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# Direct C−N Coupling of Imidazoles and Benzylic Compounds via Iron-Catalyzed Oxidative Activation of C−H Bonds

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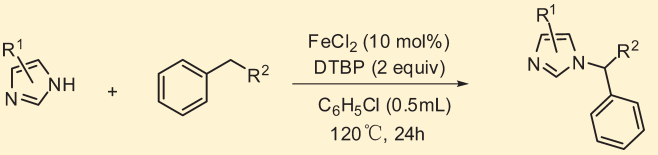
Supporting Information

**ABSTRACT:** Iron-catalyzed direct C−N bond formation between imidazoles and benzylic hydrocarbons is described. The reaction utilizes an inexpensive iron catalyst−oxidant system that is suitable for the coupling of a range of benzylic C−H bonds with various imidazoles.




The imidazole derivatives have attracted much attention for their wide applications as enzyme inhibitors,[1] drugs,[2] and polymers.[3] They have also been broadly used as the precursors of N-heterocyclic carbenes (NHC)[4] and ionic liquids.[5] It is known that N-alkylation and N-arylation of imidazoles are among the most important methods for the synthesis of imidazole derivatives. Nucleophilic substitution with alkyl halides is one of the most classical methods for the N-alkylation of imidazoles. However, this method suffers from use of alkyl halides and strong bases. Thus, a more efficient method for construction of imidazole derivatives is highly desired. In recent years, great progress has been made in transition-metal-catalyzed oxidative coupling of C−H and N−H bonds with C−H bonds to form C−C[6] and C−N[7] bonds. For example, the oxidative coupling reactions between benzylic C−H bonds and $sp^3$, $sp^2$, or sp C−H bonds have been reported.[6c,d,j,k] This strategy is an efficient and straightforward method to synthesize benzylic derivatives. Transition-metal-catalyzed C−H amination using nitrene derivatives as the nitrogen source is the most widely developed and impactful method to form C−N bonds.[8] Recently, amidation of the benzylic $sp^3$ C−H bonds with unmodified sulfonamides or carboxamides have been realized by using transition-metal salts as the catalysts.[7e−i] This strategy is an important method for the synthesis of valuable nitrogen-containing compounds without the need of a prefunctionalized starting material. However, the known benzylic C−H amination methods typically require nitrogen sources bearing powerful electron-withdrawing groups such as sulfonamides and carboxamides. As early as 1993, Hanefeld et al. had reported the direct oxidative C−N coupling reaction of indazoles and benzotriazoles with di- and triphenylmethane derivatives. However, the desired products were obtained in less than 10% yields.[9] The direct conversion of benzylic C−H bonds into C−N bonds using imidazoles as the nitrogen sources remains the great challenge. Iron is one of the most abundant and inexpensive metals on earth[10] and is an efficient catalyst for C−N cross-coupling reactions.[11] Herein, we present a direct iron-catalyzed N-alkylation of imidazoles with benzylic hydrocarbons.

Benzimidazole (**1a**) and diphenylmethane (**2a**) were selected as the model substrates to test suitable reaction conditions (Table 1). When $FeCl_3$ was used as the catalyst and di-*tert*-butyl peroxide (DTBP) as the oxidant in dichloroethane (DCE) at 80 °C, **3a** was obtained in 13% yield (Table 1, entry 1). Although copper salts are often used as catalysts for oxidative coupling reactions,[12] less than 5% yield of **3a** was observed using $Cu(OTf)_2$ and CuBr as catalysts (entries 3 and 4). DDQ, BQ, and hyperiodine compounds are well-known oxidants in oxidative C−H activation and functionalization;[13] however, they are not effective (entries 5−8). The reaction is also sensitive to solvents, and no product was obtained in DMSO and methanol (entries 9 and 10). When the reaction was carried out in chlorobenzene at 120 °C, the yield was increased to 62% (entry 13). Further increase of the temperature to 135 °C resulted in a lower yield of 41% (entry 14). The use of $FeCl_2$ instead of $FeCl_3$ as the catalyst could increase the yield to 70% (entry 15). Furthermore, we found that 10 mol % of $FeCl_2$ was the best choice for the reaction (entries 16−18). In each run of the coupling reactions, benzophenone was found to be the major side product. A large excess of diarylmethanes could significantly improve the conversion of imidazole derivatives, therefore, 6−10 equivalents of benzylic hydrocarbons were used.

