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Iodine-Mediated Aryl C–H Amination for the Synthesis of Benzimidazoles and Pyrido[1,2-*a*]benzimidazoles

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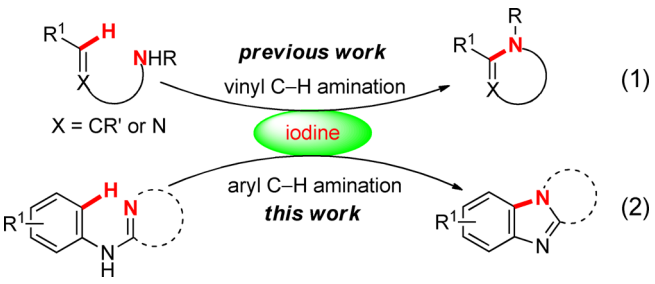
Abstract: An intramolecular aryl C–H amination reaction has been achieved using molecular iodine as the sole oxidant for the synthesis of benzimidazole derivatives. The required substrates were readily prepared by addition or coupling of arylamines with the corresponding nitriles or aryl iodides. Iodine-mediated oxidative cyclization of these substrates in the presence of potassium carbonate (K_2CO_3) as base afforded the corresponding products in moderate to good yields. The transition metal-free protocol presented here is insensitive to air and operationally simple. This versatile and eco-friendly synthetic methodology is broadly applicable to a variety of *N*-aryl-substituted amidines and pyridin-2-amines, and provides direct access to both 1*H*-benzo[*d*]imidazole and pyrido[1,2-*a*]benzimidazole derivatives from the corresponding precursors.

Keywords: amination; benzimidazoles; iodine; oxidative cyclization; pyrido[1,2-*a*]benzimidazoles

Introduction

As an inexpensive and eco-friendly oxidant, molecular iodine has been extensively applied to promote transformations, including oxidation of O/S-containing functional groups,[1] aromatization,[2] and iodocyclization/cyclodehydroiodination.[3] In recent years, numerous oxidative annulation reactions have been developed with this readily available reagent to construct diverse heterocyclic skeletons.[4] In particular, iodine (I_2)-mediated oxidative C–N bond formation is a valuable tool for the synthesis of N-containing heterocycles. For example, utilizing *in-situ* generated α-keto aldehydes through oxidation of methyl ketones by I_2/DMSO, Wu et al. have prepared compounds such as, quinazoline-4(3*H*)-ones,[5] isoquinolines,[6] and imidazo[1,2-*a*]pyridines.[7] In 2013, Zhang[8] described a route to indoles and indolines from N-protected β-2′-aminophenyl ketones in the presence of iodine. Earlier, we synthesized pyrazoles[9] and 1,3-diazaheterocyclic derivatives[10] *via* iodine-promoted, one-pot reactions, but most of these methods were achieved through functionalization of vinyl or α-C=O C–H bonds. Direct aryl C–H amination reactions using molecular iodine as the sole oxidant are rarely reported. Batra[11] and Sekar[12] disclosed such intramolecular reactions to prepare quinolines and indole-fused tetracycles, respectively, and Liang[13] and Huang[14] reported intermolecular examples for regioselective amination at C-2 of indoles. As a continuation of our research on I_2-mediated C–H functionalization, we envisioned an aryl C–H amination reaction for the synthesis of benzimidazoles from *N*-arylamidines and pyrido[1,2-*a*]benzimidazoles from *N*-aryl-2-aminopyridines, and describe the results in this paper (Scheme 1).

The benzimidazole scaffold is an important structure in medicinal chemistry.[15] Mebendazole (Figure 1), for example, is a highly effective antihelmintic for the treatment of a number of worm infec-



Scheme 1. Proposed route to benzimidazole derivatives *via* aryl C–H amination [Eq. (2)] based on the previous vinyl C–H amination reactions [Eq. (1)].

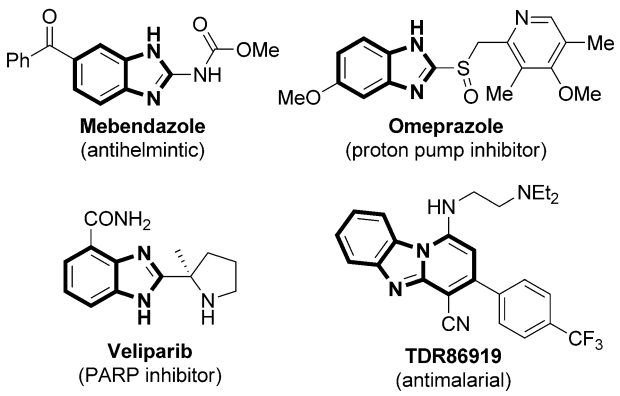


Figure 1. Representative molecules containing benzimidazole or pyrido[1,2-a]benzimidazole skeletons.

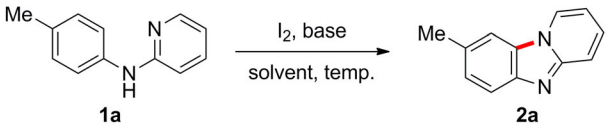
tions. As a selective and irreversible proton pump inhibitor, omeprazole is another important medication essential to a basic health system. Veliparib, a potent and orally active PARP inhibitor, is currently in phase II clinical trials[16] and TDR86919, a pyrido[1,2-*a*]benzimidazole derivative, has been identified as having promising antimalarial activity both *in vitro* and *in vivo*.[17] Furthermore, some pyrido[1,2-*a*]benzimidazoles also display interesting photophysical and fluorescence properties.[18] A variety of synthetic methods have been developed for the preparation of this class of compounds.[19] Recently, significant progress has been made in transition metal-catalyzed aerobic oxidation[20] and hypervalent iodine-mediated oxidative cyclization.[21] These reactions proceed through direct C–H cycloamination of readily available *N*-arylamidines without prefunctionalization of the reaction centers, making the synthesis simpler and more efficient. We report such a reaction employing molecular iodine.

