RSC Advances

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Advances*, 2013, **3**, 526

Palladium-catalyzed ligand-free and aqueous Suzuki reaction for the construction of (hetero)aryl-substituted triphenylamine derivatives†

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

Received 25th September 2012,
Accepted 31st October 2012

DOI: 10.1039/c2ra22275b

www.rsc.org/advances

This paper reports an efficient synthesis of triphenylamine (TPA) derivatives *via* a palladium-catalyzed Suzuki reaction of (hetero)aryl halides with 4-(diphenylamino)phenylboronic acid (**DPBA**) in aqueous ethanol under aerobic and ligand-free conditions. Heteroaryl halides, namely pyridyl bromides, quinolyl bromides, pyrimidinyl bromides, 2-chloropyrazine and sulfur-containing heteroaryl bromides, could react smoothly with **DPBA**, affording good to excellent yields under mild conditions. In addition, aryl bromides were also successfully employed in the cross-couplings with **DPBA** and furnished the products in high yields at room temperature. The cross-coupling of 4-bromobenzonitrile with **DPBA** gave the desired product in a quantitative yield within 2 min, resulting in a TOF up to 5820 h^{-1}.

Introduction

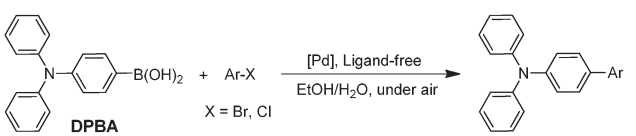
Triphenylamine (TPA) derivatives are receiving increasing attention because of their intriguing physical properties as well as being important pharmacophores in various biological compounds.[1] Moreover, due to good hole-transporting capability, strong electron-donating nature and high light-to-electrical energy conversion efficiencies, TPA derivatives are important structural motifs in organic light-emitting diodes (OLEDs)[2] and dye-sensitized solar cells (DSSCs).[3] For example, Zhou *et al.* synthesized a series of novel Ir^{III} complexes with triphenylamine dendrons and showed that the incorporation of triphenylamine units into the Ir^{III} complexes improved the HI/HT properties and the morphological stability.[4] Wang and coworkers reported a sensitizer incorporating a lipophilic alkoxy-substituted TPA electron donor, leading to a high efficiency of 10.0–10.3% for DSSCs.[5] However, these methods for the synthesis of TPA derivatives, as described in the literature, often require long reaction times, the use of harsh conditions or toxic substrates, and the yields are generally unpredictable because of side reactions such as dehalogenation and homocoupling.[6] Thus, it is still of great interest to develop a facile and robust method to synthesize this important type of compound.

The palladium-catalyzed Suzuki cross-coupling reaction has been established as one of the most versatile and powerful tools for the selective construction of aryl–aryl bonds.[7] As an intriguingly flexible reaction, it offers considerable potential in the synthesis of pharmaceuticals, fine chemicals and advanced functional materials. Generally, the Suzuki reaction is carried out in the presence of a ligand.[8] However, most ligands are air-sensitive and difficult to prepare or rather expensive. In the past few years, significant progress has been made in this area, which enables this transformation to be performed under mild conditions in the absence of a ligand.[9] Very recently, we reported a ligand-free and aerobic protocol for the synthesis of *N*-heteroaryl-substituted 9-arylcarbazolyl derivatives in aqueous ethanol.[10] Herein, we report a fast and efficient Suzuki reaction for the synthesis of TPA derivatives in aqueous ethanol under aerobic and ligand-free conditions (Scheme 1).

Results and discussion

Optimization of reaction conditions

It is known that the nature of the base is an important factor for determining the efficiency of the Suzuki reaction. Therefore, the influence of various bases on the cross-coupling reaction was first investigated. The cross-coupling of 2-bromopyridine (0.25 mmol) with 4-(diphenylamino)phenylboronic acid (**DPBA**) (0.375 mmol) was chosen as a model reaction.