Under the optimized conditions, the coupling of a variety of benzylic hydrocarbons with benzoimidazole was investigated (Table 2). A few diarylmethanes bearing either electron-withdrawing or electron-donating groups could react, and the corresponding products were provided in moderate to good yields (Table 2, entries 1−6, 8, and 9). However, strong electron-withdrawing groups considerably lower the yield (entry 7). The reaction is assumed to proceed via methylenyl cation intermediate generated by oxidation of the C−H bond, and thus, the electron-withdrawing group would destabilize the proposed intermediate (Scheme 1). The less activated **2j** and **2k** also

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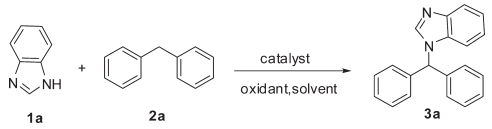
**Table 1. Optimization of Reaction Conditions**[a]




1a 2a 3a

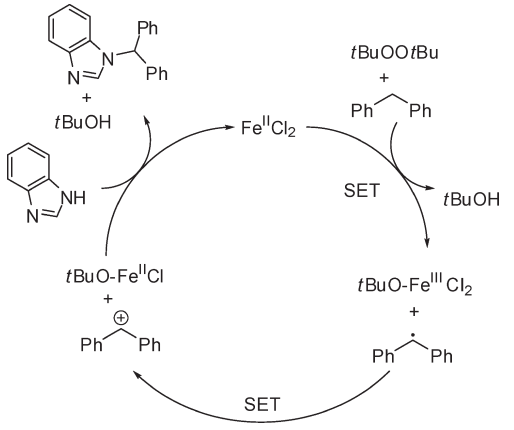
| entry | cat. | oxidant | solvent | $T$ (°C) | yield (%) |
|---|---|---|---|---|---|
| 1 | $FeCl_3$ | DTBP | DCE | 80 | 13 |
| 2 | $FeCl_2 \cdot 4H_2O$ | DTBP | DCE | 80 | trace |
| 3 | $Cu(OTf)_2$ | DTBP | DCE | 80 | trace |
| 4 | CuBr | DTBP | DCE | 80 | trace |
| 5 | $FeCl_3$ | DDQ | DCE | 80 | trace |
| 6 | $FeCl_3$ | $PhI(OAc)_2$ | DCE | 80 | trace |
| 7 | $FeCl_3$ | BQ | DCE | 80 | N.D.[b] |
| 8 | $FeCl_3$ | TBHP | DCE | 80 | trace |
| 9 | $FeCl_3$ | DTBP | $CH_3OH$ | 60 | N.D. |
| 10 | $FeCl_3$ | DTBP | DMSO | 80 | N.D. |
| 11 | $FeCl_3$ | DTBP | Toluene | 80 | trace |
| 12 | $FeCl_3$ | DTBP | $C_6H_5Cl$ | 100 | 28 |
| 13 | $FeCl_3$ | DTBP | $C_6H_5Cl$ | 120 | 62 |
| 14 | $FeCl_3$ | DTBP | $C_6H_5Cl$ | 135 | 41 |
| 15 | $FeCl_2$ | DTBP | $C_6H_5Cl$ | 120 | 70 |
| **16**[c] | **$FeCl_2$** | **DTBP** | **$C_6H_5Cl$** | **120** | **72** |
| 17[d] | $FeCl_2$ | DTBP | $C_6H_5Cl$ | 120 | 47 |
| 18 | | DTBP | $C_6H_5Cl$ | 120 | N.D. |