Results and Discussion

We used *N*-(*p*-tolyl)pyridin-2-amine (**1a**) as the model substrate in an oxidative cyclization producing pyrido[1,2-*a*]benzimidazole **2a** (Table 1). An initial screening of the reaction conditions indicated that 1,4-dioxane is the most effective solvent for this conversion. Full consumption of substrate **1a** requires at least 3.0 equiv. of iodine at 60 °C (entry 2). The conversion becomes slower at lower temperature (not shown) and produces the desired product **2a** in a lower yield at 80 °C with some by-products which remain unidentified (entry 3). The use of Cs_2CO_3 as base (entry 4) or replacement of 1,4-dioxane with DMSO (entry 5) also results in decreased yields.

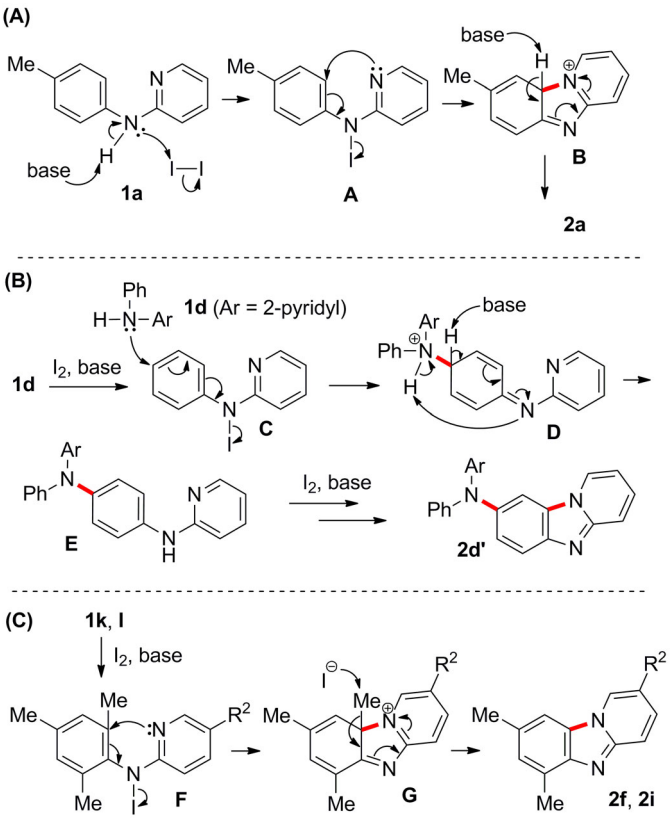
Various *N*-arylpyridin-2-amines (Table 2) were subjected to the optimal reaction conditions above (Table 1, entry 2). Substrates bearing electron-donating groups (EDGs) (**1a–c**) on the *N*-phenyl ring afford the desired pyrido[1,2-*a*]benzimidazoles (**2a–c**) in good yield; while the presence of electron-withdrawing groups (EWGs, e.g., halogen) on this ring make the reaction more complex (not shown). Interestingly, the substrate with an unsubstituted phenyl

Table 1. Optimization of the reaction conditions for the synthesis of pyrido[1,2-*a*]benzimidazole **2a**.[a]



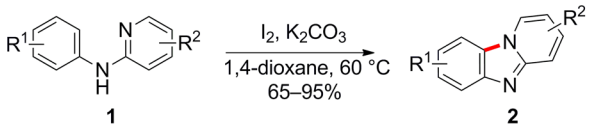
Entry	I_2 (equiv.)	Base	Solvent	Temp.	Time	Yield[b]
1	2.0	K_2CO_3	1,4-dioxane	60 °C	9 h	44%
2	3.0	K_2CO_3	1,4-dioxane	60 °C	5 h	70%
3	3.0	K_2CO_3	1,4-dioxane	80 °C	5 h	55%
4	3.0	Cs_2CO_3	1,4-dioxane	60 °C	5 h	39%
5	3.0	K_2CO_3	DMSO	60 °C	5 h	50%

[a] *Optimal reaction conditions (entry 2):* **1a** (0.5 mmol), I_2 (1.5 mmol), K_2CO_3 (2 mmol), 1,4-dioxane, 60 °C.
[b] Isolated yields.

