An efficient palladium-catalysed amination of aryl chlorides in presence of 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride

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1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (SIPr·HCl), a precursor for an *N*-heterocyclic carbene, was examined as a pro-ligand in C–N coupling reactions. Thus SIPr·HCl associated with a palladium catalyst was found to be efficient for the amination of aryl chlorides under mild conditions.

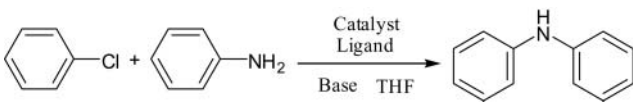
Keywords: imidazolinium chloride, *N*-heterocyclic carbene, palladium, amination, aryl chlorides

As well known, aromatic amine moieties are important building blocks for organic compounds involved in natural products, pharmaceuticals, agrochemicals, dyes and polymers.[1–8] Therefore, the development of efficient methods to synthesise these compounds attracts much attention from organic chemists.

Methods for synthesis of aromatic amines from aryl halides have been reported in recent years.[9,10] Palladium-catalysed amination of aryl halides has become one of the most widely used methods, and is now extensively used in academe and industry.[11–27] Buchwald and Hartwig, as well as other workers, have developed novel palladium catalyst systems for the cross-coupling of amines with aryl halides.[28] In most cases, aryl chlorides are cheaper and more widely available than bromides or iodides, so development of coupling reactions of aryl chlorides as substrates has been the focus of recent research.[29,30] However, amination of aryl chlorides is more difficult than that of bromides or iodides, because of their lower reactivity.

In recent years, more and more ligands have been found and applied to C–N bond-forming reactions in association with metal catalysts.[8,31–40] Typically, phosphine ligands such as $PtBu_3$ and PCy_3 were widely applied in the reactions. Recently, *N*-heterocyclic carbenes (NHCs) and their adducts were found to display good activity in coupling reactions with aryl bromides and aryl chlorides.[31,41,42] So further development of the application of NHCs and their derivatives in C–N bond-forming reactions is significant for synthetic chemistry. In our research, an imidazolinium salt, an air-stable and easily prepared[43] precursor for an NHC was used in association with Pd catalysts in the reaction, and this procedure has been found to be of good activity and efficient in the amination of aryl chlorides.

In this investigation on the amination of aryl chlorides, the coupling of chlorobenzene and aniline was selected as a model reaction (Scheme 1). Different metal catalysts were chosen, and the results are summarised in Table 1, from which we found that the combination of $NiCl_2$, or $VO(acac)_2$ with 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (SIPr·HCl) gave no reaction (entries 1 and 6 in Table 1). Although copper catalysts have been used extensively in aryl–aryl bond forming reactions,[44] when CuCl and $Cu(acac)_2$ accompanied with SIPr·HCl were employed in the reactions, there were none of the expected products found in the reactions (entries 2 and 5 in Table 1). It might be that the activities of $NiCl_2$, $VO(acac)_2$ and CuCl are too low to activate the Cl-aryl bond. Gradel *et al*. and Desmarets *et al*. reported that SIPr·HCl performed highly effectively in the $Ni(acac)_2$–NaH system.[45,46] However, in our investigation only a 40% yield occurred with NaH replaced by KO^{t}Bu (entry 3 in Table 1). The transformation was also observed when $Co(acac)_2$ was used in association with SIPr·HCl. No more conversion was observed with a longer reaction time (entry 4 in Table 1). Then we turned to another efficient catalyst palladium.