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3.0 mmol), catalyst (0.1 mmol), oxidant (1.0 mmol), 1.0 M **1a** in solvent, 24 h, under $N_2$. [b] Not detected by TLC [c] $FeCl_2$ (0.05 mmol). [d] $FeCl_2$ (0.025 mmol).

reacted with benzimidazole leading to α-aminated products (entries 10 and 11). Direct N-alkylation of **1a** with ethylbenzene and propylbenzene were also successful, but the yields are low (entries 12 and 13). Moreover, benzimidazole could also react with primary benzylic C−H bonds (entries 14−17). The amination reactions of *p*-xylene and mesitylene with benzimidazole only yielded monoaminated products. Again, 4-chlorotoluene bearing an electron-withdrawing group showed lower activity toward oxidative C−H activation.

The dehydrogenative coupling of various imidazoles and a benzylic $sp^3$ C−H bond was also examined under the reaction conditions used above (Table 3). Benzoimidazole **1b** having two methyl groups at its 5- and 6-positions shows relatively lower activity compared to **1a** (Table 3, entry 1). Unexpectedly, 2-substituted **1c**−**g** having either electron-withdrawing or electron-donating groups display higher activities than benzoimidazole itself (entries 2−6). The oxidative coupling of diphenylmethane and imidazoles bearing a electron-withdrawing group at the 4 or 5 position also proceeded well (entries 7 and 9). The reaction of 4-nitro-1*H*-imidazole would afford **4g** in 70% yield, and its structure was confirmed by NOE measurement (entry 7). Trace amount of its regioisomer 1-benzhydryl-5-nitro-1*H*-imidazole (**4g′**) was also observed from NMR analysis. 4,5-Diphenyl-1*H*-imidazole reacted with diphenylmethane to afford the corresponding product in relatively lower yield (entry 8) probably due to large steric hindrance. Interestingly, the coupling of 4,5-dicyano-1*H*-imidazole with diphenylmethane gave **4i** in almost quantitative yield (entry 9). However, imidazole is totally unreactive, and imidazole was recovered after reaction (entry 10).

**Scheme 1. Possible Mechanism of Oxidative C−N Coupling**




The reaction is assumed to proceed via diphenylmethane radical generated from the H abstraction of diphenylmethane by a di-tert-butyl peroxide molecule in the presence of $FeCl_2$ (Scheme 1). The radical could be further oxidized to benzyl cation through a single-electron transfer process assisted by Fe(III) ion.[6d] Finally, nucleophilic reaction of benzimidazole with the benzyl cation would form the product **3a**.

In summary, $FeCl_2$-catalyzed amination of benzylic C−H bonds leading to imidazole derivatives is presented. Benzylic hydrocarbons are more easily available and environmentally friendly than alkyl halides. The inexpensive and readily available catalyst−oxidant system is of practical interest for N-alkylation of imidazoles.

## EXPERIMENTAL SECTION

**General Procedure for the Synthesis of Products 3 or 4: Synthesis of 1-Benzhydryl-1*H*-benz[*d*]imidazole (3a)**[14]**.** An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (59 mg, 0.5 mmol), $FeCl_2$ (6.4 mg, 0.05 mmol), and **2a** (504 mg, 3.0 mmol). The tube was evacuated and refilled with $N_2$, and this process was repeated three times. Then ditert-butyl peroxide (146 mg, 1.0 mmol) in chlorobenzene (0.5 mL) was added. The resulting mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography eluting with ethyl acetate/petroleum (1:2): white solid; yield 72%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.0 Hz, 1H), 7.59 (s, 1H), 7.35−7.34 (m, 6H), 7.27−7.24 (m, 1H), 7.19−7.12 (m, 6H), 6.73 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 142.6, 138.1, 134.1, 129.0, 128.5, 128.2, 122.9, 122.4, 120.4, 110.7, 63.6.

