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ARTICLE

Copper/β-Diketone-Catalysed N-Arylation of Carbazoles

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A copper-catalysed C–N bond-forming reaction of carbazoles with aryl iodides is described. Several commercially available ligands such as β-diketone and diamine, are tested in the N-arylation of carbazoles. The catalytic system generated in situ from inexpensive copper salt, simple β-diketone and inorganic base efficiently N-arylated the carbazoles. A wide range of aryl iodides and carbazoles can be coupled to generate N-arylcarbazoles in the presence of various functional groups. However, the sterically hindered effect of aryl iodides is evident in this catalytic system. The selectivity of two iodine atoms on the aromatic ring of diiodobenzene is evaluated in the developed catalytic system. Results showed that the selectivity of diiodobenzene can be tuned by the reaction temperature.

Introduction

Carbazole is extensively applied as a building block in natural products,[1] pharmaceuticals,[2] dye-sensitized solar cells,[3] and advanced material science[4] because of its unique physical properties. The absorption, light-emitting properties, and electronic properties of carbazole can be tuned by introducing substituents into its structure.[5] The prevalence of substituted carbazoles in organic chemistry drives the need for a new approach to synthesize these compounds.[6]

Classical approaches to prepare N-arylcarbazoles include the aromatic nucleophilic substitution reaction[7] and copper-catalysed Ullmann coupling reaction.[8] These methods often suffer from several drawbacks such as harsh reaction conditions, the need to use stoichiometric quantities of copper, and limited substrate scope.

Since the pioneering work of Buchwald[9] and Hartwig,[10] numerous studies on the palladium- and copper-catalysed C–N bond-forming reaction have been published.[11] Copper-catalysed coupling reaction has attracted considerable interest because copper is very inexpensive, and undergoes desirable reactions for industrial applications. Different copper-fitted ligands, including α-amino acids,[12] phenanthrolines,[13] diamines,[14] diketone,[15] imines,[16] and others[17] as well as "ligand-free" systems,[18] have emerged. β-Diketone and diamine derivatives are commercially available and efficient ligands for the copper-catalysed N-arylation of aryl halides with azoles. In 2001 Buchwald et al. found that the use of diamine-based ligands greatly accelerates copper-catalysed C–N coupling reaction.[19] Subsequently, Song et al. disclosed that 2,2,6,6-tetramethylheptane-3,5-dione was an efficient ligand for copper-catalysed C–O coupling.[20] Maligres et al also recently reported a copper(II)/diketonate catalyst that showed higher catalytic activity for C–N and C–O coupling.[21] However, few studies have reported on the copper-catalysed N-arylation of carbazoles with aryl halides.

In this study, we report a simple and efficient method for the synthesis of N-arylcarbazoles via copper-diketone catalyst. The electronic and sterically hindered effect of aryl iodides and carbazoles were investigated in the developed catalytic system. A range of aryl iodides and carbazoles can be coupled to generate N-arylcarbazoles, even bearing various functional groups, such as halogen atom, that performed well under such catalytic system. The halogenated carbazoles are of great use and versatility in organic synthesis because they can be converted into useful synthetic intermediates through transition-metal-catalysed coupling.

Results and Discussion

The coupling reaction of iodobenzene and carbazole was selected as the model reaction to optimize reaction conditions. The effect of different ligands on the coupling reaction was firstly investigated.

To prove the efficiency of ligands, we designed control experiments by conducting the reaction in the presence of Cu_2O but in the absence of ligands. The results indicated that the reaction was difficult to proceed with Cu_2O in the absence of ligands, and only 16% product yield was obtained. A wide range of β-diketone ligand was initially evaluated, and the results showed that 2,2,6,6-tetramethylheptane-3,5-dione (**L**$_7$) was the most efficient for iodobenzene conversion and provided a 67% product yield. The potential catalytic efficiency of four 1,2-ethanediamine derivatives was subsequently tested

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

in the coupling of iodobenzene and carbazole. The results indicated that N,N'-dimethyl-1,2-ethanediamine (**L_{14}**) was more catalytically active than other ethanediamine derivatives. L-Proline (**L_{16}**) and *trans*-1,2-diaminocyclohexane (**L_{17}**) were also examined, but poor results were obtained.

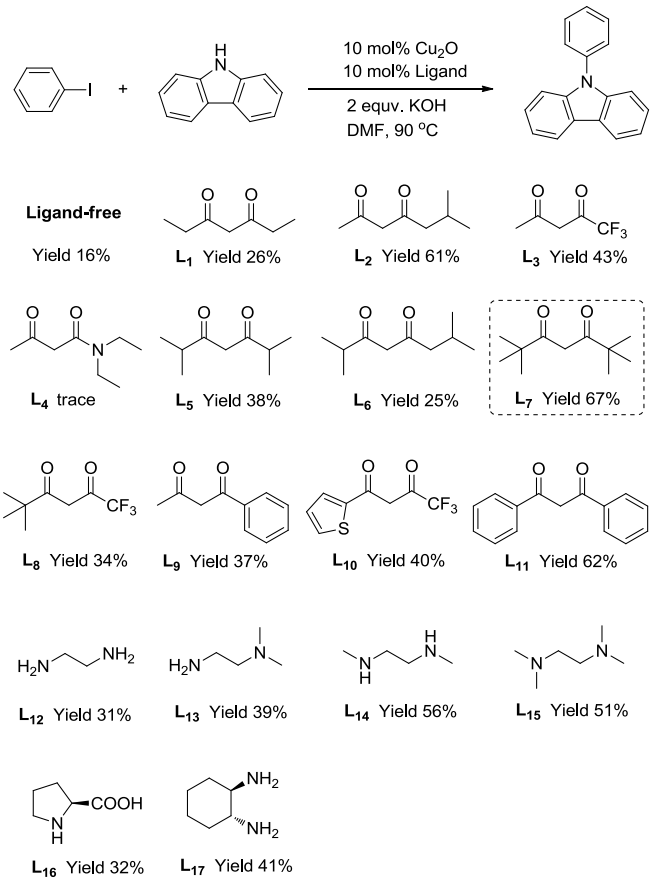


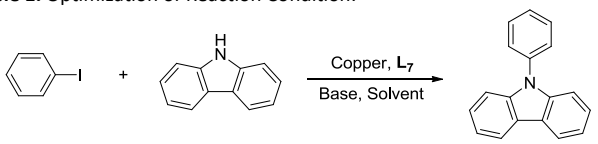
Figure 1. Ligands for Copper-Catalysed Cross-Coupling.

The cross-coupling of iodobenzene with carbazole was selected as the model reaction to optimize the reaction conditions using **L_7** as ligand, many solvent, copper sources, bases and temperature were evaluated. The effect of different solvents on the coupling between iodobenzene and carbazole was initially examined (Table 1, entries 1-4). The results showed that the solvent served a crucial function in the coupling reaction. N,N-Dimethylformamide (DMF) was the most efficient for the product formation (Table 1, entry 4).

Copper-catalysed cross-coupling is affected by the oxidation state of the copper source. Therefore, different copper sources [Cu(I), Cu(II) and Cu(0)] were evaluated. Cu(I) catalysts were more catalytically active than the other copper sources. The Cu(I) states showed moderate catalytic activity, and Cu_2O provided the best results (Table 1, entries 4 vs. 5 and 6). Among Cu(II) sources, $CuSO_4$, $Cu(OAc)_2$ and $Cu(NO_3)_2$ showed relatively higher catalytic activity than CuO (Table 1, entries 7, 8 and 9 vs. 10), and $Cu(OAc)_2$ was superior to the other Cu(II) sources (Table 1, entry 8 vs. 7, 9 and 10). Cu(0) powder yielded much slower conversion (Table 1, entry 11).

