RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

One-pot two-step synthesis of N-arylcarbazole-based skeleton

Sheng Tao, Ning Liu,* and Bin Dai*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A highly site-selective, one-pot, sequential C–N and C–C bond forming process was developed, affording carbazole-based skeleton that contained biphenyl and diarylacetylene cores. The success of this process is attributed to the use of fluorinated iodoarenes as starting material, the fluorine group of which preferentially reacts with carbazole. The subsequent coupling of the intermediate iodinated N-arylcarbazole with arylboronic acid or arylacetylene produced desired products. The intermediate underwent Pd-catalyzed Ullmann coupling with excess fluorinated iodoarenes in the absence of arylboronic acid or arylacetylene, resulting in Ullmann coupling products in a one-pot process.

Introduction

Carbazole-based skeleton that contains biphenyl and diarylacetylene cores is widely applied in dye-sensitized solar cells[1] and organic light-emitting diodes,[2] and as key component in the construction of natural products.[3]

Carbazole-based skeleton compounds are synthesized via two-pot synthetic approaches.[4] N-Arylated carbazoles are prepared through copper-catalyzed C–N forming reaction between carbazoles and dihalobenzene. After purification, the intermediate undergoes cross-coupling with arylboronic acid[5] or arylacetylene[6] in the presence of palladium as catalyst. One-pot strategy is a useful technique in synthetic organic chemistry, because it can minimizes solvent use, time, and the number of purification steps compared with individual multi-step syntheses.[7] We attempted to develop a one-pot method without purification step to prepare carbazole-based skeleton compounds. We have recently developed a copper-catalysed method for N-arylation of carbazole.[8] The study showed that halogenated fluorobenzenes undergo a highly site-selective coupling at the fluoride group with carbazole through nucleophilic substitution reaction in the metal-free condition. We infer that the metal-free condition eliminates the interference of metal for the succeeding transformation, and the tolerated halides provide an opportunity to enhance the N-arylated carbazole compounds further and convert them into useful compounds. In this paper, fluorinated iodobenzenes underwent sequential N-arylation and palladium-catalysed cross-coupling to achieve desired products with good yields. In the absence of arylboronic acids or arylacetylene, the Ullmann coupling between 9-(4-iodophenyl)-9H-carbazole and 4-fluoro-iodobenzene smoothly proceeded and then resulted in products.

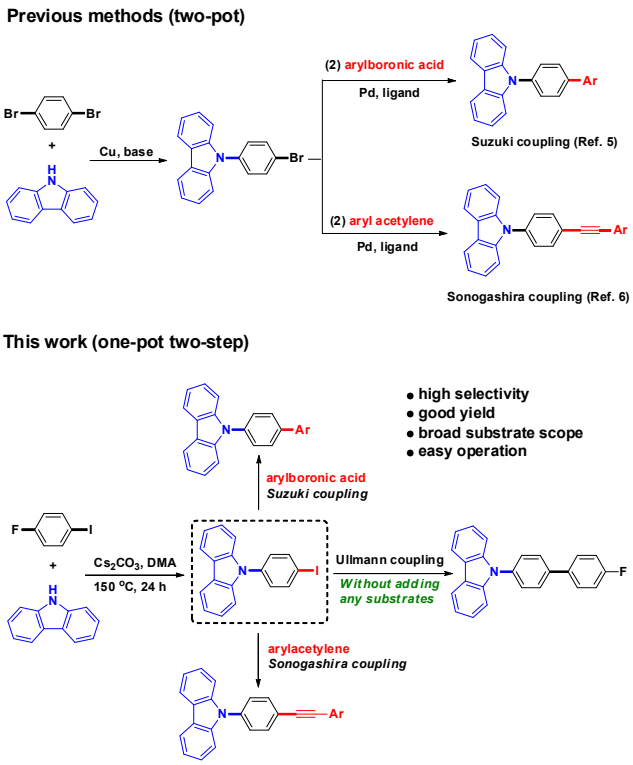


Figure 1 Methods for synthesis of carbazole-based skeleton.

Results and Discussion

One-pot two-step N-arylation and Pd-catalysed Suzuki coupling among 4-fluoro-iodobenzene, carbazole, and phenylboronic

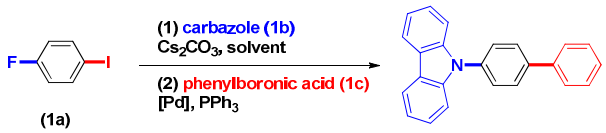
School of Chemistry and Chemical Engineering, Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, North 4th Road, Shihezi, Xinjiang 832003, China. E-mail: ninglau@163.com; dbinly@126.com; Fax: +86-0993-205-7270; Tel: +86-0993-205-7157

† 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

acid was selected as the model reaction to optimize the reaction conditions. The reaction conditions, including Pd sources, solvents, and molar ratios of substrates, were evaluated.

The effect of molar ratio of substrates on the coupling of 4-fluoro-iodobenzene with carbazole was initially examined. Molar ratio is a crucial factor for product yield. A 1.0:0.5:1.0 molar ratio of 4-fluoro-iodobenzene, carbazole, and phenylboronic acid was the optimal reaction condition for the one-pot two-step method (Table 1, entry 8).

Table 1 One-pot substitution-Suzuki coupling process: optimization of reaction condition[a]



Entry	Solvent	Molar ratio (**1a:1b:1c**)	Palladium	Yield (%)
1	DMA	0.5:0.5:0.5	$Pd(OAc)_2$	22
2	DMA	0.5:0.75:0.5	$Pd(OAc)_2$	42
3	DMA	0.5:1.0:0.5	$Pd(OAc)_2$	38
4	DMA	0.5:1.0:1.0	$Pd(OAc)_2$	31
5	DMA	1.0:0.5:0.5	$Pd(OAc)_2$	73
6	DMA	2.0:0.5:0.5	$Pd(OAc)_2$	63
7	DMA	1.0:0.5:2.0	$Pd(OAc)_2$	79
8	DMA	1.0:0.5:1.0	$Pd(OAc)_2$	83
9	DMF	1.0:0.5:1.0	$Pd(OAc)_2$	51
10	DMSO	1.0:0.5:1.0	$Pd(OAc)_2$	72
11	NMP	1.0:0.5:1.0	$Pd(OAc)_2$	49
12	DMA	1.0:.0.5:1.0	$PdCl_2$	88
13	DMA	1.0:0.5:1.0	$Pd(OH)_2$	81
14	DMA	1.0:0.5:1.0	Pd/C	74
15[b]	DMA	1.0:.0.5:1.0	$PdCl_2$	62
16[c]	DMA	1.0:.0.5:1.0	$PdCl_2$	83
17[d]	**DMA**	**1.0:.0.5:1.0**	**$PdCl_2$**	**89**
18[e]	DMA	1.0:.0.5:1.0	$PdCl_2$	80
19[f]	DMA	1.0:.0.5:1.0	$PdCl_2$	52

[a] Reaction conditions: (1) 4-fluoro-iodobenzene, carbazole, Cs_2CO_3 (1.0 mmol) in solvent (1 mL) under air, 150 °C, 24 h. [b] 130 °C. [c] 170 °C. (2) phenylboronic acid, palladium source (5 mol%), PPh_3 (10 mol%), were added without purification step, 130 °C, 6 h. Isolated yield. [d] 120 °C. [e] 110 °C. [f] 90 °C.

The effect of different solvents was also determined. The reaction carried out in DMA (N,N-dimethylacetamide) produced best yields (Table 1, entry 8). The yield decreased upon switching to DMF (N,N-dimethylformamide), NMP (N-methyl-2-pyrrolidone), or DMSO (dimethyl sulfoxide) (Table 1, entries 9, 10, and 11). Pd-catalysed cross-coupling is often affected by Pd source. Therefore, we evaluated different Pd sources. The experimental results showed that $PdCl_2$ was more catalytically active than the other Pd sources (Table 1, entry 12).

The effect of temperature for the N-arylation was investigated. The reaction rate remarkably accelerated when the increasing temperature from 130 °C to 150 °C (Table 1, entries 15, and 12). Upon further increase of the reaction temperature to 170 °C, the isolated yield slightly decreased to 83% (Table 1, entry 16). Nuclear magnetic resonance analysis showed that too high reaction temperature was likely to form disubstituted side-products due to the selectivity decrease of 4-fluoro-iodobenzene.

The effect of temperature for the Suzuki coupling was also investigated. The temperature has an evident promoting effect on the reaction rate when from 90 °C to 120 °C (Table 1, entries 17, 18, and 19). Upon further increase of the reaction temperature to 130 °C, but has no evident change in yield (Table 1, entry 12). Therefore, 120 °C was selected as the optimised reaction temperature used in subsequent studies.

