45.3 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{14}H_{13}N_3Cl$ $[M + H]^+$ 258.0798; found 258.0794.

***N*-Butyl-1*H*-benzo[*d*]imidazol-2-amine (3ag):**[20] M.p. 145–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27–7.26 (m, 2 H, ArH), 7.04–7.02 (m, 2 H, ArH), 5.19 (br. s, 1 H, NH), 3.39 (t, J = 7.1 Hz, 2 H, CH_2N), 1.55 (quint, J = 7.3 Hz, 2 H, CH_2), 1.35 (sext, J = 7.5 Hz, 2 H, CH_2), 0.84 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0, 137.8, 120.5, 111.9, 43.0, 31.9, 19.9, 13.6 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{11}H_{16}N_3$ $[M + H]^+$ 190.1344; found 190.1346.

***N*-Octyl-1*H*-benzo[*d*]imidazol-2-amine (3ah):** M.p. 139–140 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 7.17–7.16 (m, 2 H, ArH), 6.95–6.93 (m, 2 H, ArH), 3.34 (t, J = 7.1 Hz, 2 H, CH_2N), 1.64 (quint, J = 7.3 Hz, 2 H, CH_2), 1.45–1.30 (m, 10 H, 5 CH_2), 0.89 (t, J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 157.1, 139.1, 121.2, 112.6, 43.9, 33.0, 30.9, 30.5, 30.4, 28.0, 23.7, 14.4 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{15}H_{24}N_3$ $[M + H]^+$ 246.1970; found 246.1972.

***N*-Cyclopentyl-1*H*-benzo[*d*]imidazol-2-amine (3ai):** M.p. 205–206 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 7.18–7.17 (m, 2 H, ArH), 6.96–6.94 (m, 2 H, ArH), 4.09 (quint, J = 6.4 Hz, 1 H, CHN), 2.09–2.03 (m, 2 H, CH_2), 1.82–1.74 (m, 2 H, CH_2), 1.70–1.64 (m, 2 H, CH_2), 1.60–1.53 (m, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.5, 139.0, 121.2, 112.6, 55.5, 34.2, 24.6 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{12}H_{16}N_3$ $[M + H]^+$ 202.1344; found 202.1348.

***N*-Cyclohexyl-1*H*-benzo[*d*]imidazol-2-amine (3aj):**[21] M.p. 213-214 °C (ref.[21] m.p. 215.1–215.5 °C). ^{1}H NMR (500 MHz, CD_3OD): δ = 7.17–7.15 (m, 2 H, ArH), 6.94–6.93 (m, 2 H, ArH), 3.61–3.56 (m, 1 H, CHN), 2.07–2.05 (m, 2 H, CH_2), 1.80–1.78 (m, 2 H, CH_2), 1.68–1.66 (m, 1 H, CH), 1.49–1.42 (m, 2 H, CH_2), 1.32–1.22 (m, 3 H, CH_2 and CH) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.2, 139.1, 121.1, 112.6, 52.7, 34.6, 26.8, 26.1 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{13}H_{18}N_3$ $[M + H]^+$ 216.1501; found 216.1493.

***N*-(3-Phenylpropyl)-1*H*-benzo[*d*]imidazol-2-amine (3ak):** M.p. 159–161 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 7.26–7.20 (m, 4 H, ArH), 7.18–7.13 (m, 3 H, ArH), 6.96–6.94 (m, 2 H, ArH), 3.37 (t, J = 7.1 Hz, 2 H, CH_2N), 2.73 (t, J = 7.7 Hz, 2 H, CH_2Ar), 1.99–1.93 (m, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 157.0, 143.1, 139.1, 129.4, 129.3, 126.8, 121.2, 112.7, 43.4, 34.1, 32.8 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{16}H_{18}N_3$ $[M + H]^+$ 252.1501; found 252.1503.

***N*-(2-Methoxyethyl)-1*H*-benzo[*d*]imidazol-2-amine (3al):** M.p. 151–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.26 (m, 2 H, ArH), 7.05–7.03 (m, 2 H, ArH), 3.60 (t, J = 4.7 Hz, 2 H, CH_2O), 3.55 (t, J = 4.7 Hz, 2 H, CH_2N), 3.39 (s, 3 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.8, 137.5, 120.7, 112.2, 72.6, 58.9, 43.4 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{10}H_{14}N_3O$ $[M + H]^+$ 192.1137; found 192.1134.