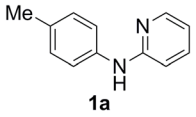
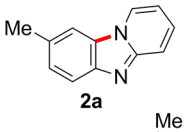
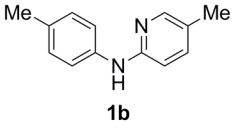
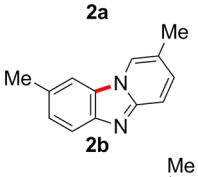
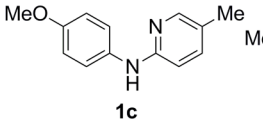
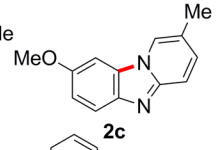
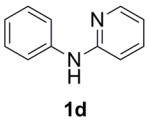
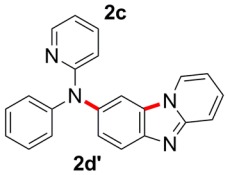
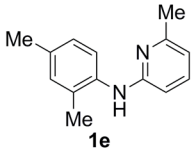
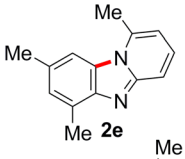
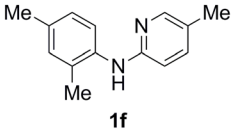
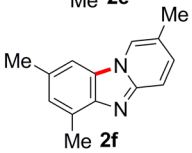
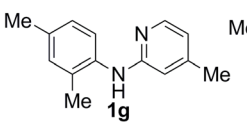
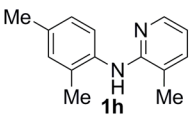
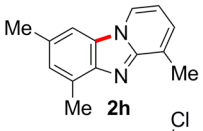
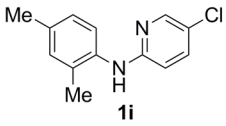
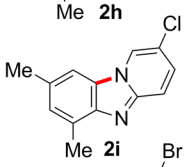
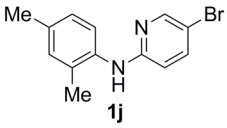
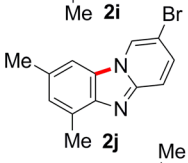
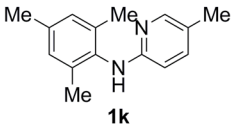
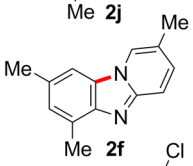
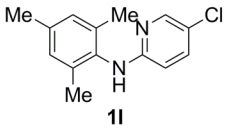
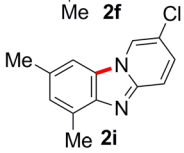


Scheme 2. Proposed mechanisms for the I_2-mediated aryl C–H amination: (**A**) oxidative cyclization of **1a** to **2a**; (**B**) formation of **2d′** from **1d**; (**C**) synthesis of **2f** and **2i** from **1k**, **l**.

Table 2. Substrate scope for the synthesis of pyrido[1,2-*a*]benzimidazoles **2**.[a]



1 **2**

Entry	Substrate	Product	Time	Yield[b]
1	 **1a**	 **2a**	5 h	70%
2	 **1b**	 **2b**	5 h	92%
3	 **1c**	 **2c**	5.5 h	91%
4	 **1d**	 **2d'**	6 h	94%
5	 **1e**	 **2e**	4.5 h	95%
6	 **1f**	 **2f**	9 h	95%
7	 **1g**	 **2g**	4 h	91%
8	 **1h**	 **2h**	3.5 h	95%
9	 **1i**	 **2i**	4 h	84%
10	 **1j**	 **2j**	5 h	65%
11[c]	 **1k**	 **2f**	6 h	81%
12[c]	 **1l**	 **2i**	6 h	69%

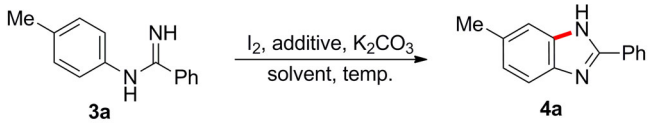
[a] *Optimal reaction conditions:* **1** (0.5 mmol), I_2 (1.5 mmol), K_2CO_3 (2 mmol), 1,4-dioxane, 60 °C.
[b] Isolated yields.
[c] 2.5 mmol of I_2 and 3 mmol of K_2CO_3 were used.

moiety (**1d**) gives the product **2d′** which when aminated by a second molecule of the substrate reacts further (Scheme 2B). This was confirmed by X-ray (see the Supporting Information).[22] This methodology can tolerate both EDGs (**1e–h**) and EWGs (**1i–j**) on the pyridine ring, with the methyl-substituted substrates giving higher yields (**2e–h**). It is worthy of note that both 2,4,6-trimethylphenylpyridin-2-amines (**1k**, **l**) also produce the cyclized products through a demethylation process. A plausible mechanism for this conversion is shown in Scheme 2C.

A plausible mechanism for this I_2-mediated aryl C–H amination reaction is proposed in Scheme 2A. Using the formation of **2a** as an example, the base-mediated oxidative iodination of substrate **1a** produces an *N*-iodo species (**A**). Then the N–I bond is cleaved, and consequently, cyclization of the iodide (**A**) generates intermediate **B** which contains a new C–N bond. Finally, the subsequent proton elimination by base and rearomatization lead to the pyrido[1,2-*a*]benzimidazole skeleton (**2a**). For substrate **1d** (Scheme 2B), due to the absence of substituents at the *para*-position of the *N*-phenyl ring (**C**), a second molecule of **1d** attacks the *para*-carbon before the cyclization step to form a dimer (**E**). Further I_2-mediated oxidative cyclization of **E** eventually affords compound **2d′**. For the substrates with a 2,4,6-trimethylphenyl moiety (**1k**, **l**) (Scheme 2C), cyclization of the iodide **F** generates first the intermediate **G**, which can then undergo demethylation to give the corresponding product.

In light of these results, we further extended the scope of this aryl C–H amination reaction to synthesize benzimidazoles from *N*-arylamidines (Table 3).

