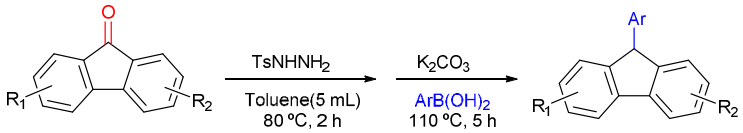
RSC Advances

This article can be cited before page numbers have been issued, to do this please use: X. Shen, N. Gu, P. Liu, X. Ma, J. Xie, Y. Liu, L. He and B. Dai, *RSC Adv.*, 2015, DOI: 10.1039/C5RA12099C.

View Article Online
DOI: 10.1039/C5RA12099C

Graphical Abstract



View Article Online
DOI: 10.1039/C5RA12099C

Journal Name

ARTICLE

A simply and efficient synthesis of 9-arylfluorenes via metal-free reductive coupling of arylboronic acids and *N*-tosylhydrazones *in situ*

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xu Shen, Ningning Gu, Ping Liu*, Xiaowei Ma, Jianwei Xie, Yan Liu*, Lin He and Bin Dai

A general, yet efficient synthesis of 9-arylfluorenes via metal-free reductive coupling of N-tosylhydrazones and arylboronic acids has been developed. This methodology is realized by a one-pot protocol in two steps involving the preparation of *N*-tosylhydrazones by reacting tosylhydrazide with 9-fluorenone derivatives, followed by the reductive coupling of arylboronic acid in the presence of potassium carbonate to afford various 9-arylfluorenes analogues in moderate to excellent yields. Importantly, the catalytic system presented here enables the use of easily accessible starting materials and can be employed on a wide variety of substrates with good functional group tolerance. This protocol could also be particularly useful for the synthesis of 9-fluorenyl-substituted carbazolyl compounds.

Introduction

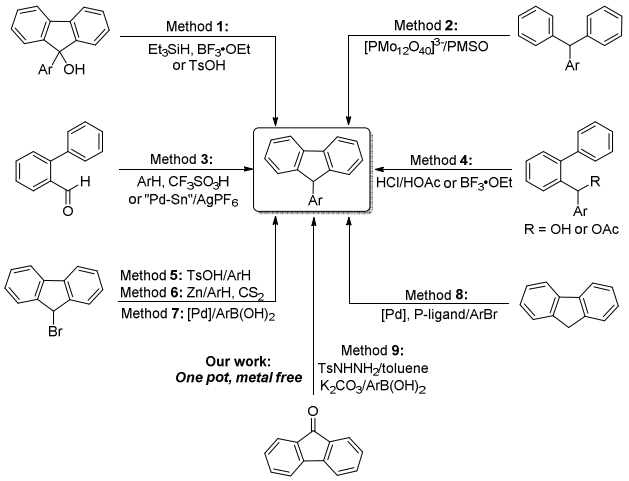
Fluorene proves to be an important structural scaffold and can be found in a variety of applications involving advanced materials, mostly due to its unique electronic and photonic properties.[1] Notably, 9-arylfluorenes have attracted considerable attention as compounds with promising properties to find use in, e.g., blue fluorescent organic light emitting materials, thin film transistors, photovoltaic cells, etc.[2] As a consequence, the development of new synthetic methods for the preparation of 9-arylfluorenes has been the main focus of related fields in recent years. In general, the reaction between 9-fluorenone and organomagnesium or organolithium compounds yields the corresponding carbinols, which can be transformed into 9-arylfluorenes by treatment with $Et_2O{\cdot}BF_3/Et_3SiH$ or TsOH (cf. Method 1).[3] Alternatively, a catalytic system consisting of phenyl methyl sulfoxide (PMSO) and the polyoxomolybdate $[PMo_{12}O_{40}]^{3-}$, triphenylmethane provides 9-phenylfluorene via a triphenylmethane cation (cf. Method 2).[4] Recently, a novel strategy for the preparation of 9-arylfluorenes via intramolecular tandem reactions of 2-arylbenzaldehydes with arenes catalyzed by CF_3SO_3H or a combination of bimetallic "Pd–Sn" and $AgPF_6$ system has been reported (cf. Method 3).[5] Additionally, Friedel-Crafts cyclization reactions of biaryl alcohols or acetates catalyzed by a Brøsted or Lewis acid, such as HCl/HOAc or $BF_3{\cdot}Et_2O$, have also been shown to furnish 9-arylfluorenes (cf. Method 4).[6] Moreover, 9-arylfluorenes can be obtained from 9-bromofluorene through *p*-toluenesulfonic acid catalyzing the intermolecular coupling reaction (cf. Method 5),[7] and the zinc-mediated radical reaction (cf. Method 6).[8] Although the methods listed above prove to be effective for the synthesis of 9-arylfluorenes, certain disadvantages particularly involving a narrow substrate scope and poor functional group tolerance need to be addressed. The 9-arylfluorene scaffold is usually constructed via multi-step reactions that sometimes require the use of a strongly acidic medium or a stoichiometric amount of a Lewis acid. However, it is worth noting that a transition metal catalyzed coupling reaction has been developed for the direct synthesis of 9-arylfluorenes. For example, Chandrasekhar *et al.* developed a catalytic protocol for the synthesis of 9-arylfluorenes via palladium-catalyzed Suzuki-Miyaura coupling of 9-bromofluorene with arylboronic acids (cf. Method 7).[9] Wu *et al.* reported a catalytic system consisting of palladium(II) acetate and tricyclohexylphosphine with the reaction of fluorene with haloarenes to provide 9-arylfluorenes in good to excellent yields (cf. Method 8). [10] The synthetic protocol proposed here will not only mitigate the mentioned disadvantages of Methods 1-6, but will also efficiently reduce the number of reaction steps needed to carry out the synthesis.