***N*-Benzyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-amine (3ba):** M.p. 179–180 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 7.38 (d, J = 7.5 Hz, 2 H, ArH), 7.31 (t, J = 7.5 Hz, 2 H, ArH), 7.23 (t, J = 7.1 Hz, 1 H, ArH), 6.97 (s, 2 H, ArH), 4.54 (s, 2 H, CH_2N), 2.26 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 156.6, 140.7, 137.6, 129.5, 129.4, 128.3, 128.2, 113.6, 47.5, 20.2 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{16}H_{18}N_3$ $[M + H]^+$ 252.1501; found 252.1504.

***N*-Butyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-amine (3bg):**[1f] M.p. 82–84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06 (s, 2 H, ArH), 4.51 (br. s, 1 H, NH), 3.38 (t, J = 7.1 Hz, 2 H, CH_2N), 2.29 (s, 6 H, 2 CH_3Ar), 1.61 (quint, J = 7.3 Hz, 2 H), 1.39 (sext, J = 7.5 Hz, 2 H), 0.92 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6, 140.7, 129.5, 129.4, 128.3, 128.2, 113.6, 47.5, 20.2 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{13}H_{20}N_3$ $[M + H]^+$ 218.1657; found 218.1658.

***N*-Benzyl-4,5-diphenyl-1*H*-imidazol-2-amine (3ca):**[22] M.p. 176–177 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 7.41 (d, J = 7.2 Hz, 2

H, ArH), 7.37–7.33 (m, 6 H, ArH), 7.26 (t, J = 7.4 Hz, 5 H, ArH), 7.20 (t, J = 7.2 Hz, 2 H, ArH), 4.50 (s, 2 H, CH_2N) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 152.1, 140.8, 134.4, 130.3, 129.5, 129.4, 128.8, 128.6, 128.2, 127.8, 48.3 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{22}H_{20}N_3$ $[M + H]^+$ 326.1657; found 326.1650.

***N*-Benzyl-5-methyl-4-phenyl-1*H*-imidazol-2-amine (3da):** M.p. 139–140 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.49–7.47 (m, 4 H, ArH), 7.41–7.37 (m, 5 H, ArH), 7.31 (br. s, 1 H, ArH), 4.53 (d, J = 6.8 Hz, 2 H), 2.25 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 146.3, 137.7, 128.8, 128.5, 128.2, 127.8, 127.4, 127.1, 126.8, 121.6, 119.1, 52.7, 45.7 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{1.7}H_{18}N_3$ $[M + H]^+$ 264.1501; found 264.1505.

***N*,1-Dibenzyl-1*H*-benzo[*d*]imidazol-2-amine (5aa):** M.p. 105–106 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.8 Hz, 1 H, ArH), 7.3–7.22 (m, 8 H, ArH), 7.17–7.13 (m, 3 H, ArH), 7.10–7.05 (m, 2 H, ArH), 5.11 (s, 2 H, CH_2N), 4.68 (d, J = 5.2 Hz, 2 H, CH_2NH), 4.25 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.1, 142.2, 138.5, 135.3, 134.9, 129.1, 128.6, 128.1, 127.5, 127.4, 126.4, 121.5, 119.9, 116.7, 107.3, 47.4, 45.7 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{21}H_{19}N_3$ $[M + H]^+$ 314.1657; found 314.1647.

***N*-(4-Methoxybenzyl)-1-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5ab):** M.p. 150–151 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.8 Hz, 1 H, ArH), 7.33–7.28 (m, 3 H, ArH), 7.17–7.15 (m, 3 H, ArH), 7.14–7.11 (m, 2 H, ArH), 7.09–7.04 (m, 2 H, ArH), 6.81 (dt, J = 8.8, J = 2.6 Hz, 2 H, ArH), 5.09 (s, 2 H, CH_2N), 4.61 (d, J = 5.4 Hz, 2 H, CH_2NH), 4.17 (br. s, 1 H, NH), 3.78 (s, 3 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0, 154.1, 142.2, 135.4, 134.8, 130.6, 129.1, 128.9, 128.0, 126.4, 121.4, 119.8, 116.6, 114.0, 107.3, 55.2, 46.9, 45.6 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{22}H_{21}N_3O$ $[M + H]^+$ 344.1763; found 344.1751.