The nature of the base is an important factor that determines the efficiency of the copper-catalysed C–N bond formation reaction. Among potassium bases, potassium hydroxide was superior to a range of other potassium bases, with carbonate, phosphate and alcoholate exhibiting lower conversion (Table 1, entries 4 vs. 12, 13 and 14). Sodium hydroxide was superior to other sodium salts (Table 1, entries 15 vs. 16-20). The strong base of cesium carbonate showed lower conversion (Table 1, entry 21).

Table 1. Optimization of Reaction Condition.[a]



Entry	Solvent	Copper	Base	T (°C)	Yield (%)[b]
1	DMA	Cu_2O	KOH	90	trace
2	NMP	Cu_2O	KOH	90	trace
3	DMSO	Cu_2O	KOH	90	16
4	DMF	Cu_2O	KOH	90	67
5	DMF	CuI	KOH	90	53
6	DMF	CuCl	KOH	90	48
7	DMF	$CuSO_4$	KOH	90	20
8	DMF	$Cu(OAc)_2$	KOH	90	39
9	DMF	$Cu(NO_3)_2$	KOH	90	30
10	DMF	CuO	KOH	90	none
11	DMF	Cu	KOH	90	24
12	DMF	Cu_2O	K_2CO_3	90	35
13	DMF	Cu_2O	$K_3PO_4{\cdot}3H_2O$	90	38
14	DMF	Cu_2O	K*t*OBu	90	33
15	DMF	Cu_2O	NaOH	90	40
16	DMF	Cu_2O	Na_2CO_3	90	21
17	DMF	Cu_2O	$NaHCO_3$	90	18
18	DMF	Cu_2O	Na*t*OBu	90	25
19	DMF	Cu_2O	CH_3ONa	90	34
20	DMF	Cu_2O	C_6H_5ONa	90	30
21	DMF	Cu_2O	Cs_2CO_3	90	25
22	**DMF**	**Cu_2O**	**KOH**	**110**	**89**
23	DMF	Cu_2O	KOH	130	80

[a] Reaction conditions: Iodobenzene (0.5 mmol), Carbazole (0.75 mmol) Copper source (10 mol%), **L_7** (10 mol%), Base (1.0 mmol) in solvent (2 ml) under N_2. [b] Isolated yield.

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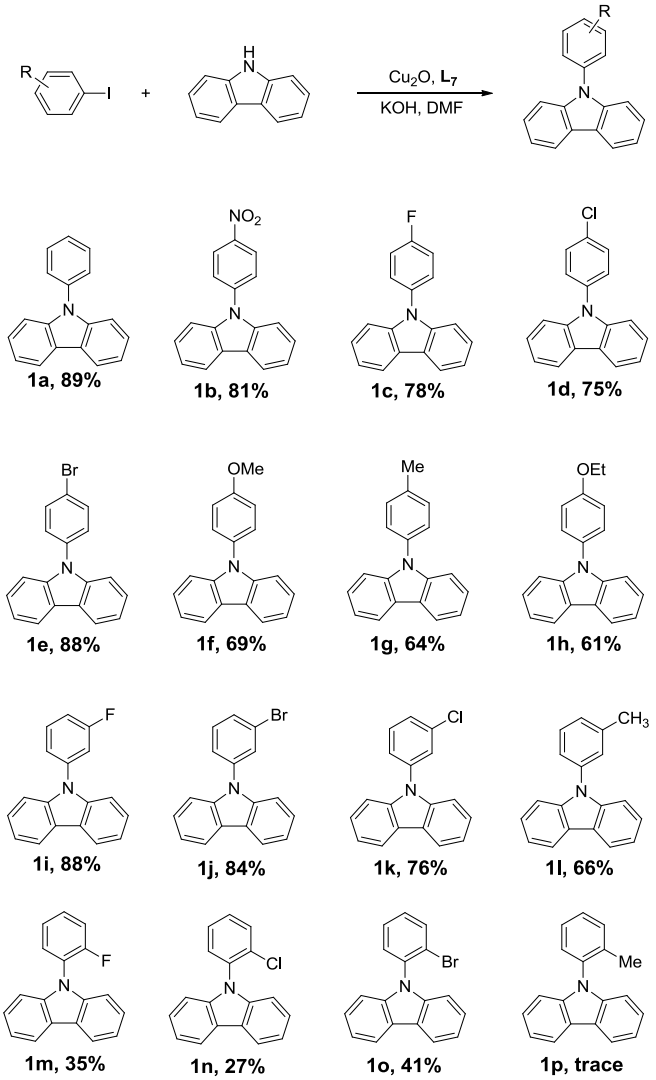
The effect of reaction temperature on cross-coupling was also explored, and the results suggested that the product yield increased with increasing temperature from 90 °C to 110 °C (Table 1, entries 4 and 22). However, when temperature reached to 130 °C, the product yield began to decrease (Table 1, entry 23). GC-MS analysis showed that small amounts of deiodinated products were also observed. This result indicated that an amount of iodobenzene consumption was responsible for the decrease in efficiency. Thus, considering efficiency and cost, 110 °C was selected as the optimized reaction temperature and used in the following studies.

The scope and limitations of coupling of aryl iodides were explored using Cu_2O as catalyst, $\mathbf{L_7}$ as ligand, KOH as base and DMF as solvent at 110 °C (Table 2).

Table 2. Copper-Catalysed Coupling of Aryl Iodides.[a]



[a] Reaction conditions: Aryl iodides (0.5 mmol), Carbazole (0.75 mmol), Cu_2O (10 mol%), $\mathbf{L_7}$ (10 mol%), KOH (1.0 mmol) in DMF (2 mL) under N_2, 110 °C, 24 h. Isolated yield.

The nature of the substituents bearing aryl iodides was initially evaluated under optimized reaction conditions. The electronic effect of *para*-substituents with the aromatic ring of aryl iodides was observed. The aryl iodides containing electron-neutral and electron-withdrawing groups such as 4-NO_2, 4-F, 4-Cl, and 4-Br, smoothly reacted with carbazole to afford the corresponding products in good to excellent yields (Table 2, **1a**-**e**). However, the aryl iodides containing electron-donating group such as 4-OMe, 4-Me, and 4-OEt, were less reactive in this system and resulted in moderate product yields (Table 2, **1f**-**h**).

The electronic effect of *meta*-substituted aryl iodides influenced the reaction rate. The reaction worked well with aryl iodides bearing the electron-withdrawing group on the *meta*-sites to afford the desired product in good yield (Table 2, **1i**-**k**). However the aryl iodides bearing the electron-donating group on the meta-sites, showed slightly slower conversion (Table 2, **1l**).

The coupling reaction of the aryl iodides bearing the sterically hindered group was also examined, and the results showed evident sterically hindered effect on the coupling reaction. The aryl iodides bearing electron-withdrawing group on the *ortho* sites yielded a low conversion (Table 2, **1m**-**o**), but the reaction with those bearing electron-donating group was difficult to trigger (Table 2, **1p**).

The scope and limitations of the coupling of carbazoles were also investigated under optimized reaction conditions (Table 3) The electronic effect of substituents bearing the aromatic ring of carbazoles was observed (Table 3, **2a**-**d**). Iodobenzene smoothly reacted with the carbazoles bearing electron-donating 3,6-di-*tert*-butyl groups to give good product yield (Table 3, **2a**). However, carbazoles bearing electron-withdrawing substituents such as 3-bromo, 3,6-dibromo and 2,7-dibromo groups, showed relatively lower reactivity in this catalytic system (Table 3, **2b**-**d**). Aryl iodides containing electron-withdrawing group such as 4-Br, 4-Cl, and 4-F, reacted with representative electron-poor, electron-neutral or electron-rich carbazoles to provide the corresponding cross-coupling products in moderate to good yields (Table 3, **2e**-**m**). Aryl iodides bearing electron-donating group showed high reactivity with carbazoles containing electron-donating group (Table 3, **2n** and **2o**), but exhibited lower reactivity with those containing electron-withdrawing group (Table 3, **2p**). In addition, the electronic effect of meta-substituents bearing the aromatic ring of aryl iodides was evaluated. The results indicated that the reaction worked well with aryl iodides bearing the electron-withdrawing group on meta-site and carbazoles to afford the desired product in good yield (Table 3, **2q** and **2r**). Steric hindrance effects of aryl iodides significantly influenced the outcome of the reaction, and the aryl iodides bearing the steric hindrance group were difficult to react (Table 3, **2s** and **2t**).

