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Site-Selective N-Arylation of Carbazoles with Halogenated Fluorobenzenes

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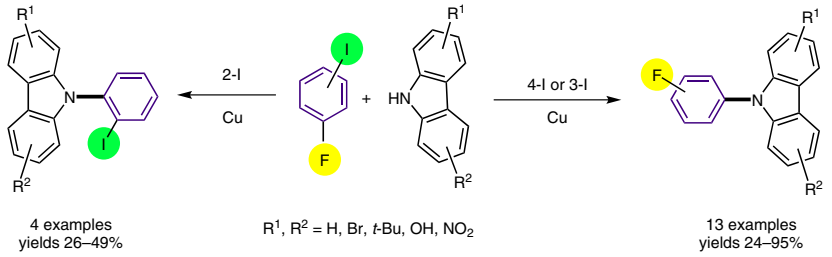

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Abstract A method for the highly site-selective C–N bond-formation reaction of halogenated fluorobenzenes with carbazoles is described. The selectivity of iodine and fluorine atoms on the aromatic ring of fluorinated iodobenzenes was initially determined with a copper–*N*,*N*-diisopropylethylamine catalytic system. By changing the position of the iodine atom on the aromatic ring from the 3- or 4-position to the 2-position, the preferred coupling site was switched from the iodine atom to the fluorine atom. Steric hindrance of the fluorinated iodobenzenes is responsible for the selectivity switch. After elucidating the reaction mechanisms of these reaction processes, a metal-free method for the highly site-selective C–N bond-formation reaction of halogenated fluorobenzenes with carbazoles was revealed through C–F bond activation. The metal-free system is able to handle a range of halogenated groups. Thus, a broad range of chlorinated, brominated, and iodinated N-arylated carbazoles were generated, which are widely useful in organic chemistry.

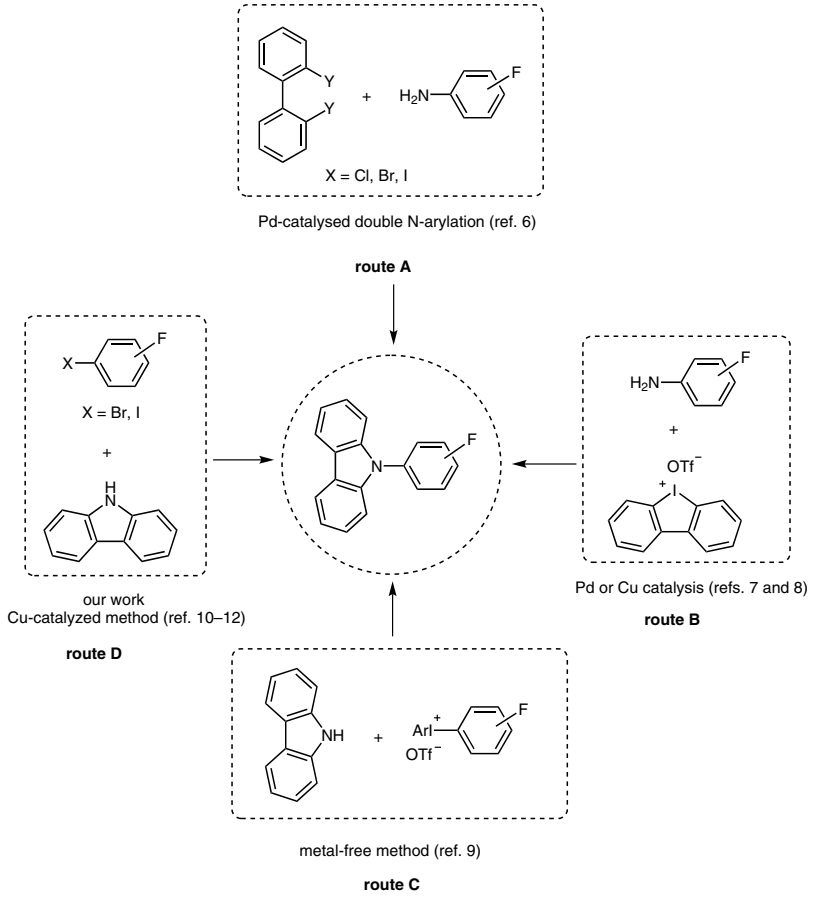
Key words N-arylation, site selectivity, halobenzenes, N-arylated carbazoles

Carbazole structural units have numerous applications in medicine as synthetic intermediates,[1] and in advanced materials as building blocks.[2] Introduction of an oganofluorine into a carbazole can efficiently tune the absorption, light-emitting, and electronic properties of materials,[3] as well as affect physical, adsorption, distribution, and metabolism properties of medicines.[4] However, naturally occurring fluorinated compounds are virtually absent from the natural world. Given the importance and rarity of this class of compounds, the search for an efficient synthetic protocol for their preparation remains an urgent priority.

Various methods to construct fluorinated N-arylated carbazoles have been described. A copper-catalysed Ullmann-type reaction was initially applied in the synthesis of fluorinated N-arylated carbazoles.[5] However, the main drawbacks of this process are the harsh reaction conditions and limited substrate scope. These limitations were overcome by the development of a method to synthesise fluorinated N-arylated carbazoles through palladium-catalysed double N-arylation by using primary amines and 2,2′-dihalobiphenyls (Scheme 1, route A).[6] Recently, cyclic diaryliodonium salts have been studied as arylation agents for use in C–N bond-formation reactions. Riedmüller and Nachtsheim reported a palladium-catalysed N-arylation of cyclic diaryliodonium salts with anilines to synthesise fluorinated N-arylated carbazoles (Scheme 1, route B).[7] Wen and co-workers have found a low-cost and environment-friendly copper catalyst, and have developed a copper-catalysed method to synthesise the same compounds by using cyclic diaryliodonium salts and amines (Scheme 1, route B).[8] Metal-free methods are an alternative synthetic strategy. Thus, Wang and co-workers have developed a metal-free method to prepare fluorinated N-arylated carbazoles (Scheme 1, route C).[9]

The limitations of Ullmann-type reactions have been reduced through the pioneering work of the Buchwald[10] and Hartwig groups.[11] Several high-performance ligands have been developed for the copper-catalysed N-arylation of carbazole (Scheme 1, route D).[12]

Carbazoles are derived from non-petroleum resources. The availability of carbazoles prompted us to develop an efficient ligand to prepare fluorinated N-arylated carbazoles via a copper-catalysed method. Diamine derivatives are commercially available, and Buchwald and co-workers have reported that these derivatives are efficient ligands for copper-catalysed N-arylation.[13] In this paper, the copper–amine-catalysed N-arylation of carbazole with fluorinated iodobenzenes is developed. Interestingly, the reactivity of the C–X bond can be tuned by adjusting the position of the iodo substituent on the aromatic ring. The preferred coupling site of the fluorinated iodobenzenes was switched



Scheme 1 Different methods towards fluorinated N-arylated carbazoles

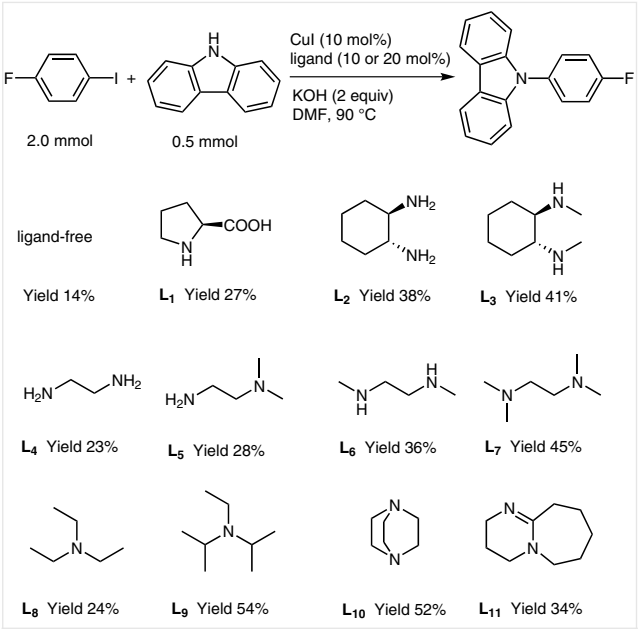
from the iodine atom to the fluorine atom when the position of the iodine atom on the aromatic ring was changed from the 3- or 4-position to the 2-position. The main factors responsible for the selectivity of halides attached to an aromatic ring are investigated in this paper.

The coupling reaction of 1-fluoro-4-iodobenzene and carbazole was selected as the model reaction to optimise the reaction conditions. First, the efficiency of different ligands on the coupling reaction was evaluated (Scheme 2).