Scheme 1

Four palladium catalysts, $Pd(OAc)_2$, $Pd(acac)_2$, $Pd_2(dba)_3$. dba and $[Pd(allyl)Cl]_2$ were used, the latter three of which were easily prepared from $PdCl_2$.[47–79] In order to investigate the activity of the catalysts in the reaction of chlorobenzene and aniline, comparative experiments were carried out and good results were obtained in the case of $[Pd(allyl)Cl]_2$ combined with SIPr·HCl (see entries 8, 10, 11 and 14 in Table 1). When $Pd(OAc)_2$ and $Pd(acac)_2$ were applied in the reaction, almost the same yields of product were obtained 5 or 10 h later (entries 7 and 8, 9 and 10 in Table 1). The yields were not further improved on prolonging the reaction time, which shows that the two catalysts were not suitable for this reaction. $Pd_2(dba)_3$·dba and $[Pd(allyl)Cl]_2$ exhibited good activities in the reaction, when they were associated with SIPr·HCl, excellent yields of products were obtained with appropriate reaction times (entries 11 and 14 in Table 1). Compared to $Pd_2(dba)_3$·dba, $[Pd(allyl)Cl]_2$ has more advantages, the reaction time is shorter and the yield is higher.[50] A widely used ligand in the Suzuki reaction,[51] however, PPh_3 combined with $[Pd(allyl)Cl]_2$, did not facilitate the reaction (entry 12 in Table 1). The use of Cs_2CO_3 (entry 13 in Table 1) as the base was entirely ineffective. It might be that this base is too weak to deprotonate SIPr·HCl to form the corresponding carbene with which $[Pd(allyl)Cl]_2$ was integrated.

Table 1 Screening of conditions for C–N coupling with amine in the presence of SIPr·HCl[a]

Entry	Catalyst (mol %)	Ligand (mol %)	Base	Time /h	Yield /%[b]
1	$NiCl_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	NR[c]
2	CuCl (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	NR
3	$Ni(acac)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	40
4	$Co(acac)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	40
5	$Cu(acac)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	NR
6	$VO(acac)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	NR
7	$Pd(OAc)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	5	48
8	$Pd(OAc)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	50
9	$Pd(acac)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	5	55
10	$Pd(acac)_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	10	55
11	$Pd_2(dba)_3$·dba (0.5)	SIPr.HCl (1)	KO^{t}Bu	5	97
12	$[Pd(allyl)Cl]_2$ (0.5)	PPh_3 (1)	KO^{t}Bu	10	NR
13	$[Pd(allyl)Cl]_2$ (0.5)	SIPr.HCl (1)	Cs_2CO_3	10	NR
14	$[Pd(allyl)Cl]_2$ (0.5)	SIPr.HCl (1)	KO^{t}Bu	3	99

[a] Reaction conditions: chlorobenzene (1.0 equiv), aniline (1.1 equiv), base (1.5 equiv), THF (65 °C).
[b] Isolated yield.
[c] NR, no reaction.

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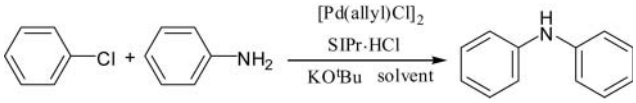


Scheme 2

In our study, we found ethers were suitable solvents for the reaction (Scheme 2), the three solvents were examined in the reaction (Table 2). It is observed from Table 2 that the reaction time was shortened when the temperature reached 100 °C (refluxing temperature in 1,4-dioxane). So 1,4-dioxane was chosen as solvent, and amination of aryl chlorides was realized at 100 °C in 1.5 h to give a good yield.

Under the optimal condition, a range of couplings between various anilines **2** and aryl chlorides **1** was carried out to give products **3** (Scheme 3); the results are summarised in Table 3.

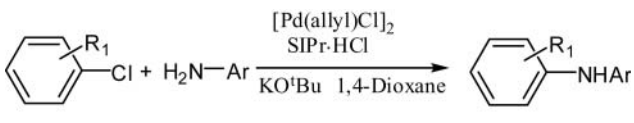
From Table 3, it is easily observed that the reactions were probably sensitive to the electronic effects of aryl chlorides. Unexpectedly, the reaction was inhibited by both electron-donating substituents and electron-withdrawing substituents on the aryl chloride. The coupling of 4-methoxychlorobenzene with amines gave only 50–55% yields (entries 20–22 in Table 3), and, according to TLC, ethoxy- and *tert*-butoxychlorobenzenes gave similar results. Coupling 4-chlorotrifluoromethylbenzene with aniline gave very low yield (entry 23 in Table 3). However, electron-donating substituents on the ring of amine did not affect the coupling reaction, the yield was very high (entries 5, 13 and 18 in Table 3). When 4-nitrobenzenamine coupled with chlorobenzene, there was no reaction (unlisted in Table 3) observed under the standard conditions. It was also observed that the yield of coupling *o*-toluidine with aryl chlorides was slightly lower than *ortho*-unsubstituted anilines (entries 2, 3, 4 and entries 15, 14, 17 in Table 3). This shows that the coupling reaction was affected by steric hindrance in the aromatic amine, which is further supported by the fact that the coupling of 2,6-diisopropylbenzenamine with chlorobenzene only gave 55% yield (entry 9 in Table 3).

