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CuCl-Catalyzed Ullmann-Type C−N Cross-Coupling Reaction of Carbazoles and 2-Bromopyridine Derivatives

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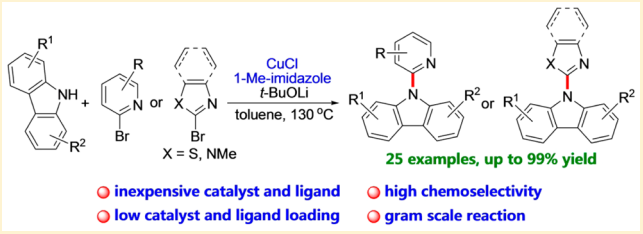
Supporting Information

ABSTRACT: A CuCl-catalyzed Ullmann-type C−N cross-coupling reaction of carbazoles and 2-bromopyridine derivatives has been developed for the synthesis of *N*-heteroarylcarbazole derivatives employing 1-methyl-imidazole and *t*-BuOLi as ligand and base, respectively, both of which are found to significantly promote the reaction. Low cost and low loading of both catalyst and ligand, together with high reaction yields, render this practical reaction to be suitable for large-scale preparations and could be useful in material science.



INTRODUCTION

N-(Hetero)arylcarbazole compounds and their derivatives are widely utilized in material science,[1] such as for energy transfer materials,[2] host materials[1b,3] and charge-transporting materials[1b,4] in the organic light-emitting devices (OLEDs) fields, due to their high thermal and electrochemical stabilities (Figure 1). Moreover, *N*-(hetero)arylcarbazole moieties are also widely incorporated into recently developed thermally activated delayed fluorescence (TADF) materials[5] and tetradentate platinum- and palladium-based phosphorescent materials[6] to serve as perfect donors and cyclometalated ligands. Both of the materials demonstrate remarkable electroluminescent properties and promising applications in low-cost displays and solid-state lighting.[7]

Generally, *N*-(hetero)arylcarbazole derivatives can be synthesized through C_{aryl}−N bond formation reactions between corresponding carbazoles and aryl halides, which has been demonstrated to have a great impact on the fields of material science, medicinal chemistry, and natural product synthesis.[8] A series of powerful approaches for the C_{aryl}−N bond formation have been developed.[9−14,19−21] Over the past two decades in particular, remarkable progress has been achieved in this field, for example, the palladium-catalyzed cross-coupling of amines and aryl halides (Buchwald−Hartwig reaction)[9] and the copper-catalyzed Ullmann-type coupling reactions promoted by bidentate ligands,[10−14] both of which demonstrated mild reaction conditions and broad reaction scopes. Because of extensive applications in both academia and industry,[8−11,15] the development of new practical methods for C_{aryl}−N bond formation has still attracted a great deal of attention in recent years. In 2011, Yum's group disclosed a LiCl-mediated *N*-arylation of carbazoles reaction to synthesize the *N*-(hetero)-arylcarbazoles;[16] meanwhile, a microwave-assisted process was also developed by the same group.[17] However, both require 10 mol % CuI as catalyst with a long reaction time of 2 days at high reaction temperature (150 and 220 °C, respectively) (Scheme 1a). Later, Wu and co-workers discovered a palladium(II)-catalyzed process to prepare 9-(2-pyridinyl)-9*H*-carbazoles through a cascade C−H bond activation/intramolecular C−N bond formation reaction with a mixture of two products owing to low chemoselectivity (Scheme 1b).[18] Moreover, in 2013, Peters and Fu developed versatile protocols for the Ullmann C_{aryl}−N coupling reactions between various heteroaryl nucleophiles and aryl halides catalyzed by CuI under ultraviolet (UV) light irradiation.[19] Recently, Kobayashi et al. performed the visible light-promoted Ullmann-type C_{aryl}−N cross-coupling of carbazole derivatives and aryl iodides in the presence of CuI and photocatalyst $Ir(ppy)_3$ (Scheme 1c),[20] and it was believed that both of the photo-promoted C_{aryl}−N cross-coupling reactions involved single electro transfer (SET) processes. In addition, an NHC-nickel(0) catalyzed C_{aryl}−N cross-coupling of indoles and carbazoles with aromatic chlorides was also achieved recently by Belderrain and Nicasio (Scheme 1d).[22] Furthermore, the Nakayama group developed an efficient palladium-catalyzed coupling reaction between (hetero)aryl chlorides and *N*-carbazolylmagnesium chloride (Scheme 1e).[8d] Thus, various approaches have been developed for forming the C_{aryl}−N bond; however, reports on the synthesis of *N*-heteroarylcarbazoles, especially for the 9-(2-pyridinyl)-9*H*-carbazole derivatives,[6c,d,18] are still rare. Furthermore, the reaction conditions had some disadvantages, including high catalyst loading,[6c,d,16,17,19] high temperature,[16,17] long reaction time,[6c,d] or incompatibility of bromine atom on the product molecules because of the palladium-[8d] and nickel-based[22] catalyst, which may result in C−Br bond reduction or cleavage. For these drawbacks to be overcome, it is highly desirable to develop a more practical method for the preparation of the *N*-heteroarylcarbazoles. Herein, we report an efficient CuCl-catalyzed Ullmann-type C_{aryl}−N cross-

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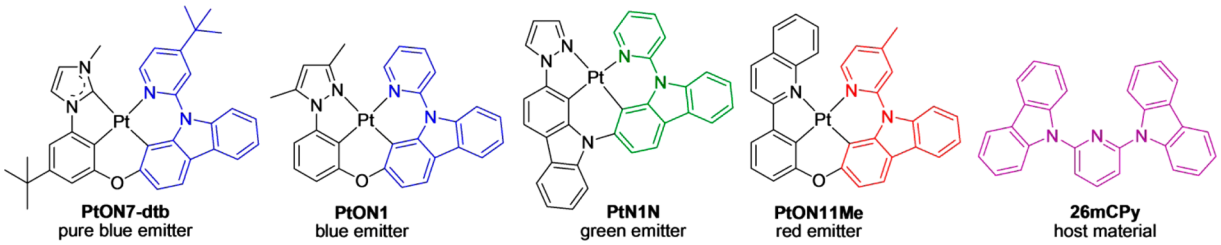
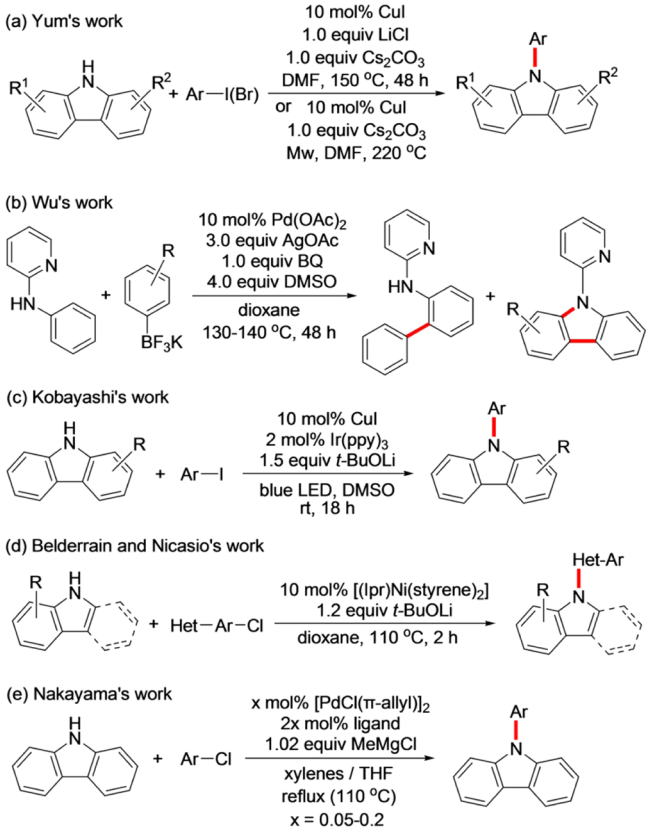


Figure 1. Selected phosphorescent emitters and host material with a 9-(2-pyridinyl)-9*H*-carbazole moiety.

