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I_2-Mediated Intramolecular C–H Amidation for the Synthesis of *N*-Substituted Benzimidazoles

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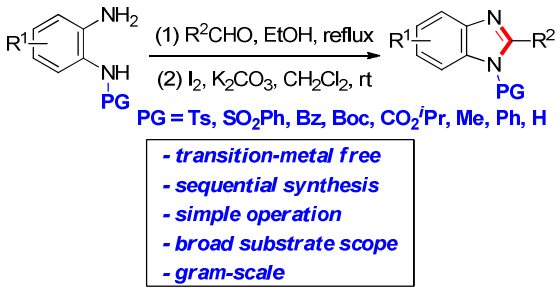
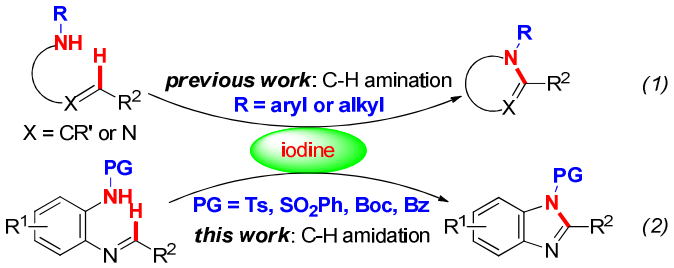


Abstract: A practical intramolecular C–H amidation methodology has been developed using molecular iodine under basic conditions. The required imine substrates were readily obtained by condensation of simple *o*-phenylenediamine derivatives and aldehydes. The transition metal-free cyclization reaction described here works well with crude imines, and allows for the sequential synthesis of *N*-protected benzimidazoles without purification of the less stable condensation intermediates. This operationally simple synthetic approach is broadly applicable to a variety of aromatic, aliphatic, and cinnamic aldehydes to produce diverse 1,2-disubstituted benzimidazole derivatives in an efficient and scalable fashion.

▪ Introduction

C−N bond formation *via* direct oxidative coupling of C–H and N–H bonds features atom- and step-economy, and has received considerable attention in recent years. Such transformations have been successfully achieved through transition metal-catalyzed[1] and hypervalent iodine-mediated C–H amination.[2] Alternatively, molecular iodine, commercially available, inexpensive, and eco-friendly, was widely used as the sole oxidant for the oxidative C–N bond construction.[3] In particular, a number of I_2-mediated amination reactions have been developed for the construction of nitrogen-containing heterocyclic skeletons.[3c, 4] However, examples of the formation of a C−N bond through direct C–H amidation has been reported only rarely,[4d, 5] probably due to the weak nucleophilicity of the nitrogen in the amide substrates. As a continuation of our previous work,[3c, 4c] we describe such an intramolecular method for benzimidazole synthesis (Scheme 1).

Scheme 1. Proposed route for direct synthesis of *N*-protected benzimidazoles through C–H amidation based on previously reported C–H amination reactions



Benzimidazole is a privileged structural unit present in many biologically active compounds.[6] Among these, *N*-protected benzimidazole derivatives possess important pharmaceutical properties (Figure 1). For example, *N*-nitrobenzenesulfonyl benzimidazole **4** can inhibit HBV DNA replication *in vitro* with low cytotoxicity[7] and

5-bromobenzimidazoles such as **5** exhibit significant activity against the H37Rv strain of mycobacterium tuberculosis.[8] *N*-Phenylsulfonyl-5-aminobenzimidazoles **6** display moderate to good anti-inflammatory and analgesic activity in animal models[9] and the *N*-isopropoxycarbonyl derivative **7** is an moderate antiviral agent which inhibits replication of coxsackie virus B2.[10] Nevertheless, of the numerous methods established for benzimidazole synthesis,[11] only a few provide direct access to *N*-protected benzimidazoles.[12,13] In 2011, Zeng[12a] reported the synthesis of *N*-tosyl benzimidazoles by $PdCl_2$-catalyzed intramolecular sulfonamidation and oxidation of imines employing $PhI(OAc)_2$ as the oxidant. Subsequently, Mal[12b] achieved an iodine(III)-mediated cyclization reaction in the absence of a palladium catalyst. In 2013, Punniyamurthy[2c] synthesized a series of 1,2-disubstituted benzimidazoles through *m*CPBA/PhI-mediated oxidative cyclization of *N′*,*N″*-disubstituted amidines. In this paper, we report a sequential approach to the synthesis of *N*-protected benzimidazoles *via* I_2-mediated direct C–H amidation, omitting purification of the less stable imine intermediates.

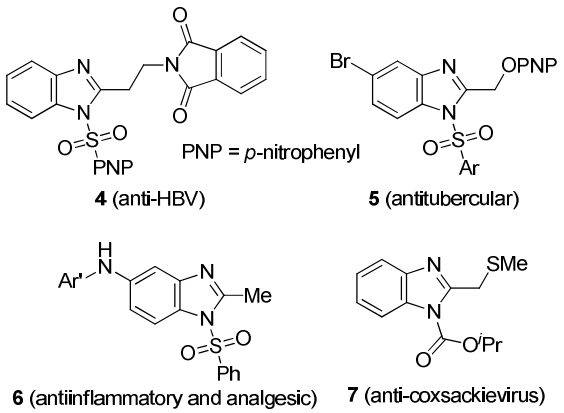
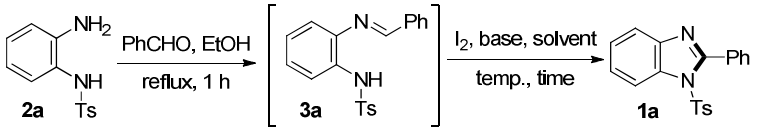


Figure 1. Representative biologically active *N*-protected benzimidazoles.

▪ Results and Discussion

The imine intermediate **3a** necessary for benzimidazole synthesis can be readily prepared by the condensation of *N*-tosyl-1,2-phenylenediamine (**2a**) with benzaldehyde in EtOH at the reflux temperature (Table 1). In view of the poor stability of imines, we initially investigated the I_2-mediated one-pot synthesis without isolation of **3a** in the absence of base,[4e] which only resulted in the trace amount of the benzimidazole **1a** (entry 1). Upon completion of the first-step condensation, the reaction mixture was treated directly with molecular iodine and K_2CO_3 in sequence, which gave the desired product in 7% yield (entry 2). We continued to optimize the reaction conditions using the crude imine **3a** obtained by removing the EtOH under reduced pressure. Screening demonstrated that CH_2Cl_2 is the optimal solvent for the second annulation step and 1.2 equiv. of the oxidant is sufficient for the transformation. In the presence of K_2CO_3, the I_2-promoted oxidative cyclization of crude **3a** at room temperature was completed within 1 h, affording product **1a** in 90% overall yield (entry 7). With weaker (entry 9) or organic bases (entry 10), yields of the expected benzimidazole were significantly reduced. Moreover, one-pot reaction of **2a** and benzaldehyde in either EtOH or CH_2Cl_2 also formed the expected product **1a**, but in lower yields (entries 11−12).