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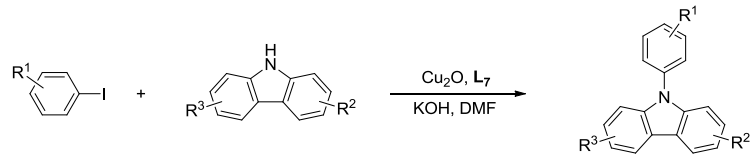
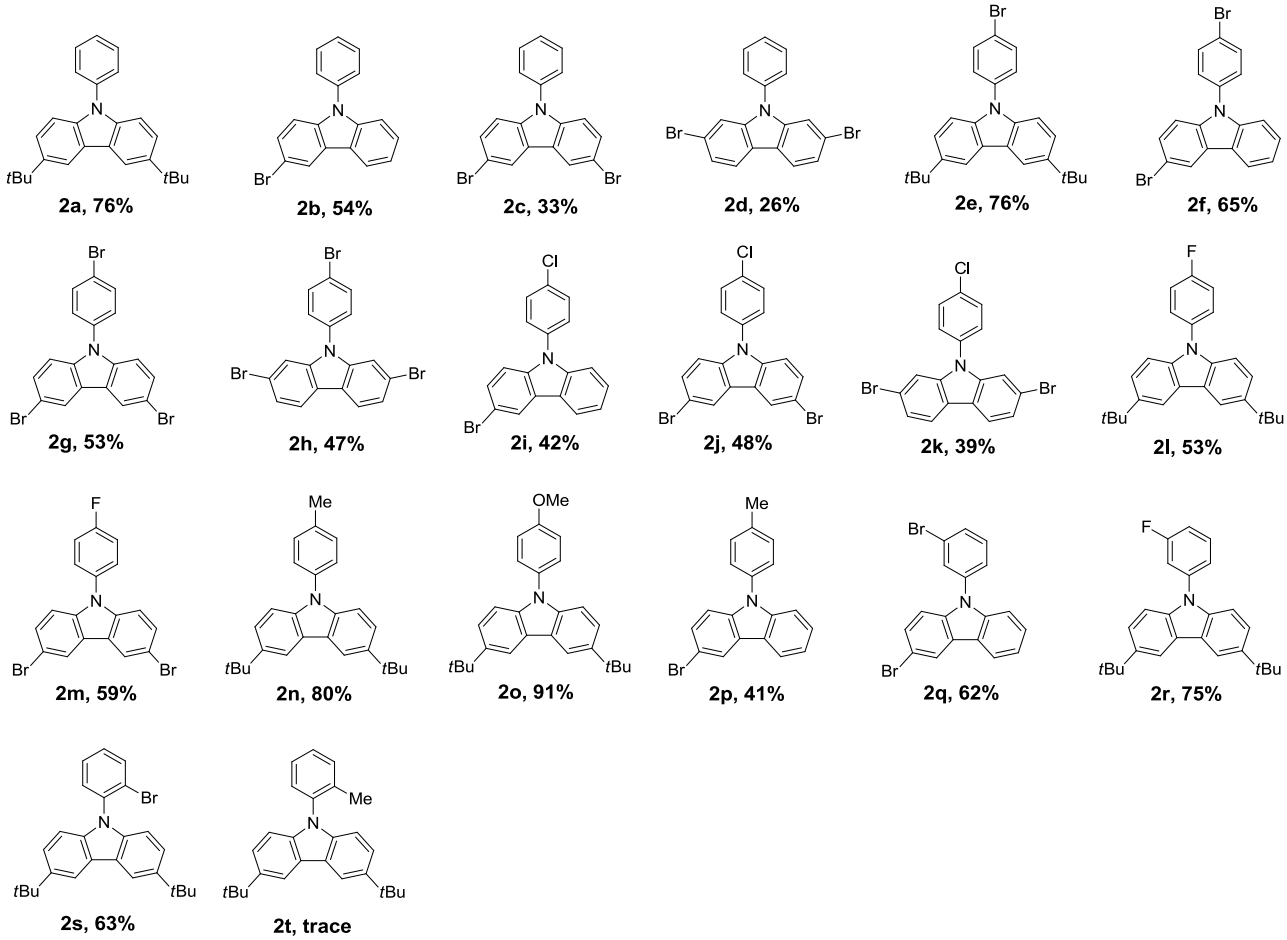
Table 3. Copper-Catalysed Coupling of Carbazoles.[a]





[a] Reaction conditions: Aryl iodides (0.5 mmol), Carbazoles (0.75 mmol), Cu_2O (10 mol%), **L_7** (10 mol%), KOH (1.0 mmol) in DMF (2 mL) under N_2, 130 °C, 24 h. Isolated yield.

Optimized reaction conditions were also applied in the coupling between diiodobenzene and carbazole, in which the selectivity of two iodine atoms on the aromatic ring was evaluated (Table 4). The electronic effect of substituents bearing the aromatic ring of carbazoles was initially explored. Carbazoles bearing electron-donating group showed higher reactivity than those bearing electron-withdrawing or -neutral group. For the carbazoles bearing electron-withdrawing or -neutral group, the selectivity for single coupling over double coupling was remarkably strong, and the product of single coupling was obtained in good yield (Table 4, entries 1-4). However, carbazoles bearing electron-donating group exhibited poor selectivity on either *para*-diiodobenzene or *meta*-diiodobenzene. NMR analysis showed varying amounts of disubstituted and deiodinated products (Table 4, entries 5 and 8). We inferred that high temperature was responsible for the poor results. Therefore, the lower temperature of 90 °C was used to test the selectivity of diiodobenzenes. As expected the coupling of *para*-diiodobenzene or *meta*-diiodobenzene with 3,6-di-*tert*-butyl carbazole proceeded smoothly and resulted in moderate product yield (Table 4, entries 6 and 9). At a higher temperature, the coupling between 3-bromocarbazole and *meta*-diiodobenzene was also prone to undergo double C–N coupling to give 78% yield of the disubstituted product (Table 4, entry 10). Single coupling resulted in 51% yield of product when the reaction temperature was reduced to 90 °C (Table 4, entry 10). These results indicated that the distribution of products was tuned by the reaction temperature.

