Full paper

Applied Organometallic Chemistry

Received: 27 January 2016 Revised: 9 April 2016 Accepted: 29 April 2016 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/aoc.3522

Poly(ethylene glycol)- and glucopyranoside-substituted N-heterocyclic carbene precursors for the synthesis of arylfluorene derivatives using efficient palladium-catalyzed aqueous Suzuki reaction

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This paper reports an environmentally friendly and highly efficient synthesis of organic semiconductor materials via a Pd/N-heterocyclic carbene (NHC)-catalyzed Suzuki reaction in aqueous ethanol with high isolated yields (86–98%). Firstly, four glucopyranoside-substituted NHC precursors with poly(ethylene glycol) (PEG) chains were synthesized and characterized. The NHC precursor with the longest PEG chain (n = 16) was found to be the most efficient ligand in the reactions of a wide range of aryl halides and arylboronic acids. The best catalyst system obtained in this work could be recycled five times without significant loss of catalytic activity.I Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: aqueous Suzuki reaction; arylfluorene derivatives; carbohydrates; N-heterocyclic carbene precursor; poly(ethylene glycol)

Introduction

Conjugated compounds based on fluorene, carbazole, triphenylamine and fluorine moieties have received much attention due to their potential application in the fields of thin-film transistors, organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).[1–5] Generally, these compounds are mainly prepared through Pd-catalyzed Suzuki reactions in the presence of phosphine ligands, which should be conducted in certain toxic organic solvents such as toluene, tetrahydrofuran or dimethyRlformamide (DMF) in inert atmosphere. All these strict requirements usually mean such reactions suffer from tedious preparation and being physiologically harmful.[6,7] It would be very meaningful if these reactions could be conducted in green solvents and with mild conditions in air, which would make them easier to handle, safer and environmentally friendly too.[8]

In recent years, significant progress has been made in the aqueous Suzuki reaction.[9–11] Since the first report on catalysts containing sulfonate- and carboxylate-functionalized N-heterocyclic carbene (NHC) ligands,[12] there have been a large number of water-soluble NHC ligands used in Pd-catalyzed cross-coupling.[13,14] Taking the hydrophilicity and flexibility of bulky poly (ethylene glycol) (PEG) chains into consideration, the incorporation of PEG chains into NHC ligands could effectively improve simultaneously the water solubility and steric hindrance of the host materials. However, up to the present, there have been only a few reports of NHC ligands containing PEG groups.[13,15–19] The first example was reported by Hong and Grubbs who used a PEG-decorated NHC–Ru compound for aqueous olefin metathesis.[17] Liu and co-workers reported short alkyl chain- and PEG chain-functionalized imidazolium salts for the efficient Pd-catalyzed Suzuki reaction in neat water.[13] Tsuji and co-workers synthesized a series of NHC–Pd catalysts bearing hydrophobic long-chain alkyl and/or hydrophilic tetraethylene glycol groups for the Suzuki reaction.[15] Shi *et al.* synthesized a series of short-chain alkyl and/or PEG chain ferrocenylphospine–imidazolium salts, and they found that the catalysts bearing PEG chains showed higher catalytic activity for Pd-catalyzed Suzuki reaction in aqueous solvents.[19] Very recently, NHCs bearing different lengths of PEG chains were synthesized by Fujihara *et al.* and used to promote Pd-catalyzed Suzuki reactions, the catalysts with longer PEG chains showing better performance.[18] We found PEG-functionalized NHC ligands were efficient for recyclable Pd-catalyzed Suzuki reactions in water,[16] and recently we utilized short alkyl chain- and

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glucopyranoside-based NHC precursors for Pd-catalyzed Suzuki reactions, which smoothly promoted the Suzuki coupling in ethanol (95%) with a typical catalyst loading of 0.1 mol%.[20] Obviously, the long flexible PEG chains wrapping the metal Pd catalyst center can stabilize the catalyst species, which is crucial in the Pd-catalyzed Suzuki reaction.

In this work, we report the synthesis and characterization of four glucopyranoside-substituted NHC precursors (**2**–**5**) bearing PEG chains with different length (Scheme 1), and develop a fast and efficient protocol for the aqueous Suzuki reaction. By using this catalyst system, we synthesized 2-arylfluorene and 2,7-diarylfluorene derivatives (eight examples each) containing carbazole, triphenylamine and fluorine moieties under aqueous conditions in air with 86–98% yields.

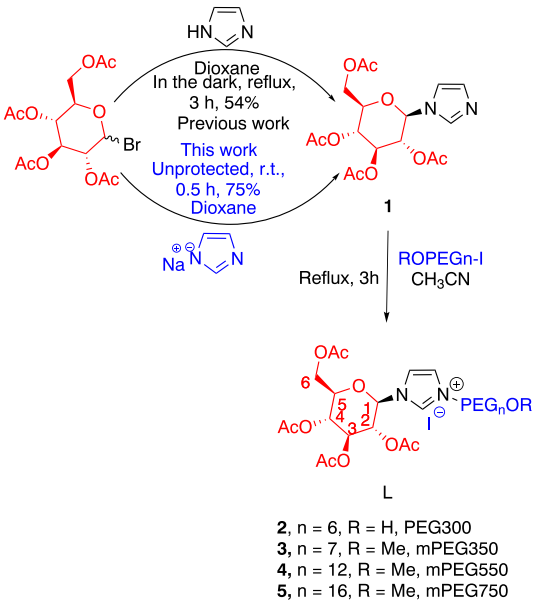
Results and discussion

The synthesis of compound **1** was started from tetra-acetyl-α-D-glucopyranosyl bromide, which was prepared on a gram scale according to a previously reported method.[21] In the earlier method, the substrates tetra-acetyl-α-D-glucopyranosyl bromide and imidazole were refluxed in freshly distilled 1,4-dioxane in the dark and an inert atmosphere for 3 h with a total yield of 54% (α:β = 1:3), and the yield of β-anomer compound **1** was 40.5%.[22,23] The relatively low yield was attributed to the sensitivity of tetra-acetyl-α-D-glucopyranosyl bromide to heat, light and water. The synthesis of compound **1** was accomplished herein using a modified procedure (Scheme 1). Firstly, deprotonation of imidazole with sodium hydride in 1,4-dioxane gave sodium imidazole salt using an ice bath. Then, a 1,4-dioxane solution of tetra-acetyl-α-D-glucopyranosyl bromide was added quickly into the sodium imidazole salt, to directly produce **1** after 0.5 h in air, with a yield of 75% higher than the previously reported yield.[22,23]

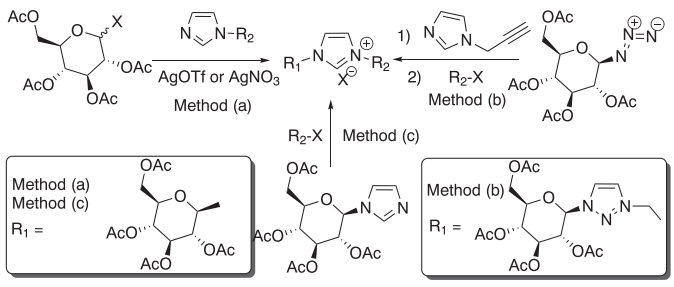
Sugar-containing imidazolium salts are usually obtained using the following three methods: (a) reaction of glycosyl bromide with *N*-substituted imidazole;[24] (b) attaching sugar units to imidazolium salts by click chemistry;[25] and (c) reaction of sugar-substituted imidazole with haloalkane or halogenoarene (Scheme 2).[22,26] Because anomeric effects will induce liability of hemiacetal groups at C-1 or C-6 for aldehydic sugars, a mixture of α- and β-epimers was obtained. Pure β-anomer was obtained when tetra-acetyl-α-D-glucopyranosyl bromide was treated with *N*-mesityl imidazole using silver triflate as additive. However, silver nitrate will lead to a mixture of epimers obtained in method (a).[24] The sugar units were not attached to imidazolium salts directly by using click chemistry and a mixture of α,β-epimers was obtained with method (b).[25] Thus, compound **1** was firstly synthesized with method (c) and purified, followed by reaction with 1-iodo-PEG derivatives to afford the target products **2**–**5**.