Table 1. Reaction Conditions Optimization for the Synthesis of 1-Tosyl Benzimidazole **1a**.



entry	I_2 (equiv.)	base	solvent	temp.	time[a]	yield[b]
1[c]	1.2	–	EtOH	reflux	6 h	trace

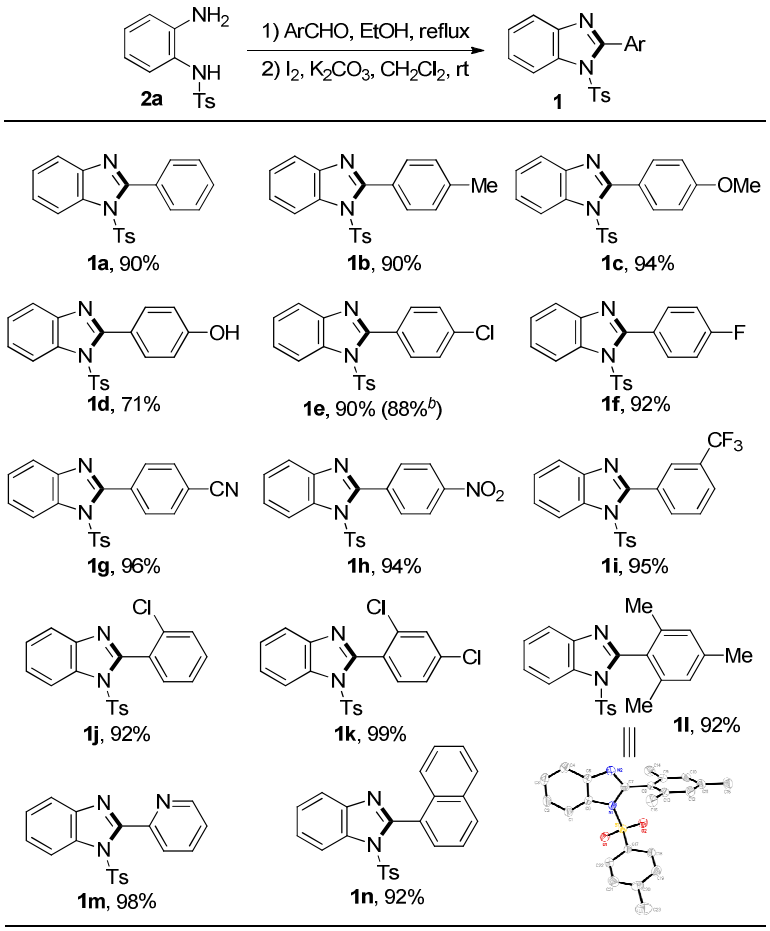
2	1.2	K_2CO_3	EtOH	reflux	1.5 h	7%
3	1.2	K_2CO_3	MeCN	rt	2 h	63%
4	1.2	K_2CO_3	1,4-dioxane	60 °C	1 h	51%
5	1.2	K_2CO_3	toluene	rt	2 h	78%
6	1.0	K_2CO_3	CH_2Cl_2	rt	2 h	86%
7[d]	1.2	**K_2CO_3**	**CH_2Cl_2**	**rt**	**1 h**	**90%**
8	1.4	K_2CO_3	CH_2Cl_2	rt	1 h	90%
9	1.2	$NaHCO_3$	CH_2Cl_2	rt	1 h	49%
10	1.2	DBU	CH_2Cl_2	rt	1 h	43%
11[c]	1.2	K_2CO_3	EtOH	reflux	4 h	38%
12[c]	1.2	K_2CO_3	CH_2Cl_2	rt	1 h	82%

[a]Reaction time for the cyclization step. [b]Isolated yields are given. [c]The reaction mixture was directly treated with iodine and then heated to reflux. [d]Optimal reaction conditions: 1) **2a** (0.5 mmol), PhCHO (0.55 mmol), EtOH, reflux; 2) iodine (0.6 mmol), K_2CO_3 (1.5 mmol), CH_2Cl_2, rt.

Having established the optimal reaction conditions, we sought to probe the substrate scope and the generality of this synthetic approach. A range of aromatic aldehydes were subjected to these sequential synthesis conditions (Scheme 2) and all were smoothly transformed into the expected benzimidazoles by condensation with *N*-tosyl-*o*-phenylenediamine (**2a**) followed by I_2-mediated intramolecular C–H amidation. Using the synthesis of product **1e** as an example, the reaction was successfully conducted on the gram scale. This method is compatible with either electron-donating groups (EDG) or electron-withdrawing groups (EWG) at the *para*, *meta*, and *ortho* positions of the phenyl ring of the aldehydes (**1a**–**1l**). The good functional group tolerance allows for the presence of a phenolic hydroxy group in the substrate, as in **1d**. 2,4,6-Trimethylbenzaldehyde was efficiently cyclized to the

expected product (**1l**), whose structure was confirmed by X-ray crystallography[14] (see Supporting Information). 2-Pyridyl- (**1m**) and 1-naphthyl-substituted benzimidazoles (**1n**) were prepared from the corresponding aldehydes in excellent yields.

Scheme 2. Scope of Aromatic Aldehydes (ArCHO)[a]

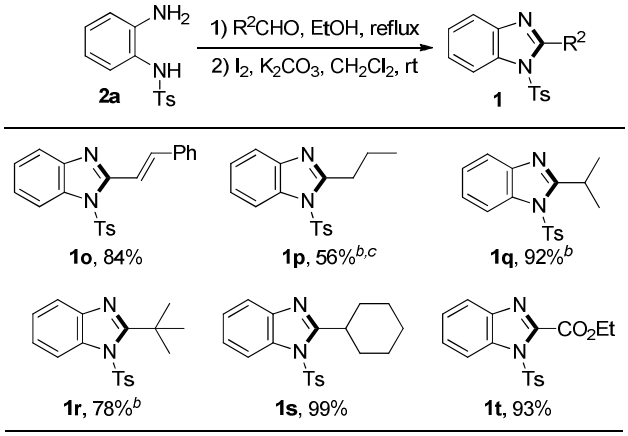


[a]Optimal reaction conditions: 1) **2a** (0.5 mmol), ArCHO (0.55 mmol), EtOH, reflux; 2) iodine (0.6 mmol), K_2CO_3 (1.5 mmol), CH_2Cl_2, rt (isolated yields are given). [b]The yield of gram-scale synthesis (4 mmol) is given in parentheses.