1,2-Dichlorobenzene **4** was coupled with two equivalent of amines **2** to give its double-substituted derivatives **5** (Scheme 4). Three amines were used for these reactions and the yields of products were very high (entries 24–26 in Table 3). Unexpectedly, however, preliminary studies of 1,4-dichlorobenzene indicated that it gave a mixture of its corresponding single and double substituted derivatives with moderate conversion even with an excess of aniline employed.

Table 2 The solvent influence on amination of chlorobenzene.

Entry	Solvent[a]	Temperature/°C	Time/h	Yield/%[b]
1	THF	65	3	99
2	DME	80	2.5	99
3	1,4-Dioxane	100	1.5	99

[a] THF (tetrahydrofuran), DME (1,2-dimethoxyethane).
[b] Isolated yield.

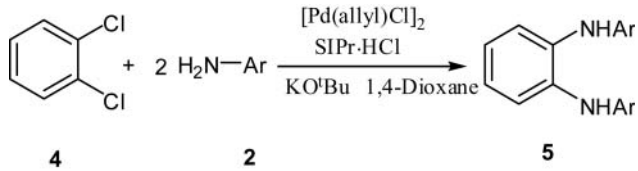


Scheme 3

Table 3 Coupling of aryl chlorides with amines catalysed by $[Pd(allyl)Cl]_2$ and SIPr·HCl[a]

Entry	R_1	Ar	Product	Yield %[b]
1	H	C_6H_5	**3a**	99
2	H	2-$CH_3C_6H_4$	**3b**	97
3	H	3-$CH_3C_6H_4$	**3c**	98
4	H	4-$CH_3C_6H_4$	**3d**	99
5	H	4-$CH_3OC_6H_4$	**3e**	99
6	H	2-$C_2H_5C_6H_4$	**3f**	95
7	H	3,5-$(CH_3)_2C_6H_3$	**3g**	98
8	H	2-Naphthyl	**3h**	98
9	H	2,6-$(^iPr)_2C_6H_3$	**3i**	55
10	2-CH_3	C_6H_5	**3b**	95
11	2-CH_3	2-$CH_3C_6H_4$	**3j**	90
12	2-CH_3	4-$CH_3C_6H_4$	**3k**	99
13	2-CH_3	4-$CH_3OC_6H_4$	**3l**	99
14	4-CH_3	C_6H_5	**3d**	99
15	4-CH_3	2-$CH_3C_6H_4$	**3k**	95
14	4-CH_3	3-$CH_3C_6H_4$	**3m**	98
17	4-CH_3	4-$CH_3C_6H_4$	**3n**	99
18	4-CH_3	4-$CH_3OC_6H_4$	**3o**	99
19	4-CH_3	3,5-$(CH_3)_2C_6H_3$	**3p**	99
20	4-CH_3O	C_6H_5	**3e**	55
21	4-CH_3O	2-$CH_3C_6H_4$	**3l**	50
22	4-CH_3O	4-$CH_3C_6H_4$	**3o**	55
23	4-CF_3	C_6H_5	**3r**	Trace
24[c]	2-Cl	C_6H_5	**5a**	99
25[c]	2-Cl	4-$CH_3C_6H_4$	**5b**	99
26[c]	2-Cl	3,5-$(CH_3)_2C_6H_3$	**5c**	98

[a] Reaction conditions: **1** (1.0 equiv), **2** (1.1 equiv), $[Pd(allyl)Cl]_2$ (0.5 mol%), SIPr·HCl (1 mol%), KO^{t}Bu (1.5 equiv), 1,4-dioxane (100 °C), 1.5 h.
[b] Isolated yield.
[c] Reaction conditions: **4** (1.0 equiv), **2** (2.2 equiv), $[Pd(allyl)Cl]_2$ (0.5 mol%), SIPr·HCl (1mol%), KO^{t}Bu (3 equiv), 1,4-dioxane (100 °C), 2 h.