Table 3. Optimization of the reaction conditions for the synthesis of benzimidazole **4a**.[a]



Entry	I_2 (equiv.)	Additive	Solvent	Temp.	Time	Yield[b]
1	3.0	–	1,4-dioxane	60 °C	22 h	trace
2	3.0	–	1,4-dioxane	reflux	11 h	34%
3	3.0	–	DMSO	120 °C	6 h	46%
4	3.0	KI	DMSO	120 °C	0.5 h	62%
5	1.5	KI	DMSO	120 °C	0.5 h	70%
6	1.2	KI	DMSO	120 °C	1 h	68%
7	1.5	KI	DMSO	110 °C	1 h	66%

[a] *Optimal reaction conditions (entry 5):* a well-stirred mixture of I_2 (0.75 mmol) and KI (0.75 mmol) in DMSO (5 mL) was treated with **3a** (0.5 mmol), followed by the addition of K_2CO_3 (1.75 mmol) and DMSO (5 mL), and then heated to 120 °C.

[b] Isolated yields.

However, the cyclization of substrate **3a** under the above conditions is very slow and only a trace amount of product **4a** was formed (entry 1). At reflux temperature the reaction produced **4a** in 34% yield (entry 2). Replacement of 1,4-dioxane with DMSO results in a better yield but the total consumption of **3a** still required a longer time (entry 3). Based upon our experience with the I_2/KI-mediated N–N bond formation reaction,[23] we added KI to the reaction system. This greatly accelerated the transformation and improved the yield of the product (entry 4). Furthermore, in the presence of KI, 120 °C is the optimal temperature and 1.5 equiv. of iodine are sufficient for the transformation (entry 5).

With the optimum reaction conditions (Table 3, entry 5) in hand, we examined the substrate scope for benzimidazole synthesis (Table 4). *N*-Arylamidines bearing both EDGs and EWGs on the *N*-phenyl ring (**3a–i**) are compatible with this oxidative cyclization protocol. The chlorinated (**3d**) and unsubstituted (**3e**) substrates give lower yields. Both 2-aryl (**4a–n**) and 2-alkyl (**4o–p**) substituted benzimidazoles were prepared by replacing the phenyl moiety at the R^3 position (Table 4) with the corresponding substituents.

Conclusions

In summary, we have established a new I_2-mediated intramolecular aryl C–H amination reaction for benzimidazole synthesis. This transition metal-free and versatile protocol is not sensitive to air and operationally simple. It works well with both *N*-aryl-substituted amidines and 2-aminopyridines to produce 1*H*-benzo[*d*]imidazole and pyrido[1,2-*a*]benzimidazole derivatives, respectively. Further application of this I_2-mediated cycloamination method to construct other heterocyclic skeletons is currently in progress in our laboratory.

Experimental Section

General Information

^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400 MHz (100 MHz for ^{13}C NMR) spectrometer. Chemical shift values are given in parts per million (ppm) with tetramethylsilane (TMS) as the internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets. The coupling constants (*J*) are reported in Hertz (Hz). Melting points were determined on an XT4A micromelting point apparatus and are uncorrected. High-resolution mass spectra (HR-MS) were obtained on a Bruker MicrOTOF-Q II mass spectrometer equipped with an electrospray ion source (ESI), operated in the positive mode. Flash column chromatography was performed over silica gel 200–300 mesh and the eluents were distilled prior to use. 1,4-Dioxane and DMSO were dried over 4 Å molecular sieves before use. All the chemicals (AR grade) were purchased from Aladdin or Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and were used without further purification.

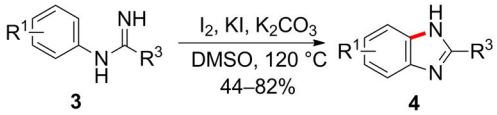
General Procedure for the Synthesis of Products 2

A stirred solution of *N*-arylpyridin-2-amine **1** (0.5 mmol) in 1,4-dioxane (10 mL) was treated sequentially with iodine (381 mg, 1.5 mmol) and K_2CO_3 (276 mg, 2 mmol). The resulting mixture was heated to 60 °C until TLC indicated that the conversion was complete. After cooling to room temperature, the reaction was quenched with 5% $Na_2S_2O_3$ (15 mL) and extracted with EtOAc (3×15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography using a mixture of EtOAc and petroleum ether as the eluent to afford product **2**.