Scheme 1 The Suzuki reaction for the synthesis of TPA derivatives in aqueous ethanol under ligand-free and aerobic conditions.

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

† Electronic supplementary information (ESI) available: Experimental details and characterization of cross-coupling products. See DOI: 10.1039/c2ra22275b

As is evidenced from Table 1, the use of inorganic bases, such as K_2CO_3, $K_3PO_4{\cdot}3H_2O$, or Na_2CO_3, delivered the desired products in high yields (Table 1, entries 1–3). On the other hand, organic bases, such as Et_3N and 1,4-diazabicyclo-[2,2,2]octance (DABCO), gave disappointing results (Table 1, entries 6 and 7). We chose K_2CO_3 for the remainder of the study as K_2CO_3 exhibited the highest activity among the bases used.

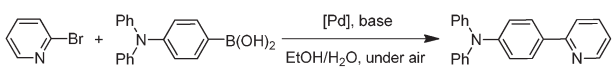
The next investigation was carried out to study the influence of different palladium species on the cross-coupling reaction, and the results are illustrated in Table 2. Precatalysts with Pd^{II} salts such as $Pd(OAc)_2$ and $PdCl_2$ exhibited high catalytic activity (Table 2, entries 1 and 2). However, the activity was decreased when Pd^{II} salt was replaced with zero-valent palladium such as $Pd_2(dba)_3$ or Pd/C (Table 2, entries 3 and 4), which is consistent with both our recent results[11] and Li's report.[12] The effect of the catalyst loading on this reaction was further evaluated. The yield decreased obviously when reducing the catalyst loading from 1.5 mol% to 1.0 mol% or 0.5 mol% (Table 2, entries 5 and 6). The effect of the temperature on the coupling reaction was also observed. The reaction performed at 50 °C provided the expected cross-coupled product in 35% yield, and the reaction was sluggish at room temperature (Table 1, entries 7 and 8). Thus, the optimum reaction conditions for this cross-coupling were found to be 1.5 mol% $Pd(OAc)_2$, 2 equiv. of K_2CO_3, 80 °C in aqueous ethanol under air.

Scope and limitations of substrates

With the optimized conditions in hand, we further explored the generality of the cross-coupling between **DPBA** with a variety of 2-pyridyl bromides using 1.5 mol% $Pd(OAc)_2$ in $EtOH/H_2O$, and the results are shown in Table 3. The coupling of 2-bromopyridine with **DPBA** exclusively gave the desired product **1** in 97% yield after 10 min (Table 3, entry 1), showing high efficiency. In 2006, a procedure was reported for the construction of *N*,*N*-diphenyl-4-(pyridin-2-yl)aniline (product **1**), which was prepared from 2-fluoropyridine in about 36% yield *via* two synthetic steps.[6b] Later, the Stille cross-coupling was used to synthesize the product **1** from 2-(tributylstannyl)-pyridine and (4-bromophenyl)diphenylamine in 75% yield in the presence of $Pd(PPh_3)_4$ for 24 h under nitrogen.[4c] Compared with the reported methods, this protocol is the fastest and simplest catalytic system for such a transformation.[4c,6b,c,13] Various 2-pyridyl bromides bearing electron-donating groups, such as methyl or methoxyl moieties, or electron-withdrawing groups, such as fluoro, nitro or cyan moieties, performed with high reactivity and delivered the desired products in high yields (Table 3, entries 2–8). For example, the cross-coupling between 2-bromo-4-methylpyridine and **DPBA** could be conducted with 96% yield after 8 min (Table 3, entry 2). Electron-poor 2-bromo-5-fluoropyridine resulted in 92% yield after 10 min (Table 3, entry 5). In particular, the cross-coupling of 2-bromo-5-(trifluoromethyl)pyridine and **DPBA** provided 95% yield in 10 min, which is much more efficient than that performed under nitrogen.[14] Furthermore, 6-substituted-2-bromopyridines were also successfully employed in the cross-coupling reactions (Table 3, entries 9–14). For example, 2-bromo-6-methoxypyridine produced the expected biaryl **10** in a 99% yield within 4 min, resulting in a TOF up to 990 h^{-1} (Table 3, entry 10).