Scheme 1. Previous Reports for the Synthesis of *N*-(Hetero)arylcarbazole Derivatives



coupling of carbazoles and 2-bromopyridine derivatives with the advantages of low catalyst and ligand loading and good functional group tolerance, especially for 2-bromo, 3-bromo, 2,7-dibromo, and 3,6-dibromo *N*-heteroarylcarbazole products, which was critical for their further functionalization. More importantly, this practical method is suitable for large-scale synthesis of *N*-heteroarylcarbazoles, which is important for the preparation of advanced materials in the material science field.

RESULTS AND DISCUSSION

2-Bromo-9-(2-pyridinyl)-9*H*-carbazole **3a** and its derivatives were critical intermediates in the synthesis of tetradentate platinum- and palladium-based phosphorescent materials.[6] Furthermore, on the basis of our previous study,[6c] it is valuable to note that starting material **1a** should be consumed completely to avoid purification problems because of the low solubility of **1a** in common solvents, such as hexane, ethyl acetate, and dichloromethane. We initially adopted 2-bromocarbazole **1a** and 2-bromopyridine **2a** as model substrates to investigate the optimal reaction conditions. To our disappointment, only 33% of desired product **3a** was obtained when the previously reported CuI-catalyzed *N*-arylation reaction condition[13a] was employed using *trans*-cyclohexanediamine (**L1**) as ligand and K_3PO_4 as base in dioxane (Table 1, entry 1). Then, the reaction was performed in toluene utilizing 1-methyl-1*H*-imidazole (**L2**) as ligand and K_2CO_3 as base to form desired product **3a** in quantitative yield with high chemoselectivity; however, 6 days was needed to complete the reaction (Table 1, entry 2). The influences of other bases on the product yields were then investigated. Both *t*-BuOK and *t*-BuONa afforded disappointing results (Table 1, entries 3 and 4). However, it was encouraging to find that *t*-BuOLi exhibited extremely high efficiency, the reaction could be accomplished in 4 h in excellent yield with good chemoselectivity (Table 1, entry 5). Decreasing the amount of *t*-BuOLi or replacing the ligand **L2** with **L1** or L-proline (**L3**) prolonged the reaction time without affecting yields and chemoselectivities (Table 1, entries 6−9). Next, control experiments were examined, and no reaction was observed in the absence of CuI, revealing that it was not a nucleophilic substitution reaction path (Table 1, entries 10−12). As expected, reducing reaction temperature also prolonged the reaction time (Table 1, entry 13). Surprisingly, both CuBr and CuCl demonstrated catalytic activation and chemoselectivities comparable with CuI (Table 1, entries 6, 14, and 15). Last, it was worth pointing out that this reaction could also be performed under air without significantly decreasing the yield and chemoselectivity (Table 1, entry 18). In consideration of the relatively low cost of catalyst and ligand, the CuCl/**L2** catalytic system was employed for the next reaction scope investigation.

With the optimized conditions in hand, we next examined the substrate scope of 2-bromocarbazole **1a** with a range of 2-bromopyridine derivatives (Table 2). To our delight, all of the target product 2-bromo-9-(2-pyridinyl)-9*H*-carbazole derivatives **3a**−**l** could be obtained with excellent chemoselectivities and purities higher than 97%. The 2-bromopyridine derivatives bearing an electron-donating group at the one of the 3, 4, or 5 positions underwent cross-coupling efficiently, affording the corresponding products **3b**−**d** in excellent yields of 91−95% with the ratios of **3**/**4** not less than 98:2. Incorporating an electron-withdrawing group, such as 5-bromo or 4-fluoro, at the pyridinyl ring also generated C_{aryl}−N cross-coupling products **3e** and **3f** in good to excellent yields, and no 2,5-di(2-bromo-9*H*-carbazol-9-yl)pyridine was observed attributed to different reaction activities of the two bromo in **2e**. In addition, all of the 2-bromopyrimidine **2g**, 2-bromopyrazine **2h**, and 2-bromoquinoline **2i** were suitable for this condition and reacted smoothly with **1a**. However, product **3j** was obtained in only 24% even though the reaction time was prolonged to 5 days with 2 mol % CuCl/4 mol % **L2** loading due to the low activity of 1-chloroisoquinoline. This result indicated that the reaction

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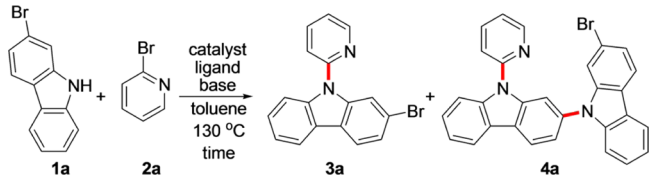
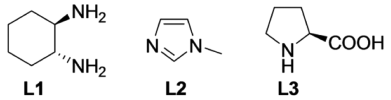
Table 1. Optimization Study on the Ullmann-Type C_{aryl}–N Cross-Coupling Reaction[a]



1a 2a 3a 4a

entry[a]	2/eq	catalyst	ligand[i]	base (equiv)	time	yield[b] (3a:4a[c])
1[d]	1.5	5 mol % CuI	50 mol % **L1**	2.1 K_3PO_4	3.0 d	33% (100:0)
2	1.2	10 mol % CuI	25 mol % **L2**	2.0 K_2C0_3	6.0 d	99% (100:0)
3	1.2	1 mol % CuI	2 mol % **L2**	2.0 *t*-BuOK	24.0 h	9% (85:15)
4	1.1	1 mol % CuI	2 mol % **L2**	1.5 *t*-BuONa	3.0 d	*e*
5	1.2	1 mol % CuI	2 mol % **L2**	2.0 *t*-BuOLi	4.0 h	98% (97:3)
6	1.1	1 mol % CuI	2 mol % **L2**	1.5 *t*-BuOLi	5.5 h	99% (97:3)
7	1.1	1 mol % CuI	2 mol % **L2**	1.2 *t*-BuOLi	9.5 h	99% (98:2)
8	1.1	1 mol % CuI	2 mol % **L1**	1.5 *t*-BuOLi	13.0 h	97% (96:4)
9	1.1	1 mol % CuI	2 mol % **L3**	1.5 *t*-BuOLi	5.2 d	90% (98:2)
10	1.2			2.0 *t*-BuOLi	24.0 h	NR[f]
11	1.1		2 mol % **L2**	1.5 *t*-BuOLi	3.0 d	NR
12	1.1	1 mol % CuI		1.5 *t*-BuOLi	3.4 d	98% (98:2)
13[g]	1.1	1 mol % CuI	2 mol % **L2**	1.5 *t*-BuOLi	11.0 h	97% (99:1)
14	1.1	1 mol % CuBr	2 mol % **L2**	1.5 *t*-BuOLi	5.4 h	94% (97:3)
15	**1.1**	**1 mol% CuCI**	**2 mol % L2**	**1.5 *t*-BuOLi**	**4.8 h**	**97% (98:2)**
16	1.1	1 mol % CuCI		1.5 *t*-BuOLi	4.8 h	76% (98:2)
17	1.1	1 mol % CuCI		1.5 *t*-BuOLi	3.4 d	92% (97:3)
18[h]	1.1	1 mol % CuCI	2 mol % **L2**	1.5 *t*-BuOLi	5.5 h	90% (96:4)

[a]All reactions were conducted on a scale of 15.0 mmol of **1a** unless otherwise noted. [b]Isolated yields after chromatography. [c]The ratio of **3a:4a** was given in parentheses, and all the ratios were determined by ^{1}H NMR of the isolated products after chromatography. [d]In dioxane at 110 °C. [e]Reaction was messy; no **3a** was observed, and 58% of **1a** was recycled. [f]NR = no reaction. [g]At 110 °C. [h]Reaction was conducted on a scale of 5.0 mmol based on **1a** under air. [i]



L1 L2 L3

activities of the aryl halides played an important role in this reaction, and high yield could be achieved if 1-bromoisoquinoline was employed. Interesting, 2-thiazolyl and 2-benzothiazolyl could be also incorporated successfully to the product (**3k**, **3l**) employing corresponding bromide substrates **2k** and **2l**. Importantly, because of the 3-bromo at the carbazolyl ring, these functional products could be further transformed easily and provided various tetradentate ligands for the platinum- and palladium-based phosphorescent materials with tunable photophysical properties.[6]