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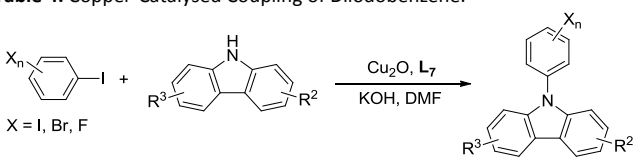
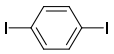
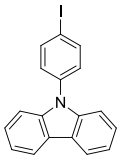
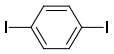
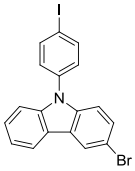
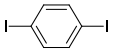
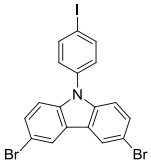
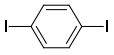
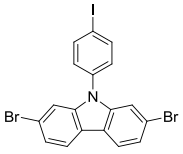
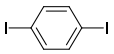
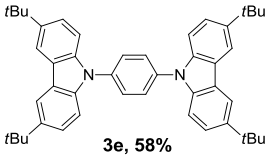
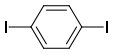
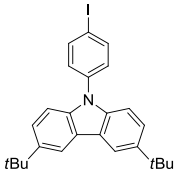
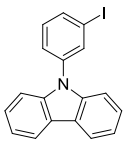
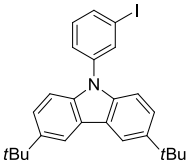
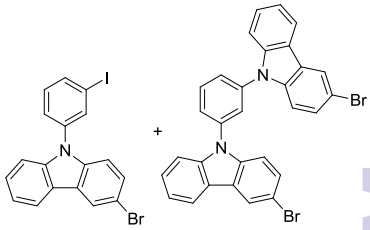
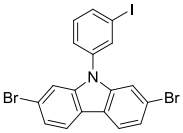
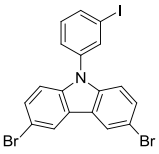
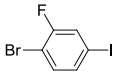
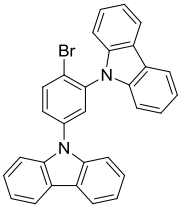
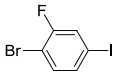
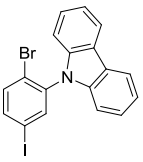
Table 4. Copper-Catalysed Coupling of Diiodobenzene.[a]



Entry	Aryl iodides	Products
1		 **3a, 72%**
2		 **3b, 47%**
3		 **3c, 54%**
4		 **3d, 55%**
5		 **3e, 58%** + **2a, 16%**
6		 **3f, 47%[b]**
7		 **3g, 33%**
8		**2a, 15%**
9		 **3h, 44%[b]**
10		 **3ia, trace (51%)[b]** **3ib, 78% (16%)[b]**
11		 **3j, 54%**
12		 **3k, 33%[c]**
13		 **3l, 53% (76%)[d]**
14		 **3m, 51%[e]**

[a] Reaction conditions: Aryl iodides (0.5 mmol), Carbazole (0.75 mmol), Cu_2O (10 mol%), **L**$_7$ (10 mol%), KOH (1.0 mmol) in DMF (2 mL) under N_2, 130 °C, 24 h. Isolated yield. [b] 90 °C. [c] 110 °C. [d] 3.0 equiv. Carbazole. [e] without Cu_2O.

Furthermore, the selective coupling of poly-halogenated benzene with carbazole was investigated in this copper/β-diketone catalytic system. The fluorine and iodine atoms on

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the benzene ring of 1-bromo-2-fluoro-4-iodobenzene showed similar reactivity and provided disubstituted product (Table 4, entry 13). Given that the formation of disubstituted product required 2.0 equiv. of carbazoles, a 3.0 equiv. of carbazoles was used to obtain higher product yield (Table 4, entry 13). To probe the main factors responsible for the selectivity of the fluoride group bearing benzene ring, control experiments were designed in the absence of Cu_2O (Table 4, entry 14). The control experiment revealed that the 1-bromo-2-fluoro-4-iodobenzene underwent highly selective coupling at the fluoride group with carbazole through nucleophilic substitution reaction in the copper-free condition. We supposed that the bromide group at the position *ortho* to the fluoride group activated C–F bond through the effect of electron-withdrawing, the effect was responsible for the selectivity of fluoride group.

Halogens, such as chlorine, bromine and iodine, on the aromatic ring are well tolerated in the developed copper/β-diketone catalytic system. This characteristic provides an opportunity to further functionalize the N-arylated carbazole compounds and convert them into useful pharmaceutical, dye-sensitized solar cells and advanced material intermediates. We selected the obtained 9-(4-iodophenyl)-carbazole as model substrate to explore its reactivity on a series of transition-metal-catalysed cross-coupling reaction. Figure 2 illustrates that 9-(4-iodophenyl)-carbazole was successfully converted into valuable intermediates via classical transition-metal-catalysed Suzuki coupling, Ullmann-type reaction, and Sonogashira coupling.

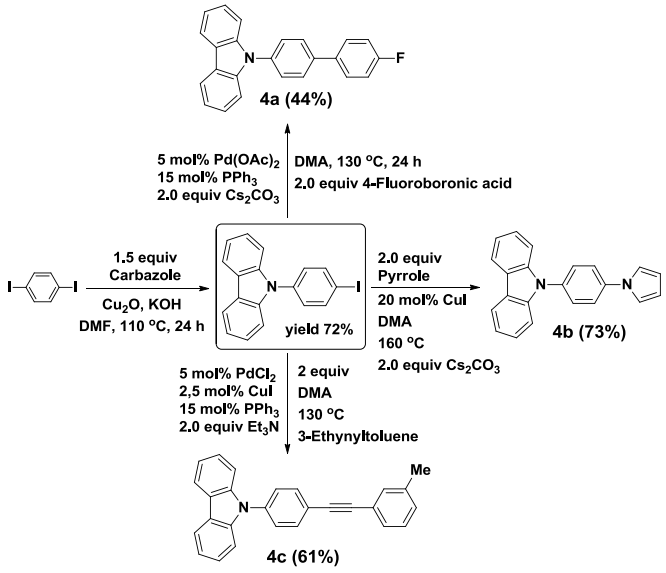

Figure 2. Functionalization of 9-(4-iodophenyl)-carbazole.

The mechanism for the copper-catalysed C–N bond-forming reaction has been well summarized by Ma.[12b] Three studies toward elucidation of the mechanism for the Ullmann-type coupling reactions have been reported: (1) oxidative addition/reductive elimination mechanism;[22] (2) π–complex mechanism;[23] (3) radical mechanism.[24] The first mechanism has well explained the phenomena observed in our reactic process. For example, the halogen displacement order of aryl halides is I > Br > Cl, and aryl halides bearing electron-withdrawing group showed relatively high reactivity tha those bearing electron-donating group. On the basis of oxidative addition/reductive elimination mechanism, a proposed mechanism for N-arylation of carbazole is depicted in Figure 3. The reaction proceeds via copper(I) complex **I**, which is in situ generated through coordination of copper(I) oxide with β-diketone. The subsequent oxidative addition of copper(I) complex **I** with PhI occurs to form copper(III) complex **II**. And then transmetalation between copper(III) complex **II** and carbazole takes place to afford a copper(III) complex **III**. At last, copper(III) complex **III** proceeds reductive elimination to provide the desired product **IV** while simultaneously releasing active copper(I) complex **I**.

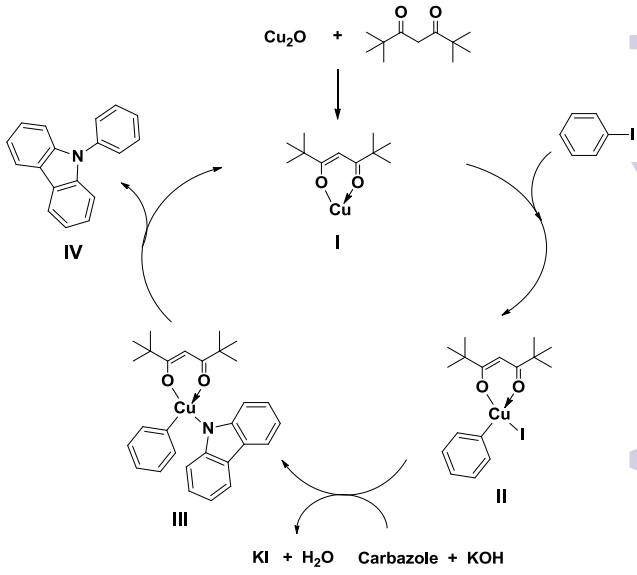

Figure 3. Proposed mechanism for N-arylation of carbazole.