To further investigate the scope and limitations of this methodology, we carried out cross-couplings of different heteroaryl halides with **DPBA** under standard conditions. The results are illustrated in Table 4. The coupling between 3-bromopyridine and **DPBA** provided 77% yield in 30 min (Table 4, entry 1). Using 5-bromo-2-methoxypyridine instead of 3-bromopyridine afforded the target product **16** in 83% for 10 min (Table 4, entry 2), which was much efficient than our previously reported method.[13a] Noticeably, 2-bromoquinoline and 3-bromoquinoline underwent cross-coupling smoothly and afforded the desired products in 97% and 85% yields, respectively (Table 4, entries 3 and 4). However, 8-bromoquinoline was less active and delivered the product in 41% yield even over a prolonged period (Table 4, entry 5). The cross-coupling of 5-bromopyrimidine and **DPBA** provided a 91% yield after 15 min (Table 4, entry 7). Due to the electronic effects of the nitrogen atoms of 2-bromopyrimidine, the reactivity decreased (Table 4, entry 8). In addition, deactivated 2-chloropyrazine is also a good coupling partner in the catalytic system (Table 4, entry 9). Furthermore, 2,6-dibromopyridine delivered the double coupling product **27** in 57% yield using a 3 mol% $Pd(OAc)_2$ loading (Table 4, entry 13). It is noteworthy that this catalytic system is also suitable for sulfur-

Table 1 The effect of base on the Suzuki reaction[a]



Entry	Base	Time (min)	Yield (%)[b]
1	$K_3PO_4{\cdot}3H_2O$	10	91
2	**K_2CO_3**	**10**	**97**
3	Na_2CO_3	10	88
4	$NaHCO_3$	10	76
5	EtONa	10	59
6	Et_3N	10	34
7	DABCO	10	40

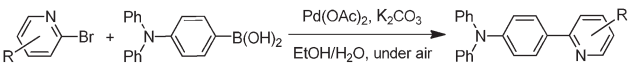
[a] Reaction conditions: 2-bromopyridine (0.25 mmol), **DPBA** (0.375 mmol), $Pd(OAc)_2$ (1.5 mol%), base (0.5 mmol), $EtOH/H_2O$ (3 mL/1 mL), under air. [b] Isolated yield.

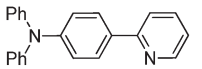
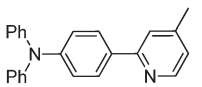
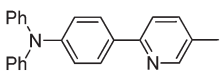
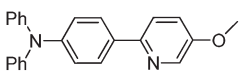
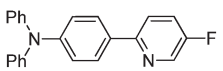
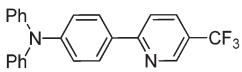
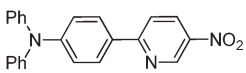
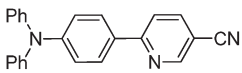
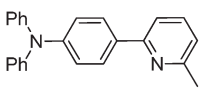
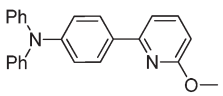
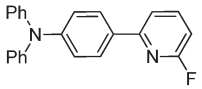
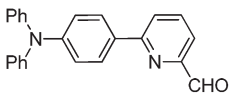
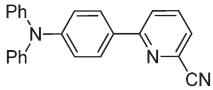
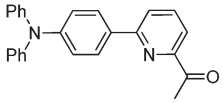
Table 2 The effects of precatalysts and temperature on the Suzuki reaction[a]