Next, we investigated the scope of the carbazole substrates (Table 3). Gratifyingly, it was found that carbazole **1b** could react with various heteroaryl bromides smoothly under the optimized reaction conditions, leading to the corresponding products incorporated with 2-pyridinyl (**3m**, **3n**), 2-benothiazolyl (**3o**), and 1-methyl-benzo[*d*]imidazol-2-yl (**3p**) groups in 50–93% yields in 8–26 h. As expected, carbazole bearing a bromo at the 3-position or dibromo at te 2,7-positions or 3,6-positions were all compatible under the reaction conditions to generate products **3q–s** in 83–95% yields. It is interesting to note that no further functionalized products like **4** were observed. Satisfactorily, carbazole substrates containing an electron-donating group, such as phenyl and 3,6-di-*tert*-butyl, also successfully coupled with 2-bromopyridine to give the products **3t** and **3u** in 99 and 96% yields, respectively. However, when 1,3,6-tri-*tert*-9*H*-butylcarbazole was introduced as the reactant, product **3v** was obtained in relative low yield (59%), mainly owing to the large steric effect of the *tert*-butyl group at the 1-position of the carbazolyl ring. In addition, we also examined the indole and phenoxazine, both of which were converted to desired products **3w** and **3y** in 97 and 40% yields, respectively. Furthermore, this CuCl-catalyzed Ullmann-type C_{aryl}–N cross-coupling reaction was successfully employed for the preparation of 9,9′-(2,6-pyridinediyl)bis-9*H*-carbazole **3x** (26mCPy) in 92% yield, which is widely used as a host material in the OLED field.[1c,3a]

For the synthetic practicality of this protocol to be demonstrated further, gram-scale experiments were carried out under the optimized conditions (Scheme 2). To our delight, coupling products **3a**, **3m**, and **3x** (26mCPy) could be prepared on large scales in 87–96% yields. More importantly, the product purifications were achieved through filtration and recrystallization without column chromatography for **3a** and **3x**, making this protocol more suitable for large-scale preparations. Furthermore, no **4a** was observed in product **3a** after recrystallization.

For gaining insight into the reaction mechanism, control experiments were subsequently performed. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger was added to the reaction mixture of **1a** and **2a** under the optimized conditions; the reaction was suppressed to a great extent, and desired product **3a** was obtained in only 7% yield (Scheme 3I). It was also found that 3 equiv of TEMPO could nearly completely hamper the reaction between **1b** and **2a** (Scheme

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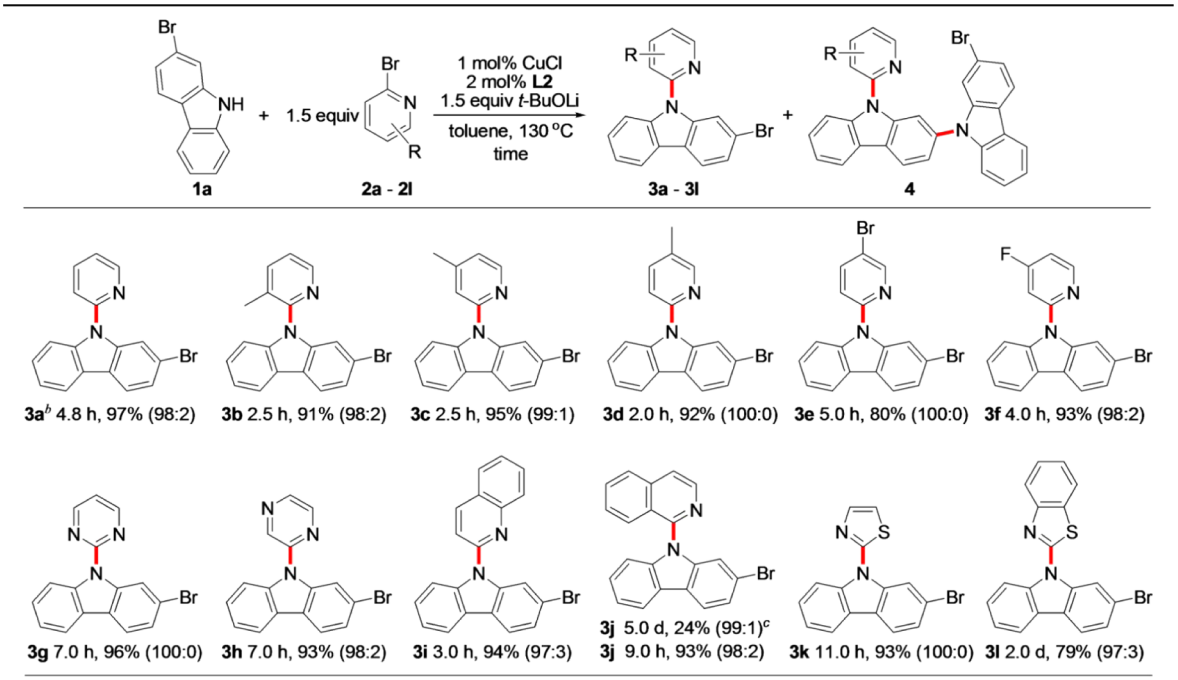
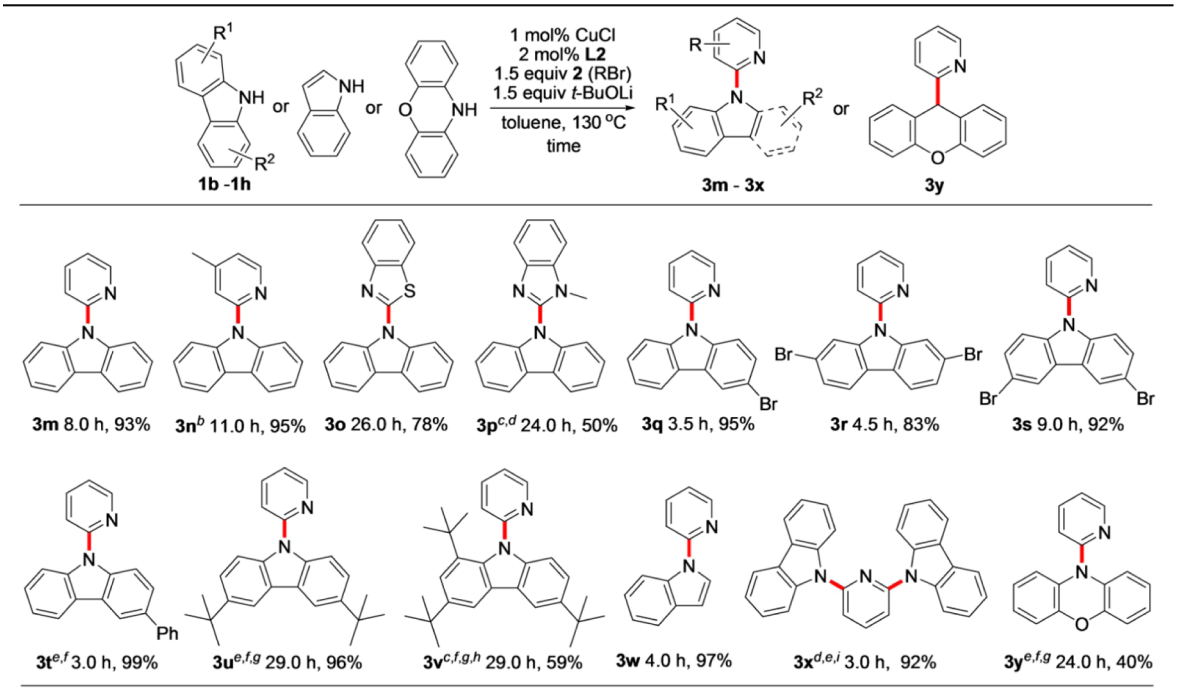
Table 2. Substrate Scope of 2-Bromopyridine/2-Bromothiazole Derivatives[a]



[a]The reactions were conducted on scales of 0.5−15.0 mmol based on **1a**. All yields are isolated yields after chromatography. The ratio of **3**/**4** is given in parentheses, and all of the ratios were determined by ^{1}H NMR of the isolated products after chromatography. [b]Using 1.1 equiv of **2a**. [c]Employing 2 mol % CuCl/4 mol % **L2** and 1-chloroisoquinoline.