Experimental

General Experimental Methods. All reactions were performed in Schlenk tubes under nitrogen atmosphere. DMF, DMSO, DMA, and NMP were distilled from 4Å-molecular sieves. All solvents and reagents were purchased from Alfa Aesar, Acros and Adamas-beta. NMR spectra were recorded on a Varian Inova-400 or a Bruke Avance III HD 400 spectrometer using TMS as internal standard (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR). The Mass data of the compounds were collected on a Bruker ultrafleXtreme mass spectrometer. All products were isolated by short chromatography on a silica gel (200–300 mesh) column.

General Procedure for N-Arylation of Carbazoles. A mixture of aryl iodides (0.5 mmol), carbazoles (0.75 mmol), copper sources (0.5 mmol), ligand (0.05 mmol) and base (1.0 mmol) in solvent (2 mL) was allowed to react under nitrogen atmosphere. The reaction

mixture was heated to the specified temperature for 24 h. After reaction, the reaction mixture was added to brine (15 mL) and extracted three times with dichloromethane (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

9-Phenyl-9*H*-carbazole (1a).[25] Purification by flash chromatography (petroleum ether): a white solid (108 mg, 89%), mp = 82-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.0 Hz, 2H), 7.66-7.59 (m, 4H), 7.52-7.48 (m, 1H), 7.46-7.42 (m, 4H), 7.36-7.29 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.94, 137.76, 129.90, 127.48, 127.19, 125.96, 123.39, 120.34, 119.94, 109.81, ppm.

9-(4-Nitrophenyl)-9*H*-carbazole (1b).[26] Purification by flash chromatography (petroleum ether): a yellow solid (117 mg, 81%), mp = 172-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.51-7.43 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.78, 142.82, 138.81, 125.70, 125.44, 124.49, 123.13, 120.17, 119.59, 108.57, ppm.

9-(4-Fluorophenyl)-9*H*-carbazole (1c).[25] Purification by flash chromatography (petroleum ether): a white solid (102 mg, 78%), mp = 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.13 (m, 2H), 7.54-7.49 (m, 2H), 7.43-7.39 (m, 2H), 7.33-7.24 (m, 6H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.60 (d, $J_{C\text{-}F}$ = 245.8 Hz), 141.07, 133.66 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.05 (d, $J_{C\text{-}F}$ = 8.5 Hz), 126.05, 123.32, 120.39, 120.04, 116.88 (d, $J_{C\text{-}F}$ = 22.6 Hz), 109.55, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.66, ppm.

9-(4-Chlorophenyl)-9*H*-carbazole (1d).[25] Purification by flash chromatography (petroleum ether): a white solid (104 mg, 75%), mp = 144-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.43-7.35 (m, 4H), 7.31-7.23 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.68, 136.25, 133.01, 130.10, 128.39, 126.05, 123.44, 120.37, 120.17, 109.53, ppm.

9-(4-Bromophenyl)-9*H*-carbazole (1e).[5c] Purification by flash chromatography (petroleum ether): a pale yellow solid (153 mg, 95%), mp = 143-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.42-7.34 (m, 6H), 7.29-7.26 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.57, 135.76, 132.07, 127.68, 125.04, 122.44, 119.85, 119.35, 119.17, 108.51, ppm.

9-(4-Methoxyphenyl)-9*H*-carbazole (1f).[25] Purification by flash chromatography (petroleum ether): a white solid (94 mg, 69%), mp = 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.6 Hz, 2H), 7.45-7.37 (m, 4H), 7.33-7.24 (m, 4H), 7.10 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.83, 141.35, 130.28, 128.55, 125.81, 123.08, 120.22, 119.61, 115.04, 109.67, 55.58, ppm.

9-(*p*-Tolyl)-9*H*-carbazole (1g).[25] Purification by flash chromatography (petroleum ether): a white solid (82 mg, 64%), mp = 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.6 Hz, 2H), 7.45-7.36 (m, 8H), 7.29-7.25 (m, 2H), 2.49 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.10, 137.39, 135.04, 130.49, 127.03, 125.88, 123.27, 120.29, 119.75, 109.82, 21.28, ppm.

9-(4-Ethoxyphenyl)-9*H*-carbazole (1h). Purification by flash chromatography (petroleum ether): a white solid (83 mg, 61%), mp = 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.6 Hz, 2H), 7.44-7.38 (m, 4H), 7.33-7.25 (m, 4H), 7.09 (d, J = 8.4 Hz, 2H), 4.13 (q, J = 6.8 Hz, 2H), 1.49 (t, J = 6.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.24, 141.37, 130.10, 128.53, 125.80, 123.07, 120.21, 119.58, 115.55, 109.69, 63.82, 14.88, ppm.

9-(3-Fluorophenyl)-9*H*-carbazole (1i). Purification by flash chromatography (petroleum ether): a white solid (115 mg, 88%), mp = 78-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (dt, J = 7.6 Hz, J = 0.8 Hz, 2H), 7.63-7.58 (m, 1H), 7.50-7.41 (m, 5H), 7.38-7.32 (m, 3H), 7.21 (ddd, J = 8.4 Hz, J = 2.8 Hz, J = 1.2 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.47 (d, $J_{C\text{-}F}$ = 246.6 Hz), 140.56, 139.34 (d, $J_{C\text{-}F}$ = 9.8 Hz), 131.08 (d, $J_{C\text{-}F}$ = 9.2 Hz), 126.16, 123.59, 122.73 (d, $J_{C\text{-}F}$ = 3 Hz), 120.44, 120.36, 114.52 (d, $J_{C\text{-}F}$ = 7.1 Hz), 114.30 (d, $J_{C\text{-}F}$ = 8.8 Hz), 109.73, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.46, ppm; HRMS (MALDI): m/z calcd for $C_{18}H_{12}FN$ $[M]^+$ 261.0948, found 261.0947.

9-(3-Bromophenyl)-9*H*-carbazole (1j).[27] Purification by flash chromatography (petroleum ether): a colorless oil (135 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 7.6 Hz, 2H), 7.70 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.41-7.37 (m, 5H), 7.28-7.25 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.59, 139.17, 131.16, 130.54, 130.17, 126.19, 125.75, 123.60, 123.28, 120.46, 120.41, 109.67, ppm.

9-(3-Chlorophenyl)-9*H*-carbazole (1k).[25] Purification by flash chromatography (petroleum ether): a pale yellow oil (106 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 1 Hz, 1H), 7.47-7.36 (m, 7H), 7.29-7.22 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.43, 138.88, 135.29, 130.75, 127.46, 127.12, 126.04, 125.10, 123.45, 120.31, 120.25, 109.54, ppm.

9-(*m*-Tolyl)-9*H*-carbazole (1l). Purification by flash chromatography (petroleum ether): a yellow oil (85 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dt, J = 7.6 Hz, J = 0.8 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.51-7.43 (m, 6H), 7.39-7.33 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.01, 139.94, 137.67, 129.68, 128.29, 127.73, 125.91, 124.21, 123.36, 120.32, 119.85, 109.90, 21.51, ppm; HRMS (MALDI): m/z calcd for $C_{19}H_{15}N$ $[M]^+$ 257.1199, found 257.1201.

9-(2-Fluorophenyl)-9*H*-carbazole (1m). Purification by flash chromatography (petroleum ether): a yellow oil (46 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (dt, J = 8.0 Hz, J = 0.8 Hz, 2H), 7.60 (td, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.55-7.50 (m, 1H), 747-7.37 (m, 4H), 7.35-7.31 (m, 2H), 7.27 (dt, J = 8.0 Hz, J = 0.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.36 (d, $J_{C\text{-}F}$ = 251.4 Hz), 140.85, 129.88 (d, $J_{C\text{-}F}$ = 1.2 Hz), 129.61 (d, $J_{C\text{-}F}$ = 7.6 Hz), 126.05, 125.10 (d, $J_{C\text{-}F}$ = 3.9 Hz), 123.55, 120.33, 120.18, 117.39 (d, $J_{C\text{-}F}$ = 19.6 Hz), 109.89 (d, $J_{C\text{-}F}$ = 1.5 Hz), ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -118.46, ppm; HRMS (MALDI): m/z calcd for $C_{18}H_{12}FN$ $[M]^+$ 261.0948, found 261.0947.