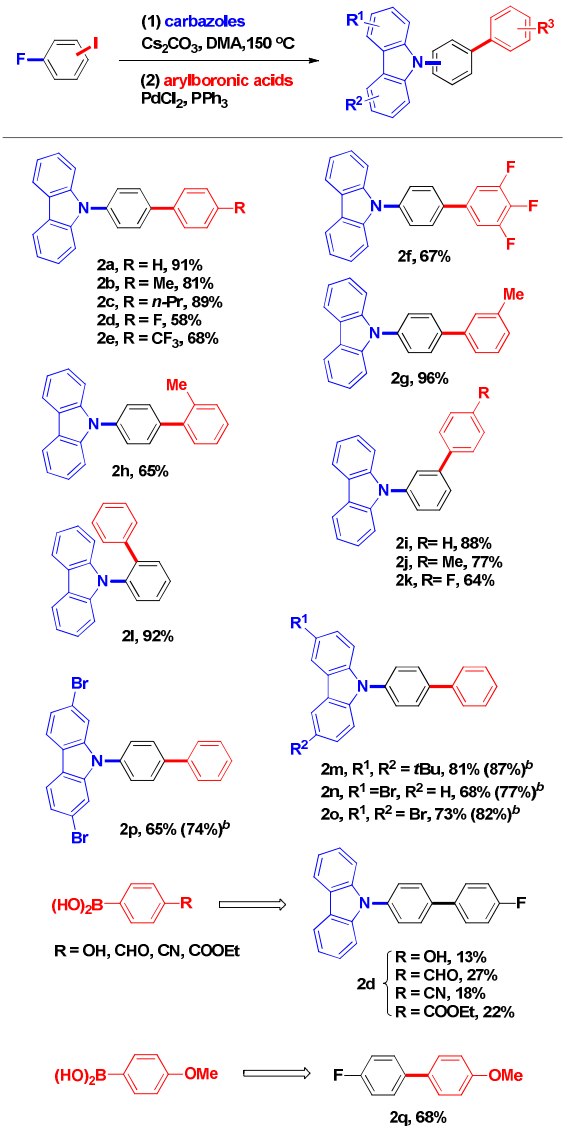
The scope and limitations for the Suzuki coupling of arylboronic acids were initially examined (Table 2).

The reactivity of arylboronic acids was tested under optimised reaction conditions. The desired products were obtained in good-to-excellent yields (Table 2, 2a-h). The electronic effect of *para*-substituents that bear the aromatic ring of boronic acids was observed. Arylboronic acids that contained electron-donating and electron-neutral groups such as 4-H, 4-Me, and 4-*n*Pr, smoothly reacted with intermediates generated from N-arylation, resulting in high-yield products (Table 2, 2a-c). However, the arylboronic acids that contained electron-withdrawing group were less reactive in the developed system and produced moderate product yields (Table 2, 2d-f). The electronic effect of *meta*-substituted arylboronic acids was not evident in the developed one-pot system. 3-Methylphenylboronic acid successfully reacted with 9-(4-iodophenyl)-9H-carbazole to provide good results (Table 2, 2g). The steric hindrance effect of *ortho*-substituted arylboronic acids presented a certain influence on the reaction rate. 2-Methylphenylboronic acid showed considerably slower conversion and obtained moderate yield (Table 2, 2h).

The Suzuki coupling was not affected by the electronic nature and steric hindrance effects of fluorinated iodobenzenes. Thus, 3-iodo- or 2-iodo-substituted carbazolylbenzene smoothly underwent coupling with arylboronic acids and resulted in moderate to good yield products (Table 2, 2i-l).

The scope of coupling for carbazoles was also investigated under optimised reaction conditions. The electronic effect of carbazoles was not evident. Thus, 3,6-di*tert*-butyl 3,6-dibromo, and 2,7-dibromo group substituted carbazoles smoothly underwent coupling and produced good yields (Table 2, 2m-p).

Table 2 One-pot substitution-Suzuki coupling process[a]



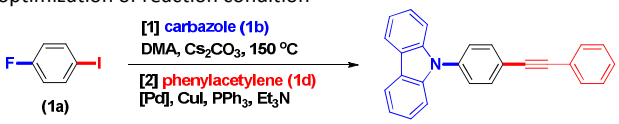
[a] Reaction conditions: (1) fluorinated iodobenzenes (1.0 mmol), carbazoles (0.5 mmol), Cs_2CO_3 (1.0 mmol) in DMA (1 mL) under air, 150 °C, 24 h. (2) phenylboronic acid (1.0 mmol), $PdCl_2$ (5 mol%), PPh_3 (10 mol%), were added without purification step, 120 °C, 6 h. Isolated yield. [b] 130 °C.

Arylboronic acids containing sensitive groups such as 4-OH, 4-CHO, 4-COOEt, 4-CN, and 4-OMe, were evaluated in the developed catalytic system. The results showed that no desired products were obtained. Arylboronic acids bearing 4-OH, 4-CHO, 4-COOEt, and 4-CN, have not participated in the reaction, but a sequential N-arylation and Ullmann coupling occurred between 4-fluoro-iodobenzene and carbazole (Table 2). 4-Methoxyphenylboronic acid preferentially reacted with 4-fluoro-iodobenzene to generate 4-fluoro-4'-methoxy-1,1'-biphenyl compound instead of attacking on the intermediate from the N-arylation between 4-fluoro-iodobenzene and carbazole (Table 2, 2q).

One-pot two-step process through N-arylation and Pd-catalyzed Sonogashira coupling among 4-fluoro-iodobenzene, carbazole, and phenylacetylene was selected as the model reaction to optimize the reaction conditions. In this model, different reaction conditions, including Pd sources, solvents, and molar ratios of substrates, were evaluated. A 1.0:0.5:1.0 molar ratio of 4-fluoro-iodobenzene, carbazole, and phenylacetylene was the optimal reaction condition for the one-pot method (Table 3, entry 5).

To probe the efficiency of CuI and Et_3N, we designed control experiments by conducting the reaction in the absence of CuI and Et_3N, respectively. The results indicated that the CuI can efficiently promote the coupling reaction from 75% to 93% of the product yield (Table 3, entry 5 vs. 11). Et_3N is crucial for the reaction. The reaction was difficult to proceed in the absence of Et_3N, and only 13% product yield was obtained (Table 3, entry 12).

Table 3. One-pot substitution-Sonogashira coupling process: optimization of reaction condition[a]



Entry	Solvent	Molar ratio (**1a:1b:1d**)	Palladium	Yield (%)
1	DMA	0.5:0.5:1.0	$PdCl_2$	67
2	DMA	0.5:0.75:1.0	$PdCl_2$	52
3	DMA	0.5:1.0:1.0	$PdCl_2$	81
4	DMA	0.5:2.0:1.0	$PdCl_2$	41
5	**DMA**	**1.0:0.5:1.0**	**$PdCl_2$**	**93**
6	DMSO	1.0:0.5:1.0	$PdCl_2$	84
7	DMF	1.0:0.5:1.0	$PdCl_2$	46
8	NMP	1.0:0.5:1.0	$Pd(OAc)_2$	78
9	DMA	1.0:0.5:1.0	$Pd(OH)_2$	68
10	DMA	1.0:0.5:1.0	Pd/C	63
11[b]	DMA	1.0:0.5:1.0	$PdCl_2$	75
12[c]	DMA	1.0:0.5:1.0	$PdCl_2$	13
13[d]	DMA	1.0:0.5:1.0	$PdCl_2$	89
14[e]	DMA	1.0:0.5:1.0	$PdCl_2$	83
15[f]	DMA	1.0:0.5:1.0	$PdCl_2$	70

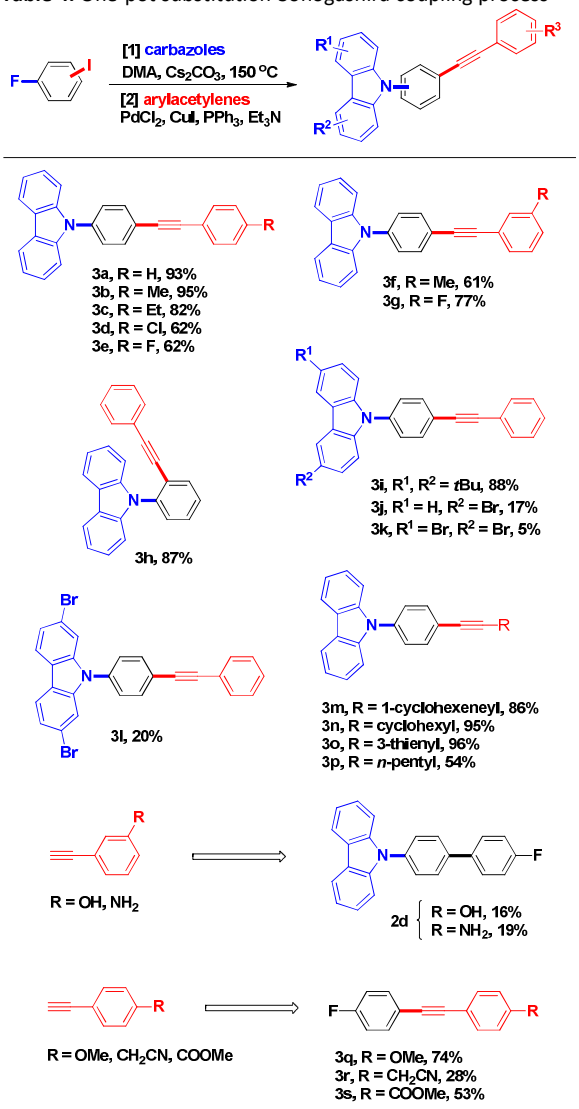
[a] Reaction conditions: (1) 4-fluoro-iodobenzene, carbazole, Cs_2CO_3 (1.0 mmol) in solvent (1 mL) under air, 150 °C, 24 h. (2) phenylacetylene (1.0 mmol), palladium source (5 mol%), CuI (2.5 mol%), PPh_3 (10 mol%), Et_3N (1 mmol), were added without purification step, 130 °C, 6 h. Isolated yield. [b] Without CuI. [c] Without Et_3N. [d] 120 °C. [e] 110 °C. [f] 90 °C.