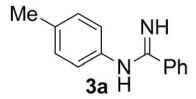
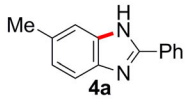
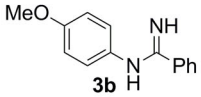
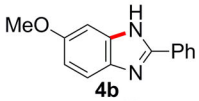
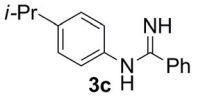
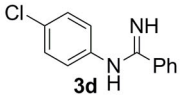
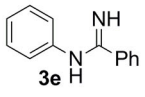
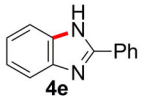
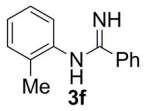
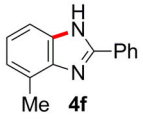
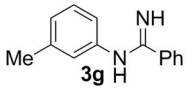
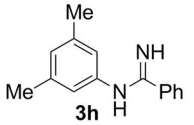
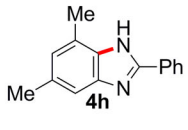
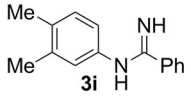
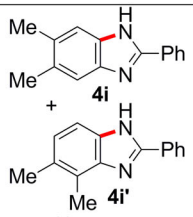
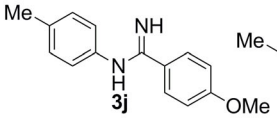
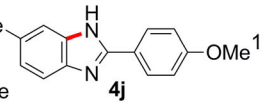
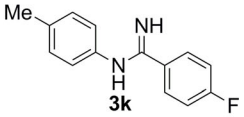
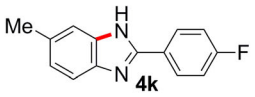
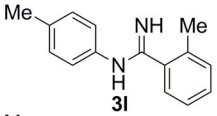
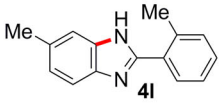
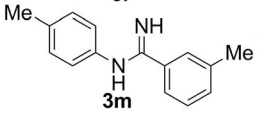
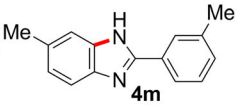
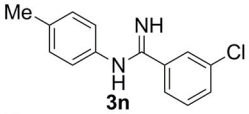
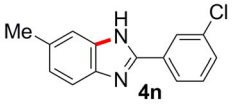
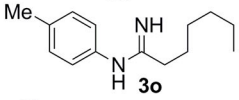
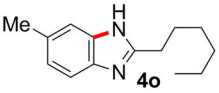
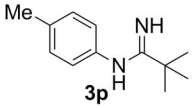
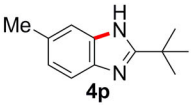
8-Methylbenzo[4,5]imidazo[1,2-*a*]pyridine (2a): 5 h; yield: 64 mg (70%); brown solid; mp 111–112 °C; R_f=0.32 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6): δ=8.96 (d, J=6.8 Hz, 1H), 8.07 (s, 1H), 7.66 (d, J=8.4 Hz, 1H), 7.60 (d, J=9.2 Hz, 1H), 7.50–7.46 (m, 1H), 7.30 (d, J=8.4 Hz, 1H), 6.94 (t, J=6.8 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=147.9, 142.4, 130.6, 130.1, 129.1, 127.5, 127.2, 119.0, 117.4, 111.8, 110.6, 21.9; HR-MS: m/z=183.0917 $[M+H]^+$, calcd. for $C_{12}H_{11}N_2$: 183.0917.

2,8-Dimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2b): 5 h; yield: 90 mg (92%); brown solid; mp 135–136 °C; R_f=0.30 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6): δ=8.78 (s, 1H), 8.00 (s, 1H), 7.64 (d, J=8.4 Hz, 1H), 7.54 (d, J=9.2 Hz, 1H), 7.37–7.34 (m, 1H), 7.29–7.26 (m, 1H), 2.50 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=147.0, 142.4, 133.2, 130.3, 129.0, 127.2, 124.4, 119.8, 118.9,

Table 4. Substrate scope for the synthesis of benzimidazoles **4**.[a]



3 **4**

Entry	Substrate	Product	Time	Yield[b]
1	 **3a**	 **4a**	0.5 h	70%
2	 **3b**	 **4b**	1 h	63%
3	 **3c**	 **4c**	1 h	81%
4	 **3d**	 **4d**	1.5 h	44%
5	 **3e**	 **4e**	0.5 h	46%
6	 **3f**	 **4f**	1 h	54%
7	 **3g**	**4a**:**4f** (1:0.8)[c]	1 h	62%
8	 **3h**	 **4h**	1 h	64%
9	 **3i**	 **4i** + **4i'**	1 h	38% + 37%
10	 **3j**	 **4j**	1.5 h	74%
11	 **3k**	 **4k**	1.5 h	64%
12	 **3l**	 **4l**	1.5 h	45%
13	 **3m**	 **4m**	1 h	82%
14	 **3n**	 **4n**	1 h	71%
15	 **3o**	 **4o**	0.5 h	47%
16	 **3p**	 **4p**	4.5 h	46%

[a] *Optimal reaction conditions:* A well-stirred mixture of I_2 (0.75 mmol) and KI (0.75 mmol) in DMSO (5 mL) was treated with **3a** (0.5 mmol), followed by the addition of K_2CO_3 (1.75 mmol) and DMSO (5 mL), and then heated to 120 °C.
[b] Isolated yields.
[c] The ratio was determined by ^{1}H NMR.

116.8, 111.7, 21.9, 18.0; HR-MS: m/z = 197.1072 $[M+H]^+$, calcd. for $C_{13}H_{13}N_2$: 197.1073.

8-Methoxy-2-methylbenzo[4,5]imidazo[1,2-*a*]pyridine (2c): 5.5 h; yield: 97 mg (91%); black solid; mp 169–170 °C; R_f = 0.36 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.79 (d, J = 1.2 Hz, 1H), 7.82 (s, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 9.6 Hz, 1H), 7.33–7.29 (m, 1H), 7.11–7.07 (m, 1H), 3.87 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.0, 146.8, 138.8, 132.3, 129.1, 124.1, 120.0, 119.6, 116.9, 116.0, 94.8, 56.2, 18.0; HR-MS: m/z = 213.1023 $[M+H]^+$, calcd. for $C_{13}H_{13}N_2O$: 213.1022.