Encouraged by the successful synthesis of *N*-tosyl-2-aryl benzimidazoles, we continued to explore the substrate scope of non-aromatic aldehydes (Scheme 3) and found that both cinnamic and aliphatic aldehydes were converted into the deisred products through the reaction with the *o*-phenylenediamine derivative **2a** under the

optimal reaction conditions. It is worth to mention that benzimidazole **1o** could be used as a substrate for aza Michael-type addition, which was previously prepared from a Boc-protected precursor over three steps.[15] Condensation of ethyl glyoxylate with **2a** followed by I_2-mediated oxidative cyclization afforded a 2-carbethoxyl-substituted benzimidazole **1t**.

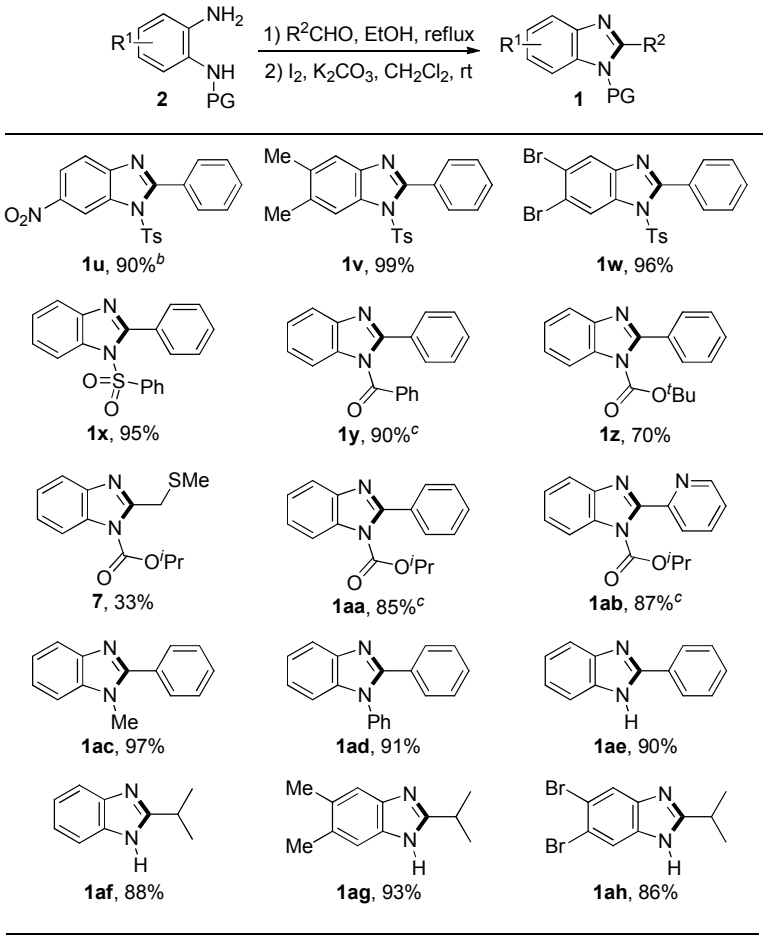
Scheme 3. Scope of Non-Aromatic Aldehydes (R^2CHO)[a]



[a]Optimal reaction conditions: 1) **2a** (0.5 mmol), R^2CHO (0.55 mmol), EtOH, reflux; 2) iodine (0.6 mmol), K_2CO_3 (1.5 mmol), CH_2Cl_2, rt (isolated yields are given). [b]Anhydrous CH_2Cl_2 was used. [c]1.5 mmol of the aldehyde was used.

The scope of *o*-phenylenediamine derivatives was also examined (Scheme 4), and it was found that substrates bearing both EDGs and EWGs were transformed into the expected benzimidazoles (**1u**–**w**). Notably, even the nitro-substituted substrate (**2u**) was cyclized into the corresponding product in 90% yield. Furthermore, a variety of benzimidazoles bearing different *N*-protecting groups (**1x**–**ad**) and no *N*-substituents (**1ae**–**ah**) were successfully synthesized from the corresponding *o*-phenylenediamine derivatives. The relatively lower yield of the antiviral agent **7**[10] might be caused by the side reactions of the methylthio moiety, as both its 2-phenyl (**1aa**) and 2-pyridyl analogs (**1ab**) were obtained in satisfactory yields.

Scheme 4. Scope of *o*-Phenylenediamine Derivatives 2[a]

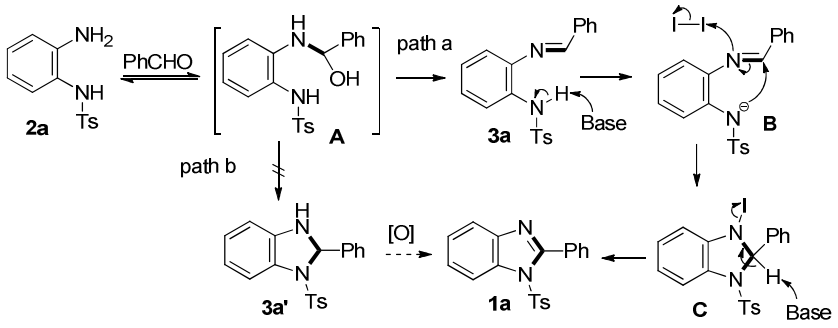


[a]Optimal reaction conditions: 1) **2** (0.5 mmol), PhCHO (0.55 mmol), EtOH, reflux; 2) iodine (0.6 mmol), K_2CO_3 (1.5 mmol), CH_2Cl_2, rt (isolated yields are given). [b]The reaction was performed at reflux temperature in CH_2Cl_2. [c]The reaction was performed at reflux temperature in 1,2-dichloroethane (DCE).

Based on these experimental results along with our previous work of I_2-mediated C–H amination,[3c, 4c] a tentative reaction mechanism for this intramolecular C–H amidation reaction is proposed (Scheme 5). Taking the formation of **1a** as an example, condensation of **2a** and benzaldehyde formed imine **3a** (*path a*), of which the structure has been confirmed by ^1H and ^{13}C NMR. Then the iodine-mediated iodocyclization of intermediate **3a** generates a plausible iodo species **C**. Finally, the

subsequent elimination of one molecule of HI promoted by base produces the benzimidazole framework **1a**. Another possible intermediate **3a'** (*path b*) was not observed, probably because the presence of *N*-sulfonyl group reduces the nucleophilicity of the nitrogen in intermediate **A**.[16]

Scheme 5. Proposed Mechanism for the Formation of 1-Tosyl Benzimidazole 1a via I_2-Mediated C–H Amidation



▪ Conclusion

We have established a practical and transition metal-free intramolecular C–H amidation reaction using molecular iodine as the sole oxidant. The sequential synthetic approach described here is operationally simple and requires no isolation of the less stable imine intermediates. Under the optimal cyclization conditions, crude imines obtained from readily available *o*-phenylenediamine derivatives and aldehydes were directly cyclized into *N*-protected benzimidazoles. This versatile methodology is broadly applicable to a variety of aromatic, aliphatic, and cinnamic aldehydes, and provides facile access to diverse 1,2-disubstituted benzimidazole derivatives in an efficient and scalable fashion.