The effect of temperature for the Sonogashira coupling was investigated (Table 3, entries 5, 13, 14, and 15). 130 °C was

selected as the optimised reaction temperature for Sonogashira coupling (Table 3, entry 5).

The scope and limitations for the Sonogashira coupling of arylacetylenes were examined. The reactivity of arylacetylenes was tested under optimised reaction conditions, and the desired products were obtained in good to excellent yields (Table 4).

Table 4. One-pot substitution-Sonogashira coupling process[a]



[a] Reaction conditions: (1) fluorinated iodobenzenes (1.0 mmol), carbazoles (0.5 mmol), Cs_2CO_3 (1.0 mmol) in DMA (1 mL) under air, 150 °C, 24 h. (2) arylacetylene (1.0 mmol), $PdCl_2$ (5 mol%), CuI (2.5 mol%), PPh_3 (10 mol%), Et_3N (1 mmol), were added without purification step, 130 °C, 6 h. Isolated yield.

The electronic effect of *para*-substituents bearing the aromatic ring of arylacetylenes was evident. Arylacetylenes containing electron-donating and electron-neutral groups were highly reactive and resulted in excellent yields (Table 4, 3a-c). However, the arylacetylenes bearing electron-withdrawing group were less reactive in the developed one-pot system and resulted in moderate product yields (Table 4, 3d and 3e). The reactivity of arylacetylenes decreased when their groups bear at the *meta*-position (Table 4, 3f and 3g). Steric hindrance effect of *ortho*-substituted arylacetylenes was not observed in the developed system (Table 4, 3h).

The scope of one-pot method for carbazoles was also investigated under the optimised reaction conditions. The electronic effect of carbazoles was significantly evident. Carbazoles bearing 3,6-di*tert*-butyl group exhibited higher reactivity than those bearing 3,6-dibromo and 2,7-dibromo groups (Table 4, 3i vs. 3j-l).

The optimised reaction conditions were also applied in the coupling of alicyclic and aliphatic alkynes. The reactivity of alicyclic alkynes was evidently higher than aliphatic alkynes (Table 4, 3m-o vs. 3p). Alicyclic alkynes were successfully converted to the desired products with excellent yields (Table 4, 3m-o). However, aliphatic alkynes showed considerably slower conversion and resulted in moderate product yield in the same reaction condition (Table 4, 3p).

Arylacetylenes containing sensitive groups such as 3-OH, 3-NH_2, 4-COOMe, 4-CH_2CN, and 4-OMe, were evaluated in the developed catalytic system. 3-Ethynylphenol and 3-ethynylaniline have not participated in the reaction, but coupling product through sequential N-arylation and Ullmann coupling was obtained (Table 4). Arylacetylenes bearing 4-COOMe, 4-CH_2CN, and 4-OMe, preferentially reacted with 4-fluoro-iodobenzene instead of attacking on the intermediate from the N-arylation between 4-fluoro-iodobenzene and carbazole (Table 4, 3q-s).

In view of the unexpected results in Table 2, and 4, arylboronic acid or arylacetylene was eliminated from the reaction system. The results showed that the reaction process was not terminated in the N-arylation of carbazole in the presence of palladium catalyst. Instead, the process continued to react with fluorinated iodobenzenes through the Ullmann coupling and yielded products.

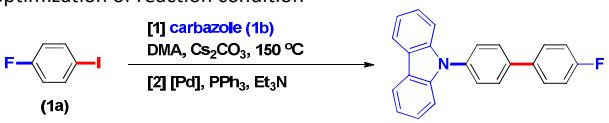
The reaction conditions of the one-pot two-step method for N-arylation and Ullmann coupling were evaluated (Table 5). A 1.5:0.5 molar ratio of 4-fluoro-iodobenzene and carbazole was the optimal reaction conditions for the one-pot two-step method in DMA in the presence of $PdCl_2$ as catalyst (Table 5, entry 3). Palladium catalyst was crucial for the Ullmann coupling between 9-(4-iodophenyl)-9H-carbazole and 4-fluoro-iodobenzene.

To investigate the efficiency of CuI, $PdCl_2$, and Et_3N, we designed three control experiments (Table 5, entries 11-13). The results showed that CuI inhibited Ullmann coupling reaction and homo-coupling of 4-fluoro-iodobenzene increased (Table 5, entry 11). Et_3N can efficiently promote the coupling reaction (Table 5, entry 12). The coupling reaction was difficult to start in the absence of Pd catalyst (Table 5, entry 13).

The effect of temperature for the Ullman coupling was investigated (Table 5, entries 3, 14, 15, and 16). The results showed that the temperature served a crucial function in the

Ullman coupling. The higher reaction temperature is necessary to activate the intermediate from N-arylation between fluorinated iodobenzenes and carbazole, so 130 °C was selected as the optimised reaction temperature (Table 5, entry 3).

Table 5. One-pot substitution-Ullmann coupling process: optimization of reaction condition[a]

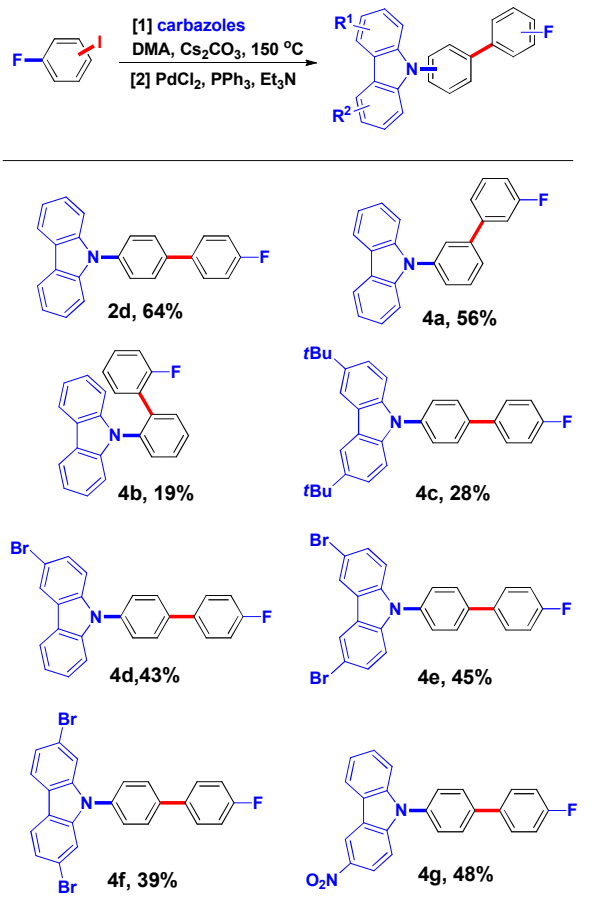


Entry	Solvent	Molar ratio (**1a:1b**)	Palladium	Yield (%)
1	DMA	0.75:0.5	$PdCl_2$	47
2	DMA	1.0:0.5	$PdCl_2$	68
3	**DMA**	**1.5:0.5**	**$PdCl_2$**	**83**
4	DMA	2.0:0.5	$PdCl_2$	85
5	DMSO	1.5:0.5	$PdCl_2$	72
6	DMF	1.5:0.5	$PdCl_2$	58
7	NMP	1.5:0.5	$PdCl_2$	64
8	DMA	1.5:0.5	$Pd(OAc)_2$	77
9	DMA	1.5:0.5	$Pd(OH)_2$	69
10	DMA	1.5:0.5	Pd/C	65
11[b]	DMA	1.5:0.5	$PdCl_2$	73
12[c]	DMA	1.5:0.5	$PdCl_2$	53
13[d]	DMA	1.5:0.5	no	0
14[e]	DMA	1.5:0.5	$PdCl_2$	66
15[f]	DMA	1.5:0.5	$PdCl_2$	57
16[g]	DMA	1.5:0.5	$PdCl_2$	35

[a] Reaction conditions: (1) 4-fluoro-iodobenzene, carbazole, Cs_2CO_3 (1.0 mmol) in solvent (1 mL) under air, 150 °C, 24 h. (2) phenylacetylene (1.0 mmol), palladium source (5 mol%), PPh_3 (10 mol%), Et_3N (1 mmol), were added without purification step, 130 °C, 6 h. Isolated yield. [b] Adding CuI (2.5 mol%). [c] Without Et_3N. [d] Without $PdCl_2$. [e] 120 °C. [f] 110 °C. [g] 90 °C.