**1-(Phenyl(*p*-tolyl)methyl)-1*H*-benz[*d*]imidazole (3b):** white solid; yield 63%; mp 115−117 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.0 Hz, 1H), 7.60 (s, 1H), 7.34−7.11 (m, 10H), 7.03 (d, $J$ = 8.0 Hz, 2H), 6.70 (s, 1H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 142.6, 138.3, 135.1, 134.1, 129.7, 128.9, 128.3, 128.2, 128.1, 122.9, 122.3, 120.4, 110.8, 63.4, 21.1; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{21}H_{18}N_2$ 298.1470, found 298.1471.

**1-(Phenyl(*o*-tolyl)methyl)-1*H*-benz[*d*]imidazole (3c):** white solid; yield 64%; mp 106−108 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (d, $J$ = 8.0 Hz, 1H), 7.54 (s, 1H), 7.37−7.35 (m, 3H), 7.30−7.26 (m, 3H), 7.21−7.18 (m, 1H), 7.14−7.11 (m, 4H), 6.88 (s, 1H), 6.76 (d, $J$ = 7.6 Hz, 1H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 142.6, 137.5, 136.4, 136.3, 134.0, 131.0, 129.0, 128.5, 128.5, 128.2, 127.8, 126.5, 123.0, 122.5, 120.4, 110.5, 60.7, 19.1; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{21}H_{18}N_2$ 298.1470, found 298.1466.


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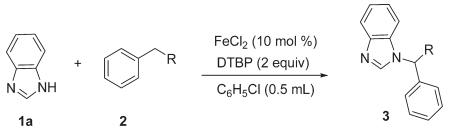
**Table 2. Reactions of Benzimidazole with Various Benzylic Hydrocarbons**[a]




| entry | 2 | product | yield (%) |
|---|---|---|---|
| 1 | **2a** | **3a** | 72 |
| 2 | **2b** | **3b** | 63 |
| 3 | **2c** | **3c** | 64 |
| 4 | **2d** | **3d** | 60 |
| 5 | **2e** | **3e** | 69 |
| 6 | **2f** | **3f** | 90 |
| 7 | **2g** | **3g** | 23 |
| 8 | **2h** | **3h** | 54 |
| 9 | **2i** | **3i** | 83 |
| 10[b] | **2j** | **3j** | 53 |
| 11[b] | **2k** | **3k** | 52 |
| 12[b] | **2l** | **3l** | 31 |
| 13[b] | **2m** | **3m** | 31 |
| 14[b] | **2n** | **3n** | 41 |
| 15[b] | **2o** | **3o** | 32 |
| 16[b] | **2p** | **3p** | 23 |
| 17[c] | **2q** | **3q** | 45 |

[a] Reaction conditions: **1a** (0.5 mmol), **2** (3.0 mmol), $FeCl_2$ (0.05 mmol), DTBP (1.0 mmol), **1a** 1.0 M in $C_6H_5Cl$, 120 °C, 24 h, under $N_2$. [b] **2** (5.0 mmol), 36 h. [c] Toluene (2 mL), 36 h.

**1-(Phenyl(*m*-tolyl)methyl)-1*H*-benz[*d*]imidazole (3d):** White solid; yield 60%; Mp 118−120 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 8.0 Hz, 1H), 7.62 (s, 1H), 7.37−7.35 (m, 3H), 7.29−7.14 (m, 7H), 7.00 (s, 1H), 6.94 (d, $J$ = 7.2 Hz, 1H), 6.72 (s, 1H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 142.6, 138.8, 138.2, 138.0, 134.1, 129.3, 128.9, 128.8, 128.4, 128.1, 125.3, 122.9, 122.3, 120.3, 110.7, 63.6, 21.4; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{21}H_{18}N_2$: 298.1470, found 298.1469.

**1-((4-Chlorophenyl)(phenyl)methyl)-1*H*-benz[*d*]imidazole (3e):** yellow solid; yield 69%; mp 119−120 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.4 Hz, 1H), 7.59 (s, 1H), 7.37−7.25 (m, 6H), 7.20−7.10 (m, 4H), 7.06 (d, $J$ = 8.4 Hz, 2H), 6.72 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 142.3, 137.6, 136.7, 134.4, 133.9, 129.4, 129.2, 129.1, 128.8, 128.2, 123.1, 122.5, 120.5, 110.6, 63.0; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{20}H_{15}ClN_2$ 318.0924, found 318.0921.

