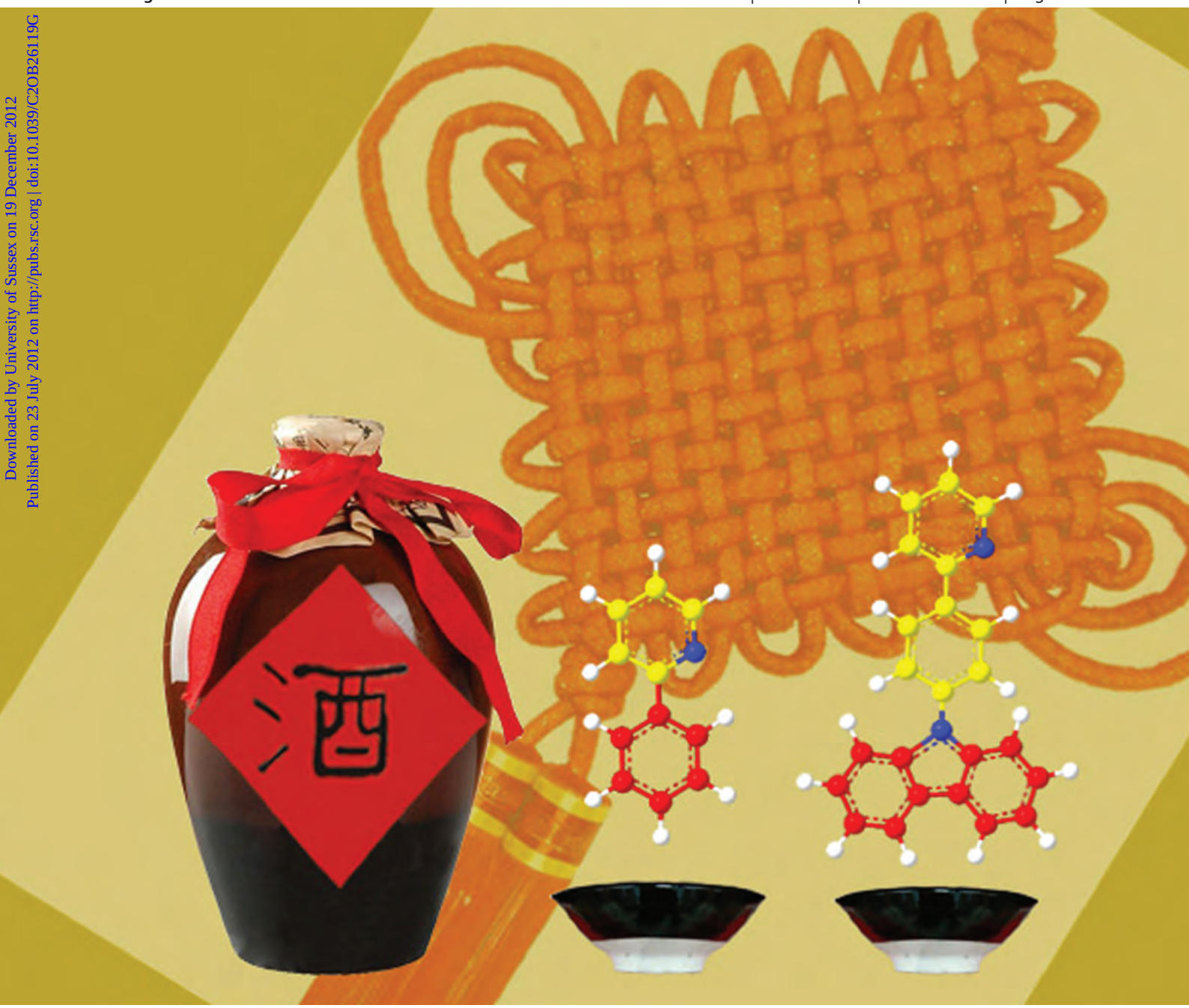
Organic & Biomolecular Chemistry

www.rsc.org/obc

Volume 10 | Number 39 | 21 October 2012 | Pages 7849–8028



ISSN 1477-0520

RSC Publishing

PAPER

Chun Liu *et al.*

A highly efficient and aerobic protocol for the synthesis of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives *via* a palladium-catalyzed ligand-free Suzuki reaction

1477-0520(2012)10:39;1-5

Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 7875

www.rsc.org/obc

PAPER

A highly efficient and aerobic protocol for the synthesis of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives *via* a palladium-catalyzed ligand-free Suzuki reaction†

Xiaofeng Rao, Chun Liu,* Jieshan Qiu and Zilin Jin

Received 11th June 2012, Accepted 19th July 2012
DOI: 10.1039/c2ob26119g

A palladium-catalyzed aerobic and ligand-free Suzuki reaction in aqueous ethanol has been developed for the synthesis of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives. A number of *N*-heteroaryl halides, namely 2-halogenated pyridines, 2-bromoquinoline, 5-bromopyrimidine and 2-chloropyrazine, were coupled with 4-(9*H*-carbazol-9-yl)phenylboronic acid (**CPBA**) or 9-phenyl-9*H*-carbazol-3-ylboronic acid (**PCBA**) efficiently to afford good to excellent yields in a short reaction time. Moreover, the catalytic system of $Pd(OAc)_2$–$EtOH/H_2O$–K_2CO_3 was successfully extended to the cross-couplings of *N*-heteroaryl halides with various arylboronic acids. The results demonstrated that the cross-coupling reaction in the present protocol was promoted by oxygen.

Introduction

Natural carbazole moieties have drawn a wide range of interest due to their being an important pharmacophore in various biological compounds as well as for their intriguing physical properties.[1] In recent years, carbazole derivatives have been extensively used as functional building blocks for the synthesis of small molecules, oligomers or polymers.[2] As is well known, carbazole derivatives with their associated ready functionalization at the 3-, 6-, or 9-position can be used as the hole-transporting components in the construction of numerous photo- and electroluminescent devices and photorefractive materials.[3] Small-molecule iridium complexes derived from carbazole units have been reported by Wong and co-workers.[4] They showed that carbazole moieties played a crucial role in alleviating the self-quenching of the luminophores and consequently increased the emission efficiency. Carbazole derivatives have also attracted interest in the field of dye-sensitized solar cells (DSSCs) for their strong electron donating nature.[5] Chen *et al.* prepared two ruthenium-based dyes modified with a carbazole unit, which provided a high solar energy conversion efficiency (η) of up to 9.72%.[6]

Numerous synthetic methodologies for the construction of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives have been developed in the past decades.[7] However, these methods, as described in the literature, are always combined with toxic solvents, harsh conditions, long reaction times and low yields. Thus far, a more effective method for synthesizing this important type of compound is still missing from the chemist's toolbox.

The palladium-catalyzed Suzuki reaction of aryl boronic acids with aryl halides is one of the most versatile and powerful tools for the construction of biaryls.[8] This reaction has been widely used to synthesize pharmaceuticals, fine chemicals and advanced materials. Generally, the Suzuki reaction is carried out in the presence of a ligand, in particular phosphine,[9] *N*-heterocyclic carbene[10] or palladacyclic complexes.[11] However, if the cross-coupling could be performed under air and ligand-free conditions, it would be considerably cheaper, safer, and more environmentally friendly. In recent years, significant progress has been made in this area, which enables this transformation to be performed in the absence of a ligand.[12] Our laboratory has documented a series of ligand-free protocols for the palladium-catalyzed Suzuki reaction over the last few years, including the activation of challenging aryl chlorides.[13]

In this paper, we report a fast and efficient ligand-free protocol for the synthesis of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives under aerobic and aqueous conditions (Scheme 1).

