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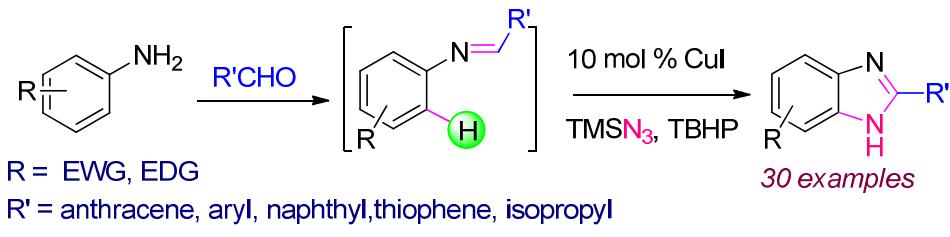
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# Copper(I)-Catalyzed Regioselective Amination of *N*-Aryl Imines Using TMSN<sub>3</sub> and TBHP: A Route to Substituted Benzimidazoles

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- one pot reaction
- broad substrate scope
- commercial starting material
- scalable

**ABSTRACT:** A novel and efficient copper-catalyzed amination of *N*-aryl imines is described. This, one-pot, multicomponent reaction, in which imine acts as a directing group by chelating to the metal center, affords a potential route for the transformation of the commercial aryl amines, aldehydes and azide into valuable benzimidazole structural units with wide substrate scope and diversity. The synthetic and mechanistic aspects are presented.

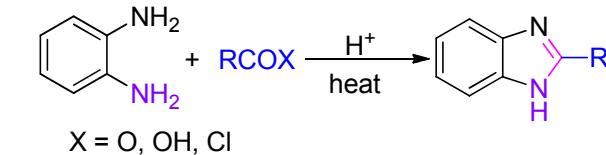
## INTRODUCTION

Transition-metal-catalyzed C-H functionalization directed by functional groups affords a powerful tool for the atom economical regioselective construction of carbon-carbon and carbon-heteroatom bonds.<sup>1</sup> For the most part, the second row transition-metals such as Ru<sup>2</sup>, Rh<sup>3</sup>, Pt<sup>4</sup> and Pd<sup>5</sup> have been studied. Few studies are focused on the copper-catalyzed systems,<sup>6</sup> which are particularly attractive

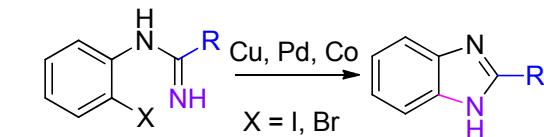
because of its high abundance and low toxicity. Herein, we report a novel one-pot multi-component copper-catalyzed imine chelated regioselective amination of *N*-aryl imines using trimethylsilyl azide ( $\text{TMNS}_3$ ) in the presence of *tert*-butyl hydroperoxide (TBHP) at moderate temperature (Scheme 1, e). This newly discovered reaction is simple, uses inexpensive copper catalyst and converts the readily available substrates into important benzimidazole core structures that tolerates an array of functional groups and substantial steric hindrance, via a sequential tandem condensation, C-H azidation and C-N bond formation.

**Scheme 1. The main strategies for benzimidazole syntheses.**

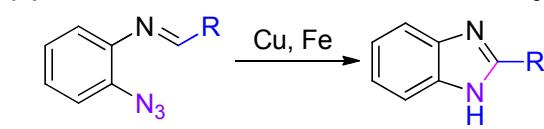
**(a) Condensation/oxidative cyclization**



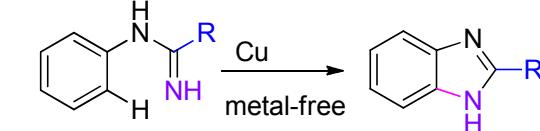
**(b) Cross-coupling reaction**



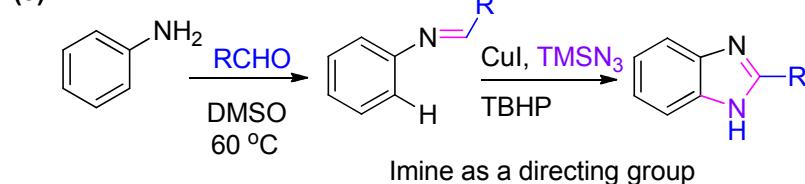
**(c) Lewis acid assisted intramolecular cyclization**



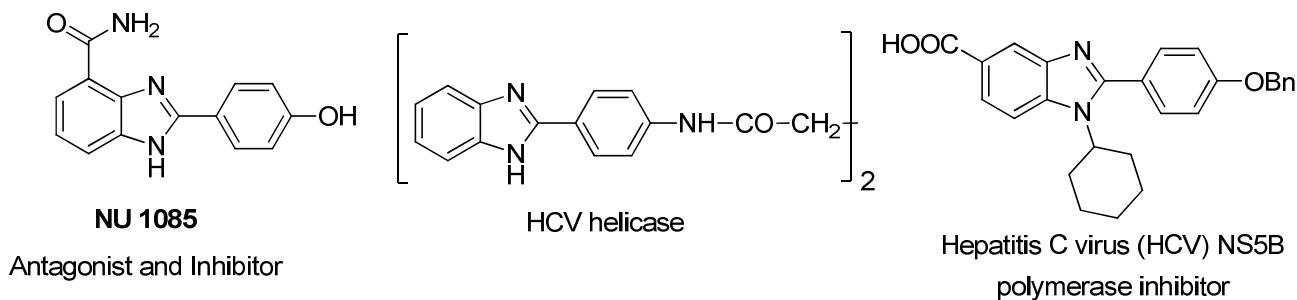
**(d) C-H functionalization**



**(e) This work**



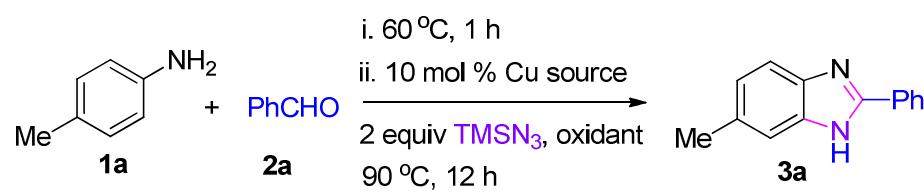
Benzimidazoles are an important class of compounds for the pharmaceutical industry.<sup>7,8</sup> The benzimidazole scaffold can be found in several commercial drugs such as Nexium, Attacand, Protonix, Prilosec, and Famvir as well as numerous experimental drug candidates (Figure 1). These structural frameworks are commonly made by condensation of 1,2-diaminoarenes with carboxylic acids or aldehydes followed by oxidative cyclization (Scheme 1, a).<sup>9</sup> However, these approaches often suffer due to limited substrate scope, and sometimes with the requirement of the strong acidic condition and high reaction temperature. Thus, an effort has been recently made on the development of new strategies to construct the benzimidazole structural motifs using C-N cross-coupling reaction of 2-haloarylamidines (Scheme 1, b),<sup>10</sup> intramolecular cyclization of 2-azido *N*-aryl imines (Scheme 1, c)<sup>11</sup> and the C-H functionalization of *N*-arylamidines (Scheme 1, d).<sup>12</sup> Hence, developing new ways to obtain benzimidazoles with structural diversity involving the direct C-H functionalization from the readily available simple substrates would be fascinating while challenging at the same time.



**Figure 1.** Examples of biologically important substituted 2-arylbenzimidazoles.

## RESULTS AND DISCUSSION

We commenced the optimization studies with *p*-toluidine **1a** and benzaldehyde **2a** as model substrates using a series of copper sources with different solvents, azides and oxidants (Table 1).

