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N-Arylation of carbazole by microwave-assisted ligand-free catalytic CuI reaction

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ABSTRACT

N-Arylation of carbazole has been achieved in high yields within 1 h using a microwave-assisted catalytic CuI reaction with no organic ligand. The N-arylation can be performed by various arylhalides, such as phenyl, pyridine, thiophene, and thiazole moieties. Specifically, *N*-arylated bromocarbazoles were converted into useful synthetic intermediates for functionalized carbazole materials.

1. Introduction

High-speed synthesis using microwave technology has attracted considerable attention in organic chemistry because it can accelerate slow thermal reactions.[1] Microwave irradiation provides advantages over conventional heating in chemical transformations, such as accelerated reaction rates, significant energy savings, high chemical yields, and cleaner reactions.[2] Recently, microwave-assisted copper (Cu)-catalyzed C–N-arylation has been shown to efficiently synthesize indoles,[3] imidazoles,[4] amines,[5] and benzothiadiazines.[6]

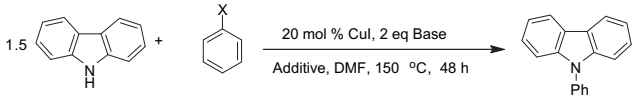
Natural carbazole moieties have interesting biological activities, such as protein kinase inhibition and antibacterial, anti-inflammatory, and antitumor properies.[7,8] Other synthetic carbazole derivatives have been used widely as functional building blocks for optoelectronic applications.[9] In the field of organic light-emitting devices (OLEDs), organometallic complexes of carbazoles have been reported as potential luminescent materials,[10] especially carbazole molecules containing a 2,7-linkage with heterocycles or diarylamine.[11] Polymeric carbazole derivatives have attracted interest as solid-state dye-sensitized solar cells.[12]

N-Arylated carbazoles are important moieties for material science. The typical preparation of *N*-arylated carbazoles has been the traditional Ullmann-type C–N coupling reaction, which requires stoichiometric amounts of copper, harsh conditions, long reaction times, and strong bases.[10d,11b,13] Although several papers have reported N-arylation of carbazoles synthesized by catalytic Cu-mediated reactions, these results show only one or several examples with long reaction times.[13,14]

As part of our continuing organometallic research regarding heterocycles, such as indoles,[15] azaindoles,[16] and quinolines,[17] we examined microwave-assisted catalytic Cu-mediated N-arylation of carbazoles with our previously reported N-arylation conditions.[16f]

2. Results and discussion

Initially, we examined the thermal catalytic N-arylation of carbazole using arylhalides (X=I, Br, Cl) under optimized reaction conditions for imidazoles,[18] alkylamine,[19] and azaindoles[16f] with a ligand-free catalytic CuI reaction. The results are presented in Scheme 1.



X = I			X = Br		
LiCl	Base	Isolated yield	LiCl	Base	Isolated yield
1 eq	K_3PO_4	87	1 eq	K_3PO_4	21
-	"	85	-	"	19
1 eq	Cs_2CO_3	90	1 eq	Cs_2CO_3	25
-	"	85	-	"	19

Scheme 1. N-Arylation of carbazole by thermal reaction conditions.

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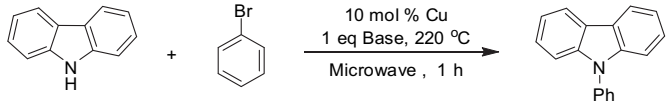
The reaction using iodobenzene provided high yields of *N*-phenylcarbazole, but the reaction with bromobenzene provided low yields of the desired product with large amounts of starting materials left. However, chlorobenzene did not react with carbazole under the reaction conditions used. The results showed that the arylhalide and heterocyclic substrates were very sensitive to the N-arylation reaction conditions. Many microwave-assisted reactions have shown advantages over conventional heating for slow organic reactions.[2] Specifically, in a previous report on microwave-assisted Cu-free N-arylation of indole with nitrobenzene containing halides (X=I, Br, Cl, and F), the reaction was efficient with F, but inefficient for I, Br, and Cl.[20] We applied the microwave-assisted Cu-free N-arylation of carbazole with variation of the arylhalide at 220 °C for 1 h, but the reaction using arylhalide (X=I, Br, Cl) afforded no *N*-arylated product. Hence, we investigated microwave-assisted Cu-mediated N-arylation of carbazole with bromobenzene to optimize the N-arylation of carbazole in a short reaction time. The results are summarized in Table 1.