***N*-Phenyl-*N*-(pyridin-2-yl)benzo[4,5]imidazo[1,2-*a*]pyridin-8-amine (2d'):** 6 h; yield: 158 mg (94%); light yellow solid; mp 189–191 °C; R_f = 0.41 (EtOAc); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.01 (d, J = 6.8 Hz, 1H), 8.26 (d, J = 2.0 Hz, 1H), 8.10–8.08 (m, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 9.2 Hz, 1H), 7.53–7.48 (m, 2H), 7.34–7.26 (m, 3H), 7.20 (s, 1H), 7.18 (s, 1H), 7.09 (t, J = 7.2 Hz, 1H), 6.92 (t, J = 7.2 Hz, 1H), 6.82–6.79 (m, 1H), 6.60 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.2, 148.9, 148.1, 146.5, 142.4, 139.2, 138.1, 130.5, 129.7, 127.6, 126.7, 126.2, 124.5, 120.4, 117.5, 116.1, 112.4, 111.9, 110.9; HR-MS: m/z = 337.1445 $[M+H]^+$, calcd. for $C_{22}H_{17}N_4$: 337.1448.

1,6,8-Trimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2e): 4.5 h; yield: 104 mg (≥95%); yellow solid; mp 154–155 °C; R_f = 0.28 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-

d_6): δ = 7.91 (s, 1H), 7.54 (d, J = 9.2 Hz, 1H), 7.43–7.39 (m, 1H), 7.17 (s, 1H), 6.73 (d, J = 6.4 Hz, 1H), 3.02 (s, 3H), 2.63 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.5, 142.5, 139.9, 129.8, 129.6, 129.4, 128.1, 126.9, 115.0, 112.9, 110.8, 22.0, 21.2, 17.3; HR-MS: m/z = 211.1229 [M+H]$^+$, calcd. for $C_{14}H_{15}N_2$: 211.1230.

2,6,8-Trimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2f): 9 h; yield: 104 mg (≥95%); black solid; mp 108–109 °C; R_f = 0.39 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.73 (s, 1H), 7.80 (s, 1H), 7.54 (d, J = 9.6 Hz, 1H), 7.33 (d, J = 9.2 Hz, 1H), 7.09 (s, 1H), 2.57 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 146.5, 142.1, 132.6, 130.2, 128.48, 128.46, 127.1, 124.4, 119.7, 117.0, 109.0, 21.9, 18.0, 17.2; HR-MS: m/z = 211.1235 [M+H]$^+$, calcd. for $C_{14}H_{15}N_2$: 211.1230.

3,6,8-Trimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2g): 4 h; yield: 96 mg (91%); gray solid; mp 136–137 °C; R_f = 0.45 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.77 (d, J = 6.8 Hz, 1H), 7.79 (s, 1H), 7.38 (s, 1H), 7.07 (s, 1H), 6.75 (dd, J = 7.2, 1.6 Hz, 1H), 2.56 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.8, 142.2, 140.3, 129.8, 128.6, 128.2, 127.1, 126.2, 115.4, 113.1, 109.0, 21.84, 21.75, 17.2; HR-MS: m/z = 211.1230 [M+H]$^+$, calcd. for $C_{14}H_{15}N_2$: 211.1230.

4,6,8-Trimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2h): 3.5 h; yield: 104 mg (≥95%); brown solid; mp 99–100 °C; R_f = 0.46 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.73 (d, J = 6.8 Hz, 1H), 7.81 (s, 1H), 7.24 (dd, J = 6.8, 1.2 Hz, 1H), 7.09 (s, 1H), 6.81 (t, J = 6.8 Hz, 1H), 2.59 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.0, 141.7, 130.3, 129.2, 128.6, 127.5, 127.3, 127.0, 124.7, 110.4, 109.2, 21.9, 17.6, 17.3; HR-MS: m/z = 211.1230 [M+H]$^+$, calcd. for $C_{14}H_{15}N_2$: 211.1230.

2-Chloro-6,8-dimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2i): 4 h; yield: 97 mg (84%); brown solid; mp 144–145 °C; R_f = 0.42 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.23 (d, J = 4.0 Hz, 1H), 7.90 (s, 1H), 7.68–7.64 (m, 1H), 7.50–7.45 (m, 1H), 7.13 (s, 1H), 2.58 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.5, 142.4, 131.2, 130.2, 128.9, 128.7, 127.8, 125.4, 118.5, 117.2, 109.5, 21.9, 17.1; HR-MS: m/z = 231.0673 [M+H]$^+$, calcd. for $C_{13}H_{12}ClN_2$: 231.0684.

2-Bromo-6,8-dimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (2j): 5 h; yield: 89 mg (65%); yellow solid; mp 138–139 °C; R_f = 0.43 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.30 (s, 1H), 7.92 (s, 1H), 7.62–7.52 (m, 2H), 7.13 (s, 1H), 2.57 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.6, 142.2, 132.3, 131.2, 128.8, 128.6, 127.8, 127.6, 118.7, 109.5, 103.9, 21.9, 17.1; HR-MS: m/z = 275.0177 [M+H]$^+$, calcd. for $C_{13}H_{12}BrN_2$: 275.0178.

General Procedure for the Synthesis of Products 4

A mixture of KI (125 mg, 0.75 mmol) and iodine (191 mg, 0.75 mmol) in DMSO (5 mL) was stirred at room temperature for 10 min and then treated with *N*-arylamidine **3** (0.5 mmol), followed by the addition of K_2CO_3 (242 mg, 1.75 mmol) and DMSO (5 mL). The reaction mixture was maintained at 120 °C until TLC indicated the conversion was complete. After cooling to room temperature, it was quenched with 5% $Na_2S_2O_3$ (5 mL), followed by the addition of 5% aqueous ammonia (15 mL), and then extracted with EtOAc (3×15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and then purified by silica gel column chromatography using a mixture of EtOAc and petroleum ether as the eluent to afford the desired product **4**.