**Table 1. Optimization of the Reaction Conditions<sup>a</sup>**

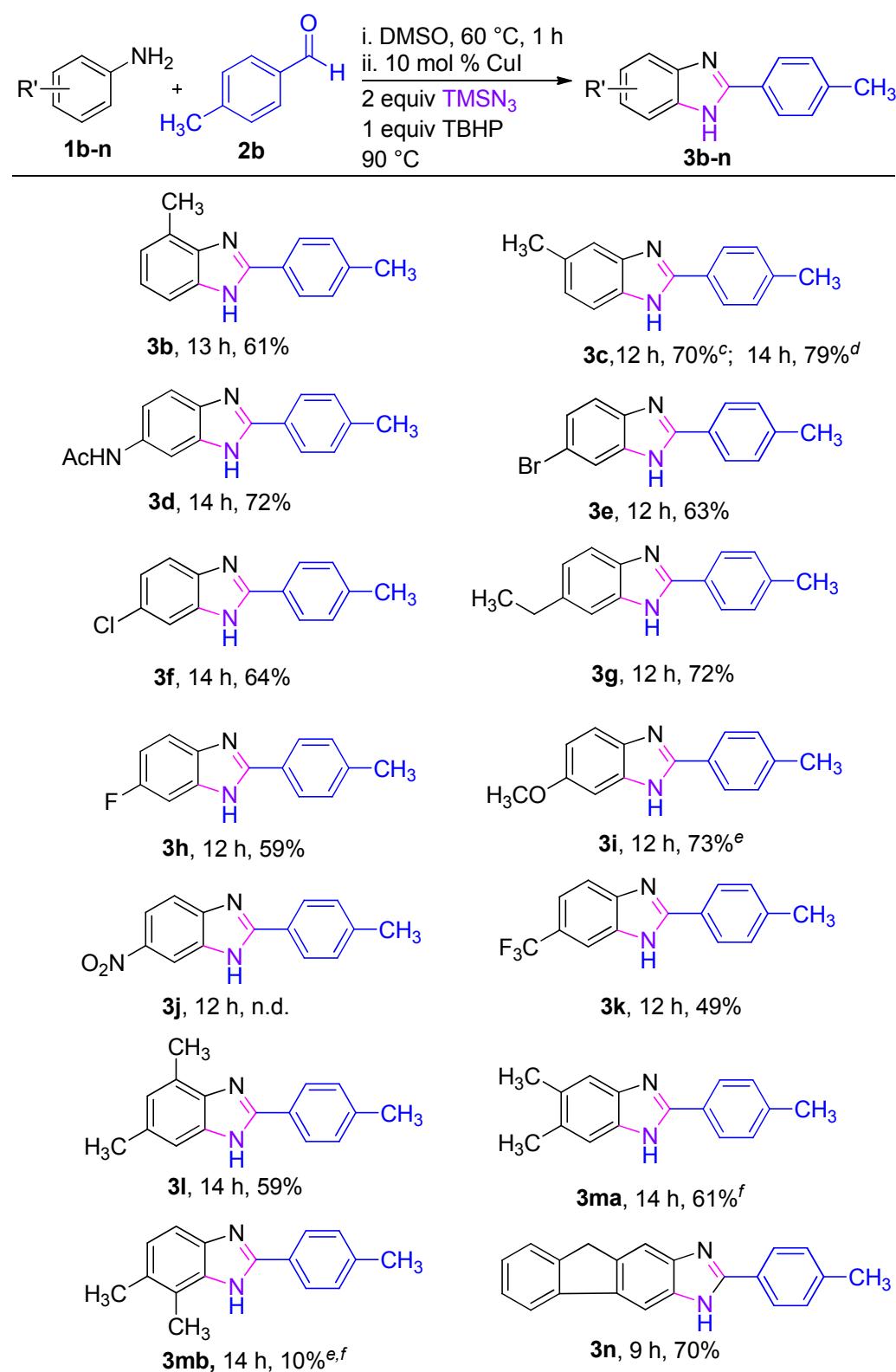
entry	[Cu] source	[N <sub>3</sub> ]	oxidant	solvent	yield (%) <sup>b</sup>
1	CuBr	TMSN <sub>3</sub>	TBHP	CH <sub>3</sub> CN	60
2	CuBr	TMSN <sub>3</sub>	TBHP	toluene	5
3	CuBr	TMSN <sub>3</sub>	TBHP	CH <sub>2</sub> Cl <sub>2</sub>	3
4	CuBr	TMSN <sub>3</sub>	TBHP	THF	3
5	CuBr	TMSN <sub>3</sub>	TBHP	DMF	16
6	CuBr	TMSN <sub>3</sub>	TBHP	DMSO	72
7	CuBr	TsN <sub>3</sub>	TBHP	DMSO	n.d.
8	CuBr	NaN <sub>3</sub>	TBHP	DMSO	n.d.
9	CuBr	TMSN <sub>3</sub>	30% H <sub>2</sub> O <sub>2</sub>	DMSO	n.d.
10	CuCl	TMSN <sub>3</sub>	TBHP	DMSO	40
11	CuI	TMSN <sub>3</sub>	TBHP	DMSO	77
12	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	TMSN <sub>3</sub>	TBHP	DMSO	66
13	CuCl <sub>2</sub>	TMSN <sub>3</sub>	TBHP	DMSO	63
14	CuBr <sub>2</sub>	TMSN <sub>3</sub>	TBHP	DMSO	64
15	Cu <sub>2</sub> O	TMSN <sub>3</sub>	TBHP	DMSO	10
16	Cu(OAc) <sub>2</sub>	TMSN <sub>3</sub>	TBHP	DMSO	68
17	CuI	TMSN <sub>3</sub>	TBHP	DMSO	56 <sup>c</sup>

1	18	CuI	TMSN <sub>3</sub>	TBHP	DMSO	59 <sup>d</sup>
2	19	CuI	TMSN <sub>3</sub>	TBHP	DMSO	61 <sup>e</sup>
3	20	-	TMSN <sub>3</sub>	TBHP	DMSO	n.d.
4	21	CuI	TMSN <sub>3</sub>	-	DMSO	n.d.

<sup>a</sup> Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), solvent (0.5 mL), 60 °C, 1 h; copper source (10 mol %), azide (1 mmol), TBHP (0.5 mmol), 90 °C, 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> 5 mol % CuI was used. <sup>d</sup> 0.75 mmol TMSN<sub>3</sub> was used. <sup>e</sup> 0.25 mmol TBHP was used. n.d. = not detected.

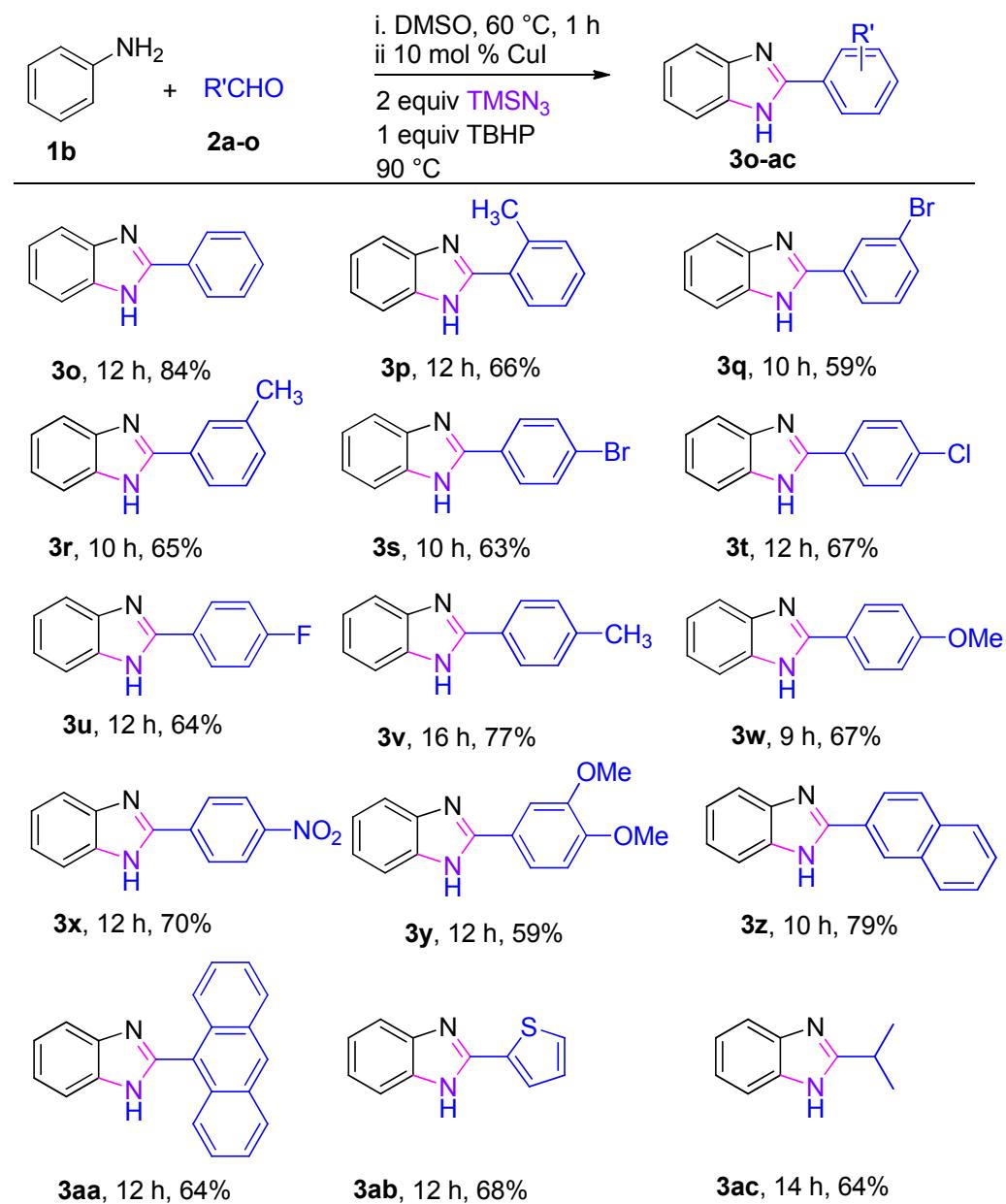
Gratifyingly, the reaction took place to give 2-phenylbenzimidazole **3a** in 60% yield when the substrates **1a** (1 equiv) and **2a** (1.2 equiv) were stirred at 60 °C for 1 h to give an imine intermediate that was reacted with CuBr (10 mol %), TMSN<sub>3</sub> (2 equiv) and TBHP (1 equiv) at 90 °C for 12 h in CH<sub>3</sub>CN (entry 1). The use of DMSO as a solvent led to an increase the product yield to 72%, whereas solvents such as DMF, CH<sub>2</sub>Cl<sub>2</sub>, THF and toluene gave inferior results (entries 2-6). Azides such as NaN<sub>3</sub> and TsN<sub>3</sub>, and oxidant, 30% H<sub>2</sub>O<sub>2</sub>, failed to react (entries 7-9). Subsequent screening of the copper sources revealed that CuI exhibited superior results, leading to **3a** in 77% yield, while CuCl, CuBr<sub>2</sub>, CuCl<sub>2</sub>, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, Cu(OAc)<sub>2</sub> and Cu<sub>2</sub>O afforded the target molecule in <68% yield (entries 10-16). Lowering the amount of the Cu-source (5 mol %), TBHP (0.5 equiv) or TMSN<sub>3</sub> (1.5 equiv) led to the formation of **3a** in <61% yield (entry 17-19). Control experiment confirmed that, in the absence of either the Cu-source or TBHP, the formation of **3a** was not observed (entries 20-21).

Having the optimal condition in hand, the scope of the protocol was investigated for the reaction of a series of substituted anilines and 2-aminofluorene with tolualdehyde **2b** as representative

**Table 2. Reaction of Aryl Amines with Tolualdehyde<sup>a</sup>**

<sup>a</sup> Reaction conditions: amine **1b-n** (1 mmol), aldehyde **2b** (1.2 mmol), DMSO (1 mL), 60 °C, 1 h; CuI (10 mol %), TMSN<sub>3</sub> (2 mmol), TBHP (1 mmol) and 90 °C. <sup>b</sup> Isolated yield. <sup>c</sup> 3-Methylaniline was used. <sup>d</sup> 4-Methylaniline was used. <sup>e</sup> Two tautomers were observed in nearly 1:1 ratios by <sup>1</sup>H NMR. <sup>f</sup> Obtained as a 1:6 mixture.