N-tosylhydrazones prove to be highly versatile synthetic intermediates that have attracted considerable interest in a variety of research fields in recent years.[11] In 2007, Valdés [12] and coworkers from Wang's group[13] developed a series of transformation reactions with tosylhydrazones. To the best of our knowledge, as early as 2009, Valdés *et al.* have developed a new metal-free C-C bond formation reaction between *N*-tosylhydrazones and boronic acid derivatives that proved to be suitable for the preparation of biarylmethane

School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, China.
E-mail: liuping1979112@aliyun.com and liuyan1979810@aliyun.com; Tel.: +86 0993 2057213; Fax: +86 0993 2057270.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C5RA12099C



Scheme 1 Synthetic methods for 9-arylfluorenes.

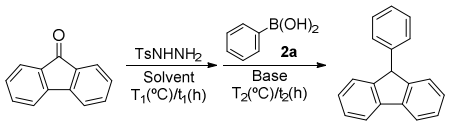
structures. This process can be carried out without the need for a metal catalyst and adapting extremely simple reaction conditions exhibiting remarkably versatile applications.[12b] Inspired by this work and in contrast to the methods mentioned above, requiring a multi-step process for the preparation of 9-arylfluorenes and the use a strongly acidic medium, a Lewis acid, or a palladium catalyst promote these catalytic reactions, we herein report a new method that employs 9-fluorenone derivatives as a simple and readily available starting material for the one-pot, two-step synthesis of 9-arylfluorenes through the metal-free reductive coupling of *N*-tosylhydrazones and arylboronic acids (cf. Method 9).

Results and discussion

Optimization of the reaction conditions

Initially, 9-fluorenone (0.5 mmol) and phenylboronic acid (0.75 mmol) were chosen as model substrates for the reductive coupling in the presence of tosylhydrazide (1.5 equivalents) and potassium carbonate (K_2CO_3, 2 equivalents). Tosylhydrazones prove to be easily accessible by reacting tosylhydrazide with a corresponding ketone. Therefore, we focussed our studies on the reductive coupling in an effort to answer the question if this reaction could be carried out in a one-pot fashion directly from 9-fluorenone and without the need to isolate the intermediate, tosylhydrazone. Indeed, this process proves to be feasible and can be carried out by simply heating 9-fluorenone with tosylhydrazide for 2 hours at 80 ºC prior to the addition of phenylboronic acid. Heating was then continued for another 5 hours at 110 ºC and the product of this reductive coupling, 9-phenyl-9*H*-fluorene, was obtained in 34% yield using 1,4-dioxane as a solvent. Furthermore, the intermediate tosylhydrazone did not have to be isolated (cf. Table 1, entry 2). A short list of solvents with similar boiling points as 1,4-dioxane have been screened for applicability in this reaction. Notably, sgnificantly higher yields have been obtained using nonpolar solvent such as toluene; a lower yield has been observed using dimethylformamide (DMF, cf. Table 1, entries 2 and 3) as solvent. The use of tetrahydrofuran (THF) was also investigated, but the high volatility of the solvent forced us to lower the reaction temperature to 65 ºC, resulting in a particularly low yield obtained (cf. Table 1, entry 4). The screening of different bases revealed that K_2CO_3 proves to be the most appropriate base for delivering the desired product in 89% yield (cf. Table 1, entry 11), while other bases such as K_3PO_4, Na_2CO_3, NaOH, KOH, and Cs_2CO_3 afforded significantly lower yields (31-70%, cf. Table 1, entries 5-9). Meanwhile, the base loading was found to be another crucial parameter with the product yield increasing from 80% to 89% as the base loading increases from 1.5 equivalents to 3.0 equivalents (cf. Table 1, entries 2, 10 and 11), respectively. In summary, the combination of 9-fluorenone (0.5 mmol), tosylhydrazide (1.5 equiv.), phenylboronic acid (0.75 mmol), K_2CO_3 (2 equivalents) at T_1 = 80 °C (t_1 = 2 hours) and T_2 = 110 °C (t_2 = 5 hours) in toluene (5 mL) were found to be the most suitable reaction conditions.

Table 1 Optimized reaction conditions[a]



1a 3a

Entry	Base	Solvent	Yield (%)[b]
1	K_2CO_3 (1.5 equiv.)	1,4-dioxane	34
2	K_2CO_3 (1.5 equiv.)	Toluene	80
3	K_2CO_3 (1.5 equiv.)	DMF	trace
4c	K_2CO_3 (1.5 equiv.)	THF	41
5	K_3PO_4 (1.5 equiv.)	Toluene	67
6	Na_2CO_3 (1.5 equiv.)	Toluene	31
7	NaOH (1.5 equiv.)	Toluene	46
8	KOH (1.5 equiv.)	Toluene	48
9	Cs_2CO_3 (1.5 equiv.)	Toluene	70
10	K_2CO_3 (2 equiv.)	Toluene	87
11	K_2CO_3 (3 equiv.)	Toluene	89

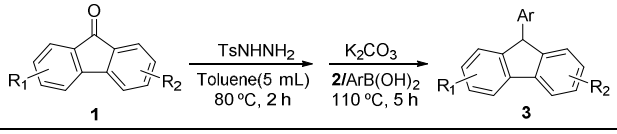
[a]Reaction conditions: Reaction conditions: 0.50 mmol 9-fluorenone, tosylhydrazide (1.5 equiv.), 0.75 mmol phenylboronic acid, 5 mL toluene, T_1 = 80 ºC/t_1 = 2 h, T_2 = 110 ºC/t_2 = 5 h. [b] GC-MS yield. [c]T_1 = T_2 = 65 ºC, yield of GC-MS.