Four chiral imidazolium salts (**2**–**5**) were synthesized in high yields from the reaction of compound **1** with various 1-iodo-PEG derivatives. The structure of these compounds was confirmed with Fourier transform infrared (FT-IR), electrospray ionization (ESI)-MS and NMR spectral analyses. All imidazolium salts were air-stable and water-soluble. In the ESI-MS spectrum of compound **3** in methanol, the gap between the adjacent two peaks was 44.0 *m/z*, which was exactly the theoretical value of the repeat ethoxyl unit, corresponding to the break of ethoxyl groups occurring in methanol. NMR spectra of these compounds clearly show four acetyl groups. The TLC and NMR results revealed that all of compounds **2**–**5** were β-anomer only. The NCHN proton in the imidazolinium salts of **2**–**5** was observed at 9.74 ppm for **2**, 10.17 ppm for **3**, 9.75 ppm for **4** and 9.77 ppm for **5** in the ^{1}H NMR spectra, because of the highly acidic character of the 2-proton of imidazolium salts. The configuration at the anomeric position can also be determined using ^{1}H NMR spectroscopy. The proton at the anomeric position (C-1) results in a doublet at 6.33 to 6.48 ppm, with coupling constant $^3J_{1,2}$ ranging from 9.2 to 9.3 Hz for **2**–**5**. This indicates a diaxial relationship of the hydrogen at C-1 and C-2, and thus just one set of proton signals observed in the ^{1}H NMR spectra suggests that no racemization occurred during the synthesis of these compounds, as shown in Scheme 1.

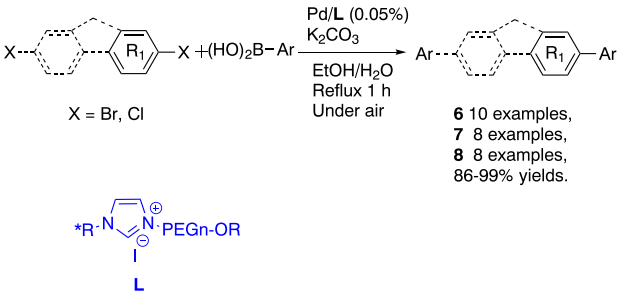
The catalytic activity of glucopyranoside-substituted NHC precursors **2**–**5** bearing PEG chains with various lengths in Pd-catalyzed Suzuki reactions was first investigated. The cross-coupling of 4-bromotoluene and phenylboronic acid was chosen as a model reaction (Scheme 3). We first explored the reaction in water, and found that just 45% of 4-bromotoluene was consumed even under refluxing (Table 1, entry 4). The partial deprotection of the acetyl groups occurred in the Pd-catalyzed Suzuki reaction in neat water, resulting in a decrease in the steric bulk of the ligand, and the relatively low catalytic activity. Then Suzuki reaction was carried out under reflux in green solvents, including methanol,



Scheme 1. Synthesis of glucopyranoside- and PEG chain-substituted NHC precursors.



Scheme 2. Synthesis of sugar-containing imidazolium salts by three different methods.



Scheme 3. Pd/L-catalyzed Suzuki reactions in aqueous ethanol.

Table 1. Conversion of Suzuki reactions using various solvents and bases[a]

Entry	Base	Solvent	Conversion (%)[b]
1	$K_3PO_4{\cdot}7H_2O$	H_2O	Trace[c]
2	$K_3PO_4{\cdot}7H_2O$	EtOH	38[c]
3	$K_3PO_4{\cdot}7H_2O$	MeOH	33[c]
4	$K_3PO_4{\cdot}7H_2O$	H_2O	45
5	$K_3PO_4{\cdot}7H_2O$	EtOH	80
6	$K_3PO_4{\cdot}7H_2O$	MeOH	78
7	$K_3PO_4{\cdot}7H_2O$	EtOH–H_2O = 1/1	87
8	$K_3PO_4{\cdot}7H_2O$	EtOH–H_2O = 2/1	93
9	$K_3PO_4{\cdot}7H_2O$	EtOH–H_2O = 3/1	96
10	$K_3PO_4{\cdot}7H_2O$	EtOH (95%)	91
11	$K_3PO_4{\cdot}7H_2O$	*i*PrOH–H_2O = 3/1	65
12	$K_3PO_4{\cdot}7H_2O$	*n*BuOH–H_2O = 3/1	68
13	$K_3PO_4{\cdot}7H_2O$	DMF–H_2O = 3/1	81
14	Na_2CO_3	EtOH–H_2O = 3/1	85
15	NaOH	EtOH–H_2O = 3/1	92
16	K_2CO_3	EtOH–H_2O = 3/1	98
17	Et_3N	EtOH–H_2O = 3/1	42
18	DABCO	EtOH–H_2O = 3/1	21
19	NaOMe	EtOH–H_2O = 3/1	88
20	—	EtOH–H_2O = 3/1	Trace

[a]Reaction conditions: 4-bromotoluene (0.5 mmol), phenylboronic acid (0.75 mmol), Pd $(OAc)_2$/**3** = 1:2 (0.1 mol%), base (1.0 mmol), solvent (3.0 ml), reflux in air, 1 h.
[b]Measured by GC–MS.
[c]Room temperature, 12 h.

ethanol and 95% aqueous ethanol solution, leading to moderate to excellent conversions (Table 1, entries 5, 6 and 10). The high yield of these reactions confirmed that the PEG chain increased both the water solubility and the steric bulk of the ligand.

As is evident from Table 1, a high conversion of 91% is obtained from 95% aqueous ethanol solution, which implies that the amount of water in the reaction solvent is an important factor affecting the catalytic activity of the catalyst system.[27,28] We changed the content of water in the ethanol–water reaction solvents in subsequent experiments. When the volume ratio of ethanol and water changed from 1:1 to 3:1 (Table 1, entries 7–9), the conversion of 4-bromotoluene increased from 87 to 96% (Table 1, entry 9). Our results agreed with those of a previous study,[29] and 3:1 ethanol–water mixture was used to check the various catalytic systems.

It is well known that base is a crucial factor in the Pd-catalyzed Suzuki reaction. Therefore, the effect of various organic and inorganic bases was investigated for the Pd $(OAc)_2$/**3**-catalyzed Suzuki reaction in 3:1 ethanol–water mixture (Table 1, entries 9 and 14–19). The results in Table 1 show that K_2CO_3 (Table 1, entry 16) was the best base for the reaction in our work. The widely used base 1,4-diazabicyclo[2.2.2] octane (DABCO) was inefficient (Table 1, entry 18). The base Et_3N has a greater tendency to coordinate to NHC–Pd active species, and extend the lifetime of NHC–Pd active species during the catalytic cycle of the Suzuki reaction.[30] This may be attributed to the coordinated space of NHC occupied by the bulky PEG chain and sugar group.