**Table 3. Reaction of Aniline with Various Aldehydes<sup>a</sup>**



<sup>1</sup> Reaction conditions: aniline **1b** (1 mmol), aldehyde **2a-o** (1.2 mmol), DMSO (1 mL), 60 °C, 1 h;  
<sup>2</sup> CuI (10 mol %), TMSN<sub>3</sub> (2 mmol), TBHP (1 mmol) and 90 °C. <sup>b</sup> Isolated yield.

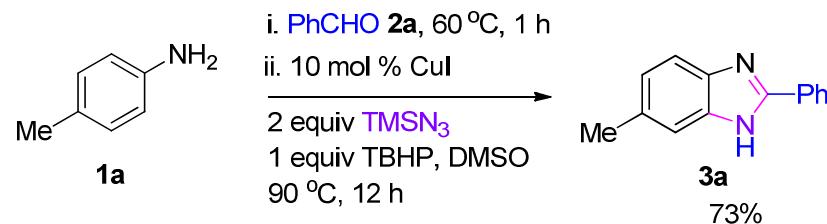
<sup>3</sup> example (Table 2). Aniline bearing electron donating and electron withdrawing substituents readily  
<sup>4</sup> proceeded reaction, and a substituent at 2-position had little effect on the yield. Reaction of 2-methyl  
<sup>5</sup> aniline gave benzimidazole **3b** in 61% yield, while 3-methyl aniline underwent reaction to afford the  
<sup>6</sup> desired **3c** in 70% yield. The reactions of anilines having 4-acetamide, 4-bromo, 4-chloro, 4-ethyl, 4-  
<sup>7</sup> fluoro, 4-methyl, 4-methoxy and 4-trifluoromethyl groups produced the corresponding  
<sup>8</sup> benzimidazoles **3c-i** and **3k** in 49-73% yields. In contrast, in aniline with a strong electron  
<sup>9</sup> withdrawing group, 4-nitro, failed to react, which suggests that the electronic nature of the aryl ring  
<sup>10</sup> is crucial for the reaction. The reaction conditions are also effective for disubstituted substrates. 2,4-  
<sup>11</sup> Dimethylaniline underwent reaction to furnish benzimidazole **3l** in 59% yield, while the reaction of  
<sup>12</sup> 3,4-dimethylaniline led to the formation of a 1:6 mixture of **3ma** and **3mb** in 71% yield, which can  
<sup>13</sup> be easily separated by column chromatography. In addition, 2-aminofluorene readily underwent  
<sup>14</sup> reaction to afford the target product **3n** in 70% yield. Recrystallization of **3e** yielded single crystals  
<sup>15</sup> whose structure was confirmed by X-ray analysis (see Supporting Information). Benzimidazoles **3i**  
<sup>16</sup> and **3mb** produced nearly a 1:1 mixture of tautomers.<sup>11a,18</sup>

<sup>17</sup> Next, we applied the protocol for the reactions of aldehydes with aniline **1b** as a standard  
<sup>18</sup> substrate (Table 3). The reaction of benzaldehyde **1a** produced benzimidazole **3o** in 84% yield.  
<sup>19</sup> Substituted aromatic aldehydes with electron donating and electron withdrawing groups, 2-methyl,  
<sup>20</sup> 3-bromo, 3-methyl, 4-bromo, 4-chloro, 4-fluoro, 4-methoxy, 4-methyl and 4-nitro substituents,  
<sup>21</sup> underwent reaction to give the corresponding benzimidazoles **3p-x** in 59-77% yields. The reaction of  
<sup>22</sup> 3,4-dimethoxybenzaldehyde afforded **3y** in 59% yield, while 2-naphthaldehyde underwent reaction  
<sup>23</sup> to furnish **3z** in 79% yield. Anthracene-9-carbaldehyde underwent reaction to provide the substituted  
<sup>24</sup> benzimidazole **3aa** in 70% yield. The reaction of 2,4-diformylphenylhydrazine with aniline **1b** provided  
<sup>25</sup> the corresponding benzimidazole **3ab** in 70% yield. The reaction of 2-formylbenzaldehyde with aniline  
<sup>26</sup> **1b** provided the corresponding benzimidazole **3ac** in 70% yield. The reaction of 2-formylbenzylamine  
<sup>27</sup> with aniline **1b** provided the corresponding benzimidazole **3ad** in 70% yield. The reaction of 2-formyl-4-  
<sup>28</sup> methoxyphenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3ae** in 70% yield.  
<sup>29</sup> The reaction of 2-formyl-4-methoxyphenylhydrazine with aniline **1b** provided the corresponding  
<sup>30</sup> benzimidazole **3af** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided  
<sup>31</sup> the corresponding benzimidazole **3ag** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine  
<sup>32</sup> with aniline **1b** provided the corresponding benzimidazole **3ah** in 70% yield. The reaction of 2-formyl-4-  
<sup>33</sup> nitrophenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3ai** in 70% yield.  
<sup>34</sup> The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided the corresponding  
<sup>35</sup> benzimidazole **3aj** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided  
<sup>36</sup> the corresponding benzimidazole **3ak** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine  
<sup>37</sup> with aniline **1b** provided the corresponding benzimidazole **3al** in 70% yield. The reaction of 2-formyl-4-  
<sup>38</sup> nitrophenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3am** in 70% yield.  
<sup>39</sup> The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided the corresponding  
<sup>40</sup> benzimidazole **3an** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided  
<sup>41</sup> the corresponding benzimidazole **3ao** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine  
<sup>42</sup> with aniline **1b** provided the corresponding benzimidazole **3ap** in 70% yield. The reaction of 2-formyl-4-  
<sup>43</sup> nitrophenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3aq** in 70% yield.  
<sup>44</sup> The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided the corresponding  
<sup>45</sup> benzimidazole **3ar** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided  
<sup>46</sup> the corresponding benzimidazole **3as** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine  
<sup>47</sup> with aniline **1b** provided the corresponding benzimidazole **3at** in 70% yield. The reaction of 2-formyl-4-  
<sup>48</sup> nitrophenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3au** in 70% yield.  
<sup>49</sup> The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided the corresponding  
<sup>50</sup> benzimidazole **3av** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided  
<sup>51</sup> the corresponding benzimidazole **3aw** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine  
<sup>52</sup> with aniline **1b** provided the corresponding benzimidazole **3ax** in 70% yield. The reaction of 2-formyl-4-  
<sup>53</sup> nitrophenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3ay** in 70% yield.  
<sup>54</sup> The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided the corresponding  
<sup>55</sup> benzimidazole **3az** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided  
<sup>56</sup> the corresponding benzimidazole **3ba** in 70% yield. The reaction of 2-formyl-4-nitrophenylhydrazine  
<sup>57</sup> with aniline **1b** provided the corresponding benzimidazole **3bb** in 70% yield. The reaction of 2-formyl-4-  
<sup>58</sup> nitrophenylhydrazine with aniline **1b** provided the corresponding benzimidazole **3bc** in 70% yield.  
<sup>59</sup> The reaction of 2-formyl-4-nitrophenylhydrazine with aniline **1b** provided the corresponding  
<sup>60</sup> benzimidazole **3bd** in 70% yield.

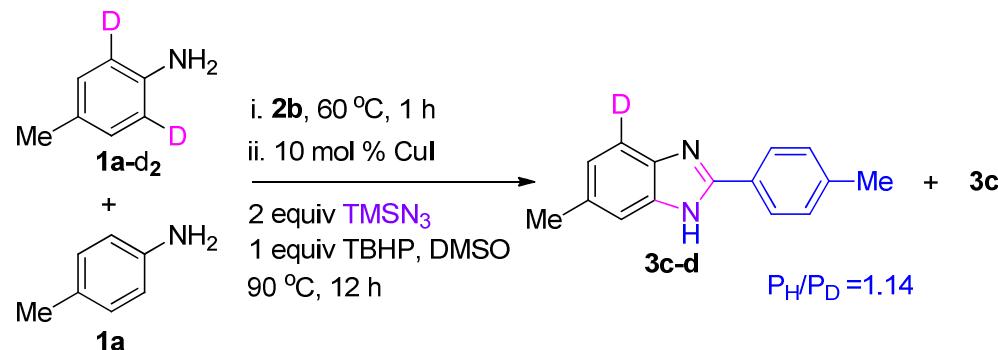
benzimidazole **3aa** in 64% yield. The reaction of the heterocyclic aldehyde, thiophene-2-aldehyde, occurred to afford the target product **3ab** in 68% yield. In addition, an aliphatic aldehyde, isobutyraldehyde, underwent reaction to give 2-isopropylbenzimidazole **3ac** in 64% yield.