Table 1
Optimization of conditions for Cu-catalyzed N-arylation of carbazoles

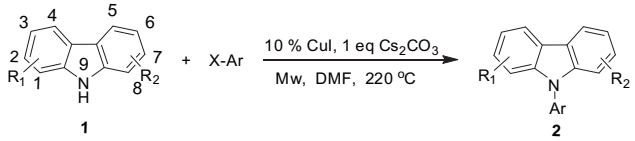


Entry[a,b]	Cu Source	Additive	Base	Solvent	Yield (%)
1	CuI	LiCl	K_2CO_3	DMF	57
2	CuI	—	K_2CO_3	DMF	62
3	CuI	LiCl	Cs_2CO_3	DMF	75
4	CuI	—	Cs_2CO_3	DMF	85
5	CuI	LiCl	K_3PO_4	DMF	52
6	CuI	—	K_3PO_4	DMF	61
7	CuI	—	DBU	DMF	48
8	CuI	—	Cs_2CO_3	DMA	65
9	CuI	—	Cs_2CO_3	NMP	58
10	CuBr	—	Cs_2CO_3	DMF	70
11	CuCl	—	Cs_2CO_3	DMF	70
12	$Cu(OAc)_2$	—	Cs_2CO_3	DMF	72

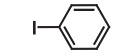
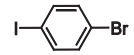
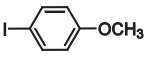
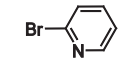
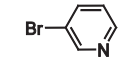
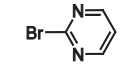
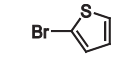
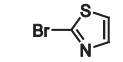
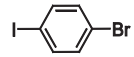
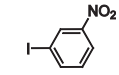
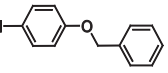
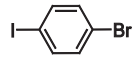
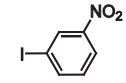
[a] All reactions were conducted on a 1.0-mmol scale under 2 mL of solvent in a Biotage 5-mL vial sealed crimp cap using an initiator instrument (EXP EU, Biotage, 400 W, 2450 MHz).
[b] Vapor pressure of the reaction mixture in the vial was monitored as 5–7 bar at 220 °C.

Reactions carried out at 210 °C usually required twice the time to reach completion, compared with reactions at 220 °C. Yields were higher when no chloride source was used than when LiCl was added (Table 1, entries 1–6). We also examined the effects of several Cu species that are used frequently for Cu-coupling reactions. N-Arylation of carbazoles using CuI produced higher yields of the desired product compared to the reactions using other copper sources (Table 1, entries 4 and 10–12). The yields were slightly lower with the use of alternative Cu species, such as CuBr, CuCl, and $Cu(OAc)_2$. Reactions using Cs_2CO_3 as a base also produced good yields of the desired product. However, reactions using K_2CO_3, K_3PO_4, and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as bases only produced moderate yields of the desired product (Table 1, entries 1–7). We also investigated the effect of different solvents under the same temperature conditions (Table 1, entries 4 and 8–9). The reaction using DMF as the solvent produced good yields of the desired product, but the yields changed from slightly to dramatically lower in different solvents. The vapor pressure of the reaction mixture in the vial was monitored as 5–7 bar using an online programmed Biotage microwave reactor at 220 °C. The results showed that the optimal conditions for N-arylation of carbazoles were 1 equiv Cs_2CO_3, 10 mol % CuI, and DMF at 220 °C. N-Arylation was examined using various aryliodides or bromides under optimal reaction conditions to diversify the *N*-arylated carbazole products. The results are summarized in Table 2. The reaction using substituted iodobenzene produced high yields of *N*-arylated carbazoles (Table 2, entries 1–4). Specifically, the reaction using 1-bromo-4-iodobenzene produced *N*-substituted 4-bromophenyl carbazole with excellent selectivity for the iodo substituent (Table 2, entry 2). Additionally, reactions using heteroaryl bromides, such as pyridine, thiophene, and thiazole, produced reasonable yields of *N*-heteroarylated carbazoles (Table 2, entries 5–8). These results indicate that reactions using nitrogen-containing heterocycles produced the same reactivity of the benzene ring, but reactions using diheteroarylbromide produced lower yields of the desired product. The optimized reaction conditions were applied for the diversification of substituted carbazoles using substituted aryliodides (Table 2, entries 10–13). Good yields of *N*-arylated carbazole were obtained