Various catalyst systems were studied in the Suzuki reaction including Pd source, Pd and ligand molar ratio, and catalyst loading (Table 2). The catalytic activity of Pd $(OAc)_2$/**3** was obviously higher than that of commercially available Pd $(PPh_3)_4$ (Table 2, entry 6). Trace product was detected in the reaction without any addition of Pd source (Table 2, entry 1). We observed that a 1:2 Pd/ligand molar ratio afforded a highest conversion of 98% (Table 2, entry 5), which was slightly higher than the conversion (95%) at 1:1.5 molar ratio with 0.1 mol% catalyst loading (Table 2, entry 8). Ligands **2**, **4** and **5** were also explored (Table 2, entries 14–16). We found that a 1:2 molar ratio of $Pd(OAc)_2$/**5** afforded the highest conversion of 99% with 0.05 mol% catalyst loading (Table 2, entry 16). Under the same reaction conditions, decreasing the amount of catalyst to 0.01 mol% and extending the reaction time to 12 h gave a conversion of 80% (Table 2, entry 17). Compared with the short alkyl chain- and glucopyranoside-based NHC precursor,[20] the longer PEG chain (n = 16) not only increased the water solubility and steric bulk of glucopyranoside-based NHC precursor, but also improved the catalytic activity considerably.

Table 2. Conversion of Suzuki reactions using various precatalysts, ligands and molar ratios[a]

Entry	Precatalyst (Pd)	Pd/**L** (%)	Time (h)	Conversion (%)[b]
1	—	Pd/**3** = 0:2, —	3.0	Trace
2	$Pd_2(dba)_3$	Pd/**3** = 1:2, 0.1	1.0	93
3	$Pd(CH_3CN)_2Cl_2$	Pd/**3** = 1:2, 0.1	1.0	71
4	$PdCl_2$	Pd/**3** = 1:2, 0.1	1.0	95
5	$Pd(OAc)_2$	Pd/**3** = 1:2, 0.1	1.0	98
6	$Pd(PPh_3)_4$	Without **L**, 0.1	1.0	75
7	$Pd(OAc)_2$	Without **L**, 0.1	1.0	35
8	$Pd(OAc)_2$	Pd/**3** = 1:1.5, 0.1	3.0	95
9	$Pd(OAc)_2$	Pd/**3** = 1:1.2, 0.1	3.0	85
10	$Pd(OAc)_2$	Pd/**3** = 1:1, 0.1	3.0	78
11	$Pd(OAc)_2$	Pd/**3** = 1:3, 0.1	3.0	90
12	$Pd(OAc)_2$	Pd/**3** = 1:4, 0.1	3.0	78
13	$Pd(OAc)_2$	Pd/**3** = 1:2, 0.05	1.0	97
14	$Pd(OAc)_2$	Pd/**2** = 1:2, 0.05	1.0	91
15	$Pd(OAc)_2$	Pd/**4** = 1:2, 0.05	1.0	96
16	$Pd(OAc)_2$	Pd/**5** = 1:2, 0.05	1.0	99
17	$Pd(OAc)_2$	Pd/**5** = 1:2, 0.01	12.0	80

[a]Reaction conditions: 4-bromotoluene (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst, K_2CO_3 (1.0 mmol), EtOH–H_2O = 3:1 (3.0 ml), reflux in air.
[b]Measured by GC–MS.

The best conditions for the Suzuki reaction obtained in this work were as follow: 0.17 mmol ml^{-1} aryl halide and 2.0 mol equiv. of K_2CO_3 stirred at 110 °C for 1.0 h in air using 0.05 mol% Pd/**5** (1:2) as catalyst. A range of aryl halides were studied further in the protocol (Fig. 1). As expected, all these reactions gave biaryl derivatives with high yields. Various 4-substituted aryl bromides bearing electron-donating or electron-withdrawing groups, including methyl, methoxy, cyano and acetyl groups, reacted with phenylboronic acid providing the corresponding biaryl products in yields above 92% (**6a**–**6g**, Fig. 1). Further studies indicated that the activated aryl chloride *p*-(trifluoromethyl) chlorobenzene was suitable for this Pd-catalyzed Suzuki coupling (91%, **6j**, Fig. 1).

With the optimum conditions mentioned above, various arylboronic acids containing carbazole, triphenylamine and fluorine moieties were explored to couple with 2-bromofluorene and 2,7-dibromofluorene (Figs 2 and 3). Notably, the results revealed that the electronic nature of the substituent group on arylboronic acids had little effect on the reactivity of Suzuki coupling. As shown in Fig. 2, the coupling of 2-bromofluorene with 2-methylbenzeneboronic acid gave **7b** in 92% yield, showing a slightly lower efficiency, while 1-naphthylboronic acid and 3,5-dimethylbenzeneboronic acid reacted smoothly and afforded **7a** and **7c** in 94 and 95% yields, respectively. Fluorine moieties are popular groups for modifying the carrier transporting property and energy levels of organic semiconductor materials. It was noteworthy that the Suzuki coupling of 2-bromofluorene with 3,5-bis (trifluoromethyl) fluorobenzeneboronic acid, 3,5-difluorobenzeneboronic acid and 3,4,5-trifluorobenzeneboronic acid could be completed in 97, 93 and 97% yields, respectively (**7d**, **7e** and **7f**), which represent high reactivity. Because of the good hole transporting/electron donating ability of carbazole and triphenylamine building blocks, they have been widely used in the field of photoelectronics to construct OLEDs, OPVs and perovskite solar cells.[3,5] We also carried out the reaction of 2-bromofluorene with 4-(diphenylamino) phenylboronic acid and 9-phenyl-3-carbazoleboronic acid using the same catalyst system, to provide the corresponding products **7g** and **7h** in 97 and 89% yields, respectively.

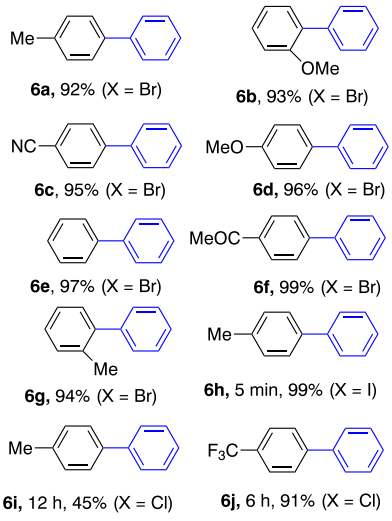


Figure 1. Scope and limitation of Suzuki reaction. (Reaction conditions: catalyst: Pd $(OAc)_2$/**5** (1:2), 0.05 mol%; 0.21 mmol ml^{-1} phenylboronic acid; base: 2.0 mol equiv. of K_2CO_3; solvent: 3:1 ethanol–water mixture; with 0.17 mmol ml^{-1} aryl halide; reaction maintained at 110 °C in an oil bath, stirred in air for about 1.0 h except special instructions. The isolated yields are presented.)

