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Solvent-free Buchwald–Hartwig amination with low palladium loadings

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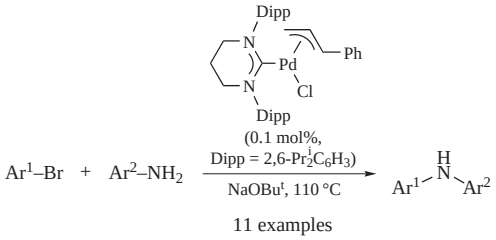
A highly efficient 'green' solvent-free monoarylation of primary anilines with aryl bromides mediated by the expanded-ring N-heterocyclic carbene palladium complex (THP-Dipp)Pd(cinn)Cl [THP-Dipp is 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene; cinn is cinnamyl] can be performed at low catalyst loadings (0.1 mol%) to provide excellent yields and remarkable selectivities for various substrates.



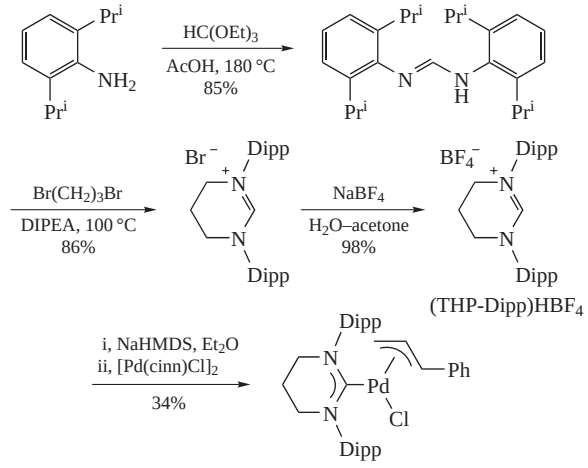
Organic light emitting diode (OLED) technology, first introduced in 1987,[1] has undergone significant development in recent years.[2] In multilayered structures of small-molecule OLEDs, emitting layers are positioned between electron- and hole-transporting layers, and the electrode materials. Hole-transporting materials usually consist of polyaromatic amines bearing triarylamine moieties.[3,4] Thus, efficient methods for the synthesis of such triarylamines are constantly sought.

Convenient precursors of triarylamines are obviously diarylamines.[5] Palladium mediated Buchwald–Hartwig amination of aryl halides is arguably the most versatile and efficient synthetic entry to them.[6–9] However, arylation of anilines with bulky aryl bromides proceeds rather sluggishly even with state-of-the-art catalysts.[10–12] Usually, high loadings of catalysts exceeding 1 mol% are required. Moreover, significant quantities of hard-to-separate diarylation products are also obtained, which demands for specific isolation procedures to purify diarylamines. Most of these hardens can be overcome using a new catalytic system based on expanded-ring N-heterocyclic carbene palladium complex (THP-Dipp)Pd(cinn)Cl [THP-Dipp is 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene; cinn is cinnamyl] and a solvent-free protocol for the Buchwald–Hartwig amination recently developed in our group.[5]

In this contribution, we aimed at developing a highly selective and easily scalable monoarylation procedure operative at high substrate concentrations (solvent-free conditions), low catalyst loadings (0.1 mol%), and equimolar (no excess of aryl halide or aniline) amounts of the coupling partners. It was previously reported that carbene and phosphine palladium complexes bearing indenyl ligands (L)Pd(3-Bu^{t}Ind)Cl (3-Bu^{t}Ind is 3-*tert*-butyl-1-indenyl) exhibited higher catalytic activities than their cinnamyl counterparts.[13] Presumably, this was due to easier activation of the precatalyst in case of indenyl derivatives. Therefore, we performed comparative catalytic studies of cinnamyl and indenyl palladium complexes in the Buchwald–Hartwig amination.