Finally, the scale up of the procedure was investigated using **1a** and **2a** as representative examples (Scheme 2). The reaction was efficient and the target product was obtained in 73% yield. To insight into the reaction pathway, an intermolecular kinetic isotope experiment between equimolar amounts of **1a-d<sub>2</sub>** and **2b** was performed (Scheme 3). At 1 h with 23% conversion, the

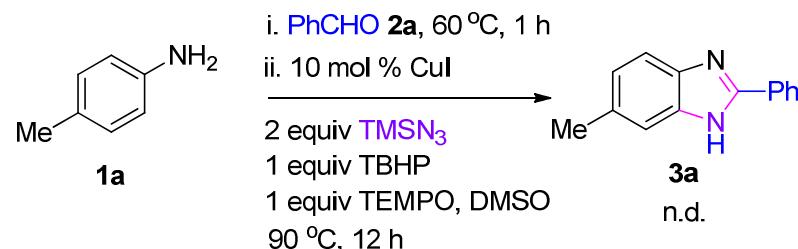
### Scheme 2. Gram Scale Synthesis

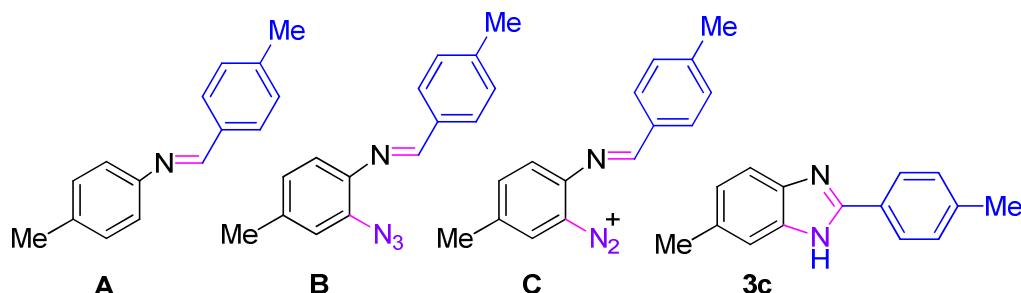


### Scheme 3. Kinetic Isotope Experiment



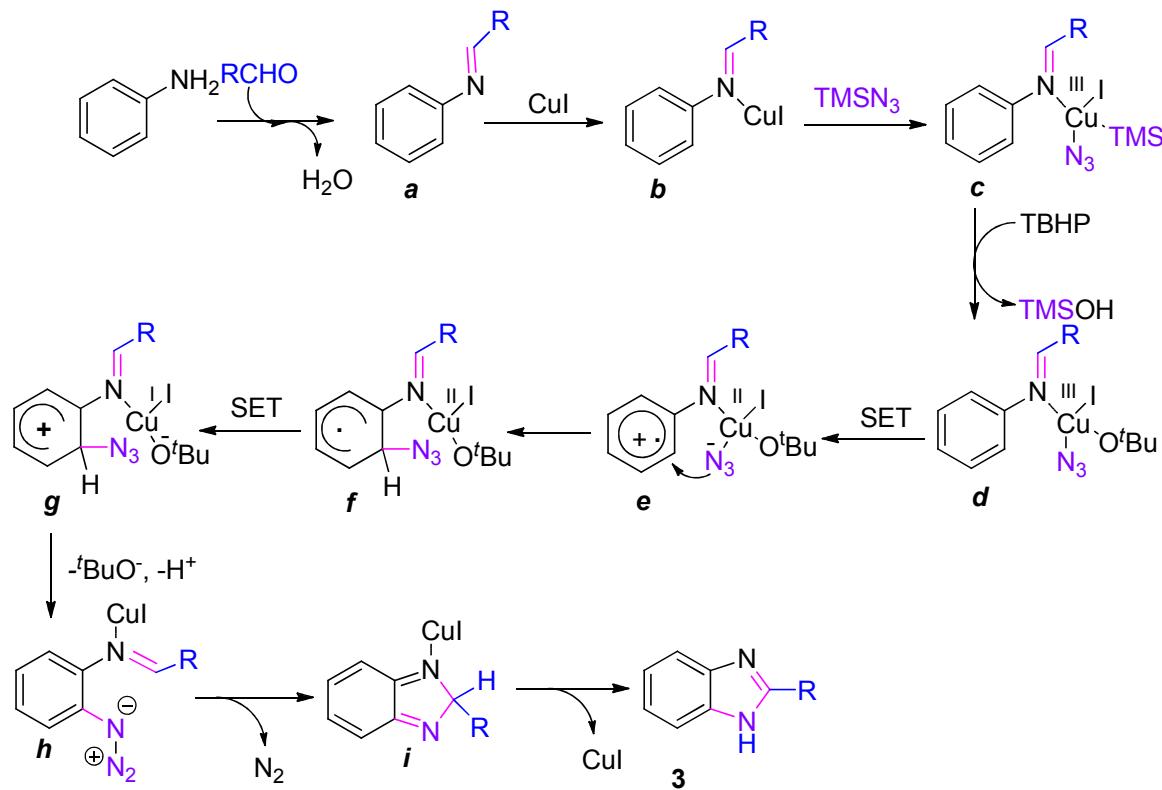
### Scheme 4. Radical Scavenger Experiment





**Figure 2.** Major species identified using ESI-MS of the reaction mixture of **1a**, **2b** and  $\text{TMSN}_3$  after 3 h (see Supporting Information).<sup>6k</sup>

**Scheme 5. Proposed Reaction Pathway**



reaction afforded  $P_{\text{H}}/P_{\text{D}} = 1.14$ , which suggests that the C-H bond cleavage is not involved in the product determining step.<sup>13</sup> In addition, the radical scavenger experiment using TEMPO exhibited no reaction, which suggests that the reaction involves a radical intermediate (Scheme 4).<sup>14</sup> Furthermore, the ESI-MS analyses of the reaction mixture of **1a**, **2b** and  $\text{TMSN}_3$  after 3 h revealed the presence of

1 four major species **A**, **B**, **C** and **3a** (Figure 2).<sup>6i,k</sup> Thus, the condensation of aldehyde with amine can  
2 give *N*-aryl imine **a** that may undergo chelation with CuI to afford **b**. Oxidative addition of **b** with  
3 TMSN<sub>3</sub> can produce **c** that can react with TBHP to afford **d**. The latter can convert into copper(II)  
4 species **e** by a single electron transfer (SET).<sup>6a,f,h</sup> Intramolecular N<sub>3</sub> transfer to aryl cation radical can  
5 give **f** that may lead to the formation of **h** via aryl cation **g** by SET. Cyclization of **h** may give **i** that  
6 can furnish the target product **3** by tautomerization to complete the catalytic cycle.  
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## CONCLUSIONS

19 In summary, we have found that copper(I)-catalyzed imine directed amination of *N*-aryl imines  
20 proceeds smoothly to afford substituted benzimidazoles. The use of inexpensive copper catalysts, the  
21 commercially available starting material and the broad substrate scope are significant practical  
22 advantages. The tolerance of the functional groups is a synthetically useful feature.  
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## EXPERIMENTAL SECTION

32 **General Information:** Cu(OAc)<sub>2</sub> (99%), CuCl<sub>2</sub> (99%), CuI (98%), CuBr (97%), CuCl (90%), Cu<sub>2</sub>O  
33 (97%), TMSN<sub>3</sub> (95%) and TBHP (98%, 5.5 M in decane) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (98%) were  
34 purchased from commercial sources. The solvents were purchased and dried according to standard  
35 procedure prior to use.<sup>15</sup> Purification of the reaction products was carried out by column  
36 chromatography using silica gel (60-120 mesh). Analytical TLC was performed on silica gel G/GF  
37 254 plate. NMR spectra were recorded on DRX-400 and 600 MHz using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as  
38 solvents and Me<sub>4</sub>Si as internal standard. Chemical shifts ( $\delta$ ) were reported in ppm and spin-spin  
39 coupling constants ( $J$ ) were given in Hz. Melting points were determined using melting point  
40 apparatus and are uncorrected. FT-IR spectra were recorded using IR spectrometer. Mass spectra  
41 were recorded on a Q-Tof ESI-MS Instrument. X-Ray data were collected with a CCD area detector  
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1 using Mo/K $\alpha$  radiation. The structures were solved by direct method using SHELLX-97 (Göttingen,  
2  
3 Germany).  
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5