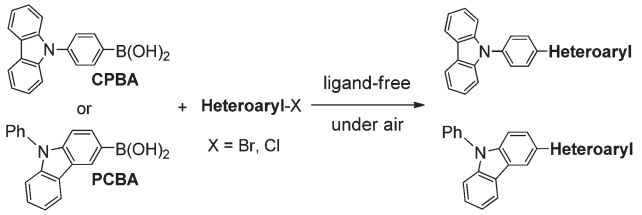
Results and discussion

Optimization of reaction conditions

In accordance with the literature reports, a suitable amount of water is important for the efficiency of the palladium-catalyzed ligand-free Suzuki reaction.[14] Therefore, we initially investigated

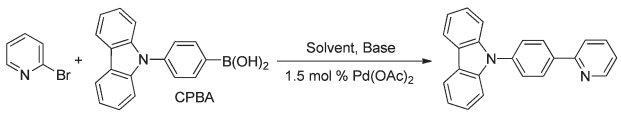
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Linggong Road 2, Dalian, 116024, China. E-mail: chunliu70@yahoo.com; Fax: (+86) 411-8498-6812; Tel: (+86) 411-8498-6182

†Electronic supplementary information (ESI) available: Experimental details and characterization of cross-coupling products. See DOI: 10.1039/c2ob26119g



Scheme 1 Ligand-free protocol for the synthesis of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives.

Table 1 Effect of solvent and base on the Suzuki reaction[a]



Entry	Solvent (v/v)	Base	Time/min	Yield[b] [%]
1	Pure water	K_2CO_3	20	Trace
2	EtOH–H_2O (1 : 1)	K_2CO_3	20	33
3	EtOH–H_2O (2 : 1)	K_2CO_3	20	75
4	EtOH–H_2O (3 : 1)	K_2CO_3	15	99
5	EtOH–H_2O (4 : 1)	K_2CO_3	20	92
6	Neat EtOH	K_2CO_3	20	51
7	*i*-PrOH–H_2O (3 : 1)	K_2CO_3	20	74
8	DMF–H_2O (3 : 1)	K_2CO_3	20	58
9	EG–H_2O (3 : 1)	K_2CO_3	20	52
10	Neat EG	K_2CO_3	20	39
11	EtOH–H_2O (3 : 1)	$K_3PO_4 \cdot 7H_2O$	20	98
12	EtOH–H_2O (3 : 1)	Na_2CO_3	20	95
13	EtOH–H_2O (3 : 1)	NaOH	40	84
14	EtOH–H_2O (3 : 1)	EtONa	40	79
15	EtOH–H_2O (3 : 1)	Et_3N	40	48
16	EtOH–H_2O (3 : 1)	DABCO	40	35

[a] Reaction conditions: 2-bromopyridine (0.25 mmol), **CPBA** (0.375 mmol), $Pd(OAc)_2$ (1.5 mol%), solvent (4 mL), base (0.5 mmol), 80 °C, under air. The reaction was monitored by TLC. [b] Isolated yields.

the effect of the water content on the reaction. The cross-coupling reaction of 2-bromopyridine (0.25 mmol) with **CPBA** (0.375 mmol) using $Pd(OAc)_2$ (1.5 mol%) and K_2CO_3 (0.5 mmol) at 80 °C under air, was chosen as a model reaction. As is evidenced from Table 1, the reaction in pure water was sluggish (Table 1, entry 1). However, the addition of an incremental amount of ethanol led to a very rapid increase in the reactivity, and a nearly quantitative isolated yield was obtained when the volume ratio of ethanol to water was 3 : 1 within 15 min (Table 1, entry 4). While further increasing the amount of ethanol, the isolated yield of the cross-coupling product decreased a little and only a 51% yield was obtained when the reaction was carried out in neat ethanol (Table 1, entries 5 and 6). These results show that the volume ratio of ethanol and water plays a crucial role in the cross-coupling reaction. We also investigated the effect of different solvents on the cross-coupling reaction. The use of *i*-PrOH, ethylene glycol (EG) or *N*,*N*-dimethylformamide (DMF) as co-solvents gave moderate to good yields (Table 1, entries 7–9). Although the $Pd(OAc)_2$–ethylene glycol system could activate a wide range of *N*-heteroaryl halides for the Suzuki reaction in the absence of a ligand,[13c] only a 39% yield was obtained in 20 min (Table 1, entry 10).

Table 2 Effect of precatalyst and temperature on the Suzuki reaction[a]

Entry	Precatalyst	Temp./°C	Time/min	Yield[b] [%]
1	—	80	15	No reaction
2	$Pd(OAc)_2$	80	15	99
3	$PdCl_2$	80	40	83
4	$Pd_2(dba)_3$	80	40	58
5	5% Pd/C	80	40	71
6	$Pd(OAc)_2$	80	15	60[c]
7	$Pd(OAc)_2$	50	15	30
8	$Pd(OAc)_2$	25	15	Trace

[a] Reaction conditions: 2-bromopyridine (0.25 mmol), **CPBA** (0.375 mmol), palladium loading (1.5 mol%), K_2CO_3 (0.5 mmol), EtOH–H_2O (3 mL–1 mL), under air. The reaction was monitored by TLC. [b] Isolated yields. [c] $Pd(OAc)_2$ (0.5 mol%).

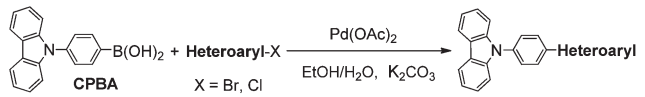
We next studied the effects of different bases on the same model reaction. The use of inorganic bases, such as K_2CO_3, $K_3PO_4 \cdot 7H_2O$, or Na_2CO_3, delivered the desired product in high yields (Table 1, entries 4, 11 and 12). On the other hand, an organic base, such as Et_3N and 1,4-diazabicyclo-[2,2,2]octane (DABCO), gave disappointing results in the catalytic system (Table 1, entries 15 and 16). The results reveal that an inorganic base is better than an organic base in this catalytic system. We chose K_2CO_3 as the optimal base for further study.

The next investigation was carried out to screen palladium species. The results are illustrated in Table 2. It is clear that the reaction could not occur without palladium (Table 2, entry 1). Palladium(II) salts such as $Pd(OAc)_2$ and $PdCl_2$ exhibited high catalytic activity, respectively (Table 2, entries 2 and 3). However, the activity was decreased when palladium(II) salt was replaced with zero-valent palladium such as $Pd_2(dba)_3$ or Pd/C (Table 2, entries 4 and 5), which is consistent with both our recent results[15] and Li and Venkatraman's report.[16] Among the palladium species screened, $Pd(OAc)_2$ is the preferred catalyst in the reaction system. However, decreasing the loading of $Pd(OAc)_2$ from 1.5 mol% to 0.5 mol% led to the desired product in 60% isolated yield (Table 2, entry 6). In addition, the effect of temperature on the reaction was observed. When the temperature was dropped to 50 °C, only 30% isolated yield was obtained and it was difficult for the reaction to proceed at room temperature (Table 2, entries 7 and 8). Therefore, the optimized conditions for the cross-couplings of *N*-heteroaryl halides with **CPBA** were 1.5 mol% $Pd(OAc)_2$, K_2CO_3 as a base at 80 °C under air.