Scheme 4

Nolan and coworkers [22] reported that an adduct of $[Pd(allyl)Cl]_2$, and NHC, prepared in advance, could readily mediate the arylation of anilines in a nitrogen glove box. Also other researchers reported that an NHC/Pd adduct had a good result in the amination of aryl chlorides under similar conditions.[52] As a contrast, however, the reaction was examined under our present conditions (without a glove box) and we found that almost no product was obtained. It might be due to NHC or the process of the reaction being sensitive to air and moisture.

In conclusion, we have developed an efficient palladium-catalysed amination of aryl chlorides. Coupling of aryl chlorides with aromatic amines catalysed by $[Pd(allyl)Cl]_2$ in association with SIPr·HCl, a precursor for NHC, in presence of KO^{t}Bu has been achieved.

Experimental

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were determined on a Varian Plus 500 instrument using TMS as an internal standard and $CDCl_3$ as a solvent. ESI-MS spectra were performed on an AEI MS-902 apparatus. Elemental analyses were performed on a Carlo-Erba 1106 analytical instrument.

General procedure for preparation of **3a–p**

CAUTION: 2-Naphthylamine (β-naphthylamine, naphthalene-2-amine) is a known potent carcinogen. A series of studies of workers with occupational exposure to it has shown clear evidence of a link between exposure and bladder cancer. In the UK, it appears in Schedule 2 of the Control of Substances Hazardous to Health Regulations (COSSH) 1999 which prohibits its "manufacture and use for all purposes".

To a dried tube was added under nitrogen atmosphere chlorobenzene (1 mmol), the amine (1.1 mmol) and dry 1,4-dioxane (2 mL). Then the reaction tube was charged with KO^{t}Bu (1.5 mmol, 148 mg), $[Pd(allyl)Cl]_2$ (0.5 mol%, 1.8 mg) and SIPr·HCl (1 mol%, based on aryl chloride, 4.3 mg) and the reaction mixture was heated at 100 °C for 1.5 h. The reaction mixture was allowed to cool to room temperature and was filtered through a pad of silica gel. The silica gel pad was washed with ethyl acetate (10 mL×3). The combined organic phases were evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (10:1) eluant to give the diarylamine.

Diphenylamine (**3a**):^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.70 (s, br, 1H), 6.91–6.94 (m, 2H), 7.05–7.08 (m, 4H), 7.24–7.28 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.1, 129.3, 121.0, 117.8; m.p. 76–77 °C [lit.[53] 78–79 °C].

2-Methyl-N-phenylbenzenamine (**3b**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 5.33 (s, br, 1H), 6.86–6.94 (m, 4H), 7.10–7.13 (m, 1H), 7.17–7.21 (m, 1H), 7.22–7.24 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =144.1, 141.3, 131.0, 129.4, 128.4, 126.8, 122.1, 120.5, 119.0, 117.5, 18.0; m.p. 35–36 °C [lit.[54] 37 °C].

3-Methyl-N-phenylbenzenamine (**3c**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 5.66 (s, br, 1H), 6.74–6.76 (m, 1H), 6.87–6.93 (m, 3H), 7.04–7.07 (m, 2H), 7.13–7.14 (m, 1H), 7.23–7.27 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 143.2, 139.3, 129.4, 129.2, 122.0, 120.9, 118.6, 117.9, 115.0, 21.6. oil [lit.[55] 30–31 °C].