Ligand efficiency was verified by designing control experiments in the absence of a ligand. Results show that the reaction had difficulty proceeding with copper(I) iodide in the absence of a ligand, with a 14% product yield. A number of diamine ligands were initially evaluated, and N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (L_7) was more catalytically efficient than other ethanediamine derivatives. Encouraged by these results, the catalytic efficiency of another four tertiary amine derivatives (L_8–L_{11}) was subsequently tested in the coupling of 1-fluoro-4-iodobenzene and carbazole, with the commercially available *N*,*N*-diisopropylethylamine (L_9) proving the most efficient (Scheme 2).

The N-arylation of carbazole with 1-fluoro-4-iodobenzene was also used as the model reaction to further optimise the reaction conditions, in which a range of temperatures, solvents, and bases was investigated (Table 1).

The effect of reaction temperature on this cross-coupling was evaluated, and the results show that the reaction temperature plays an important role in the reaction. The coupling reaction was slow at 90 °C, with a mere 54% isolated yield obtained (Table 1, entry 1). The cross-coupling was remarkably accelerated when the temperature was raised to 110 °C, with an increased yield of 76% (Table 1, entry 2). Upon further increase of the reaction temperature to 130 °C, the isolated yield reached 82% (Table 1, entry 3). However, NMR analysis showed that the higher reaction temperature led to low selectivity of the C–X bond and resulted in the formation of a mixture of products, namely 9-(4-fluorophenyl)-9*H*-carbazole and 9-(4-iodophenyl)-9*H*-carbazole, from which the desired product is often difficult to isolate.



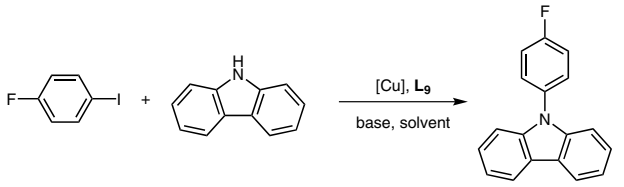
Scheme 2 Ligands for the copper-catalysed cross-coupling of 1-fluoro-4-iodobenzene with carbazole

The effect of different solvents was also determined. The reaction carried out in *N*,*N*-dimethylformamide (DMF) gave a good yield (Table 1, entry 2), while the yields were decreased when *N*,*N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidinone (NMP), or dimethyl sulfoxide (DMSO) was employed (Table 1, entries 4–6).

Copper-catalysed cross-coupling is often affected by the oxidation state of the copper source. Therefore, different copper sources [Cu(I), Cu(II), and Cu(0)] were evaluated for the N-arylation of carbazole with 1-fluoro-4-iodobenzene when using *N*,*N*-dimethylformamide as the solvent. The copper(I) catalysts were more catalytically active than the other copper sources. Thus, the copper(I) states showed moderate to good catalytic activity, with copper(I) iodide providing the best results (Table 1, entry 2 vs entries 7 and 8). Among the copper(II) sources, copper(II) sulfate, copper(II) acetate, and copper(II) nitrate showed relatively higher catalytic activity than copper(II) oxide (Table 1, entries 9–11 vs entry 12). The use of copper powder resulted in a moderate conversion (Table 1, entry 13).

A series of bases was also evaluated. Strong bases showed higher catalytic activity than weak bases. The activity of potassium hydroxide was superior to other potassium bases, with potassium phosphate giving lowest conversion (Table 1, entry 2 vs entries 14–16). The activity of sodium hydroxide was superior to a range of other sodium bases (Table 1, entry 17 vs entries 18–20). By contrast, cesium carbonate showed moderate catalytic activity (Table 1, entry 21).

Table 1 Optimisation of the Reaction Conditions[a]

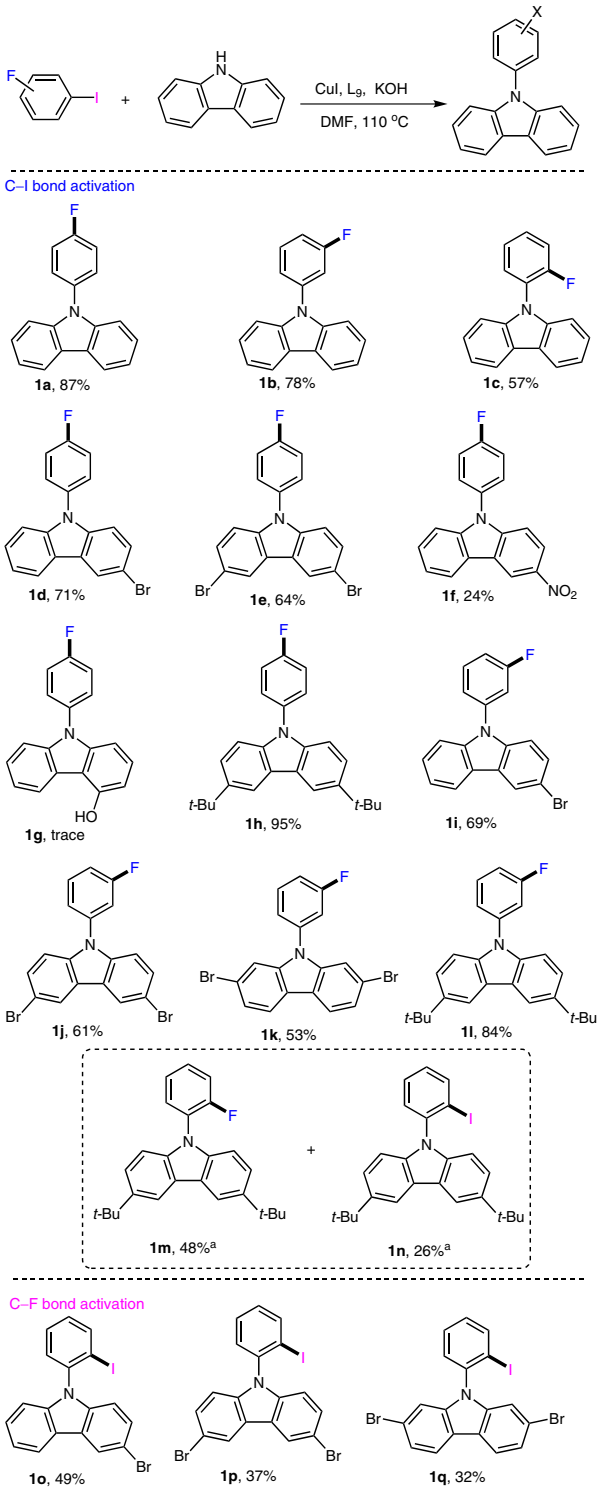


Entry	Solvent	Copper source	Base	Temp (°C)	Yield (%)
1	DMF	CuI	KOH	90	54
2	**DMF**	**CuI**	**KOH**	**110**	**76**
3	DMF	CuI	KOH	130	82
4	DMA	CuI	KOH	110	37
5	NMP	CuI	KOH	110	26
6	DMSO	CuI	KOH	110	23
7	DMF	Cu_2O	KOH	110	72
8	DMF	CuCl	KOH	110	64
9	DMF	$CuSO_4·5H_2O$	KOH	110	59
10	DMF	$Cu(OAc)_2·H_2O$	KOH	110	57
11	DMF	$Cu(NO_3)_2$	KOH	110	49
12	DMF	CuO	KOH	110	14
13	DMF	Cu	KOH	110	42
14	DMF	CuI	K_2CO_3	110	55
15	DMF	CuI	$K_3PO_4·3H_2O$	110	33
16	DMF	CuI	*t*-BuOK	110	57
17	DMF	CuI	NaOH	110	65
18	DMF	CuI	Na_2CO_3	110	16
19	DMF	CuI	$NaHCO_3$	110	24
20	DMF	CuI	*t*-BuONa	110	45
21	DMF	CuI	Cs_2CO_3	110	51

[a] Reaction conditions: 1-fluoro-4-iodobenzene (2.0 mmol), carbazole (0.5 mmol), copper source (10 mol%), L_9 (20 mol%), base (1.0 mmol), solvent (2 mL), 12 h, under N_2; isolated yields are given.

Soulé, Doucet, and co-workers[14] have described a palladium-catalysed methodology for the synthesis of fluorinated biphenyls through C–H bond activation of halogenated fluorobenzenes. However, no biaryl product generated from C–H bond activation of halogenated fluorobenzene was observed in the developed copper-catalysed system.