Table 3. Substrate Scope of Carbazole Derivatives and Other *N*-Heterocycles[a]



[a]Reactions were conducted on scales of 0.25−2.0 mmol based on **1.** All yields are isolated yields after chromatography. [b]With 1.1 equiv of 2-bromo-4-methylpyridine. [c]With 5 mol % CuCl/10 mol % **L2.** [d]With 3.0 equiv of *t*-BuOLi. [e]With 2 mol % CuCl/4 mol % **L2**. [f]With 2.0 equiv of *t*-BuOLi. [g]With 2.0 equiv of 2-bromopyridine. [h]Recycling 25% of 1,3,6-tri-*t*-butyl-9*H*-carbazole. [i]With 2.2 equiv of carbazole.

3II). Moreover, an electron paramagnetic resonance (EPR) experiment was also performed using 5,5-dimethy-1-pyrroline-*N*-oxide (DMPO) as radical probe. As shown in Figure 2, two kinds of radical signals were detected after a reaction mixture of **1a**, **2a**, CuCl, **L2**, and *t*-BuOLi in toluene was heated for 1 h at 130 °C in the presence of DMPO. These results indicated that the reactions involved radical-mediated pathways.

On the basis of these results and previous literature reports,[20,21a,c,23] a plausible catalytic cycle is depicted in Scheme 4. Initially, ligand **L2** coordinated with CuCl to

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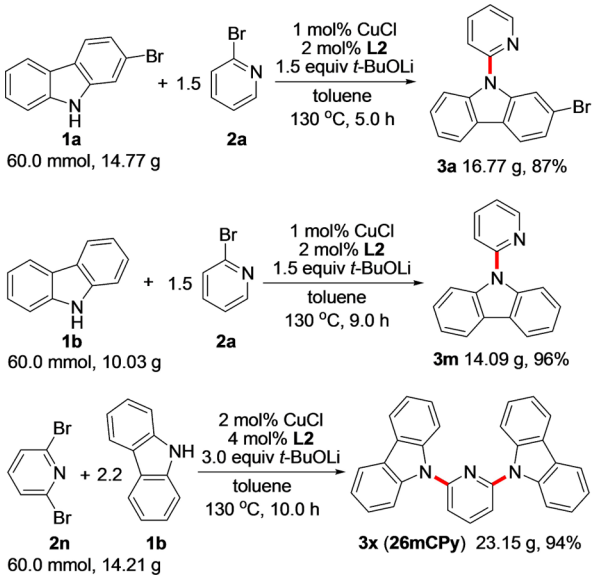
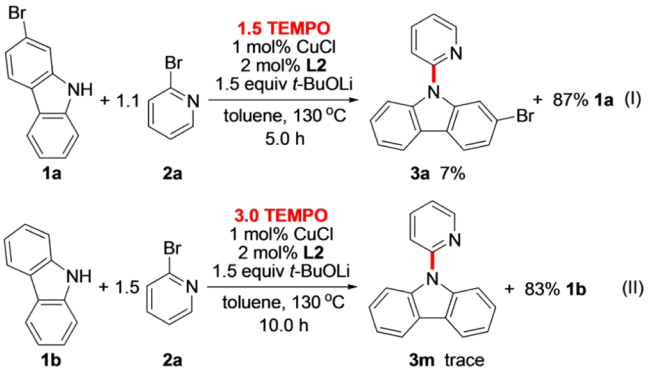
Scheme 2. Gram-Scale Experiments and Application for the Synthesis of 26mCPy



Scheme 3. Control Experiments



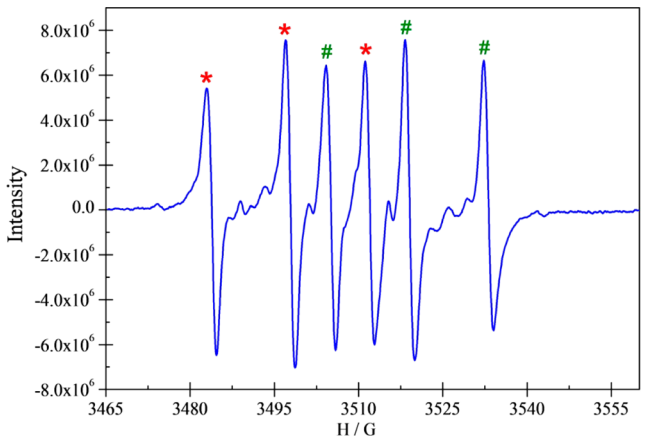
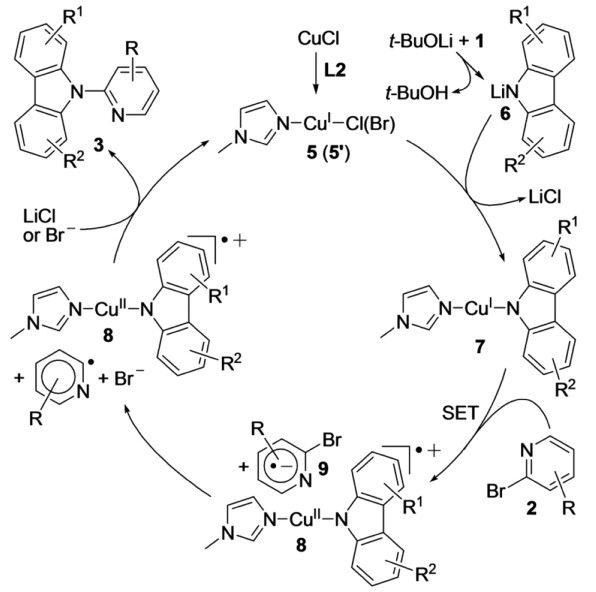


Figure 2. EPR measurement of **1a** (1.0 equiv), **2a** (1.1 equiv), CuCl (1 mol %), **L2** (2 mol %), and *t*-BuOLi (1.5 equiv) in toluene in the presence of DMPO (2.2 equiv).

generate Cu^{I} complex **5**, which was subsequently attacked by intermediate **6** at the metal center to give the other Cu^{I} complex **7**. Oxidative addition might be unfavorable because of the high energy of the Cu^{III} intermediate reported by Houk, Buchwald, and co-workers[23d] and also its steric hindrance.

Scheme 4. Proposed Mechanistic Pathway



Then, a SET reaction between Cu^{I} complex **7** and **2** occurred to form caged radical pairs[23d] of Cu^{II} complex **8** and 2-bromopyridine derivatives radical anion **9**. Thereafter, **9** could fragment to generate bromide anion and the pyridinyl radical, which rapidly reacted with **8** to deliver the corresponding final product **3** along with the regeneration of the Cu^{I} complex **5** or **5′**.

CONCLUSIONS

In summary, we have developed a facile and efficient CuCl-catalyzed Ullmann-type C−N cross-coupling reaction of carbazoles and 2-bromopyridine derivatives using the 1-methyl-1*H*-imidazole and *t*-BuOLi as ligand and base, respectively. It was found that both the ligand and base could significantly promote the reaction. This reaction could be employed to efficiently synthesis various *N*-heteroarylcarbazole derivatives in good to excellent yields under mild conditions. Furthermore, the low cost and low loading of both catalyst and ligand rendered this cross-coupling reaction suitable for large-scale preparation, and further applications of this approach in material science for the synthesis and development of new functional materials are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 126 MHz, respectively, with NMR instruments in $CDCl_3$ solutions, and chemical shifts were referenced to residual signal of TMS or $CDCl_3$. ^{1}H NMR spectra were recorded with residual TMS (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. The following abbreviations (or combinations thereof) were used to explain ^{1}H NMR multiplicities: s = singlet, d = doublet, t = triplet, and m = multiplet. All of the new compounds were analyzed for HRMS on an ESI-QTOF mass spectrometer using electrospray ionization in positive ion mode. All of the ratios of 3:4 were determined by ^{1}H NMR of the isolated products after chromatography. EPR spectra were recorded on an EPR spectrometer. All chemicals and reagents were purchased from commercial sources and used directly without further purification. Toluene was dried with Na_2SO_4 overnight before being used.