**1-((4-Fluorophenyl)(phenyl)methyl)-1*H*-benz[*d*]imidazole (3f):** light yellow oil; yield 90%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 7.6 Hz, 1H), 7.57 (s, 1H), 7.33 (s, 3H), 7.24 (t, $J$ = 7.6 Hz, 1H), 7.18−7.00 (m, 8H), 6.72 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.5 (d, $J_{C-F}$ = 247.2 Hz), 144.1, 142.4, 137.8, 133.9 (d, $J_{C-F}$ = 3.1 Hz), 130.0, 129.9 (d, $J_{C-F}$ = 8.4 Hz), 129.1, 128.7, 128.0, 123.1, 122.5, 120.5, 116.0


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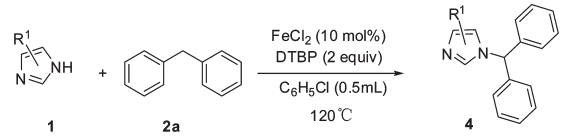
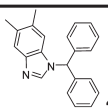
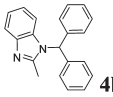
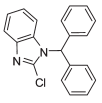
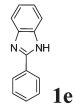
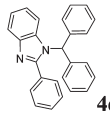
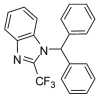
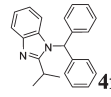
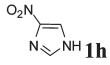
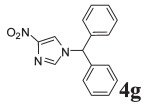
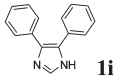
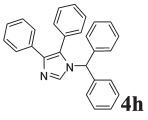
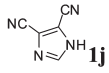
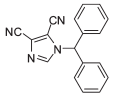
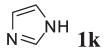
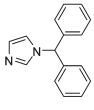
**Table 3. Reactions of Various Imidazoles with Diphenylmethane**[a]




1 2a 4

| entry | 1 | product | yield % |
|---|---|---|---|
| 1 |  1b |  4a | 48 |
| 2 |  1c |  4b | 83 |
| 3 |  1d |  4c | 80 |
| 4 |  1e |  4d | 84 |
| 5 |  1f |  4e | 80 |
| 6 |  1g |  4f | 71 |
| 7 |  1h |  4g | 70 |
| 8 |  1i |  4h | 48 |
| 9 |  1j |  4i | 95 |
| 10 |  1k |  4j | 0 |

[a] Reaction conditions: **1** (0.5 mmol), **2a** (3.0 mmol), $FeCl_2$ (0.05 mmol), DTBP (1.0 mmol), **1** 1.0 M in $C_6H_5Cl$, 120 °C, 24 h, under $N_2$.

(d, $J_{C-F}$ = 21.8 Hz), 115.9, 110.7, 62.9; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{20}H_{15}FN_2$ 302.1219, found 302.1212.

**1-(Phenyl(4-(trifluoromethyl)phenyl)methyl)-1*H*-benz[*d*]-imidazole (3g):** light yellow oil; yield 23%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 8.0 Hz, 1H), 7.62 (s, 1H), 7.60 (d, $J$ = 5.2 Hz, 2H), 7.39 (t, $J$ = 3.2 Hz, 3H), 7.40−7.10 (m, 7H), 6.79 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 142.3, 142.2, 137.0, 126.2, 133.8, 130.7 (q, $J_{C-F}$ = 32.5 Hz), 129.3, 129.0, 128.5, 128.3, 126.0 (q, $J_{C-F}$ = 3.5 Hz), 123.7 (q, $J_{C-F}$ = 270.6 Hz), 123.2, 122.7, 120.6, 110.5; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{21}H_{15}F_3N_2$ 352.1187, found 352.1188.