The scope and limitations for the cross-coupling of iodinated fluorobenzenes with a range of carbazoles was examined using the optimised reaction conditions, namely copper(I) iodide as catalyst, *N*,*N*-diisopropylethylamine (L_9) as ligand, potassium hydroxide as base, and *N*,*N*-dimethylformamide as solvent at 110 °C (Scheme 3).

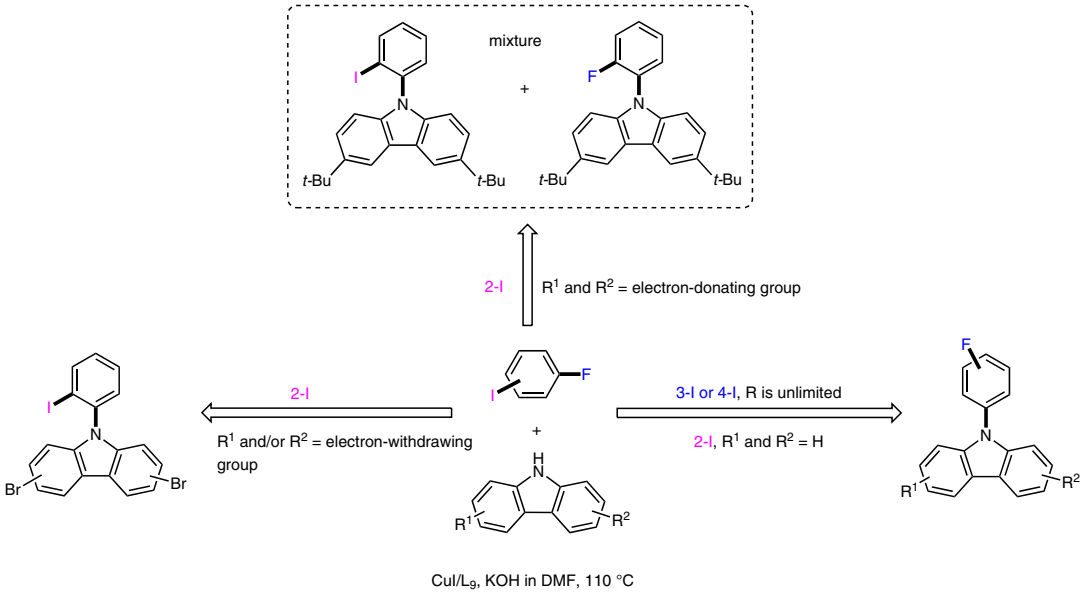


Scheme 3 Copper-catalysed cross-coupling of iodinated fluorobenzenes with carbazoles. *Reagents and conditions*: fluorinated iodobenzene (2.0 mmol), carbazole (0.5 mmol), CuI (10 mol%), L_9 (20 mol%), KOH (1.0 mmol), DMF (2 mL), under N_2, 110 °C, 24 h; isolated yields are given, except where otherwise indicated. [a] NMR yield.

The effect of a fluoro substituent at the different positions of iodobenzene on the copper-catalysed coupling reaction with carbazole was initially examined. N-Arylation was not affected by the electronic effect of an aromatic fluoro substituent; thus, 4-fluoro- or 3-fluoro-substituted iodobenzene smoothly underwent coupling to give corresponding products in good yields (Scheme 3, 1a and **1b**). However, steric hindrance of fluorinated iodobenzene was evident; the 2-fluoro-substituted iodobenzene resulted in low conversion, and gave 57% yield (Scheme 3, 1c). Subsequently, the electronic nature of substituents on carbazole was also investigated, and an electronic effect of substituents attached to the aromatic rings of carbazole was observed. Thus, carbazoles bearing the electron-donating *tert*-butyl group reacted with 4-fluoro- or 3-fluoro-substituted iodobenzene to produce high yields (Scheme 3, 1h and **1l**). However, carbazoles bearing electron-withdrawing substituents such as 3-bromo, 3,6-dibromo, 2,7-dibromo, and 3-nitro groups, showed relatively lower reactivity in the developed catalytic system (Scheme 3, 1d–f and **1i**–**k**). The coupling with 4-hydroxycarbazole failed to furnish the desired product (Scheme 3, 1g).

Steric hindrance effects of the fluorinated iodobenzenes significantly influenced the selectivity of the reaction. 1-Fluoro-2-iodobenzene was selected as the model substrate to explore the selectivity of the reaction under the optimised conditions. Carbazole itself, bearing the electron-neutral hydrogen group, preferentially reacted with the C–I bond (Scheme 3, 1c). Carbazoles bearing electron-donating groups, such as 3,6-di-*tert*-butyl groups, showed poor selectivity and reacted with the C–I and C–F bonds to yield a mixture of products (Scheme 3, 1m and **1n**). Finally, carbazoles bearing electron-withdrawing groups, such as 3-bromo, 3,6-dibromo, and 2,7-dibromo groups, preferentially reacted with the C–F bond (Scheme 3, 1o–q).

Scheme 4 summarises the reaction rules for the coupling of fluorinated iodobenzenes with carbazoles. The position effect of the iodine atom is crucial to the selectivity of this coupling. Fluorobenzenes with the iodo substituent at the para or meta position to the fluorine atom show higher reactivity with the C–I bond of the benzene ring than with the C–F bond in the presence of a copper catalyst. Steric hindrance significantly affects the copper-catalysed N-arylation of carbazoles and inhibits the reaction. Carbazole bearing the electron-neutral hydrogen group showed relatively high reactivity and selectivity, and reacted with the C–I bond of the benzene ring to provide the desired products. However, carbazoles bearing electron-donating groups, such as 3,6-di-*tert*-butyl groups, exhibited low selectivity with 1-fluoro-2-iodobenzene, to give a mixture of C–F and C–I bond activation. In the case of the *ortho*-iodinated fluorobenzene, the preferred coupling site switched from the iodine atom to the fluorine atom with carbazoles bearing electron-withdrawing groups, such as 3-bromo, 3,6-dibromo, and 2,7-dibromo groups.



Scheme 4 Selective synthesis of N-arylated carbazoles

Control experiments in the absence of a copper source and ligand were designed to probe the main reason for the selectivity of the aromatic halide group (Scheme 5). Such a control experiment showed that 3,6-dibromocarbazole preferentially reacted with the fluoro group of 1-fluoro-2-iodobenzene to generate the monosubstituted product through a nucleophilic substitution reaction (Scheme 5, equation 1). The selectivity of aromatic polyhalides was explored in the presence and absence of a copper source. The results revealed that the C–I and C–F bonds of 1-bromo-2-fluoro-4-iodobenzene exhibited similar reactivity in the presence of copper and were simultaneously activated to give the disubstituted product **2a**. However, in the absence of copper, 1-bromo-2-fluoro-4-iodobenzene underwent highly selective coupling at the fluorine group with carbazole through a nucleophilic substitution reaction (Scheme 5, equation 2). The results indicate that nucleophilic attack is likely to occur at the fluoro-substituted carbon atom of the aromatic ring. The metal-free method shows excellent selectivity for the halogen atoms of the aromatic ring, leading to the creation of the desired product with a minimal amount of byproducts.

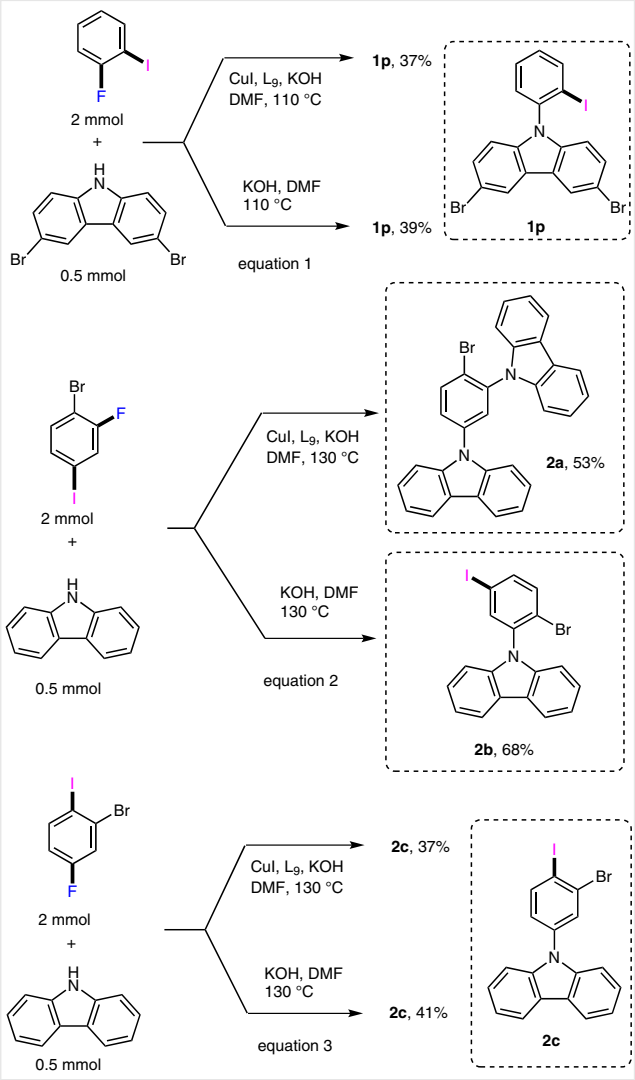
Our results indicated that copper-catalysed C–I bond activation is significantly affected by steric hindrance. However, steric hindrance only slightly affects the metal-free nucleophilic substitution reaction. This hypothesis was tested by selecting 2-bromo-4-fluoro-1-iodobenzene, containing steric hindrance at the ortho position of the iodine atom, to elucidate the reaction process (Scheme 5, equation 3). As shown, 2-bromo-4-fluoro-1-iodobenzene preferentially reacted at the fluorine group of the aromatic ring with carbazole, both in the presence and absence of a copper catalyst. In summary, copper-catalysed coupling of halogenated benzenes with carbazole is significantly affected by steric hindrance; however, steric hindrance has a slight effect on the nucleophilic substitution reaction.