Scope and limitations of substrates

Under the optimal conditions, the scope and limitations of various *N*-heteroaryl halides were investigated. The results are summarized in Table 3. A quantitative yield of product **1** was obtained within 15 min in 75% aqueous ethanol (Table 3, entry 1). Compared with the reported methods,[4d,7a] operational simplicity, a short reaction time and good yield are the key advantages of this protocol. A wide range of 2-halogenated pyridines bearing either an electron-donating group or an electron-withdrawing group performed well and delivered the desired products in high yields. These results illustrate that the electronic nature of the substituent group has a small influence on the reactivity.

Table 3 Suzuki reactions of *N*-heteroaryl halides with **CPBA**[a]



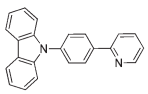
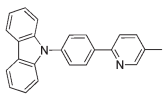
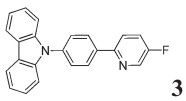
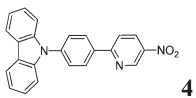
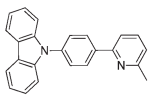
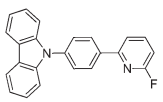
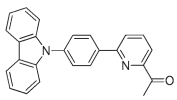
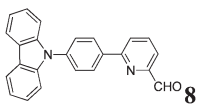
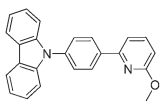
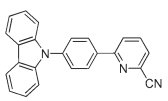
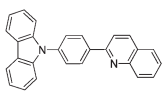
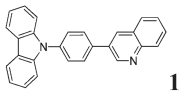
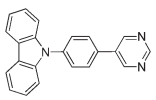
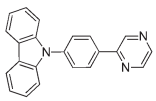
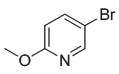
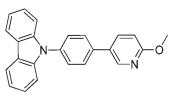
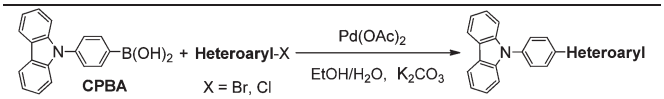
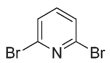
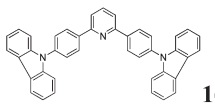
Entry	Heteroaryl-X	Product	Time/min	Yield[b] [%]
1		 **1**	15	99
2		 **2**	20	99
3		 **3**	10	91
4		 **4**	20	93
5		 **5**	5	99
6		 **6**	10	96
7		 **7**	5	99
8		 **8**	20	96
9		 **9**	5	98
10		 **10**	15	90
11		 **11**	40	92
12		 **12**	60	77
13		 **13**	40	96
14		 **14**	40	81
15		 **15**	20	74

Table 3 *(Contd.)*



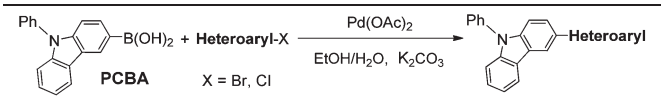
Entry	Heteroaryl-X	Product	Time/min	Yield[b] [%]
16		 **16**	15	38[c]

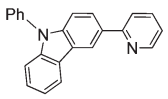
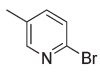
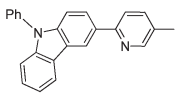
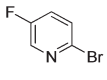
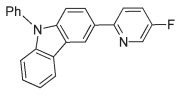
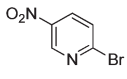
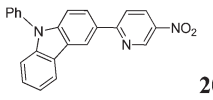
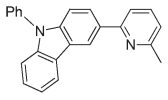
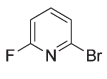
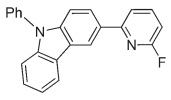
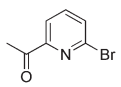
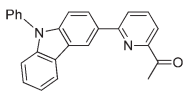
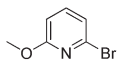
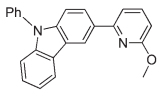
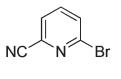
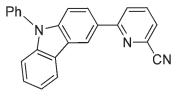
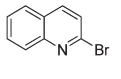
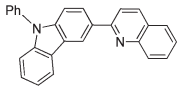
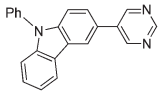
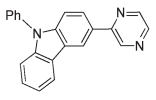
[a] Reaction conditions: *N*-heteroaryl halide (0.25 mmol), **CPBA** (0.375 mmol), $Pd(OAc)_2$ (1.5 mol%), K_2CO_3 (0.5 mmol), EtOH–H_2O (3 mL–1 mL), 80 °C, under air. The reaction was monitored by TLC. [b] Isolated yields. [c] Reaction conditions: 2,6-dibromopyridine (0.25 mmol), **CPBA** (0.75 mmol), $Pd(OAc)_2$ (3.0 mol%), K_2CO_3 (1.0 mmol), EtOH–H_2O (3 mL–1 mL), 80 °C, under air.

As shown in Table 3, the coupling of 2-bromo-5-methyl-pyridine with **CPBA** gave the product **2** in 99% yield after 20 min (Table 3, entry 2), showing high efficiency. Moreover, 2-bromo-5-fluoropyridine and 2-bromo-5-nitropyridine underwent the cross-coupling smoothly and afforded the desired products in 91% and 93% yields, respectively (Table 3, entries 3 and 4). It is noteworthy that the cross-coupling between 2-bromo-6-methyl-pyridine and **CPBA** could be conducted with a 99% yield after 5 min, resulting in a TOF up to 792 h^{-1} (Table 3, entry 5). The reaction system exhibited similar high reactivity for the couplings of **CPBA** with 2-bromo-6-methoxylpyridine or 1-(6-bromopyridin-2-yl)ethanone (Table 3, entries 7 and 9). In addition to 2-halogenated pyridines, other 2-halogenated heteroarenes as one of the cross-coupling partners also performed well and afforded good to excellent yields of the expected products. For example, 2-bromoquinoline produced the product **11** in a 92% yield within 40 min (Table 3, entry 11). Noticeably, 5-bromopyrimidine was also successfully used in the reaction to afford a 96% yield in 40 min (Table 3, entry 13). In general, *N*-heteroaryl chlorides are less reactive than *N*-heteroaryl bromides and require drastic reaction conditions for arylation. To our delight, the coupling of 2-chloropyrazine with **CPBA** produced the biaryl **14** in an 81% yield within 40 min (Table 3, entry 14). However, 3-halogenated heteroarenes were less active and gave moderate yields (Table 3, entries 12 and 15). More significantly, 2,6-dibromopyridine also delivered the double cross-coupled product **16** in 38% yield using 3 mol% $Pd(OAc)_2$ and 4 equiv. of the base (Table 3, entry 16).

In the field of OLEDs, carbazole derivatives with a functional group at the 3- or 6-position are important building blocks because of their high triplet energy and good hole-transporting ability. Organometallic complexes of carbazoles have been reported as potential luminescent materials, especially carbazoles containing a 3,6-linkage with heterocycles or diarylamines.[4a,17] Encouraged by the successful cross-coupling mentioned-above, we tried to carry out the Suzuki reaction of *N*-heteroaryl halides with **PCBA** under the same catalytic system ($Pd(OAc)_2$–EtOH/H_2O–K_2CO_3), and the results are illustrated in Table 4. The coupling of 2-bromopyridine with **PCBA** provided the corresponding product **17** in 91% yield within 25 min (Table 4,

Table 4 Suzuki reactions of *N*-heteroaryl halides with **PCBA**[a]



Entry	Heteroaryl-X	Product	Time/min	Yield[b] [%]
1		 **17**	25	91
2		 **18**	20	84
3		 **19**	15	71
4		 **20**	40	81
5		 **21**	40	90
6		 **22**	40	89
7		 **23**	30	86
8		 **24**	60	75
9		 **25**	40	81
10		 **26**	60	72
11		 **27**	60	75
12		 **28**	60	73

[a] Reaction conditions: *N*-heteroaryl halide (0.25 mmol), **PCBA** (0.375 mmol), $Pd(OAc)_2$ (1.5 mol%), K_2CO_3 (0.5 mmol), EtOH–H_2O (3 mL–1 mL), 80 °C, under air. The reaction was monitored by TLC. [b] Isolated yields.

