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Aerobic Copper-Catalyzed Halocyclization of Methyl *N*-Heteroaromatics with Aliphatic Amines: Access to Functionalized Imidazo-Fused *N*-Heterocycles

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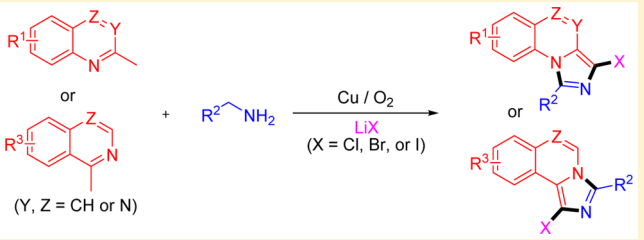
Supporting Information

ABSTRACT: A new aerobic copper-catalyzed halocyclization reaction of methyl *N*-heteroaromatics and aliphatic amines has been developed, which enables straightforward access to functionalized imidazo-fused *N*-heterocycles with the merits of good functional tolerance, use of easily available copper salts as the catalysts, lithium halides as the halogen sources, and O_2 as a sole oxidant. Due to the reaction features' selective introduction of halogen functionalities to the newly formed imidazo ring, further extensions of the developed chemistry toward synthetic diversity, including effective access to functional materials, are easily envisioned.



INTRODUCTION

Aerobic copper-catalyzed C−H functionalization constitutes one of the most powerful tools for carbon−carbon and carbon−heteroatom bond formations.[1] Among which, the direct aryl C−H halogenation is of particular importance in both laboratory chemical preparation and industry applications.[2] Conventionally, such a goal was realized on the basis of using various halogen sources such as bromine, iodine, hypobromites, etc.[3] To obtain more green and efficient halogenated aromatics, contributions on aerobic copper-catalyzed halogenation of arenes and heteroarenes have also been elegantly demonstrated.[4] However, direct access to aryl halides from readily available raw materials, through in situ introduction of halogens to the newly constructed aryl ring in one operation, has been rarely studied.

Imidazo[1,5-*a*]- and imidazo[1,5-*c*]-*N*-heteroaromatics constitute a significant important class of compounds that exhibit diverse bioactivities[5] and interesting optoelectronic properties.[6] Therefore, the search for alternative approaches to obtain these products has long been an attractive topic in synthetic organic chemistry. Pioneered by Vilsmeier-type cyclization,[7] various new protocols[8] have also been developed during the past decade, and representative examples mainly involve the iodine-mediated cyclization of *N*-2-pyridylmethyl thioamides,[8a] oxidative condensation−cyclization of aldehydes with aryl 2-pyridylmethylamines in the presence of elemental sulfur,[8b] dehydrative aromatization of *N*-(2-pyridinylmethyl)-benzamide,[8c] and the oxidative coupling of 2-carbonyl *N*-heteroaromatics with amines[9] or amino acids.[10] Interestingly, direct oxidative cyclization of 2-alkyl-*N*-heteroaromatics with alkyl amines has also been recently explored.[11] Despite these important advances, the halocyclization of heteroaromatics with aliphatic amines, leading to imidazo-fused *N*-heteroaryl halides, still remains unresolved.

Considering the catalytic aminohalogenation of alkenes reported by our group,[12] we set out to address the above-described synthetic issue. Herein, we report a new aerobic copper-catalyzed halocyclization reaction of methyl *N*-heteroaromatics **1** with alkyl amines **2** by employing easily available lithium halides as the halogen sources, which enables versatile access to imidazo[1,5-*a*]- and imidazo[1,5-*c*]-*N*-heteroaryl halides in a straightforward manner (Scheme 1).

RESULTS AND DISCUSSION

To initiate our study, we chose the coupling of 2-methylquinoline **1a** with benzylamine **2a** as a model reaction to evaluate different parameters. First, in the presence of 6 equiv of LiBr, the reaction in chlorobenzene was performed at 120 °C for 22 h under 1 atm of O_2. Gratifyingly, all the tested copper salts could afford the desired halocyclization product **3aa** (Table 1, entries 1−7), and $CuBr_2$ exhibited the best activity. However, the absence of copper salt failed to give any product (entry 8). Next, we examined several polar and less-polar solvents with a catalytic amount of $CuBr_2$, but they were less effective or totally ineffective for the product formation (entries 9−11). Decrease or increase of reaction temperature led to diminished yield (entry 12). Further, the absence of LiBr gave only 8% yield (entry 13), showing that LiBr served as the halogen source. Finally, decreasing the catalyst loading (entry 14) and replacing LiBr with NaBr or KBr (entry 15) significantly decreased the

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Scheme 1. Halocyclization of Methyl *N*-Heteroaromatics with Aliphatic Amines

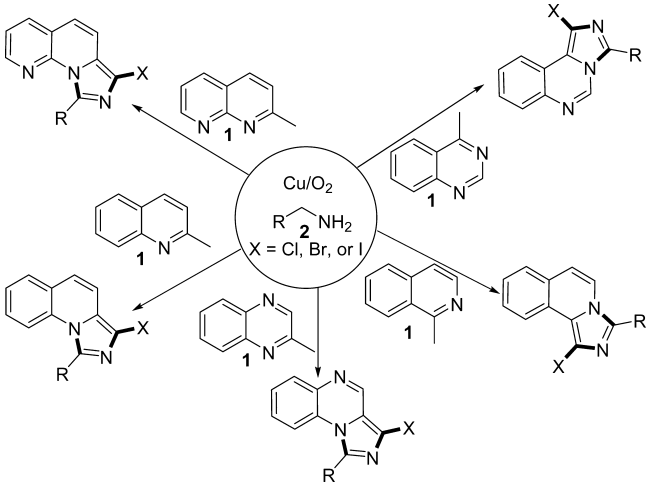
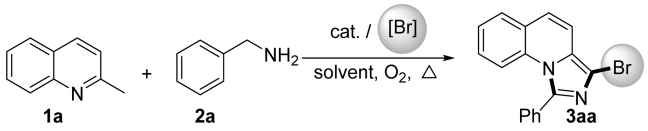