General Experimental Procedure for the Synthesis of Compounds 3a−y. Carbazole derivatives **1**, heteroaryl bromide **2** (if solid), CuCl, and *t*-BuOLi were added to a dry three-necked flask

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equipped with a magnetic stir bar and a condenser. The flask was then evacuated and backfilled with nitrogen; this evacuation and backfill procedure was repeated twice. Then, ligand 1-methyl-1*H*-imidazole **L2**, heteroaryl bromide **2** (if liquid), and the solvent toluene were added under nitrogen. The mixture was then stirred under reflux at 130 °C until carbazole derivative **1** was consumed completely as monitored by TLC. The reaction mixture was allowed to cool to room temperature and quenched with a solution of Na_2SO_3, diluted with EtOAc, filtered through a pad of Celite, and washed with EtOAc. The organic layer was then separated, dried over Na_2SO_4, and filtered, and the filtrate was concentrated to remove the solvent and excess heteroaryl bromide **2** (if liquid) under reduced pressure. The residue was purified through column chromatography on silica gel to afford desired product **3**. Note: It was better to remove heteroaryl bromide **2** (if liquid) as much as possible from the crude product before purification; otherwise, it might result in separation problems with the desired product in some cases.

*2-Bromo-9-(pyridin-2-yl)-9H-carbazole (**3a**).* Following the general procedure, 2-bromocarbazole **1a** (3.69 g, 15.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (1.57 mL, 16.50 mmol, 1.1 equiv) using CuCl (14.9 mg, 0.15 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (23.8 uL, 0.30 mmol, 0.02 equiv), and *t*-BuOLi (1.80 g, 22.50 mmol, 1.5 equiv) in toluene (56.6 mL) for 4.8 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 1:1−0:1) afforded the title compound as a white solid (4.70 g in 97% yield with a ratio of **3a**:**4a** = 98:2). **3a**: mp 169.5−170.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31−7.34 (m, 2H), 7.42 (dd, J = 8.0, 1.5 Hz, 1H), 7.44−7.47 (m, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.93−7.96 (m, 2H), 8.01 (d, J = 1.5 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 8.73 (dd, J = 5.0, 1.5 Hz, 1H). MS (ESI): calcd for $C_{17}H_{11}BrN_2$ M^+ 323.0, found 323.2. The ^{1}H NMR data are in agreement with that previously reported.[6c] 2-(2-Bromocarbazol-9-yl)-9-(pyridin-2-yl)-carbazole (**4a**) was confirmed by HPLC-MS spectra analysis. Column: C18 250 × 4.6 mm, H_2O/CH_3CN = 85:15−5:95, flow 1.0 mL/min, 254 nm. (See Supporting Information for the spectra.) MS (ESI): calcd for $C_{29}H_{18}BrN_3$ $[M + H]^+$ 488.1, found 488.2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28−7.31 (m, 2H), 7.37−7.42 (m, 4H), 7.46 (dd, J = 8.0, 1.5 Hz, 1H), 7.50−7.53 (m, 1H), 7.56 (d, J = 1.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.90−7.94 (m, 1H), 8.00 (d, J = 1.0 Hz, 1H), 8.01 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.68 (ddd, J = 5.0, 2.0, 1.0 Hz, 1H).

*2-Bromo-9-(3-methylpyridin-2-yl)-9H-carbazole (**3b**).* Following the general procedure, 2-bromocarbazole **1a** (492.2 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromo-3-methylpyridine **2b** (334.2 μl, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 2.5 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/EtOAc = 40:1−1:1) afforded the title compound as a white solid (611.9 mg in 91% yield with a ratio of **3b**:**4b** = 98:2). **3b**: mp 182.1−183.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.08 (s, 3H), 7.08 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 1.5 Hz, 1H), 7.27−7.31 (m, 1H), 7.38−7.42 (m, 3H), 7.83 (dd, J = 7.5, 1.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H), 8.58 (dd, J = 5.0, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.4, 110.3, 113.2, 119.5, 120.4, 120.5, 121.5, 122.5, 122.9, 123.3, 123.9, 126.4, 131.5, 140.3, 140.7, 141.0, 147.9, 149.1. HRMS (ESI): calcd for $C_{18}H_{14}BrN_2$ $[M + H]^+$ 337.0335, found 337.0347.

*2-Bromo-9-(4-methylpyridin-2-yl)-9H-carbazole (**3c**).* Following the general procedure, 2-bromocarbazole **1a** (492.2 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromo-4-methylpyridine **2c** (334.0 μl, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 2.5 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid (643.2 mg in 95% yield with a ratio of **3c**:**4c** = 99:1). **3c**: mp 181.4−183.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.13 (d, J = 5.0 Hz, 1H), 7.29−7.32 (m, 1H), 7.39−7.46 (m, 3H), 7.72 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 1.5 Hz, 1H), 8.06 (d, J = 7.5 Hz, 1H), 8.56 (d, J = 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 111.1, 114.3, 119.7, 119.7, 120.2, 121.1, 121.2, 122.9, 123.1, 123.5, 123.9, 126.5, 139.7, 140.4, 149.4, 150.2, 151.3. HRMS (ESI): calcd for $C_{18}H_{14}BrN_2$ $[M + H]^+$ 337.0335, found 337.0321.

*2-Bromo-9-(5-methylpyridin-2-yl)-9H-carbazole (**3d**).* Following the general procedure, 2-bromocarbazole **1a** (492.2 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromo-5-methylpyridine **2d** (516.1 mg, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 2.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid 617.1 mg in 92% yield with a ratio of **3d**:**4d** = 100:0. **3d**: mp. 189.1−190.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.30 (t, J = 7.5 Hz, 1H), 7.41 (dd, J = 8.0, 1.5 Hz, 1H), 7.42−7.45 (m, 1H), 7.47 (d, J = 8.0, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.72 (dd, J = 8.5, 2.5 Hz, 1H), 7.93 (s, 1H), 7.94 (d, J = 6 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.54 (d, J = 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.0, 111.0, 114.2, 118.7, 119.7, 120.2, 121.0, 121.2, 123.0, 123.5, 123.8, 126.5, 131.5, 139.2, 139.8, 140.5, 148.8, 149.9. HRMS (ESI): calcd for $C_{18}H_{14}BrN_2$ $[M + H]^+$ 337.0335, found 337.0347.

*2-Bromo-9-(5-bromopyridin-2-yl)-9H-carbazole (**3e**).* Following the general procedure, 2-bromocarbazole **1a** (246.1 mg, 1.00 mmol, 1.0 equiv) was coupled with 2,5-dibromopyridine **2e** (355.3 mg, 1.50 mmol, 1.5 equiv) using CuCl (1.0 mg, 0.01 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (1.6 μl, 0.02 mmol, 0.02 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 1.5 equiv) in toluene (3.8 mL) for 5.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid (311.6 mg in 80% yield with a ratio of **3e**:**4e** = 100:0). **3e**: mp 193.1−194.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 7.5 Hz, 1H), 7.42 (dd, J = 8.5, 1.5 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 1.5 Hz, 1H), 8.01 (dd, J = 8.5, 2.5 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 8.75 (d, J = 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.0, 114.4, 117.4, 119.9, 119.9, 120.3, 121.3, 121.6, 123.3, 123.8, 124.4, 126.7, 139.3, 140.0, 141.2, 149.9, 150.7. HRMS (ESI): calcd for $C_{17}H_{11}Br_2N_2$ $[M + H]^+$ 400.9284, found 400.9290.

*2-Bromo-9-(5-fluoropyridin-2-yl)-9H-carbazole (**3f**).* Following the general procedure, 2-bromocarbazole **1a** (246.1 mg, 1.00 mmol, 1.0 equiv) was coupled with 2-bromo-4-fluoro-pyridine **2f** (155.0 μl, 1.50 mmol, 1.5eq) using CuCl (1.0 mg, 0.01 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (1.6 μl, 0.02 mmol, 0.02 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 1.5 equiv) in toluene (3.8 mL) for 4.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 5:1−1:1) afforded the title compound as a white solid (319.1 mg in 93% yield with a ratio of **3f**:**4f** = 98:2). **3f**: mp 206.7−207.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05−7.08 (m, 1H), 7.32−7.36 (m, 2H), 7.44 (dd, J = 8.0, 1.5 Hz, 1H), 7.45−7.48 (m, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 1.5 Hz, 1H), 8.68 (dd, J = 8.5, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 106.3 (d, J = 20.0 Hz), 109.7 (d, J = 17.4 Hz), 111.2, 114.7, 120.0, 120.3, 121.2, 121.8, 123.4, 123.9, 124.6, 126.8, 139.6 (d, J = 98.75 Hz), 151.8 (d, J = 8.8 Hz), 153.5 (d, J = 10.0 Hz), 168.9, 171.0. HRMS (ESI): for $C_{17}H_{11}BrFN_2$ $[M + H]^+$ calcd 341.0084, found 341.0082.