***N*-(4-Methylbenzyl)-1-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5ac):** M.p. 123–124 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.8 Hz, 1 H, ArH), 7.31–7.30 (m, 3 H, ArH), 7.17–7.05 (m, 9 H, ArH), 5.10 (s, 2 H, CH_2N), 4.64 (d, J = 4.1 Hz, 2 H, CH_2NH), 4.29 (br. s, 1 H, NH), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.1, 142.1, 137.2, 135.4, 135.3, 134.8, 129.3, 129.2, 128.1, 127.6, 126.5, 121.5, 119.9, 116.7, 107.3, 47.2, 45.7, 21.0 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{22}H_{22}N_3$ $[M + H]^+$ 328.1814; found 328.1806.

***N*-(4-Bromobenzyl)-1-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5ae):** M.p. 147–148 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.6 Hz, 1 H, ArH), 7.37 (d, J = 8.3 Hz, 1 H, ArH), 7.38–7.30 (m, 3 H, ArH), 7.18–7.13 (m, 3 H, ArH), 7.11–7.07 (m, 3 H, ArH), 5.14 (d, J = 5.1 Hz, 2 H, CH_2N), 4.63 (d, J = 5.6 Hz, 2 H, CH_2N), 4.46 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 141.8, 137.6, 135.3, 134.8, 131.6, 129.2, 129.1, 128.2, 126.5, 121.6, 121.2, 120.1, 116.7, 107.4, 46.6, 45.7 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{21}H_{19}N_3Br$ $[M + H]^+$ 392.0762; found 392.0760.

***N*-(4-Chlorobenzyl)-1-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5am):** M.p. 130–132 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.8 Hz, 1 H, ArH), 7.32–7.30 (m, 3 H, ArH), 7.21 (d, J = 8.5 Hz, 2 H, ArH), 7.17–7.06 (m, 7 H, ArH), 5.12 (s, 2 H, CH_2N), 4.62 (d, J = 4.9 Hz, 2 H, CH_2NH), 4.43 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.9, 141.9, 137.1, 135.3, 134.8, 133.1, 129.2, 128.8, 128.6, 128.1, 126.4, 121.6, 120.0, 116.6, 107.4, 46.5, 45.7 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{21}H_{19}N_3Cl$ $[M + H]^+$ 348.1268; found 348.1270.

***N*-(2,4-Dichlorobenzyl)-1-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5an):** M.p. 101–103 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.7 Hz, 1 H, ArH), 7.30 (d, J = 8.1 Hz, 4 H, ArH), 7.24 (s, 1 H), 7.16–7.06 (m, 6 H, ArH), 5.12 (s, 2 H, CH_2N), 4.71 (d, J = 4.9 Hz, 2 H, CH_2NH), 4.55 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 141.9, 135.2, 134.9, 134.6, 134.0, 133.7, 130.5, 129.2, 129.1, 128.2, 127.1, 126.5, 121.6, 120.0, 116.7, 107.3, 45.7, 44.5 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{21}H_{18}N_3Cl_2$ $[M + H]^+$ 382.0878; found 382.0872.

***N*-[3-(Trifluoromethyl)benzyl]-1-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5ao):** M.p. 136–138 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 6.6 Hz, 1 H, ArH), 7.50–7.29 (m, 7 H, ArH), 7.18–7.08 (m, 5 H, ArH), 5.15 (s, 2 H, CH_2N), 4.74 (s, 2 H,CH_2NH), 4.48 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 141.9, 139.7, 135.2, 134.9, 130.88 (q, $J_{C,F}$ = 32.1 Hz), 130.9, 129.2, 129.0, 128.3, 126.4, 124.2, 124.00 (q, $J_{C,F}$ = 270.9 Hz), 123.98, 121.6, 120.2, 116.8, 107.4, 46.7, 45.8 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{22}H_{19}N_3F_3$ $[M + H]^+$ 382.1531; found 382.1539.

1-Benzyl-*N*-(naphthalen-2-ylmethyl)-1*H*-benzo[*d*]imidazol-2-amine (5ap): M.p. 132–133 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (t, J = 4.6 Hz, 1 H, ArH), 7.75 (d, J = 8.5 Hz, 1 H, ArH), 7.72 (t, J = 4.7 Hz, 1 H, ArH), 7.61 (s, 1 H, ArH), 7.56 (d, J = 7.7 Hz, 1 H, ArH), 7.46–7.45 (m, 2 H, ArH), 7.35 (dd, J = 8.4, J = 1.6 Hz, 1 H, ArH), 7.31–7.30 (m, 3 H, ArH), 7.18–7.07 (m, 5 H, ArH), 5.12 (s, 2 H, CH_2N), 4.84 (d, J = 5.0 Hz, 2 H, CH_2NH), 4.35 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.1, 142.2, 135.9, 135.3, 134.9, 133.2, 132.7, 129.1, 128.3, 128.1, 127.7, 127.6, 126.4, 126.1, 125.9, 125.8, 125.7, 121.5, 119.9, 116.7, 107.3, 47.4, 45.6 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{25}H_{22}N_3$ $[M + H]^+$ 364.1814; found 364.1811.