Table 2
N-Arylation of carbazoles with arylhalides

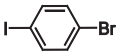
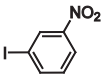
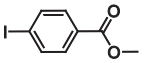
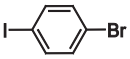
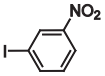
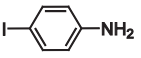


1 2

Entry[a,b]	R_1	R_2	XAr	Time (min)	Product	Yield (%)
1	H	H		20	**2a**	96
2	H	H		30	**2b**	79
3	H	H		40	**2c**	85
4	H	H		40	**2d**	91
5	H	H		40	**2e**	82
6	H	H		40	**2f**	61
7	H	H		40	**2g**	89
8	H	H		40	**2h**	44
9	2-Ph	H		30	**2i**	76
10	2-Ph	H		30	**2j**	77
11	2-Ph	H		30	**2k**	82
12	2-Br	H		30	**2l**	82
13	2-Br	H		30	**2m**	85

(*continued on next page*)

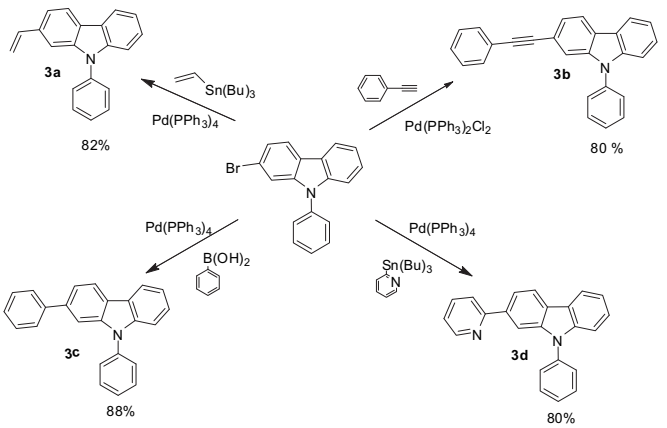
Table 2 (*continued*)

Entry[a,b]	R_1	R_2	XAr	Time (min)	Product	Yield (%)
14	3-Br	6-Br		30	**2n**	75
15	3-Br	6-Br		30	**2o**	79
16	3-Br	6-Br		30	**2p**	82
17	2-Br	7-Br		30	**2q**	80
18	2-Br	7-Br		30	**2r**	88
19	2-Br	7-Br		30	**2s**	78

[a] All reactions were conducted on a 1.0-mmol scale under 2 mL of solvent in a Biotage 5-mL vial sealed crimp cap using an initiator instrument (EXP EU, Biotage, 400 W, 2450 MHz).

with substituent variations. N-Arylation of 2,7- and 3,6-dibromocarbazole were also examined using aryliodo compounds. The reactions produced *N*-arylated dibromocarbazoles in good-to-excellent yields (Table 2, entries 14–19). However, N-arylation of dibromocarbazole with arylbromide produced low yields of the desired product due to nonselective Cu-catalyst reactivity for arylbromide and bromocarbazole.

The *N*-arylated bromocarbazoles could be converted into useful OLED or solar-cell intermediates by conventional palladium-catalyzed Heck-, Suzuki-, and Stille-coupling reaction conditions (Scheme 2).



Scheme 2. Functionalization of *N*-arylated bromocarbazole by palladium-catalyzed coupling reactions.

3. Conclusions

Simple and efficient N-arylation of carbazoles was achieved using microwave-assisted catalytic CuI reactions without an organic ligand in a short reaction time. The selective reactivity of arylhalide could be extended to various halocarbazoles. *N*-Arylated halocarbazoles gave promising results for the functionalization of carbazole moieties with palladium-catalyzed coupling reactions. We will examine the synthesized *N*-arylated dibromocarbazole intermediates for possible applications in material science.[12a,21]

4. Experimental

4.1. Instrumentation and analysis

All ^{1}H and ^{13}C NMR spectra were recorded on a Jeol 400 MHz spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard. The GC–MS spectra were obtained using a Shimadzu QP 1000 GC-MS. Elemental analyses were carried out by Chungnam National University using an elemental analyzer (EA-1110). Microwave-assisted reactions were performed with an initiator instrument (EXP EU, Biotage, 400 W, 2450 MHz). Each reaction was carried out in a 5-mm-thickness Biotage 5-mL vial sealed with a crimp cap. Reaction temperatures were measured using infrared sensors on the outer surface of the reaction vial. Products were purified by flash chromatography on 230–400-mesh ASTM 60 silica gel. All base and Cu species were purchased from Sigma–Aldrich Chemical Co. Chemicals were used directly as obtained from commercial sources unless otherwise noted.