Entry	Precatalyst	Temp. (°C)	Yield (%)[b]
1	$PdCl_2$	80	82
2	**$Pd(OAc)_2$**	**80**	**97**
3	$Pd_2(dba)_3$	80	43
4	5% Pd/C	80	55
5	$Pd(OAc)_2$	80	79[c]
6	$Pd(OAc)_2$	80	43[d]
7	$Pd(OAc)_2$	50	35
8	$Pd(OAc)_2$	room temperature	trace

[a] Reaction conditions: 2-bromopyridine (0.25 mmol), **DPBA** (0.375 mmol), [Pd] (1.5 mol%), K_2CO_3 (0.5 mmol), $EtOH/H_2O$ (3 mL/1 mL), 10 min, in air. [b] Isolated yields. [c] $Pd(OAc)_2$ (1.0 mol%). [d] $Pd(OAc)_2$ (0.5 mol%).

Table 3 The Suzuki reaction of **DPBA** with pyridyl bromides[a]



Entry	R	Product	Time (min)	Yield (%)[b]
1	H	 **1**	10	97
2	4-CH_3	 **2**	8	96
3	5-CH_3	 **3**	20	94
4	5-OCH_3	 **4**	25	87
5	5-F	 **5**	10	92
6	5-CF_3	 **6**	10	95
7	5-NO_2	 **7**	10	91
8	5-CN	 **8**	30	90
9	6-CH_3	 **9**	4	98
10	6-OCH_3	 **10**	4	99
11	6-F	 **11**	8	89
12	6-CHO	 **12**	10	92
13	6-CN	 **13**	10	90
14	6-$COCH_3$	 **14**	6	95

[a] Reaction conditions: pyridyl bromide (0.25 mmol), **DPBA** (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.

containing heteroaryl bromides. The reaction between 2-bromothiophene and **DPBA** could be conducted with a 98% yield after 30 min and 3-bromothiophene produced the expected biaryl **25** in 81% yield within 60 min, respectively (Table 4, entries 10 and 11). Moreover, 2-bromothiazole coupling with **DPBA** afforded the target product in 62% yield after 4 h (Table 4, entry 12), which was comparable with the result in the presence of $Pd(PPh_3)_4$ under nitrogen in toluene at 110 °C for 24 h.[15]

In addition to heteroaryl halides, aryl bromides as one of the cross-coupling partners also exhibited high reactivity and afforded excellent yields. As shown in Table 4, the electronic nature of the substituent group has a small influence on the reactivity of the cross-coupling reactions (Table 4, entries 14–17). The coupling of 4-bromobenzonitrile with **DPBA** gave the desired product **28** in a quantitative isolated yield after 2 min, resulting in a TOF up to 5820 h^{-1} (Table 4, entry 14). To our delight, *ortho*-substituted substrate 2-bromobenzonitrile exhibited almost the same reactivity, and the coupling was completed in 4 min (Table 4, entry 15). A quantitative yield of product **32** was obtained by using 4-bromo-*N*,*N*-diphenylaniline as a coupling partner in 10 min (Table 4, entry 18). To the best of our knowledge, product **32** is commonly used as hole transport material in OLEDs,[16] and the present approach is the most efficient one for such a transformation.[17] Thus, this work provides a simple, fast and practical method for the synthesis of aryl-substistuted TPA derivatives, which are the potential building blocks for the construction of various important intermediates and advanced functional materials.