**1-((4-*tert*-Butylphenyl)(phenyl)methyl)-1*H*-benz[*d*]imidazole (3h):** white solid; yield 54%; mp 123−125 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (d, $J$ = 8.0 Hz, 1H), 7.64 (s, 1H), 7.40−7.35 (m, 5H), 7.28−7.09 (m, 7H), 6.74 (s, 1H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 151.6, 144.2, 142.7, 138.4, 135.0, 134.1, 128.9, 128.3, 128.0, 128.0, 125.9, 122.8, 122.3, 120.4, 110.8, 63.3, 34.6, 31.2; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{24}H_{24}N_2$ 340.1939, found 340.1938.

**1-(Biphenyl-4-yl(phenyl)methyl)-1*H*-benz[*d*]imidazole (3i):**[15] white solid; yield 83%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (d, $J$ = 7.6 Hz, 1H), 7.69 (s, 1H), 7.61−7.58 (m, 4H), 7.47−7.37 (m, 6H), 7.30−7.21 (m, 7H), 6.81 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.6, 141.4, 140.1, 138.0, 137.0, 129.1, 128.8, 128.6, 128.5, 128.2, 127.7, 127.1, 123.0, 122.4, 120.4, 110.8, 63.3.

**1-(1,2,3,4-Tetrahydronaphthalen-1-yl)-1*H*-benz[*d*]imidazole (3j):** light yellow oil; yield 53%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (d, $J$ = 8.0 Hz, 1H), 7.68 (s, 1H), 7.31−7.24 (m, 5H), 7.11 (t, $J$ = 8.0 Hz, 1H), 6.93 (d, $J$ = 7.6 Hz, 1H), 5.68 (t, $J$ = 6.2 Hz, 1H), 3.02−2.93 (m, 2H), 2.33−2.26 (m, 2H), 1.93−1.88 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 142.9, 137.8, 133.4, 133.1, 129.5, 128.8, 128.3, 126.7, 122.7, 122.1, 120.5, 110.4, 54.5, 30.1, 29.0, 19.9; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{17}H_{16}N_2$ 248.1313, found 248.1311.

**1-(2,3-Dihydro-1*H*-inden-1-yl)-1*H*-benz[*d*]imidazole (3k):** light yellow oil; yield 52%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (d, $J$ = 8.0 Hz, 1H), 7.77 (s, 1H), 7.41−7.33 (m, 2H), 7.30−7.18 (m, 4H), 7.11 (d, $J$ = 7.2 Hz,1H), 5.97 (t, $J$ = 7.2 Hz, 1H), 3.18−3.15 (m, 1H), 3.10−3.04 (m, 1H), 2.76−2.72 (m, 1H), 2.37−2.31 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 141.0, 140.7, 133.6, 129.0, 128.1, 125.9, 122.8, 122.2, 120.3, 110.6, 55.2, 21.6; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{16}H_{14}N_2$ 234.1157, found 234.1151.

**1-(1-Phenylethyl)-1*H*-benz[*d*]imidazole (3l):**[16] white solid; yield 31%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09 (s, 1H), 7.82 (d, $J$ = 8.4 Hz, 1H), 7.34−7.24 (m, 4H), 7.20−7.19 (m, 4H), 5.65−5.61 (m, 1H), 2.01 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.1, 141.0, 140.7, 133.6, 129.0, 128.1, 125.9, 122.8, 122.2, 120.3, 110.6, 55.2, 21.6.

**1-(1-Phenylpropyl)-1*H*-benz[*d*]imidazole (3m):** light yellow oil; yield 31%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.12 (s, 1H), 7.82 (d, $J$ = 7.6 Hz, 1H), 7.36−7.21 (m, 8H), 5.31 (t, $J$ = 7.6 Hz, 1H), 2.49−2.37 (m, 2H), 1.01 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 141.1, 139.5, 133.7, 128.9, 128.1, 126.5, 122.8, 122.2, 120.3, 110.5, 61.7, 27.9, 11.2; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{16}H_{16}N_2$ 236.1313, found 236.1316.