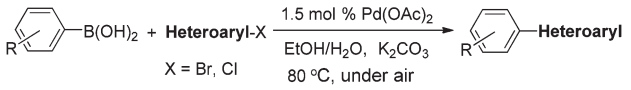
entry 1), which indicated that the catalytic system also showed high activity in the cross-coupling of *N*-heteroaryl halides with **PCBA**. We next explored the reactivity of various *N*-heteroaryl halides in the catalytic system. The cross-couplings between **PCBA** and 5- or 6-substituted 2-bromopyridines provided the products in good to excellent yields (Table 4, entries 2–9). As far as we know, the carbazole derivatives with an *N*-heteroaryl group on the 3- or 6-position, such as products **17**, **18** and **19**, are important ligands for the synthesis of iridium complexes used in OLEDs.[4a,d] To the best of our knowledge, the present protocol for the formation of these carbazole derivatives is simpler and much more efficient than the reported procedures.[4a,d,18] Other *N*-heteroaryl halides also exhibited high reactivity in this protocol. For example, 2-bromoquinoline produced the expected biaryl **26** in 72% yield within 60 min (Table 4, entry 10). Finally, the cross-coupling of 2-chloropyrazine coupled with **PCBA** under the reaction conditions afforded a yield of 73% in 60 min (Table 4, entry 12). Thus, this work provides a fast and very practical method for the synthesis of *N*-heteroaryl substituted 9-arylcarbazole derivatives, which are the potential building blocks for the construction of various intermediates and advanced functional materials.

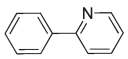
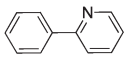
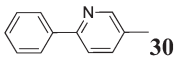
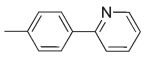
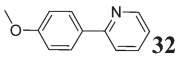
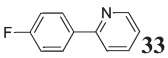
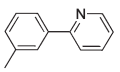
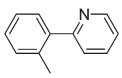
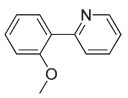
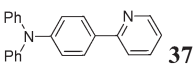
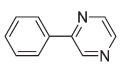
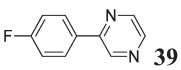
To further investigate the scope and limitations of this methodology, cross-couplings of different aryl boronic acids with *N*-heteroaryl halides were carried out. The results are summarized in Table 5. The coupling of 2-bromopyridine with phenylboronic acid gave 2-phenylpyridine in a quantitative isolated yield after 10 min (Table 5, entry 1). Even decreasing the catalyst loading to 0.25 mol%, the cross-coupling was completed in 60 min (Table 5, entry 2). As far as we know, this is the most efficient catalytic system for such a transformation under ligand-free conditions.[13b,19] Both electron-rich and electron-poor aryl boronic acids proceeded smoothly. For example, using 4-methylphenyl boronic acid instead of phenyl boronic acid, the coupling was completed in 5 min (Table 5, entry 4), resulting in a TOF of 784 h^{-1}. In addition, 4-methoxyphenyl boronic acid was coupled with 2-bromopyridine giving the product **32** in 92% yield for 10 min (Table 5, entry 5). Moreover, electron-poor 4-fluorophenyl boronic acid afforded the target product **33** in 95% for 30 min (Table 5, entry 6). While increasing the steric hindrance of arylboronic acid, the reactivity decreased (Table 5, entries 8 and 9). Note that a nearly quantitative yield of product **37** was obtained when using 4-(diphenylamino)phenylboronic acid as a coupling partner in 10 min (Table 5, entry 10). To the best of our knowledge, the present protocol for the formation of product **37** is simpler and more efficient than the methods described in the literature.[13f,20] Moreover, 2-chloropyrazine is a good coupling partner in the catalytic system (Table 5, entries 11 and 12).

Effect of atmosphere on the Suzuki reaction

As we reported previously,[13a,b,21] oxygen served as a promoter in the palladium-catalyzed ligand-free Suzuki reaction, which inspired us to speculate whether oxygen could also promote the Suzuki reaction of carbazole boronic acid with *N*-heteroaryl halides in the present catalytic system. Consequently, the effects of different atmospheres on the cross-couplings were investigated. The results are illustrated in Table 6. It is clear that the couplings gave higher yields under air than in nitrogen (Table 6, entries 1a–4a *vs.* 1b–4b). For example, the cross-coupling between 2-bromopyridine and **CPBA** in open air resulted in 99% isolated yield in 15 min (Table 6, entry 2a), while the isolated yield was decreased to 51% in nitrogen (Table 6, entry 2b).

Table 5 Suzuki reactions of *N*-heteroaryl halides with arylboronic acids[a]



Entry	Heteroaryl-X	Product	Time/min	Yield[b] [%]
1		 **29**	10	99
2		 **29**	60	96[c]
3		 **30**	20	96
4		 **31**	5	98
5		 **32**	10	92
6		 **33**	30	95
7		 **34**	10	98
8		 **35**	180	60
9		 **36**	120	81
10		 **37**	10	97
11		 **38**	30	94
12		 **39**	30	90

[a] Reaction conditions: *N*-heteroaryl halide (0.25 mmol), arylboronic acid (0.375 mmol), $Pd(OAc)_2$ (1.5 mol%), K_2CO_3 (0.5 mmol), EtOH–H_2O (3 mL–1 mL), 80 °C, under air. The reaction was monitored by TLC. [b] Isolated yields. [c] $Pd(OAc)_2$ (0.25 mol%).

Gratifyingly, it took only 9 min to complete the same reaction in oxygen (Table 6, entry 2c). Using **PCBA** instead of **CPBA**, it took 15 min to complete the coupling in oxygen (Table 6, entry 4c), faster than that in nitrogen (Table 6, entry 4b). Therefore, we can conclude that oxygen serves as a promoter in the $Pd(OAc)_2$-catalyzed ligand-free Suzuki reaction in EtOH–H_2O. It is proposed that a peroxo-palladium complex might be formed in the presence of oxygen,[22] which accelerates the oxidative addition step due to the enhanced electron density of the palladium. However, the details of the mechanism are ambiguous at present and will be the subject of the further study.

Conclusions

In summary, we have developed a very fast and highly efficient catalytic system of $Pd(OAc)_2$–EtOH/H_2O–K_2CO_3 for the synthesis of *N*-heteroaryl substituted 9-arylcarbazolyl derivatives under aerobic and ligand-free conditions. A wide range of *N*-heteroaryl halides readily underwent the Suzuki reaction with **CPBA** or **PCBA** to provide good to excellent yields of the cross-coupled products. Moreover, the present approach was successfully extended to the cross-couplings of *N*-heteroaryl halides with various arylboronic acids. This aerobic and water-involved protocol is in accordance with the concept of green chemistry and is of great interest for the synthesis of advanced functional materials. Further investigations including photophysical properties of these *N*-heteroaryl substituted 9-arylcarbazolyl derivatives and synthetic applications of this methodology are in progress in our laboratory.