Halogens including chlorine, bromine, and iodine on the aromatic ring are well-tolerated in metal-free N-arylation, thus providing an opportunity to functionalise the resulting halogenated N-arylated carbazoles and to convert them into useful pharmaceuticals, dye-sensitised solar cells, and advanced materials intermediates. We chose 9-(4-iodophenyl)-9*H*-carbazole (**4r**, see Scheme 7) as a model substrate to explore its reactivity in a series of transition-metal-catalysed cross-coupling reactions. As illustrated in Scheme 6, iodo derivative **4r** could be successfully converted into valuable intermediates through classical transition-metal-catalysed Suzuki coupling, Ullmann-type reaction, and Sonogashira coupling.

The N-arylation of carbazole with 1-fluoro-4-iodobenzene was also selected as the model reaction to optimise the metal-free reaction conditions (Table 2).

The amount of base, crucial for the nucleophilic substitution reaction to activate the N–H bond of carbazole, was investigated under metal-free conditions. The amount of base had an effect on the product yield (Table 2, entry 1 vs entry 2); thus, considering efficiency, four equivalents of base was selected as the optimised mole ratio.

The effect of reaction temperature on the cross-coupling was evaluated. The results show that the reaction temperature plays an important role in metal-free N-aryla-



Scheme 5 Control experiments to probe the coupling selectivity

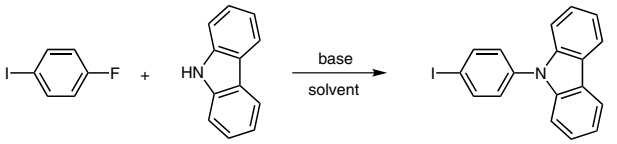
tion. The N-arylation of carbazole with 1-fluoro-4-iodobenzene was slow at 110 °C, with merely 35% isolated yield (Table 2, entry 2). The cross-coupling was remarkably accelerated when the temperature was increased to 150 °C, with 48% yield (Table 2, entry 4). Upon further increase of the reaction temperarure to 170 °C, the isolated yield reached 52% (Table 2, entry 5). However, HPLC–MS analysis showed that the higher reaction temperature was likely to result in disubstituted and dehalogenated side products. In view of this, 150 °C was selected as the optimised reaction temperature for use in subsequent studies.

The nature of the base is crucial to the efficiency of metal-free N-arylation. Therefore, various bases were evaluated for the cross-coupling of carbazole with 1-fluoro-4-iodobenzene when using *N*,*N*-dimethylformamide as the solvent. Among the potassium bases, potassium hydroxide and potassium carbonate were superior to other potassium bases, with potassium *tert*-butoxide giving lower conversion and potassium phosphate yielding a trace of product (Table 2, entries 4 and 6 vs entries 7 and 8). Sodium *tert*-butoxide was superior to a range of other sodium bases, but promoted byproduct formation (Table 2, entry 9 vs entries 10–12). Cesium carbonate was the most efficient base of all tested bases (Table 2, entry 13).

The reaction was promoted with an increased amount of 1-fluoro-4-iodobenzene, but the increasing rate slowed down when the concentration was 6 equivalents (Table 2, entries 13–15); 4 equivalents of 1-fluoro-4-iodobenzene was the best compromise between cost and product yield (Table 2, entry 13).

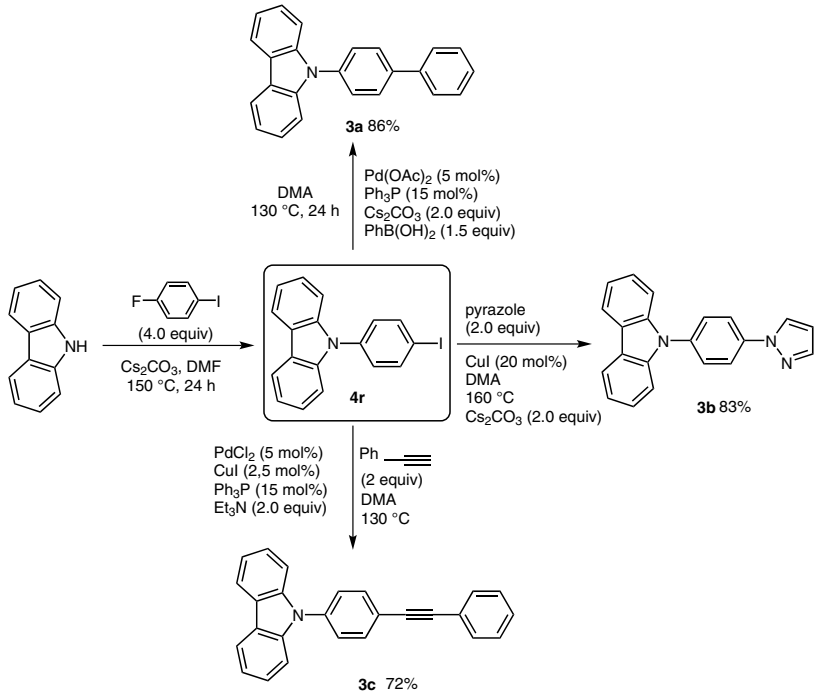
The effect of various solvents was also determined. The reaction carried out in *N*,*N*-dimethylformamide, dimethyl sulfoxide, or *N*,*N*-dimethylacetamide produced good to ex-

Table 2 Optimisation of the Metal-Free Reaction Conditions[a]



Entry	Solvent	Base	Temp (°C)	Yield (%)
1	DMF	KOH	110	27[b]
2	DMF	KOH	110	35
3	DMF	KOH	130	43
4	DMF	KOH	150	48
5	DMF	KOH	170	52
6	DMF	K_2CO_3	150	36
7	DMF	*t*-BuOK	150	13
8	DMF	$K_3PO_4·3H_2O$	150	trace
9	DMF	*t*-BuONa	150	36
10	DMF	NaOH	150	28
11	DMF	Na_2CO_3	150	trace
12	DMF	$NaHCO_3$	150	trace
13	**DMF**	**Cs_2CO_3**	**150**	**92**
14	DMF	Cs_2CO_3	150	74[c]
15	DMF	Cs_2CO_3	150	94[d]
16	DMSO	Cs_2CO_3	150	85
17	DMA	Cs_2CO_3	150	71
18	NMP	Cs_2CO_3	150	54
19	toluene	Cs_2CO_3	150	trace

[a] Reaction conditions: 1-fluoro-4-iodobenzene (2.0 mmol), carbazole (0.5 mmol), base (2.0 mmol), solvent (2 mL), 24 h; isolated yields are given.
[b] Base (1.0 mmol).
[c] 1-Fluoro-4-iodobenzene (1.0 mmol).
[d] 1-Fluoro-4-iodobenzene (3.0 mmol).



Scheme 6 Functionalisation of 9-(4-iodophenyl)-9*H*-carbazole (**4r**)

cellent yields (Table 2; entries 13, 16, and 17). The yield decreased upon switching to *N*-methyl-2-pyrrolidinone as the solvent (Table 2, entry 18), while the nonpolar solvent toluene gave a poor result (Table 2, entry 19).