9-(2-Chlorophenyl)-9*H*-carbazole (1n).[28] Purification by flash chromatography (petroleum ether): a pale yellow solid (38 mg, 27%), mp = 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 7.6 Hz, 2H), 7.66-7.64 (m, 1H), 7.49-7.42 (m, 3H), 7.38 (t, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.80, 133.98, 132.67, 129.96, 129.79, 128.71, 127.01, 124.87, 122.24, 119.26, 118.94, 108.90, ppm.

9-(2-Bromophenyl)-9*H*-carbazole (1o).[29] Purification by flash chromatography (petroleum ether): a white solid (66 mg, 41%), mp = 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.0 Hz, 2H), 7.84 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.52-7.43 (m, 2H), 7.39 (t, J = 8.0 Hz, 3H), 7.28 (t, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.79, 136.69, 134.18, 131.09, 130.10, 128.77, 125.89, 123.79, 123.20, 120.31, 119.94, 109.98, ppm.

3,6-Di-*tert*-butyl-9-phenyl-9*H*-carbazole (2a).[30] Purification by flash chromatography (petroleum ether): a white solid (135 mg, 76%), mp = 155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 1.6 Hz, 2H), 7.66-7.61 (m, 4H), 7.54-7.46 (m, 3H), 7.42 (d, J = 8.8 Hz, 2H), 1.54 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.84, 139.33, 138.26, 129.79, 127.01, 126.83, 123.63, 123.39, 116.26, 109.25, ppm.

3-Bromo-9-phenyl-9*H*-carbazole (2b).[31] Purification by flash chromatography (petroleum ether): a white solid (87 mg, 54%), mp = 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 1.2 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 8.0 Hz, 2H), 7.57-7.51 (m, 4H), 7.48-7.42 (m, 2H), 7.36-7.30 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.25, 139.58, 137.28, 130.03, 128.63, 127.80, 127.07, 126.72, 125.14, 123.09, 122.32, 120.53, 120.37, 112.73, 111.30, 110.05, ppm.

3,6-Dibromo-9-phenyl-9*H*-carbazole (2c).[32] Purification by flash chromatography (petroleum ether): a white solid (66 mg, 33%), mp = 164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 2H), 7.64 (t, J = 7.2 Hz, 2H), 7.53-7.51 (m, 5H), 7.27 (d, J = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.87, 136.79, 130.12, 129.38, 128.11, 126.96, 123.93, 123.21, 113.05, 111.51, ppm.

2,7-Dibromo-9-phenyl-9*H*-carbazole (2d).[31] Purification by flash chromatography (petroleum ether): a white solid (52 mg, 26%), mp = 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.4 Hz, 2H), 7.69-7.64 (m, 2H), 7.57-7.51 (m, 5H), 7.42 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.90, 136.44, 130.28, 128.39, 127.12, 123.62, 121.68, 121.47, 120.00, 113.04, ppm.

9-(4-Bromophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (2e).[33] Purification by flash chromatography (petroleum ether): a white solid (165 mg, 76%), mp = 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 2.0 Hz, 2H), 7.71 (dt, J = 8.8 Hz, J = 2.8 Hz, 2H), 7.48-7.42 (m, 4H), 7.32 (dt, J = 8.4 Hz, J = 0.4 Hz, 2H), 1.47 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.15, 138.93, 137.27, 132.95, 128.28, 123.71, 123.46, 120.24, 116.30, 108.96, 34.73, 31.98, ppm.

3-Bromo-9-(4-bromophenyl)-9*H*-carbazole (2f).[29] Purification by flash chromatography (petroleum ether): a white solid (130 mg, 65%), mp = 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.50-7.40 (m, 4H), 7.36-7.29 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.95, 139.30, 136.32, 133.25, 128.76, 128.64, 126.83, 125.23, 123.15, 122.40, 121.31, 120.62, 120.57, 112.98, 111.03, 109.78, ppm.

3,6-Dibromo-9-(4-bromophenyl)-9*H*-carbazole (2g).[8a] Purification by flash chromatography (petroleum ether): a white solid (127 mg, 53%), mp = 217-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.62, 135.85, 133.39, 129.56, 128.56, 124.06, 123.33, 121.72, 113.37, 111.28, ppm.

2,7-Dibromo-9-(4-bromophenyl)-9*H*-carbazole (2h).[34] Purification by flash chromatography (petroleum ether): a white solid (113 mg, 47%), mp = 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.[illegible] Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.46-7.38 (m, 6H), ppm; ^{13}C NM[illegible] (100 MHz, $CDCl_3$): δ 141.63, 135.48, 133.55, 128.72, 123.92, 122.07, 121.80, 121.55, 120.13, 112.87, ppm.

3-Bromo-9-(4-chlorophenyl)-9*H*-carbazole (2i). Purification by flash chromatography (petroleum ether): a white solid (75 mg, 42%), mp = 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.05 (d, J 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.47-7.40 (m, 4H), 7.33-7.27 (m, 2H), 7.19 (d, J = 8.0 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.95, 138.29, 134.71, 132.34, 129.18, 127.68, 127.24, 125.75, 124.13, 122.07, 121.30, 119.53, 119.51, 111.90, 109.95, 108.71, ppm; HRMS (MALDI): *m/z* calcd for $C_{18}H_{11}BrClN$ $[M]^+$ 354.9758, found 354.9751.

3,6-Dibromo-9-(4-chlorophenyl)-9*H*-carbazole (2j).[35] Purification by flash chromatography (petroleum ether): a white solid (105 m[illegible] 48%), mp = 214-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.71, 135.32, 133.85, 130.40, 129.54, 128.26, 124.03, 123.32, 113.34, 111.28, ppm.

2,7-Dibromo-9-(4-chlorophenyl)-9*H*-carbazole (2k). Purification by flash chromatography (petroleum ether): a white solid (85 mg, 39%) mp = 166-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.46-7.40 (m, 6H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.71, 134.94, 134.18, 130.56, 128.43, 123.89, 121.77, 121.55, 120.11, 112.87, ppm; HRMS (MALDI): *m/z* calcd for $C_{18}H_{10}Br_2ClN$ $[M]^+$ 432.8863, found 432.8859.

3,6-Di-*tert*-butyl-9-(4-fluorophenyl)-9*H*-carbazole (2l). Purification by flash chromatography (petroleum ether): a pale yellow solid (99 mg, 53%), mp = 192-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 1.6 Hz, J = 0.4 Hz, 2H), 7.53-7.49 (m, 2H), 7.47 (dd, J = 8.4 Hz, J = 2.0 Hz, 2H), 7.30-7.25 (m, 4H), 1.47 (s, 18H), ppm; ^{13}C NMR (10[illegible] MHz, $CDCl_3$): δ 161.29 (d, $J_{C\text{-}F}$ = 245.5 Hz), 142.86, 139.36, 134.05 ([illegible] $J_{C\text{-}F}$ = 2.9 Hz), 128.56 (d, $J_{C\text{-}F}$ = 8.4 Hz), 123.60, 123.20, 116.65 (d, $J_{C\text{-}F}$ = 22.6 Hz), 116.22, 108.86, 34.69, 31.96, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -36.65 – -36.72 (m), ppm; HRMS (MALDI): *m/z* calcd for $C_{26}H_{28}FN$ $[M]^+$ 373.2200, found 373.2199.