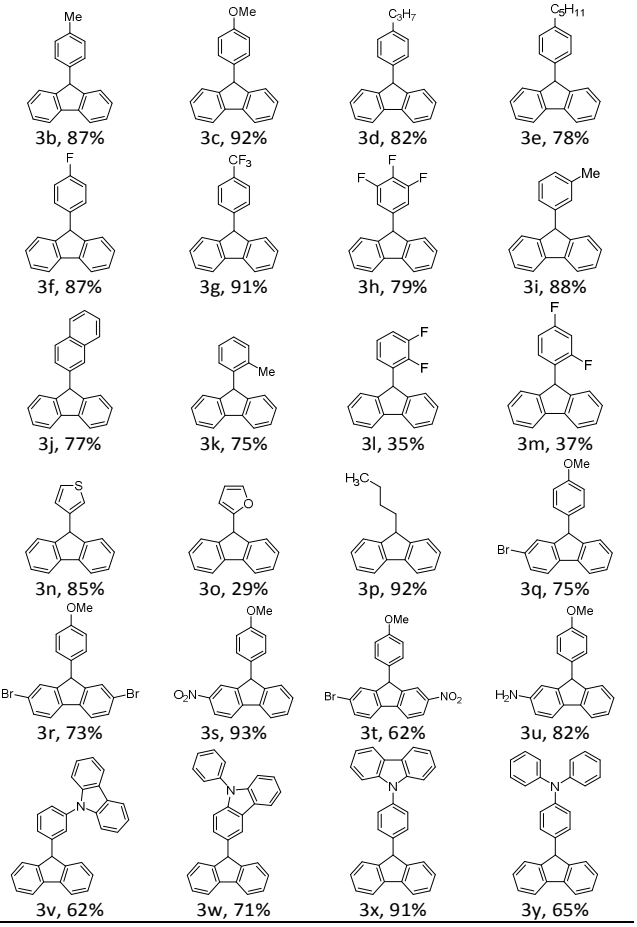
Scope and limitations of substrates

Upon optimizing the reaction conditions, we further investigated the substrate scope of this one pot, two-step reductive coupling reaction. As shown in Table 2, the 4-substituted arylboronic acid substrates bearing electron-withdrawing or electron-donating groups constantly afford the desired products **3b-3g** in good to excellent yields (78-92%). Moreover, (3,4,5-trifluorophenyl)boronic acid and m-tolylboronic acid were found to produce the desired coupling products **3h** and **3i** in 79% and 88% yields, respectively. Naphthalene-2-ylboronic acid has also been used as a coupling partner to provide the product **3j** in 77% yield. Furthermore, the reductive coupling reactions involving orth-substituted arylboronic acids with 9-fluorenone have been investigated. Both the electronic properties and the steric hindrance of the substrates seem to influence the coupling reaction. For example, the coupling reaction of *o*-tolylboronic acid with 9-fluorenone to afford the product **3k** proceeds in 75% yield.

View Article Online
DOI: 10.1039/C5RA12099C

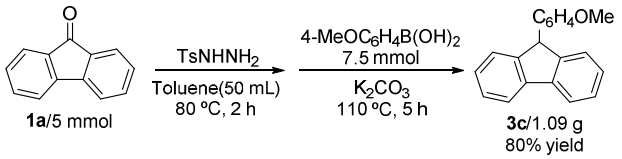
Table 2 One-pot reductive coupling of substituted 9-fluorenones with boronic acids[a]





[a]Reaction conditions: 0.50 mmol substituted 9-fluorenone, 0.75 mmol phenylboronic acid, 1.5 equiv. base, 5 mL toluene, T_1 = 80 °C/t_1 = 2 h, T_2 = 110 °C/t_2 = 5 h. The yields of isolated products are given.

However, (2,3-difluorophenyl)boronic acid and (2,4-difluorophenyl)boronic acid as substrates result in the formation of the corresponding coupling products **3l** and **3m** in low yields of 35% and 37%, respectively. Similarly, while thiophen-3-ylboronic acid shows good reactivity towards conversion into the corresponding product **3n** in 85% yield, the use of furan-2-ylboronic acid as the substrate results in the formation of product **3o** only in 29% yield. Noteworthy, the reaction of butylboronic acid with 9-fluorenone has also been attempted using standard reaction conditions. The desired product **3p** was obtained in 92% yield. To further investigate the range of substrates that can be used in this process, a variety of substituted 9-fluorenone derivatives have been studied. The results show that the coupling reactions involving substituted 9-fluorenone and (4-methoxyphenyl)boronic acid work to our satifsaction and afford the corresponding products



Scheme 1 A gram-scale synthesis of product **3c**

3q-3u in yields ranging from 62% to 93%. The synthesis of substituted carbazolyl compounds has attracted considerable interest due to the importance of this compound in numerous photo devices, electroluminescent devices and photorefractive materials.[18] However, to the best of our knowledge no reports on the synthesis of 9-fluorenyl-substituted carbazolyl compounds via metal free reductive coupling reactions have been published to date. Therefore, this method provided further incentive to be applied to the synthesis of 9-fluorenyl-substituted carbazolyl compounds. The reaction of 9-fluorenone with (3-(9H-carbazol-9-yl)phenyl)boronic acid, (9-phenyl-9H-carbazol-3-yl)boronic acid and (4-(9H-carbazol-9-yl)phenyl)boronic acid was carried out efficiently and the desired products **3v-3x** have been isolated in high yields ranging from 62 to 91%. Furthermore, (4-(diphenylamino)phenyl)boronic acid can also react with 9-fluorenone to afford the functionalized coupling product **3y** in 65% yield.