Experimental section

General remarks

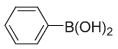
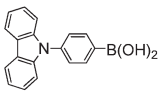
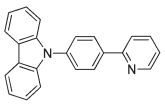
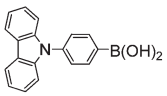
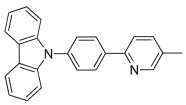
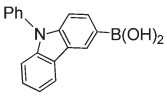
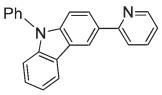
Unless otherwise noted, all the reactions were carried out in air. All *N*-heteroaryl halides were purchased from Alfa Aesar or Avocado. 4-(9*H*-carbazol-9-yl)phenylboronic acid (**CPBA**) and 9-phenyl-9*H*-carbazol-3-ylboronic acid (**PCBA**) were purchased from Trusyn Chem-Tech Co., Ltd, China. Other chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Brucker Advance II 400 spectrometer using TMS as internal standard (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Mass spectroscopy data of the products were collected with a MS-EI instrument. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C). Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

General procedure for the Suzuki cross-coupling of *N*-heteroaryl halides with CPBA or PCBA. A mixture of *N*-heteroaryl halide (0.25 mmol), **CPBA** or **PCBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.00375 mmol), distilled water (1 mL) and ethanol (3 mL) was stirred at 80 °C in air for the indicated time. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4 × 15 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200–300 mesh).

General procedure for the Suzuki cross-coupling of *N*-heteroaryl halides with arylboronic acids. A mixture of *N*-heteroaryl halide (0.25 mmol), arylboronic acid (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.00375 mmol), distilled water (1 mL) and ethanol (3 mL) was stirred at 80 °C in air for the indicated time. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4 × 15 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200–300 mesh).

9-(4-(5-Methylpyridin-2-yl)phenyl)-9*H*-carbazole (2). Yield: 99%; white solid, m.p. 212–213 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.58 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.62 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.93, 150.29, 140.80, 138.48,

Table 6 Effect of atmosphere on the Suzuki reaction[a]

Entry	Ar-B(OH)$_2$	Product	Atmosphere	Time/min	Yield[b] [%]
1a			Open air	10	99
1b			N_2	10	76
1c			O_2 balloon	8	98
2a			Open air	15	99
2b			N_2	15	51
2c			O_2 balloon	9	99
3a			Open air	20	99
3b			N_2	20	73
3c			O_2 balloon	12	99
4a			Open air	25	91
4b			N_2	25	77
4c			O_2 balloon	15	92

[a] Reaction conditions: *N*-heteroaryl bromide (0.25 mmol), arylboronic acid (0.375 mmol), $Pd(OAc)_2$ (1.5 mol%), K_2CO_3 (0.5 mmol), EtOH–H_2O (3 mL–1 mL), 80 °C. The reaction was monitored by TLC. [b] Isolated yields.

138.05, 137.50, 132.01, 128.18, 127.21, 126.01, 123.50, 120.33, 120.04, 109.88, 18.23 ppm. MS (EI): *m*/*z* = 334.1467 $[M]^+$.

9-(4-(5-Fluoropyridin-2-yl)phenyl)-9*H*-carbazole (3). Yield: 91%; white solid, m.p. 210–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.60 (d, *J* = 2.8 Hz, 1H), 8.19–8.15 (m, 4H), 7.83–7.81 (m, 1H), 7.70–7.68 (m, 2H), 7.56–7.51 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.45–7.40 (m, 2H), 7.32–7.28 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.28, 157.72, 152.88, 152.84, 140.75, 138.42, 138.12, 137.88, 137.38, 128.29, 127.28, 126.05, 123.82, 123.64, 123.58, 121.35, 121.31, 120.37, 120.14, 109.83 ppm. MS (EI): *m*/*z* = 338.1223 $[M]^+$.

9-(4-(5-Nitropyridin-2-yl)phenyl)-9*H*-carbazole (4). Yield: 93%; light-yellow solid, m.p. 266–267 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.55 (d, *J* = 2.4 Hz, 1H), 8.61–8.58 (m, 1H), 8.36–8.34 (m, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.79–7.76 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.46–7.42 (m, 2H), 7.34–7.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.44, 145.45, 143.01, 140.44, 140.33, 135.70, 132.15, 129.28, 127.29, 126.17, 123.77, 120.47, 119.99, 109.78 ppm. MS (EI): *m*/*z* = 365.1167 $[M]^+$.

9-(4-(6-Methylpyridin-2-yl)phenyl)-9*H*-carbazole (5). Yield: 99%; white solid, m.p. 201–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.23–8.21 (m, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 7.72–7.66 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.45–7.41 (m, 2H), 7.32–7.28 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.64, 156.07, 140.85, 138.84, 138.21, 137.12, 128.55, 127.22, 126.02, 123.53, 121.95, 120.34, 120.05, 117.68, 109.88, 24.76 ppm. MS (EI): *m*/*z* = 334.1470 $[M]^+$.

9-(4-(6-Fluoropyridin-2-yl)phenyl)-9*H*-carbazole (6). Yield: 96%; white solid, m.p. 137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.25–8.23 (m, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.93–7.88 (m, 1H), 7.73–7.68 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.45–7.41 (m, 2H), 7.32–7.29 (m, 2H), 6.94–6.91 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.72, 162.34, 155.45, 155.31, 141.90, 141.82, 140.66, 139.01, 136.47, 128.48, 127.51, 127.18, 126.09, 123.62, 120.40, 120.23, 120.13, 117.35, 117.31, 109.84, 108.25, 107.87 ppm. MS (EI): *m*/*z* = 338.1222 $[M]^+$.

1-(6-(4-(9*H*-Carbazol-9-yl)phenyl)pyridin-2-yl)ethanone (7). Yield: 99%; white solid, m.p. 161–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.36–8.34 (m, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 8.05–8.02 (m, 2H), 7.96 (t, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46–7.42 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 2.87 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 200.40, 155.60, 153.59, 140.69, 138.93, 137.89, 137.33, 128.42, 127.28, 126.07, 123.61, 123.46, 120.41, 120.21, 120.09, 109.83, 25.81 ppm. MS (EI): *m*/*z* = 362.1428 $[M]^+$.

6-(4-(9*H*-Carbazol-9-yl)phenyl)picolinaldehyde (8). Yield: 96%; white solid, m.p. 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.22 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.03–7.96 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 193.78, 157.02, 152.89, 140.65, 139.12, 138.05, 137.02, 128.58, 127.34, 126.12, 124.44, 123.63, 120.44, 120.27, 120.05, 109.83 ppm. MS (EI): *m*/*z* = 348.1268 $[M]^+$.

9-(4-(6-Methoxypyridin-2-yl)phenyl)-9*H*-carbazole (9). Yield: 98%; white solid, m.p. 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.71–7.65 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.30 (t, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.09 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.94, 153.77, 140.81, 139.35, 138.24, 138.11, 128.18, 127.09, 126.03, 123.54, 120.37, 120.09, 112.89, 109.91, 109.72, 53.31 ppm. MS (EI): *m*/*z* = 350.1422 $[M]^+$.

6-(4-(9*H*-Carbazol-9-yl)phenyl)picolinonitrile (10). Yield: 90%; white solid, m.p. 180–181 °C. ^{1}H NMR (400 MHz,

$CDCl_3$, 25 °C): δ = 8.28 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.6 Hz, 1H), 7.95 (t, J = 7.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.07, 140.56, 139.65, 137.95, 135.98, 134.07, 128.64, 127.31, 126.79, 126.12, 123.68, 123.40, 120.42, 120.33, 117.32, 109.78 ppm. MS (EI): m/z = 345.1269 $[M]^+$.