Table 1. Screening of the Reaction Conditions[a]



entry	catalyst (mol %)	Br source	solvent	yields of 3aa[b]
1	CuCl	LiBr	chlorobenzene	11
2	$CuCl_2$	LiBr	chlorobenzene	4
3	CuI	LiBr	chlorobenzene	9
4	$CuBr_2$	LiBr	chlorobenzene	90
5	CuBr	LiBr	chlorobenzene	70
6	$Cu(OAc)_2$	LiBr	chlorobenzene	85
7	$Cu(OTf)_2$	LiBr	chlorobenzene	51
8		LiBr	chlorobenzene	0
9	$CuBr_2$	LiBr	*p*-xylene	44
10	$CuBr_2$	LiBr	DMSO	0
11	$CuBr_2$	LiBr	DMF	0
12	$CuBr_2$	LiBr	chlorobenzene	(48, 88)[c]
13	$CuBr_2$		chlorobenzene	8
14	$CuBr_2$	LiBr	chlorobenzene	(28, 66)[d]
15	$CuBr_2$	(NaBr or KBr)	chlorobenzene	(18, 15)[e]

[a]Unless otherwise stated, the reaction was performed with **1a** (0.25 mmol), **2a** (0.5 mmol), cat. (20 mol %), Br source (1.5 mmol) in solvent (1.5 mL) at 120 °C for 22 h using an O_2 balloon. [b]GC yield (%). [c]Yields are with respect to 110 and 130 °C. [d]Yields are with respect to catalyst loadings of 15 and 18 mol %. [e]Yields are with respect to using NaBr and KBr as the bromine sources.

product yields. Hence, the optimal reaction conditions are as described in entry 4 of Table 1.

With the optimal conditions established, we then examined the generality and limitations of the synthetic protocol. By using 2-methylquinoline **1** as the benchmark substrate and LiBr as the halogen source, we evaluated a number of readily available aliphatic amines **2** (**2a**−**2j**: for structures, see Supporting Information Scheme S1). Gratifyingly, all the reactions proceeded smoothly and furnished the desired products in good to excellent yields upon isolation (**3aa**−**3aj**). Substituents such as −Me, −OMe, and other functional ones (−CN, −Cl, −Br) on the aryl ring of **2** were well-tolerated, and the electronic property of which affected the product yields to some extent. Specifically, electron-rich ones enabled better results (**3ab**−**3ad**) than those of electron-deficient ones (**3ae**−**3ah**). Notably, heteroaryl methylamine **2j** also served as an effective coupling partner to afford the desired product **3aj**, a potential hemilabile bidentate ligand that could be applied in the fields of catalysis and organometallic chemistry. Aliphatic amine **2k** also could be transformed into the 2-alkyl product, although the yield was somewhat low (**3ak**).

Next, we turned our attention to apply different types of *o*-methyl heteroaromatics **1**. The combinations of various 2-methylquinolines **1** with different benzylic amines **2** (for structures, see Supporting Information) were first examined. Analogous to the results described in Scheme 2, all of the reactions afforded the imidazo-fused *N*-heterocycles by selectively introducing bromo functionality to C-3 (Scheme 3). It was found that substrates **1** possessing electron-donating groups (**3ba**, **3bj**, **3ca**) gave yields much higher than those of relatively electron-poor ones (**3da**, **3db**, **3ea**). Then, dinitrogen heteroaromatics such as 4-methylquinazoline (**1f**), 2-methylquinoxaline (**1g**), and 2-methyl-1,8-naphthyridine (**1h**) also underwent smooth bromocyclization reactions to give the desired products in moderate to high yields (**3fa**, **3ga**, **3ha**). Finally, the reaction of 1-methylisoquinoline **1i** with benzylamine **2a** could produce a 1-bromo-3-phenyl product **3ia** in 72% yield.

In addition to the above bromocyclization reaction, we further wished to incorporate other halogen functionalities into the product skeletons in the presence of suitable copper catalysts and lithium halides. As shown in Scheme 4, replacing $CuBr_2$/LiBr of the optimal conditions with different copper catalysts and LiF failed to give the fluorinated product, whereas the combination of $CuCl_2$/LiCl enabled the chlorocyclization reactions, affording the chlorinated products in good yields (**4aa**, **4ab**, **4ia**). Pleasingly, by employing $Cu(OAc)_2$ as an effective catalyst and LiI as the iodine source, the catalytic cyclization reactions also proceeded smoothly to afford the iodinated products within a shorter time (**5aa** and **5ab**).

To gain insight into the reaction information, several control experiments were performed. First, the reaction of **1a** and **2a** under standard conditions was interrupted after 1.5 h to analyze the intermediates (Scheme 5, eq 1). Except for the generation of nonbrominated product **3aa-1** (33.7% yield), compounds **1a-1** and **1a-2** arising from methyl bromination and oxidation were observed in 15.5 and 7% yields, respectively. Further, both **1a-1** and **1a-2** were able to couple with **2a** to afford **3aa** in 91 and 65% yields (eq 2), respectively. Similarly, **3aa-1** underwent direct bromocyclization reaction to give **3aa** in almost quantitative yield (eq 3). These results suggest that **1a-1**, **1a-2**, and **3aa-1** are the reaction intermediates. However, upon addition of radical scavengers (TEMPO), the bromination of **3aa-1** only led to a 13% product yield (eq 4), indicating that the transformation of **3aa-1** into the final product **3aa** mainly undergoes a radical pathway. Under the same conditions, the bromocyclization of **1a** and **2a** was totally suppressed (eq 5),[11] showing that radical intermediates are also involved to generate **3aa-1**, which is in agreement with previously reported references.[13]

Based on the above findings, a tentative reaction pathway is depicted in Scheme 6. Initially, aldehyde **1a-2** is generated from **1a** through an aerobic Cu-catalyzed single electron transfer (SET) process,[13] in which the carbocupration intermediate **B** is oxidized to hypervalent species **D** in the presence of X^-, H^+,