Conclusions

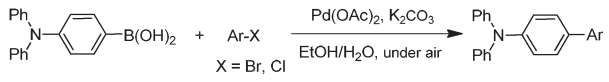
In summary, a very fast and highly efficient method for the synthesis of (hetero)aryl-substituted TPA derivatives has been developed. Operational simplicity, short reaction time and good yield are the key advantages of the present protocol. This aerobic and water-involved protocol is in accordance with the concept of green chemistry and is of great interest for the synthesis of various intermediates and advanced functional materials. Further investigations including photophysical properties of these TPA derivatives and synthetic applications of this methodology are currently under-way 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-(Diphenylamino)phenylboronic acid (**DPBA**) was 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 ^1H NMR and 100 MHz for ^{13}C NMR). Mass spectroscopy data of the products were collected with a

Table 4 The Suzuki reactions of **DPBA** with heteroaryl halides or aryl bromides[a]



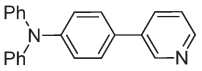
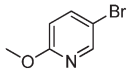
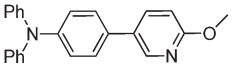
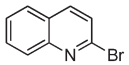
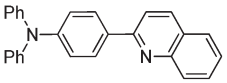
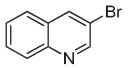
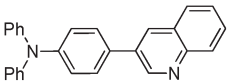
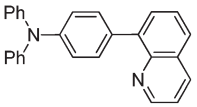
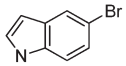
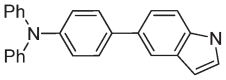
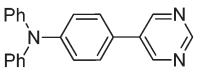
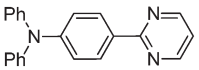
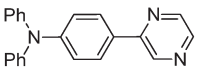
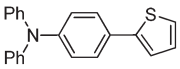
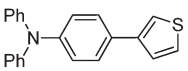
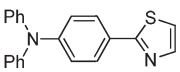
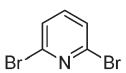
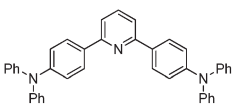
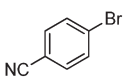
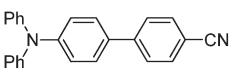
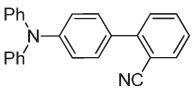
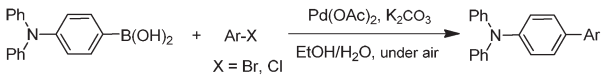
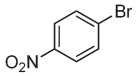
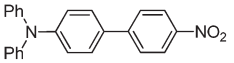
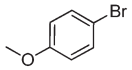
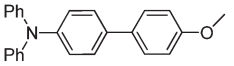
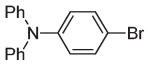
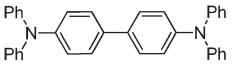
Entry	Ar–X	Product		Time (min)	Yield (%)[b]
1			**15**	30	77
2			**16**	10	83
3			**17**	8	97
4			**18**	20	85
5			**19**	120	41
6			**20**	10	95
7			**21**	15	91
8			**22**	60	71
9			**23**	15	84
10			**24**	30	98
11			**25**	60	81
12			**26**	240	62
13			**27**	60	57[c]
14			**28**	2	97[d]
15			**29**	4	95[d]

Table 4 (*Continued*)



Entry	Ar–X	Product	Time (min)	Yield (%)[b]
16		 **30**	10	91[d]
17		 **31**	10	92[d]
18		 **32**	10	86[d]

[a] Reaction conditions: heteroaryl halide (0.25 mmol), **DPBA** (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), **DPBA** (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. [d] Reaction conditions: aryl bromide (0.25 mmol), **DPBA** (0.375 mmol), $Pd(OAc)_2$ (0.5 mol%), K_2CO_3 (0.5 mmol), $EtOH/H_2O$ (3 mL/1 mL), room temperature, under air.

MS-EI instrument. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Compounds described in the literature were characterized by ^{1}H NMR spectra compared to reported data.

General procedure for the Suzuki cross-coupling of DPBA with heteroaryl halides

A mixture of heteroaryl halide (0.25 mmol), **DPBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (1.5 mol%), ethanol (3 mL) and distilled water (1 mL) was stirred at 80 °C in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted four times 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 DPBA with aryl bromides

A mixture of aryl bromide (0.25 mmol), **DPBA** (0.375 mmol), K_2CO_3 (0.5 mmol), $Pd(OAc)_2$ (0.5 mol%), ethanol (3 mL) and distilled water (1 mL) was stirred at room temperature in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted four times 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).