▪ Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz (100 MHz for ^{13}C NMR) spectrometer. Chemical shift values are given in parts per million (ppm) relative to the internal standard, tetramethylsilane (TMS). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; hept, heptet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; tt, triplet of triplets. The coupling constants (*J*) are reported in Hertz (Hz). Melting points were determined on a micromelting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on an FT-IR spectrometer. High-resolution mass spectra (HRMS) were obtained on a TOF-Q mass spectrometer equipped with an electrospray ion source (ESI) and operated in the positive mode. Flash column chromatography was performed over 200–300 mesh silica gel and the solvents were distilled prior to use. EtOH, for the first-step condensation, was analytical reagent (AR) grade and used was without any pretreatment. CH_2Cl_2 and 1,2-dichloroethane (DCE), used in the sequential oxidative cylization, were dried over 4 Å molecular sieves (for the synthesis of **1p**–**r**, CH_2Cl_2 was distilled from calcium hydride) prior to use.

General Procedure for the Synthesis of *N*-Substituted Benzimidazoles 1. A mixture of *o*-phenylenediamine derivative (**2**, 0.5 mmol) and the corresponding aldehyde (0.55 mmol) in EtOH (6 mL) was refluxed for 1 h. Then the solvent was evaporated under reduced pressure to give the crude imine **3** [The structure of **3a** was characterized by NMR: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.79-7.77 (m, 1H), 7.72 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.53-7.47 (m, 3H), 7.21 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 7.04-7.02 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 143.5, 140.9, 136.1, 135.6, 132.3, 132.1, 129.4, 129.0, 128.9, 127.7, 127.1, 125.4, 121.2, 116.9, 21.5], which was redissolved in

CH_2Cl_2 (6 mL), followed by the sequential addition of iodine (152 mg, 0.6 mmol) and K_2CO_3 (207 mg, 1.5 mmol). The reaction mixture was stirred at room temperature (for the synthesis of **1u**, the reaction was performed in CH_2Cl_2 at reflux temperature; for **1y** and **1aa**–**ab** in DCE at reflux temperature) for the indicated time. Upon completion of the reaction, it was quenched with 5% $Na_2S_2O_3$ (15 mL), and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, concentrated, and then purified through silica gel column chromatography to afford the desired product **1**.

2-Phenyl-1-tosyl-1*H*-benzo[*d*]imidazole (1a).[17] 1 h; eluent: EtOAc/petroleum ether (PE) 5:95; yield: 156 mg, 90%; white solid, mp 103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.48-7.37 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 145.7, 142.6, 135.0, 133.9, 130.9, 130.5, 130.0, 129.7, 127.7, 127.0, 125.5, 125.3, 120.4, 115.2, 21.6; IR (film) 3056(w), 1597(w), 1449(w), 1387(m), 1176(s), 1119(m), 1083(m), 1010(w), 816(w), 768(m), 740(vs), 701(s), 668(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2O_2S$ 349.1005, found 349.1005.

2-(*p*-Tolyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1b). 1 h; eluent: EtOAc/PE 5:95; yield: 162 mg, 90%; white solid, mp 127-128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.18 (m, 1H), 7.72-7.70 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44-7.33 (m, 4H), 7.28-7.26 (m, 2H, overlapped with the peak of chloroform), 7.09 (d, *J* = 8.4 Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 145.6, 142.7, 140.8, 135.0, 133.9, 130.8, 129.7, 128.4, 127.1, 127.0, 125.31, 125.27, 120.3, 115.2, 21.7, 21.6; IR (film) 2921(w), 1596(w), 1497(w), 1445(w), 1374(s), 1253(w), 1174(vs), 1118(w), 1062(m), 996(m), 823(m), 805(m), 767(s), 757(s), 703(w), 669(s); HRMS (m/z) $[M + H]^+$ calcd

for $C_{21}H_{19}N_2O_2S$ 363.1162, found 363.1151.

2-(4-Methoxyphenyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1c).[12b] 0.5 h; eluent: EtOAc/PE 15:85; yield: 178 mg, 94%; white solid, mp 132-133 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.18 (m, 1H), 7.71-7.68 (m, 1H), 7.61-7.57 (m, 2H), 7.43-7.35 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00-6.97 (m, 2H), 3.91 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 154.3, 145.6, 142.8, 134.9, 134.0, 132.5, 129.7, 126.9, 125.3, 125.2, 122.2, 120.2, 115.3, 113.1, 55.4, 21.6; IR (film) 2966(w), 1609(w), 1494(m), 1441(w), 1376(s), 1304(m), 1251(m), 1175(vs), 1117(w), 1063(m), 1010(m), 833(s), 807(w), 769(s), 750(m), 704(w), 676(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{19}N_2O_3S$ 379.1111, found 379.1104.

4-(1-Tosyl-1*H*-benzo[*d*]imidazol-2-yl)phenol (1d). 1 h; eluent: EtOAc/PE 25:75; yield: 130 mg, 71%; light brown solid, mp 163-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.47-7.37 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 154.7, 145.9, 141.6, 134.8, 133.7, 132.6, 129.7, 127.1, 125.50, 125.49, 120.5, 119.7, 115.4, 115.1, 21.6; IR (film) 1594(w), 1486(w), 1452(w), 1386(m), 1274(m), 1179(s), 1128(w), 1083(m), 837(m), 809(w), 745(s), 675(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{17}N_2O_3S$ 365.0954, found 365.0948.

2-(4-Chlorophenyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1e). 1 h; eluent: EtOAc/PE 95:5; yield: 171 mg, 90% (0.5 mmol scale); 1.35 g, 88% (4 mmol scale); white solid, mp 138-139 ºC (lit.[18] mp 140-141 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.19 (m, 1H), 7.73-7.71 (m, 1H), 7.58 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.46-7.38 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 145.9, 142.6, 136.9, 134.9, 133.9,132.2, 129.8, 128.5, 128.0, 126.9, 125.7, 125.5, 120.5, 115.2, 21.7; IR (film) 1596(w), 1480(w), 1453(w), 1373(s), 1304(w),

1175(s), 1116(w), 1092(m), 1063(s), 1013(m), 994(m), 834(m), 808(m), 758(s), 702(w), 666(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}ClN_2O_2S$ 383.0616, found 383.0603.