4.2. General experimental procedure for microwave-assisted N-arylation of carbazoles

9*H*-Carbazole (1.0 mmol), Cs_2CO_3 (1.0 mmol), iodobenzene (1.1 mmol), CuI (0.1 mmol), and DMF (2 mL) were added to a 5-mL vial. The vial was sealed with a crimp cap and placed in a Biotage initiator microwave cavity. After irradiation at 220 °C for the appropriate time and subsequent cooling, the reaction mixture was diluted with saturated aqueous ammonium chloride. Products were isolated by extraction into ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Products were purified by silica gel column chromatography using a hexane/ethyl acetate solvent. *N*-Phenyl-carbazole (**2a**)[22] was obtained (96% yield) as a white solid. Mp 86–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, 2H, J=7.6 Hz), 7.61 (m, 4H), 7.50 (t, 1H), 7.44 (d, 4H, J=7.6 Hz), 7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.6, 104.5, 96.6, 94.2, 93.9, 92.7, 90.1, 87.0, 86.6, 76.5; MS (*m*/*z*, relative intensity): 243 (M^+, 100), 140 (11), 120 (16); Anal. Calcd for $C_{18}H_{13}N_1$: C, 88.89; H, 5.35; N, 5.76. Found: C, 88.73; H, 5.29, N, 5.98.

The following compounds (**2b**–**s**) were prepared with microwave-assisted general experimental procedures.

*4.2.1. 9-(4-Bromophenyl)-9H-carbazole (**2b**)*[23]. The product (**2b**) was obtained as a white solid in 79% isolated yield from 9*H*-carbazole and 1-bromo-4-iodobenzene. Mp 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 2H, J=4.4 Hz), 7.89 (d, 1H, J=4.4 Hz), 7.70 (d, 1H, J=8.4 Hz), 7.40 (m, 5H), 7.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.1, 133.1, 128.9, 128.7, 126.1, 123.5, 120.4, 120.2, 109.5; MS (*m*/*z*, relative intensity): 322 (M^+, 100), 321 (97), 241 (75), 121 (20).

*4.2.2. 9-(4-Methoxyphenyl)-9H-carbazole (**2c**).* Product (**2c**) was obtained as a white solid in 85% isolated yield from 9*H*-carbazole and 4-bromoanisole. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 2H, J=7.6 Hz), 7.44 (m, 4H), 7.14 (m, 6H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 140.8, 138.8, 130.5, 125.9, 123.3, 120.2, 119.9, 119.3, 113.2, 112.6, 109.9, 55.4; MS (*m*/*z*, relative intensity): 273 (M^+, 77), 230 (12), 228 (10), 182 (21), 181 (100), 180 (77), 152 (17); Anal. Calcd for $C_{19}H_{15}N_1$: C, 88.71; H, 5.84; N, 5.45. Found: C, 88.73; H, 5.79, N, 5.48.

*4.2.3. 9-(Pyridin-2-yl)-9H-carbazole (**2d**).* Product (**2d**) was obtained as a white solid in 91% isolated yield from 9*H*-carbazole and 2-bromopyridine. Mp 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.71 (d, 1H, *J*=7.6 Hz), 8.11 (d, 2H, *J*=7.6 Hz), 7.89 (d, 1H, *J*=7.6, 1.6 Hz), 7.82 (d, 2H, *J*=4.4 Hz), 7.61 (d, 1H, *J*=4.4 Hz), 7.42 (t, 2H, *J*=7.2 Hz), 7.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 149.6, 139.5, 138.5, 126.2, 124.3, 121.2, 120.9, 120.2, 119.1, 111.1; MS (*m*/*z*, relative intensity): 244 (M^+, 100), 243 (73), 242 (10), 121 (13); Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.52; H, 4.96; N, 11.52.