The scope and limitations for N-arylation and Pd-catalyzed Ullmann coupling were evaluated (Table 6). The electronic effect of the fluorine group bearing the iodobenzene ring was not observed. The iodobenzene with fluorine substitution at the *para* or *meta* position to the aromatic ring showed similar reactivity and produced moderate yield (Table 6, 2d and 4a). The steric hindrance effect of fluorinated iodobenze was evident and only 19% desired product yield was obtained (Table 6, 4b). The electronic effect of carbazole was also evident for Ullmann coupling. The carbazole with electronic-withdrawing group at the para position to the aromatic ring showed higher reactivity than that with electronic-donating group (Table 6, 4c vs. 4d-g).

Table 6. One-pot substitution-Ullmann coupling process[a]



[a] Reaction conditions: (1) fluorinated iodobenzenes (1.0 mmol), carbazoles (0.5 mmol), Cs_2CO_3 (1.0 mmol) in DMA (1 mL) under air, 150 °C, 24 h. (2) $PdCl_2$ (5 mol%), PPh_3 (10 mol%), and Et_3N (1.0 mmol), were added without purification step, 130 °C, 6 h. Isolated yield.

To simplify the operating procedures, we simultaneously conducted N-arylation and Pd-catalysed cross coupling reactions in one-pot (Figure 2). Interestingly, the one-pot method for N-arylation and Pd-catalysed Sonogashira coupling showed a slight decrease in yield and achieve high conversion (Figure 2). However, N-arylation and Pd-catalysed Suzuki coupling in one-pot is difficult to perform simultaneously (Figure 2). In the presence of Pd-catalyst, 4-fluoro-iodobenzene preferred to react with phenylboronic acid or undergo homo-couple to afford products **5a** and **5b**. The one-pot method for N-arylation and Pd-catalysed Ullmann coupling showed evident decrease in yield and achieved high conversion (Figure 2). The product analysis revealed that the Pd-catalyst activated the C–I bond of fluorinated iodobenzene and lead to decrease reaction selectivity.

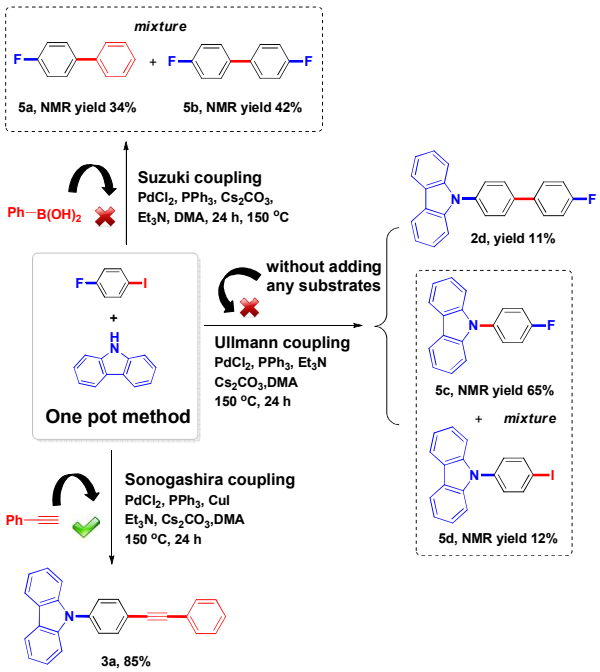


Figure 2 Trial experiments for the one-pot synthesis of N-arylcarbazole-based skeleton.

One-pot four-compound competing reaction was conducted as shown in Figure 3. The reaction processes were composed of competing reactions, namely, Suzuki coupling reaction, Sonogashira coupling reaction and Ullmann coupling reaction. The one-pot procedure for N-arylation and Pd-catalysed Sonogashira performed coupling smoothly and produced good yield (Figure 3).

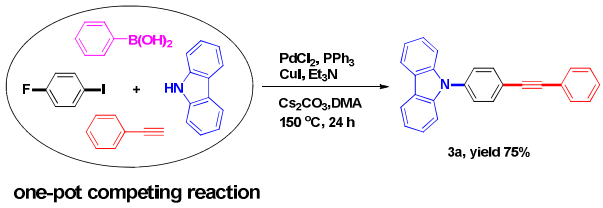


Figure 3 One-pot competing reaction.

Experimental

General experimental methods. All reactions were performed in glass vial under air atmosphere. DMF, DMSO, DMA, and NMP were distilled from 4Å-molecular sieves. Other reagents were purchased from commercial sources used without additional purification. NMR spectra were recorded on 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 substitution-Suzuki coupling process. A mixture of 4-fluoro-iodobenzene (1.0 mmol), carbazoles (0.5 mmol), Cs_2CO_3 (0.05 mmol) was added to a glass vial in solvent (1 mL) under air atmosphere. The reaction mixture was heated to 150 °C for 24 h. The reaction mixture was cooled to room temperature. To this mixture was added arylboronic acid (1.0 mmol), palladium sources (0.025 mmol), and PPh_3 (0.05 mmol), and the mixture was heated to 130 °C for 6 h. 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.

General procedure for substitution-Sonogashira coupling process. A mixture of 4-fluoro-iodobenzene (1.0 mmol), carbazoles (0.5 mmol), Cs_2CO_3 (0.05 mmol) was added to a glass vial in solvent (1 mL) under air atmosphere. The reaction mixture was heated to 150 °C for 24 h. The reaction mixture was cooled to room temperature. To this mixture was added arylacetylene (1.0 mmol), palladium sources (0.025 mmol), PPh_3 (0.05 mmol), CuI (0.0125 mmol), and Et_3N (1 mmol), and the mixture was heated to 130 °C for 6 h. 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.

General procedure for substitution-Ullmann coupling process. A mixture of 4-fluoro-iodobenzene (1.0 mmol), carbazoles (0.5 mmol), Cs_2CO_3 (0.05 mmol) was added to a glass vial in solvent (1 mL) under air atmosphere. The reaction mixture was heated to 150 °C for 24 h. The reaction mixture was cooled to room temperature. To this mixture was added palladium sources (0.025 mmol), PPh_3 (0.05 mmol), CuI (0.0125 mmol), and Et_3N (1 mmol), and the mixture was heated to 130 °C for 6 h. 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-([1,1'-Biphenyl]-4-yl)-9H-carbazole (2a).[4c] Purification by flash chromatography (petroleum ether): a white solid (145 mg, 91%), mp = 227-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 1.2 Hz, J = 0.8 Hz, 1H), 8.17 (dd, J = 1.2 Hz, J = 0.8 Hz, 1H), 7.86-7.83 (m, 2H), 7.73-7.70 (m, 2H), 7.68-7.65 (m, 2H), 7.55-7.41 (m, 7H), 7.35-7.31 (m, 2H), ppm; ^{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, ppm.

9-(4'-Methyl-[1,1'-biphenyl]-4-yl)-9H-carbazole (2b). Purification by flash chromatography (petroleum ether): a white solid (135 mg, 81%), mp = 235-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.67-7.62 (m, 4H), 7.53-7.45 (m, 4H), 7.36-7.32 (m, 4H), 2.48 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.93, 140.28, 137.52, 137.42, 136.60, 129.72, 128.31, 127.34, 127.00, 125.99, 123.44, 120.35, 119.97, 109.90, 21.21, ppm; HRMS (EI): m/z calcd for $C_{25}H_{19}N$ $[M]^+$ 333.1517, found 333.1520.

9-(4'-Propyl-[1,1'-biphenyl]-4-yl)-9H-carbazole (2c). Purification by flash chromatography (petroleum ether): a white solid (161 mg, 89%), mp = 161-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.64 (q, J = 4.0 Hz, 4H), 7.51-7.43 (m, 4H), 7.36-7.31 (m, 4H), 2.70 (t, J = 7.6 Hz, 2H), 1.75 (sext, J = 7.6 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.31, 140.90, 140.30, 137.62, 136.55, 129.09, 128.30, 127.30, 126.96, 125.94, 123.40, 120.30, 119.92, 109.86, 37.74, 24.57, 13.91, ppm; HRMS (EI): m/z calcd for $C_{27}H_{23}N$ $[M]^+$ 361.1830, found 361.1834.

9-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-9H-carbazole (2d).[8] Purification by flash chromatography (petroleum ether): a white solid (98 mg, 58%), mp = 186-187 °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'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)-9H-carbazole (2e). Purification by flash chromatography (petroleum ether): a white solid (132 mg, 68%), mp = 251-252 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.6 Hz, 2H), 7.87-7.78 (m, 6H), 7.72 (d, J = 8.4 Hz, 2H), 7.53-7.45 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.76, 140.72, 138.71, 137.82, 128.72, 127.49, 127.43, 126.05, 125.95, 125.91, 123.54, 120.40, 120.16, 109.77, 29.72, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.41, ppm.