6 **General Procedure for Amination of N-Aryl Imines.** Aniline **1**(1.0 mmol) and benzaldehyde **2**  
7 (1.2 mmol) were stirred at 60 °C for 1 h in DMSO (1 mL) under air. The mixture was then cooled to  
8 room temperature and treated with CuI (10 mol %, 0.1 mmol, 19 mg), TMSN<sub>3</sub> (2 equiv, 2.0 mmol,  
9 230 mg) and TBHP (1 equiv, 1 mmol, 181 $\mu$ L). The resultant mixture was stirred at 90 °C for the  
10 appropriate time (Table 1 and 2). The progress of the reaction was monitored by TLC using ethyl  
11 acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and was  
12 extracted with ethyl acetate (3 x 10 mL) and washed with brine (2 x 5 mL) and water (2 x 5 mL).  
13 The solution was dried over Na<sub>2</sub>SO<sub>4</sub>, passed through a short pad of celite and evaporated on a rotary  
14 evaporator to give a residue that was purified on silica gel column chromatography using n-hexane  
15 and ethyl acetate as eluent.  
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18 **6-Methyl-2-phenyl-1H-benzo[d]imidazole 3a.**<sup>11a</sup> Analytical TLC on silica gel, 1:3 ethyl  
19 acetate/hexane R<sub>f</sub> = 0.41; pale yellow solid; 160 mg, yield 77%; mp 243-244 °C; <sup>1</sup>H NMR (400  
20 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.77 (br s, 1H), 8.17 (d, J = 7.2 Hz, 2H), 7.55-7.32 (m, 5H), 7.05-7.00 (m, 1H),  
21 2.43 (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>)  $\delta$  150.9, 144.2, 142.0, 135.3, 133.1, 131.9, 130.7,  
22 126.1, 123.3, 118.5, 111.1, 21.4; FT-IR (KBr) 3447, 3047, 2920, 2110, 1632, 1595, 1460, 1403,  
23 1313, 1272, 1108, 969, 801, 699 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>H 209.1079,  
24 found 209.1073.  
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27 **4-Methyl-2-(*p*-tolyl)-1H-benzo[d]imidazole 3b.** Analytical TLC on silica gel, 1:3 ethyl  
28 acetate/hexane R<sub>f</sub> = 0.41; liquid; 135 mg, yield 61%; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.74 (br s,  
29 1H), 8.10 (s, 2H), 7.36 (d, J = 7.8 Hz, 3H), 7.08 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 6.6 Hz, 1H), 2.56 (s,  
30 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 140.5, 129.9, 127.4, 126.7, 123.6, 123.0,  
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1           21.6, 17.2; FT-IR (neat) 3402, 3029, 2917, 2115, 1620, 1504, 1485, 1439, 1373, 1285, 1117, 958,  
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3           827, 748 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>H 223.1235, found 223.1234.  
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7           **5-Methyl-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3c.** Analytical TLC on silica gel, 1:3 ethyl  
8           acetate/hexane R<sub>f</sub> = 0.41; white solid; 155 mg, yield 70% (using 3-methylaniline) and 175 mg, yield  
9           79% (using 4-methyl aniline); mp 163-164 °C; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ 12.62 (br s, 1H),  
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11           8.02 (s, 2H), 7.48-7.32 (m, 4H), 7.05-6.98 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (150 MHz,  
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13           DMSO-d<sub>6</sub>) δ 152.5, 140.3, 139.2, 138.0, 132.7, 129.9, 127.5, 126.9, 124.4, 115.2, 114.6, 21.8, 21.5;  
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15           FT-IR (KBr) 3440, 2922, 2852, 1627, 1449, 1385, 1284, 1225, 1109, 1026, 922, 804, 741 cm<sup>-1</sup>.  
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17           HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>H 223.1235, found 223.1230.  
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21           **N-(2-(*p*-tolyl)-1*H*-benzo[*d*]imidazol-6-yl)acetamide 3d.** Analytical TLC on silica gel, 1:2 ethyl  
22           acetate/hexane R<sub>f</sub> = 0.41; pale yellow solid; 191 mg, yield 72%; mp 273-274 °C; <sup>1</sup>H NMR (400  
23  
24           MHz, DMSO-d<sub>6</sub>) δ 12.69 (br s, 1H), 9.97 (br s, 1H), 8.09 (d, J = 7.2 Hz, 1H), 8.03 (d, J = 8.0 Hz,  
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26           2H), 7.51 (s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.20 (s, 1H), 2.36 (s, 3H), 2.07 (s, 3H); <sup>13</sup>C NMR (150  
27  
28           MHz, DMSO-d<sub>6</sub>) δ 167.9, 139.3, 134.6, 129.5, 127.5, 126.1, 118.4, 114.3, 101.5, 24.0, 20.9; FT-IR  
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30           (KBr) 3439, 3200, 2920, 2854, 1671, 1609, 1563, 1456, 1391, 1272, 1156, 1033, 824, 715 cm<sup>-1</sup>.  
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32           HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>OH 266.1293, found 266.1297.  
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40           **6-Bromo-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3e.**<sup>16</sup> Analytical TLC on silica gel, 1:3 ethyl  
41           acetate/hexane R<sub>f</sub> = 0.41; white solid; 180 mg, yield 63%; mp 232-233 °C; <sup>1</sup>H NMR (400 MHz,  
42  
43           DMSO-d<sub>6</sub>) δ 13.03 (br s, 1H), 8.06 (d, J = 7.6 Hz, 2H), 7.77 (s, 1H), 7.52 (s, 1H), 7.37 (d, J = 6.8  
44  
45           Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 2.38 (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub> + CDCl<sub>3</sub>) δ 152.0,  
46  
47           139.1, 128.4, 126.1, 125.7, 125.6, 123.8, 20.3; FT-IR (KBr) 3449, 3015, 2917, 2110, 1620, 1448,  
48  
49           1378, 1303, 1275, 1112, 1015, 911, 823, 729 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for  
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51           C<sub>14</sub>H<sub>11</sub>BrN<sub>2</sub>H 287.0184, found 287.0191.  
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**6-Chloro-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3f.** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f = 0.41$ ; white solid; 155 mg, yield 64%; mp 234-235 °C;  $^1\text{H}$  NMR (600 MHz, DMSO-d<sub>6</sub>) δ 13.01 (br s, 1H), 8.06 (d,  $J = 7.8$  Hz, 2H), 7.69-7.65 (m, 1H), 7.53 (d,  $J = 9.0$  Hz, 1H), 7.37 (d,  $J = 8.4$  Hz, 2H), 7.21 (s, 1H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz, DMSO-d<sub>6</sub> + CDCl<sub>3</sub>) δ 152.1, 139.0, 128.3, 126.1, 125.9, 125.6, 121.2, 20.2; FT-IR (KBr) 3435, 2922, 2857, 2110, 1620, 1583, 1439, 1378, 1308, 1275, 1219, 1061, 963, 809, 725 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>2</sub>H 243.0689, found 243.0691.

**6-Ethyl-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3g.** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f = 0.41$ ; liquid; 170 mg, yield 72%;  $^1\text{H}$  NMR (600 MHz, DMSO-d<sub>6</sub>) δ 12.66 (br s, 1H), 8.04 (d,  $J = 8.4$  Hz, 2H), 7.53 (d,  $J = 7.2$  Hz, 1H), 7.45 (s, 1H), 7.35 (d,  $J = 8.4$  Hz, 2H), 7.06-7.04 (m, 1H), 2.71 (s, 2H), 2.37 (s, 3H), 1.26-1.22 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>) δ 152.8, 140.2, 139.3, 129.8, 127.5, 123.3, 115.2, 113.5, 29.2, 21.4, 16.4; FT-IR (neat) 3417, 2962, 2925, 2859, 2103, 165, 1559, 1493, 1449, 1389, 1324, 1378, 1186, 1120, 1019, 965, 821, 728 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>H 237.1392, found 237.1399.

**6-Fluoro-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3h.** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f = 0.41$ ; white solid; 134 mg, yield 59%; mp 231-232 °C;  $^1\text{H}$  NMR (600 MHz, DMSO-d<sub>6</sub>) δ 12.94 (br s, 1H), 8.05 (d,  $J = 7.8$  Hz, 2H), 7.63 (s, 1H), 7.50 (s, 1H), 7.37 (d,  $J = 7.8$  Hz, 2H), 7.04 (s, 1H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz, DMSO-d<sub>6</sub>) δ 140.4, 130.1, 127.6, 126.9, 112.3, 110.7, 110.3, 21.8; FT-IR (KBr) 3058, 2855, 2752, 2113, 1901, 1734, 1653, 1630, 1595, 1577, 1497, 1443, 1422, 1365, 1309, 1220, 1141, 1022, 824, 727 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>11</sub>FN<sub>2</sub>H 227.0985, found 227.0990.

**6-Methoxy-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3i.** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f = 0.41$ ; liquid; 174 mg, yield 73%; mixture of tautomers (1:1);  $^1\text{H}$  NMR (600

1 MHz, DMSO-d<sub>6</sub>) δ 12.65 (br s, 2H), 8.02 (s, 4H), 7.52 (s, 1H), 7.38 (s, 1H), 7.33 (s, 4H), 7.18 (s,  
2 1H), 6.97 (s, 1H), 6.81 (s, 2H), 3.87 (s, 6H), 2.37 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.8,  
3 152.2, 140.3, 129.9, 127.4, 126.6, 116.2, 112.5, 97.8, 56.0, 21.6; FT-IR (neat) 3430, 2927, 2857,  
4 2110, 1630, 1597, 1453, 1425, 1392, 1266, 1201, 1159, 1107, 1033, 949, 823, 729 cm<sup>-1</sup>. HRMS  
5 (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>OH 239.1184, found 239.1189.

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14 **2-(*p*-Tolyl)-6-(trifluoromethyl)-1*H*-benzo[d]imidazole 3k.**<sup>17</sup> Analytical TLC on silica gel, 1:3  
15 ethyl acetate/hexane R<sub>f</sub> = 0.31; white solid; 135 mg, yield 49%; mp 192-193 °C; <sup>1</sup>H NMR (400  
16 MHz, DMSO-d<sub>6</sub>) δ 13.28 (br s, 2H), 8.10 (d, J = 7.6 Hz, 2H), 7.84-7.81 (m, 1H), 7.72 (d, J = 8.8 Hz,  
17 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-  
18 d<sub>6</sub>) δ 153.9, 140.2, 129.6, 126.7, 119.0; FT-IR (KBr) 3464, 3124, 2924, 1889, 1615, 1562, 1509,  
19 1427, 1329, 1239, 1218, 1055, 1022, 936, 826, 728 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for  
20 C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>F<sub>3</sub>H 277.0953, found 277.0961.

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31 **4,6-Dimethyl-2-(*p*-tolyl)-1*H*-benzo[d]imidazole 3l.** Analytical TLC on silica gel, 1:3 ethyl  
32 acetate/hexane R<sub>f</sub> = 0.41; liquid; 140 mg, yield 59%; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ 12.57 (br s,  
33 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.15 (s, 1H), 6.81 (s, 1H), 2.52 (s, 3H), 2.38  
34 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 151.4, 140.2, 132.8, 129.9, 127.6, 126.7, 125.2, 21.8, 21.6,  
35 17.2; FT-IR (neat) 3444, 2917, 2857, 1901, 1630, 1593, 1429, 1387, 1257, 1182, 1033, 958, 827,  
36 725 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>H 237.1392, found 237.1392.

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46 **5,6-Dimethyl-2-(*p*-tolyl)-1*H*-benzo[d]imidazole 3ma.** Analytical TLC on silica gel, 1:3 ethyl  
47 acetate/hexane R<sub>f</sub> = 0.41; white solid; 144 mg, yield 61%; mp 233-224 °C; <sup>1</sup>H NMR (600 MHz,  
48 DMSO-d<sub>6</sub>) δ 12.52 (br s, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.40 (s, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.26  
49 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 150.5, 142.5,  
50 139.1, 133.4, 130.8, 129.4, 129.1, 127.7, 126.1, 118.8, 111.2, 20.9, 20.0; FT-IR (KBr) 3435, 3015,

2917, 2087, 1900, 1625, 1588, 1499, 1448, 1387, 1308, 1289, 1121, 1308, 1121, 1005, 827, 720 cm<sup>-1</sup>

<sup>1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>H 237.1392, found 237.1390.

**6,7-dimethyl-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole 3mb.** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R<sub>f</sub> = 0.31; yellow solid; 24 mg, yield 10%; mp 190-191 °C; mixture of tautomers (1:1); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.64 (br s, 1H), 12.30 (br s, 1H), 8.16 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 7.6 Hz, 2H), 7.38-7.36 (m, 5H), 7.24 (d, J = 8.0 Hz, 1H), 7.03-7.00 (m, 2H), 2.53 (s, 6H), 2.40 (s, 6H), 2.36 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 151.3, 140.2, 132.0, 129.9, 127.5, 126.7, 126.5, 21.6, 20.6; FT-IR (KBr) 3596, 2919, 2102, 1625, 1503, 1437, 1384, 1310, 1260, 1122, 1019, 958, 827, 727 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>H 237.1392, found 237.1399.