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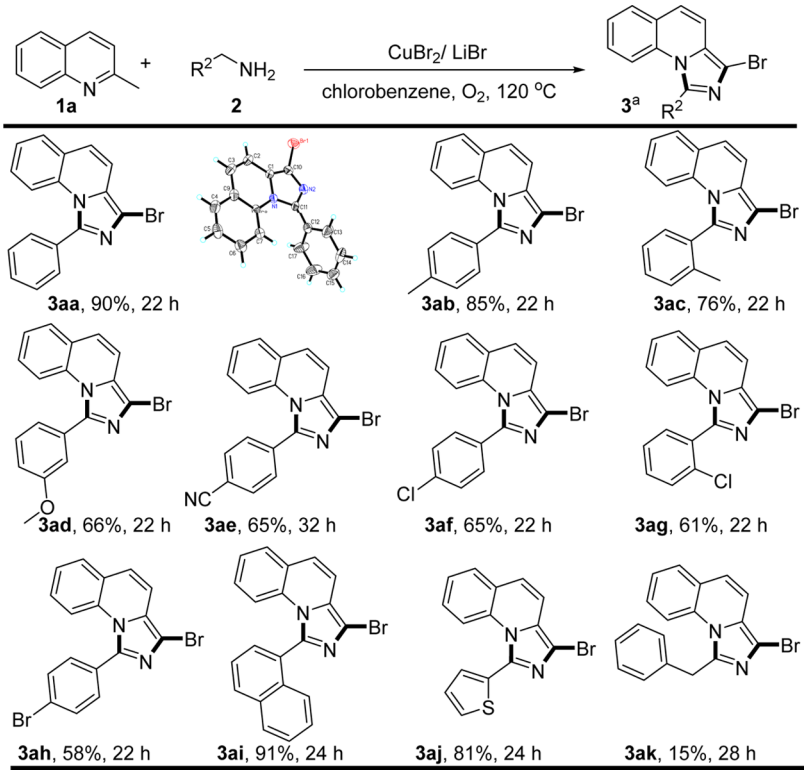
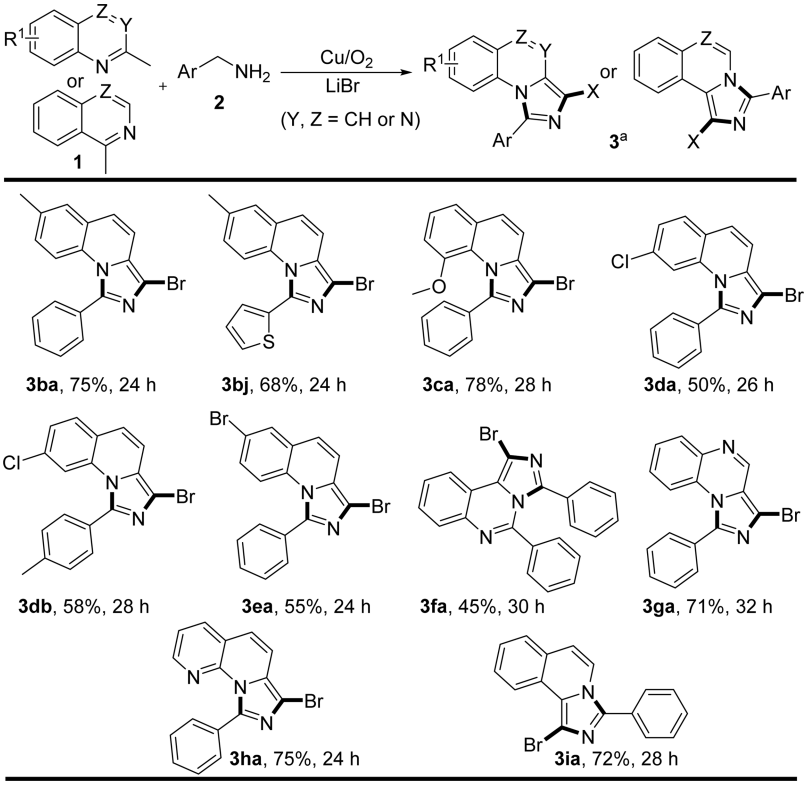
Scheme 2. Variation of Aliphatic Amines



[a]The reaction was performed with **1a** (0.25 mmol), **2** (0.5 mmol), $CuBr_2$ (20 mol %), LiBr (1.5 mmol) in chlorobenzene (1.5 mL) at 120 °C for 22−32 h using an O_2 balloon.

Scheme 3. Variation of Methyl *N*-Heteroaromatics



[a]The reaction was performed with **1** (0.25 mmol), **2** (0.5 mmol), $CuBr_2$ (20 mol %), LiBr (1.5 mmol) in chlorobenzene (1.5 mL) at 120 °C for 24−32 h using an O_2 balloon.

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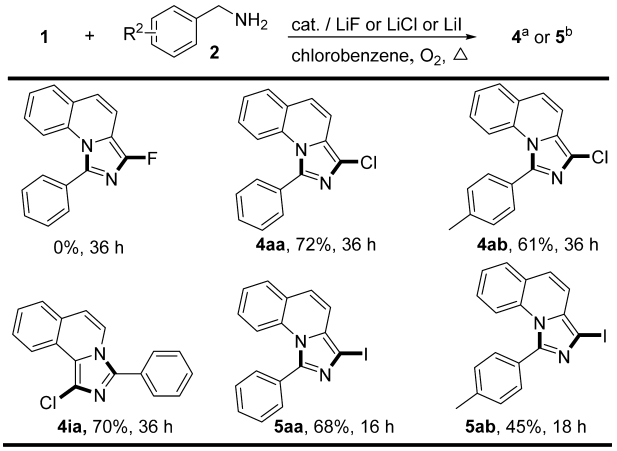
Scheme 4. Variation of Halogen Sources



[a]The reaction was performed with **1** (0.25 mmol), **2a** (0.5 mmol), $CuCl_2$ (20 mol %), LiCl (1.5 mmol) in chlorobenzene (1.5 mL) at 120 °C for 36 h using an O_2 balloon. [b]The reaction was performed with **1a** (0.25 mmol), **2a** (0.5 mmol), $Cu(OAc)_2$ (20 mol %), LiI (1.5 mmol) in chlorobenzene (1.5 mL) at 120 °C for 16−18 h using an O_2 balloon.

and O_2 and the reductive elimination (RE) of **D** leads to form a benzyl halogenated intermediate **1a-1**. Then, the oxidative coupling of **1a-1** with amine **2a** or the condensation of **1a-2** with **2a** gives imine **E**, which undergoes intramolecular oxidative cyclization to afford heterocycle **3aa-1**.[9a] Further, the acidic C−H bond of **3aa-1** reacts with [Cu^n] followed by SET from Cu to O_2, affording the [Cu^{n+1}]-superoxo radical **F**. SET from electron-rich imidazo ring to the oxygen radical forms a radical cation **G**. Finally, the H^+ abstraction by the oxygen anion of **G**, elimination of [Cu^nOOH], and nucleophilic addition of X^- to the cationic heterocyclic ring yielded product **3**. Alternatively, successive oxidation of carbocupration species **H** and RE of **I** also rationalized the product formation. Moreover, other Cu-oxidized forms, serving as oxidants to regenerate the catalytic species, can also be possible in the transformation.[1d,f,14]