9-(3',4',5'-Trifluoro-[1,1'-biphenyl]-4-yl)-9H-carbazole (2f). Purification by flash chromatography (petroleum ether): a white solid (125 mg, 67%), mp = 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (m, 2H), 7.76-7.68 (m, 4H), 7.51-7.45 (m, 4H), 7.38-7.30 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.66 (ddd, $J_{C\text{-}F}$ = 248.4 Hz, $J_{C\text{-}F}$ = 10.0 Hz, $J_{C\text{-}F}$ = 4.3 Hz), 140.67, 138.01, 137.07 (dd, $J_{C\text{-}F}$ = 3.7 Hz, $J_{C\text{-}F}$ = 2.1 Hz), 136.39 (ddd, $J_{C\text{-}F}$ = 12.4 Hz, $J_{C\text{-}F}$ = 7.7 Hz, $J_{C\text{-}F}$ = 4.6 Hz), 128.33, 128.32, 127.52, 126.13, 123.61, 120.46, 120.29, 111.13 (dd, $J_{C\text{-}F}$ = 16.0 Hz, $J_{C\text{-}F}$ = 6.1 Hz), 109.74, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -133.58 (d, $J_{F\text{-}F}$ = 20.3 Hz), 161.89 (t, $J_{F\text{-}F}$ = 20.3 Hz), ppm.

9-(3'-Methyl-[1,1'-biphenyl]-4-yl)-9H-carbazole (2g). Purification by flash chromatography (petroleum ether): a white solid (160 mg, 96%), mp = 153-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.55-7.41 (m, 7H), 7.36-7.32 (m, 2H), 7.26 (d, J = 7.6 Hz, 2H), 2.51 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.89, 140.47, 140.29, 138.58, 136.77, 128.87, 128.53, 128.40, 127.98, 127.29, 125.96, 124.26, 123.42, 120.33, 119.95, 109.86, 21.61, ppm; HRMS (EI): m/z calcd for $C_{25}H_{19}N$ $[M]^+$ 333.1517, found 333.1520.

9-(2'-Methyl-[1,1'-biphenyl]-4-yl)-9H-carbazole (2h). Purification by flash chromatography (petroleum ether): a white solid (104 mg, 65%), mp = 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.0 Hz, 2H), 7.67-7.46 (m, 8H), 7.41-7.33 (m, 6H), 2.44 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.12, 141.08, 140.93, 136.40, 135.45, 130.69, 130.58, 129.88, 127.66, 126.66, 126.02, 125.99, 123.46, 120.38, 120.01, 109.92, 20.66, ppm; HRMS (EI): m/z calcd for $C_{25}H_{19}N$ $[M]^+$ 333.1517, found 333.1520.

9-([1,1'-Biphenyl]-3-yl)-9H-carbazole (2i).[9] Purification by flash chromatography (petroleum ether): a white solid (140 mg, 88%), mp = 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 7.6 Hz, 2H), 7.85 (t, J = 2.0 Hz, 1H), 7.75-7.68 (m, 4H), 7.61-7.58 (m, 1H), 7.53-7.40 (m, 7H), 7.36-7.32 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.14, 140.90, 140.14, 138.24, 130.28, 128.98, 127.87, 127.19, 126.14, 126.00, 125.83, 125.75, 123.43, 120.36, 119.99, 109.84, ppm.

9-(4'-Methyl-[1,1'-biphenyl]-3-yl)-9H-carbazole (2j). Purification by flash chromatography (petroleum ether): a white solid (128 mg, 77%), mp = 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 7.6 Hz, 2H), 7.84 (t, J = 2.0 Hz, 1H), 7.74-7.68 (m, 2H), 7.61-7.45 (m, 7H), 7.37-7.31 (m, 4H), 2.45 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.07, 140.92, 138.19, 137.76, 137.27, 130.23, 129.71, 127.02, 126.00, 125.94, 125.53, 123.43, 120.36, 119.97, 109.89, 21.17, ppm; HRMS (EI): m/z calcd for $C_{25}H_{19}N$ $[M]^+$ 333.1517, found 333.1520.

9-(4'-Fluoro-[1,1'-biphenyl]-3-yl)-9H-carbazole (2k). Purification by flash chromatography (petroleum ether): a white solid (108 mg, 64%), mp = 67 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.22 (m, 2H), 7.85-7.81 (m, 1H), 7.73-7.59 (m, 5H), 7.55-7.46 (m, 4H), 7.40-7.35 (m, 2H), 7.23-7.18 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.81 (d, $J_{C\text{-}F}$ = 245.8 Hz), 142.16, 140.91, 138.35, 136.27 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.40, 129.74, 128.82 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.04, 126.08, 126.00, 125.87, 125.62, 123.50, 120.44, 120.10, 115.93 (d, $J_{C\text{-}F}$ = 21.4 Hz), 109.82, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.60 - -114.62 (m), ppm; HRMS (MALDI): *m/z* calcd for $C_{24}H_{16}FN$ $[M]^+$ 337.1261, found 337.1263.

9-([1,1'-Biphenyl]-2-yl)-9H-carbazole (2l). Purification by flash chromatography (petroleum ether): a white solid (147 mg, 92%), mp = 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.6 Hz, 2H), 7.71 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H), 7.65-7.51 (m, 3H), 7.32-7.29 (m, 2H), 7.23-7.19 (m, 2H), 7.12-7.00 (m, 7H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.15, 141.08, 138.61, 134.80, 131.55, 129.80, 128.80, 128.74, 128.07, 127.76, 127.25, 125.62, 123.06, 120.04, 119.44, 109.98, ppm; HRMS (EI): m/z calcd for $C_{24}H_{17}N$ $[M]^+$ 319.1361, found 319.1369.

9-([1,1'-Biphenyl]-4-yl)-3,6-di-tert-butyl-9H-carbazole (2m). Purification by flash chromatography (petroleum ether): a white solid (175 mg, 81%), mp = 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.73 (), (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.56-7.51 (m, 4H), 7.45 (d, J = 8.8 Hz, 3H), 1.52 (d, J = 1.6 Hz, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.95, 140.40, 139.80, 139.28, 137.44, 128.98, 128.43, 127.60, 127.16, 126.97, 123.69, 123.49, 116.31, 109.35, 34.82, 32.11, ppm.

9-([1,1'-Biphenyl]-4-yl)-3-bromo-9H-carbazole (2n).[10] Purification by flash chromatography (petroleum ether): a white solid (135 mg, 68%), mp = 153-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 1.6 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.74-7.71 (m,

2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.57-7.53 (m, 3H), 7.50-7.44 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.22, 140.67, 140.14, 139.55, 136.38, 129.03, 128.67, 128.64, 127.79, 127.26, 127.17, 126.75, 125.20, 123.10, 122.38, 120.55, 120.43, 112.79, 111.37, 110.12, ppm.

9-([1,1'-Bphenyl]-4-yl)-3,6-dibromo-9H-carbazole (2o). Purification by flash chromatography (petroleum ether): a white solid (174 mg, 73%), mp = 218-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (d, *J* = 1.6 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.72-7.69 (m, 2H), 7.59-7.52 (m, 6H), 7.47-7.43 (m, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.03, 139.98, 139.85, 135.88, 129.43, 129.03, 128.74, 127.87, 127.18, 127.16, 124.01, 123.25, 113.14, 111.59, ppm; HRMS (EI): m/z calcd for $C_{24}H_{15}Br_2N$ $[M]^+$ 474.9571, found 474.9580.

9-([1,1'-Biphenyl]-4-yl)-2,7-dibromo-9H-carbazole (2p). Purification by flash chromatography (petroleum ether): a white solid (155 mg, 65%), mp = 199-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.98 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.60-7.53 (m, 6H), 7.47-7.43 (m, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.89, 141.37, 139.99, 135.49, 129.02, 128.92, 127.88, 127.34, 127.22, 123.69, 121.75, 121.50, 120.04, 113.12, ppm; HRMS (EI): m/z calcd for $C_{24}H_{15}Br_2N$ $[M]^+$ 474.9571, found 474.9580.

4-Fluoro-4'-methoxy-1,1'-biphenyl (2q).[11] Purification by flash chromatography (petroleum ether): a white solid (138 mg, 68%), mp = 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53-7.48 (m, 4H), 7.12 (t, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), pmm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.09 (d, $J_{C\text{-}F}$ = 244.0 Hz), 159.11, 136.96 (d, $J_{C\text{-}F}$ = 3.3 Hz), 132.84, 128.21 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.03, 115.52 (d, $J_{C\text{-}F}$ = 21.1 Hz), 114.25, 55.37, ppm.

9-(4-(Phenylethynyl)phenyl)-9H-carbazole (3a).[6a] Purification by flash chromatography (petroleum ether): a white solid (160 mg, 93%), mp = 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.17 (t, *J* = 1.2 Hz, 1H), 8.15 (dd, *J* = 1.2 Hz, *J* = 0.8 Hz, 1H), 7.79 (t, *J* = 2.0 Hz, 1H), 7.77 (t, *J* = 2.0 Hz, 1H), 7.62-7.58 (m, 4H), 7.46-7.38 (m, 7H), 7.34-7.30 (m, 2H), ppm; ^{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, ppm.