2-(4-Fluorophenyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1f). 2 h; eluent: EtOAc/PE 10:90; yield: 168 mg, 92%; white solid, mp 118-119 ºC (lit.[12b] mp 118-120 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.64-7.60 (m, 2H), 7.46-7.38 (m, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.18-7.09 (m, 4H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3 (d, $J_{C\text{-}F}$ = 249.8 Hz), 153.1, 145.9, 142.5, 134.9, 133.9, 133.0 (d, $J_{C\text{-}F}$ = 8.7 Hz), 129.8, 126.9, 126.1 (d, $J_{C\text{-}F}$ = 3.4 Hz), 125.6, 125.4, 120.4, 115.2, 115.0 (d, $J_{C\text{-}F}$ = 21.9 Hz), 21.6; IR (film) 1593(w), 1494(m), 1447(w), 1372(m), 1303(w), 1223(m), 1175(s), 1158(m), 1117(m), 1060(s), 997(m), 840(s), 798(s), 756(vs), 703(w), 668(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}FN_2O_2S$ 367.0911, found 367.0905.

4-(1-Tosyl-1*H*-benzo[*d*]imidazol-2-yl)benzonitrile (1g). 0.5 h; eluent: EtOAc/PE 15:85; yield: 180 mg, 96%; white solid, mp 147-149 ºC (lit.[12b] mp 146-148 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.0 Hz, 1H), 7.78 (s, 4H), 7.74 (d, J = 7.6 Hz, 1H), 7.50-7.40 (m, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 146.2, 142.6, 134.7, 134.6, 133.8, 131.6, 131.4, 130.0, 126.8, 126.2, 125.7, 120.8, 118.3, 115.2, 114.2, 21.7; IR (film) 2231(w), 1599(w), 1495(w), 1448(w), 1382(m), 1303(w), 1174(s), 1119(w), 1070(m), 1005(w), 852(s), 807(w), 748(s), 676(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{16}N_3O_2S$ 374.0958, found 374.0952.

2-(4-Nitrophenyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1h). 1.5 h; eluent: EtOAc/PE 15:85; yield: 185 mg, 94%; yellow solid, mp 168-170 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 2H),

7.75 (d, J = 7.6 Hz, 1H), 7.51-7.41 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 149.0, 146.3, 142.6, 136.3, 134.7,133.8, 132.0, 130.0, 126.8, 126.3, 125.8, 122.8, 120.8, 115.1, 21.7; IR (film) 1599(w), 1515(m), 1450(w), 1381(m), 1350(s), 1275(w), 1172(s), 1122(w), 1076(m), 1011(w), 855(s), 812(m), 747(m), 701(w), 670(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}N_3O_4S$ 394.0856, found 394.0852.

1-Tosyl-2-(3-(trifluoromethyl)phenyl)-1*H*-benzo[*d*]imidazole (1i). 0.5 h; eluent: EtOAc/PE 5:95; yield: 197 mg, 95%; white solid, mp 62-63 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.71 (s, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.50-7.41 (m, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 146.2, 142.4, 134.9, 134.4, 133.9, 130.9, 130.3 (q, $J_{C\text{-}F}$ = 32.7 Hz), 129.9, 128.3, 127.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 127.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 126.9, 126.0, 125.5, 123.7 (q, $J_{C\text{-}F}$ = 271.1 Hz), 120.6, 115.1, 21.6; IR (film) 1597(w), 1431(w), 1384(m), 1335(s), 1300(w), 1269(m), 1230(w), 1174(s), 1117(s), 1074(m), 1035(w), 908(w), 855(w), 813(m), 742(m), 702(vs), 674(m); HRMS (m/z) $[M + H]^+$ calcd for $C_{21}H_{16}F_3N_2O_2S$ 417.0879, found 417.0871.

2-(2-Chlorophenyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1j). 1.5 h; eluent: EtOAc/PE 5:95; yield: 176 mg, 92%; white solid, mp 145-146 ºC (lit.[17] mp 147-148 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.50-7.45 (m, 3H), 7.43-7.37 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 146.0, 142.3, 135.2, 135.0, 132.9, 132.3, 131.6, 130.0, 129.9, 129.4, 127.4, 126.0, 125.7, 125.0, 120.8, 114.2, 21.7; IR (film) 1596(w), 1450(w), 1366(s), 1251(w), 1174(s), 1126(m), 1088(m), 1054(m), 806(m), 766(vs), 749(s), 678(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}ClN_2O_2S$

383.0616, found 383.0613.

2-(2,4-Dichlorophenyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1k). 1.5 h; eluent: EtOAc/PE 10:90; yield: 207 mg, 99%; white solid, mp 139-140 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.54-7.51 (m, 3H), 7.49-7.35 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 146.2, 142.2, 137.2, 136.1, 134.9, 133.1, 132.9, 130.0, 129.4, 128.6, 127.3, 126.5, 125.9, 125.2, 120.8, 114.2, 21.7; IR (film) 1596(w), 1446(w), 1381(m), 1307(w), 1280(w), 1245(w), 1176(vs), 1123(m), 1085(m), 1051(m), 1013(w), 823(m), 785(m), 770(w), 753(w), 743(m), 669(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}Cl_2N_2O_2S$ 417.0226, found 417.0213.

2-Mesityl-1-tosyl-1*H*-benzo[*d*]imidazole (1l).[12b] 1 h; eluent: EtOAc/PE 10:90; yield: 179 mg, 92%; white solid, mp 161-162 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.48-7.39 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 1.76 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 145.9, 142.3, 139.9, 138.7, 135.2, 133.1, 129.7, 127.9, 127.7, 126.8, 125.2, 124.6, 120.5, 114.2, 21.7, 21.4, 20.0; IR (film) 2920(w), 1611(w), 1545(w), 1449(w), 1381(s), 1296(w), 1251(m), 1179(s), 1125(w), 1092(w), 1061(m), 1014(m), 861(w), 812(m), 741(s), 678(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_2S$ 391.1475, found 391.1471.

2-(Pyridin-2-yl)-1-tosyl-1*H*-benzo[*d*]imidazole (1m). 0.5 h; eluent: EtOAc/PE 20:80; yield: 170 mg, 98%; white solid, mp 136-138 ºC (lit.[12b] mp 129-131 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.8 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.88-7.86 (m, 2H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.46-7.38 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 149.6, 148.5, 145.6, 142.3, 136.4, 135.8, 133.5, 129.7, 127.9, 125.7, 125.6, 125.0, 124.7, 120.9,

114.3, 21.7; IR (film) 1591(w), 1449(w), 1436(w), 1365(s), 1254(w), 1174(s), 1132(w), 1088(m), 1012(w), 811(w), 766(m), 750(m), 669(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{16}N_3O_2S$ 350.0958, found 350.0954.