*4.2.4. 9-(Pyridin-3-yl)-9H-carbazole (**2e**).* The product (**2e**) was obtained as a white solid in 82% isolated yield from 9*H*-carbazole and 3-bromopyridine. Mp 109–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.72 (d, 1H, *J*=4.4 Hz), 8.14 (d, 2H, *J*=7.6 Hz), 7.91 (d, 1H, *J*=8.0 Hz), 7.56 (dd, 1H, *J*=8.0, 4.8 Hz), 7.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 148.5, 140.6, 134.6, 134.5, 126.2, 124.4, 123.7, 120.5, 120.5, 109.3; MS (*m*/*z*, relative intensity): 244 (M^+, 100), 243 (43), 242 (16), 121 (13); Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.54; H, 4.97; N, 11.49.

*4.2.5. 9-(Pyrimidin-2-yl)-9H-carbazole (**2f**).* The product (**2f**) was obtained as a white solid in 61% isolated yield from 9*H*-carbazole and 2-bromopyrimidine. Mp 112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (m, 4H), 8.06 (d, 2H, *J*=7.6 Hz), 7.50 (t, 2H, *J*=7.6 Hz), 7.36 (t, 2H, *J*=7.6 Hz), 7.08 (t, 1H, *J*=4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 139.1, 126.6, 125.8, 122.3, 119.5, 116.2, 116.0; Anal. Calcd for $C_{17}H_{12}N_3$: C, 78.37; H, 4.49; N, 17.14. Found: C, 78.32; H, 4.47; N, 17.21.

*4.2.6. 9-(Thiophen-2-yl)-9H-carbazole (**2g**).* The product (**2g**) was obtained as a yellow oil in 89% isolated yield from 9*H*-carbazole and 2-bromothiophene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, 2H, *J*=7.6, 0.8 Hz), 7.47 (m, 4H), 7.55 (dd, 1H, *J*=7.6, 0.8 Hz) 7.33 (m, 2H) 7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 138.7, 126.2, 126.1, 124.8, 124.2, 123.4, 120.5, 120.2, 110.2; MS (*m*/*z*, relative intensity): 250 (M+1, 38), 249 (M^+, 100), 248 (12), 247 (10), 204 (40); Anal. Calcd for $C_{16}H_{11}N_1S_1$: C, 77.11; H, 4.44; N, 5.62. Found: C, 77.08; H, 4.46; N, 5.58.

*4.2.7. 2-(9H-Carbazol-9-yl)thiazole (**2h**).* The product (**2h**) was obtained as a white solid in 44% isolated yield from the CuI-mediated reaction of 9*H*-carbazole and 2-bromothiazole. Mp 83–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, 2H, *J*=7.6 Hz), 8.06 (d, 2H, *J*=7.6 Hz), 7.75 (d, 1H, *J*=2.8 Hz), 7.49 (t, 2H, *J*=7.6 Hz), 7.35 (t, 2H, *J*=7.6 Hz), 7.21 (t, 2H, *J*=2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 139.8, 139.3, 126.8, 124.7, 122.1, 120.1, 114.5, 112.8; MS (*m*/*z*, relative intensity): 250 (M^+, 100), 249 (12), 224 (13), 191 (13), 125 (12), 58 (14); Anal. Calcd for $C_{15}H_{10}N_2S_1$: C, 71.97; H, 4.06; N, 11.17. Found: C, 71.95; H, 4.03; N, 11.20.

*4.2.8. 9-(4-Bromophenyl)-2-phenyl-9H-carbazole (**2i**).* The product (**2i**) was obtained as a white solid in 76% isolated yield from 2-phenyl-9*H*-carbazole and 1-bromo-4-iodobenzene. Mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (t, 2H, *J*=8.0 Hz), 7.76 (d, 2H, *J*=8.0 Hz), 7.67 (d, 2H, *J*=7.2 Hz), 7.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.1, 141.0, 139.5, 139.0, 137.3, 136.6, 133.1, 128.8, 128.7, 127.1, 126.0, 120.9, 120.6, 120.4, 119.8, 109.5, 107.9; MS (*m*/*z*, relative intensity): 399 (M+2, 98), 397 (M^+, 100), 317 (26), 241 (12).