9-(4-(Quinolin-2-yl)phenyl)-9*H*-carbazole (11). Yield: 92%; white solid, m.p. 155–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.41 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.79–7.74 (m, 3H), 7.58 (t, J = 8.8 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.44, 148.39, 140.77, 138.78, 138.72, 137.05, 129.89, 129.80, 129.10, 127.54, 127.30, 126.54, 126.05, 123.58, 120.36, 120.13, 118.85, 109.88 ppm. MS (EI): m/z = 370.1479 $[M]^+$.

9-(4-(Quinolin-3-yl)phenyl)-9*H*-carbazole (12). Yield: 77%; white solid, m.p. 261–262 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.30 (d, J = 2.0 Hz, 1H), 8.42 (d, J = 2.0 Hz, 1H), 8.18 (t, J = 7.6 Hz, 3H), 7.95 (t, J = 8.0 Hz, 3H), 7.79–7.74 (m, 3H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.72, 147.56, 140.76, 137.79, 136.93, 133.37, 132.98, 129.68, 129.37, 128.87, 128.09, 128.03, 127.72, 127.24, 126.08, 123.57, 120.42, 120.19, 109.79 ppm. MS (EI): m/z = 370.1476 $[M]^+$.

9-(4-(Pyrimidin-5-yl)phenyl)-9*H*-carbazole (13). Yield: 96%; white solid, m.p. 188–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.27 (s, 1H), 9.07 (s, 2H), 8.17 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.49–7.42 (m, 4H), 7.34–7.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.78, 154.91, 140.60, 138.75, 133.60, 133.17, 128.51, 127.91, 126.14, 123.66, 120.46, 120.36, 109.67 ppm. MS (EI): m/z = 321.1257 $[M]^+$.

9-(4-(Pyrazin-2-yl)phenyl)-9*H*-carbazole (14). Yield: 81%; white solid, m.p. 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.14 (d, J = 1.6 Hz, 1H), 8.71–8.69 (m, 1H), 8.57 (d, J = 2.4 Hz, 1H), 8.28–8.26 (m, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.77–7.73 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.45–7.42 (m, 2H), 7.33–7.29 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.06, 144.38, 143.04, 142.01, 140.59, 139.47, 135.13, 128.50, 127.43, 126.11, 123.67, 120.42, 120.31, 109.79 ppm. MS (EI): m/z = 321.1267 $[M]^+$.

9-(4-(6-Methoxypyridin-3-yl)phenyl)-9*H*-carbazole (15). Yield: 74%; white solid, m.p. 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.50 (d, J = 2.4 Hz, 1H), 8.16 (d, J = 7.6 Hz, 2H), 7.91–7.88 (m, 1H), 7.76–7.74 (m, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.45–7.41 (m, 2H), 7.33–7.29 (m, 2H), 6.89 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.88, 145.10, 140.83, 137.42, 137.02, 136.97, 129.24, 128.05, 127.58, 126.04, 123.49, 120.39, 120.09, 111.09, 109.82, 53.68 ppm. MS (EI): m/z = 350.1418 $[M]^+$.

2,6-Bis(4-(9*H*-carbazol-9-yl)phenyl)pyridine (16). Yield: 38%; white solid, m.p. 253–254 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.43 (d, J = 8.4 Hz, 4H), 8.17 (d, J = 7.6 Hz, 4H), 7.96 (t, J = 8.0 Hz, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 8.8 Hz, 4H), 7.52 (d, J = 8.0 Hz, 4H), 7.46–7.42 (m, 4H), 7.31 (t, J = 7.2 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.15, 140.75, 138.74, 138.25, 137.88, 128.70, 127.21, 126.06, 123.59, 120.37, 120.15, 119.21, 109.89 ppm. MS (EI): m/z = 561.2205 $[M]^+$.

3-(5-Methylpyridin-2-yl)-9-phenyl-9*H*-carbazole (18). Yield: 84%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.78 (d, J = 1.2 Hz, 1H), 8.55 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 8.03–8.01 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.63–7.55 (m, 5H), 7.49–7.44 (m, 2H), 7.41 (d, J = 4.0 Hz, 2H), 7.32–7.29 (m, 1H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.47, 149.93, 141.48, 141.31, 137.64, 137.42, 131.61, 130.75, 129.93, 127.56, 127.09, 126.15, 124.95, 123.91, 123.74, 120.61, 120.23, 119.86, 118.81, 109.95, 109.89, 18.15 ppm. MS (EI): m/z = 334.1466 $[M]^+$.

3-(5-Nitropyridin-2-yl)-9-phenyl-9*H*-carbazole (20). Yield: 81%; yellow solid, m.p. 196–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.52 (d, J = 2.4 Hz, 1H), 8.94 (d, J = 1.6 Hz, 1H), 8.54–8.51 (m, 1H), 8.25 (d, J = 7.6 Hz, 1H), 8.18–8.15 (m, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.67–7.63 (m, 2H), 7.60–7.78 (m, 2H), 7.55–7.42 (m, 4H), 7.38–7.34 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.06, 145.38, 142.52, 142.17, 141.68, 137.08, 131.86, 130.09, 128.99, 128.01, 127.09, 126.73, 125.71, 124.13, 123.38, 120.79, 120.64, 120.38, 119.37, 110.34, 110.26 ppm. MS (EI): m/z = 365.1159 $[M]^+$.

3-(6-Methylpyridin-2-yl)-9-phenyl-9*H*-carbazole (21). Yield: 90%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.79 (d, J = 1.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.06–8.04 (m, 1H), 7.64–7.63 (m, 2H), 7.61–7.57 (m, 4H), 7.49–7.45 (m, 2H), 7.42–7.41 (m, 2H), 7.33–7.30 (m, 1H), 7.08–7.06 (m, 1H), 2.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.29, 157.65, 141.45, 141.37, 137.64, 136.90, 132.03, 129.93, 127.55, 127.09, 126.10, 125.28, 123.85, 123.75, 120.87, 120.66, 120.18, 119.17, 117.45, 109.93, 109.90, 24.89 ppm. MS (EI): m/z = 334.1464 $[M]^+$.

3-(6-Fluoropyridin-2-yl)-9-phenyl-9*H*-carbazole (22). Yield: 89%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.84 (d, J = 1.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.07–8.05 (m, 1H), 7.88–7.82 (m, 1H), 7.75–7.72 (m, 1H), 7.65–7.61 (m, 2H), 7.59–7.57 (m, 2H), 7.51–7.47 (m, 1H), 7.46–7.40 (m, 3H), 7.35–7.31 (m, 1H), 6.84–6.82 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.70, 162.34, 157.14, 157.00, 141.78, 141.62, 141.54, 137.42, 130.00, 129.68, 127.73, 127.07, 126.39, 125.04, 123.91, 123.59, 120.67, 120.47, 119.32, 116.93, 116.89, 110.06, 109.96, 106.72, 106.34 ppm. MS (EI): m/z = 338.1217 $[M]^+$.

1-(6-(9-Phenyl-9*H*-carbazol-3-yl)pyridin-2-yl)ethanone (23). Yield: 86%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.86 (d, J = 1.6 Hz, 1H), 8.25 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.89 (t, J = 7.6 Hz, 1H), 7.66–7.58 (m, 4H), 7.52–7.47 (m, 2H), 7.45–7.42 (m, 2H), 7.36–7.32 (m, 1H), 2.89 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 200.88, 157.21, 153.39, 141.73, 141.53, 137.55, 137.44, 130.64, 130.00, 127.74, 127.09, 126.39, 125.15, 123.88, 123.55, 123.21, 120.49, 120.39, 119.00, 110.11, 25.93 ppm. MS (EI): m/z = 362.1415 $[M]^+$.