9-(4-(p-Tolylethynyl)phenyl)-9H-carbazole (3b). Purification by flash chromatography (petroleum ether): a white solid (170 mg, 95%), mp = 200-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.17 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.52-745 (m, 6H), 7.35-7.31 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.59, 138.70, 137.37, 133.04, 131.58, 129.21, 126.85, 126.05, 123.53, 122.52, 120.36, 120.18, 119.95, 109.76, 90.54, 88.03, 21.57, ppm; HRMS (EI): m/z calcd for $C_{27}H_{19}N$ $[M]^+$ 357.1512, found 357.1513.

9-(4-((4-Ethylphenyl)ethynyl)phenyl)-9H-carbazole (3c). Purification by flash chromatography (petroleum ether): a white solid (152 mg, 82%), mp = 191-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.49-7.43 (m, 4H), 7.35-7.31 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.01, 140.60, 137.38, 133.06, 131.68, 128.03, 126.85, 126.06, 123.55, 122.54, 120.37, 120.19, 109.77, 90.59, 88.04, 28.90, 15.39, ppm; HRMS (EI): m/z calcd for $C_{28}H_{21}N$ $[M]^+$ 371.1674, found 371.1680.

9-(4-((4-Chlorophenyl)ethynyl)phenyl)-9H-carbazole (3d). Purification by flash chromatography (petroleum ether): a white solid (117 mg, 62%), mp = 234-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48-7.43 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.52, 137.80, 134.55, 133.12, 132.89, 128.80, 126.88, 126.08, 123.59, 121.89, 121.55, 120.40, 120.27, 109.73, 89.61, 89.18, ppm; HRMS (EI): m/z calcd for $C_{26}H_{16}ClN$ $[M]^+$ 377.0971, found 377.0975.

9-(4-((4-Fluorophenyl)ethynyl)phenyl)-9H-carbazole (3e). Purification by flash chromatography (petroleum ether): a white solid (92 mg, 51%), mp = 254 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.62-7.58 (m, 4H), 7.48-7.43 (m, 4H), 7.35-7.31 (m, 2H), 7.11 (t, *J* = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.67 (d, $J_{C\text{-}F}$ = 248.5 Hz), 140.56, 137.67, 133.60 (d, $J_{C\text{-}F}$ = 8.3 Hz), 133.08, 126.89, 126.09, 123.60, 122.09, 120.41, 120.27, 119.16 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.78 (d, $J_{C\text{-}F}$ = 21.9 Hz), 109.75, 89.26, 88.39 (d, $J_{C\text{-}F}$ = 1.5 Hz), ppm.

9-(4-(m-Tolylethynyl)phenyl)-9H-carbazole (3f).[8] Purification by flash chromatography (petroleum ether): a white solid (109 mg, 61%), mp = 109-110 °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.

9-(4-((3-Fluorophenyl)ethynyl)phenyl)-9H-carbazole (3g). Purification by flash chromatography (petroleum ether): a white solid (139 mg, 77%), mp = 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.49-7.43 (m, 4H), 7.40-7.29 (m, 5H), 7.14-7.08 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.45 (d, $J_{C\text{-}F}$ = 245.1 Hz), 140.52, 137.91, 133.21, 130.03 (d, $J_{C\text{-}F}$ = 8.6 Hz), 127.57 (d, $J_{C\text{-}F}$ = 3.1 Hz), 126.88, 126.09, 124.90 (d, $J_{C\text{-}F}$ = 9.4 Hz), 123.60, 121.74, 120.30 (d, $J_{C\text{-}F}$ = 11.7 Hz), 118.46 (d, $J_{C\text{-}F}$ = 22.7 Hz), 115.81 (d, $J_{C\text{-}F}$ = 21.1 Hz), 109.74, 89.54, 89.01 (d, $J_{C\text{-}F}$ = 3.3 Hz), ppm.

9-(2-(Phenylethynyl)phenyl)-9H-carbazole (3h). Purification by flash chromatography (petroleum ether): a white solid (149 mg, 87%), mp = 108-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.27 (d, *J* = 8.4 Hz, 2H), 7.87 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 7.68-7.54 (m, 3H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 4H), 7.23-7.12 (m, 3H), 6.71 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.04, 139.13, 133.47, 131.38, 129.50, 129.08, 128.38, 128.16, 128.08, 125.89, 123.48, 123.09, 122.61, 120.32, 119.94, 110.70, 95.57, 86.24, ppm; HRMS (EI): m/z calcd for $C_{26}H_{17}N$ $[M]^+$ 343.1361, found 343.1362.

3,6-Di-*tert*-butyl-9-(4-(phenylethynyl)phenyl)-9H-carbazole (3i).[6a] Purification by flash chromatography (petroleum ether): a white solid (188 mg, 87%), mp = 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 2.0 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.62-7.58 (m, 4H), 7.50 (dd, J = 8.4 Hz, J = 2.0 Hz, 2H), 7.43-7.40 (m, 5H), 1.49 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.21, 138.93, 138.13, 133.06, 131.70, 128.46, 126.42, 123.76, 123.61, 123.16, 121.69, 116.33, 109.25, 90.16, 88.86, 34.80, 32.05, ppm.

3-Bromo-9-(4-(phenylethynyl)phenyl)-9H-carbazole (3j). Purification by flash chromatography (petroleum ether): a white solid (36 mg, 17%), mp = 206-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 2.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.62-7.53 (m, 5H), 7.48-7.40 (m, 5H), 7.36-7.32 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.92, 139.26, 137.03, 133.21, 131.70, 128.74, 128.58, 128.45, 126.81, 126.80, 125.30, 123.13, 122.95, 122.71, 122.47, 120.62, 120.56, 112.98, 111.24, 109.98, 90.57, 88.48, ppm; HRMS (EI): m/z calcd for $C_{26}H_{16}BrN$ $[M]^+$ 421.0466, found 421.0473.

3,6-Dibromo-9-(4-(phenylethynyl)phenyl)-9H-carbazole (3k). Purification by flash chromatography (petroleum ether): a white solid (13 mg, 5%), mp = 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 2.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.62-7.60 (m, 2H), 7.56-7.51 (m, 4H), 7.43-7.40 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.59, 136.51, 133.31, 131.70, 129.53, 128.65, 128.46, 126.74, 124.13, 123.31, 123.14, 122.85, 113.35, 111.48, 90.80, 88.30, ppm.

2,7-Dibromo-9-(4-(phenylethynyl)phenyl)-9H-carbazole (3l). Purification by flash chromatography (petroleum ether): a white solid (50 mg, 20%), mp = 228-229 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.63-7.61 (m, 2H), 7.53 (d, J = 8.0 Hz, 4H), 7.45 (d, J = 1.6 Hz, 1H), 7.43-7.41 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.61, 136.12, 133.45, 131.73, 128.64, 128.46, 126.92, 123.90, 123.47, 122.87, 121.85, 121.54, 120.10, 113.05, 90.92, 88.26, ppm HRMS (EI): m/z calcd for $C_{26}H_{15}Br_2N$ $[M]^+$ 498.9571, found 498.9567.

9-(4-(Cyclohex-1-en-1-ylethynyl)phenyl)-9H-carbazoleb (3m). Purification by flash chromatography (petroleum ether): a white solid (149 mg, 86%), mp = 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.45-7.44 (m, 4H), 7.35-7.30 (m, 2H), 6.33-630 (m, 1H), 2.33-2.28 (m, 2H), 2.24-2.19 (m, 2H), 1.78-1.65 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.61, 137.02, 135.73, 132.91, 126.78, 126.01, 123.49, 122.86, 120.63, 120.33, 120.12, 109.75, 92.26, 86.09, 29.23, 25.84, 22.36, 21.53, ppm; HRMS (EI): m/z calcd for $C_{26}H_{21}N$ $[M]^+$ 347.1674, found 347.1680.

9-(4-(Cyclohexylethynyl)phenyl)-9H-carbazole (3n). Purification by flash chromatography (petroleum ether): a white solid (166 mg, 95%), mp = 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.46-7.41 (m, 4H), 7.34-7.30 (m, 2H), 2.71-2.65 (m, 1H), 1.98-1.80 (m, 4H), 1.67-1.57 (m, 4H), 1.47-1.38 (m, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.67, 136.75, 133.07, 126.78, 125.99, 123.45, 123.29, 120.33, 120.06, 109.73, 95.61, 79.90, 32.71, 29.74, 25.95, 24.94, ppm; HRMS (EI): m/z calcd for $C_{26}H_{23}N$ $[M]^+$ 349.1830, found 349.1839.

9-(4-(Thiophen-3-ylethynyl)phenyl)-9H-carbazole (3o). Purification by flash chromatography (petroleum ether): a white solid (168 mg, 96%), mp = 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 7.6 Hz, 2H), 7.62-7.58 (m, 3H), 7.48-7.43 (m, 4H), 7.38-7.27 (m, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.56, 137.52, 133.02, 129.89, 128.95, 126.86, 126.06, 125.53, 123.55, 122.23, 122.09, 120.37, 120.21, 109.75, 88.19, 85.46, ppm; HRMS (EI): m/z calcd for $C_{24}H_{15}NS$ $[M]^+$ 349.0925, found 349.0923.