*4.2.9. 9-(3-Nitrophenyl)-2-phenyl-9H-carbazole (**2j**).* The product (**2j**) was obtained in 77% isolated yield from 2-phenyl-9*H*-carbazole and 1-iodo-3-nitrobenzene. Mp 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.27 (d, 1H, *J*=7.2 Hz), 8.12 (t, 2H, *J*=7.8 Hz), 7.91 (t, 1H, *J*=7.8 Hz), 7.75 (d, 1H, *J*=8.4 Hz), 7.45–7.60 (m, 4H), 7.25–7.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 130.9, 128.8, 127.5, 127.3, 126.4, 124.8, 124.2, 123..9, 123.1, 122.1, 121.0, 120.8, 120.6, 109.3, 107.7, 100.1; MS (*m*/*z*, relative intensity): 364 (M^+, 100), 318 (45), 241 (17).

*4.2.10. 9-(4-(Benzyloxy)phenyl)-2-phenyl-9H-carbazole (**2k**).* The product (**2k**) was obtained as a white solid in 82% isolated yield from 2-phenyl-9*H*-carbazole and 1-(benzyloxy)-4-iodobenzene. Mp 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 2H, *J*=8.4 Hz), 7.6 (d, 2H, *J*=8.4 Hz), 7.2–7.5 (m, 15H), 7.12 (d, 2H, *J*=8.4 Hz), 5.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 141.9, 139.3, 136.6, 130.3, 128.7, 128.1, 127.9, 127.5, 127.0, 125.9, 122.9, 122.3, 120.9, 120.5, 120.3, 116.0, 114.8, 109.7, 108.2, 70.3; MS (*m*/*z*, relative intensity): 425 (M^+, 50), 334 (100), 304 (19), 91 (55).

*4.2.11. 2-Bromo-9-(4-bromophenyl)-9H-carbazole (**2l**).* The product (**2l**) was obtained as a white solid in 82% isolated yield from 2-bromo-9*H*-carbazole and 1-bromo-4-iodobenzene. Mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 1H, *J*=8.0 Hz), 7.93 (d, 1H, *J*=8.0 Hz), 7.72 (d, 1H, *J*=8.0 Hz), 7.47 (d, 1H, *J*=1.6 Hz), 7.39 (m, 4H), 7.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.6, 139.1, 135.9, 133.1, 128.7, 128.5, 126.3, 123.2, 122.6, 122.2, 121.2, 120.5, 120.2, 119.4, 112.4, 109.5; MS (*m*/*z*, relative intensity): 403 (M+2, 50), 401 (M^+, 100), 399 (M−2, 50), 241 (91), 121 (35).

*4.2.12. 2-Bromo-9-(3-nitrophenyl)-9H-carbazole (**2m**).* The product (**2m**) was obtained as a yellow solid in 85% isolated yield from 2-bromo-9*H*-carbazole and 1-iodo-3-nitrobenzene. Mp 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, 1H, *J*=8.0 Hz), 8.12 (d, 1H, *J*=8.0 Hz), 7.89 (m, 2H), 7.4 (m, 4H), 7.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 143.2, 138.1, 132.6, 132.1, 130.8, 130.4, 126.6, 123.8, 122.4, 121.7, 121.5, 121.1, 120.3, 112.1, 109.2; MS (*m*/*z* , relative intensity): 368 (M+2, 98), 366 (M^+,100), 241 (50),120 (35).

*4.2.13. 3,6-Dibromo-9-(4-bromophenyl)-9H-carbazole (**2n**).* The product (**2n**) was obtained as a white solid in 75% isolated yield from 3,6-dibromo-9*H*-carbazole and 1-bromo-4-iodobenzene. Mp 181–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H, *J*=8.4 Hz), 7.71 (d, 2H, *J*=8.4 Hz), 7.47 (dd, 2H, *J*=8.4, 1.6 Hz), 7.34 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 137.6, 131.6, 127.7, 126.9, 126.7, 122.2, 121.5, 111.6, 109.4; MS (*m*/*z*, relative intensity): 483 (M+4, 36), 481 (M+2, 98), 479 (M^+, 88), 477 (M−2, 36), 239 (100).