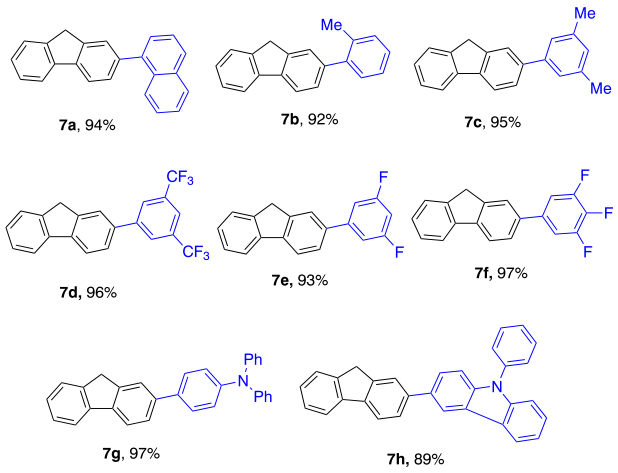


Figure 2. 2-Arylfluorene derivatives obtained from Suzuki reaction. (Reaction conditions: catalyst: Pd $(OAc)_2$/**5** (1:2), 0.05 mol%; 0.21 mmol ml^{-1} arylboronic acid; base: 2.0 mol equiv. of K_2CO_3; solvent: 3:1 ethanol–water mixture; with 0.17 mmol ml^{-1} 2-bromofluorene; reaction maintained at 110 °C in an oil bath, stirred about 1.0 h in air. The isolated yields are presented.)

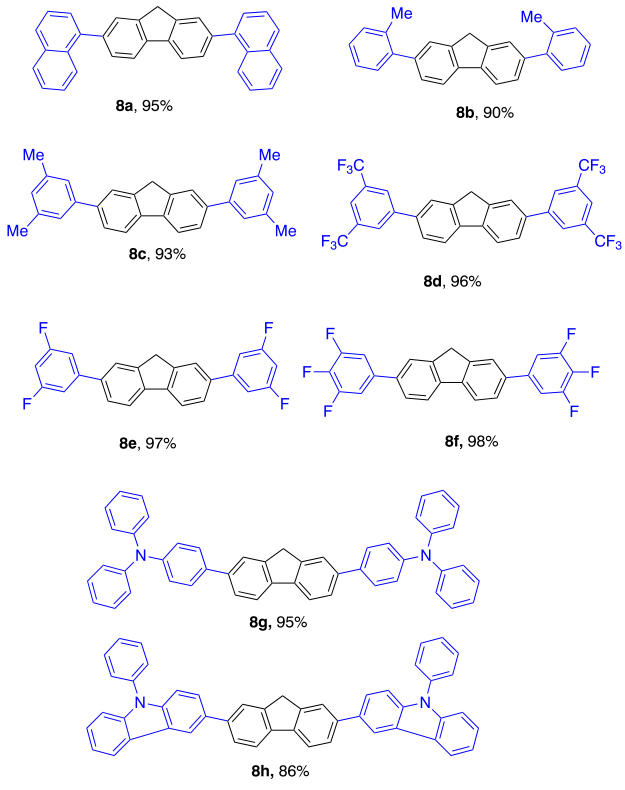


Figure 3. 2,7-Diarylfluorene derivatives obtained from Suzuki reaction. (Reaction conditions: catalyst: Pd $(OAc)_2$/**5** (1:2), 0.05 mol%; 0.21 mmol ml^{-1} arylboronic acids; base: 2.0 mol equiv. of K_2CO_3; solvent: 3:1 ethanol–water mixture; with 0.17 mmol ml^{-1} 2,7-dibromofluorene; reaction maintained at 110 °C in an oil bath, stirred about 1.0 h in air. The isolated yields are presented.)

Table 3. Reusability of catalyst in Suzuki reaction[a]

Run	Time (min)	Conversion (%)[b]	Yield (%)[c]
1	5	99	98
2	5	98	96
3	10	98	95
4	20	95	92
5	30	93	91

[a]Reaction conditions: phenylboronic acid (3.0 mmol), 4-iodotoluene (2.0 mmol), catalyst (Pd $(OAc)_2$:**5** = 1:2, 0.05 mol%), K_2CO_3 (4.0 mmol), ethanol–water (3:1, 12.0 ml), 110 °C, stirred in air.
[b]Measured by GC–MS.
[c]Isolated yield.

To investigate the universality of the new catalyst system, cross-coupling reactions of 2,7-dibromofluorene with various arylboronic acids were carried out. The yields of these reactions are summarized in Fig. 3. The results were similar to those for the Suzuki reaction of 2-bromofluorene (Fig. 2), which illustrated that the catalyst system worked smoothly between 2-bromofluorene/2,7-dibromofluorene and a range of arylboronic acids, affording high yields of 2-arylfluorene and 2,7-diarylfluorene derivatives.

The reusability of our best catalyst system (Pd $(OAc)_2$/**5** = 1:2, 0.05 mol%) was tested with the coupling of 4-iodotoluene with phenylboronic acid using K_2CO_3 as base at 110 °C. Since the product 4-phenyltoluene was soluble and the precatalyst (Pd$(OAc)_2$/**5**) was insoluble in diethyl ether, 4-phenyltoluene was easily purified by extraction using diethyl ether. Precatalyst combined with solution was recovered and recycled to be used for another run. The reuse reactions occurred very fast, complete conversions were achieved after recycling three times within 20 min, and 91% isolated yield was achieved when prolonging the reaction time to 30 min after recycling four times (Table 3). Our catalyst system could be recycled five times with some decrease in activity (Table 3).

Conclusions

In summary, four NHC precursors bearing glucopyranoside and PEG chains with various lengths were synthesized, and employed in Pd-catalyzed aqueous Suzuki reaction. In the coupling of arylboronic acids with aryl bromides and activated aryl chlorides, 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-mPEG750-imidazolium iodide with the longest PEG chain (n = 16) was found to be the most efficient ligand. The PEG chains increased both the water solubility and steric bulk of NHC precursors, and improved their catalytic activity considerably. Organic semiconductor materials based on 2-arylfluorene derivatives (eight examples) and 2,7-diarylfluorene derivatives (eight examples) were synthesized using Suzuki coupling with high isolated yields (86–98%) using the new catalyst system. Such catalyst system could be recycled five times with little decrease in activity. Combining the high yields and wide feasibility, the catalyst system will have potential in the efficient preparation of functional conjugated compounds in an environmentally friendly solvent.

Experimental

General notes

All aryl bromides, aryl chlorides and arylboronic acids (Aldrich or Acros) were used as received directly, except 2-bromofluorene and 2,7-dibromofluorene.[31] $Pd_2(dba)_3$, Pd $(CH_3CN)_2Cl_2$, $PdCl_2$, Pd $(OAc)_2$ and Pd $(PPh_3)_4$ were purchased from Strem Chemical Company. $K_3PO_4{\cdot}7H_2O$, K_2CO_3, Na_2CO_3, Et_3N, DABCO, NaOMe and NaOH were used as received purchased from Sinopharm Chemical Reagent Limited Corporation. 1-Iodo-PEG derivatives[32,33] HO-PEG300-I (Mw: 300 g mol^{-1}), MeO-PEG350-I (Mw: 350 g mol^{-1}), MeO-PEG550-I (Mw: 550 g mol^{-1}) and MeO-PEG750-I (Mw: 750 g mol^{-1}) were synthesized according to the literature method. 1,4-Dioxane was stored over sodium wire, and distilled from sodium benzophenone ketyl prior to use. Silica gel HF_{254} and silica gel 200–300 mesh were used for TLC and column chromatography, respectively. NMR spectra were recorded with a Bruker Avance III 400 spectrometer at 298 K with tetramethylsilane as internal standard. MS was conducted with a Bruker Daltonics Flex-Analysis. Most of the Suzuki reactions were monitored with an Agilent 6890 GC with 5973 MS detector. CHN elemental analysis was performed with an elemental analyzer (Vario Micro Cube, Germany). FT-IR spectra were recorded neat using the smart OMNI-transmission accessories for a Nicolet FT-IR spectrometer and frequencies were reported as cm^{-1}.