1-Benzyl-*N*-butyl-1*H*-benzo[*d*]imidazol-2-amine (5ag): M.p. 86–88 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.9 Hz, 1 H, ArH), 7.36–7.31 (m, 3 H, ArH), 7.16 (d, J = 7.0 Hz, 2 H, ArH), 7.13 (t, J = 7.4 Hz, 1 H, ArH), 7.08–7.02 (m, 2 H, ArH), 5.08 (s, 2 H, CH_2Ph), 3.89 (br. s, 1 H, NH), 3.48 (q, J = 6.6 Hz, 2 H, CH_2N), 1.54 (quint, J = 7.4 Hz, 2 H, CH_2), 1.28 (sext, J = 7.4 Hz, 2 H, CH_2), 0.87 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 142.3, 135.4, 134.8, 129.1, 128.1, 126.4, 121.3, 119.6, 116.4, 107.1, 45.6, 43.1, 31.7, 19.8, 13.7 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{18}H_{22}N_3$ $[M + H]^+$ 280.1814; found 280.1807.

1-Benzyl-*N*-octyl-1*H*-benzo[*d*]imidazol-2-amine (5ah): M.p. 82–83 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.9 Hz, 1 H, ArH), 7.36–7.31 (m, 3 H, ArH), 7.17 (d, J = 7.2 Hz, 2 H, ArH), 7.13 (t, J = 7.4 Hz, 1 H, ArH), 7.08–7.02 (m, 2 H, ArH), 5.08 (s, 2 H, CH_2N), 3.88 (br. s, 1 H, NH), 3.47 (q, J = 6.6 Hz, 2 H, CH_2NH), 1.55 (quint, J = 7.0 Hz, 2 H, CH_2), 1.29–1.23 (m, 10 H, 5 CH_2), 0.87 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 142.3, 135.5, 134.8, 129.1, 128.1, 126.5, 121.3, 119.6, 116.5, 107.1, 45.7, 43.4, 31.7, 29.6, 29.2, 29.1, 26.7, 22.6, 14.0 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{22}H_{30}N_3$ $[M + H]^+$ 336.2440; found 336.2439.

1-Benzyl-*N*-cyclohexyl-1*H*-benzo[*d*]imidazol-2-amine (5aj): M.p. 169–171 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.9 Hz, 1 H, ArH), 7.56–7.31 (m, 3 H, ArH), 7.17 (d, J = 7.2 Hz, 2 H, ArH), 7.12 (d, J = 7.5 Hz, 1 H, ArH), 7.07–7.00 (m, 2 H, ArH), 5.07 (s, 2 H, CH_2N), 3.95–3.88 (m, 1 H, CH), 3.78 (d, J = 7.8 Hz, 1 H, NH), 2.03–2.01 (m, 2 H, CH_2), 1.62–1.56 (m, 3 H, CH_2 and CH), 1.44–1.36 (m, 2 H, CH_2), 1.18–1.06 (m, 3 H, CH_2 and CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 142.5, 135.5, 134.7, 129.1, 128.1, 126.5, 121.3, 119.4, 116.4, 107.0, 51.3, 45.6, 33.5, 25.6, 24.5 ppm. HRMS-EI (70 eV): m/z calcd. for $C_{20}H_{24}N_3$ $[M + H]^+$ 3061970; found 306.1972.

***N*,1-Dibenzyl-4,5-diphenyl-1*H*-imidazol-2-amine (5ba):** M.p. 129–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.6 Hz, 2 H, ArH), 7.34–7.18 (m, 15 H, ArH), 7.11 (d, J = 7.3 Hz, 1 H, ArH), 7.07 (d, J = 7.3 Hz, 2 H, ArH), 4.79 (s, 2 H, CH_2N), 4.62 (d, J = 5.7 Hz, 2 H, CH_2NH), 3.61 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.5, 139.4, 136.4, 135.1, 133.6, 131.3, 131.0, 129.1, 128.9, 128.4, 128.1, 128.0, 127.8, 127.7, 127.2, 126.6, 126.1, 125.8, 125.1, 47.9, 45.9 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{29}H_{26}N_3$ [M + H]$^+$ 416.2127; found 416.2133.