4-methyl-N-phenylbenzenamine (**3d**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 5.89 (s, br, 1H), 6.87–6.90 (m, 1H), 7.00–7.03 (m, 4H), 7.09–7.10 (m, 2H), 7.22–7.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.9, 140.3, 131.0, 129.8, 129.3, 120.3, 118.9, 114.9, 20.7; m.p. 84–85 °C [lit.[39] 85–86 °C]

4-Methoxy-N-phenylbenzenamine (**3e**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 5.52 (s, br, 1H), 6.81–6.91 (m, 5H), 7.06–7.08 (m, 2H), 7.19–7.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =155.3, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.5; m.p. 100–101 °C [lit.[55] 101–103 °C].

2-Ethyl-N-phenylbenzenamine (**3f**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31–1.36 (m, 3H), 2.71 (q, 7.0 Hz, 2H), 5.48 (s, br, 1H), 6.96–7.03 (m, 3H), 7.08–7.11 (m, 1H), 7.21–7.28 (m, 1H), 7.33–7.36 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ =144.6, 140.6, 134.9, 129.4, 129.0, 126.7, 122.7, 120.3, 120.2, 117.1, 24.4, 14.0. oil.[46]

3,5-Dimethyl-N-phenylbenzenamine (**3g**):^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26 (m, 6H), 5.58 (s, br, 1H), 6.58 (s, 1H), 6.70 (s, 2H), 6.92 (t, 7.0Hz, 1H), 7.03–7.05 (m, 2H), 7.22–7.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 143.1, 139.1, 129.3, 122.9, 120.8, 117.9,115.7, 21.4; m.p. 52–53 °C [lit.[56] 52–53 °C].

N-Phenylnaphthalen-2-amine(**3h**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.95 (s, br, 1H), 6.96–6.99 (m, 1H), 7.15–7.17 (m, 2H), 7.20–7.23 (m, 1H), 7.28–7.32 (m, 3H), 7.38–7.43 (m, 2H), 7.64 (d, 8.0 Hz, 1H), 7.74 (d, 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.9, 140.9, 134.6, 129.5, 129.2, 129.1, 126.5, 126.4, 123.5, 121.5, 120.1, 118.3, 111.7; m.p. 109–110 °C [lit.[55] 108–110 °C].

2,6-Diisopropyl-N-phenylbenzenamine (**3i**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, 7.0Hz,12H), 3.14–3.24 (m, 2H), 5.11 (s, br, 1H), 6.47–6.48 (m, 2H), 6.69–6.72 (m, 1H), 7.12–7.30 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.3, 147.8, 135.4, 129.4, 127.4, 124.0, 117.9, 113.2, 28.4, 24.1. oil.[46]

Di-o-tolylamine (**3j**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 6H), 5.13 (s, br, 1H), 6.88–6.91 (m, 2H), 6.97–6.99 (m, 2H), 7.09–7.12 (m, 2H), 7.18–7.22 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.1, 130.9, 127.6, 126.9, 121.5, 118.4, 17.9; m.p. 46–48 °C [lit.[57] 47–49 °C].

2-Methyl-N-p-tolylbenzenamine (**3k**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.29 (s, 3H), 5.26 (s, br, 1H), 6.86–6.90 (m, 3H), 7.05–7.09 (m, 3H), 7.14–7.14 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.1, 141.2, 130.9, 130.5, 129.9, 127.1, 126.8, 121.2, 118.7, 117.4, 20.7, 17.9; m.p. 50–52 °C [lit.[58] 53 °C].

N-(4-Methoxyphenyl)-2-methylbenzenamine (**3l**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.80 (s, 3H), 5.25 (s, br, 1H), 6.80–6.87 (m, 3H), 6.99–7.15 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.1, 143.3, 136.3, 130.8, 126.8, 125.3, 122.1, 120.0, 115.3, 114.7, 55.6, 17.8; m.p. 81–82 °C [lit.[59] 81.5–82 °C].