2-(Naphthalen-1-yl)-1-tosyl-1*H*-benzo[*d*]imidazole (1n).[12b] 1 h; eluent: EtOAc/PE 10:90; yield: 184 mg, 92%; white solid, mp 125-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.83-7.81 (m, 1H), 7.62-7.55 (m, 2H), 7.53-7.42 (m, 3H), 7.27-7.22 (m, 2H，overlapped with the peak of chloroform), 7.19 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 145.6, 142.3, 134.7, 133.5, 133.0, 132.5, 130.8, 130.0, 129.5, 128.1, 127.2, 126.7, 126.0, 125.6, 125.2, 125.0, 124.3, 120.6, 114.7, 21.5; IR (film) 3056(w), 1594(w), 1449(w), 1371(s), 1302(w), 1256(w), 1173(s), 1131(m), 1085(m), 1043(m), 1014(w), 801(m), 778(m), 743(vs), 701(m), 682(s), 659(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{24}H_{19}N_2O_2S$ 399.1162, found 399.1156.

(*E*)-2-Styryl-1-tosyl-1*H*-benzo[*d*]imidazole (1o).[19] 0.5 h; eluent: EtOAc/PE 10:90; yield: 157 mg, 84%; white solid, mp 155-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (m, 1H), 7.93 (s, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.70-7.65 (m, 3H), 7.46-7.39 (m, 3H), 7.36-7.34 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 145.9, 142.7, 139.8, 135.8, 135.3, 133.2, 130.2, 129.6, 129.0, 127.8, 126.8, 125.3, 125.1, 119.9, 114.4, 114.0, 21.6; IR (film) 1623(w), 1506(w), 1448(w), 1374(s), 1342(w), 1232(w), 1198(m), 1162(s), 1089(m), 1050(m), 976(w), 925(w), 817(m), 760(m), 741(s), 672(vs), 645(m); HRMS (m/z) $[M + H]^+$ calcd for $C_{22}H_{19}N_2O_2S$ 375.1162, found 375.1160.

2-Propyl-1-tosyl-1*H*-benzo[*d*]imidazole (1p). 0.5 h; eluent: EtOAc/PE 10:90; yield: 88 mg, 56%; white solid, mp 99-100 ºC (lit.[20] mp 102-104 ºC); ^{1}H NMR (400

MHz, $CDCl_3$): δ 8.04-8.02 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.67-7.65 (m, 1H), 7.35-7.31 (m, 2H), 7.30-7.26 (m, 2H, overlapped with the peak of chloroform), 3.13 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.94 (sext, *J* = 7.6 Hz, 2H), 1.06 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 145.9, 142.0, 135.6, 133.2, 130.2, 126.7, 124.7, 124.6, 119.8, 113.7, 31.8, 21.7, 21.2, 14.0; IR (film) 2962(w), 1595(w), 1543(w), 1452(w), 1367(s), 1303(w), 1231(w), 1197(m), 1169(s), 1147(m), 1086(m), 1053(w), 878(w), 823(w), 764(w), 745(s), 667(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{17}H_{19}N_2O_2S$ 315.1162, found 315.1161.

2-Isopropyl-1-tosyl-1*H*-benzo[*d*]imidazole (1q).[12b] 0.5 h; eluent: EtOAc/PE 10:90; yield: 145 mg, 92%; white solid, mp 102-103 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06-8.04 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.70-7.66 (m, 1H), 7.36-7.29 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H, overlapped with the peak of chloroform), 3.83 (hept, *J* = 6.8 Hz, 1H), 2.38 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 145.8, 142.0, 135.9, 133.0, 130.2, 126.6, 124.7, 124.6, 119.8, 114.0, 28.5, 22.3, 21.6; IR (film) 2970(w), 1595(w), 1534(w), 1454(w), 1383(s), 1257(w), 1175(vs), 1139(m), 1087(s), 1035(m), 817(w), 768(w), 746(s), 692(s), 659(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{17}H_{19}N_2O_2S$ 315.1162, found 315.1161.

2-(*tert*-Butyl)-1-tosyl-1*H*-benzo[*d*]imidazole (1r). 0.5 h; eluent: EtOAc/PE 5:95; yield: 128 mg, 78%; white solid, mp 70-71 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.30-7.21 (m, 4H, overlapped with the peak of chloroform), 2.36 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 145.2, 140.7, 136.6, 134.8, 129.9, 126.5, 124.8, 124.5, 120.1, 114.6, 37.0, 30.1, 21.6; IR (film) 2970(w), 1594(w), 1523(w), 1456(w), 1379(s), 1255(w), 1189(m), 1178(s), 1130(m), 1081(m), 1010(m), 817(w), 746(m), 704(w), 675(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{18}H_{21}N_2O_2S$ 329.1318, found 329.1316.

2-Cyclohexyl-1-tosyl-1*H*-benzo[*d*]imidazole (1s).[12b] 0.5 h; eluent: EtOAc/PE 5:95; yield: 175 mg, 99%; white solid, mp 125-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.03 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.70-7.66 (m, 1H), 7.35-7.30 (m, 2H), 7.28-7.26 (m, 2H, overlapped with the peak of chloroform), 3.49 (tt, *J* = 11.6, 3.2 Hz, 1H), 2.38 (s, 3H), 1.94-1.84 (m, 4H), 1.78-1.66 (m, 3H), 1.47-1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 145.8, 142.0, 135.9, 132.9, 130.2, 126.6, 124.7, 124.6, 119.8, 114.0, 38.1, 32.6, 26.3, 25.8, 21.7; IR (film) 2922(w), 2846(w), 1448(w), 1370(m), 1247(w), 1194(m), 1162(s), 1120(m), 1087(m), 1047(m), 884(w), 805(w), 765(w), 748(s), 704(w), 669(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{23}N_2O_2S$ 355.1475, found 355.1476.

Ethyl 1-tosyl-1*H*-benzo[*d*]imidazole-2-carboxylate (1t).[12a] 0.5 h; eluent: EtOAc/PE 10:90; yield: 159 mg, 93%; white solid, mp 105-106 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 1H), 7.42-7.38 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.56 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 146.3, 143.4, 141.5, 134.6, 132.2, 130.1, 128.1, 126.9, 125.3, 121.7, 113.7, 63.4, 21.8, 14.0; IR (film) 2981(w), 1732(s), 1596(w), 1524(w), 1380(m), 1370(m), 1328(w), 1255(w), 1200(s), 1171(s), 1087(m), 1050(w), 1010(m), 860(w), 817(w), 749(s), 670(vs); HRMS (m/z) $[M + Na]^+$ calcd for $C_{17}H_{16}N_2NaO_4S$ 367.0723, found 367.0726.