The scope for the N-arylation of a range of carbazoles with halogenated fluorobenzenes was explored under the optimised metal-free reaction conditions (Scheme 7).

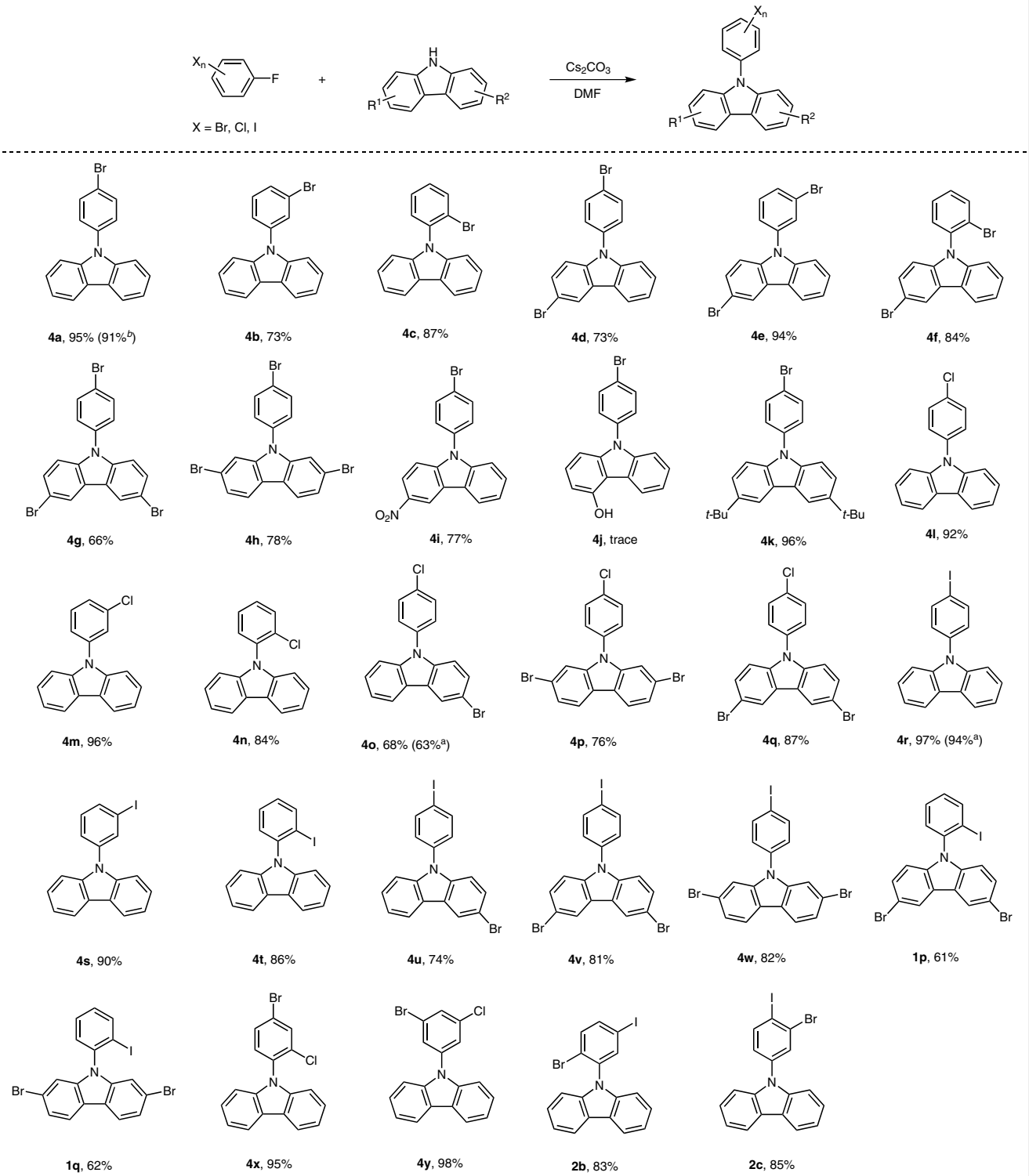
The electronic and steric hindrance effects of brominated fluorobenzenes in reactions with carbazoles were first studied. Electronic and steric hindrance effects were not apparent in the metal-free catalytic system. Thus, 4-bromo-, 3-bromo-, and the sterically hindered 2-bromo-substituted fluorobenzene smoothly reacted with carbazole to give the corresponding products in good to excellent yields (Scheme 7, 4a–c). The nature of substituents on carbazole was then investigated. The results show an evident electronic effect of substituents attached to the aromatic rings of carbazole. 1-Bromo-4-fluorobenzene smoothly reacted with carbazoles bearing electron-neutral or electron-donating 3,6-di-*tert*-butyl groups to produce excellent yields (Scheme 7, 4a and **4k**). However, carbazoles bearing electron-withdrawing substituents such as 3-bromo, 3,6-dibromo, 2,7-dibromo, 3-nitro, and 4-hydroxy groups, showed relatively lower reactivity (Scheme 7, 4d and **4g**–**j**).

Brominated fluorobenzenes were replaced by a series of other halogenated fluorobenzenes to extend the scope of N-arylation. As listed in Scheme 7, chlorinated and iodinated fluorobenzenes showed similar reactivities as the brominated fluorobenzenes upon metal-free N-arylation, successfully converting various carbazoles into the corresponding N-arylated products in moderate to excellent yields (Scheme 7; **4l**–**w**, **1p**, and **1q**).

Encouraged by the success of monohalogenated fluorobenzenes, fluorobenzenes bearing an additional two different halogen groups were also investigated for reactivity and selectivity with the metal-free catalytic system. Four dihalogenated fluorobenzenes were examined under the optimised conditions. Remarkably, there was full conversion of all four dihalogenated fluorobenzenes, resulting in excellent product yields (Scheme 7; **4x**, **4y**, **2b**, and **2c**). Controlling the selectivity of multiple halogens on an aromatic ring to avoid the formation of various byproducts has been a challenge in previous studies. Interestingly, this metal-free method showed excellent selectivity of the aromatic halogen atoms, yielding the desired products with minimal amounts of byproducts. The results indicate that nucleophilic attack is likely to occur at the fluoro-substituted carbon atom of the halogenated aromatic ring.

The reaction is scalable, and could be scaled up to a gram scale without any setbacks (Scheme 7; **4a**[a], **4o**[a], and **4r**[a]).

In summary, the catalytic system generated in situ from an inexpensive copper salt, the commercially available ligand *N*,*N*-diisopropylethylamine, and a simple inorganic base is able to perform the C–N bond-formation reaction of halogenated fluorobenzenes with carbazoles with high selectivity. The selectivity of iodine and fluorine atoms on the aromatic ring was evaluated in the developed catalytic sys-



Scheme 7 Metal-free N-arylation of carbazoles with halogenated fluorobenzenes. *Reagents and conditions*: fluorinated halobenzene (2.0 mmol), carbazole (0.5 mmol), Cs_2CO_3 (2.0 mmol), DMF (2 mL), under air, 150 °C, 24 h; isolated yields are given. [a] The reaction was performed with a 10-fold amount of the reactants in DMF (20 mL) at 150 °C for 24 h.

tem. The selectivity of fluorinated iodobenzenes can be tuned by adjusting the position of the iodine atom on the aromatic ring. The preferred coupling site of the fluorinated iodobenzenes was switched from the iodine atom to the fluorine atom when the position of the iodine atom on the aromatic ring was changed from the 3- or 4-position to the 2-position. The main factor that affects the selectivity of halides attached to aromatic rings is steric hindrance. These reaction processes are composed of two competing reactions: a metal-free nucleophilic substitution reaction and a copper-catalysed C–N bond formation. Control experiments showed that the copper-catalysed coupling of halogenated benzenes with carbazole was significantly affected by steric hindrance; however, steric hindrance has only a slight effect on the nucleophilic substitution reaction. Therefore, fluorinated iodobenzenes containing a sterically demanding group preferentially react at the C–F bond rather than the C–I bond. The major advantage of the metal-free process is that the selectivity of halogen atoms on the aromatic ring can be completely controlled, giving a range of N-arylated carbazoles bearing chlorine, bromine, and iodine groups. The resulting halogenated N-arylated carbazoles are synthetically useful intermediates for the pharmaceutical, agrochemical, and materials science fields.

All copper-catalysed reactions were performed in Schlenk tubes under nitrogen atmosphere. DMF, DMSO, DMA, and NMP were distilled from 4-Å molecular sieves. All reagents were purchased from commercial sources and used without additional purification. NMR spectra were recorded on a Varian Inova 400 or a Bruker 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). 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.