To explore the utility of the developed synthetic method, the synthesis of compound **3aa** was scaled up by using 5 mmol of **1a**, which still afforded a good product yield (62%). Then, **3aa** was applied to synthesize products **6a** (78% yield) and **7a** (65% yield) via Suzuki and Sonogashira coupling reactions, respectively (Figure 1). Through determination of their photophysical and thermal properties (see Supporting Information), it showed that the absorption and emission spectra of **6a** and **7a** exhibited a typical bathochromic shift compared to **3aa**. Moreover, the coupling products (**6a** and **7a**) showed intense fluorescence in both solution (quantum efficiencies, $\Phi_{F,s}$ = 52.6 and 52.5%) and crystalline solid ($\Phi_{F,c}$ = 12 and 10.2%) states, typical crystallization-induced emission enhancement characteristics, and excellent thermal stability (T_d = 381 and 328 °C). These results indicate that the developed halocyclization reaction, enabling versatile access to imidazo-fused *N*-heterocycles, offers the potential to effectively obtain optoelectronic materials with excellent performance.

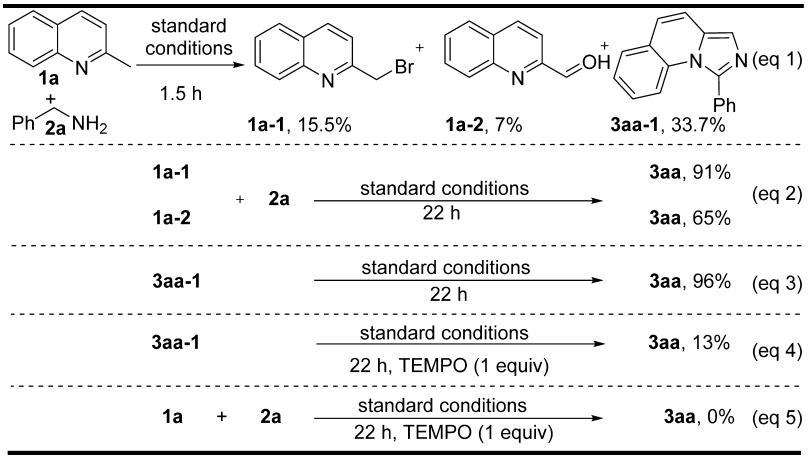
CONCLUSION

In summary, we have demonstrated a new aerobic copper-catalyzed halocyclization reaction of methyl *N*-heteroaromatics with aliphatic amines, which enables straightforward access to functionalized imidazo-fused *N*-heterocycles with the merits of good functional group tolerance, use of easily available copper salts as the catalysts, lithium halides as the halogen sources, and O_2 as a sole oxidant. One of the obtained products was utilized for classical cross-coupling reactions, and the resulting products exhibited unique photophysical properties and excellent thermal stability. Due to the reaction features' selective and versatile introduction of halogen functionalities to the newly formed imidazo ring, further extensions of the developed chemistry toward synthetic diversity, including facile access to functional materials, are easily envisioned.

EXPERIMENTAL SECTION

General Methods. Melting points were measured by a melting point instrument and were uncorrected. ^1H and ^{13}C NMR spectra were recorded by using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, and chloroform is used as a solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared spectrometer. GC-MS was obtained using electron ionization. The data of HRMS were carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed by using commercially available 100−400 mesh silica gel plates. Unless otherwise noted, all purchased chemicals were used without further purification. The absorption and fluorescence spectra were recorded. The solution fluorescence quantum yield was

Scheme 5. Control Experiments



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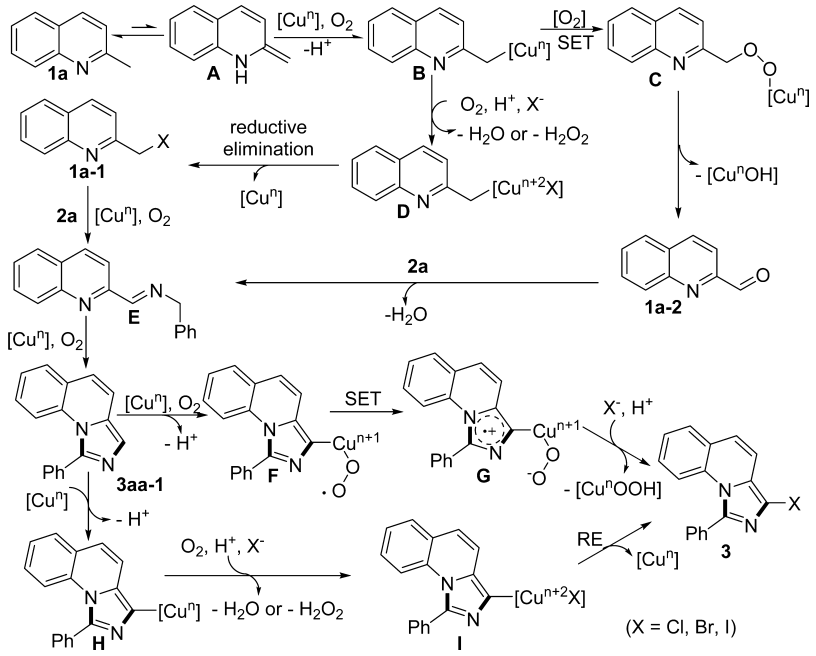
Scheme 6. Proposed Reaction Pathway



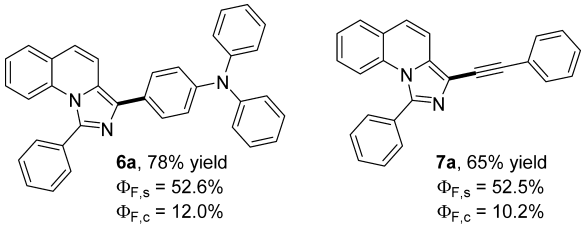


Figure 1. Synthetic utility of the halocyclization reaction.

estimated by using 9,10-diphenylanthracene as the standard (Φ_F = 90% in cyclohexane). Solid-state efficiencies were determined with the excitation wavelength of 365 nm. Glass transition temperature was determined by DSC measurements. Thermal stability was determined by a thermogravimetric analyzer over a temperature range of 28−600 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

General Procedure for the Synthesis of 3. The mixture of 2-methylquinoline (0.25 mmol), benzylamine (0.5 mmol), lithium bromide (1.5 mmol), and $CuBr_2$ (0.05 mmol) in chlorobenzene (1.5 mL) was stirred at 120 °C for 22 h under 1 atm of O_2 atmosphere (using an O_2 balloon). After being cooled to room temperature, the resulting mixture was extracted with chloroform, washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica (petroleum ether/ethyl acetate) to give 3-bromo-1-phenylimidazo[1,5-*a*]quinoline **3**.