3-Methyl-N-p-tolylbenzenamine (**3m**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.30 (s, 3H), 5.55 (s, br, 1H), 6.69–6.71 (m, 1H), 6.81–6.82 (m, 2H), 6.98–6.99 (m, 2H), 7.07–7.23 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0, 140.4, 139.2, 130.8, 129.9, 129.2, 121.2, 119.0, 117.6, 114.0, 21.6, 20.7. oil. [58]

Di-p-tolylamine (**3n**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 6H), 5.83 (s, br, 1H), 6.95 (d, 8.0 Hz, 2H), 7.06 (d, 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 130.2, 129.8, 118.0, 20.6; m.p. 58–60 °C [lit.[58] 60–61 °C].

4-Methoxy-N-p-tolylbenzenamine (**3o**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, br, 3H) , 3.79 (s, 3H), 5.79 (s, br, 1H), 6.83–6.85 (m, 4H), 7.03–7.04 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.9, 142.4, 136.6, 129.8, 129.4, 121.2, 114.6, 114.7, 55.6, 20.6; m.p. 79–80 °C [lit.[60] 80–81 °C].

3,5-Dimethyl-N-p-tolylbenzenamine (**3p**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 6H), 2.30 (s, 3H), 5.65 (s, br, 1H), 6.54 (s, 1H), 6.65 (s, 2H), 6.98–7.0 (m, 2H), 7.07–7.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.9, 140.5, 139.0, 130.8, 129.8, 122.3, 119.1, 114.7, 21.4, 20.7. oil.[61]

General procedure for amination of 1,2-dichlorobenzene **5a–c**

To a dried tube was added under nitrogen atmosphere 1,2-dichlorobenzene (1 mmol), amine (2.2 mmol) and dry 1,4-dioxane (2 mL). Then the reaction tube was charged with KO^{t}Bu (3 mmol, 330 mg), $[Pd(allyl)Cl]_2$ (0.5 mol%, 1.8 mg) and SIPr·HCl (1 mol%, based on aryl chloride, 4.3 mg) and the reaction mixture was heated at 100 °C for 2 h. The reaction mixture was allowed to cool to room temperature and filtered through a pad of silica gel. The silica gel pad was washed with ethyl acetate (10 mL×3). The combined organic phases were evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (10:1) to give the *N,N′*-diarylbenzene-1,2-diamine.

N,N′-Diphenylbenzene-1,2-diamine (**5a**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.67 (s, br, 2H), 6.88–6.98 (m, 8H), 7.22–7.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0, 135.0, 129.4, 123.1, 120.7, 120.3, 117.3; m.p. 100–101 °C [lit.[62]109 °C].

N,N′-Di-p-tolylbenzene-1,2-diamine (**5b**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, 6H), 5.50 (s, br, 2H), 6.83–6.86 (m, 4H), 6.90–6.92 (m, 2H), 7.04 (d, 8.0 Hz, 4H), 7.19–7.23 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.4, 135.3, 130.2, 129.9, 122.6, 119.6, 117.9, 20.6; m.p. 35–36 °C.[63]

N,N′-Di(3,5-dimethylphenyl)benzene-1,2-diamine (**5c**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.24 (s, 12H), 5.50 (s, br, 2H), 6.55–6.56 (m, 6H), 6.95–6.97 (m, 2H), 7.25–7.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0, 139.0, 135.1, 122.8, 122.5, 120.5, 115.0, 21.4. ESI-MS: 317 ($M+H^+$). Elemental Anal. Calcd C, 83.50; H, 7.64; N, 8.85. Found: C, 83.40; H, 7.58; N, 8.81%; m.p. 45–47 °C.

N,N′-Diphenylbenzene-1,4-diamine: ^{1}H NMR (500 MHz, DMSO-d^6): δ = 7.85 (s, 2H), 7.15–7.19 (m, 4H), 7.03 (s, 4H), 6.96 (d, *J* = 8Hz, 4H), 6.68–6.72 (m, 2H); m.p. 143–145 °C [lit.[64] 146–148 °C].

Received 14 November 2009; accepted 4 March 2010
Paper 090872 doi: 10.3184/030823410X12680525004303
Published online: 23 March 2010

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