*4.2.14. 3,6-Dibromo-9-(3-nitrophenyl)-9H-carbazole (**2o**).* The product (**2o**) was obtained as a yellow solid in 79% isolated yield from 3,6-dibromo-9*H*-carbazole and 1-iodo-3-nitrobenzene. Mp 173–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.71 (d, 2H, *J*=8.0 Hz), 7.47 (dd, 2H, *J*=8.0, 1.2 Hz), 7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.2, 130.9, 129.2, 128.4, 122.0, 121.2, 120.3, 109.5, 108.6; MS (*m*/*z*, relative intensity): 448 (M+2, 34), 446 (M^+, 61), 444 (M−2, 32), 321 (61), 239 (100).

*4.2.15. Methyl 4-(3, 6-dibromo-9H-carbazol-9-yl)benzoate (**2p**).* The product (**2p**) was obtained as a white solid in 82% isolated yield from 3,6-dibromo-9*H*-carbazole and methyl 4-iodobenzoate. Mp 125–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, 1H, *J*=8.4, 1.6 Hz), 8.14 (d, 1H, *J*=1.6 Hz), 8.05 (d, 1H, *J*=1.6 Hz), 7.68 (t, 1H, *J*=7.4 Hz), 7.53 (m, 3H), 7.27 (m, 3H), 4.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 130.7, 128.7, 128.1, 125.4, 122.2, 110.5, 109.2, 51.5; MS (*m*/*z*, relative intensity): 461 (M+2, 57), 459 (M^+, 100), 457 (M−2, 48), 321 (40), 239 (97).

*4.2.16. 2,7-Dibromo-9-(4-bromophenyl)-9H-carbazole (**2q**).* The product (**2q**) was obtained as a white solid in 80% isolated yield from 2,7-dibromo-9*H*-carbazole and 1-bromo-4-iodo- benzene. Mp 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 2H, *J*=8.8 Hz), 7.75 (d, 2H, *J*=8.8 Hz), 7.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 137.2, 131.3, 126.4, 126.4, 121.6, 119.5, 119.3, 117.4, 116.4, 110.5; MS (*m*/*z*, relative intensity): 483 (M+4, 30), 481 (M+2, 98), 479 (M^+, 98), 477 (M−2, 30), 239 (100).

*4.2.17. 2,7-Dibromo-9-(3-nitrophenyl)-9H-carbazole (**2r**).* The product (**2r**) was obtained as a yellow solid in 88% isolated yield from 2,7-dibromo-9*H*-carbazole and 1-iodo-3-nitrobenzene. Mp 126–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, 1H, *J*=8.4 Hz), 8.22 (d, 1H, *J*=8.4 Hz), 7.94 (d, 1H, *J*=1.6 Hz), 7.67 (m, 3H), 7.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 131.4, 129.3, 125.1, 124.6, 123.5, 122.8, 121.8, 112.6; MS (*m*/*z*, relative intensity): 448 (M+2, 52), 446 (M^+, 100), 444 (M−2, 50), 319 (41), 239 (58).

*4.2.18. 4-(2,7-Dibromo-9H-carbazol-9-yl)aniline (**2s**)[21].* The product (**2s**) was obtained as a white solid in 78% isolated yield from 2,7-dibromo-9*H*-carbazole and 4-iodoaniline. Mp 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 2H, *J*=8.0 Hz), 7.36 (m, 4H), 7.18 (d, 2H, *J*=8.0 Hz), 6.81 (d, 2H, *J*=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 142.9, 128.5, 127.0, 123.2, 121.4, 117.3, 116.0, 113.1; MS (*m*/*z*, relative intensity): 418 (M+2, 52), 416 (M^+, 100), 414 (M−2, 50), 256 (70).

4.3. Functionalization of 2-bromo-9-phenyl-carbazole by palladium-catalyzed coupling reactions

*4.3.1. 9-Phenyl-2-vinyl-9H-carbazole (**3a**).* $Pd(PPh_3)_4$ (60 mg, 0.05 mmol), 2-bromo-9-phenylcarbazole (321 mg, 1 mmol), and tributyl(vinyl)stannane (475 mg, 1.5 mmol) were dissolved in 3 mL of 1,4-dioxane in a 10-mL vial with a screw cap. The reaction was stirred at 100 °C in oil bath for 6 h, the reaction mixture was diluted with saturated aqueous ammonium chloride, and the products were isolated by extraction into ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Product (**3a**) was obtained as a white solid in 82% isolated yield by silica gel column chromatography using a hexane/ethyl acetate solvent. Mp 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, 2H, *J*=8.0, 1.2 Hz), 7.41 (m, 4H), 7.34 (m, 5H), 7.20 (m, 1H), 6.78 (d, 1H, *J*=17.6 Hz), 5.73 (d, 1H, *J*=17.6 Hz), 5.19 (d, 1H, *J*=10.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 141.1, 137.5, 135.1, 129.9, 127.5, 127.1, 125.9, 123.2, 120.3, 120.0, 118.3, 113.3, 109.1, 107.6; MS (*m*/*z*, relative intensity): 270 (M+1, 24), 269 (M^+, 100), 268 (M−1, 13).