*3-Bromo-1-phenylimidazo[1,5-a]quinoline (**3aa**):* Pale yellow solid (72.4 mg, 90% yield), mp 163−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.59 (m, 3H), 7.56−7.46 (m, 4H), 7.33 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 9.4 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 132.7, 132.2, 129.7, 129.7, 128.9, 128.9, 127.9, 127.7, 125.7, 125.6, 122.4, 117.3, 116.1, 109.3; IR (KBr) 3061, 2954, 2924, 2852, 1622, 1604, 1452, 1393, 1360, 793, 754, 700, 559 cm^{-1}; MS (EI, m/z) 322 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{11}BrN_2Na$ $[M + Na]^+$ 344.9998; found 344.9996.

*3-Bromo-1-(p-tolyl)imidazo[1,5-a]quinoline (**3ab**):* Pale yellow solid (71.4 mg, 85% yield), mp 167−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.8, 1.1 Hz, 1H), 7.56−7.48 (m, 3H), 7.35−7.29 (m, 3H), 7.27 (d, J = 9.4 Hz, 1H), 7.22−7.16 (m, 1H), 7.06 (d, J = 9.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 139.8, 132.3, 129.7, 129.6, 129.5, 128.9, 127.8, 127.7, 125.7, 122.2, 117.3, 116.0, 109.1, 21.6; IR (KBr) 3024, 2953, 2921, 2856, 1606, 1552, 1526, 1475, 1451, 1359, 793, 754, 722, 558 cm^{-1}; MS (EI, m/z) 336 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{13}BrN_2Na$ $[M + Na]^+$ 359.0154; found 359.0149.

*3-Bromo-1-(o-tolyl)imidazo[1,5-a]quinoline (**3ac**):* Pale yellow solid (63.8 mg, 76% yield), mp 155−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.47 (dd, J = 13.8, 7.2 Hz, 2H), 7.40−7.29 (m, 4H), 7.22−7.13 (m, 2H), 7.09 (d, J = 9.4 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 138.5, 132.7, 132.4, 130.6, 130.5, 130.2, 128.8, 128.3, 127.3, 126.5, 125.7, 125.4, 122.2, 116.1, 115.9, 108.7, 19.6; IR (KBr) 3059, 2952, 2922, 2855, 1619, 1605, 1552, 1508, 1475, 1448, 1359, 795, 757, 728, 596 cm^{-1}; MS (EI, m/z) 336 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{13}BrN_2Na$ $[M + Na]^+$ 359.0154; found 359.0151.

*3-Bromo-1-(3-methoxyphenyl)imidazo[1,5-a]quinoline (**3ad**):* Pale yellow oil liquid (58.0 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.59 (m, 1H), 7.56−7.48 (m, 1H), 7.46−7.13 (m, 6H), 7.09 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 141.4, 133.8, 132.1, 129.9, 128.9, 127.9, 127.8, 125.8, 125.6, 122.4, 122.0, 117.4, 116.2, 115.99, 114.6, 109.1, 55.5; IR (KBr) 3066, 3001, 2958, 2927, 2852, 2834, 1603, 1580, 1469, 1434, 1359, 1249, 1228, 792, 754, 703, 556 cm^{-1}; MS (EI, m/z) 352 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{14}BrN_2O$ $[M + H]^+$ 353.0284; found 353.0276.

*4-(3-Bromoimidazo[1,5-a]quinolin-1-yl)benzonitrile (**3ae**):* Pale yellow solid (56.4 mg, 65% yield), mp 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.75 (m, 4H), 7.71 (d, J = 7.8 Hz, 1H), 7.50−7.38 (m, 2H), 7.31 (dd, J = 19.5, 9.1 Hz, 2H), 7.18 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 136.8, 132.5, 131.6, 130.1, 129.4, 128.9, 128.0, 126.3, 125.8, 123.2, 118.3, 117.2, 116.0, 113.2, 110.3; IR (KBr) 3062, 2925, 2853, 2228, 1752, 1684, 1606, 1452, 1426, 1363, 843, 796, 754, 594, 543 cm^{-1}; MS (EI, m/z) 347 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{11}BrN_3$ $[M + H]^+$ 348.0131; found 348.0127.

*3-Bromo-1-(4-chlorophenyl)imidazo[1,5-a]quinoline (**3af**):* Pale yellow solid (57.8 mg, 65% yield), mp 213−214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 8.2 Hz, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.33−7.22 (m, 2H), 7.11 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 135.8, 132.0, 131.1, 131.0, 129.2, 129.1, 128.2, 127.9, 126.0, 125.7, 122.6, 117.2, 116.0, 109.5; IR (KBr) 3062, 2954, 2923, 2852, 1625, 1476, 1447, 1359, 831, 789, 754, 588 cm^{-1}; MS (EI, m/z) 356 $[M]^+$; HRMS

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(ESI) calcd for $C_{17}H_{10}BrClN_2Na$ $[M + Na]^+$ 378.9608; found 378.9607.

3-Bromo-1-(2-chlorophenyl)imidazo[1,5-a]quinoline (**3ag**): White solid (54.3 mg, 61% yield), mp 181−182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.59 (m, 2H), 7.58−7.49 (m, 2H), 7.46 (t, J = 7.1 Hz, 1H), 7.38−7.29 (m, 2H), 7.25−7.17 (m, 2H), 7.13 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 135.3, 132.5, 132.4, 132.3, 131.5, 129.9, 128.9, 128.4, 127.8, 127.5, 125.9, 125.3, 122.7, 115.9, 115.9, 108.9; IR (KBr) 3059, 2955, 2924, 2853, 1622, 1475, 1438, 1365, 862, 794, 757, 666, 593 cm^{-1}; MS (EI, m/z) 356 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{10}BrClN_2Na$ $[M + Na]^+$ 378.9608; found 378.9609.