6-Nitro-2-phenyl-1-tosyl-1*H*-benzo[*d*]imidazole (1u). 3 h; eluent: EtOAc/PE 10:90; yield: 178 mg, 90%; white solid, mp 164-166 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, *J* = 2.0 Hz, 1H), 8.32 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.63-7.59 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 146.7, 146.6, 145.3,

134.3, 133.5, 131.4, 130.9, 130.0, 129.0, 127.9, 127.3, 120.9, 120.6, 111.9, 21.7; IR (film) 3067(w), 1594(w), 1516(m), 1435(w), 1380(m), 1337(m), 1272(m), 1235(w), 1170(s), 1123(w), 1082(m), 1019(m), 890(w), 835(m), 811(m), 762(m), 734(w), 698(s), 664(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{16}N_3O_4S$ 394.0856, found 394.0856.

5,6-Dimethyl-2-phenyl-1-tosyl-1*H*-benzo[*d*]imidazole (1v). 1 h; eluent: EtOAc/PE 10:90; yield: 187 mg, 99%; white solid, mp 134-135 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47-7.42 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 145.5, 141.2, 135.2, 134.8, 134.3, 132.3, 130.9, 130.3, 130.2, 129.6, 127.6, 126.9, 120.4, 115.4, 21.6, 20.8, 20.2; IR (film) 2924(w), 1595(w), 1465(w), 1361(s), 1287(w), 1164(m), 1110(w), 1083(m), 1071(w), 1010(m), 867(w), 810(m), 771(s), 689(s), 663(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{22}H_{21}N_2O_2S$ 377.1318, found 377.1316.

5,6-Dibromo-2-phenyl-1-tosyl-1*H*-benzo[*d*]imidazole (1w). 2 h; eluent: EtOAc/PE 5:95; yield: 243 mg, 96%; white solid, mp 182-183 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.98 (s, 1H), 7.59-7.55 (m, 3H), 7.48-7.44 (m, 2H), 7.28-7.26 (m, 2H, overlapped with the peak of chloroform), 7.12 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 146.3, 142.8, 134.5, 133.9, 131.0, 130.9, 129.9, 129.1, 127.8, 127.1, 124.7, 121.1, 121.0, 119.7, 21.7; IR (film) 1624(w), 1494(w), 1429(w), 1377(m), 1236(w), 1158(vs), 1082(w), 1031(w), 1010(m), 935(w), 810(w), 769(w), 740(w), 666(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}Br_2N_2O_2S$ 504.9216, found 504.9200.

2-Phenyl-1-(phenylsulfonyl)-1*H*-benzo[*d*]imidazole (1x).[21] 0.5 h; eluent: EtOAc/PE 10:90; yield: 158 mg, 95%; white solid, mp 64-66 ºC; ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.23-8.21 (m, 1H), 7.75-7.72 (m, 1H), 7.60-7.57 (m, 2H), 7.55-7.49 (m, 2H), 7.47-7.38 (m, 6H), 7.33-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 142.6, 138.0, 134.4, 133.9, 130.9, 130.6, 129.9, 129.1, 127.7, 127.0, 125.6, 125.4, 120.5, 115.2; IR (film) 3057(w), 1536(w), 1445(m), 1381(s), 1275(w), 1184(s), 1122(m), 1067(m), 1016(w), 826(w), 764(m), 750(s), 729(s), 687(vs); HRMS (m/z) $[M + Na]^+$ calcd for $C_{19}H_{15}N_2O_2S$ 335.0849, found 335.0846.

Phenyl(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)methanone (1y).[22] 12 h; eluent: EtOAc/PE 10:90; yield: 134 mg, 90%; white solid, mp 142-143 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.62-7.60 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.41-7.27 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 154.0, 142.7, 134.9, 134.1, 133.1, 130.6, 130.3, 129.9, 129.3, 128.8, 128.4, 124.8, 124.6, 120.2, 113.1; IR (film) 3029(w), 1698(m), 1597(w), 1450(m), 1333(w), 1282(m), 1265(m), 1147(m), 1026(w), 932(w), 899(m), 839(w), 748(s), 696(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{15}N_2O$ 299.1179, found 299.1179.

***tert*-Butyl 2-phenyl-1*H*-benzo[*d*]imidazole-1-carboxylate (1z).** 0.5 h; eluent: EtOAc/PE 5:95; yield: 103 mg, 70%; brown oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06-8.04 (m, 1H), 7.80 (dd, J = 5.6, 2.4 Hz, 1H), 7.64-7.62 (m, 2H), 7.48-7.45 (m, 3H), 7.42-7.36 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 148.6, 142.5, 133.8, 132.4, 129.6, 129.2, 128.0, 125.0, 124.5, 120.1, 114.7, 85.3, 27.6; IR (film) 2979(w), 2930(w), 1741(vs), 1539(w), 1452(m), 1327(s), 1262(m), 1221(m), 1149(s), 1059(m), 846(w), 764(m), 746(m), 697(m); HRMS (m/z) $[M + H]^+$ calcd for $C_{18}H_{19}N_2O_2$ 295.1441, found 295.1453.

Isopropyl 2-((methylthio)methyl)-1*H*-benzo[*d*]imidazole-1-carboxylate (7).[10] 0.5 h; eluent: EtOAc/PE 15:85; yield: 43 mg, 33%; brown oil; ^1H NMR (400 MHz, $CDCl_3$):

δ 7.98-7.95 (m, 1H), 7.72-7.70 (m, 1H), 7.37-7.32 (m, 2H), 5.34 (hept, *J* = 6.4 Hz, 1H), 4.19 (s, 2H), 2.15 (s, 3H), 1.52 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.5, 149.7, 141.9, 133.3, 124.9, 124.4, 119.9, 115.1, 73.1, 33.3, 21.9, 15.4; IR (Film) 2920(w), 1743(s), 1533(w), 1453(m), 1367(s), 1339(m), 1323(m), 1287(m), 1259(m), 1211(s), 1147(m), 1103(s), 1089(vs), 908(w), 839(w), 765(m), 744(m); HRMS (m/z) $[M + Na]^+$ calcd for $C_{13}H_{16}N_2NaO_2S$, 287.0825, found 287.0833.

Isopropyl 2-phenyl-1*H*-benzo[*d*]imidazole-1-carboxylate (1aa). 3 h; eluent: EtOAc/PE 20:80; yield: 122 mg, 87%; white solid, mp 83-84ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.07-8.04 (m, 1H), 7.81-7.78 (m, 1H), 7.66-7.63 (m, 2H), 7.51-7.45 (m, 3H), 7.41-7.37 (m, 2H), 5.14 (hept, *J* = 6.4 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.9, 149.7, 142.7, 133.7, 132.1, 129.7, 129.4, 127.9, 125.1, 124.6, 120.3, 114.9, 72.8, 21.5; IR (film) 2983(w), 1738(s), 1538(w), 1454(m), 1364(m), 1328(m), 1311(m), 1280(m), 1208(m), 1154(w), 1145(w), 1098(s), 1059(m), 903(w), 846(w), 760(s), 743(vs), 696(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_2$, 281.1285, found 281.1283.