3-(6-Methoxypyridin-2-yl)-9-phenyl-9*H*-carbazole (24). Yield: 75%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.82 (d, J = 1.2 Hz, 1H), 8.24–8.22 (m, 1H), 8.15–8.12 (m, 1H), 7.67–7.57 (m, 5H), 7.50–7.46 (m, 2H), 7.45–7.44 (m, 1H), 7.42 (d, J = 4.0 Hz, 2H), 7.35–7.29 (m, 1H), 6.68–6.66 (m, 1H), 4.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.81, 155.56, 141.47, 139.24, 137.61, 131.42, 129.96, 127.61, 127.10, 126.18, 125.12, 123.75, 123.72, 120.51, 120.24, 118.81, 112.52, 110.00, 109.83, 108.11, 53.32 ppm. MS (EI): m/z = 350.1419 $[M]^+$.

6-(9-Phenyl-9*H*-carbazol-3-yl)picolinonitrile (25). Yield: 81%; white solid, m.p. 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.85 (d, J = 1.2 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.11–8.06 (m, 2H), 7.88 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 8.0 Hz, 2H), 7.60–7.57 (m, 3H), 7.53–7.42 (m, 4H), 7.37–7.33 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.58, 142.04, 141.57, 137.54, 137.25, 133.70, 130.02, 129.20, 127.84, 127.07, 126.53, 125.75, 125.04, 123.96, 123.43, 123.16, 120.63, 120.56, 119.47, 117.73, 110.16, 110.12 ppm. MS (EI): m/z = 345.1261 $[M]^+$.

9-Phenyl-3-(quinolin-2-yl)-9*H*-carbazole (26). Yield: 72%; yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.99 (d, J = 1.6 Hz, 1H), 8.29–8.21 (m, 4H), 8.04 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.76–7.72 (m, 1H), 7.67–7.61 (m, 4H), 7.53 (d, J = 8.4 Hz, 2H), 7.51–7.48 (m, 1H), 7.45–7.43 (m, 2H), 7.36–7.32 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.95, 148.48, 141.75, 141.55, 137.54, 136.69, 131.80, 129.99, 129.64, 129.57, 127.67, 127.54, 127.11, 126.99, 126.29, 125.89, 125.83, 124.00, 123.75, 120.72, 120.38, 119.87, 119.15, 110.09, 110.05 ppm. MS (EI): m/z = 370.1471 $[M]^+$.

9-Phenyl-3-(pyrimidin-5-yl)-9*H*-carbazole (27). Yield: 75%; white solid, m.p. 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.20 (s, 1H), 9.08 (s, 2H), 8.35 (d, J = 1.6 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.66–7.57 (m, 5H), 7.54–7.50 (m, 2H), 7.49–7.43 (m, 2H), 7.37–7.33 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.79, 154.90, 141.51, 141.17, 137.24, 135.12, 130.06, 127.90, 127.10, 126.73, 126.00, 124.81, 124.33, 122.99, 120.53, 120.50, 118.89, 110.81, 110.18 ppm. MS (EI): m/z = 321.1265 $[M]^+$.

9-Phenyl-3-(pyrazin-2-yl)-9*H*-carbazole (28). Yield: 73%; brown solid, m.p. 156–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.16 (d, J = 1.2 Hz, 1H), 8.84 (d, J = 1.6 Hz, 1H), 8.65 (t, J = 2.0 Hz, 1H), 8.48 (d, J = 2.8 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.10–8.07 (m, 1H), 7.64 (t, J = 8.0 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.53–7.50 (m, 2H), 7.47–7.42 (m, 2H), 7.36–7.32 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.58, 144.07, 142.13, 142.00, 141.94, 141.57, 137.32, 130.02, 128.31, 127.83, 127.12, 126.52, 124.87, 124.10, 123.42, 120.62, 120.53, 119.28, 110.32, 110.11 ppm. MS (EI): m/z = 321.1256 $[M]^+$.

Acknowledgements

The authors thank the financial support from the National Natural Science Foundation of China (21076034, 20923006, 20836002), the Fundamental Research Funds for the Central Universities (DUT11LK15), and the Ministry of Education (the Program for New Century Excellent Talents in University).

Notes and references

1 (*a*) G. H. Kirsch, *Curr. Org. Chem.*, 2001, **5**, 507; (*b*) H.-J. Knölker and K. R. Reddy, *Chem. Rev.*, 2002, **102**, 4303; (*c*) M. P. Krahl, A. Jager, T. Krause and H. J. Knolker, *Org. Biomol. Chem.*, 2006, **4**, 3215; (*d*) F. F. Zhang, L. L. Gan and C. H. Zhou, *Bioorg. Med. Chem.*, 2010, **20**, 1881; (*e*) C. Zhao, Y. Zhang, X. Li, D. Wen and X. Tang, *J. Hazard. Mater.*, 2011, **190**, 253; (*f*) K. R. Wee, W. S. Han, D. W. Cho, S. Kwon, C. Pac and S. O. Kang, *Angew. Chem., Int. Ed.*, 2012, **51**, 2677.

2 (*a*) K. Brunner, A. v. Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. W. Langeveld, *J. Am. Chem. Soc.*, 2004, **126**, 6035; (*b*) K.-T. Wong, Y.-M. Chen, Y.-T. Lin, H.-C. Su and C.-C. Wu, *Org. Lett.*, 2005, **7**, 5361; (*c*) P.-I. Shih, C.-L. Chiang, A. K. Dixit, C.-K. Chen, M.-C. Yuan, R.-Y. Lee, C.-T. Chen, E. W.-G. Diau and C.-F. Shu, *Org. Lett.*, 2006, **8**, 2799; (*d*) J. Li and A. C. Grimsdale, *Chem. Soc. Rev.*, 2010, **39**, 2399; (*e*) S. Lengvinaite, J. V. Grazulevicius, S. Grigalevicius, B. Zhang and Z. Xie, *React. Funct. Polym.*, 2010, **70**, 477; (*f*) P. Moonsin, N. Prachumrak, R. Rattanawan, T. Keawin, S. Jungsuttiwong, T. Sudyoadsuk and V. Promarak, *Chem. Commun.*, 2012, **48**, 3382; (*g*) Y.-L. Chu, C.-C. Cheng, Y.-C. Yen and F.-C. Chang, *Adv. Mater.*, 2012, **24**, 1894.

3 (*a*) Y. Zhang, T. Wada and H. Sasabe, *J. Mater. Chem.*, 1998, **8**, 809; (*b*) A. v. Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel and K. Brunner, *J. Am. Chem. Soc.*, 2004, **126**, 7718; (*c*) J.-F. Morin, N. Drolet, Y. Tao and M. Leclerc, *Chem. Mater.*, 2004, **16**, 4619; (*d*) M. H. Tsai, H. W. Lin, H. C. Su, T. H. Ke, C. C. Wu, F. C. Fang, Y. L. Liao, K. T. Wong and C. I. Wu, *Adv. Mater.*, 2006, **18**, 1216; (*e*) Y. Tao, Q. Wang, C. Yang, Z. Zhang, T. Zou, J. Qin and D. Ma, *Angew. Chem., Int. Ed.*, 2008, **47**, 8104; (*f*) D. Kim, V. Coropceanu and J.-L. Brédas, *J. Am. Chem. Soc.*, 2011, **133**, 17895; (*g*) K. R. Justin Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404.