4-(4-Methylpyridin-2-yl)-*N*,*N*-diphenylaniline (2)

Yield: 96%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.50 (d, J = 2.4 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.49 (s, 1H), 7.28–7.25 (m, 4H), 7.14–7.12 (m, 6H), 7.06–7.02 (m, 3H), 2.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 157.16, 149.50, 148.72, 147.76, 147.70, 133.51, 129.46, 127.91, 124.83, 123.49, 123.31, 122.73, 121.04, 21.47 ppm. MS (EI): m/z = 336.1632 $[M]^+$.

4-(5-Methoxypyridin-2-yl)-*N*,*N*-diphenylaniline (4)

Yield: 87%; purple solid, mp 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.35 (d, J = 4.4 Hz, 1H), 7.81–7.79 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.28–7.23 (m, 5H), 7.14–7.11 (m, 6H), 7.05–7.01 (m, 2H), 3.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 154.47, 149.89, 148.01, 147.61, 136.83, 133.11, 129.29, 127.25, 124.55, 123.63, 123.05, 121.54, 120.22, 55.71 ppm. MS (EI): m/z = 352.1585 $[M]^+$.

6-(4-(Diphenylamino)phenyl)nicotinonitrile (8)

Yield: 90%; yellow solid, mp 144–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.87 (s, 1H), 7.92–7.90 (m, 3H), 7.74 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 8.0 Hz, 4.4 Hz, 4H), 7.16–7.11 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 159.97, 152.46, 150.30, 146.94, 139.57, 130.01, 129.51, 128.31, 125.42, 124.05,121.88, 118.90, 117.32, 106.63 ppm. MS (EI): m/z = 347.1426 $[M]^+$.

6-(4-(Diphenylamino)phenyl)picolinaldehyde (12)

Yield: 92%; yellow solid, mp 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 10.14 (s, 1H), 7.97–7.94 (m, 2H), 7.89–7.83 (m, 3H), 7.31–7.27 (m, 4H), 7.19–7.14 (m, 6H), 7.10–7.06 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 194.08, 157.60, 152.70, 149.40, 147.31, 137.65, 131.49, 129.43, 127.87, 125.01, 123.75, 123.59, 122.85, 119.06 ppm. MS (EI): m/z = 350.1421 $[M]^+$.

N,*N*-Diphenyl-4-(quinolin-8-yl)aniline (19)

Yield: 41%; white solid, mp 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.97–8.96 (m, 1H), 8.21–8.18 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.80–7.74 (m, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.43–7.40 (m, 1H), 7.30–7.26 (m, 4H), 7.21–7.17 (m, 6H), 7.03 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 150.08, 147.81, 147.05, 146.04, 140.34, 136.36, 133.35, 131.47, 130.14, 129.25, 128.85, 127.15, 126.37, 124.73, 122.92, 122.84, 120.93 ppm. MS (EI): m/z = 372.1631 $[M]^+$.

Acknowledgements

The authors thank the financial support from the National Natural Science Foundation of China (21276043, 21076034, 20836002), the Fundamental Research Funds for the Central Universities (DUT11LK15), and the Ministry of Education (the Program for New Century Excellent Talents in University).

References

1 (*a*) Y. Shirota and H. kageyama, *Chem. Rev.*, 2007, **107**, 953; (*b*) Y.-J. Pu, M. Soma, J. Kido and H. Nishide, *Chem. Mater.*, 2001, **13**, 3817; (*c*) C. S. K. Mak, D. Pentlehner, M. Stich, O. S. Wolfbeis, W. K. Chan and H. Yersin, *Chem. Mater.*, 2009, **21**, 2173; (*d*) S.-H. Cheng, S.-H. Hsiao, T.-H. Su and G.-S. Liou, *Macromolecules*, 2005, **38**, 307; (*e*) P. Wei, X. Bi, Z. Wu and Z. Xu, *Org. Lett.*, 2005, **7**, 3199; (*f*) Z. Fang, T.-L. Teo, L. Cai, Y.-H. Lai, A. Samoc and M. Samoc, *Org. Lett.*, 2009, **11**, 1; (*g*) M. Grigoras, L. Vacareanu, T. Ivan and G. L. Ailiesei, *Org. Biomol. Chem.*, 2010, **8**, 3638; (*h*) W. Z. Yuan, P. Lu, S. Chen, J. W. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159.