6-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole (4a): 0.5 h; yield: 73 mg (70%); yellow solid; mp 251–252 °C; R_f = 0.26 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.76 (br, s, 1H), 8.17–8.15 (m, 2H), 7.56–7.45 (m, 4H), 7.38 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 151.0, 131.3, 130.4, 129.6, 128.9, 126.4, 123.6, 21.4; HR-MS: m/z = 209.1074 [M+H]$^+$, calcd. for $C_{14}H_{13}N_2$: 209.1073.

6-Methoxy-2-phenyl-1*H*-benzo[*d*]imidazole (4b): 1 h; yield: 71 mg (63%); yellow solid; mp 152–153 °C; R_f = 0.53 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6, mixture of tautomers, *peaks of the minor tautomer): δ = 12.78* (br, s, 0.41H), 12.76 (br, s, 0.53H), 8.16–8.12 (m, 2H), 7.56–7.41 (m, 4H), 7.22* (s, 0.40H), 7.00 (s, 0.54H), 6.87–6.82 (m, 1H), 3.82 (s, 1.74H), 3.81* (s, 1.25H); ^{13}C NMR (100 MHz, DMSO-d_6, mixture of tautomers, *peaks of the minor tautomer): δ = 156.1, 155.4*, 151.4*, 150.4, 144.7*, 138.3, 135.7, 130.4, 129.6*, 129.4, 128.9, 126.2*, 126.1, 119.4, 112.3*, 111.6*, 111.2, 101.3*, 94.4, 55.5; HR-MS: m/z = 225.1021 [M+H]$^+$, calcd. for $C_{14}H_{13}N_2O$: 225.1022.

6-Isopropyl-2-phenyl-1*H*-benzo[*d*]imidazole (4c): 1 h; yield: 96 mg (81%); brown solid; mp 90–91 °C; R_f = 0.33 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.76 (br, s, 1H), 8.17–8.14 (m, 2H), 7.55–7.44 (m, 4H), 7.41 (s, 1H), 7.09 (dd, J = 8.4, 1.6 Hz, 1H), 3.05–2.94 (m, 1H), 1.25 (d, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 151.5, 143.2, 130.8, 130.1, 129.4, 126.7, 121.5, 34.1, 24.94, 24.89; HR-MS: m/z = 237.1391 [M+H]$^+$, calcd. for $C_{16}H_{17}N_2$: 237.1386.

6-Chloro-2-phenyl-1*H*-benzo[*d*]imidazole (4d): 1.5 h; yield: 50 mg (44%); white solid; mp 176–177 °C; R_f = 0.41 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6, mixture of tautomers, *peaks of the minor tautomer): δ = 13.11 (s, 0.51), 13.08* (s, 0.45H), 8.18–8.16 (m, 2H), 7.72* (s, 0.45H), 7.67 (d, J = 8.8 Hz, 0.52H), 7.58–7.49 (m, 4H), 7.25–7.20 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.1, 130.7, 130.1, 129.5, 127.0, 122.8; HR-MS: m/z = 229.0527 [M+H]$^+$, calcd. for $C_{13}H_{10}ClN_2$: 229.0527.

2-Phenyl-1*H*-benzo[*d*]imidazole (4e): 0.5 h; yield: 45 mg (46%); brown solid; mp 278–279 °C; R_f = 0.34 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.92 (br, s, 1H), 8.19–8.16 (m, 2H), 7.60–7.46 (m, 5H), 7.21–7.18 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 151.6, 130.6, 130.3, 129.4, 126.9, 122.5; HR-MS: m/z = 195.0916 [M+H]$^+$, calcd. for $C_{13}H_{11}N_2$: 195.0917.

4-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole (4f): 1 h; yield: 56 mg (54%); yellow solid; mp 251–252 °C; R_f = 0.32 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.79 (br, s, 1H), 8.19 (d, J = 6.8 Hz, 2H), 7.55–7.38 (m, 4H), 7.08 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 130.8, 130.1, 129.3, 127.0, 17.4; HR-MS: m/z = 209.1071 [M+H]$^+$, calcd. for $C_{14}H_{13}N_2$: 209.1073.

5,7-Dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (4h): 1 h; yield: 71 mg (64%); yellow solid; mp 190–191 °C; R_f = 0.31 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.62 (br, s, 1H), 8.17 (d, J = 7.6 Hz, 2H), 7.54–7.49 (m, 2H), 7.47–7.42 (m, 1H), 7.16 (s, 1H), 6.80 (s, 1H), 2.52 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ =

130.5, 129.5, 128.8, 126.4, 21.3, 16.8; HR-MS: m/z = 223.1231 $[M+H]^+$, calcd. for $C_{15}H_{15}N_2$: 223.1230.

5,6-Dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (4i): 1 h; yield: 42 mg (38%); yellow solid; mp 255–256 °C; R_f = 0.22 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.63 (br, s, 1H), 8.14–8.11 (m, 2H), 7.53–7.48 (m, 2H), 7.45–7.41 (m, 1H), 7.34 (s, 2H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.8, 130.9, 129.9, 129.3, 126.6, 20.5; HR-MS: m/z = 223.1230 $[M+H]^+$, calcd. for $C_{15}H_{15}N_2$: 223.1230.