1-(4-Methylbenzyl)-*N*-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5ca): M.p. 135–136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.9 Hz, 1 H, ArH), 7.30–7.24 (m, 3 H, ArH), 7.22 (d, J = 7.8 Hz, 1 H, ArH), 7.15 (t, J = 7.4 Hz, 1 H, ArH), 7.11–7.06 (m, 4 H, ArH), 7.03 (d, J = 8.1 Hz, 2 H, ArH), 5.06 (s, 2 H, CH_2N), 4.68 (d, J = 5.3 Hz, 2 H, CH_2NH), 4.27 (br. s, 1 H, NH), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.2, 142.2, 138.6, 137.9, 134.9, 132.3, 129.8, 128.5, 127.5, 127.4, 126.4, 121.4, 119.8, 116.6, 107.3, 47.4, 45.5, 21.0 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{22}H_{22}N_3$ [M + H]$^+$ 328.1814; found 328.1804.

1-(4-Fluorobenzyl)-*N*-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5da):[20] M.p. 150–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.9 Hz, 1 H, ArH), 7.30–7.24 (m, 5 H, ArH), 7.18–7.13 (m, 1 H, ArH), 7.10 (m, 2 H, ArH), 7.07 (d, J = 4.1 Hz, 2 H, ArH), 6.99 (t, J = 8.6 Hz, 2 H, ArH), 5.08 (s, 2 H, CH_2N), 4.69 (d, J = 4.9 Hz, 2 H, CH_2NH), 4.33 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.4 (d, $J_{C,F}$ = 245.7 Hz), 154.0, 142.1, 138.4, 134.7, 131.1 (d, $J_{C,F}$ = 11.0 Hz), 128.6, 128.1 (d, $J_{C,F}$ = 32.5 Hz), 127.6, 127.5, 121.5, 120.0, 116.7, 116.1 (d, $J_{C,F}$ = 21.7 Hz), 107.3, 47.4, 45.0 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{21}H_{19}N_3$ [M + H]$^+$ 314.1657; found 314.1647.

1-(4-Chlorobenzyl)-*N*-benzyl-1*H*-benzo[*d*]imidazol-2-amine (5ea): M.p. 149–151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.0 Hz, 1 H, ArH), 7.31–7.24 (m, 7 H, ArH), 7.16 (t, J = 7.1 Hz, 1 H, ArH), 7.08–7.04 (m, 4 H, ArH), 5.07 (s, 2 H, CH_2N), 4.69 (d, J = 4.3 Hz, 2 H, CH_2NH), 4.29 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.9, 142.2, 138.4, 134.6, 134.0, 133.8, 129.3, 128.6, 127.7, 127.6, 127.5, 121.7, 120.0, 116.8, 107.3, 47.5, 45.0 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{21}H_{18}ClN_3$ [M + H]$^+$ 348.1268; found 348.1269.

***N*-Benzyl-1-phenethyl-1*H*-benzo[*d*]imidazol-2-amine (5fa):** M.p. 122–123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.7 Hz, 1 H, ArH), 7.32–7.28 (m, 3 H, ArH), 7.21–7.14 (m, 6 H, ArH), 7.13–7.08 (m, 2 H, ArH), 7.01 (t, J = 3.5 Hz, 2 H, ArH), 4.40 (t, J = 4.7 Hz, 2 H, CH_2NH), 4.13 (t, J = 4.9 Hz, 2 H, CH_2N), 3.48 (br. s, 1 H, NH), 3.04 (t, J = 6.4 Hz, 2 H, $ArCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.2, 142.1, 138.3, 138.2, 134.1, 129.0, 128.8, 128.5, 128.0, 127.5, 127.2, 121.4, 120.0, 116.7, 107.2, 47.6, 44.5, 35.3 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{22}H_{22}N_3$ [M + H]$^+$ 328.1814; found 328.1812.

***N*-Benzyl-1-ethyl-1*H*-benzo[*d*]imidazol-2-amine (5ga):** M.p. 152–153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.8 Hz, 1 H, ArH), 7.42 (d, J = 7.5 Hz, 2 H, ArH), 7.36 (t, J = 7.3 Hz, 2 H, ArH), 7.31 (t, J = 7.2 Hz, 1 H, ArH), 7.13 (t, J = 7.1 Hz, 1 H, ArH), 7.10–7.06 (m, 2 H, ArH), 4.76 (d, J = 5.0 Hz, 2 H, CH_2NH), 4.37 (br. s, 1 H, NH), 3.93 (q, J = 7.3 Hz, 2 H, CH_2N), 1.35 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 142.2, 138.7, 134.0, 128.7, 127.9, 127.6, 121.2, 119.6, 116.5, 107.1, 47.6, 36.8, 14.0 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{16}H_{18}N_3$ [M + H]$^+$ 252.1501; found 252.1508.