*4.3.2. 9-Phenyl-2-(phenylethynyl)-9H-carbazole (**3b**).* $Pd(PPh_3)_2Cl_2$ (60 mg, 0.05 mmol), 2-bromo-9-phenyl-carbazole (321 mg, 1 mmol), ethynylbenzene (153 mg, 1.5 mmol), and CuI (0.01 mmol) were dissolved in 3 mL of Et_3N in 10 mL vials. The reaction mixture was stirred at 80 °C in oil bath for 6 h. The reaction mixture was diluted with saturated aqueous ammonium chloride. Products were isolated by extraction into ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The product (**3b**) was obtained as a white solid in 80% isolated yield. Mp 83–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 2H, *J*=8.4, 1.6 Hz), 7.57 (s, 1H), 7.51 (m, 5H), 7.48 (t, 2H, *J*=7.4 Hz), 7.34 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.9, 136.6, 130.9, 129.3, 127.7, 127.5, 126.5, 125.8, 123.0, 122.8, 122.3, 119.9, 119.7, 119.6, 112.3, 109.2, 90.1, 88.5; MS (*m*/*z*, relative intensity): 343 (M^+, 100), 342 (M−1, 7).

*4.3.3. 2,9-Diphenyl-9H-carbazole (**3c**).* $Pd(PPh_3)_4$ (60 mg, 0.05 mmol), 2-bromo-9-phenyl-carbazole (231 mg, 1 mmol), phenylboronic acid (181 mg, 1.5 mmol), and K_2CO_3 (2 mmol) were dissolved in 3 mL of toluene in 10 mL vial sealed with screw cap. The reaction mixture was stirred at 100 °C in oil bath for 6 h. The reaction mixture was diluted with saturated aqueous ammonium chloride. Products were isolated by extraction into ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Product (**3c**) was obtained as a white solid in 88% isolated yield by silica gel column chromatography using a hexane/ethyl acetate solvent. Mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, 2H, *J*=8.0, 1.2 Hz), 7.61 (d, 2H, *J*=8.0 Hz), 7.54 (d, 2H, *J*=1.2 Hz), 7.40 (m, 3H), 7.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.1, 141.0, 139.5, 139.0, 137.3, 136.6, 133.1, 128.9, 128.7, 127.1, 126.0, 120.9, 120.6, 120.4, 119.8, 109.5, 107.9; MS (*m*/*z*, relative intensity): 319 (M^+, 100).

*4.3.4. 9-Phenyl-2-(pyridin-2-yl)-9H-carbazole (**3d**).* $Pd(PPh_3)_4$ (60 mg, 0.05 mmol), 2-bromo-9-phenyl-carbazole (321 mg, 1 mmol), and 2-(tributylstannyl)pyridine (552 mg, 1.5 mmol) were dissolved in 3 mL of 1,4-dioxane in 10 mL vial with screw cap. The reaction was stirred at 100 °C in oil bath for 5 h. The reaction mixture was diluted with saturated aqueous ammonium chloride. Products were isolated by extraction into ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The product (**3c**) was obtained as a white solid in 80% isolated yield. Mp 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, 1H, *J*=8.0 Hz), 8.17 (dd, 2H, *J*=8.0, 1.2 Hz), 8.04 (s, 1H), 7.87 (d, 1H, *J*=8.4 Hz), 7.72 (q, 2H), 7.58 (m, 4H), 7.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 148.6, 140.7, 140.4, 136.5, 136.5, 135.1, 128.9, 126.6, 125.3, 123.0, 122.0, 120.8, 120.0, 119.5, 118.1, 108.9, 107.3; MS (*m*/*z*, relative intensity): 320 (M^+, 100), 319 (M−1, 69).

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