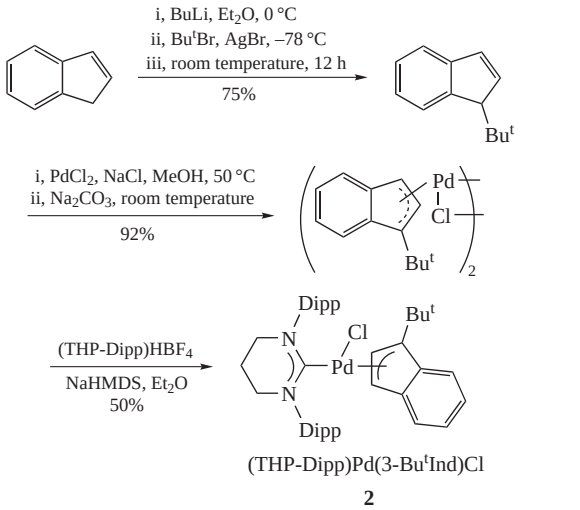
Cinnamyl-containing complex **1** was prepared as outlined in Scheme 1.† The reaction between cyclic amidinium salt (THP-Dipp)HBF$_4$ and palladium source [Pd(3-Bu^{t}Ind)Cl]$_2$ afforded new complex (THP-Dipp)Pd(3-Bu^{t}Ind)Cl **2** (Scheme 2).[13]

Catalytic tests of the Buchwald–Hartwig amination were performed using equimolar amounts of arylamine and aryl bromide, 0.1 mol% of palladium complexes, 1.2 equiv. of NaOBu^t as a



Scheme 1

† *Complex (THP-Dipp)Pd(cinn)Cl* **1**. A 10 ml Schlenk flask equipped with a magnetic stirring bar and rubber septum was charged with (THP-Dipp)-HBF$_4$[14] (492 mg, 1 equiv.) and dry diethyl ether (5 ml). Then, a solution of NaHMDS in THF (2.0 M, 0.5 ml) was added. The mixture was stirred at room temperature for 1 h, then it was transferred to another 10 ml Schlenk flask containing a suspension of [Pd(cinn)Cl]$_2$ (258 mg, 0.5 equiv.) in dry diethyl ether (2 ml) and stirred overnight. The mixture was filtered through Celite® pad and the filtrate was discarded. The pad was washed with dichloromethane to give dark yellow solution, which was evaporated to dryness and purified by column chromatography (CH_2Cl_2 and CH_2Cl_2–MeOH, 10 : 1) to give 226 mg (34%) of complex **1** as a bright yellow powder. Analytical data were consistent with those previously reported.[14]



(THP-Dipp)Pd(3-Bu^{t}Ind)Cl

2

Scheme 2

strong base, in melt at 110 °C. Activities of **1** and **2** were compared using a challenging substrate, 3-methylpyridine-2-amine, and bromobenzene. At 0.1 mol% loading, both complexes showed moderate activities. The resulting product, 3-methyl-*N*-phenylpyridin-2-amine, was isolated in 27% yield for **1** and 20% for **2** (Table 1, entry 1). Thus, cinnamyl complex **1** exhibits higher activity under solvent-free conditions. Further catalytic studies were performed for complex **1**.

Note that the reaction proceeds quite fast during the initiation even at rather low catalyst loading. After mixing the reaction components and immersing the flask into preheated oil bath (110 °C), the reaction initiates in a period of *ca*. 0.5–1.5 min. Initiation is accompanied by a strong flux of white dense vapors of Bu^{t}OH in the condenser. After several dozens of seconds, the reaction continues to proceed more steadily.

To determine the scope of this solvent-free procedure (0.1 mol% of **1**), we performed coupling of various (het)aryl bromides and anilines (see Table 1).§ Phenyl and *o*-tolyl bromides are aminated with anilines bearing donor, acceptor and bulky groups,

Table 1 Buchwald–Hartwig amination catalyzed by complex **1**.[a]

Entry	(Het)aryl bromide R^1Br	(Het)arylamine R^2NH_2	Yield of product R^1NHR^2 (%)
1	PhBr	3-methylpyridin-2-amine	27 (20[b])
2	PhBr	2-Me$C_6H_4NH_2$	>99
3	PhBr	2-Et$C_6H_4NH_2$	>99
4	2-MeC_6H_4Br	2-MeO$C_6H_4NH_2$	>99
5	2-MeC_6H_4Br	1-aminonaphthalene	99
6	2-MeC_6H_4Br	4-F$C_6H_4NH_2$	>99
7	2-MeC_6H_4Br	3-F_3C$C_6H_4NH_2$	68 (98[c])
8	PhBr	2,4-Me$_2C_6H_3NH_2$	>99
9	PhBr	2,4,6-Me$_3C_6H_2NH_2$	>99
10	3-bromopyridine	2-Me$C_6H_4NH_2$	95
11	3-bromothiophene	2-Me$C_6H_4NH_2$	41 (84[d])

[a] Aryl bromide (20 mmol, 1 equiv.), arylamine (20 mmol, 1 equiv.), NaOBu^t (24 mmol, 1.2 equiv.), complex **1** (0.02 mmol, 0.001 equiv.), 110 °C. [b] 0.1 mol% of **2**. [c] 0.5 mol% of **1**. [d] 0.2 mol% of **1**.