4 (*a*) W. Y. Wong, C. L. Ho, Z. Q. Gao, B. X. Mi, C. H. Chen, K. W. Cheah and Z. Lin, *Angew. Chem., Int. Ed.*, 2006, **45**, 7800; (*b*) C. L. Ho, W. Y. Wong, Z. Q. Gao, C. H. Chen, K. W. Cheah, B. Yao, Z. Y. Xie, Q. Wang, D. G. Ma, L. X. Wang, X. M. Yu, H. S. Kwok and Z. Y. Lin, *Adv. Funct. Mater.*, 2008, **18**, 319; (*c*) C. L. Ho, W. Y. Wong, G. J. Zhou, B. Yao, Z. Xie and L. Wang, *Adv. Funct. Mater.*, 2007, **17**, 2925; (*d*) C.-L. Ho, W.-Y. Wong, B. Yao, Z. Xie, L. Wang and Z. Lin, *J. Organomet. Chem.*, 2009, **694**, 2735.

5 (*a*) Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube and K. Hara, *Chem. Mater.*, 2008, **20**, 3993; (*b*) 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.

6 C. Y. Chen, J. G. Chen, S. J. Wu, J. Y. Li, C. G. Wu and K. C. Ho, *Angew. Chem., Int. Ed.*, 2008, **47**, 7342.

7 (*a*) K. Ono, M. Joho, K. Saito, M. Tomura, Y. Matsushita, S. Naka, H. Okada and H. Onnagawa, *Eur. J. Inorg. Chem.*, 2006, 3676; (*b*) J. K. Kwon, J. H. Cho, Y.-S. Ryu, S. H. Oh and E. K. Yum, *Tetrahedron*, 2011, **67**, 4820.

8 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*b*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176; (*c*) J. Hassan and M. Sévignon, *Chem. Rev.*, 2002, **102**, 1359; (*d*) M. Miura, *Angew. Chem., Int. Ed.*, 2004, **43**, 2201; (*e*) A. Cwik, Z. Hell and F. Figueras, *Org. Biomol. Chem.*, 2005, **3**, 4307; (*f*) F. Alonso, I. P. Beletskaya and M. Yus, *Tetrahedron*, 2008, **64**, 3047; (*g*) V. Polshettiwar, A. Decottignies, C. Len and A. Fihri, *ChemSusChem*, 2010, **3**, 502.

9 (*a*) A.-E. Wang, J. Zhong, J.-H. Xie, K. Li and Q.-L. Zhou, *Adv. Synth. Catal.*, 2004, **346**, 595; (*b*) K. Billingsley and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3358; (*c*) R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461.

10 (*a*) G. Altenhoff, R. Goddard, C. W. Lehmann and F. Glorius, *J. Am. Chem. Soc.*, 2004, **126**, 15195; (*b*) N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.*, 2006, **128**, 4101; (*c*) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (*d*) M. Sreenivasulu, K. S. Kumar, P. R. Kumar, K. B. Chandrasekhar and M. Pal, *Org. Biomol. Chem.*, 2012, **10**, 1670.
11 (*a*) S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633; (*b*) C.-L. Chen, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Organometallics*, 2005, **24**, 1075.
12 (*a*) N. E. Leadbeater and M. Marco, *Org. Lett.*, 2002, **4**, 2973; (*b*) L. Liu, Y. Zhang and Y. Wang, *J. Org. Chem.*, 2005, **70**, 6122; (*c*) Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Commun.*, 2007, 5069; (*d*) T. M. Razler, Y. Hsiao, F. Qian, R. Fu, R. K. Khan and W. Doubleday, *J. Org. Chem.*, 2009, **74**, 1381; (*e*) Y. Kitamura, S. Sako, A. Tsutsui, Y. Monguchi, T. Maegawa, Y. Kitade and H. Sajiki, *Adv. Synth. Catal.*, 2010, **352**, 718.
13 (*a*) W. Han, C. Liu and Z.-L. Jin, *Org. Lett.*, 2007, **9**, 4005; (*b*) C. Liu and W. Yang, *Chem. Commun.*, 2009, 6267; (*c*) C. Liu, N. Han, X. Song and J. Qiu, *Eur. J. Org. Chem.*, 2010, 5548; (*d*) W. Yang, C. Liu and J. Qiu, *Chem. Commun.*, 2010, **46**, 2659; (*e*) C. Liu, Q. Ni, F. Bao and J. Qiu, *Green Chem.*, 2011, **13**, 1260; (*f*) C. Liu, Q. Ni and J. Qiu, *Eur. J. Org. Chem.*, 2011, 3009.
14 (*a*) N. E. Leadbeater, *Chem. Commun.*, 2005, 2881; (*b*) L. Liu, Y. Zhang and B. Xin, *J. Org. Chem.*, 2006, **71**, 3994; (*c*) T. Maegawa, Y. Kitamura, S. Sako, T. Udzu, A. Sakurai, A. Tanaka, Y. Kobayashi, K. Endo, U. Bora, T. Kurita, A. Kozaki, Y. Monguchi and H. Sajiki, *Chem.–Eur. J.*, 2007, **13**, 5937; (*d*) R. Nencka, D. Sinnaeve, I. Karalic, J. C. Martins and S. Van Calenbergh, *Org. Biomol. Chem.*, 2010, **8**, 5234.
15 C. Liu, Q. Ni, P. Hu and J. Qiu, *Org. Biomol. Chem.*, 2011, **9**, 1054.
16 S. Venkatraman and C.-J. Li, *Org. Lett.*, 1999, **1**, 1133.
17 (*a*) K. Zhang, Z. Chen, C. Yang, X. Zhang, Y. Tao, L. Duan, L. Chen, L. Zhu, J. Qin and Y. Cao, *J. Mater. Chem.*, 2007, **17**, 3451; (*b*) C.-L. Ho, L.-C. Chi, W.-Y. Hung, W.-J. Chen, Y.-C. Lin, H. Wu, E. Mondal, G.-J. Zhou, K.-T. Wong and W.-Y. Wong, *J. Mater. Chem.*, 2012, **22**, 215.
18 M. Tobisu, Y. Ano and N. Chatani, *Chem.–Asian J.*, 2008, **3**, 1585.
19 (*a*) A. Del Zotto, F. Amoroso, W. Baratta and P. Rigo, *Eur. J. Org. Chem.*, 2009, 110; (*b*) C. Pan, M. Liu, L. Zhang, H. Wu, J. Ding and J. Cheng, *Catal. Commun.*, 2008, **9**, 508.
20 (*a*) Z. He, W.-Y. Wong, X. Yu, H.-S. Kwok and Z. Lin, *Inorg. Chem.*, 2006, **45**, 10922; (*b*) C. Liu, Y. Wu, N. Han and J. Qiu, *Appl. Organomet. Chem.*, 2011, **25**, 862; (*c*) G. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder and A. Beeby, *Adv. Funct. Mater.*, 2008, **18**, 499; (*d*) W. Wu, C. Cheng, W. Wu, H. Guo, S. Ji, P. Song, K. Han, J. Zhao, X. Zhang, Y. Wu and G. Du, *Eur. J. Org. Chem.*, 2010, 4683.
21 W. Han, C. Liu and Z. Jin, *Adv. Synth. Catal.*, 2008, **350**, 501.
22 (*a*) C. Adamo, C. Amatore, I. Ciofini, A. Jutand and H. Lakmini, *J. Am. Chem. Soc.*, 2006, **128**, 6829; (*b*) G.-J. T. Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636.