4,5-Dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (4i'): 1 h; yield: 41 mg (37%); yellow solid; mp 197–198 °C; R_f = 0.33 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.58 (br, s, 1H), 8.18 (d, J = 7.2 Hz, 2H), 7.54–7.50 (m, 2H), 7.47–7.43 (m, 1H), 7.27 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 2.49 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 130.9, 130.0, 129.2, 126.9, 124.8, 19.5, 14.0; HR-MS: m/z = 223.1229 $[M+H]^+$, calcd. for $C_{15}H_{15}N_2$: 223.1230.

2-(4-Methoxyphenyl)-6-methyl-1*H*-benzo[*d*]imidazole (4j): 1.5 h; yield: 88 mg (74%); yellow solid; mp 159–160 °C; R_f = 0.53 (EtOAc/PE 50:50); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.59 (br, s, 1H), 8.08 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.08 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.9, 151.5, 128.3, 123.6, 123.3, 114.8, 55.8, 21.8; HR-MS: m/z = 239.1179 $[M+H]^+$, calcd. for $C_{15}H_{15}N_2O$: 239.1179.

2-(4-Fluorophenyl)-6-methyl-1*H*-benzo[*d*]imidazole (4k): 1.5 h; yield: 72 mg (64%); yellow solid; mp 180–181 °C; R_f = 0.40 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.75 (br, s, 1H), 8.21–8.16 (m, 2H), 7.46–7.35 (m, 4H), 7.02 (d, J = 8.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.6, 162.2, 129.0 (d, J = 8.6 Hz), 127.4 (d, J = 3.0 Hz), 116.4 (d, J = 21.7 Hz), 21.8; HR-MS: m/z = 227.0984 $[M+H]^+$, calcd. for $C_{14}H_{12}FN_2$: 227.0979.

6-Methyl-2-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (4l): 1.5 h; yield: 50 mg (45%); yellow solid; mp 157–158 °C; R_f = 0.38 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.47 (br, s, 1H), 7.71 (d, J = 6.8 Hz, 1H), 7.47 (d, J = 6.8 Hz, 1H), 7.40–7.31 (m, 4H), 7.01 (d, J = 8.4 Hz, 1H), 2.59 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.4, 131.7, 130.7, 129.8, 129.6, 126.4, 21.8, 21.5; HR-MS: m/z = 223.1234 $[M+H]^+$, calcd. for $C_{15}H_{15}N_2$: 223.1230.

6-Methyl-2-(*m*-tolyl)-1*H*-benzo[*d*]imidazole (4m): 1 h; yield: 91 mg (82%); yellow solid; mp 209–210 °C; R_f = 0.42 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.70 (br, s, 1H), 7.99 (s, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.47–7.35 (m, 3H), 7.27 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.5, 130.7, 130.7, 129.2, 127.3, 123.9, 21.8, 21.5; HR-MS: m/z = 223.1230 $[M+H]^+$, calcd. for $C_{15}H_{15}N_2$: 223.1230.

2-(3-Chlorophenyl)-6-methyl-1*H*-benzo[*d*]imidazole (4n): 1 h; yield: 86 mg (71%); yellow solid; mp 147–148 °C; R_f = 0.49 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.92 (br, s, 1H), 8.21 (s, 1H), 8.14–8.11 (m, 1H), 7.60–7.49 (m, 3H), 7.40 (s,1H), 7.05 (d, J = 8.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 149.8, 134.2, 132.7, 131.4, 129.8, 126.3, 125.3, 124.4, 21.8; HR-MS: m/z = 243.0675 $[M+H]^+$, calcd. for $C_{14}H_{12}ClN_2$: 243.0684.

2-Hexyl-6-methyl-1*H*-benzo[*d*]imidazole (4o): 0.5 h; yield: 51 mg (47%); brown oil; R_f = 0.24 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.31 (d, J = 8.0 Hz, 1H), 7.22 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 2.75 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.76–1.68 (m, 2H), 1.32–1.21 (m, 6H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.2, 130.4, 122.8, 31.4, 29.0, 28.8, 28.0, 22.5, 21.7, 14.4; HR-MS: m/z = 217.1692 $[M+H]^+$, calcd. for $C_{14}H_{21}N_2$: 217.1699.

2-(*tert*-Butyl)-6-methyl-1*H*-benzo[*d*]imidazole (4p): 4.5 h; yield: 43 mg (46%); yellow solid; mp 205–206 °C; R_f = 0.25 (EtOAc/PE 25:75); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.94 (br, s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.25 (s, 1H), 6.93 (d, J = 8.0 Hz, 1H), 2.39 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.2, 130.5, 122.8, 33.6, 29.7, 21.8; HR-MS: m/z = 189.1386 $[M+H]^+$, calcd. for $C_{12}H_{17}N_2$: 189.1386.

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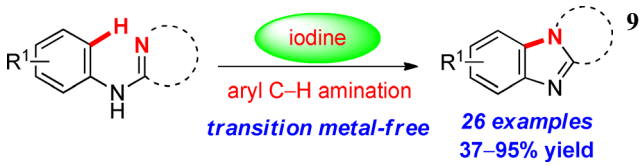
Iodine-Mediated Aryl C–H Amination for the Synthesis of Benzimidazoles and Pyrido[1,2-*a*]benzimidazoles



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