A gram-scale synthesis was performed to verify the practical application using this synthesis system. Fortunately, the reaction was performed using 5 mmol of 9-fluorenone and 7.5 mmol (4-methoxyphenyl)boronic acid, and proceeded in 80% yield leading to 1.08 g of the desired product **3c**(**Scheme 1**).

Conclusions

To summarize, a simple and efficient method for the synthesis of 9-arylfluorenes via metal-free reductive coupling of arylboronic acids with *N*-tosylhydrazones *in situ* has been developed, affording the corresponding target molecules in moderate to excellent yields. Moreover, isolation of the desired tosylhydrazones is not required and the reaction can be carried out in one pot and in two steps, directly from the 9-fluorenone derivatives. Potential substrates for this reaction are diverse, exhibiting a superior functional-group tolerance. Furthermore, no sophisticated experimental setups, e.g. involving inert gasses or dry solvents, are required. Notably, this protocol also proves suitable for the synthesis of 9-fluorenyl-substituted carbazolyl compounds. Further studies to investigate employing this system to other related reactions are currently underway in our laboratory.

Experimental

Materials and instruments

Chemicals were obtained commercially and used as received. NMR spectra were recorded on a Bruker DPX–400 spectrometer using TMS as the internal standard. EI–Mass spectrum was measured on a LC/Q–TOF MS (Micromass,

View Article Online
DOI: 10.1039/C5RA12099C

England) All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. 9-fluorenone and its derivatives, and arylboronic acids were of analytical grade quality, purchased from Adamas-beta Pharmaceuticals, Inc.

General procedure for the one-pot two-steps reductive coupling of *N*-tosylhydrazones and arylboronic acids

A solution of the 9-fluorenone derivatives **1** (0.5 mmol) and tosylhydrazide (0.75 mmol) in 5 mL of toluene was stirred at 80 ºC for 2 h in a reaction tube. Potassium carbonate (1.0 mmol) and the appropriate boronic acid **2** (0.75 mmol) were added to the reaction mixture. The system was refluxed at 110 ºC for 5 h with stirring. When the reaction was complete, the crude mixture was allowed to reach room temperature. Dichloromethane and a saturated solution of $NaHCO_3$ were added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with a saturated solution of $NaHCO_3$, one portion of brine and then dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The products were purified by chromatography on silica gel.

9-(4-propylphenyl)-9H-fluorene[3d]

Mp. 88-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.29 – 7.22 (m, 2H), 7.03 (ddd, *J* = 9.8, 7.2, 1.9 Hz, 4H), 5.02 (s, 1H), 2.57 – 2.51 (m, 2H), 1.61 (ddd, *J* = 9.1, 7.5, 4.1 Hz, 2H), 0.96 – 0.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09 (s), 141.20 (s), 140.98 (s), 138.68 (s), 128.76 (s), 128.13 (s), 127.25 (dd, *J* = 3.0, 2.1 Hz), 125.35 (s), 119.83 (s), 77.36 (s), 77.04 (s), 76.72 (s), 54.13 (s), 37.74 (s), 24.52 (s), 13.94 (s). HRMS(EI):m/z calcd for $C_{22}H_{24}$ $[M]^+$ 284.1565,found 284.1563. IR (KBr, cm^{-1}): 2953, 2928, 2826, 1510, 1448, 738.

9-(4-pentylphenyl)-9H-fluorene[3e]

Mp.74-75 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.25 (td, *J* = 7.2, 1.1 Hz, 3H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.97 (m, 2H), 5.02 (s, 1H), 2.58 – 2.52 (m, 2H), 1.63 – 1.53 (m, 3H), 1.34 – 1.24 (m, 5H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.07 (s), 141.45 (s), 140.97 (s), 138.61 (s), 128.68 (s), 128.13 (s), 127.23 (d, *J* = 4.2 Hz), 125.34 (s), 119.82 (s), 77.34 (s), 77.02 (s), 76.71 (s), 54.11 (s), 35.61 (s), 31.61 (s), 31.14 (s), 22.56 (s), 14.05 (s). HRMS(EI):m/z calcd for $C_{24}H_{24}$ $[M]^+$ 312.1878, found 312.1873. IR (KBr, cm^{-1}): 3048, 2951, 2876, 1510, 1449, 739.

9-(3,4,5-trifluorophenyl)-9H-fluorene[3h]

Mp.115.7-116.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.9, 0.7 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.30 – 7.27 (m, 4H), 6.70 (dd, *J* = 8.5, 6.5 Hz, 2H), 4.95 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.28 (s), 140.94 (s), 127.96 (s), 127.62 (s), 125.14 (s), 120.18 (s), 112.20 (dd, *J* = 15.6, 5.8 Hz), 86.82 (s), 77.35 (s), 77.03 (s), 76.71 (s), 53.39 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.06 (d, *J* = 20.7 Hz), -162.77 (t, *J* = 20.6 Hz). HRMS(EI):m/z calcd for $C_{19}H_{11}F_3$ $[M]^+$ 296.0813, found 296.0810. IR (KBr, cm^{-1}): 3048, 2951, 2876, 1510, 1449, 739.