9-(4-(Hept-1-yn-1-yl)phenyl)-9H-carbazole (3p). Purification by flash chromatography (petroleum ether): a white solid (91 mg, 54%), mp = 60-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.6 Hz, 2H), 7.69 (dd, J = 8.4 Hz, J = 2.0 Hz, 2H), 7.55 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.47 (d, J = 8.0 Hz, 4H), 7.38-7.33 (m, 2H), 2.53 (t, J = 7.2 Hz, 2H), 1.73 (q, J = 6.8 Hz, 2H), 1.59-1.44 (m, 4H), 1.03 (d, J = 7.2 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.72, 136.87, 133.10, 126.84, 126.07, 123.54, 123.31, 120.40, 120.15, 109.80, 91.71, 80.05, 31.27, 28.55, 22.38, 19.56, 14.15, ppm.

Fluoro-4-((4-methoxyphenyl)ethynyl)benzene (3q).[12] Purification by flash chromatography (petroleum ether): a white solid (167 mg, 74%), mp = 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.47 (m, 4H), 7.06 (t, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), ppm.

2-(4-((4-Fluorophenyl)ethynyl)phenyl)acetonitrile (3r). Purification by flash chromatography (petroleum ether): a white solid (66 mg, 28%), mp = 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 4H), 7.35 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 8.8 Hz, 2H), 3.80 (s, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.63 (d, $J_{C\text{-}F}$ = 248.5 Hz), 133.54 (d, $J_{C\text{-}F}$ = 8.3 Hz), 132.23, 129.90, 127.99, 123.4, 119.03 (d, $J_{C\text{-}F}$ = 34.6 Hz), 117.40, 115.72 (d, $J_{C\text{-}F}$ = 22.1 Hz), 89.17, 88.14, 23.60, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.52, ppm.

Methyl 4-((4-fluorophenyl)ethynyl)benzoate (3s).[13] Purification by flash chromatography (petroleum ether): a white solid (134 mg, 53%), mp = 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 2H), 7.61-7.53 (m, 4H), 7.09 (t, J = 8.8 Hz, 2H), 3.95 (s, 3H), ppm.

9-(3'-Fluoro-[1,1'-biphenyl]-3-yl)-9H-carbazole (4a). Purification by flash chromatography (petroleum ether): a white solid (94 mg, 56%), mp = 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, J = 8.0 Hz, J = 1.2 Hz, 2H), 7.83 (s, 1H), 7.74-7.70 (m, 2H), 7.65-7.61 (m, 1H), 7.52-7.45 (m, 6H), 7.40-7.33 (m, 3H), 7.16-7.09 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.27 (d, $J_{C\text{-}F}$ = 244.6 Hz), 142.38 (d, $J_{C\text{-}F}$ = 7.6 Hz), 141.86 (d, $J_{C\text{-}F}$ = 2.2 Hz), 140.85, 138.40, 130.54, 130.46, 126.43, 126.09, 126.07, 125.72, 123.49, 122.83 (d, $J_{C\text{-}F}$ = 2.8 Hz), 120.42, 120.10, 114.70 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.12 (d, $J_{C\text{-}F}$ = 22.0 Hz), 109.76, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.58, ppm; HRMS (MALDI): *m/z* calcd for $C_{24}H_{16}FN$ $[M]^+$ 337.1261, found 337.1263.

9-(2'-Fluoro-[1,1'-biphenyl]-2-yl)-9H-carbazole (4b). Purification by flash chromatography (petroleum ether): a colorless oil (32 mg, 19%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.0 Hz, 2H), 7.72-7.68 (m, 1H), 7.65-7.56 (m, 3H), 7.35-7.30 (m, 2H), 7.23-7.16 (m, 4H),

7.02-6.96 (m, 1H), 6.89-6.83 (m, 2H), 6.69-6.65 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.11 (d, J_{C-F} = 245.3 Hz), 141.19, 135.83, 135.14, 132.46 (d, J_{C-F} = 2.1 Hz), 130.22 (d, J_{C-F} = 3.1 Hz), 129.59, 129.46, 129.33 (d, J_{C-F} = 8.2 Hz), 128.28, 125.64, 123.58 (d, J_{C-F} = 3.6 Hz), 123.05, 120.00, 119.53, 115.51 (d, J_{C-F} = 22.1 Hz), 109.85, 109.84; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.28, ppm; HRMS (MALDI): *m/z* calcd for $C_{24}H_{16}FN$ $[M]^+$ 337.1261, found 337.1263.

3,6-Di-tert-butyl-9-(4'-fluoro-[1,1'-biphenyl]-4-yl)-9H-carbazole (4c). Purification by flash chromatography (petroleum ether): a white solid (63 mg, 28%), mp = 192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 1.6 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.69-7.64 (m, 4H), 7.50 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 8.4 Hz, 2H), 1.50 (s, 18H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.94, 139.18, 138.76, 137.41, 136.50 (d, J_{C-F} = 3.1 Hz), 128.68 (d, J_{C-F} = 8.0 Hz), 128.26 (d, J_{C-F} = 0.6 Hz), 126.98, 123.63, 123.43, 116.27, 115.82 (d, J_{C-F} = 21.3 Hz), 109.22, 34.76, 32.03, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.29, ppm; HRMS (EI): m/z calcd for $C_{32}H_{32}FN$ $[M]^+$ 449.2519, found 449.2528.

3-Bromo-9-(4'-fluoro-[1,1'-biphenyl]-4-yl)-9H-carbazole (4d). Purification by flash chromatography (petroleum ether): a white solid (89 mg, 43%), mp = 189-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 2.0 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.68-7.61 (m, 4H), 7.53 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.48-7.47 (m, 2H), 7.36-7.32 (m, 2H), 7.22 (t, *J* = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.74 (d, J_{C-F} = 145.7 Hz), 141.18, 139.69, 139.52, 136.40, 136.26 (d, J_{C-F} = 3.3 Hz), 128.79, 128.68 (d, J_{C-F} = 4.4 Hz), 128.50, 127.33, 126.73, 125.19, 123.10, 122.37, 120.49 (d, J_{C-F} = 9.9 Hz), 116.02, 115.81, 112.79, 111.29, 110.04, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.87, ppm; HRMS (EI): m/z calcd for $C_{24}H_{15}BrFN$ $[M]^+$ 415.0372, found 415.0374.

3,6-Dibromo-9-(4'-fluoro-[1,1'-biphenyl]-4-yl)-9H-carbazole (4e). Purification by flash chromatography (petroleum ether): a white solid (111 mg, 45%), mp = 217 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 2.0 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.67-7.64 (m, 2H), 7.58-7.53 (m, 4H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.78 (d, J_{C-F} = 245.9 Hz), 140.04, 139.83, 136.10 (d, J_{C-F} = 3.3 Hz), 135.91, 129.45, 128.76 (d, J_{C-F} = 8.1 Hz), 128.61, 127.25, 124.02, 123.27, 115.96 (d, J_{C-F} = 21.5 Hz), 113.17, 111.53, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.65, ppm; HRMS (EI): m/z calcd for $C_{24}H_{14}Br_2FN$ $[M]^+$ 492.9477, found 492.9474.

2,7-Dibromo-9-(4'-fluoro-[1,1'-biphenyl]-4-yl)-9H-carbazole (4f). Purification by flash chromatography (petroleum ether): a white solid (97 mg, 39%), mp = 172-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.69-7.66 (m, 2H), 7.60-7.56 (m, 4H), 7.44 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 2H), 7.23 (t, *J* = 8.4 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.81 (d, J_{C-F} = 245.8 Hz), 141.86, 140.36, 136.12 (d, J_{C-F} = 3.3 Hz), 135.53, 128.86, 128.78 (d, J_{C-F} = 1.0 Hz), 127.42, 123.72, 121.76, 121.52, 120.05, 115.96 (d, J_{C-F} = 21.4 Hz), 113.07, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.68, ppm; HRMS (EI): m/z calcd for $C_{24}H_{14}Br_2FN$ $[M]^+$ 492.9477, found 492.9474.

9-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-3-nitro-9H-carbazole (4g). Purification by flash chromatography (petroleum ether): a yellow solid (92 mg, 48%), mp = 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.70-7.63 (m, 4H), 7.50-7.43 (m, 4H), 7.24 (t, *J* = 8.8 Hz, 2H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.86 (d, J_{C-F} = 246.1 Hz), 143.93, 142.33, 141.50, 140.64, 136.00 (d, J_{C-F} = 4.0 Hz), 135.44, 128.82 (d, J_{C-F} = 8.1 Hz), 128.76, 127.70, 127.47, 123.21, 123.09, 121.88, 121.68, 120.98, 117.34, 116.12, 115.96 (d, J_{C-F} = 21.4 Hz), 110.71, 109.57, ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.47, ppm.