General procedure for Pd-Catalyzed aqueous suzuki reactions

In air, the appropriate amounts of NHC precursor, base and Pd source were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was fitted with a rubber septum, evacuated and then refilled three times with nitrogen. 1,4-Dioxane (3.0 ml) was added via syringe, and then the mixture was stirred for 0.5 h at 80 °C to generate NHC-coordinated Pd complex. Then 1,4-dioxane was evaporated under reduced pressure. Aryl halide, arylboronic acid (1.25 equiv. based on aryl halide) and solvent were sequentially added, and decane was used as internal standard. The Schlenk tube was sealed and immersed in an oil bath at 110 °C and the course of reaction was monitored using GC–MS. When the reaction was completed, the mixture was cooled to room temperature, and the product was extracted three times with ether or ethyl acetate, and then purified by column chromatography (PE/EA = 20/1 to 10/1).

Synthesis of compounds 1–5

*1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl) imidazole (**1**).*

A mixture of sodium hydride (0.45 g, 13 mmol) and imidazole (0.60 g, 8.8 mmol) in 20 ml of freshly distilled 1,4-dioxane was stirred for 30 min at room temperature. To the mixture a 1,4-dioxane solution of tetra-acetyl-α-D-glucopyranosyl bromide (4.75 g, 9.0 mmol), which was synthesized according to a procedure analogous to a previously reported method,[21] was added and stirred at room temperature for 0.5 h. The pale yellow solid formed was filtered off, washed three times with brine and dried with $MgSO_4$, then evaporated *in vacuo*. Recrystallization from methanol three times afforded compound **1** as white needles (2.69 g, 75%), m.p. 206–208 °C.

*1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3-PEG300-imidazolium iodide (**2**)*

Compound **1** (1.0 g, 2.5 mmol), 25.0 ml of CH_3CN and the corresponding reagent HO-PEG300 iodide (1.17 g, 2.75 mmol) were added into a 50 ml flask, and the mixture was stirred under reflux for 3 h in air. After cooling to room temperature, CH_3CN was removed under reduced pressure and the residue was purified by chromatography (dichloromethane–methanol, 10:1) to afford the title compound **2** (2.01 g, 95%) as a pale yellow viscous compound, which was characterized using ^1H, ^{13}C, DEPT135, DEPT45, DEPT90, ^1H–^1H COSY, ^1H–^{13}C HSQC and ^1H–^{13}C HMBC.

^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.74 (s, 1H, 2-Im), 7.79 (s, 1H, 4-Im), 7.56 (s, 1H, 5-Im), 6.35 (d, J = 8.0 Hz, 1H, 1-carbohydrate), 5.29 (t, J = 8.0 Hz, 1H, 3-carbohydrate), 5.17 (s, 1H, OH), 5.16–5.05 (m, 2H, 2 and 4-carbohydrate), 4.55–4.43 (m, 2H, CH_2), 4.24–4.20 (m, 1H, 5-carbohydrate), 4.18–4.14 (m, 1H, 6-carbohydrate), 4.01–3.98 (m, 1H, 6-carbohydrate), 3.80–3.68 (m, 2H, CH_2), 3.57–3.38 (m, 48H, CH_2-CH_2), 3.37–3.34 (m, 2H, CH_2), 1.91 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.83 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 170.14 (C= O), 169.29 (C=O), 169.16 (C=O), 169.09 (C=O), 136.40 (2-Im), 124.11 (4-Im), 119.24 (5-Im), 83.45 (1-carbohydrate), 74.48 (5-carbohydrate), 72.00 (3-carbohydrate), 71.55 (CH_2), 70.34 (2-carbohydrate), 70.15 (CH_2), 70.03 (CH_2), 70.01 (CH_2), 69.96 (CH_2), 69.87 (CH_2), 68.31 (CH_2), 67.13 (4-carbohydrate), 61.06 (6-carbohydrate), 58.68 (CH_2), 53.54 (CH_2), 50.09 (CH_2), 20.56 (CH_3, AcO), 20.34 (CH_3, AcO), 20.30 (CH_3, AcO), 20.24 (CH_3, AcO). MS (ESI): m/z (%) = 697.2 $[M - I]^+$. Elemental analysis: calcd for $C_{29}H_{46}IN_2O_{16}$ (%): C, 43.24; H, 5.76; found (%): C, 43.20; H, 5.79. FT-IR (neat): 3399, 3154, 2979, 1749, 1636, 1558, 1456, 1369, 1223, 1155, 1105, 1038, 939, 716.

*1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3-mPEG350-imidazolium iodide (**3**)*

Compound **3** was obtained as described for the synthesis of **2**. Yield 96% starting from compound **1** and mPEG350 iodide, pale yellow viscous compound. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 10.17 (s, 1H, 2-Im), 7.81 (s, 1H, 4-Im), 7.59 (s, 1H, 5-Im), 6.49 (d, J = 8.0 Hz, 1H, 1-carbohydrate), 5.44 (t, J = 12.0 Hz, 1H, 3-carbohydrate), 5.30–5.20 (m, 2H, 2 and 4-carbohydrate), 4.70–4.57 (m, 2H, CH_2), 4.37–4.30 (m, 2H, 5 and 6-carbohydrate), 4.18–4.13 (m, 1H, 6-carbohydrate), 3.90 (t, J = 4.0 Hz, 2H, CH_2), 3.75–3.54 (m, 31H, CH_2– CH_2), 3.52–3.54 (m, 2H, CH_2), 3.33 (s, 3H, OCH_3), 2.05 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.97 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 170.19 (C= O), 169.34 (C=O), 169.28 (C=O), 136.93 (2-Im), 124.16 (4-Im), 118.93 (5-Im), 83.65 (1-carbohydrate), 74.77 (5-carbohydrate), 72.25 (3-carbohydrate), 71.73 (2-carbohydrate), 70.32 (CH_2), 70.29 (CH_2), 70.23 (CH_2), 70.18 (CH_2), 70.16 (CH_2), 70.13 (CH_2), 70.09 (CH_2), 68.55 (CH_2), 67.26 (4-carbohydrate), 61.13 (6-carbohydrate), 58.79 (CH_2), 50.24 (CH_2), 20.58 (CH_3, AcO), 20.47 (CH_3, AcO), 20.34 (CH_3, AcO), 20.27 (CH_3, AcO). MS (ESI): m/z (%) = 853.3 $[M - Na]^+$. Elemental analysis: calcd for $C_{32}H_{52}IN_2O_{17}$ (%): C, 44.50; H, 6.07; found (%): C, 44.47; H, 6.12. FT-IR (neat): 3359, 2923, 2850, 1749, 1654, 1558, 1556, 1369, 1437, 1369, 1234, 1144, 1106, 963, 939, 918, 704.