**2-(*p*-tolyl)-3,9-dihydrofluoreno[2,3-d]imidazole 3n.** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R<sub>f</sub> = 0.41; thick brown gummy liquid; 207 mg, yield 70%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.91 (br s, 1H), 8.11 (s, 1H), 8.07 (d, J = 7.2 Hz, 2H), 7.94 (s, 1H), 7.79-7.68 (m, 1H), 7.55 (s, 1H), 7.37 (d, J = 7.2 Hz, 3H), 7.27 (s, 1H), 3.98 (s, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 151.6, 142.4, 139.5, 139.4, 129.5, 127.5, 126.7, 126.4, 126.3, 125.1, 125.0, 57.9, 20.9; FT-IR (neat) 3435, 2924, 2257, 1644, 1431, 1382, 1272, 1047, 1030, 998, 826, 764 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>H 297.1392, found 297.1393.

**2-Phenyl-1*H*-benzo[*d*]imidazole 3o.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R<sub>f</sub> = 0.41; pale yellow solid; 163 mg, yield 84%; mp 292-293 °C; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ 12.92 (br s, 1H), 8.18 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 7.2 Hz, 1H), 7.56-7.49 (m, 4H), 7.22-7.19 (m, 2H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 151.3, 143.8, 135.0, 130.2, 129.9, 129.0, 126.5, 122.6, 121.8, 118.2, 111.4; FT-IR (KBr) 3442, 2961, 2919, 2112, 1565, 1440, 1360, 1283, 1120, 1088, 995, 893, 743 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>H 195.0922, found 195.0922.

1           **2-(*o*-tolyl)-1*H*-benzo[*d*]imidazole 3p.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f$  =  
2           0.41; white solid; 137 mg, yield 66%; mp 223-224 °C; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ 12.62 (br s,  
3           1H), 7.73 (d,  $J$  = 7.2 Hz, 1H), 7.67 (s, 1H), 7.53 (s, 1H), 7.41-7.35 (m, 3H), 7.21 (s, 2H), 2.59 (s,  
4           3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 152.0, 143.7, 137.0, 131.3, 130.1, 129.5, 129.4, 126.0,  
5           122.4, 121.5, 119.0, 111.3, 21.0; FT-IR (KBr) 3440, 3048, 2973, 2721, 1938, 1619, 1597, 1448,  
6           1406, 1369, 1275, 1229, 1047, 972, 879 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>H  
7           209.1079, found 209.1077.  
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2-(3-Bromophenyl)-1*H*-benzo[*d*]imidazole 3q.<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f$  = 0.41; pale yellow solid; 161 mg, yield 59%; mp 223-224 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 13.05 (br s, 1H), 8.37 (s, 1H), 8.19 (d,  $J$  = 8.0 Hz, 1H), 7.70 (d,  $J$  = 6.4 Hz, 2H), 7.56-7.50 (m, 2H), 7.25-7.21 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 149.6, 143.7, 135.0, 132.5, 132.4, 131.1, 128.9, 125.4, 122.9, 122.3, 121.9, 119.1, 111.5; FT-IR (KBr) 3326, 3048, 2529, 2112, 1698, 1649, 1595, 1544, 1445, 1315, 1226, 1156, 970, 743 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>9</sub>BrN<sub>2</sub>H 273.0027, found 273.0030.

2-(*m*-tolyl)-1*H*-Benzo[*d*]imidazole 3r.<sup>19</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f$  = 0.41; white solid; 135 mg, yield 65%; mp 231-232 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.88 (br s, 1H), 8.02 (s, 1H), 7.97 (d,  $J$  = 7.6 Hz, 1H), 7.64 (s, 1H), 7.53 (d,  $J$  = 4.4 Hz, 1H), 7.45 (t,  $J$  = 7.6 Hz, 1H), 7.31 (d,  $J$  = 7.2 Hz, 1H), 7.20 (d,  $J$  = 3.6 Hz, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 151.8, 144.2, 138.6, 135.4, 130.9, 130.5, 129.3, 127.4, 124.0, 122.9, 122.0, 119.2, 111.7, 21.5; FT-IR (KBr) 3439, 2920, 2859, 2114, 1685, 1554, 1443, 1308, 1239, 1122, 1039, 957, 822, 728 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>H 209.1079, found 209.1088.

2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole 3s.<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f$  = 0.41; pale yellow solid; 172 mg, yield 63%; mp 255-256 °C; <sup>1</sup>H NMR (400

1 MHz, DMSO-d<sub>6</sub>) δ 13.00 (br s, 1H), 8.13 (m, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.66 (s, 1H), 7.55 (s,  
2 1H), 7.22 (s, 2H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 150.2, 143.7, 135.1, 129.4, 129.0, 128.3, 123.4,  
3 123.2, 122.3, 118.9, 111.7; FT-IR (KBr) 3449, 3052, 2112, 1622, 1590, 1490, 1427, 1300, 1273,  
4 1224, 1114, 1069, 1009, 963, 828, 745 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>9</sub>BrN<sub>2</sub>H  
5 273.0027, found 273.0036.

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14 **2-(4-Chlorophenyl)-1*H*-benzo[d]imidazole 3t.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl  
15 acetate/hexane R<sub>f</sub> = 0.41; pale yellow solid; 153 mg, yield 67%; mp 265-266 °C; <sup>1</sup>H NMR (600  
16 MHz, DMSO-d<sub>6</sub>) δ 12.97 (br s, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* =  
17 8.4 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.23-7.20 (m, 2H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 150.1,  
18 143.7, 135.0, 134.4, 129.0, 128.7, 128.1, 122.7, 121.8, 118.9, 111.4; FT-IR (KBr) 3442, 2997, 2951,  
19 2112, 1630, 1587, 1486, 1429, 1300, 1273, 1225, 1089, 1015, 965, 831, 746 cm<sup>-1</sup>. HRMS (ESI) m/z:  
20 [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>9</sub>ClN<sub>2</sub>H 229.0533, found 229.0533.

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31 **2-(4-Fluorophenyl)-1*H*-benzo[d]imidazole 3u.**<sup>20</sup> Analytical TLC on silica gel, 1:3 ethyl  
32 acetate/hexane R<sub>f</sub> = 0.41; pale yellow solid; 136 mg, yield 64%; mp 240-241 °C; <sup>1</sup>H NMR (400  
33 MHz, DMSO-d<sub>6</sub>) δ 12.93 (br s, 1H), 8.23 (m, 2H), 7.66 (d, *J* = 6.4 Hz, 1H), 7.53 (d, *J* = 6.4 Hz,  
34 1H), 7.42-7.38 (m, 2H), 7.20 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 164.7, 162.3, 150.8, 144.2,  
35 135.4, 129.2, 127.2, 123, 122.1, 119.2, 111.6, 111.7; FT-IR (KBr) 3443, 2917, 2854, 2113, 1603,  
36 1497, 1475, 1433, 1276, 1229, 1157, 1111, 967, 838, 747 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for  
37 C<sub>13</sub>H<sub>9</sub>FN<sub>2</sub>H 213.0828, found 213.0820.

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49 **2-(*p*-tolyl)-1*H*-benzo[d]imidazole 3v.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R<sub>f</sub> =  
50 0.41; white solid; 160 mg, yield 77%; mp 275-276 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 12.85 (br s,  
51 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 7.63 (s, 1H), 7.52 (s, 1H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.19 (s, 2H), 2.37  
52 (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 151.4, 143.8, 139.6, 135.0, 129.5, 127.5, 126.4, 122.4,