Isopropyl 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole-1-carboxylate (1ab). 1.5 h; eluent: EtOAc/PE 25:75; yield: 120 mg, 85%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.71-8.69 (m, 1H), 8.02-8.00 (m, 1H), 7.90-7.82 (m, 3H), 7.45-7.37 (m, 3H), 5.15 (hept, *J* = 6.4 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.0, 150.7, 149.6, 149.0, 142.5, 136.5, 133.7, 125.6, 124.6, 124.2, 124.0, 120.5, 114.3, 72.8, 21.5; IR (film) 2983(w), 1746(s), 1589(w), 1449(s), 1365(s), 1322(s), 1291(m), 1218(vs), 1103(s), 1066(m), 849(w), 763(m), 746(m); HRMS (m/z) $[M + H]^+$ calcd for $C_{16}H_{16}N_3O_2$, 282.1237, found 282.1247.

1-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole (1ac). *N*-Methyl-1,2-benzenediamine dihydrochloride (98 mg, 0.5 mmol) was used as the substrate in the presence of

NaOAc (82 mg, 1 mmol). 3 h; eluent: EtOA/PE 20:80; yield: 101 mg, 97%; white solid, mp 93-94ºC (lit.[11e] mp 96-49 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.81 (m, 1H), 7.78-7.75 (m, 2H), 7.55-7.50 (m, 3H), 7.40-7.37 (m, 1H), 7.34-7.29 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 143.0, 136.6, 130.3, 129.7, 129.5, 129.5, 128.7, 122.8, 122.5 119.9, 109.6, 31.7; IR (film) 1614(w), 1468(m), 1441(m), 1383(m), 1329(w), 1277(w), 1242(w), 1155(w), 1060(w), 1022(w), 927(w), 818(w), 754(vs), 700(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{14}H_{13}N_2$, 209.1073, found 209.1077.

1,2-Diphenyl-1*H*-benzo[*d*]imidazole (1ad). 3 h; eluent: EtOA/PE 15:85; yield: 123 mg, 91%; white solid, mp 108-109 ºC (lit.[11e] mp 109-110 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 1H), 7.58-7.56 (m, 2H), 7.52-7.46 (m, 3H), 7.34-7.25 (m, 8H, overlapped with the peak of chloroform); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 143.0, 137.2, 137.0, 130.0, 129.9, 129.5, 129.4, 128.6, 128.3, 127.4, 123.3, 123.0, 119.9, 110.5; IR (film) 3050(w), 1595(w), 1491(m), 1476(m), 1444(m), 1381(m), 1328(w), 1260(w), 1181(w), 1077(w), 1027(w), 996(w), 977(w), 932(w), 832(w), 763(s), 750(s), 698(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{15}N_2$, 271.1230, found 271.1245.

2-Phenyl-1*H*-benzo[*d*]imidazole (1ae). Eluent: EtOAc/PE 30:70 (enriched with 3% of MeOH); yield: 87 mg, 90%; white solid, mp 285-286 ºC (lit.[4e] mp 282-284 ºC); ^{1}H NMR (400 MHz, CD_3OD): δ 8.10 (d, J = 6.8 Hz, 2H), 7.63-7.61 (m, 2H), 7.57-7.49 (m, 3H), 7.28-7.26 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 152.0, 130.0, 129.6, 128.8, 126.4, 122.5, 114.5; IR (film) 1542(w), 1463(m), 1444(m), 1411(m), 1315(w), 1277(w), 1227(w), 1120(w), 971(m), 927(w), 764(w), 738(vs), 702(s), 686(m); HRMS (m/z) $[M + H]^+$ calcd for $C_{13}H_{11}N_2$, 195.0917, found 195.0918.

2-Isopropyl-1*H*-benzo[*d*]imidazole (1af). Eluent: EtOAc/PE 30:70 (enriched with 3%

of MeOH); yield: 70 mg, 88%; white solid, mp 217-218 ºC (lit.[23] mp 220-225 ºC); ^{1}H NMR (400 MHz, CD_3OD): δ 7.52-7.50 (m, 2H), 7.21-7.19 (m, 2H), 3.24 (hept, *J* = 7.2 Hz, 1H), 1.44(d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_3OD): δ 160.2, 137.8, 121.8, 113.9, 28.7, 20.3; IR (film) 2971(w), 1533(w), 1455(m), 1414(s), 1321(m), 1273(s), 1158(w), 1091(m), 1014(w), 995(m), 929(w), 879(w), 742(vs); HRMS (m/z) $[M + H]^+$ calcd for $C_{10}H_{13}N_2$, 161.1073, found 161.1073.

2-Isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1ag). Eluent: EtOAc/PE 20:80 (enriched with 3% of MeOH); yield: 87 mg, 93%; white solid, mp 204-206 ºC (lit.[24] mp 210 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 2H), 3.24 (hept, *J* = 6.8 Hz, 1H), 2.33(s, 6H), 1.44(d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_3OD): δ 159.2, 136.9, 130.9, 114.9, 29.0, 21.6, 20.3; IR (film) 2963(m), 1541(w), 1445(vs), 1377(w), 1309(s), 1238(w), 1166(m), 1111(m), 1087(m), 1071(w), 1000(s), 928(w), 850(s); HRMS (m/z) $[M + H]^+$ calcd for $C_{12}H_{17}N_2$, 189.1386, found 189.1387.

5,6-Dibromo-2-isopropyl-1*H*-benzo[*d*]imidazole (1ah). Eluent: EtOAc/PE 25:75 (enriched with 3% of MeOH); yield: 136 mg, 86%; white solid, mp 203-205 ºC; ^{1}H NMR (400 MHz, CD_3OD): δ 7.83 (s, 2H), 3.22 (hept, *J* = 7.2 Hz, 1H), 1.43(d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_3OD): δ 162.9, 124.8, 116.4, 28.8, 20.1; IR (film) 2972(m), 1532(w), 1437(s), 1356(m), 1295(m), 1276(m), 1095(s), 1078(w), 1003(w), 928(w), 858(vs), 846(s), 609(w); HRMS (m/z) $[M + H]^+$ calcd for $C_{10}H_{11}Br_2N_2$, 316.9283, found 316.9287.

▪ Associated Content

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products **1** and **7**, and imine **3a**, and X-ray structures and data of compound **1l** (CIF). This material is available free of charge via

the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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a large amount of substrate **2a** left. This also supports that the present C–H amidation reaction more likely undergoes the *path a* mechanism, and the formation of imine **3a** is necessary. Moreover, a similar mechanism has been demonstrated in our previous work for pyrazole synthesis (ref 4c).

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