*1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3-mPEG550-imidazolium iodide (**4**)*

Compound **4** was obtained as described for the synthesis of **2**. Yield 97% starting from compound **1** and mPEG550 iodide, pale yellow viscous compound. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.75 (s, 1H, 2-Im), 7.78 (s, 1H, 4-Im), 7.56 (s, 1H, 5-Im), 6.33 (d, J = 12.0 Hz, 1H, 1-carbohydrate), 5.31 (t, J = 12.0 Hz, 1H, 3-carbohydrate), 5.18 (s, 1H, OH), 5.17–5.07 (m, 2H, 2 and 4-carbohydrate), 4.57–4.39 (m, 2H, CH_2), 4.27–4.12 (m, 2H, 5 and 6-carbohydrate), 4.07–3.97 (m, 1H, 6-carbohydrate), 3.78–3.73 (m, 2H, CH_2), 3.61–3.40 (m, 44H, CH_2– CH_2), 3.37–3.34 (m, 2H, CH_2), 3.24 (s, 3H, OCH_3), 1.92 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.84 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 170.20 (C= O), 169.33 (C=O), 169.20 (C=O), 169.13 (C=O), 136.41 (2-Im), 124.11 (4-Im), 119.24 (5-Im), 83.50 (1-carbohydrate), 74.51 (5-carbohydrate), 72.02 (3-carbohydrate), 71.56 (CH_2), 70.36 (CH_2), 70.15 (2-carbohydrate), 70.10 (CH_2), 70.04 (CH_2), 69.97 (CH_2), 69.89 (CH_2), 68.33 (CH_2), 67.14 (4-carbohydrate), 61.08 (6-carbohydrate), 58.69 (CH_2), 53.50 (CH_2), 50.10 (CH_2), 49.84 (CH_2), 20.56 (CH_3, AcO), 20.32 (CH_3, AcO), 20.30 (CH_3, AcO), 20.24 (CH_3, AcO). MS (ESI): m/z (%) = 914.1 $[M - I - Na]^+$. Elemental analysis: calcd for $C_{42}H_{72}IN_2O_{22}$ (%): C, 46.54; H, 6.70; found (%): C, 46.49; H, 6.73. FT-IR (neat): 3394, 2969, 2896, 1748, 1555, 1434, 1369, 1221, 1175, 1144, 1065, 1037, 915, 756.

*1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3-mPEG750-imidazolium iodide (**5**).*

Compound **5** was obtained as described for the synthesis of **2**. Yield 94% starting from compound **1** and mPEG750 iodide, pale yellow viscous compound. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.77 (s, 1H, 2-Im), 7.78 (s, 1H, 4-Im), 7.56 (s, 1H, 5-Im), 6.35 (d, J = 8.0 Hz, 1H, 1-carbohydrate), 5.30 (t, J = 8.0 Hz, 1H, 3-carbohydrate), 5.18–5.07 (m, 2H, 2 and 4-carbohydrate), 4.57–4.39 (m, 2H, CH_2), 4.25–4.15 (m, 2H, 5 and 6-carbohydrate), 4.02–3.98 (m, 1H, 6-carbohydrate), 3.74 (t, J = 4.0 Hz, 2H, CH_2), 3.60–3.32 (m, 70H, CH_2– CH_2), 3.18 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.83 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 170.15 (C= O), 169.30 (C=O), 169.18 (C=O), 169.12 (C=O), 136.47 (2-Im), 124.12 (4-Im), 119.22 (5-Im), 83.47 (1-carbohydrate), 74.49 (5-carbohydrate), 72.02 (3-carbohydrate), 71.56 (CH_2), 70.35 (2-carbohydrate), 70.17 (CH_2), 70.03 (CH_2), 69.97 (CH_2), 69.89 (CH_2), 68.34 (CH_2), 67.13 (4-carbohydrate), 61.06 (6-carbohydrate), 58.68 (CH_2), 50.08 (CH_2), 20.55 (CH_3, AcO), 20.33 (CH_3, AcO), 20.30 (CH_3, AcO), 20.24 (CH_3, AcO). MS (ESI): m/z (%) = 623.0 $[M - I - R^*]^+$. Elemental analysis: calcd for $C_{50}H_{88}IN_2O_{26}$ (%): C, 47.66; H, 7.04; found (%): C, 47.60; H, 7.10. FT-IR (neat): 3418, 3054, 2959, 2867, 1749, 1573, 1554, 1437, 1369, 1218, 1173, 1106, 1064, 1037, 914, 706.

Characterization of 2-Arylfluorene and 2,7-Diarylfluorene derivatives

*2-(Naphthalen-1-yl)-9H-fluorene (**7a**)*

White solid, m.p. 172–173 °C. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.15 (d, J = 8.0 Hz, 1H, Ar-H), 8.04 (d, J = 8.0 Hz, 1H, Ar-H), 8.02–7.93 (m, 3H, Ar-H), 7.78 (s, 1H, Ar-H), 7.70–7.59 (m, 5H, Ar-H), 7.55 (dd, J = 17.4, 8.4 Hz, 2H, Ar-H), 7.46 (t, J = 7.2 Hz, 1H, Ar-H), 4.05 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 143.38 (Ar-C), 143.27 (Ar-C), 141.42 (Ar-C), 140.80 (Ar-C), 140.51 (Ar-C), 139.27 (Ar-C), 133.85 (Ar-C), 131.77 (Ar-C), 128.80 (Ar-C), 128.25 (Ar-C), 127.50 (Ar-C), 126.94 (Ar-C), 126.79 (Ar-C), 126.71 (Ar-C), 126.65 (Ar-C), 126.09 (Ar-C), 125.95 (Ar-C), 125.69 (Ar-C), 125.34 (Ar-C), 125.01 (Ar-C), 119.91 (Ar-C), 119.54 (Ar-C), 36.89 (C, CH_2). MS (ESI): m/z calcd for $C_{23}H_{15}$ $[M - H]^+$ 291.1; found 291.2. Elemental analysis: calcd for $C_{23}H_{16}$ (%): C, 94.48; H, 5.52; found (%): C, 94.50; H, 5.50.

*2-(3,5-Dimethylphenyl)-9H-fluorene (**7c**)*

Light yellow solid, m.p. 165–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.85 (t, J = 7.0 Hz, 2H, Ar-H), 7.81 (s, 1H, Ar-H), 7.66 (d, J = 7.9 Hz, 1H, Ar-H), 7.60 (d, J = 7.4 Hz, 1H, Ar-H), 7.44 (t, J = 7.4 Hz, 1H, Ar-H), 7.37 (d, J = 7.4 Hz, 3H, Ar-H), 7.34 (s, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 3.99 (s, 2H, CH_2), 2.46 (s, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 143.83 (Ar-C), 143.51 (Ar-C), 141.55 (Ar-C), 140.82 (Ar-C), 140.18 (Ar-C), 138.29 (Ar-C), 128.83 (Ar-C), 126.84 (Ar-C), 126.68 (Ar-C), 126.06 (Ar-C), 125.18 (Ar-C), 125.07 (Ar-C), 123.84 (Ar-C), 120.04 (Ar-C), 119.96 (Ar-C), 37.03 (C, CH_2), 21.49 (C, CH_3). MS (ESI): *m/z* calcd for $C_{21}H_{17}$ $[M - H]^+$ 269.1; found 269.2. Elemental analysis: calcd for $C_{23}H_{16}$ (%): C, 93.71; H, 6.29; found (%): C, 93.76; H, 6.24.