Copper-Catalysed N-Arylation of Carbazoles; General Procedure

A mixture of a fluorinated aryl iodide (2.0 mmol), a carbazole (0.5 mmol), a copper source (0.05 mmol), a ligand (0.05 or 0.1 mmol), and a 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 completion, the mixture was added to brine (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined extract was concentrated under reduced pressure and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

Metal-Free N-Arylation of Carbazoles; General Procedure

A mixture of a fluorinated aryl halide (2.0 mmol), a carbazole (0.5 mmol), and a base (2.0 mmol) in solvent (2 mL) was allowed to react under air atmosphere. The reaction mixture was heated to the specified temperature for 24 h. After reaction completion, the mixture was added to brine (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined extract was concentrated under reduced pressure and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

9-(4-Fluorophenyl)-9*H*-carbazole (1a)[6d]

Purification by flash chromatography [petroleum ether (PE)]; white solid; yield: 114 mg (87%); mp 113–115 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.6 Hz, 2 H), 7.56–7.53 (m, 2 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.37–7.30 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.60 (d, J_{C-F} = 246.0 Hz), 141.01, 133.60 (d, J_{C-F} = 3.1 Hz), 129.00 (d, J_{C-F} = 8.5 Hz), 125.99, 123.26, 120.33, 119.98, 116.82 (d, J_{C-F} = 22.6 Hz), 109.49.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –35.9 to –35.98 (m).

9-(3-Fluorophenyl)-9*H*-carbazole (1b)

Purification by flash chromatography (PE); white solid; yield: 102 mg (78%); mp 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (dt, *J* = 7.6, 0.8 Hz, 2 H), 7.63–7.58 (m, 1 H), 7.50–7.41 (m, 5 H), 7.38–7.32 (m, 3 H), 7.21 (ddd, *J* = 8.4, 2.8, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.47 (d, J_{C-F} = 246.6 Hz), 140.56, 139.34 (d, J_{C-F} = 9.8 Hz), 131.08 (d, J_{C-F} = 9.2 Hz), 126.16, 123.59, 122.73 (d, J_{C-F} = 3.2 Hz), 120.44, 120.36, 114.52 (d, J_{C-F} = 7.1 Hz), 114.30 (d, J_{C-F} = 8.8 Hz), 109.73.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.46.

HRMS (MALDI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{12}FN$: 261.0948; found: 261.0947.

9-(2-Fluorophenyl)-9*H*-carbazole (1c)

Purification by flash chromatography (PE); yellow oil; yield: 74 mg (57%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (dt, *J* = 8.0, 0.8 Hz, 2 H), 7.60 (td, *J* = 8.0, 1.6 Hz, 1 H), 7.55–7.50 (m, 1 H), 7.47–7.37 (m, 4 H), 7.35–7.31 (m, 2 H), 7.27 (dt, *J* = 8.0, 0.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.36 (d, J_{C-F} = 251.4 Hz), 140.85, 129.88 (d, J_{C-F} = 1.2 Hz), 129.61 (d, J_{C-F} = 7.6 Hz), 126.05, 125.10 (d, J_{C-F} = 3.9 Hz), 123.55, 120.33, 120.18, 117.39 (d, J_{C-F} = 19.6 Hz), 109.89 (d, J_{C-F} = 1.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –118.46.

HRMS (MALDI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{12}FN$: 261.0948; found: 261.0954.

3-Bromo-9-(4-fluorophenyl)-9*H*-carbazole (1d)

Purification by flash chromatography (PE); yellow oil; yield: 121 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 1.6 Hz, 1 H), 8.12 (d, *J* = 7.2 Hz, 1 H), 7.54–7.46 (m, 4 H), 7.37–7.31 (m, 4 H), 7.22 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.81 (d, J_{C-F} = 246.4 Hz), 141.38, 139.71, 133.18 (d, J_{C-F} = 3.0 Hz), 129.02, 128.83 (d, J_{C-F} = 20.4 Hz), 126.81, 125.06, 123.13, 122.25, 120.58, 120.47, 117.03 (d, J_{C-F} = 22.6 Hz), 112.83, 111.03, 109.79.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.99 to –113.01 (m).

HRMS (MALDI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{11}BrFN$: 339.0053; found: 339.0053.

3,6-Dibromo-9-(4-fluorophenyl)-9*H*-carbazole (1e)

Purification by flash chromatography (PE); white solid; yield: 134 mg (64%); mp 164–166 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dd, *J* = 2.0, 0.4 Hz, 2 H), 7.51 (dd, *J* = 8.8, 2.0 Hz, 2 H), 7.48–7.45 (m, 2 H), 7.33–7.29 (m, 2 H), 7.17 (dd, *J* = 8.4, 0.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.19, 160.71, 140.01, 132.69, 132.66, 129.46, 128.95, 128.87, 123.86, 123.25, 117.25, 117.03, 113.16, 111.24.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –34.72 to –34.79 (m).

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{10}Br_2FN$: 416.9159; found: 416.9159.

9-(4-Fluorophenyl)-3-nitro-9*H*-carbazole (1f)[15]

Purification by flash chromatography (PE–EtOAc, 10:1); yellow solid; yield: 37 mg (24%); mp 145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (d, *J* = 2.0 Hz, 1 H), 8.33 (dd, *J* = 8.8, 2.0 Hz, 1 H), 8.22 (d, *J* = 7.6 Hz, 1 H), 7.56–7.53 (m, 3 H), 7.45–7.32 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.29 (d, J_{C-F} = 247.9 Hz), 144.06, 142.46, 141.51, 132.25 (d, J_{C-F} = 3.3 Hz), 129.13 (d, J_{C-F} = 8.6 Hz), 127.76, 123.08, 122.94, 121.89, 121.70, 120.98, 117.40 (d, J_{C-F} = 16.9 Hz), 117.25, 110.46, 109.31.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.63.

3,6-Di-*tert*-butyl-9-(4-fluorophenyl)-9*H*-carbazole (1h)

Purification by flash chromatography (PE); pale yellow solid; yield: 176 mg (95%); mp 192–193 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 1.6, 0.4 Hz, 2 H), 7.53–7.49 (m, 2 H), 7.47 (dd, *J* = 8.4, 2.0 Hz, 2 H), 7.30–7.25 (m, 4 H), 1.47 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.52, 160.06, 142.86, 139.36, 134.07, 134.04, 128.61, 128.52, 123.60, 123.20, 116.76, 116.53, 116.22, 108.86, 34.69, 31.96.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –36.65 to –36.72 (m).

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{26}H_{28}FN$: 373.2200; found: 373.2199.

3-Bromo-9-(3-fluorophenyl)-9*H*-carbazole (1i)

Purification by flash chromatography (PE); colourless oil; yield: 117 mg (69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (m, 1 H), 8.11 (d, *J* = 8.0 Hz, 1 H), 7.63–7.58 (m, 1 H), 7.55–7.45 (m, 3 H), 7.37–7.29 (m, 4 H), 7.26–7.21 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.45 (d, J_{C-F} = 247.2 Hz), 140.86, 139.20, 138.82 (d, J_{C-F} = 9.7 Hz), 131.23 (d, J_{C-F} = 9.2 Hz), 128.81, 126.90, 125.32, 123.18, 122.62 (d, J_{C-F} = 3.3 Hz), 122.47, 120.75, 120.61, 114.80 (d, J_{C-F} = 20.9 Hz), 114.30 (d, J_{C-F} = 22.7 Hz), 113.13, 111.19, 109.93.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.04 (m).

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrFN$: 339.0053; found: 339.0053.

3,6-Dibromo-9-(3-fluorophenyl)-9*H*-carbazole (1j)

Purification by flash chromatography (PE); white solid; yield: 128 mg (61%); mp 154–155 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 2 H), 7.61 (q, *J* = 8.0 Hz, 1 H), 7.55–7.52 (m, 2 H), 7.34–7.22 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.44 (d, J_{C-F} = 247.6 Hz), 139.49, 138.31 (d, J_{C-F} = 9.8 Hz), 131.38 (d, J_{C-F} = 9.1 Hz), 129.58, 124.10, 123.32, 122.53 (d, J_{C-F} = 3.3 Hz), 115.16 (d, J_{C-F} = 20.9 Hz), 114.26 (d, J_{C-F} = 22.7 Hz), 113.47, 111.39.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –109.75 to –109.77 (m).

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{10}Br_2FN$: 416.9159; found: 416.9159.