9-(2,3-difluorophenyl)-9H-fluorene[3l]

Mp. 100-101 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.28 (td, *J* = 7.4, 1.1 Hz, 2H), 7.07 – 6.98 (m, 1H), 6.84 (tdd, *J* = 8.1, 5.0, 1.7 Hz, 1H), 6.42 (dd, *J* = 7.7, 6.3 Hz, 1H), 5.49 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.20 (d, *J* = 1.1 Hz), 141.16 (s), 131.22 (d, *J* = 11.9 Hz), 127.57 (d, *J* = 17.4 Hz), 125.19 (d, *J* = 1.2 Hz), 124.15 (dd, *J* = 7.0, 4.7 Hz), 123.80 (s), 120.07 (s), 115.58 (d, *J* = 17.0 Hz), 77.34 (s), 77.02 (s), 76.71 (s), 29.72 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.94 – -138.01 (m), -143.90 (d, *J* = 19.9 Hz). HRMS(EI):m/z calcd for $C_{19}H_{12}F_2$ $[M]^+$ 278.0907, found 278.0909. IR (KBr, cm^{-1}): 1485, 1446, 1280, 945, 800, 779, 742.

9-(2,4-difluorophenyl)-9H-fluorene[3m]

Mp. 94.6-95.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.28 (dd, *J* = 7.4, 1.0 Hz, 2H), 6.94 – 6.87 (m, 1H), 6.70 – 6.59 (m, 2H), 5.42 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.55 (s), 141.11 (s), 127.51 (d, *J* = 12.4 Hz), 125.13 (d, *J* = 1.2 Hz), 120.05 (s), 111.74 – 111.25 (m), 104.12 (s), 103.87 (s), 77.34 (s), 77.02 (s), 76.70 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.22 (dd, *J* = 6.8, 1.1 Hz), -114.77 (s). HRMS(EI):m/z calcd for $C_{19}H_{12}F_2$ $[M]^+$ 278.0907, found 278.0909. IR (KBr, cm^{-1}): 1620, 1604, 1500, 1447, 1267, 964, 852, 739.

2-bromo-9-(4-methoxyphenyl)-9H-fluorene[3q]

Mp. 107-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.49 (ddd, *J* = 8.1, 1.8, 0.7 Hz, 1H), 7.44 – 7.32 (m, 2H), 7.32 – 7.23 (m, 2H), 7.02 – 6.94 (m, 2H), 6.86 – 6.79 (m, 2H), 4.97 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.74 (s), 150.23 (s), 147.90 (s), 139.88 (d, *J* = 2.1 Hz), 132.57 (s), 130.43 (s), 129.29 (s), 128.54 (s), 127.73 (s), 127.47 (s), 125.35 (s), 121.11 (d, *J* = 14.6 Hz), 119.92 (s), 114.26 (s), 55.27 (s), 53.61 (s). HRMS(**EI**): m/z calcd for $C_{20}H_{15}BrO$ $[M]^+$ 350.0306, found 350.0305. IR (KBr, cm^{-1}): 1508, 1460, 1258, 1176, 742.

2,7-dibromo-9-(4-methoxyphenyl)-9H-fluorene[3r]

Mp. 153.5-155.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 (ddd, *J* = 8.1, 1.8, 0.7 Hz, 2H), 7.40 – 7.36 (m, 2H), 6.92 (s, 2H), 6.81 (s, 2H), 4.92 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95 (s), 149.88 (s), 138.85 (s), 131.60 (s), 130.69 (s), 129.29 (d, *J* = 1.0 Hz), 128.61 (s), 121.52 (s), 121.25 (s), 114.42 (s), 77.36 (s), 77.04 (s), 76.73 (s), 55.30 (s), 53.50 (s). HRMS(**EI**):m/z calcd for $C_{20}H_{14}Br_2O$ $[M]^+$ 429.9391, found 429.9387. IR (KBr, cm^{-1}): 1510, 1456, 1258, 964, 806.

9-(4-methoxyphenyl)-2-nitro-9H-fluorene[3s]

Mp. 149.8-151.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 15.8 Hz, 1H), 8.15 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 5.8, 1.0 Hz, 3H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.09 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98 (s), 149.76 (s), 149.22 (s), 147.22 (s), 138.63 (s), 131.39 (s), 129.33 (d, *J* = 19.9 Hz), 127.90 (s), 125.70 (s), 123.57 (s), 121.26 (s), 120.77 (s), 119.97 (s), 114.46 (s), 77.33 (s), 77.01 (s), 76.69 (s), 55.29 (s), 53.72 (s). HRMS(EI):m/z calcd for $C_{20}H_{15}NO_3$ $[M-H]^+$ 316.0968, found 316.0973. IR (KBr, cm^{-1}): 1510, 1333, 1258, 1030, 752.

2-bromo-9-(4-methoxyphenyl)-7-nitro-9H-fluorene[3t]

Mp. 191.5-192.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.16 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.03 – 6.98 (m, 2H), 6.90 – 6.85 (m, 2H), 5.10 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.20 (s), 151.59 (s), 148.94 (s), 147.48 (s), 146.10 (s), 137.55 (s), 131.23 (s), 130.45 (s), 129.24 (s), 129.02 (s), 123.70 (d, *J* = 8.0 Hz), 122.50 (s), 120.85 (s), 120.12 (s), 114.63 (s),

View Article Online
DOI: 10.1039/C5RA12099C

77.33 (s), 77.01 (s), 76.69 (s), 55.32 (s), 53.64 (s). HRMS(EI):m/z calcd for $C_{20}H_{14}BrNO_3$ $[M-H]^+$ 394.0073, found 394.0080. IR (KBr, cm^{-1}): 1600, 1510, 1337, 1250, 1028, 818, 737.