3-Bromo-1-(4-bromophenyl)imidazo[1,5-a]quinoline (**3ah**): Pale yellow solid (58.0 mg, 58% yield), mp 173−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 3H), 7.57−7.48 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.33−7.22 (m, 2H), 7.12 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 132.1, 132.0, 131.5, 131.2, 129.1, 128.3, 127.9, 126.0, 125.7, 124.1, 122.6, 117.2, 116.0, 109.6; IR (KBr) 3061, 2954, 2923, 2852, 1676, 1592, 1473, 1448, 1398, 1361, 1010, 828, 793, 754, 588 cm^{-1}; MS (EI, m/z) 400 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{11}Br_2N_2$ $[M + H]^+$ 400.9283; found 400.9285.

3-Bromo-1-(naphthalen-1-yl)imidazo[1,5-a]quinoline (**3ai**): White solid (84.6 mg, 91% yield), mp 185−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 6.9 Hz, 1H), 7.61 (t, J = 8.5 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.42−7.28 (m, 3H), 7.22 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 9.5 Hz, 1H), 6.99−6.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 133.7, 132.4, 132.1, 130.5, 130.4, 129.1, 128.8, 128.5, 128.1, 127.8, 127.4, 126.6, 125.6, 125.6, 125.5, 125.4, 122.5, 116.9, 116.0, 109.2; IR (KBr) 3053, 2954, 2924, 2853, 1607, 1473, 1448, 1360, 1247, 798, 777, 752, 741, 561, 527 cm^{-1}; MS (EI, m/z) 372 $[M]^+$; HRMS (ESI) calcd for $C_{21}H_{13}BrN_2Na$ $[M + Na]^+$ 395.0154; found 395.0158.

3-Bromo-1-(thiophen-2-yl)imidazo[1,5-a]quinoline (**3aj**): Pale yellow solid (66.4 mg, 81% yield), mp 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 6.8 Hz, 2H), 7.40−7.33 (m, 2H), 7.28 (dd, J = 12.7, 6.2 Hz, 2H), 7.23−7.18 (m, 1H), 7.11 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 132.9, 132.2, 130.1, 129.0, 128.8, 128.6, 128.1, 127.5, 126.0, 125.6, 122.9, 116.9, 115.8, 109.4; IR (KBr) 3068, 2954, 2924, 2852, 1620, 1473, 1447, 1361, 1251, 794, 751, 741, 706, 672, 555 cm^{-1}; MS (EI, m/z) 328 $[M]^+$; HRMS (ESI) calcd for $C_{15}H_9BrN_2NaS$ $[M + Na]^+$ 350.9562; found 350.9568.

1-Benzyl-3-bromoimidazo[1,5-a]quinoline (**3ak**): Pale yellow solid (12.6 mg, 15% yield), mp 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.87 (m, 1H), 7.63−7.53 (m, 1H), 7.39−7.10 (m, 8H), 7.00 (d, J = 9.3 Hz, 1H), 4.78 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 136.3, 132.3, 129.0, 128.8, 128.2, 128.0, 126.9, 125.6, 125.6, 122.0, 116.8, 116.1, 107.9, 37.6; IR (KBr) 3060, 3029, 2923, 2852, 1604, 1494, 1377, 1076, 792, 751, 721, 694, 512 cm^{-1}; MS (EI, m/z) 336 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{14}BrN_2$ $[M + H]^+$ 337.0335; found 337.0336.

3-Bromo-7-methyl-1-phenylimidazo[1,5-a]quinoline (**3ba**): Gray solid (63.0 mg, 75% yield), mp 189−190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.8 Hz, 2H), 7.51 (d, J = 5.1 Hz, 3H), 7.42 (s, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.02 (t, J = 9.7 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 135.6, 132.7, 130.1, 129.7, 129.7, 128.8, 128.8, 127.9, 125.7, 122.3, 117.1, 115.9, 109.1, 20.8; IR (KBr) 3055, 2953, 2920, 2854, 1603, 1562, 1482, 1448, 1366, 803, 767, 697, 592 cm^{-1}; MS (EI, m/z) 336 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{13}BrN_2Na$ $[M + Na]^+$ 359.0154; found 359.0158.

3-Bromo-7-methyl-1-(thiophen-2-yl)imidazo[1,5-a]quinoline (**3bj**): Gray solid (58.1 mg, 68% yield), mp 182−183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 5.1 Hz, 1H), 7.51−7.42 (m, 2H), 7.36 (d, J = 2.9 Hz, 1H), 7.27 (d, J = 9.6 Hz, 1H), 7.20 (t, J = 4.3 Hz, 1H), 7.08 (t, J = 8.8 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 134.0, 132.9, 130.2, 130.1, 129.2, 128.8, 128.7, 128.5, 127.4, 125.6, 122.8, 116.7, 115.7, 109.2, 20.9; IR (KBr) 3062, 2956, 2922, 2854, 1615, 1591, 1563, 1479, 1365, 1258, 806, 704, 553 cm^{-1}; MS (EI, m/z) 342 $[M]^+$; HRMS (ESI) calcd for $C_{16}H_{11}BrN_2NaS$ $[M + Na]^+$ 364.9719; found 364.9721.

3-Bromo-9-methoxy-1-phenylimidazo[1,5-a]quinoline (**3ca**): Pale yellow oil liquid (68.6 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.3 Hz, 2H), 7.40−7.26 (m, 4H), 7.21 (t, J = 8.5 Hz, 2H), 6.97 (d, J = 9.3 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 2.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 146.1, 135.5, 129.0, 128.7, 128.1, 128.0, 126.6, 125.2, 122.2, 121.8, 119.7, 116.7, 110.4, 110.3, 53.7; IR (KBr) 3061, 3005, 2963, 2932, 2838, 1600, 1558, 1463, 1442, 1358, 1319, 1278, 1253, 1133, 1077, 960, 803, 737, 697, 593 cm^{-1}; MS (EI, m/z) 352 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{14}BrN_2O$ $[M + H]^+$ 353.0284; found 353.0289.

3-Bromo-8-chloro-1-phenylimidazo[1,5-a]quinoline (**3da**): Pale yellow solid (44.5 mg, 50% yield), mp 180−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.51 (m, 6H), 7.44 (s, 1H), 7.33−7.22 (m, 2H), 7.03 (d, J = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 133.3, 132.6, 132.0, 130.2, 129.8, 129.5, 129.1, 127.8, 126.1, 124.1, 121.5, 117.5, 116.3, 109.7; IR (KBr) 3062, 2955, 2923, 2853, 1608, 1474, 1447, 1385, 1091, 840, 692, 582 cm^{-1}; MS (EI, m/z) 356 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{10}BrClN_2Na$ $[M + Na]^+$ 378.9608; found 378.9615.