2,7-Dibromo-9-(3-fluorophenyl)-9*H*-carbazole (1k)

Purification by flash chromatography (PE); white solid; yield: 111 mg (53%); mp 149 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.0 Hz, 2 H), 7.62 (q, *J* = 8.0 Hz, 1 H), 7.54 (s, 2 H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.30–7.22 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.50 (d, J_{C-F} = 248.0 Hz), 141.46, 137.93 (d, J_{C-F} = 9.7 Hz), 131.58 (d, J_{C-F} = 9.2 Hz), 124.02, 122.70 (d, J_{C-F} = 3.3 Hz), 121.83, 121.55, 120.20, 115.49 (d, J_{C-F} = 20.8 Hz), 114.39 (d, J_{C-F} = 22.8 Hz), 112.94.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –109.17 to –109.22 (m).

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{10}Br_2FN$: 416.9159; found: 416.9159.

3,6-Di-*tert*-butyl-9-(3-fluorophenyl)-9*H*-carbazole (1l)

Purification by flash chromatography (PE); white solid; yield: 156 mg (84%); mp 143–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 2.0 Hz, 2 H), 7.59–7.53 (m, 1 H), 7.50 (dd, *J* = 4.8, 2.0 Hz, 2 H), 7.42–7.38 (m, 3 H), 7.35–7.31 (m, 1 H), 7.18–7.13 (m, 1 H), 1.50 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.60, 162.13, 143.22, 139.80, 139.71, 138.81, 130.89, 130.80, 123.72, 123.50, 122.19, 122.16, 116.27, 113.91, 113.70, 113.68, 109.10, 34.71, 31.96.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –33.09 to –33.15 (m).

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{26}H_{28}FN$: 373.2200; found: 373.2198.

3,6-Di-*tert*-butyl-9-(2-fluorophenyl)-9*H*-carbazole (1m) and 3,6-Di-*tert*-butyl-9-(2-iodophenyl)-9*H*-carbazole (1n)

Compounds **1m** and **1n** are difficult to isolate by chromatography. The molar ratio **1m**/**1n** was 2:1, as determined by NMR spectroscopy.

3-Bromo-9-(2-iodophenyl)-9*H*-carbazole (1o)

Purification by flash chromatography (PE); yellow oil; yield: 110 mg (49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 2.0 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 2 H), 7.60 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.51 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.48–7.43 (m, 2 H), 7.36–7.29 (m, 2 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 6.94 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.05, 140.61, 139.87, 139.33, 130.66, 130.54, 129.88, 128.68, 126.74, 125.01, 123.20, 122.20, 120.60, 120.43, 112.89, 111.69, 110.37, 99.04.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrIN$: 446.9114; found: 446.9112.

3,6-Dibromo-9-(2-iodophenyl)-9*H*-carbazole (1p)

Purification by flash chromatography (PE); white solid; yield: 97 mg (37%); mp 162–164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (dd, *J* = 1.6, 0.4 Hz, 2 H), 8.12 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.60 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.53 (d, *J* = 2.0 Hz, 1 H), 7.51 (d, *J* = 2.0 Hz, 1 H), 7.42 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.34–7.29 (m, 1 H), 6.92 (dd, *J* = 8.4, 0.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.69, 139.64, 139.36, 130.91, 130.40, 129.96, 129.48, 123.85, 123.37, 113.27, 111.86, 98.81.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{10}Br_2IN$: 526.8200; found: 526.8211.

2,7-Dibromo-9-(2-iodophenyl)-9*H*-carbazole (1q)

Purification by flash chromatography (PE); white solid; yield: 84 mg (32%); mp 162–163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.61 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.43–7.40 (m, 3 H), 7.32 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.15 (d, *J* = 1.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.51, 140.71, 138.97, 131.02, 130.39, 130.02, 123.71, 121.57, 121.53, 119.98, 113.32, 98.80.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{10}Br_2IN$: 526.8200; found: 526.8211.

9,9′-(4-Bromo-1,3-phenylene)bis(9*H*-carbazole) (2a)

Purification by flash chromatography (PE); white solid; yield: 65 mg (53%); mp 226 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.12 (m, 5 H), 7.79 (d, *J* = 2.4 Hz, 1 H), 7.73 (dd, *J* = 8.4, 2.3 Hz, 1 H), 7.55–7.45 (m, 6 H), 7.35 (q, *J* = 8.0 Hz, 4 H), 7.27 (d, *J* = 8.0 Hz, 2 H).

^{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.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{30}H_{19}BrN_2$: 486.0726; found: 486.0726.

9-(2-Bromo-5-iodophenyl)-9*H*-carbazole (2b)

Purification by flash chromatography (PE); white solid; yield: 152 mg (68%); mp 138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.6 Hz, 2 H), 7.85 (d, *J* = 2.0 Hz, 1 H), 7.75 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.61 (d, *J* = 8.4 Hz, 1 H), 7.48–7.44 (m, 2 H), 7.37–7.33 (m, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H).

^{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.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrIN$: 446.9114; found: 446.9119.

9-(3-Bromo-4-iodophenyl)-9*H*-carbazole (2c)

Purification by flash chromatography (PE); pale yellow solid; yield: 83 mg (37%); mp 168–170 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.0 Hz, 2 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 2.4 Hz, 1 H), 7.41–7.35 (m, 4 H), 7.28 (t, *J* = 8.0 Hz, 2 H), 7.20 (dd, *J* = 8.0, 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.32, 140.24, 138.89, 130.99, 130.89, 127.00, 126.28, 123.67, 120.62, 120.51, 109.52, 99.15.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrIN$: 446.9114; found: 446.9113.

9-(1,1′-Biphenyl-4-yl)-9*H*-carbazole (3a)[16]

Purification by flash chromatography (PE); white solid; yield: 138 mg (86%); mp 218–219 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dd, *J* = 1.2, 0.8 Hz, 1 H), 8.17 (dd, *J* = 1.2, 0.8 Hz, 1 H), 7.86–7.83 (m, 2 H), 7.73–7.70 (m, 2 H), 7.68–7.65 (m, 2 H), 7.55–7.41 (m, 7 H), 7.35–7.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.81, 140.26, 140.23, 136.82, 128.91, 128.46, 127.60, 127.28, 127.10, 125.91, 123.38, 120.28, 119.92, 109.79.

9-(4-(1*H*-Pyrazol-1-yl)phenyl)-9*H*-carbazole (3b)

Purification by flash chromatography (PE–EtOAc, 40:1); white solid; yield: 128 mg (83%); mp 185–186 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dd, *J* = 8.0, 0.8 Hz, 2 H), 8.05 (d, *J* = 2.0 Hz, 1 H), 7.98–7.94 (m, 2 H), 7.81 (d, *J* = 1.2 Hz, 1 H), 7.70–7.66 (m, 2 H), 7.47–7.42 (m, 4 H), 7.34–7.30 (m, 2 H), 6.56 (dd, *J* = 2.4, 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.47, 140.78, 139.07, 135.79, 128.12, 126.79, 126.01, 123.38, 120.47, 120.33, 120.06, 109.57, 108.02.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{15}N_3$: 309.1260; found: 309.1260.

9-(4-(Phenylethynyl)phenyl)-9*H*-carbazole (3c)[2h]

Purification by flash chromatography (PE); white solid; yield: 124 mg (72%); mp 144–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (t, *J* = 1.2 Hz, 1 H), 8.15 (dd, *J* = 1.2, 0.8 Hz, 1 H), 7.79 (t, *J* = 2.0 Hz, 1 H), 7.77 (t, *J* = 2.0 Hz, 1 H), 7.62–7.58 (m, 4 H), 7.46–7.38 (m, 7 H), 7.34–7.30 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.51, 137.50, 133.06, 131.63, 128.45, 128.38, 126.80, 126.00, 123.49, 122.98, 122.23, 120.31, 120.15, 109.69, 90.26, 88.60.

9-(4-Bromophenyl)-9*H*-carbazole (4a)[17]

Purification by flash chromatography (PE); pale yellow solid; yield: 153 mg (95%); mp 143–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.42–7.34 (m, 6 H), 7.29–7.26 (m, 2 H).

^{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.

9-(3-Bromophenyl)-9*H*-carbazole (4b)[18]

Purification by flash chromatography (PE); colourless oil; yield: 118 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 2 H), 7.70 (s, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.41–7.37 (m, 5 H), 7.28–7.25 (m, 2 H).

^{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.

9-(2-Bromophenyl)-9*H*-carbazole (4c)[19]

Purification by flash chromatography (PE); white solid; yield: 140 mg (87%); mp 95–96 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.0 Hz, 2 H), 7.84 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.52–7.43 (m, 2 H), 7.39 (t, *J* = 8.0 Hz, 3 H), 7.28 (t, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H).