9-(4-methoxyphenyl)-9H-fluoren-2-amine[3u]

Mp. 161.4-162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.14 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.83 – 6.78 (m, 2H), 6.70 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.63 (s, 1H), 4.89 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.45 (s), 150.13 (s), 147.34 (s), 141.36 (s), 133.98 (s), 129.35 (s), 127.13 (s), 125.63 (s), 125.00 (s), 120.68 (s), 118.54 (s), 114.42 (s), 114.05 (s), 112.01 (s), 77.34 (s), 77.02 (s), 76.71 (s), 55.24 (s), 53.54 (s). HRMS(EI):m/z calcd for $C_{20}H_{17}NO$ $[M]^+$ 287.1305, found 287.1311. IR (KBr, cm^{-1}): 3564, 3412, 1609, 1510, 1456, 1252, 1179, 1034, 825, 741.

9-(3-(9H-fluoren-9-yl)phenyl)-9H-carbazole[3v]

Mp. 200.3-201.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.00 (m, 2H), 7.79 (dd, *J* = 7.5, 0.8 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.23 (m, 14H), 7.19 (s, 1H), 5.15 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.39 (s), 143.82 (s), 141.08 (s), 140.69 (s), 137.96 (s), 130.13 (s), 127.53 (d, *J* = 15.0 Hz), 127.24 (s), 126.88 (s), 125.89 (s), 125.29 (d, *J* = 2.2 Hz), 123.35 (s), 120.38 – 119.80 (m), 109.76 (s), 77.36 (s), 77.04 (s), 76.72 (s), 54.17 (s). HRMS(EI):m/z calcd for $C_{31}H_{21}N$ $[M]^+$ 407.1674, found 407.1672. IR (KBr, cm^{-1}): 3045, 1599, 1449, 1334, 1226, 1179, 1034, 825, 741.

3-(9H-fluoren-9-yl)-9-phenyl-9H-carbazole[3w]

Mp. 101.1-101.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.51 (m, 4H), 7.39 (ddd, *J* = 11.5, 9.8, 7.3 Hz, 7H), 7.29 – 7.25 (m, 3H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 1H), 5.24 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72 (s), 141.04 (d, *J* = 19.5 Hz), 137.73 (s), 133.02 (s), 129.83 (s), 127.25 (dd, *J* = 22.9, 11.6 Hz), 126.33 (s), 125.92 (s), 125.47 (s), 123.61 (s), 123.14 (s), 120.37 (s), 120.07 (s), 119.86 (d, *J* = 2.3 Hz), 110.08 (s), 109.77 (s), 77.35 (s), 77.03 (s), 76.71 (s), 54.64 (s). HRMS(EI):m/z calcd for $C_{31}H_{21}N$ $[M]^+$ 407.1674, found 407.1672. IR (KBr, cm^{-1}): 3267, 1595, 1501, 1448, 1323, 1234, 806, 735.

9-(4-(9H-fluoren-9-yl)phenyl)-9H-carbazole[3x]

Mp. 243.5-244.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 0.8 Hz, 2H), 7.84 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.48 – 7.38 (m, 10H), 7.37 – 7.25 (m, 6H), 5.18 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.53 (s), 141.19 – 140.76 (m), 136.35 (s), 129.70 (s), 127.82 – 127.10 (m), 125.87 (s), 125.43 (s), 123.32 (s), 120.28 (s), 119.96 (d, *J* = 20.0 Hz), 109.85 (s), 77.35 (s), 77.04 (s), 76.72 (s), 54.07 (s). HRMS(EI):m/z calcd for $C_{31}H_{21}N$ $[M]^+$ 407.1674, found 407.1672. IR (KBr, cm^{-1}): 3059, 1599, 1510, 1450, 1223, 745.

4-(9H-fluoren-9-yl)-N,N-diphenylaniline[3y]

Mp. 174.2-175.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.38 (d, *J* = 8.3 Hz, 4H), 7.29 (s, 2H), 7.19 (s, 4H), 7.05 (ddd, *J* = 4.4, 3.4, 1.8 Hz, 4H), 6.95 (s, 6H), 5.00 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.85 (d, *J* = 10.8 Hz), 140.96 (s), 129.09 (d, *J* = 15.2 Hz), 127.26 (d, *J* = 2.8 Hz), 125.36 (s), 124.16 (d, *J* = 7.2 Hz), 122.61 (s), 119.87 (s), 77.34 (s), 77.02 (s), 76.70 (s), 53.84 (s). HRMS(EI):m/z calcd for $C_{31}H_{23}N$ $[M]^+$ 409.1830, found 409.1823. IR (KBr, cm^{-1}): 3036, 1585, 1495, 1448, 1328, 1273, 738, 649.

Acknowledgements

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (No. 21103114, No. 21463022), and Shihezi University Training Programme for Distinguished Youth Scholars (No.2014ZRKXJQ05), Key Scientific and Technological Project of Shihezi University (gxjs2013-zdgg0201), and Start-Up Foundation for Young Scientists of Shihezi University (RCZX201408).