*2-Bromo-9-(pyrimidin-2-yl)-9H-carbazole (**3g**).* Following the general procedure, 2-bromocarbazole **1a** (492.2 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromopyrimidine **2g** (476.9 mg, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 7.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 5:1−1:1) afforded the title compound as a white solid (621.7 mg in 96% yield with a ratio of **3g**:**4g** = 100:0). **3g**: mp 215.3−216.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (t, J = 4.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 8.0, 1.5 Hz, 1H), 7.48−7.52 (m, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.5 Hz, 1H), 8.80 (d, J = 4.5 Hz, 2H), 8.82 (d, J = 8.5 Hz, 1H), 9.06 (d, J = 2.0 Hz, 1H); ^{13}C

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NMR (126 MHz, $CDCl_3$): δ 116.2, 116.5, 119.4, 119.5, 120.1, 120.4, 122.6, 124.7, 125.0, 125.4, 127.0, 139.2, 139.7, 157.8, 158.8. HRMS (ESI): calcd for $C_{16}H_{11}BrN_3$ $[M + H]^+$ 324.0131, found 324.0127.

*2-Bromo-9-(pyrazin-2-yl)-9H-carbazole (**3h**).* Following the general procedure, 2-bromocarbazole **1a** (246.1 mg, 1.00 mmol, 1.0 equiv) was coupled with 2-bromopyrazine **2h** (135.7 μl, 1.50 mmol, 1.5 equiv) using CuCl (1.0 mg, 0.01 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (1.6 μl, 0.02 mmol, 0.02 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 1.5 equiv) in toluene (3.8 mL) for 7.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 5:1−1:1) afforded the title compound as a white solid (300.6 mg in 93% yield with a ratio of **3h**:**4h** = 98:2). **3h**: mp 207.9−208.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.0 Hz, 1H), 7.43−7.49 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 5.0 Hz, 1H), 8.06 (s, 1H), 8.56 (d, *J* = 2.5 Hz, 1H), 8.67 (dd, *J* = 2.0, 1.5 Hz, 1H), 9.01 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 110.9, 114.4, 120.1, 120.4, 121.3, 122.1, 123.6, 124.1, 124.9, 126.9, 139.0, 139.8, 140.5, 141.5, 143.5, 148.3. HRMS (ESI): calcd for $C_{16}H_{11}BrN_3$ $[M + H]^+$ 324.0131, found 324.0143.

*2-Bromo-9-(quinolin-2-yl)-9H-carbazole (**3i**).* Following the general procedure, 2-bromocarbazole **1a** (246.1 mg, 1.00 mmol, 1.0 equiv) was coupled with 2-bromoquinoline **2i** (312.1 mg, 1.50 mmol, 1.5 equiv) using CuCl (1.0 mg, 0.01 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (1.6 μl, 0.02 mmol, 0.02 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 1.5 equiv) in toluene (3.8 mL) for 3.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 5:1−3:1) afforded the title compound as a white solid (351.6 mg in 94% yield with a ratio of **3i**:**4i** = 97:3). **3i**: mp 199.6−200.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.5 Hz, 1H), 7.42−7.48 (m, 2H), 7.60 (td, *J* = 7.5, 1.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.78−7.81 (m, 1H), 7.91 (t, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 1.5 Hz, 1H), 8.35 (d, J = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.5, 114.8, 117.5, 119.9, 120.3, 121.3, 121.6, 123.4, 123.9, 124.3, 126.6, 126.6, 126.7, 127.6, 128.8, 130.5, 139.0, 139.6, 140.3, 147.7, 150.3. HRMS (ESI): calcd for $C_{21}H_{14}BrN_2$ $[M + H]^+$ 373.0335, found 373.0342.

*2-Bromo-9-(isoquinolin-2-y)-9H-carbazole (**3j**).* Following the general procedure, 2-bromocarbazole **1a** (626.2 mg, 2.54 mmol, 1.0 equiv) was coupled with 1-chloroisoquinoline **2j** (624.2 mg, 3.82 mmol, 1.5 equiv) using CuCl (5.0 mg, 0.05 mmol, 0.02 equiv), 1-methyl-1*H*-imidazole **L2** (8.2 μl, 0.10 mmol, 0.04 equiv), and *t*-BuOLi (305.0 mg, 3.82 mmol, 1.5 equiv) in toluene (9.7 mL) for 5.0 days. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid (228.6 mg in 24% yield with a ratio of **3j**:**4j** = 99:1). **3j**: mp 70.3−71.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.0 Hz, 1H), 7.30−7.38 (m, 3H), 7.42 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.50−7.53 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.77−7.80 (m, 1H), 7.86 (d, *J* = 5.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.1, 114.0, 119.6, 120.3, 120.9, 121.5, 121.6, 122.9, 123.3, 123.7, 125.0, 125.5, 126.4, 127.3, 128.3, 131.2, 138.7, 141.4, 142.0, 142.3, 149.6. HRMS (ESI): calcd for $C_{21}H_{14}BrN_2$ $[M + H]^+$ 373.0335, found 373.0319.

*2-Bromo-9-(thiazol-2-yl)-9H-carbazole (**3k**).* Following the general procedure, 2-bromocarbazole **1a** (492.2 mg, 2.0 mmol, 1.0 equiv) was coupled with 2-bromothiazole **2k** (270.4 μl, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.0 mmol, 1.5 equiv) in toluene (7.8 mL) for 11.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 3:1−1:1) afforded the title compound as a white solid (613.2 mg in 93% yield with a ratio of **3k**:**4k** = 100:0). **3k**: mp 189.5−190.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, *J* = 4 Hz, 1H), 7.35−7.38 (m, 1H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.0 Hz, 1H), 7.79 (d, *J* = 3.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 112.1, 115.1, 115.9, 120.2, 120.4, 121.1, 122.5, 123.5, 124.1, 125.4, 127.2, 139.3, 140.0, 140.1, 158.5. HRMS (ESI): calcd for $C_{15}H_{10}BrN_2S$ $[M + H]^+$ 328.9743, found 328.9753.

*2-Bromo-9-(benzothiazol-2-yl)-9H-carbazole (**3l**).* Following the general procedure, 2-bromocarbazole **1a** (123.1 mg, 0.50 mmol, 1.0 equiv) was coupled with 2-bromobenzothiazole **2l** (160.6 mg, 0.75 mmol, 1.5 equiv) using CuCl (0.5 mg, 0.005 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (0.8 μl, 0.01 mmol, 0.02 equiv), and *t*-BuOLi (60.0 mg, 0.75 mmol, 1.5 equiv) in toluene (4.0 mL) for 2 days. Purification of the crude product by flash chromatography on silica gel (eluent: PE/EtOAc = 20:1) afforded the title compound as a white solid (149.1 mg in 79% yield with a ratio of **3l**:**4l** = 97:3). **3l**: mp 209.1−209.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39−7.44 (m, 2H), 7.52 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54−7.58 (m, 2H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.71 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 112.9, 116.7, 120.2, 120.6, 121.1, 121.2, 122.5, 123.0, 124.0, 124.6, 124.9, 125.9, 126.7, 127.3, 132.1, 139.1, 140.0, 150.1, 157.2. HRMS (ESI): calcd for $C_{19}H_{12}BrN_2S$ $[M + H]^+$ 378.9899, found 378.9918.