**1-(3,5-Dimethylbenzyl)-1*H*-benz[*d*]imidazole (3n):**[17] white solid; yield 41%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 (s, 1H), 7.86−7.84 (m, 1H), 7.34−7.27 (m, 3H), 6.96 (s, 1H), 6.82 (s, 2H), 5.28 (s, 2H), 2.28 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 143.2, 138.7, 135.3, 134.0, 129.9, 124.9, 123.0, 122.1, 120.3, 110.0, 48.7, 21.2.

**1-(4-Methylbenzyl)-1*H*-benz[*d*]imidazole (3o):**[17] white solid; yield 32%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (s, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.33−7.26 (m, 3H), 7.16 (d, $J$ = 8.4 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 5.31 (s, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 143.1, 138.1, 133.9, 132.3, 129.6, 127.1, 123.0, 122.2, 120.3, 110.0, 48.6, 21.1.

**1-(4-Chlorobenzyl)-1*H*-benz[*d*]imidazole (3p):**[17] light yellow oil; yield 23%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95 (s, 1H), 7.84 (d, $J$ = 7.2 Hz, 1H), 7.32−7.25 (m, 5H), 7.11 (d, $J$ = 8.0 Hz, 2H), 5.33 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 143.1, 134.1, 133.9, 133.7, 129.2, 128.3, 123.2, 122.4, 120.5, 109.9, 48.1.

**1-Benzyl-1*H*-benz[*d*]imidazole (3q):**[17] white solid; yield 45%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 (s, 1H), 7.86 (d, $J$ = 8.0 Hz, 1H), 7.35−7.26 (m, 6H), 7.18 (d, $J$ = 6.4 Hz, 2H), 5.34 (s, 2H); $^{13}$C NMR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(100 MHz, $CDCl_3$) $\delta$ 143.9, 143.2, 135.4, 133.9, 129.0, 128.2, 127.0, 123.1, 122.2, 120.4, 110.0, 48.8.

**1-Benzhydryl-5,6-dimethyl-1*H*-benz[*d*]imidazole (4a):** white solid; yield 48%; mp 253−255 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.55 (s, 1H), 7.46 (s, 1H), 7.33−7.31 (m, 6H), 7.11−7.09 (m, 4H), 6.89 (s, 1H), 6.67 (s, 1H), 2.31 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.6, 141.8, 138.3, 132.6, 132.1, 131.3, 128.9, 128.4, 128.2, 120.3, 110.7, 63.3, 20.5, 20.2; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{22}H_{20}N_2$ 312.1626, found 312.1625.

**1-Benzhydryl-2-methyl-1*H*-benz[d]imidazole (4b):** Yellow solid; yield 83%; Mp 141−142 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.70 (d, $J$ = 8.0 Hz, 1H), 7.34−7.13 (m, 11H), 6.95 (t, $J$ = 7.8 Hz, 1H), 6.87 (s, 1H), 6.59 (d, $J$ = 8.0 Hz, 1H), 2.53 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.3, 142.4, 137.7, 135.0, 128.8, 128.3, 128.2, 122.1, 121.8, 119.0, 111.8, 63.1, 15.1; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{21}H_{18}N_2$ 298.1470, found 298.1475.

**1-Benzhydryl-2-chloro-1*H*-benz[*d*]imidazole (4c):** white solid; yield 80%; mp 135−137 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 (d, $J$ = 8.4 Hz, 1H), 7.36−6.98 (m, 13H), 6.60 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.9, 141.3, 137.0, 134.7, 128.8, 128.4, 128.2, 123.0, 122.5, 119.5, 112.2, 63.9; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{20}H_{15}ClN_2$ 318.0924, found 318.0928.

**1-Benzhydryl-2-phenyl-1*H*-benz[*d*]imidazole (4d):** white solid; yield 84%; mp 184−186 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (d, $J$ = 8.0 Hz, 1H), 7.65 (d, $J$ = 7.2 Hz, 2H), 7.51−7.46 (m, 3H), 7.34−7.33 (m, 6H), 7.26−7.16 (m, 5H), 7.04−7.01 (m, 2H), 6.87 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 154.9, 143.5, 138.3, 134.8, 130.6, 129.9, 129.6, 128.7, 128.1, 128.0, 122.6, 122.2, 120.0, 113.4, 63.7; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{26}H_{20}N_2$ 360.1626, found 360.1621.