‡ *Complex (THP-Dipp)Pd(3-Bu^{t}Ind)Cl* **2**. A 10 ml Schlenk flask equipped with a magnetic stirring bar and rubber septum was charged with (THP-Dipp)HBF_4 (492 mg, 1 equiv.) and dry diethyl ether (5 ml) followed by addition of solution of NaHMDS in THF (2.0 M, 0.5 ml). The mixture was stirred at room temperature for 1 h, then it was transferred to another 10 ml Schlenk flask containing a suspension of [Pd(3-Bu^{t}Ind)Cl]$_2$ (314 mg, 0.5 equiv.) in dry diethyl ether (2 ml) and stirred overnight. The mixture was filtered through Celite® pad and the filtrate was discarded. The pad was washed with dichloromethane to give red solution, which was evaporated to dryness, and the residue was recrystallized from the hexane–dichloromethane mixture to give 204 mg (28%) of product **2** as bright red crystals. The supernatant solution was concentrated to dryness and purified by column chromatography (CH_2Cl_2) to give additional 227 mg (31%) of product as a red solid. The total yield was 431 mg (59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38–7.29 (m, 4H), 7.15 (d, 2H, *J* 8.4 Hz), 6.93 (d, 1H, *J* 7.6 Hz), 6.64 (t, 1H, *J* 7.6 Hz), 6.19 (t, 1H, *J* 7.4 Hz), 5.74 (d, 1H, *J* 7.4 Hz), 5.41 (d, 1H, *J* 2.7 Hz), 5.23 (d, 1H, *J* 2.6 Hz), 3.62–3.45 (m, 8H), 2.30 (p, 2H, *J* 5.8 Hz), 1.58 (d, 7H, *J* 6.6 Hz), 1.27 (d, 6H, *J* 6.7 Hz), 1.15–1.06 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 204.9, 146.7, 146.5, 144.0, 139.1, 138.6, 128.7, 124.7, 124.2, 123.5, 118.2, 116.9, 113.2, 107.9, 63.5, 50.3, 33.6, 29.4, 28.9, 28.3, 26.8, 26.7, 24.6, 23.5, 21.3.

§ *Solvent-free Buchwald–Hartwig amination reaction (general procedure)*. A 50 ml round-bottom flask equipped with a magnetic stirring bar and a reflux condenser with argon inlet was charged with complex **1** (13.3 mg, 0.02 mmol), aryl bromide (20 mmol) and arylamine (20 mmol). The mixture was deaerated by 3 evacuate/refill cycles. Then NaOBu^t (2.306 g, 24 mmol, 1.2 equiv.) was added and the resulting mixture was manually homogenized with a magnet. The flask was immediately immersed into preheated (110 °C) oil bath and allowed to stir for 18 h at this temperature. After cooling to ambient temperature, the mixture was partitioned between CH_2Cl_2 (30 ml) and water (30 ml). The organic phase was collected and the aqueous one was extracted with CH_2Cl_2 (2×20 ml). The combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo*. The resulting oil was passed through a small pad of silica gel with CH_2Cl_2 as eluent to give pure product.

2-Methyl-N-*phenylaniline*[16] was obtained from bromobenzene (3.140 g) and *o*-toluidine (2.143 g) as yellow oil. Yield 3.658 g (99.8%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31–7.27 (m, 3H), 7.24 (d, 1H, *J* 7.5 Hz), 7.20–7.16 (m, 1H), 7.02–6.96 (m, 3H), 6.95 (tt, 1H, *J* 7.4, 1.1 Hz), 5.39 (s, 0H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 141.3, 131.1, 129.4, 126.9, 122.2, 120.6, 119.0, 117.6, 18.0.