2 (*a*) P. Moonsin, N. Prachumrak, R. Rattanawan, T. Keawin, S. Jungsuttiwong, T. Sudyoadsuk and V. Promarak, *Chem. Commun.*, 2012, **48**, 3382; (*b*) N. Tamoto, C. Adachi and K. Nagai, *Chem. Mater.*, 1997, **9**, 1077; (*c*) K. Walzer, B. Maennig, M. Pfeiffer and K. Leo, *Chem. Rev.*, 2007, **107**, 1233; (*d*) J. Liu, X. Guo, L. J. Bu, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2007, **17**, 1917; (*e*) P. Jiang, D. D. Zhao, X. L. Yang, X. L. Zhu, J. Chang and H. J. Zhu, *Org. Biomol. Chem.*, 2012, **10**, 4704.

3 (*a*) M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen and Z. Li, *J. Phys. Chem. C*, 2007, **111**, 4465; (*b*) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and h. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (*c*) X. Lu, Q. Feng, T. Lan, G. Zhou and Z.-S. Wang, *Chem. Mater.*, 2012, **24**, 3179; (*d*) D. W. Chang, H. N. Tsao, P. Salvatori, F. De Angelis, M. Grätzel, S.-M. Park, L. Dai, H. J. Lee, J.-B. Baek and M. K. Nazeeruddin, *RSC Adv.*, 2012, **2**, 6209.

4 (*a*) G. Zhou, W. Y. Wong, B. Yao, Z. Xie and L. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1149; (*b*) G. Zhou, Q. Wang, C. L. Ho, W. Y. Wong, D. Ma, L. Wang and Z. Lin, *Chem.–Asian J.*, 2008, **3**, 1830; (*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.

5 W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915.

6 (*a*) H. J. Lee, J. Sohn, J. Hwang and S. Y. Park, *Chem. Mater.*, 2004, **16**, 456; (*b*) K. Ono, M. Joho, K. Saito, M. Tomura, Y. Matsushita, S. Naka, H. Okada and H. Onnagawa, *Eur. J. Inorg. Chem.*, 2006, 3676; (*c*) 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. Inorg. Chem.*, 2010, 4683; (*d*) K. Kowalski, N. J. Long, M. K. Kuimova, A. A. Kornyshev, A. G. Taylor and A. J. P. White, *New J. Chem.*, 2009, **33**, 598.

7 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*b*) R. B. Bedford, C. S. J. Cazin and D. Holder, *Coord. Chem. Rev.*, 2004, **248**, 2283; (*c*) A.-E. Wang, J. Zhong, J.-H. Xie, K. Li and Q.-L. Zhou, *Adv. Synth. Catal.*, 2004, **346**, 595; (*d*) F. Alonso, I. P. Beletskaya and M. Yus, *Tetrahedron*, 2008, **64**, 3047; (*e*) V. Polshettiwar, A. Decottignies, C. Len and A. Fihri, *ChemSusChem*, 2010, **3**, 502; (*f*) R. Ciriminna, V. Pandarus, G. Gingras, F. Béland, P. Demma Carà and M. Pagliaro, *RSC Adv.*, 2012, **2**, 10798.