3,6-Dibromo-9-(4-fluorophenyl)-9*H*-carbazole (2m). Purification by flash chromatography (petroleum ether): a white solid (124 mg, 59%), mp = 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 2.0 Hz, J = 0.4 Hz, 2H), 7.51 (dd, J = 8.8 Hz, J = 2.0 Hz, 2H), 7.48-7.45 (m, 2H), 7.33-7.29 (m, 2H), 7.17 (dd, J = 8.4 Hz, J = 0.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.95 (d, $J_{C\text{-}F}$ = 247.4 Hz), 140.01, 132.67 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.46, 128.91 (d, $J_{C\text{-}F}$ = 8.7 Hz), 123.86, 123.25, 117.14 (d, $J_{C\text{-}F}$ = 22.8 Hz), 113.16, 111.24, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -34.72 – -34.79 (m), ppm; HRMS (MALDI): *m/z* calcd for $C_{18}H_{10}Br_2FN$ $[M]^+$ 416.9159, found 416.9159.

3,6-Di-*tert*-butyl-9-(*p*-tolyl)-9*H*-carbazole (2n).[36] Purification by flash chromatography (petroleum ether): a yellow oil (148 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 1.2 Hz, 2H), 7.53-7.47 (m, 4H), 7.43 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 2.53 (s, 3H), 1.54 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.64, 139.51, 136.86, 135.55, 130.40, 126.71, 123.56, 123.27, 116.23, 109.26, 34.79, 32.12, 21.28, ppm.

3,6-Di-*tert*-butyl-9-(4-methoxyphenyl)-9*H*-carbazole (2o).[37] Purification by flash chromatography (petroleum ether): a white solid (176 mg, 91%), mp = 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 2.0 Hz, J = 0.8 Hz, 2H), 7.49-7.45 (m, 4H), 7.29 (d, J = 8.8 Hz, 2H), 7.14-7.10 (m, 2H), 3.94 (s, 3H), 1.50 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.54, 142.49, 139.77, 130.83, 128.27, 123.49, 123.04, 116.17, 114.95, 109.07, 55.59, 34.73, 32.06, ppm.

3-Bromo-9-(*p*-tolyl)-9*H*-carbazole (2p).[38] Purification by flash chromatography (petroleum ether): a white solid (69 mg, 41%), mp = 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 1.6 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.51-7.38 (m, 7H), 7.33-7.25 (m, 2H), 2.52 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.40, 139.74, 137.76, 134.54, 130.59, 128.52, 126.91, 126.59, 124.98, 122.99, 122.17, 120.44, 120.15, 21.17, ppm.

3-Bromo-9-(3-bromophenyl)-9*H*-carbazole (2q).[29] Purification by flash chromatography (petroleum ether/EtOAc = 40:1): a white solid (124 mg, 62%), mp = 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.63-7.59 (m, 1H), 7.50-7.25 (m, 7H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.87, 139.22, 138.61, 131.22, 130.86, 130.07, 128.78, 126.85, 125.64, 125.25, 123.32, 123.13, 122.41, 120.71, 120.55, 113.08, 111.09, 109.82, ppm.

3,6-Di-*tert*-butyl-9-(3-fluorophenyl)-9*H*-carbazole (2r). Purification by flash chromatography (petroleum ether): a white solid (140 mg, 75%), mp = 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 2.0 Hz, 2H), 7.59-7.53 (m, 1H), 7.50 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 7.42-7.38 (m, 3H), 7.33 (dt, J = 7.6 Hz, J = 0.8 Hz, 2H), 7.42-7.38 (m, 3H), 7.18-7.13 (m, 1H), 1.50 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.36 (d, $J_{C\text{-}F}$ = 246.5 Hz), 143.22, 139.75 (d, $J_{C\text{-}F}$ = 9.9 Hz), 138.81, 130.84 (d, $J_{C\text{-}F}$ = 9.3 Hz), 123.72, 123.50, 122.18 (d, $J_{C\text{-}F}$ = 3.2 Hz), 116.27, 113.91, 113.69 (d, $J_{C\text{-}F}$ = 2.3 Hz), 109.10, 34.71, 31.96, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -33.09 – -33.15 (m), ppm; HRMS (MALDI): *m/z* calcd for $C_{26}H_{28}FN$ $[M]^+$ 373.2200, found 373.2198.

9-(2-Bromophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (2s).[39] Purification by flash chromatography (petroleum ether): a white solid (137 mg, 63%), mp = 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 2.0 Hz, 2H), 7.89 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.55-7.38 (m, 5H), 7.03 (d, J = 8.4 Hz, 2H), 1.51 (s, 18H), ppm.

9-(4-Iodophenyl)-9*H*-carbazole (3a).[40] Purification by flash chromatography (petroleum ether): a white solid (98 mg, 53%), mp = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dt, J = 8.0 Hz, J = 1.2 Hz, 2H), 7.95-7.91 (m, 2H), 7.44-7.37 (m, 4H), 7.35-7.28 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.50, 139.07, 137.50, 128.92, 126.06, 123.50, 120.37, 120.21, 109.55, 92.02, ppm.

3-Bromo-9-(4-iodophenyl)-9*H*-carbazole (3b). Purification by flash chromatography (petroleum ether): a white solid (105 mg, 47%), mp = 171-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.49-7.41 (m, 2H), 7.36-7.28 (m, 5H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.84, 139.20, 137.04, 128.81, 128.74, 126.81, 125.24, 123.13, 122.41, 120.62, 120.56, 112.99, 111.03, 109.78, 92.47, ppm; HRMS (MALDI): *m/z* calcd for $C_{18}H_{11}BrIN$ $[M]^+$ 446.9114, found 446.9112.

3,6-Dibromo-9-(4-iodophenyl)-9*H*-carbazole (3c).[40] Purification by flash chromatography (petroleum ether): a white solid 142 mg, 54%), mp = 188-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.53, 139.36, 136.56, 129.55, 128.74, 124.09, 123.32, 113.38, 111.29, 92.93, ppm.

2,7-Dibromo-9-(4-iodophenyl)-9*H*-carbazole (3d).[41] Purification by flash chromatography (petroleum ether): a white solid (145 mg, 55%), mp = 207-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 4H), 7.46 (s, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.54, 139.52, 136.19, 128.89, 123.93, 121.83, 121.55, 120.13, 112.88, 93.32, ppm.

1,4-Bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzene (3e).[42] Purification by flash chromatography (petroleum ether): a white solid (184 mg, 58%), mp = 297-298 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 4H), 7.81 (s, 4H), 7.58-7.51 (m, 8H), 1.53 (s, 36H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.16, 139.18, 136.73, 127.84, 123.77, 123.54, 116.36, 109.24, 34.80, 32.06, ppm;

3,6-di-*tert*-butyl-9-(4-iodophenyl)-9*H*-carbazole (3f).[5d] Purification by flash chromatography (petroleum ether): a white solid (113 mg, 47%), mp = 177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 2.0 Hz, J = 0.4 Hz, 2H), 7.94-7.90 (m, 2H), 7.48 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.36-7.33 (m, 4H), 1.49 (s, 18h), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.20, 138,94, 138.85, 138.01, 128.53, 123.73, 123.52, 116.33, 109.01, 99.99, 91.34, 34.76, 32.00, ppm.

9-(3-Iodophenyl)-9*H*-carbazole (3g).[43] Purification by flash chromatography (petroleum ether): a white solid (61 mg, 33%), mp = 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.6 Hz, 2H), 7.93 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 4H), 7.30 (q, J = 8.0 Hz, 3H), ppm; ^{13}C NMR (100 MHz,

$CDCl_3$): δ 140.57, 138.98, 136.46, 136.00, 131.25, 126.44, 126.11, 123.51, 120.38, 120.31, 109.61, 94.58, ppm.