1       121.6, 118.7, 111.2, 21.0; FT-IR (KBr) 3440, 2927, 2852, 2106, 1630, 1457, 1261, 1196, 1038, 823,  
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3       715 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>H 209.1079, found 209.1087.  
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7       **2-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole 3w.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl  
8       acetate/hexane R<sub>f</sub> = 0.41; pale yellow solid ; 151 mg, yield 67%; mp 218-219 °C; <sup>1</sup>H NMR (400  
9       MHz, DMSO-d<sub>6</sub>) δ 12.76 (br s, 1H), 8.13 (d, J = 7.2 Hz, 2H), 7.56 (s, 2H), 7.17-7.10 (m, 4H), 3.83  
10      (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 160.6, 151.4, 128.0, 122.7, 121.7, 114.4, 114.3, 111.2,  
11      55.3; FT-IR (KBr) 3472, 2921, 2836, 2113, 1611, 1501, 1476, 1453, 1295, 1254, 1179, 1124, 1034,  
12      965, 845, 745 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>OH 225.1028, found 225.1033.  
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22       **2-(4-Nitrophenyl)-1*H*-benzo[*d*]imidazole 3x.**<sup>11b</sup> Analytical TLC on silica gel, 1:3 ethyl  
23       acetate/hexane R<sub>f</sub> = 0.41; Brown solid; 167 mg, yield 70%; mp 260-261 °C; <sup>1</sup>H NMR (400 MHz,  
24       DMSO-d<sub>6</sub>) δ 13.30 (br s, 1H), 8.40-8.37 (m, 4H), 7.67 (s, 2H), 7.27 (s, 2H); <sup>13</sup>C NMR (150 MHz,  
25       DMSO-d<sub>6</sub>) δ 150.0, 149.0, 147.7, 136.0, 134.5, 127.32, 127.3, 124.14, 124.1, 122.9, 114.9; FT-IR  
26       (KBr) 3451, 2661, 2110, 1667, 1603, 1516, 1433, 1340, 1290, 1101, 1008, 967, 854, 742 cm<sup>-1</sup>.  
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34       HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>H 240.0773, found 240.0770.  
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37       **2-(3,4-Dimethoxyphenyl)-1*H*-benzo[*d*]imidazole 3y.**<sup>21</sup> Analytical TLC on silica gel, 1:3 ethyl  
38       acetate/hexane; R<sub>f</sub> = 0.41; Pale Yellow solid; 150 mg, yield 59%; mp 181-182 °C; <sup>1</sup>H NMR (400  
39       MHz, DMSO-d<sub>6</sub>) δ 12.77 (br s, 1H), 7.75 (s, 2H), 7.63 (s, 1H), 7.51 (s, 1H), 7.17 (s, 3H), 3.88 (s,  
40       3H), 3.84 (s, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 151.6, 150.5, 150.3, 149.0, 122.8, 122.4, 121.8,  
41       119.5, 119.4, 111.8, 109.8, 55.6; FT-IR (KBr) 3195, 2987, 2842, 1620, 1508, 1481, 1432, 1264,  
42       1198, 1115, 1039, 945, 847, 743 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>H 255.1134,  
43       found 255.1140.  
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1           **2-(Naphthalen-2-yl)-1*H*-benzo[*d*]imidazole 3z.**<sup>21</sup> Analytical TLC on silica gel, 1:3 ethyl  
2 acetate/hexane  $R_f = 0.41$ ; pale yellow solid; 194 mg, yield 79%; mp 192-193 °C; <sup>1</sup>H NMR (600  
3 MHz, DMSO-d<sub>6</sub>) δ 13.07 (br s, 1H), 8.74 (s, 1H), 8.33-8.29 (m, 1H), 8.09 (d,  $J = 8.4$  Hz, 1H), 8.05  
4 (d,  $J = 6.6$  Hz, 1H), 7.99 (d,  $J = 6.6$  Hz, 1H), 7.71 (d,  $J = 5.4$  Hz, 1H), 7.61-7.58 (m, 3H), 7.23 (s,  
5 2H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub> + CDCl<sub>3</sub>) δ 151.1, 133.1, 133.0, 132.4, 127.7, 127.6, 127.1,  
6 126.9, 126.6, 126.1, 125.9, 125.6, 125.4, 123.3, 121.6, 114.4, 113.4; FT-IR (KBr) 3450, 3053, 2111,  
7 1653, 1588, 1504, 1441, 1405, 1334, 1282, 1136, 1096, 982, 907, 18, 742 cm<sup>-1</sup>. HRMS (ESI) m/z:  
8 [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>H 245.1079, found 245.1091.  
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11           **2-(Anthracen-9-yl)-1*H*-benzo[*d*]imidazole 3aa.**<sup>22</sup> Analytical TLC on silica gel, 1:3 ethyl  
12 acetate/hexane  $R_f = 0.71$ ; yellow solid; 188 mg, yield 64%; mp 261-262 °C; <sup>1</sup>H NMR (600 MHz,  
13 DMSO-d<sub>6</sub>) δ 13.0 (br s, 1H), 8.85 (s, 1H), 8.22 (d,  $J = 8.4$  Hz, 2H), 7.83 (d,  $J = 7.2$  Hz, 1H), 7.69 (d,  
14  $J = 9.0$  Hz, 2H), 7.61-7.57 (m, 3H), 7.53-7.50 (m, 2H), 7.33-7.31 (m, 2H); <sup>13</sup>C NMR (150 MHz,  
15 DMSO-d<sub>6</sub>) δ 149.5, 130.6, 130.5, 128.8, 128.5, 126.8, 125.8, 125.64, 125.6, 122.5, 121.6, 119.1,  
16 111.4; FT-IR (KBr) 3435, 3398, 2922, 2106, 1625, 1448, 1401, 1373, 1331, 1271, 1229, 1033, 921,  
17 883, 790, 743 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>14</sub>N<sub>2</sub>H 295.1235, found 295.1233.  
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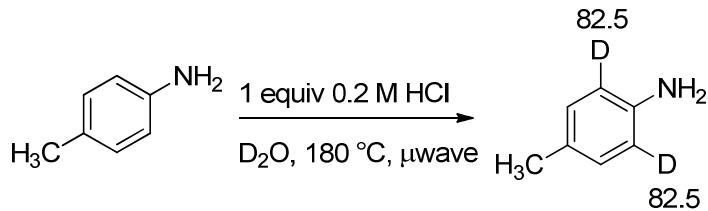
20           **2-(Thiophen-2-yl)-1*H*-benzo[*d*]imidazole 3ab.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl  
21 acetate/hexane  $R_f = 0.41$ ; pale yellow solid; 136 mg, yield 68%; mp 343-344 °C; <sup>1</sup>H NMR (600  
22 MHz, DMSO-d<sub>6</sub>) δ 12.95 (br s, 1H), 7.82 (d,  $J = 3.6$  Hz, 1H), 7.71 (d,  $J = 5.4$  Hz, 1H), 7.60 (s, 1H),  
23 7.50 (s, 1H), 7.23-7.19 (m, 3H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ 147.4, 143.9, 135.0, 134.0,  
24 129.1, 128.7, 127.1, 123.0, 122.2, 118.9, 111.5; FT-IR (KBr) cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd  
25 for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>SH 201.0486, found 201.0491.  
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28           **2-Isopropyl-1*H*-benzo[*d*]imidazole 3ac.**<sup>18</sup> Analytical TLC on silica gel, 1:3 ethyl acetate/hexane  $R_f$   
29 = 0.31; pale yellow solid; 102 mg, yield 64%; mp 232-233 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.31-  
30 7.21 (m, 1H), 7.04 (d,  $J = 7.8$  Hz, 1H), 6.94 (d,  $J = 7.8$  Hz, 1H), 6.84 (d,  $J = 7.8$  Hz, 1H), 6.74 (d,  $J = 7.8$  Hz,  
31 1H), 6.64 (d,  $J = 7.8$  Hz, 1H), 6.54 (d,  $J = 7.8$  Hz, 1H), 6.44 (d,  $J = 7.8$  Hz, 1H), 6.34 (d,  $J = 7.8$  Hz, 1H), 6.24 (d,  $J = 7.8$  Hz,  
32 1H), 6.14 (d,  $J = 7.8$  Hz, 1H), 6.04 (d,  $J = 7.8$  Hz, 1H), 5.94 (d,  $J = 7.8$  Hz, 1H), 5.84 (d,  $J = 7.8$  Hz, 1H), 5.74 (d,  $J = 7.8$  Hz,  
33 1H), 5.64 (d,  $J = 7.8$  Hz, 1H), 5.54 (d,  $J = 7.8$  Hz, 1H), 5.44 (d,  $J = 7.8$  Hz, 1H), 5.34 (d,  $J = 7.8$  Hz, 1H), 5.24 (d,  $J = 7.8$  Hz,  
34 1H), 5.14 (d,  $J = 7.8$  Hz, 1H), 5.04 (d,  $J = 7.8$  Hz, 1H), 4.94 (d,  $J = 7.8$  Hz, 1H), 4.84 (d,  $J = 7.8$  Hz, 1H), 4.74 (d,  $J = 7.8$  Hz,  
35 1H), 4.64 (d,  $J = 7.8$  Hz, 1H), 4.54 (d,  $J = 7.8$  Hz, 1H), 4.44 (d,  $J = 7.8$  Hz, 1H), 4.34 (d,  $J = 7.8$  Hz, 1H), 4.24 (d,  $J = 7.8$  Hz,  
36 1H), 4.14 (d,  $J = 7.8$  Hz, 1H), 4.04 (d,  $J = 7.8$  Hz, 1H), 3.94 (d,  $J = 7.8$  Hz, 1H), 3.84 (d,  $J = 7.8$  Hz, 1H), 3.74 (d,  $J = 7.8$  Hz,  
37 1H), 3.64 (d,  $J = 7.8$  Hz, 1H), 3.54 (d,  $J = 7.8$  Hz, 1H), 3.44 (d,  $J = 7.8$  Hz, 1H), 3.34 (d,  $J = 7.8$  Hz, 1H), 3.24 (d,  $J = 7.8$  Hz,  
38 1H), 3.14 (d,  $J = 7.8$  Hz, 1H), 3.04 (d,  $J = 7.8$  Hz, 1H), 2.94 (d,  $J = 7.8$  Hz, 1H), 2.84 (d,  $J = 7.8$  Hz, 1H), 2.74 (d,  $J = 7.8$  Hz,  
39 1H), 2.64 (d,  $J = 7.8$  Hz, 1H), 2.54 (d,  $J = 7.8$  Hz, 1H), 2.44 (d,  $J = 7.8$  Hz, 1H), 2.34 (d,  $J = 7.8$  Hz, 1H), 2.24 (d,  $J = 7.8$  Hz,  
40 1H), 2.14 (d,  $J = 7.8$  Hz, 1H), 2.04 (d,  $J = 7.8$  Hz, 1H), 1.94 (d,  $J = 7.8$  Hz, 1H), 1.84 (d,  $J = 7.8$  Hz, 1H), 1.74 (d,  $J = 7.8$  Hz,  
41 1H), 1.64 (d,  $J = 7.8$  Hz, 1H), 1.54 (d,  $J = 7.8$  Hz, 1H), 1.44 (d,  $J = 7.8$  Hz, 1H), 1.34 (d,  $J = 7.8$  Hz, 1H), 1.24 (d,  $J = 7.8$  Hz,  
42 1H), 1.14 (d,  $J = 7.8$  Hz, 1H), 1.04 (d,  $J = 7.8$  Hz, 1H), 0.94 (d,  $J = 7.8$  Hz, 1H), 0.84 (d,  $J = 7.8$  Hz, 1H), 0.74 (d,  $J = 7.8$  Hz,  
43 1H), 0.64 (d,  $J = 7.8$  Hz, 1H), 0.54 (d,  $J = 7.8$  Hz, 1H), 0.44 (d,  $J = 7.8$  Hz, 1H), 0.34 (d,  $J = 7.8$  Hz, 1H), 0.24 (d,  $J = 7.8$  Hz,  
44 1H), 0.14 (d,  $J = 7.8$  Hz, 1H), 0.04 (d,  $J = 7.8$  Hz, 1H), -0.14 (d,  $J = 7.8$  Hz, 1H), -0.24 (d,  $J = 7.8$  Hz, 1H), -0.34 (d,  $J = 7.8$  Hz,  
45 1H), -0.44 (d,  $J = 7.8$  Hz, 1H), -0.54 (d,  $J = 7.8$  Hz, 1H), -0.64 (d,  $J = 7.8$  Hz, 1H), -0.74 (d,  $J = 7.8$  Hz, 1H), -0.84 (d,  $J = 7.8$  Hz,  
46 1H), -0.94 (d,  $J = 7.8$  Hz, 1H), -1.04 (d,  $J = 7.8$  Hz, 1H), -1.14 (d,  $J = 7.8$  Hz, 1H), -1.24 (d,  $J = 7.8$  Hz, 1H), -1.34 (d,  $J = 7.8$  Hz,  
47 1H), -1.44 (d,  $J = 7.8$  Hz, 1H), -1.54 (d,  $J = 7.8$  Hz, 1H), -1.64 (d,  $J = 7.8$  Hz, 1H), -1.74 (d,  $J = 7.8$  Hz, 1H), -1.84 (d,  $J = 7.8$  Hz,  
48 1H), -1.94 (d,  $J = 7.8$  Hz, 1H), -2.04 (d,  $J = 7.8$  Hz, 1H), -2.14 (d,  $J = 7.8$  Hz, 1H), -2.24 (d,  $J = 7.8$  Hz, 1H), -2.34 (d,  $J = 7.8$  Hz,  
49 1H), -2.44 (d,  $J = 7.8$  Hz, 1H), -2.54 (d,  $J = 7.8$  Hz, 1H), -2.64 (d,  $J = 7.8$  Hz, 1H), -2.74 (d,  $J = 7.8$  Hz, 1H), -2.84 (d,  $J = 7.8$  Hz,  
50 1H), -2.94 (d,  $J = 7.8$  Hz, 1H), -3.04 (d,  $J = 7.8$  Hz, 1H), -3.14 (d,  $J = 7.8$  Hz, 1H), -3.24 (d,  $J = 7.8$  Hz, 1H), -3.34 (d,  $J = 7.8$  Hz,  
51 1H), -3.44 (d,  $J = 7.8$  Hz, 1H), -3.54 (d,  $J = 7.8$  Hz, 1H), -3.64 (d,  $J = 7.8$  Hz, 1H), -3.74 (d,  $J = 7.8$  Hz, 1H), -3.84 (d,  $J = 7.8$  Hz,  
52 1H), -3.94 (d,  $J = 7.8$  Hz, 1H), -4.04 (d,  $J = 7.8$  Hz, 1H), -4.14 (d,  $J = 7.8$  Hz, 1H), -4.24 (d,  $J = 7.8$  Hz, 1H), -4.34 (d,  $J = 7.8$  Hz,  
53 1H), -4.44 (d,  $J = 7.8$  Hz, 1H), -4.54 (d,  $J = 7.8$  Hz, 1H), -4.64 (d,  $J = 7.8$  Hz, 1H), -4.74 (d,  $J = 7.8$  Hz, 1H), -4.84 (d,  $J = 7.8$  Hz,  
54 1H), -4.94 (d,  $J = 7.8$  Hz, 1H), -5.04 (d,  $J = 7.8$  Hz, 1H), -5.14 (d,  $J = 7.8$  Hz, 1H), -5.24 (d,  $J = 7.8$  Hz, 1H), -5.34 (d,  $J = 7.8$  Hz,  
55 1H), -5.44 (d,  $J = 7.8$  Hz, 1H), -5.54 (d,  $J = 7.8$  Hz, 1H), -5.64 (d,  $J = 7.8$  Hz, 1H), -5.74 (d,  $J = 7.8$  Hz, 1H), -5.84 (d,  $J = 7.8$  Hz,  
56 1H), -5.94 (d,  $J = 7.8$  Hz, 1H), -6.04 (d,  $J = 7.8$  Hz, 1H), -6.14 (d,  $J = 7.8$  Hz, 1H), -6.24 (d,  $J = 7.8$  Hz, 1H), -6.34 (d,  $J = 7.8$  Hz,  
57 1H), -6.44 (d,  $J = 7.8$  Hz, 1H), -6.54 (d,  $J = 7.8$  Hz, 1H), -6.64 (d,  $J = 7.8$  Hz, 1H), -6.74 (d,  $J = 7.8$  Hz, 1H), -6.84 (d,  $J = 7.8$  Hz,  
58 1H), -6.94 (d,  $J = 7.8$  Hz, 1H), -7.04 (d,  $J = 7.8$  Hz, 1H), -7.14 (d,  $J = 7.8$  Hz, 1H), -7.24 (d,  $J = 7.8$  Hz, 1H), -7.34 (d,  $J = 7.8$  Hz,  
59 1H), -7.44 (d,  $J = 7.8$  Hz, 1H), -7.54 (d,  $J = 7.8$  Hz, 1H), -7.64 (d,  $J = 7.8$  Hz, 1H), -7.74 (d,  $J = 7.8$  Hz, 1H), -7.84 (d,  $J = 7.8$  Hz,  
60 1H), -7.94 (d,  $J = 7.8$  Hz, 1H), -8.04 (d,  $J = 7.8$  Hz, 1H), -8.14 (d,  $J = 7.8$  Hz, 1H), -8.24 (d,  $J = 7.8$  Hz, 1H), -8.34 (d,  $J = 7.8$  Hz,  
61 1H), -8.44 (d,  $J = 7.8$  Hz, 1H), -8.54 (d,  $J = 7.8$  Hz, 1H), -8.64 (d,  $J = 7.8$  Hz, 1H), -8.74 (d,  $J = 7.8$  Hz, 1H), -8.84 (d,  $J = 7.8$  Hz,  
62 1H), -8.94 (d,  $J = 7.8$  Hz, 1H), -9.04 (d,  $J = 7.8$  Hz, 1H), -9.14 (d,  $J = 7.8$  Hz, 1H), -9.24 (d,  $J = 7.8$  Hz, 1H), -9.34 (d,  $J = 7.8$  Hz,  
63 1H), -9.44 (d,  $J = 7.8$  Hz, 1H), -9.54 (d,  $J = 7.8$  Hz, 1H), -9.64 (d,  $J = 7.8$  Hz, 1H), -9.74 (d,  $J = 7.8$  Hz, 1H), -9.84 (d,  $J = 7.8$  Hz,  
64 1H), -9.94 (d,  $J = 7.8$  Hz, 1H), -10.04 (d,  $J = 7.8$  Hz, 1H), -10.14 (d,  $J = 7.8$  Hz, 1H), -10.24 (d,  $J = 7.8$  Hz, 1H), -10.34 (d,  $J = 7.8$  Hz,  
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100 1H), -27.94 (d,  $J = 7.8$  Hz, 1H), -28.04 (d,  $J = 7.8$  Hz, 1H), -28.14 (d,  $J = 7.8$  Hz, 1H), -28.24 (d,  $J = 7.8$  Hz, 1H), -28.34 (d,  $J = 7.8$  Hz,  
101 1H),