3-Bromo-8-chloro-1-(p-tolyl)imidazo[1,5-a]quinoline (**3db**): Red solid (53.6 mg, 58% yield), mp 213−214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.47 (m, 4H), 7.35 (d, J = 7.7 Hz, 2H), 7.32−7.22 (m, 2H), 7.02 (d, J = 9.4 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 140.3, 133.2, 132.7, 129.7, 129.4, 129.0, 127.7, 126.1, 124.2, 121.4, 117.5, 116.4, 109.5, 21.6; IR (KBr) 3072, 3041, 2922, 2853, 1602, 1455, 1415, 1355, 1247, 1091, 828, 739, 577 cm^{-1}; MS (EI, m/z) 370 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{12}BrClN_2Na$ $[M + Na]^+$ 392.9765; found 392.9775.

3,7-Dibromo-1-phenylimidazo[1,5-a]quinoline (**3ea**): Red solid (55.0 mg, 55% yield), mp 203−204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.56−7.47 (m, 3H), 7.38−7.24 (m, 3H), 6.98 (d, J = 9.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 132.2, 131.1, 131.0, 130.5, 130.0, 129.6, 129.1, 127.7, 127.5, 121.1, 119.0, 118.8, 117.4, 110.0; IR (KBr) 3056, 2954, 2922, 2852, 1600, 1546, 1469, 1448, 1362, 962, 798, 699, 590 cm^{-1}; MS (EI, m/z) 400 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{10}Br_2N_2Na$ $[M + Na]^+$ 422.9103; found 422.9107.

1-Bromo-3,5-diphenylimidazo[1,5-c]quinazoline (**3fa**): Yellow solid (44.9 mg, 45% yield), mp 229−230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 7.4 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H), 7.67−7.52 (m, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.22−6.97 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 141.8, 138.5, 133.4, 130.5, 130.1, 129.2, 128.8, 128.7, 128.5, 128.4, 128.2, 127.8, 127.5, 125.6, 121.7, 118.9, 109.0; IR (KBr) 3052, 2954, 2922, 2852, 1605, 1566, 1532, 1462, 1329, 1234, 949, 753, 695, 541 cm^{-1}; MS (EI, m/z) 399 $[M]^+$; HRMS (ESI) calcd for $C_{22}H_{15}BrN_3$ $[M + H]^+$ 400.0444; found 400.0449.

3-Bromo-1-phenylimidazo[1,5-a]quinoxaline (**3ga**): Pale yellow solid (57.3 mg, 71% yield), mp 206−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.97 (d, J = 7.0 Hz, 1H), 7.67 (d, J = 6.7 Hz, 2H), 7.64−7.53 (m, 3H), 7.52−7.42 (m, 2H), 7.30−7.20 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 143.1, 137.3, 131.1, 130.5, 130.5, 129.7, 129.0, 128.0, 127.3, 126.2, 123.3, 116.4, 114.1; IR (KBr) 3067, 2954, 2922, 2851, 1612, 1585, 1465, 1440, 1387, 1257, 762, 695, 587 cm^{-1}; MS (EI, m/z) 323 $[M]^+$; HRMS (ESI) calcd for $C_{16}H_{11}BrN_3$ $[M + H]^+$ 324.0131; found 324.0134.

7-Bromo-9-phenylimidazo[1,5-a][1,8]naphthyridine (**3ha**): Pale yellow solid (60.5 mg, 75% yield), mp 183−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 4.5 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.80−7.70 (m, 2H), 7.48−7.38 (m, 3H), 7.35−7.26 (m, 2H), 6.98 (d, J = 9.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 143.9, 143.1, 136.3, 132.5, 130.4, 128.8, 128.7, 127.27, 122.0, 120.3, 120.2, 117.4, 110.6; IR (KBr) 3055, 2954, 2922, 2853, 1617, 1593, 1422, 1366, 814, 761, 699, 675, 590 cm^{-1}; MS (EI, m/z) 323 $[M]^+$; HRMS (ESI) calcd for $C_{16}H_{11}BrN_3$ $[M + H]^+$ 324.0131; found 324.0132.

1-Bromo-3-phenylimidazo[5,1-a]isoquinoline (**3ia**): White green solid (57.9 mg, 72% yield), mp 155−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.60−7.41 (m, 6H), 6.77 (d, J = 7.5 Hz, 1H); ^{13}C

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NMR (101 MHz, $CDCl_3$) δ 140.1, 129.5, 129.0, 129.0, 128.6, 128.4, 127.5, 127.3, 127.0, 124.7, 124.3, 122.5, 120.3, 115.0, 108.3; IR (KBr) 3060, 2955, 2923, 2852, 1602, 1476, 1457, 1364, 1237, 787, 695, 567 cm^{-1}; MS (EI, *m/z*) 322 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{11}BrN_2Na$ $[M + Na]^+$ 344.9998; found 344.9999.

General Procedure for the Synthesis of 4. The mixture of 2-methylquinoline (0.25 mmol), benzylamine (0.5 mmol), lithium chloride (1.5 mmol), and $CuCl_2$ (0.05 mmol) in chlorobenzene (1.5 mL) was stirred at 120 °C for 36 h under 1 atm of O_2 atmosphere (using an O_2 balloon). After being cooled to room temperature, the resulting mixture was extracted with chloroform, washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica (petroleum ether/ethyl acetate) to give 3- chloro-1-phenylimidazo[1,5-*a*]quinoline **4**.

*3-Chloro-1-phenylimidazo[1,5-a]quinoline (**4aa**):* Brownish red solid (50.0 mg, 72% yield), mp 145−146 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.8 Hz, 3H), 7.55−7.47 (m, 4H), 7.33 (t, *J* = 8.6 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 132.7, 132.1, 129.7, 129.7, 128.9, 128.9, 127.7, 125.8, 125.7, 125.4, 122.2, 122.0, 117.3, 115.5; IR (KBr) 3061, 2924, 2853, 1605, 1553, 1477, 1448, 1364, 799, 755, 700, 595 cm^{-1}; MS (EI, *m/z*) 278 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{11}ClN_2Na$ $[M + Na]^+$ 301.0503; found 301.0504.