Notes and references

1 (a) H. Reisch, U. Wiester, U. Scherf and N. Tuytuylkov, *Macromolecules*., 1996, **29**, 8204; (b) C. Xia and R. C. Advincula, *Macromolecules.*, 2001, **34**, 6922; (c) M. Ranger, D. Rondeau and M. Leclerc, *Macromolecules.*, 2002, **35**, 2426; (d) S. Merlet, M. Birau and Z. Y. Wang, *Org. Lett*., 2002, **4**, 2157; (e) U. Scherf and E. J. W. List, *Adv. Mater*., 2002, **14**, 477; (f) D. Katsis, Y. H. Geng, J. J. Ou, S. W. Culligan, A. Trajkovska, S. H.Chen and L. J. Rothberg, *Chem. Mater*., 2002, **14**, 1332; (g) X. Cao, W. Zhang, J. Wang, X. Zhou, H. Lu and J. J. Pei, *Am. Chem*., *Soc*. 2003, **125**, 12430; (h) T. Hadizad, J. Zhang, Z. Y. Wang, T. C. Gorjanc and C. Py, *Org. Lett*., 2005, **7**, 795; (i) F. Jaramillo-Isaza and M. L. J. Turner, *Mater. Chem*., 2006, **16**, 83; (j) L. Xie, T. Fu, X. Hou, C. Tang, Y. Hua, R. Wang, Q. Fan, B. Peng, W. Wei and W. Huang, *Tetrahedron Lett*., 2006, **47**, 6421; (k) K. Wong, L. Chi, S. L. Huang, Y. iao, Y. Liu, and Y. Wang, *Org. Lett*., 2006, **8**, 5029; (l) K. Wong, T. Hwu, A. Balaiah, T. Chao, F. Fang, C. Lee and Y. Peng, *Org. Lett.*, 2006, **8**, 1415.

2 (a) K.-T. Wong, T.-Y. Hwu, A. Balaiah, T.-C. Chao, F.-C. Fang, C.-T. Lee and Y.-C. Peng, *Org. Lett*., 2006, **8**, 1415; (b) F. C. Fang, C. C. Chu, C. H. Huang, G. Raffy, A. Del Guerzo, K. T. Wong and D. M. Bassani, *Chem. Commun*., 2008, 6369; (c) Z. Peng, S. Tao and X. Zhang, J. Phys. *Chem. C.*, 2008, **113**, 2165; (d) L. Rong, Q. Liu, Y. Shi and J. Tang, *Chem. Commun*., 2011, **47**, 2155; (e) H.-g. Li, G. Wu, H.-Z. Chen and M. Wang, *Org. Electron*., 2011, **12**, 70. (f) L. H. Xie, X. Y. Hou, Y. R. Hua, C. Tang, F. Liu, Q. L. Fan and W. Huang, *Org. Lett.*, 2006, **8**, 3701.

3 (a) G. C. Vougioukalakis, M. M. Roubelakis, M. Orfanopoulos, *J. Org. Chem*. 2010, **75**, 4124. (b) M. Y. Teng, Y. Liu, S. L. Li, G. Huang, J. Jiang, and L. Wang, *RSC Adv.*, 2013, **3**, 9016.

4 A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc*., 2002, **124**, 4198.

5 (a) Q. Li, W. Xu, J. Hu, X. Chen, F. Zhang and H. Zheng, TfOH catalyzed synthesis of 9-arylfluorenes via tandem reaction under warm and efficient conditions. *RSC Adv.*, 2014, ***4***, 27722. (b) D. Das, S. Pratihar and S. Roy, *Org. Lett*., 2012, ***14***, 4870.

6 (a) S. Sarkar, S. Maiti, K. Bera, S. Jalal and U. Jana, *Tetrahedron Lett*., 2012, ***53***, 5544. (b) K. Kobiro, M. Matsura, H. Kojima and K. Nakahara, *Tetrahedron.*, 2009, ***65***, 807. (c) G. Li, E. Wang, H. Chen, H. Li, Y. Liu and P. G. Wang, *Tetrahedron*., 2008, ***64***, 9033.

7 M. P. D. Mahindaratne, K, J. Wimalasena, *Org. Chem*., 1998, **63**, 2858.

8 J. Wang, W. Wan, H. Jiang, Y. Gao, X. Jiang, H. Lin, W. Zhao and J. Hao, *Org. Lett*., 2010, **12**, 3874.

9 V. Chandrasekhar, R. S. Narayanan, P. Thilagar, *Organometallics.,* 2009, **28**, 5883.

10 J. J. Chen, S. Onogi, Y. C. Hsieh, C. C. Hsiao, S. Higashibayashi, H. Sakurai and Y. T. Wu, *Adv. Synth. Catal.*, 2012, **354**, 1551.

11 11 (a) V. K. Aggarwal, E. Alonso, G. Fang, M. Ferrara, G. Hynd, M. Porcelloni, *Angew*. *Chem*., 2001, **113**, 1482; *Angew.*

View Article Online
DOI: 10.1039/C5RA12099C

Chem. Int. Ed., 2001, **40**, 1433; (b) V. K. Aggarwal, E. Alonso, G. Hynd, K. M. Lydon, M. J. Palmer, M. Porcelloni, J. R. Studley, *Angew. Chem*., 2001, **113**, 1479; *Angew. Chem. Int. Ed*., 2001, **40**, 1430; (c) V. K. Aggarwal, J. R. Fulton, C. G. Sheldon, J. de Vicente, *J. Am. Chem. Soc*., 2003, **125**, 6034; (d) K. Inamoto, T. Saito, M. Katsuno, T. Sakamoto, K. Hiroya, *Org. Lett.*, 2007, **9**, 2931.