8 (*a*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176; (*b*) M. Miura, *Angew. Chem., Int. Ed.*, 2004, **43**, 2201; (*c*) K. L. Billingsley, K. W. Anderson and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2006, **45**, 3484; (*d*) H. H. Zhang, C. H. Xing and Q. S. Hu, *J. Am. Chem. Soc.*, 2012, **134**, 13156; (*e*) N. Liu, C. Liu and Z. Jin, *Green Chem.*, 2012, **14**, 592.

9 (*a*) L. Liu, Y. Zhang and Y. Wang, *J. Org. Chem.*, 2005, **70**, 6122; (*b*) C.-L. Deng, S.-M. Guo, Y.-X. Xie and J.-H. Li, *Eur. J. Org. Chem.*, 2007, 1457; (*c*) C. Pan, M. Liu, L. Zhang, H. Wu, J. Ding and J. Cheng, *Catal. Commun.*, 2008, **9**, 508; (*d*) Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Commun.*, 2007, 5069; (*e*) 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; (*f*) W. Han, C. Liu and Z.-L. Jin, *Org. Lett.*, 2007, **9**, 4005; (*g*) C. Liu and W. Yang, *Chem. Commun.*, 2009, 6267; (*h*) R. Nencka, D. Sinnaeve, I. Karalic, J. C. Martins and S. Van Calenbergh, *Org. Biomol. Chem.*, 2010, **8**, 5234.

10 X. Rao, C. Liu, J. Qiu and Z. Jin, *Org. Biomol. Chem.*, 2012, **10**, 7875.

11 (*a*) W. Han, C. Liu and Z. Jin, *Adv. Synth. Catal.*, 2008, **350**, 501; (*b*) C. Liu, Q. Ni, P. Hu and J. Qiu, *Org. Biomol. Chem.*, 2011, **9**, 1054; (*c*) C. Liu, Q. Ni, F. Bao and J. Qiu, *Green Chem.*, 2011, **13**, 1260; (*d*) C. Liu, Y. Zhang, N. Liu and J. Qiu, *Green Chem.*, 2012, **14**, 2999.

12 S. Venkatraman and C.-J. Li, *Org. Lett.*, 1999, **1**, 1133.

13 (*a*) C. Liu, Y. Wu, N. Han and J. Qiu, *Appl. Organomet. Chem.*, 2011, **25**, 862; (*b*) C. Liu, Q. Ni and J. Qiu, *Eur. J. Org. Chem.*, 2011, 3009.

14 J.-i. Nishida, H. Echizen, T. Iwata and Y. Yamashita, *Chem. Lett.*, 2005, **34**, 1378.

15 X. Yang, Y. Zhao, X. Zhang, R. Li, J. Dang, Y. Li, G. Zhou, Z. Wu, D. Ma, W.-Y. Wong, X. Zhao, A. Ren, L. Wang and X. Hou, *J. Mater. Chem.*, 2012, **22**, 7136.

16 (*a*) V. Coropceanu, N. E. Gruhn, S. Barlow, C. Lambert, J. C. Durivage, T. G. Bill, G. Nöll, S. R. Marder and J.-L. Brédas, *J. Am. Chem. Soc.*, 2004, **126**, 2727; (*b*) P. J. Low, M. A. J. Paterson, D. S. Yufit, J. A. K. Howard, J. C. Cherryman, D. R. Tackley, R. Brook and B. Brown, *J. Mater. Chem.*, 2005, **15**, 2304; (*c*) J.-H. Pan, Y.-M. Chou, H.-L. Chiu and B.-C. Wang, *J. Phys. Org. Chem.*, 2007, **20**, 743.

17 (*a*) K. Sreenath, C. V. Suneesh, V. K. R. Kumar and K. R. Gopidas, *J. Org. Chem.*, 2008, **73**, 3245; (*b*) K. Y. Chiu, T. X. Su, J. H. Li, T. H. Lin, G. S. Liou and S. H. Cheng, *J. Electroanal. Chem.*, 2005, **575**, 95.