***N*-Benzyl-1-butyl-1*H*-benzo[*d*]imidazol-2-amine (5ha):** M.p. 134–135 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.8 Hz, 1 H, ArH), 7.42 (d, J = 7.6 Hz, 2 H, ArH), 7.37 (t, J = 7.4 Hz, 2 H, ArH), 7.31 (t, J = 7.2 Hz, 1 H, ArH), 7.13 (t, J = 7.1 Hz, 1 H, ArH), 7.10–7.05 (m, 2 H, ArH), 4.76 (d, J = 5.5 Hz, 2 H, CH_2NH), 4.33 (br. s, 1 H, NH), 3.87 (t, J = 7.2 Hz, 2 H, CH_2N), 1.72 (quint, J = 7.5 Hz, 2 H, CH_2), 1.37 (sext, J = 7.5 Hz, 2 H, CH_2), 0.93 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 142.1, 138.7, 134.5, 128.6, 127.8, 127.5, 121.0, 119.5, 116.4, 107.3, 47.5, 42.0, 31.0, 20.1, 13.6 ppm. HRMS-EI (70 eV): *m*/*z* calcd. for $C_{18}H_{21}N_3$ [M + H]$^+$ 280.1814; found 280.1811.

Procedure for the Condensation of 1*H*-Benzo[*d*]imidazol-2-amine with Benzaldehyde: 1a (1 mmol), benzaldehyde **6** (1 mmol), and 1-butanol (0.4 mL) were added to an oven-dried, nitrogen-purged 20 mL Schlenk tube. The resulting mixture was then heated at 130 °C for 12 h, at which point the reaction mixture was allowed to cool to ambient temperature. The mixture was concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetate to give the corresponding product.

***N*-Benzylidene-1*H*-benzo[*d*]imidazol-2-amine (7):**[23] M.p. 183–184 °C (ref.[23] m.p. 201–203 °C). ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 12.7 (br. s, 1 H, NH), 9.47 (s, 1 H, N=CHAr), 8.08 (d, J = 7.0 Hz, 2 H, ArH), 7.66–7.58 (m, 4 H, ArH), 7.45–7.42 (m, 1 H, ArH), 7.20–7.18 (m, 2 H, ArH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 165.4, 155.7, 142.4, 135.1, 134.3, 132.8, 129.5, 129.1, 122.1, 121.9, 118.7, 111.2 ppm.

Procedure for the Reaction of 7 with 2g Catalyzed by the $[Cp^*IrCl_2]_2/K_2CO_3$ System: 7 (1 mmol), 1-butanol **2g** (4 mmol), $[Cp^*IrCl_2]_2$ (0.002 mmol, 0.2 mol-%), and K_2CO_3 (0.1 mmol, 10 mol-%) were added to an oven-dried, nitrogen-purged 20 mL Schlenk tube. The resulting mixture was then heated at 130 °C for 12 h, at which point the reaction mixture was allowed to cool to ambient temperature. The mixture was concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetate to give the corresponding product (i.e., **3aa**).

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR and ^{13}C NMR spectra for all *N*-alkylated products.

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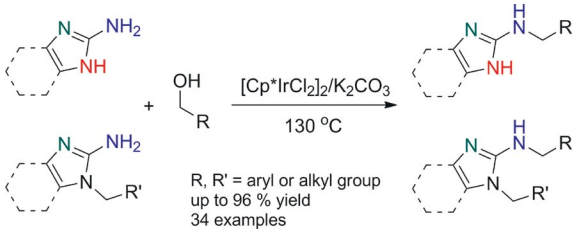

The direct *N*-alkylation of 2-aminoimidazoles to give the corresponding 2-(*N*-alkylamino)imidazoles was accomplished using alcohols as alkylating agents in the presence of a $[Cp^*IrCl_2]_2/K_2CO_3$ system. The iridium-catalyzed regioselective reaction is simple, efficient, general, and environmentally benign.

Keywords: Synthetic methods / Homogeneous catalysis / Iridium / Regioselectivity / Hydrogen transfer / Nitrogen heterocycles