*3-Chloro-1-(p-tolyl)imidazo[1,5-a]quinoline (**4ab**):* Brownish red solid (44.5 mg, 61% yield), mp 153−154 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 8.6 Hz, 3H), 7.36−7.27 (m, 4H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 9.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 139.8, 132.2, 129.7, 129.6, 129.5, 128.8, 127.7, 125.7, 125.3, 122.1, 121.8, 117.3, 115.5, 21.5; IR (KBr) 3062, 2922, 2855, 1620, 1553, 1452, 1405, 1362, 822, 793, 593 cm^{-1}; MS (EI, *m/z*) 292 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{13}ClN_2Na$ $[M + Na]^+$ 315.0659; found 315.0664.

*1-Chloro-3-phenylimidazo[5,1-a]isoquinoline (**4ia**):* White green solid (48.6 mg, 70% yield), mp 161−162 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.56−7.34 (m, 6H), 6.71 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 129.4, 129.0, 129.0, 128.5, 128.5, 127.3, 127.1, 126.9, 124.6, 122.7, 122.3, 122.2, 120.2, 114.9; IR (KBr) 3066, 3027, 2919, 2849, 1602, 1553, 1477, 1453, 1364, 977, 790, 737, 691, 596 cm^{-1}; MS (EI, *m/z*) 278 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{11}ClN_2Na$ $[M + Na]^+$ 301.0503; found 301.0511.

General Procedure for the Synthesis of 5. The mixture of 2-methylquinoline (0.25 mmol), benzylamine (0.5 mmol), lithium iodide (1.5 mmol), and $Cu(OAc)_2$ (0.05 mmol) in chlorobenzene (1.5 mL) was stirred at 120 °C for 16 h under 1 atm of O_2 atmosphere (using an O_2 balloon). After being cooled to room temperature, the resulting mixture was extracted with chloroform, washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica (petroleum ether/ethyl acetate) to give 3- iodo-1-phenylimidazo[1,5-*a*]quinoline **5**.

*3-Iodo-1-phenylimidazo[1,5-a]quinoline (**5aa**):* White solid (62.9 mg, 68% yield), mp 149−150 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65−7.58 (m, 3H), 7.56−7.48 (m, 3H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 9.4 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 132.8, 132.4, 132.3, 129.7, 129.7, 128.9, 128.9, 127.7, 125.7, 122.9, 117.2, 117.1, 77.9; IR (KBr) 3061, 2923, 2853, 1605, 1473, 1450, 1359, 795, 754, 699, 587, 512, 463 cm^{-1}; MS (EI, *m/z*) 370 $[M]^+$; HRMS (ESI) calcd for $C_{17}H_{11}IN_2Na$ $[M + Na]^+$ 392.9859; found 392.9854.

*3-Iodo-1-(p-tolyl)imidazo[1,5-a]quinoline (**5ab**):* White solid (43.2 mg, 45% yield), mp 180−181 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 8.9 Hz, 3H), 7.38−7.28 (m, 3H), 7.27−7.15 (m, 2H), 7.08 (d, *J* = 9.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 139.8, 132.4, 132.3, 129.8, 129.6, 129.5, 128.8, 127.6, 125.7, 125.6, 122.8, 117.2, 117.2, 77.7, 21.6; IR (KBr) 3056, 3023, 2921, 2853, 1606, 1471, 1449, 1356, 793, 752, 585, 471 cm^{-1}; MS (EI, *m/z*) 384 $[M]^+$; HRMS (ESI) calcd for $C_{18}H_{13}IN_2Na$ $[M + Na]^+$ 407.0016; found 407.0021.

General Procedure for the Synthesis of 6a. Under N_2 atmosphere, **3aa** (1 mmol), (4-(diphenylamino)phenyl)boronic acid (1.2 mmol), $Pd_2(dba)_3$ (5 mol %), P(*t*-Bu)$_3$ (10 mol %), KOH (2 mmol), and DMF (1.5 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed, and the resulting mixture was stirred at 100 °C for 10 h. After being cooled to room temperature, the resulting mixture was extracted with chloroform, washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica (petroleum ether/ethyl acetate/dichloromethane) to **6a**.

*N,N-Diphenyl-4-(1-phenylimidazo[1,5-a]quinolin-3-yl)aniline (**6a**):* Yellow solid (379.8 mg, 78% yield), mp 231−232 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.77−7.71 (m, 2H), 7.69 (d, *J* = 9.5 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.61−7.53 (m, 3H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.37- 7.26 (m, 5H), 7.25−7.14 (m, 7H), 7.06 (dd, *J* = 17.0, 8.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.9, 142.0, 133.6, 132.5, 129.8, 129.5, 129.3, 129.0, 128.9, 128.5, 128.4, 127.5, 126.1, 125.9, 125.3, 124.3, 124.3, 122.8, 122.6, 121.8, 117.6, 117.6; IR (KBr) 3057, 3027, 2923, 2853, 1589, 1489, 1315, 1276, 751, 696 cm^{-1}; HRMS (ESI) calcd for $C_{35}H_{26}N_3$ $[M + H]^+$ 488.2121; found 488.2137.

General Procedure for the Synthesis of 7a. Under N_2 atmosphere, **3aa** (1 mmol), ethynylbenzene (1.25 mmol), $PdCl_2$ (5 mol %), CuI (20 mol %), PPh_3 (10 mol %), N(C_2H_5)$_3$ (3 mmol), and DMF (1.5 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed, and the resulting mixture was stirred at 90 °C for 12 h. After being cooled to room temperature, the resulting mixture was extracted with chloroform, washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica (petroleum ether/ethyl acetate/dichloromethane) to **7a**.

*1-Phenyl-3-(phenylethynyl)imidazo[1,5-a]quinoline (**7a**):* Brown solid (223.6 mg, 65% yield), mp 186−187 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.57 (m, 5H), 7.57−7.44 (m, 5H), 7.40−7.25 (m, 4H), 7.22−7.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 133.3, 133.1, 132.4, 131.4, 129.7, 129.7, 128.8, 128.4, 128.1, 127.9, 125.8, 125.6, 123.5, 123.2, 117.4, 116.9, 116.7, 93.1, 82.5; IR (KBr) 3056, 2924, 2209, 1599, 1556, 1445, 1359, 1111, 798, 753, 705, 690, 611 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{17}N_2$ $[M + H]^+$ 345.1386; found 345.1395.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02117.

Copies of ^1H and ^{13}C NMR spectra data for all compounds (PDF)

X-ray crystallographic data for **3aa** (CIF)

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Notes

The authors declare no competing financial interest.

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