2-Ethyl-N-*phenylaniline*[17] was obtained from bromobenzene (3.140 g) and 2-ethylaniline (2.424 g) as yellow oil. Yield 3.943 g (99.9%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.33–7.27 (m, 4H), 7.20 (td, 1H, *J* 7.7, 1.6 Hz), 7.06 (td, 1H, *J* 7.4, 1.2 Hz), 7.00–6.97 (m, 2H), 6.94 (tt, 1H, *J* 7.4, 1.0 Hz), 5.45 (s, 1H), 2.68 (q, 2H, *J* 7.5 Hz), 1.31 (t, 3H, *J* 7.5 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 129.4, 129.1, 126.8, 122.7, 120.3, 120.2, 117.2, 24.4, 14.0.

2-Methoxy-N-*(o-tolyl)aniline*[18] was obtained from 2-bromotoluene (3.421 g) and *o*-anisidine (2.463 g) as yellow oil. Yield 4.247 g (99.5%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.41–7.38 (m, 1H), 7.28 (d, 1H, *J* 7.4 Hz), 7.23 (t, 1H, *J* 7.7 Hz), 7.11 (dd, 1H, *J* 7.6, 1.8 Hz), 7.02 (td, 1H, *J* 7.4, 1.2 Hz), 6.97–6.88 (m, 3H), 5.96 (s, 1H), 3.96 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.1, 141.0, 134.0, 131.0, 129.4, 126.8, 122.2, 121.0, 119.6, 119.4, 114.5, 110.5, 55.7, 18.0.

N-*(o-Tolyl)naphthalen-1-amine*[19] was obtained from 2-bromotoluene (3.421 g) and 1-naphthylamine (2.864 g) as yellow oil. Yield 4.660 g (99.9%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08–8.00 (m, 1H), 7.90 (d, 1H, *J* 7.9 Hz), 7.56 (d, 1H, *J* 8.2 Hz), 7.52 (dtd, 2H, *J* 9.5, 8.1, 7.4, 6.2 Hz), 7.39 (t, 1H, *J* 7.8 Hz), 7.27 (d, 1H, *J* 7.6 Hz), 7.13 (t, 1H, *J* 7.7 Hz), 7.10 (d, 1H, *J* 7.4 Hz), 7.00–6.94 (m, 2H), 5.78 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.7, 131.0, 128.7, 127.0, 126.3, 126.2, 125.7, 122.3, 121.8, 121.7, 118.8, 115.1, 18.0.

N-*(4-Fluorophenyl)-2-methylaniline*[20] was obtained from 2-bromotoluene (3.421 g) and 4-fluoroaniline (2.222 g) as yellow oil. Yield 4.023 g (99.9%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.20 (d, 1H, *J* 7.4 Hz), 7.16–7.10 (m, 2H), 7.01–6.94 (m, 4H), 6.92 (td, 1H, *J* 7.3, 1.3 Hz), 5.34 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 158.0 (d, *J* 239.6 Hz), 142.2, 139.8, 131.1, 127.3, 127.0, 121.6, 120.3 (d, *J* 7.8 Hz), 117.4, 116.0 (d, *J* 22.4 Hz), 17.9.

2-Methyl-N-*[3-(trifluoromethyl)phenyl]aniline*[21] was obtained from 2-bromotoluene (3.421 g) and 3-(trifluoromethyl)aniline (3.222 g) as yellow oil. Yield 3.418 g (68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.32 (t, 1H, *J* 7.9 Hz), 7.28–7.23 (m, 2H), 7.22–7.18 (m, 1H), 7.11 (m, 2H), 7.07–7.02 (m, 2H), 5.54 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 145.2, 139.9, 131.9 (q, *J* 32.5 Hz), 131.4, 130.3, 129.9, 127.1, 124.3 (q, *J* 272.2 Hz), 123.8, 121.0, 119.2, 116.4 (q, *J* 3.4 Hz), 112.8 (q, *J* 3.6 Hz), 18.0.

giving products in virtually quantitative yields (entries 2–6, 8–10). In reactions of 2-bromotoluene with 3-(trifluoromethyl)aniline, and 3-bromothiophene with 2-methylaniline the yields were significantly lower (entries 7, 11). In these cases, the unreacted starting compounds were recovered along with the products. However, raising the catalyst loading to 0.5 and 0.2 mol% provided 98 and 84% yields, respectively (see Table 1).