Conclusions

We developed a series of efficient one-pot N-arylation and Pd-catalysed cross-coupling procedure to produce a carbazole-based skeleton with good yield and high selectivity. The carbazole-based skeleton contained biphenyl and diarylacetylene cores. A wide range of functional groups, including aryl acetylene, boronic acid, and fluorinated iodobenzene, are compatible in the developed one-pot reaction conditions. The use of metal-free N-arylation is the key starting reaction to form iodinated N-arylcarbazole which is not isolated, but submitted to further structure elongation. N-Arylation and Pd-catalysed Sonogashira coupling via one-pot process was successfully obtained in contrast to N-arylation and Pd-catalysed Suzuki or Ullmann coupling. The Pd-catalyst activated the C–I bond of fluorinated iodobenzene to decrease reaction selectivity, which is responsible for the poor results. The competing reaction showed that N-arylation and Pd-catalysed Sonogashira coupling was superior among the one-pot four-compound processes.

Acknowledgements

The authors thank the financial support from the National Natural Science Foundation of China (grant number 21466033).

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.

1 a) C. Teng, X. C. Yang, C. Z. Yuan, C. Y. Li, R. K. Chen, H. N. Tian, S. F. Li, A. Hagfeldt and L. C. Sun, *Org. Lett.*, 2009, **11**, 5542–5545; b) J. Tang, J. L. Hua, W. J. Wu, J. Li, Z. G. Jin, Y. T. Long and H. Tian, *Energy Environ. Sci.*, 2010, **3**, 1736–1745; c) E. M. Barea, C. Zafer, B. Gultekin, B. Aydin, S. Koyuncu, S. Icli, F. F. Santiago and J. Bisquert, *J. Phys. Chem. C*, 2010, **114**, 19840–19848; d) B. J. Song, H. M. Song, I. T. Choi, S. K. Kim, K. D. Seo, M. S. Kang, M. J. Lee, D. W. Cho, M. J. Ju and H. K. Kim, *Chem. Eur. J.*, 2011, **17**, 11115–11121.

2 a) K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404–9411; b) H. Jian and J. M. Tour, *J. Org. Chem.*, 2003, **68**, 5091–5103; c) W.-Y. Wong, L. Liu, D. M. Cui, L. M. Leung, C.-F. Kwong, T.-H. Lee and H.-F.

Ng, *Macromolecules*, 2005, **38**, 4970–4976; d) W. Y. Wong, C.-L. Ho, Z. Q. Gao, B.-X. Mi, C.-H. Chen, K. W. Cheah and Z. Y. Lin, *Angew. Chem. Int. Ed.*, 2006, **45**, 7800–7803; e) W. Y. Wong, C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah and Z. Y. Lin, *Angew. Chem. Int. Ed.*, 2006, **45**, 7800–7803; f) Y.-C. Chen, G.-S. Huang, C.-C. Hsiao and S.-A. Chen, *J. Am. Chem. Soc.*, 2006, **128**, 8549–8558; g) Y. Liu, M. Nishiura, Y. Wang and Z. Hou, *J. Am. Chem. Soc.*, 2006, **128**, 5592–5593; h) L. Liu, W.-Y. Wong, J.-X. Shi, K. W. Cheah, T.-H. Lee and L. M. Leung, *J. Organomet. Chem.*, 2006, **691**, 4028–4041; i) C.-S. Wu, J.-W. Wu and Y. Chen, *J. Mater. Chem.*, 2012, **22**, 23877–23884.

3 a) A. W. Schmidt, K. R. Reddy and H.-J. Knölker, *Chem. Rev.*, 2012, **112**, 3193–3328; b) C. Börger, O. Kataeva and H.-J. *Knölker, Org. Biomol. Chem.*, 2012, **10**, 7269–7273.

4 a) L.-L. Tan, L.-J. Xie, Y. Shen, J.-M. Liu, L.-M. Xiao, D.-B. Kuang and C.-Y. Su, *Dyes Pigments*, 2014, **100**, 269–277; b) S. Riedmüller and B. J. Nachtsheim, *Beilstein J. Org. Chem.*, 2013, **9**, 1202–1209; c) P. E. Maligres, S. W. Krska and P. G. Dormer, *J. Org. Chem.*, 2012, **77**, 7646−7651.

5 a) J. Kwak, Y.-Y. Lyu, H. Lee, B. Choi, K. Char and C. Lee, *J. Mater. Chem.*, 2012, **22**, 6351–6355; b) J. Q. Ding, B. H. Zhang, J. H. Lü, Z. Y. Xie, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Mater.*, 2009, **21**, 4983–4986; c) B. Wei, J.-Z. Liu, Y. Zhang, J.-H. Zhang, H.-N. Peng, H.-L. Fan, Y.-B. He and X.-C. Gao, *Adv. Funct. Mater.*, 2010, **20**, 2448–2458.

6 a) R. M. Adhikari, R. Mondal, B. K. Shah and D. C. Neckers, *J. Org. Chem.*, 2007, **72**, 4727–4732; b) R. M. Adhikari, L. Duan, L. Hou, Y. Qiu, D. C. Neckers and B. K. Shah, *Chem. Mater.*, 2009, **21**, 4638–4644; c) Y. Wang, B. Chen, W. Wu, X. Li, W. Zhu, H. Tian and Y. Xie, *Angew. Chem. Int. Ed.*, 2014, **53**, 10779–10783; d) M. A. Reddy, A. Thomas, G. Mallesham, B. Sridhar, V. J. Rao and K. Bhanuprakash, *Tetrahedron Lett.*, 2011, **52**, 6942–6947; e) S.-H. Lee, C. T.-L. Chan, K. M.-C. Wong, W. H. Lam, W.-M. Kwok and V. W.-W. Yam, *Dalton Trans.*, 2014, **43**, 17624–17634.

7 a) E. D. D. Calder, M. W. Grafton and A. Sutherland, *Synlett*, 2014, **25**, 1068–1080; b) K. Kashinath and D. S. Reddy, *Org. Biomol. Chem.*, 2015, **13**, 970–973; c) J. B. Bharate, R. A. Vishwakarma and S. B. Bharate, *RSC Adv.*, 2015, **5**, 42020–42053; d) F. Diness and D. P. Fairlie, *Angew. Chem. Int. Ed.*, 2012, **51**, 8012–8016.

8 F. Chen, N. Liu, E. Ji and B. Dai, *RSC Adv.*, 2015, **5**, 51512–51523.

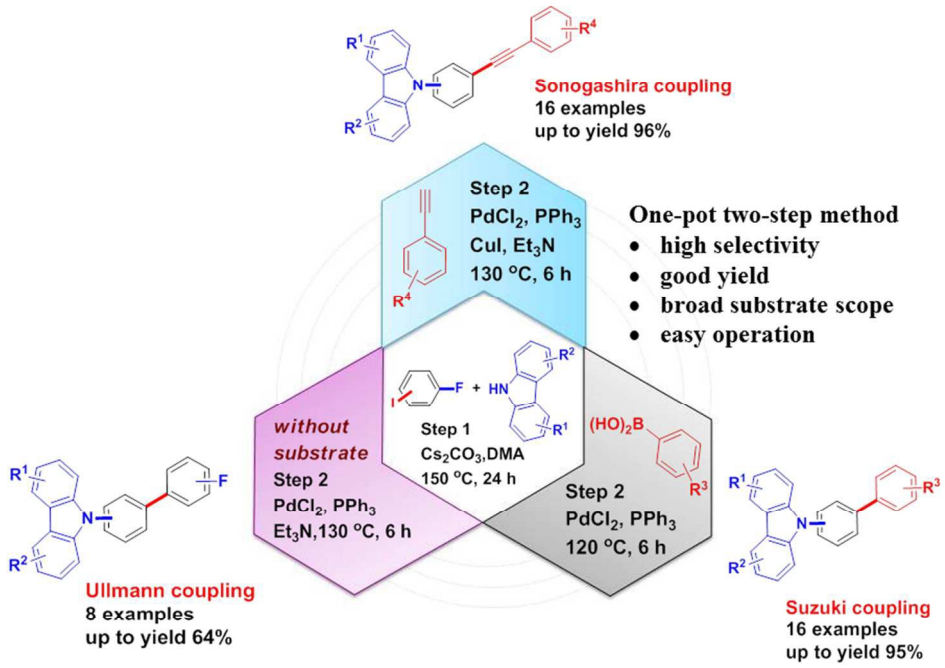
9 J.-H. Pan, Y.-M. Chou, H.-L. Chiu and B.-C. Wang, *Aust. J. Chem.*, 2009, **62**, 483–492.

10 F.-F. Yu, H.-L. Fan, H.-F. Huang, Q.-Y. Cao, Y.-F. Dai, X.-C. Gao, Y.-Z. Shang, M.-Y. Zhang, L. Long, H. Xu, X.-F. Li and B. Wei, *Inorg. Chim. Acta*, 2012, **390**, 119–122.

11 N. Liu, C. Liu, B. Yan and Z. Jin, *Appl. Organometal. Chem.*, 2011, **25**, 168–172.

12 N. Liu, C. Liu, B. Yan and Z. Jin, *Eur. J. Org. Chem.*, 2011, 4422–4428.

13 E. Paegle, S. Belyakov, M. Petrova, E. Liepinsh and P. Arsenyan, *Eur. J. Org. Chem.*, 2015, 4389–4399.



254x190mm (96 x 96 DPI)