*9-(Pyridin-2-yl)-9H-carbazole (**3m**).* Following the general procedure, carbazole **1b** (334.4 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (286.1 μl, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 8.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 5:1−1:1) afforded the title compound as a white solid (455.0 mg in 93% yield). Mp 159.7−160.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (ddd, *J* = 8.5, 5.0, 1.0 Hz, 1H), 7.29−7.32 (m, 2H), 7.43 (td, *J* = 8.5, 1.5 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.88 (td, *J* = 8.0, 2.0 Hz, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 8.71 (dd, *J* = 5.0, 1.0 Hz, 1H). The ^{1}H NMR data are consistent with that previously reported.[8d]

*9-(4-Methylpyridin-2-yl)-9H-carbazole (**3n**).* Following the general procedure, carbazole **1b** (334.4 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromo-4-methylyridine **2d** (245.0 μl, 2.20 mmol, 1.1 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 11.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 3:1−1:1) afforded the title compound as a light yellow sticky liquid (489.4 mg in 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.09 (d, *J* = 5.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.41−7.44 (m, 3H), 7.80 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.55 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 111.1, 119.7, 120.1, 120.7, 122.4, 124.2, 126.1, 139.6, 149.2, 149.9, 151.8. The ^{1}H NMR data are consistent with that previously reported.[24]

*9-(Benzo[d]thiazol-2-yl)-9H-carbazole (**3o**).* Following the general procedure, carbazole **1b** (41.8 mg, 0.25 mmol, 1.0 equiv) was coupled with 2-bromopbenzo[*d*]thiazole **2l** (80.3 mg, 0.38 mmol, 1.5 equiv) using CuCl (0.3 mg, 0.003 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (0.4 μl, 0.005 mmol, 0.02 equiv), and *t*-BuOLi (30.0 mg, 0.38 mmol, 1.5 equiv) in toluene (2.0 mL) for 26.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1) afforded the title compound as a light yellow sticky liquid (58.6 mg in 78% yield). Mp 138.3−139.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.42 (m, 3H), 7.52−7.57 (m, 3H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 8.49 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 113.3, 120.1, 121.1, 122.3, 122.7, 124.6, 125.3, 126.6, 127.0, 132.1, 139.3, 150.3, 157.8. The ^{13}C NMR data are consistent with that previously reported.[25]

*9-(1-Methylbenzo[d]imidazol-2-yl)-9H-carbazole (**3p**).* Following the general procedure, carbazole **1b** (83.6 mg, 0.5 mmol, 1.0 equiv) was coupled with 2-bromopbenzo[*d*]imidazole **2m** (158.3 mg, 0.75 mmol, 1.5 equiv) using CuCl (0.3 mg, 0.025 mmol, 0.05eq), 1-methyl-1*H*-imidazole **L2** (4.0 μl, 0.05 mmol, 0.10 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 3.0eq) in toluene (2.0 mL) for 24.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/EtOAc = 10:1) afforded the title compound as a white solid (74.3 mg in 50% yield). Mp 195.2−160.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.52 (s, 3H), 7.30−7.34 (m, 4H), 7.37−7.44 (m, 5H) 7.87−7.90 (m, 1H), 8.10 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 30.6, 109.7, 110.7, 120.2, 120.5, 121.4, 122.9, 123.3, 124.0, 126.6, 135.2,

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140.4, 141.6, 144.6. HRMS (ESI): calcd for $C_{20}H_{16}N_3$ $[M + H]^+$ 298.1339, found 298.1337.

*3-Bromo-9-(pyridin-2-yl)-9H-carbazole (**3q**).* Following the general procedure, 3-bromo-9*H*-carbazole **1c** (492.2 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (286.1 μl, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 3.5 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 3:1−0:1) afforded the title compound as a white solid (613.7 mg in 95% yield). Mp 191.9−192.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29−7.33 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.91 (td, *J* = 8.0, 1.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 8.71 (dd, *J* = 4.5, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.2, 112.8, 113.7, 118.9, 120.4, 121.2, 121.5, 122.9, 123.2, 126.0, 126.9, 128.8, 138.2, 138.6, 139.8, 149.7, 151.4. HRMS (ESI): calcd for $C_{17}H_{12}BrN_2$ $[M + H]^+$ 323.0178, found 323.0178.

*2,7-Dibromo-9-(pyridin-2-yl)-9H-carbazole (**3r**).* Following the general procedure, 2,7-dibromo-9*H*-carbazole **1d** (325.0 mg, 1.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (143.0 μl, 1.50 mmol, 1.5 equiv) using CuCl (1.0 mg, 0.01 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (1.6 μl, 0.02 mmol, 0.02 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 1.5 equiv) in toluene (3.8 mL) for 4.5 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/EtOAc = 10:1−1:1) afforded the title compound as a white solid (332.9 mg in 83% yield). Mp 208.0−209.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.0, 5.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 0.5 Hz, 2H), 7.97 (td, *J* = 8.0, 1.5 Hz, 1H), 8.74 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 114.4, 119.0, 120.2, 121.3, 122.1, 122.5, 124.5, 138.9, 140.4, 150.0, 150.7. The ^{1}H NMR and ^{13}C NMR data are consistent with that previously reported.[24]

*3,6-Dibromo-9-(pyridin-2-yl)-9H-carbazole (**3s**).* Following the general procedure, 3,6-dibromo-9*H*-carbazole **1e** (650.0 mg, 2.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (286.1 μl, 3.00 mmol, 1.5 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.02 equiv), and *t*-BuOLi (240.2 mg, 3.00 mmol, 1.5 equiv) in toluene (7.6 mL) for 9.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/EtOAc = 20:1−5:1) afforded the title compound as a white solid (738.0 mg in 92% yield). Mp 256.8−257.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 7.0, 5.0 Hz, 1H), 7.53 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 2H), 7.95 (td, *J* = 7.5, 1.5 Hz, 1H), 8.17 (d, *J* = 1.5 Hz, 2H), 8.72 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 112.9, 114.1, 118.9, 121.8, 123.1, 124.9, 129.6, 138.7, 138.5, 149.8, 151.1. The ^{1}H NMR and ^{13}C NMR data are consistent with that previously reported.[24]

*3-Phenyl-9-(pyridin-2-yl)-9H-carbazole (**3t**).* Following the general procedure, 3-phenyl-9*H*-carbazole **1f** (60.8 mg, 0.25 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (35.8 μl, 0.375 mmol, 1.5 equiv) using CuCl (0.5 mg, 0.005 mmol, 0.02 equiv), 1-methyl-1*H*-imidazole **L2** (0.8 μl, 0.01 mmol, 0.04 equiv), and *t*-BuOLi (40.0 mg, 0.50 mmol, 2.0 equiv) in toluene (1.0 mL) for 3.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 5:1−1:1) afforded the title compound as a white solid (79.0 mg in 99% yield). Mp 178.9−179.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27−7.35 (m, 3H), 7.42−7.45 (m, 3H), 7.55 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.63−7.67 (m, 3H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.89 (td, *J* = 8.0, 2.0 Hz, 1H), 8.02 (d, *J* = 1.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.72 (dd, *J* = 4.5, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 109.7, 111.1, 119.2, 120.2, 120.4, 120.6, 121.0, 121.3, 123.5, 124.0, 126.2, 127.0, 127.6, 128.7, 138.5, 139.7, 140.0, 140.1, 142.0, 149.7, 151.7. HRMS (ESI): calcd for $C_{23}H_{17}N_2$ $[M + H]^+$ 321.1386, found 321.1378.

*3,6-Di-tert-butyl-9-(pyridin-2-yl)-9H-carbazole (**3u**).* Following the general procedure, 3,6-di-*tert*-butyl-9*H*-carbazole **1g** (89.1 mg, 0.25 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (47.7 μl, 0.50 mmol, 2.0 equiv) using CuCl (0.5 mg, 0.005 mmol, 0.02 equiv), 1-methyl-1*H*-imidazole **L2** (0.8 μl, 0.01 mmol, 0.04 equiv), and *t*-BuOLi (40.0 mg, 0.50 mmol, 2.0 equiv) in toluene (1.0 mL) for 29.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid (85.4 mg in 96% yield). Mp 217.0−217.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (s, 18H), 7.21−7.23 (m, 1H), 7.49 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.87 (td, *J* = 8.0, 2.0 Hz, 1H), 8.11 (d, *J* = 2.0 Hz, 2H), 8.68 (dd, *J* = 5.0, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 31.9, 34.7, 110.7, 116.1, 118.3, 120.5, 123.9, 124.4, 137.9, 138.2, 143.8, 149.5, 152.2. HRMS (ESI): calcd for $C_{25}H_{29}N_2$ $[M + H]^+$ 357.2325, found 357.2326.