1      7.26 (m, 2H), 6.98-6.92 (m, 2H), 3.04-2.99 (m, 1H), 1.27-1.20 (m, 6H);  $^{13}\text{C}$  NMR (150 MHz,  
2      DMSO-d<sub>6</sub>)  $\delta$  160.1, 121.2, 28.7, 21.3; FT-IR (KBr) 3441, 2973, 2887, 2114, 1622, 1535, 1455, 1415,  
3      1323, 1273, 1092, 995, 750 cm<sup>-1</sup>. HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>H 161.1079, found  
4      161.1087.

11     **Kinetic Isotope Studies:**

12     **Preperation of *p*-Toluidine-d<sub>2</sub> (Scheme 6).** The titled compound was perpared according to the  
13     reported procedure.<sup>2</sup> Deuterium incorporation (82.5%) was determined by <sup>1</sup>H NMR analysis of the  
14     mixture. Characterization data for the deuterated product: analytical TLC on silica gel, 1/4 ethyl  
15     acetate/hexane R<sub>f</sub> = 0.32; pale brown solid; 185 mg, yield 85%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.96  
16     (s, 2H), 3.47 (br s, 2H), 2.23 (s, 3H).



34     **Scheme 6**

35     **Intermolecular Kinetic Isotope Study (Scheme 4).**<sup>23</sup> *p*-Toluidine **1a** (64 mg), *p*-toluidine-d<sub>2</sub> **1a-d<sub>2</sub>**  
36     (100 mg) and *p*-tolualdehyde **2b** (1.2 equiv, 1.82 mmol, 218 mg) were stirred at 60 °C for 1 h in  
37     DMSO (1 mL) under air. The reaction mixture was then cooled to room temperature and treated with  
38     CuI (10 mol %, 0.152 mmol, 29 mg), TMSN<sub>3</sub> (2 equiv, 3.0 mmol, 350 mg) and TBHP (1 equiv, 1.52  
39     mmol, 275  $\mu$ L). The resultant mixture was stirred at 90 °C for 1 h to give 24% conversion. The  
40     resulting mixture was extracted with ethyl acetate (3 x 10 mL) and washed with brine (2 x 5 mL) and  
41     water (2 x 5 mL). Drying (Na<sub>2</sub>SO<sub>4</sub>) and passing through celite gave a clear solution, which was  
42     evaporated on a rotary evaporator to give a residue that was purified on silica gel column  
43     chromatography using n-hexane and ethyl acetate as eluent (40 mg, yield 18%). The ratio of  
44     2b to **1a-d<sub>2</sub>** was determined by <sup>1</sup>H NMR analysis of the crude reaction mixture. The ratio of 2b to  
45     **1a-d<sub>2</sub>** was 1.00 ± 0.05. The ratio of 2b to **1a** was 1.00 ± 0.05. The ratio of **1a-d<sub>2</sub>** to **1a** was 0.18 ± 0.02.

1 deuterium to hydrogen was determined from the  $^1\text{H}$  NMR relative integration values of  $\text{H}_\text{a}$  (7.47  
2 ppm) based on  $\text{H}_\text{b}$  (7.05 ppm).

## ASSOCIATED CONTENT

### Supporting Information

Mass spectrum of the reaction mixture of **1a** and **2b** with  $\text{TMSN}_3$ , crystal data of **3e** and NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$ ) of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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