12 (a) J. Barluenga, P. Moriel, C. Valdes, F. Aznar, *Angew. Chem*., 2007, **119**, 5683; *Angew. Chem. Int. Ed*., 2007, **46**, 5587; (b) J. Barluenga, M. Tomás-Gamasa, F. Aznar, C. Valdés, *Nat. Chem*., 2009, **1**, 494; c) J. Barluenga, M. Escribano, F. Aznar, C. Valdés, *Angew. Chem*., 2010, **122**, 7008; *Angew. Chem. Int. Ed*., 2010, **49**, 6856; d) J. Barluenga, L. Florentino, F. Aznar, C. Valdés, *Org. Lett.,* 2011, **13**, 510; (e) J. Barluenga, M. Tomás-Gamasa, F. Aznar, C. Valdés, *Angew. Chem*., 2010, **122**, 5113; *Angew. Chem. Int. Ed*., 2010, **49**, 4993; f) J. Barluenga, N. Quinones, M. P. Cabal, F. Aznar, C. Valdes, *Angew. Chem*., 2011, **123**, 2398; *Angew. Chem. Int. Ed*., 2011, **50**, 2350; g) J. Barluenga, C. Valdés, *Angew. Chem*., 2011, **123**, 7626; *Angew. Chem. Int. Ed*., 2011, **50**, 7486; h) R. Barroso, RA. Valencia, MP. Cabal, C. Valdés. *Org. Lett*., 2014, **16**, 2264; i) L. Florentino, F. Aznar, C. Valdés, *Chemistry*., 2013, **19**, 10506; j) MC. Pérez-Aguilar, C. Valdés, *Angew. Chem. Int. Ed*., 2012, **51**, 5953; k) J. Barluenga, M. Tomás-Gamasa, C. Valdés, *Angew. Chem. Int.* Ed., 2012, **51**, 5950; l) L. Florentino, F. Aznar, C. Valdés, *Org. Lett*., 2012, **14**, 2323; m) MC. Pérez-Aguilar, C. Valdés. *Angew. Chem. Int. Ed*., 2013, **52**, 7219.

13 (a) Q. Xiao, J. Ma, Y. Yang, Y. Zhang, J. B. Wang, *Org. Lett*., 2009, **11**, 4732; b) L. Zhou, F. Ye, Y. Zhang, J. B. Wang, *J. Am. Chem. Soc*., 2010, **132**, 13590; c) Q. Xiao, Y. Xia, H. A. Li, Y. Zhang, J. B. Wang, *Angew. Chem*., 2011, **123**, 1146; *Angew. Chem. Int. Ed*., 2011, **50**, 1114; d) L. Zhou, Y. Shi, Q. Xiao, Y. Z. Liu, F. Ye, Y. Zhang, J. B. Wang, *Org. Lett*., 2011, **13**, 968; e) L. Zhou, F. Ye, J. C. Ma, Y. Zhang, J. B. Wang, *Angew. Chem.*, 2011, **123**, 3572; *Angew. Chem. Int. Ed*., 2011, **50**, 3510; f) X. Zhao, G. Wu, Y. Zhang, J. Wang, *J. Am. Chem. Soc*., 2011, **133**, 3296; g) F. Ye, X. Ma, Q. Xiao, Y. Zhang, J. Wang, *J. Am. Chem. Soc*., 2012, **134**, 5742; h) Q. Xiao, L. Ling, F. Ye, R. Tan, L. Tian, Y. Zhang, Y. Li, J. Wang, *J. Org. Chem.*, 2013, **78**, 3879; i) S. Xu, G. Wu, F. Ye, X. Wang, H. Li, X. Zhao, Y. Zhang and J. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 4669; j) Z. Zhang, Q. Zhou, W. Yu, T. Li, G. Wu, Y. Zhang, J. Wang, *Org. Lett*., 2015, **17**, 2474; k) Z. Zhang, Q. Zhou, F. Ye, Y. Xia, G. Wu, M. L. Hossain, Y. Zhang and J. Wang, *Adv. Synth. Cat.*, 2015, **357**, accepted; l) Z. Zhang, J. Feng, Y. Xu, S. Zhang, Y. Ye, T. Li, X. Wang, J. Chen, Y. Zhang and J. Wang, *Synlett*., 2015, **26**, 59; m) F. Ye, C. Wang, X. Ma, M. L. Hossain, Y. Xia, Y. Zhang and J. Wang, *J. Org. Chem*., 2015, **80**, 647; n) Y. Xia, Y. Xia, Y. Zhang, and J. Wang, *Org. Biomol. Chem.*, 2014, **12**, 9333; o) M. L. Hossain, F. Ye, Z. Liu, Y. Xia, Y. Shi, L. Zhou, Y. Zhang and J. Wang, *J. Org. Chem.*, 2014, **79**, 8689; p) F. Hu, Y. Xia, Z. Liu, C. Ma, Y. Zhang and J. Wang, *Org. Biomol. Chem.*, 2014, **12**, 3590; q) Z. Liu, L. Wang, H. Tan, S. Zhou, T. Fu, Y. Xia, Y. Zhang and J. Wang, *Chem. Commun.*, 2014, **50**, 5061; r) F. Hu, Y. Xia, F. Ye, Z. Liu, C. Ma, Y. Zhang and J. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 1364; s) M. Hossain, F. Ye, Y. Zhang and J. Wang, 2013, **78**, 1236; t) Z. Liu, Y. Zhang and J. Wang, *Chin. J. Org. Chem.*, 2013, **33**, 687; u) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.*, 2013, **46**, 236.