*1,3,6-Tri-tert-butyl-9-(pyridin-2-yl)-9H-carbazole (**3v**).* Following the general procedure, 1,3,6-tri-*tert*-butyl-9*H*-carbazole **1h** (167.8 mg, 0.50 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (95.4 μl, 1.00 mmol, 2.0 equiv) using CuCl (2.5 mg, 0.025 mmol, 0.05 equiv), 1-methyl-1*H*-imidazole **L2** (4.0 μl, 0.05 mmol, 0.1 equiv), and *t*-BuOLi (80.1 mg, 1.00 mmol, 2.0 equiv) in toluene (2.0 mL) for 29.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid (121.5 mg in 59%). The recovery of 1,3,6-tri-*tert*-butyl-9*H*-carbazole was 42.5 mg in 25% yield. **3v**: mp 211.4−212.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9H), δ 1.41 (s, 9H), δ 1.46 (s, 9H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.24−7.27 (m, 2H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.72 (td, *J* = 8.0, 2.0 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 1.5 Hz, 1H), 8.62 (dd, *J* = 5.0, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 31.6, 31.9, 31.9, 34.6, 34.8, 35.4, 112.1, 114.0, 115.6, 122.2, 122.3, 123.8, 124.5, 125.7, 129.0, 137.0, 138.0, 139.7, 143.9, 144.4, 144.6, 149.2, 158.2. HRMS (ESI): calcd for $C_{29}H_{37}N_2$ $[M + H]^+$ 413.2951, found 413.2935.

*1-(Pyridin-2-yl)-1H-indole (**3w**).* Following the general procedure, indole **1i** (117.2 mg, 1.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (143.0 μl, 1.50 mmol, 1.5 equiv) using CuCl (1.0 mg, 0.01 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (1.6 μl, 0.02 mmol, 0.02 equiv), and *t*-BuOLi (120.1 mg, 1.50 mmol, 1.5 equiv) in toluene (4.0 mL) for 4.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−3:1) afforded the title compound as a yellow liquid (188.4 mg in 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.71 (d, *J* = 3.5 Hz, 1H), 7.16 (dd, *J* = 7.0, 5.0 Hz, 1H), 7.20 (dd, *J* = 7.5 Hz, 1H), 7.28−7.31 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 3.5 Hz, 1H), 7.80−7.83 (m, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.57 (dd, *J* = 5.5, 1.5 Hz, 1H). The ^{1}H NMR data are consistent with that previously reported.[22]

*9,9′-(2,6-Pyridinediyl)bis-9H-carbazole (**3x**, 26-mCPy).* Following the general procedure, carbazole **1b** (735.7 mg, 4.4 mmol, 2.2 equiv) was coupled with 2,6-dibromopyridine **2n** (473.8 mg, 2.00 mmol, 1.0 equiv) using CuCl (4.0 mg, 0.04 mmol, 0.02 equiv), 1-methyl-1*H*-imidazole **L2** (6.4 μl, 0.08 mmol, 0.04 equiv), and *t*-BuOLi (480.3 mg, 6.0 mmol, 3.0 equiv) in toluene (8.0 mL) for 3.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 1:1) afforded the title compound as a yellow liquid (751.3 mg in 92% yield). Mp 243.1−245.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31−7.34 (m, 4H), 7.39−7.42 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 4H), 8.08 (t, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 111.9, 114.9, 120.1, 121.2, 124.5, 126.3, 139.5, 140.3, 151.5. The ^{1}H NMR data are consistent with that previously reported.[3a]

*10-(Pyridin-2-yl)-10H-phenoxazine (**3y**).* Following the general procedure, phenoxazine **1j** (183.2 mg, 1.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (190.7 μl, 2.00 mmol, 2.0 equiv) using CuCl (2.0 mg, 0.02 mmol, 0.02 equiv), 1-methyl-1*H*-imidazole **L2** (3.2 μl, 0.04 mmol, 0.04 equiv), and *t*-BuOLi (160.1 mg, 2.00 mmol, 2.0 equiv) in toluene (3.8 mL) for 24.0 h. Purification of the crude product by flash chromatography on silica gel (eluent: PE/DCM = 10:1−1:1) afforded the title compound as a white solid (104.1 mg in 40% yield). Mp 179.3−180.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 6.42 (dd, *J* = 7.5, 1.5 Hz, 2H), 6.69−6.72 (m, 2H), 6.75−6.80 (m, 4H), 7.28 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.84 (td, *J* = 7.5, 2.0 Hz, 1H), 8.68 (dd, *J* = 5.0, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 115.9, 116.0, 122.0, 122.1, 122.8, 123.2, 132.8, 139.5, 145.7, 150.4, 153.9. HRMS (ESI): calcd for $C_{17}H_{13}N_2O$ $[M + H]^+$ 261.1022, found 261.1015.

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Procedure for the Gram-Scale Synthesis of 3a. Following the general procedure, 2-bromocarbazole **1a** (14.77 g, 60.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (8.58 mL, 90.00 mmol, 1.5 equiv) using CuCl (60.0 mg, 0.60 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (95.1 μl, 1.20 mmol, 0.02 equiv), and *t*-BuOLi (7.20 g, 90.00 mmol, 1.5 equiv) in toluene (240 mL) for 5.0 h. The reaction mixture was allowed to cool to room temperature, quenched with a solution of Na_2SO_3 (100 mL), filtered through a pad of Celite, and washed with EtOAc three times. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times (100 mL × 3). The combined organic layer was washed with water (50 mL), dried over Na_2SO_4, and filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in DCM (100 mL), and silica gel (4.0 g) was added. The mixture was stirred under reflux for 3.0 h to remove the little colored impurities. The reaction mixture was allowed to cool to room temperature, filtered, and washed with DCM. The filtrate was concentrated under reduced pressure to remove the solvent and excess 2-bromopyridine. The residue was recrystallized in PE/DCM (40 mL/5 mL) to afford the desired product as a white solid (16.77 g in 87% yield). The ^{1}H NMR shows that the product did not contain **4a**. The mother liquor was concentrated, and the residue was purified through column chromatography on silica gel using PE/DCM = 3:1−1:1 as eluent to afford the product as a white solid (1.07 g in 5% yield). The total yield was 92%.

Procedure for the Gram-Scale Synthesis of 3m. Following the general procedure, carbazole **1b** (10.03 g, 60.00 mmol, 1.0 equiv) was coupled with 2-bromopyridine **2a** (8.58 mL, 90.00 mmol, 1.5 equiv) using CuCl (60.0 mg, 0.60 mmol, 0.01 equiv), 1-methyl-1*H*-imidazole **L2** (95.1 μl, 1.20 mmol, 0.02 equiv), and *t*-BuOLi (7.21 g, 90.00 mmol, 1.5 equiv) in toluene (240 mL) for 9.0 h, cooled to room temperature, quenched with a solution of Na_2SO_3 (100 mL), filtered through a pad of Celite, and washed with EtOAc three times. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times (100 mL × 3). The combined organic layer was washed with water (50 mL) and then dried over Na_2SO_4 and filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in DCM (100 mL), and silica gel (4.0 g) was added; the mixture was stirred under reflux for 3.0 h to remove the little colored impurities. The reaction mixture was allowed to cool to room temperature, filtered, and washed with DCM. The filtrate was concentrated under reduced pressure to remove the solvent and excess 2-bromopyridine. The residue was recrystallized in PE/EtOAc (90 mL/10 mL) to afford the desired product as a white solid (8.61 g in 59% yield). The mother liquor was concentrated, and the residue was purified through column chromatography on silica gel using PE/DCM = 5:1−1:1 as eluent to afford the product as a white solid (5.48 g in 37% yield). The total yield was 96%.

Procedure for the Gram-Scale Synthesis of 3x (26-mCPy). Following the general procedure, carbazole **1b** (22.07 g, 132.00 mmol, 2.2 equiv) was coupled with 2,6-dibromopyridine **2n** (14.21 g, 60.00 mmol, 1.0 equiv) using CuCl (120.0 mg, 1.20 mmol, 0.02 equiv), 1-methyl-1*H*-imidazole **L2** (190.2 μl, 2.40 mmol, 0.04 equiv), and *t*-BuOLi (14.41 g, 180.00 mmol, 3.0 equiv) in toluene (240 mL) for 10.0 h, and the product precititated. The reaction mixture was allowed to cool to room temperature, diluted with $CHCl_3$, filtered through a pad of silica gel to remove the salt, and washed with $CHCl_3$ several times to collect all of the product. The filtrated was concentrated under reduced pressure to remove the solvent. The residue was stirred in MeOH/toluene (100 mL/34 mL) at 75 °C for 2 h, cooled to room temperature slowly, kept stirring overnight, and then filtered and washed with *n*-hexane to afford the desired product as a white solid (23.15 g in 94% yield).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02595.

^{1}H and ^{13}C NMR for all of the compounds, HPLC-MS spectra for **3a** and its impurity, and the EPR experiment (PDF)

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Notes

The authors declare no competing financial interest.

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