To make solvent-free protocol for Buchwald–Hartwig amination more environmentally friendly, we performed a medium-scale (0.2 mol) synthesis of 2-methyl-*N*-phenylaniline and improved the product isolation procedure. Catalyst loading was decreased to 0.05 mol%. After completion of the reaction, the condenser was replaced by a distillation head and the reaction mixture was vacuum distilled to give pure product in 96% yield. Thus, we eliminated the use of organic solvents in product isolation and purification steps. This makes the new protocol 'greener', calculated Sheldon's E-factor[15] being only 1.08. Obviously, such a protocol is suitable for large-scale synthesis and is economically more feasible due to low palladium loadings.

In summary, a scalable procedure for the Buchwald–Hartwig amination reaction of various substrates at low palladium-catalyst loadings (0.1 mol%) has been developed. Diarylamines can be obtained on a large scale with no use of organic solvents both in synthesis and product isolation steps.

2,4-Dimethyl-N-*phenylaniline*[22] was obtained from bromobenzene (3.140 g) and 2,4-xylidine (2.424 g) as yellow oil. Yield 3.847 g (97.5%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.27–7.23 (m, 2H), 7.17 (d, 1H, *J* 8.0 Hz), 7.07 (s, 1H), 7.01–6.98 (m, 1H), 6.91–6.86 (m, 3H), 5.34 (s, 1H), 2.34 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 145.0, 138.3, 132.4, 131.8, 129.9, 129.4, 127.4, 120.9, 119.8, 116.4, 20.9, 18.0.

2,4,6-Trimethyl-N-*phenylaniline*[18] was obtained from bromobenzene (3.140 g) and 2,4,6-trimethylaniline (2.704 g) as yellow oil. Yield 4.211 g (99.6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.16 (dd, 2H, *J* 7.8, 7.4 Hz), 6.74 (t, 1H, *J* 7.3 Hz), 6.51 (d, 2H, *J* 7.8 Hz), 5.17 (s, 1H), 2.32 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.6, 135.9, 135.5, 135.4, 129.2, 117.8, 113.2, 20.9, 18.2.

N-*(*o-*Tolyl)pyridin-3-amine*[23] was obtained from 3-bromopyridine (3.160 g) and *o*-toluidine (2.143 g) as yellow oil. Yield 3.504 g (95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.28 (d, 1H, *J* 2.4 Hz), 8.11 (dd, 1H, *J* 4.6, 1.4 Hz), 7.22 (d, 1H, *J* 7.5 Hz), 7.19 (m, 2H), 7.16 (t, 1H, *J* 7.6 Hz), 7.11 (dd, 1H, *J* 8.2, 4.6 Hz), 7.00 (td, 1H, *J* 7.4, 1.4 Hz), 5.77 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 141.1, 139.5, 131.2, 126.9, 123.7, 123.3, 122.7, 120.0, 17.9.

N-*(*o-*Tolyl)thiophen-3-amine* was obtained from 3-bromothiophene (3.261 g) and *o*-toluidine (2.143 g) as yellow oil. Yield 1.560 g (41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.29–7.25 (m, 1H), 7.16 (d, 1H, *J* 7.3 Hz), 7.15–7.11 (m, 2H), 6.95 (dd, 1H, *J* 5.0, 1.4 Hz), 6.87–6.82 (m, 1H), 6.68 (dd, 1H, *J* 3.0, 1.4 Hz), 5.45 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.1, 130.8, 127.1, 125.3, 123.3, 120.3, 115.1, 107.2, 17.8. Found (%): C, 69.15; H, 5.80, N, 7.33. Calc. for $C_{11}H_{11}NS$ (%): C, 69.80; H, 5.86; N, 7.40.

3-Methyl-N-*phenylpyridin-2-amine*[24] was obtained from bromobenzene (3.140 g) and 3-methylpyridin-2-amine (2.163 g) as yellow oil. Yield 0.995 g (27%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.12 (d, 1H, *J* 4.3 Hz), 7.55 (d, 2H, *J* 8.0 Hz), 7.37 (d, 1H, *J* 7.2 Hz), 7.32 (t, 2H, *J* 7.9 Hz), 7.01 (t, 1H, *J* 7.4 Hz), 6.72 (dd, 1H, *J* 7.2, 5.0 Hz), 6.18 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 154.0, 145.4, 140.8, 138.1, 129.1, 122.2, 119.7, 115.4, 77.2, 17.6.

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