**1-Benzhydryl-2-(trifluoromethyl)-1*H*-benz[*d*]imidazole (4e):** white solid; yield 80%; mp 132−134 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 (d, $J$ = 8.4 Hz, 1H), 7.37−7.28 (m, 7H), 7.19−7.11 (m, 6H), 6.78 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.5, 141.3 (q, $J_{C-F}$ = 37.5 Hz), 137.1, 135.1, 128.8, 128.5, 128.0, 125.2, 123.4, 121.7, 119.3 (q, $J_{C-F}$ = 269.5 Hz), 114.0, 63.8; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{21}H_{15}F_3N_2$ 352.1187, found 352.1182.

**1-Benzhydryl-2-isopropyl-1*H*-benz[d]imidazole (4f):** yellow solid; yield 71%; mp 173−175 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.0 Hz, 1H), 7.35−7.16 (m, 11H), 7.00 (s, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 6.58 (d, $J$ = 8.4 Hz, 1H), 3.27 (m, 1H), 1.39 (d, $J$ = 6.4 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.5, 142.8, 138.1, 134.8, 128.8, 128.1, 121.9, 121.5, 119.4, 112.3, 62.3, 27.0, 21.9; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{23}H_{22}N_2$ 326.1783, found 326.1786.

**1-Benzhydryl-4-nitro-1*H*-imidazole (4g):** light yellow oil; yield 70%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.65 (d, $J$ = 1.6 Hz, 1H), 7.41−7.40 (m, 7H), 7.15−7.13 (m, 4H), 6.63 (s, 1H); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.31 (s, 1H), 7.92 (s, 1H), 7.43−7.39 (m, 6H), 7.24 (d, $J$ = 7.2 Hz, 4H), 7.03 (s, 1H) ;$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.8, 137.1, 136.2, 129.3, 129.1, 127.9, 119.6, 66.3; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{16}H_{13}N_3O_2$ 279.1008, found 279.1005.

**1-Benzhydryl-5-nitro-1*H*-imidazole (4g′):** light yellow oil; yield <5%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.23 (s, 1H), 7.49 (s, 1H), 7.44−7.35 (m, 7H), 7.18 (d, $J$ = 7.2 Hz, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 142.1, 139.2, 138.1, 134.4, 129.4, 128.9, 128.5, 64.7; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{16}H_{13}N_3O_2$ 279.1008, found 279.1010.

**1-Benzhydryl-4,5-diphenyl-1*H*-imidazole (4h):** white solid; yield 48%; mp 133−135 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.51 (d, $J$ = 7.2 Hz, 2H), 7.43−7.33 (m, 10H), 7.22−7.13 (m, 5H), 7.05−7.04 (m, 3H), 6.23(s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.2, 138.0, 136.4, 134.4, 131.1, 130.6, 129.2, 128.9, 128.8, 128.8, 128.2, 128.1, 128.1, 126.4, 126.3, 62.9; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{28}H_{22}N_2$ 386.1783, found 386.1790.

**1-Benzhydryl-1*H*-imidazole-4,5-dicarbonitrile (4i):** white solid; yield 95%; mp 128−130 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47−7.43 (m, 7H), 7.15−7.13 (m, 4H), 6.74 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.0, 135.5, 129.7, 129.6, 128.0, 123.6, 112.8, 111.5, 107.6, 66.5; HRMS (TOF MS EI$^+$) $m/z$ calcd for $C_{18}H_{12}N_4$ 284.1062, found 284.1065.

## ■ ASSOCIATED CONTENT

**Supporting Information.** $^1$H and $^{13}$C NMR spectra for **3a**−**q** and **4a**−**i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ NOTE ADDED AFTER ASAP PUBLICATION

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