*2-(3,5-Bis (trifluoromethyl)phenyl)-9H-fluorene (**7d**)*

Light yellow solid, m.p. 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.10 (s, 2H), 7.95–7.80 (m, 3H), 7.79 (s, 1H, Ar-H), 7.61 (dd, J = 11.0, 7.6 Hz, 2H, Ar-H), 7.44 (t, J = 7.6 Hz, 1H, Ar-H), 7.38 (t, J = 7.6 Hz, 1H, Ar-H), 3.98 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 144.36 (Ar-C), 143.61 (Ar-C), 143.58 (Ar-C), 142.56 (Ar-C), 140.81 (Ar-C), 136.58 (Ar-C), 132.32 (q, Ar-C), 127.56 (Ar-C), 127.36 (Ar-C), 127.09 (Ar-C), 127.01 (Ar-C), 126.08 (Ar-C), 125.16 (Ar-C), 124.85 (Ar-C), 123.80 (Ar-C), 122.14 (Ar-C), 120.64 (Ar-C), 120.51 (Ar-C), 120.29 (Ar-C), 119.43 (Ar-C), 36.96 (C, CH_2). MS (ESI): *m/z* calcd for $C_{21}H_{11}F_6$ $[M - H]^+$ 377.1; found 377.5. Elemental analysis: calcd for $C_{21}H_{18}$ (%): C, 93.29; H, 6.71; found (%): C, 93.31; H, 6.69.

*2-(3,5-Difluorophenyl)-9H-fluorene (**7e**)*

Light yellow solid, m.p. 148–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.83 (t, J = 7.3 Hz, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 7.57 (dd, J = 7.2, 4.2 Hz, 2H, Ar-H), 7.40 (d, J = 7.4 Hz, 1H, Ar-H), 7.35 (d, J = 7.4 Hz, 1H, Ar-H), 7.17 (d, J = 7.6 Hz, 2H, Ar-H), 6.79 (s, 1H, Ar-H), 3.95 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 164.61 (d, J = 13.1 Hz, Ar-C), 162.15 (d, J = 13.2 Hz, Ar-C), 144.88 (t, J = 9.5 Hz, Ar-C), 144.07 (Ar-C), 143.55 (Ar-C), 142.13 (Ar-C), 141.03 (Ar-C), 137.40 (Ar-C), 127.13 (Ar-C), 126.94 (Ar-C), 125.86 (Ar-C), 125.10 (Ar-C), 123.60 (Ar-C), 120.26 (Ar-C), 120.16 (Ar-C), 109.95 (d, J = 7.1 Hz, Ar-C), 109.76 (d, J = 7.1 Hz, Ar-C), 102.24 (t, J = 25.5 Hz, Ar-C), 36.96 (C, CH_2). MS (ESI): *m/z* calcd for $C_{19}H_{11}F_2$ $[M - H]^+$ 277.1; found 277.1. Elemental analysis: calcd for $C_{19}H_{12}F_2$ (%): C, 82.00; H, 4.35; found (%): C, 82.05; H, 4.33.

*2-(3,4,5-Trifluorophenyl)-9H-fluorene (**7f**)*

Light yellow solid, m.p. 188–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.83 (d, J = 8.0 Hz, 2H, Ar-H), 7.65 (s, 1H, Ar-H), 7.58 (d, J = 7.2 Hz, 1H, Ar-H), 7.50 (d, J = 8.0 Hz, 1H, Ar-H), 7.42 (t, J = 7.4 Hz, 1H, Ar-H), 7.36 (t, J = 7.2 Hz, 1H, Ar-H), 7.30–7.19 (m, 2H, Ar-H), 3.94 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 152.73 (d, Ar-C), 152.63 (d, Ar-C), 150.25 (d, Ar-C), 150.15 (d, Ar-C), 144.12 (Ar-C), 143.47 (Ar-C), 140.88 (Ar-C), 137.64 (m, Ar-C), 136.58 (Ar-C), 127.17 (Ar-C), 126.94 (Ar-C), 125.88 (Ar-C), 125.09 (Ar-C), 123.41 (Ar-C), 120.28 (Ar-C), 120.14 (Ar-C), 111.00 (Ar-C), 110.94 (Ar-C), 110.84 (Ar-C), 110.78 (Ar-C), 36.91 (C, CH_2). MS (ESI): *m/z* calcd for $C_{19}H_{10}F_3$ $[M - H]^+$ 295.1; found 295.1. Elemental analysis: calcd for $C_{19}H_{11}F_3$ (%): C, 77.02; H, 3.74; found (%): C, 77.06; H, 3.70.

*4-(9H-Fluoren-2-yl)-N,N-diphenylaniline (**7g**)*

Yellow solid, m.p. 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.79 (t, J = 8.2 Hz, 2H), 7.73 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H, Ar-H), 7.53 (d, J = 7.8 Hz, 3H, Ar-H), 7.36 (t, J = 7.6 Hz, 1H, Ar-H), 7.31–7.19 (m, 5H, Ar-H), 7.14 (dd, J = 8.2, 3.2 Hz, 6H, Ar-H), 7.02 (t, J = 7.3 Hz, 2H, Ar-H), 3.93 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 147.77 (Ar-C), 147.10 (Ar-C), 143.86 (Ar-C), 143.37 (Ar-C), 141.52 (Ar-C), 140.55 (Ar-C), 139.38 (Ar-C), 135.53 (Ar-C), 129.22 (Ar-C), 127.76 (Ar-C), 126.77 (Ar-C), 126.56 (Ar-C), 125.47 (Ar-C), 124.96 (Ar-C), 124.38 (Ar-C), 124.03 (Ar-C), 123.23 (Ar-C), 122.85 (Ar-C), 120.04 (Ar-C), 119.81 (Ar-C), 36.95 (C, CH_2). MS (ESI): *m/z* calcd for $C_{21}H_{22}N$ $[M - H]^+$ 408.2; found 408.2. Elemental analysis: calcd for $C_{31}H_{23}N$ (%): C, 90.92; H, 5.66; found (%): C, 90.96; H, 5.64.

*3-(9H-Fluoren-2-yl)-9-phenyl-9H-carbazole (**7h**)*

Yellow solid, m.p. 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.50 (s, 1H, Ar-H), 8.30 (d, J = 7.6 Hz, 1H, Ar-H), 7.96 (s, 1H, Ar-H), 7.90 (dd, J = 14.6, 7.7 Hz, 2H, Ar-H), 7.84–7.74 (m, 2H, Ar-H), 7.64 (m, J = 13.4, 5H, Ar-H), 7.53 (d, J = 8.6 Hz, 4H, Ar-H), 7.47 (t, J = 7.5 Hz, 1H, Ar-H), 7.44–7.35 (m, 2H, Ar-H), 4.03 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 144.06 (Ar-C), 143.53 (Ar-C), 141.70 (Ar-C), 141.48 (Ar-C), 140.77 (Ar-C), 140.42 (Ar-C), 140.35 (Ar-C), 137.82 (Ar-C), 133.86 (Ar-C), 129.98 (Ar-C), 127.54 (Ar-C), 127.13 (Ar-C), 126.89 (Ar-C), 126.62 (Ar-C), 126.24 (Ar-C), 126.22 (Ar-C), 125.66 (Ar-C), 125.12 (Ar-C), 124.07 (Ar-C), 123.97 (Ar-C), 123.68 (Ar-C), 120.49 (Ar-C), 120.22 (Ar-C), 120.19 (Ar-C), 119.97 (Ar-C), 118.87 (Ar-C), 110.10 (Ar-C), 110.03 (Ar-C), 37.13 (C, CH_2). MS (ESI): *m/z* calcd for $C_{21}H_{20}N$ $[M - H]^+$ 406.2; found 406.3. Elemental analysis: calcd for $C_{31}H_{21}N$ (%): C, 91.37; H, 5.19; found (%): C, 91.42; H, 5.15.