3,6-di-tert-butyl-9-(3-iodophenyl)-9H-carbazole (3h). Purification by flash chromatography (petroleum ether): a white solid (106 mg, 44%), mp = 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 2.0 Hz, 2H), 7.98 (t, J = 2.0 Hz, 1H), 7.81-7.79 (m, 1H), 7.61-7.58 (m, 1H), 7.52 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.40-7.32 (m, 3H), 1.52 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.30, 139.50, 138.93, 135.94, 135.60, 131.18, 126.00, 123.80, 123.56, 116.35, 109.09, 99.99, 94.56, 34.79, 32.04, ppm.

3-Bromo-9-(3-iodophenyl)-9*H*-carbazole (3ia).[43] Purification by flash chromatography (petroleum ether): a colorless oil (114 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 2.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.86-7.83 (m, 1H), 7.54-7.45 (m, 3H), 7.41-7.26 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.90, 139.24, 138.50, 136.81, 135.90, 131.40, 128.82, 126.91, 126.35, 125.27, 123.18, 122.43, 120.76, 120.61, 113.13, 111.13, 109.88, 94.76, ppm.

1,3-Bis(3-bromo-9*H*-carbazol-9-yl)benzene (3ib).[44] Purification by flash chromatography (petroleum ether): a white solid (221 mg, 78%), mp = 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 2.0 Hz, 2H), 8.12 (d, J = 7.6 Hz, 2H), 7.89 (t, J = 8.0 Hz, 1H), 7.77 (t, J = 2.0 Hz, 1H), 7.71 (dd, J = 8.0 Hz, J = 2.0 Hz, 2H), 7.56-7.47 (m, 6H), 7.41 (d, J = 8.8 Hz, 2H), 7.37-7.33 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.90, 139.24, 139.05, 131.49, 128.86, 126.95, 126.07, 125.39, 125.17, 123.26, 122.55, 120.82, 120.69, 113.18, 111.10, 109.84, ppm.

2,7-Dibromo-9-(3-iodophenyl)-9*H*-carbazole (3j). Purification by flash chromatography (petroleum ether): a white solid (142 mg, 54%), mp = 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.94 (s, 1H), 7.91-7.87 (m, 2H), 7.52-7.37 (m, 6H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.68, 137.64, 137.60, 136.08, 131.64, 126.65, 124.00, 121.77, 121.55, 120.16, 112.90, 94.95, ppm; Anal. Calcd. for $C_{18}H_{10}Br_2IN$: C, 41.02; H, 1.91; N, 2.66. Found: C, 41.22; H, 1.99; N, 2.69.

3,6-Dibromo-9-(3-iodophenyl)-9*H*-carbazole (3k). Purification by flash chromatography (petroleum ether): a white solid (87 mg, 33%), mp = 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 2.0 Hz, 2H), 7.89-7.85 (m, 2H), 7.56-7.50 (m, 3H), 7.37 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.59, 138.03, 137.17, 135.85, 131.49, 129.60, 126.29, 124.07, 123.32, 113.47, 111.36, 94.78, pmm; Anal. Calcd. for $C_{18}H_{10}Br_2IN$: C, 41.02; H, 1.91; N, 2.66. Found: C, 41.97; H, 2.28; N, 2.61.

9,9'-(4-Bromo-1,3-phenylene)bis(9*H*-carbazole) (3l). Purification by flash chromatography (petroleum ether): a white solid (185 mg, 76%), mp = 226 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.12 (m, 5H), 7.79 (d, J = 2.4 Hz, 1H), 7.73 (dd, J = 8.4 Hz, J = 2.3 Hz, 1H), 7.55-7.45 (m, 6H), 7.35 (q, J = 8.0 Hz, 4H), 7.27 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.66, 140.23, 138.51, 138.38, 135.50, 129.17, 128.32, 126.33, 126.19, 123.76, 123.50, 121.89, 120.69, 120.56, 120.54, 120.37, 110.00, 109.48, ppm; HRMS (MALDI): m/z calcd for $C_{30}H_{19}BrN_2$ $[M]^+$ 486.0726, found 486.0726.

9-(2-Bromo-5-iodophenyl)-9*H*-carbazole (3m). Purification by flash chromatography (petroleum ether): a white solid (114 mg, 51%), mp = 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 2.0 Hz, 1H), 7.75 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.48-7.44 (m, 2H), 7.37-7.33 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.59, 139.90, 139.14, 138.23, 135.54, 126.13, 123.95, 123.42, 120.47, 120.38, 110.00, 92.40, ppm; HRMS (MALDI): m/z calcd for $C_{18}H_{11}BrIN$ $[M]^+$ 446.9120, found 446.9119.

9-(4'-fluoro-[1,1'-biphenyl]-4-yl)-9*H*-carbazole (4a). Purification by flash chromatography (petroleum ether): a white solid (74 mg, 44%), mp = 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.70-7.66 (m, 4H), 7.51-7.44 (m, 4H), 7.34 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.69 (d, $J_{C\text{-}F}$ = 245.4 Hz), 140.85, 139.32, 136.91, 136.42 (d, $J_{C\text{-}F}$ = 3.2 Hz), 128.74 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.40, 127.41, 126.01, 123.47, 120.37, 120.04, 115.89 (d, $J_{C\text{-}F}$ = 21.3 Hz), 109.81, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.04, ppm; HRMS (MALDI): m/z calcd for $C_{24}H_{16}FN$ $[M]^+$ 337.1261, found 337.1263.

9-(4-(1*H*-pyrrol-1-yl)phenyl)-9*H*-carbazole (4b). Purification by flash chromatography (petroleum ether): a white solid (113 mg, 73%), mp = 208-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.0 Hz, 2H), 7.65 (s, 4H), 7.50-7.44 (m, 4H), 7.37-7.33 (m, 2H), 7.23-7.22 (s, 2H), 6.47-6.46 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.93, 139.76, 135.05, 128.35, 126.09, 123.45, 121.66, 120.44, 120.13, 119.40, 111.00, 109.70, ppm; HRMS (MALDI): m/z calcd for $C_{22}H_{16}N_2$ $[M]^+$ 308.1308, found 308.1306.

9-(4-(*m*-tolylethynyl)phenyl)-9*H*-carbazole (4c). Purification by flash chromatography (petroleum ether): a white solid (109 mg, 61%), mp = 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.0 Hz, 2H), 7.81-7.77 (m, 2H), 7.62-7.59 (m, 2H), 7.50-7.42 (m, 6H), 7.36-7.29 (m, 3H), 7.22 (d, J = 7.6 Hz, 1H), 2.42 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.61, 138.18, 137.53, 133.14, 132.31, 129.48, 128.84, 128.40, 126.88, 126.12, 123.61, 122.90, 122.43, 120.43, 120.27, 109.81, 90.61, 88.42, 21.34, ppm; HRMS (MALDI): m/z calcd for $C_{27}H_{19}N$ $[M]^+$ 357.1512, found 357.1513.

Conclusions

We have developed a copper/β-diketone-catalysed method for C–N bond-forming reaction of carbazoles with aryl iodides. Aryl iodides bearing electron-withdrawing group showed slightly higher reactivity than those bearing electron-donating group in this catalytic system. Aryl iodides bearing sterically hindered group were difficult to react with carbazoles. Reaction temperature significantly affected the site-selectivity of diiodobenzene. At high reaction temperature, carbazoles bearing electron-withdrawing group were prone to undergo single coupling with diiodobenzene with high selectivity. However, carbazoles bearing electron-donating group underwent double coupling and formed disubstituted or

deiodinated product, but the trend was inhibited by reduced reaction temperature. The resulting iodinated N-arylated carbazoles have been proven to be useful intermediates in organic synthesis.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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