^{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.

3-Bromo-9-(4-bromophenyl)-9*H*-carbazole (4d)[19]

Purification by flash chromatography (PE); white solid; yield: 146 mg (73%); mp 138–139 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.50–7.40 (m, 4 H), 7.36–7.29 (m, 2 H), 7.23 (d, *J* = 8.0 Hz, 1 H).

^{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.

3-Bromo-9-(3-bromophenyl)-9*H*-carbazole (4e)[19]

Purification by flash chromatography (PE–EtOAc, 40:1); white solid; yield: 188 mg (94%); mp 80–82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.70 (s, 1 H), 7.63–7.59 (m, 1 H), 7.50–7.25 (m, 7 H).

^{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.

3-Bromo-9-(2-bromophenyl)-9*H*-carbazole (4f)[19]

Purification by flash chromatography (PE); colourless oil; yield: 168 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (dd, *J* = 2.0, 0.4 Hz, 1 H), 8.15–8.12 (m, 1 H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.57–7.51 (m, 2 H), 7.49–7.42 (m, 3 H), 7.37–7.33 (m, 1 H), 7.11 (dt, *J* = 8.4, 0.8 Hz, 1 H), 6.98 (dd, *J* = 8.4, 0.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.19, 139.47, 136.22, 134.32, 130.99, 130.46, 128.94, 128.67, 126.76, 125.02, 123.69, 123.16, 122.20, 120.56, 120.46, 112.92, 111.57, 110.26.

3,6-Dibromo-9-(4-bromophenyl)-9*H*-carbazole (4g)[20]

Purification by flash chromatography (PE); white solid; yield: 158 mg (66%); mp 217–218 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H).

^{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.

2,7-Dibromo-9-(4-bromophenyl)-9*H*-carbazole (4h)[20]

Purification by flash chromatography (PE); white solid; yield: 186 mg (78%); mp 190–192 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.46–7.38 (m, 6 H).

^{13}C NMR (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.

9-(4-Bromophenyl)-3-nitro-9*H*-carbazole (4i)

Purification by flash chromatography (PE–EtOAc, 10:1); yellow solid; yield: 141 mg (77%); mp 192 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (d, *J* = 2.0 Hz, 1 H), 8.34 (dd, *J* = 8.8, 2.0 Hz, 1 H), 8.22 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.57–7.52 (m, 1 H), 7.47–7.36 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.67, 142.07, 141.63, 135.39, 133.57, 128.75, 127.82, 123.27, 123.08, 122.40, 121.94, 121.85, 121.03, 117.32, 110.46, 109.35.

HRMS (MALDI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{11}BrN_2O_2$: 365.9998; found: 365.9993.

9-(4-Bromophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (4k)[21]

Purification by flash chromatography (PE); white solid; yield: 208 mg (96%); mp 158–159 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.0 Hz, 2 H), 7.71 (dt, *J* = 8.8, 2.8 Hz, 2 H), 7.48–7.42 (m, 4 H), 7.32 (dt, *J* = 8.4, 0.4 Hz, 2 H), 1.47 (s, 18 H).

^{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.

9-(4-Chlorophenyl)-9*H*-carbazole (4l)[22]

Purification by flash chromatography (PE); white solid; yield: 129 mg (92%); mp 144–147 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.43–7.35 (m, 4 H), 7.31–7.23 (m, 2 H).

^{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.

9-(3-Chlorophenyl)-9*H*-carbazole (4m)[6d]

Purification by flash chromatography (PE); pale yellow oil; yield: 133 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 2 H), 7.54 (t, *J* = 1.6 Hz, 1 H), 7.47–7.36 (m, 7 H), 7.29–7.22 (m, 2 H).

^{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.

9-(2-Chlorophenyl)-9*H*-carbazole (4n)[23]

Purification by flash chromatography (PE); pale yellow solid; yield: 117 mg (84%); mp 98–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.6 Hz, 2 H), 7.66–7.64 (m, 1 H), 7.49–7.42 (m, 3 H), 7.38 (t, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H).

^{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.

3-Bromo-9-(4-chlorophenyl)-9*H*-carbazole (4o)

Purification by flash chromatography (PE); white solid; yield: 121 mg (68%); mp 131–133 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.47–7.40 (m, 4 H), 7.33–7.27 (m, 2 H), 7.19 (d, *J* = 8.0 Hz, 1 H).

^{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.

HRMS (MALDI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{11}BrClN$: 354.9758; found: 354.9751.

2,7-Dibromo-9-(4-chlorophenyl)-9*H*-carbazole (4p)

Purification by flash chromatography (PE); white solid; yield: 165 mg (76%); mp 166–168 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.46–7.40 (m, 6 H).

^{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.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{10}Br_2ClN$: 432.8863; found: 432.8859.

3,6-Dibromo-9-(4-chlorophenyl)-9*H*-carbazole (4q)[24]

Purification by flash chromatography (PE); white solid; yield: 189 mg (87%); mp 214–216 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H).

^{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.

9-(4-Iodophenyl)-9*H*-carbazole (4r)[25]

Purification by flash chromatography (PE); white solid; yield: 179 mg (97%); mp 133–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dt, *J* = 8.0, 1.2 Hz, 2 H), 7.95–7.91 (m, 2 H), 7.44–7.37 (m, 4 H), 7.35–7.28 (m, 4 H).

^{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.

9-(3-Iodophenyl)-9*H*-carbazole (4s)[26]

Purification by flash chromatography (PE); white solid; yield: 166 mg (90%); mp 111–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.6 Hz, 2 H), 7.93 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.40 (q, *J* = 8.0 Hz, 4 H), 7.30 (q, *J* = 8.0 Hz, 3 H).

^{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.

9-(2-Iodophenyl)-9*H*-carbazole (4t)

Purification by flash chromatography (PE); pale yellow solid; yield: 159 mg (86%); mp 130–131 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.0 Hz, 2 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.41–7.37 (m, 3 H), 7.30–7.21 (m, 3 H), 7.02 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.65, 140.44, 140.33, 130.59, 130.30, 129.71, 125.89, 123.19, 120.33, 119.92, 110.09, 99.19.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{12}IN$: 369.0014; found: 369.0015.

3-Bromo-9-(4-iodophenyl)-9*H*-carbazole (4u)

Purification by flash chromatography (PE); pale yellow solid; yield: 166 mg (74%); mp 171–172 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 7.49–7.41 (m, 2 H), 7.36–7.22 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.84, 139.20, 137.01, 128.81, 128.74, 126.81, 125.24, 123.13, 122.41, 120.62, 120.56, 112.99, 111.03, 109.78, 92.47.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrIN$: 446.9114; found: 446.9114.

3,6-Dibromo-9-(4-iodophenyl)-9*H*-carbazole (4v)[25]

Purification by flash chromatography (PE); pale yellow solid; yield: 212 mg (81%); mp 188–190 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 2 H), 7.94 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 4 H).

^{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.

2,7-Dibromo-9-(4-iodophenyl)-9*H*-carbazole (4w)[27]

Purification by flash chromatography (PE); white solid; yield: 216 mg (82%); mp 207–208 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.92 (m, 4 H), 7.46 (s, 2 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H).

^{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.

9-(4-Bromo-2-chlorophenyl)-9*H*-carbazole (4x)

Purification by flash chromatography (PE); pale yellow solid; yield: 170 mg (95%); mp 145–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (t, *J* = 0.8 Hz, 1 H), 8.15 (t, *J* = 0.8 Hz, 1 H), 7.87 (d, *J* = 2.4 Hz, 1 H), 7.63 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.45–7.38 (m, 3 H), 7.34–7.30 (m, 2 H), 7.09 (dt, *J* = 8.4, 0.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.59, 134.83, 134.31, 133.75, 131.91, 131.43, 126.04, 123.41, 122.62, 120.39, 120.25, 109.80.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrClN$: 354.9758; found: 354.9752.

9-(3-Bromo-5-chlorophenyl)-9*H*-carbazole (4y)

Purification by flash chromatography (PE); white solid; yield: 177 mg (98%); mp 147–148 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 2 H), 7.62 (s, 1 H), 7.59 (s, 1 H), 7.52 (s, 1 H), 7.43–7.40 (m, 4 H), 7.30 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.13, 139.86, 136.17, 130.20, 128.25, 126.26, 125.88, 123.66, 123.47, 120.69, 120.44, 109.46.

HRMS (MALDI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{11}BrClN$: 354.9758; found: 354.9755.

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Supporting Information

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