*2,7-Di(3,5-dimethylphenyl)-9H-fluorene (**8c**)*

Light yellow solid, m.p. 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.77 (d, J = 8.0 Hz, 2H, Ar-H), 7.71 (s, 2H, Ar-H), 7.55 (d, J = 8 Hz, 1H, Ar-H), 7.22 (s, 4H, Ar-H), 3.94 (s, 2H, CH_2), 2.35 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 144.38 (Ar-C), 141.50 (Ar-C), 140.55 (Ar-C), 140.07 (Ar-C), 138.27 (Ar-C), 128.79 (Ar-C), 126.09 (Ar-C), 125.12 (Ar-C), 123.81 (Ar-C), 120.04 (Ar-C), 37.05 (C, CH_2), 21.45 (C, CH_3). MS (ESI): *m/z* calcd for $C_{29}H_{25}$ $[M - H]^+$ 373.2; found 373.3. Elemental analysis: calcd for $C_{29}H_{26}$ (%): C, 93.00; H, 7.00; found (%): C, 93.02; H, 6.98.

*2,7-Di(3,5-bis (trifluoromethyl)phenyl)-9H-fluorene (**8d**)*

Yellow solid, m.p. 190–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.09 (s, 4H, Ar-H), 7.95 (d, J = 8.0 Hz, 2H, Ar-H), 7.86 (t, J = 12.0 Hz, 4H, Ar-H), 7.68 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H, Ar-H), 4.10 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 144.68 (Ar-C), 143.36 (Ar-C), 141.57 (Ar-C), 137.26 (Ar-C), 132.16 (q, Ar-C), 127.17 (Ar-C), 126.41 (Ar-C), 124.76 (Ar-C), 124.02 (Ar-C), 122.05 (Ar-C), 122.10 (Ar-C), 122.84 (Ar-C), 37.05 (C, CH_2). MS (ESI): *m/z* calcd for $C_{29}H_{13}F_{12}$ $[M - H]^+$ 590.1; found 590.3. Elemental analysis: calcd for $C_{29}H_{14}F_{12}$ (%): C, 59.00; H, 2.39; found (%): C, 59.04; H, 2.36.

*2,7-Bis(3,5-difluorophenyl)-9H-fluorene (**8e**)*

Yellow solid, m.p. 185–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.85 (d, J = 8.0 Hz, 2H, Ar-H), 7.73 (s, 2H, Ar-H), 7.58 (d, J = 8.0 Hz, 2H, Ar-H), 7.19–7.14 (m, 4H, Ar-H), 7.83–6.77 (m, 2H, Ar-H), 3.99 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 164.50 (d, Ar-C), 162.13 (d, Ar-C), 144.64 (t, Ar-C), 144.37 (Ar-C), 141.35 (Ar-C), 137.79 (Ar-C), 126.05 (Ar-C), 123.67 (Ar-C), 120.56 (Ar-C), 109.87 (q, Ar-C), 102.38 (t, Ar-C), 36.97 (C, CH_2). MS (ESI): *m/z* calcd for $C_{25}H_{13}F_4$ $[M - H]^+$ 390.1; found 390.2. Elemental analysis: calcd for $C_{25}H_{14}F_4$ (%): C, 76.92; H, 3.61; found (%): C, 76.96; H, 3.57.

*2,7-Bis(3,4,5-trifluorophenyl)-9H-fluorene (**8f**)*

Yellow solid, m.p. 198–199 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.86 (d, J = 8.0 Hz, 2H, Ar-H), 7.70 (s, 2H, Ar-H), 7.54 (d, J = 8.0 Hz,

2H, Ar-H), 7.29–7.21 (m, 4H, Ar-H), 4.01 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 152.70 (q, Ar-C), 150.22 (q, Ar-C), 144.41 (Ar-C), 141.21 (Ar-C), 140.45 (t, Ar-C), 137.95 (t, Ar-C), 137.45 (m, Ar-C), 137.16 (Ar-C), 125.95 (Ar-C), 123.57 (Ar-C), 120.65 (Ar-C), 111.10 (q, Ar-C), 36.98 (C, CH_2). MS (ESI): *m/z* calcd for $C_{25}H_{11}F_6$ $[M - H]^+$ 426.1; found 426.2. Elemental analysis: calcd for $C_{25}H_{12}F_6$ (%): C, 70.43; H, 2.84; found (%): C, 70.48; H, 2.80.

*4,4′-(9H-Fluorene-2,7-diyl) bis (N,N-diphenylaniline) (**8g**)*

Yellow solid, m.p. 187–188 °C. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.82 (d, J = 8.0 Hz, 2H, Ar-H), 7.76 (s, 2H, Ar-H), 7.60 (d, J = 8.0 Hz, 2H, Ar-H), 7.54 (d, J = 8.0 Hz, 4H, Ar-H), 7.27 (t, J = 8.0 Hz, 8H, Ar-H), 7.15 (d, J = 8.0 Hz, 12H, Ar-H), 7.04 (t, J = 8.0 Hz, 4H, Ar-H), 4.00 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 147.73 (Ar-C), 147.08 (Ar-C), 144.10 (Ar-C), 140.30 (Ar-C), 139.24 (Ar-C), 135.47 (Ar-C), 129.24 (Ar-C), 127.74 (Ar-C), 125.56 (Ar-C), 124.40 (Ar-C), 124.03 (Ar-C), 123.24 (Ar-C), 122.89 (Ar-C), 120.07 (Ar-C), 37.06 (C, CH_2). MS (ESI): *m/z* calcd for $C_{49}H_{35}N_2$ $[M - H]^+$ 652.3; found 652.2. Elemental analysis: calcd for $C_{49}H_{36}N_2$ (%): C, 90.15; H, 5.56; found (%): C, 90.20; H, 5.51.

*2,7-Bis(9-phenyl-9H-carbazol-3-yl)-9H-fluorene (**8h**)*

Yellow solid, m.p. 199–200 °C. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.44 (d, J = 1.6 Hz, 2H), 8.23 (d, J = 8.0 Hz, 2H, Ar-H), 7.93 (d, J = 8.0 Hz, 2H, Ar-H), 7.79–7.74 (m, 4H, Ar-H), 7.66–7.61 (m, 8H, Ar-H), 7.52–7.44 (m, 8H, Ar-H), 7.35–7.31 (m, 2H, Ar-H), 4.10 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 144.21 (Ar-C), 141.37 (Ar-C), 140.55 (Ar-C), 140.15 (Ar-C), 137.75 (Ar-C), 133.79 (Ar-C), 129.92 (Ar-C), 127.50 (Ar-C), 127.09 (Ar-C), 126.25 (Ar-C), 126.11 (Ar-C), 125.56 (Ar-C), 123.95 (Ar-C), 123.53 (Ar-C), 120.38 (Ar-C), 120.14 (Ar-C), 120.06 (Ar-C), 118.79 (Ar-C), 110.02 (Ar-C), 109.92 (Ar-C), 36.07 (C, CH_2). MS (ESI): *m/z* calcd for $C_{49}H_{31}N_2$ $[M - H]^+$ 647.3; found 647.4. Elemental analysis: calcd for $C_{49}H_{32}N_2$ (%): C, 90.71; H, 4.97; found (%): C, 90.76; H, 4.92.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (nos. 21574021, 21562002, 51573026 and 21461002), Natural Science Foundation of Fujian Province (2016J01211) and Program for Innovative Research Team in Science and Technology in Fujian Province University (IRTSTFJ).

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