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# Novel robust benzimidazolylidene palladium complexes: synthesis, structure, and catalytic applications in amination of chloroarenes

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ABSTRACT

A series of novel pyridine stabilized Pd–NHC complexes were developed, which revealed high activities and broad substrates tolerance in the amination of various (hetero)-aryl chlorides. Besides various secondary amines, a wide range of primary anilines and aliphatic amines were also well tolerated. The results highlight us a new strategy to increase catalyst activity in the future catalyst design by alternating the σ-donor property and flexibility of NHC ligands.



## 1. Introduction

During the last several decades, significant efforts have been devoted to the development of transition metal catalyzed cross-coupling reactions,[1] which implicated the fact that these reactions have been constituted as the most powerful and practical protocols to construct carbon–carbon or carbon–heteroatom bonds. Until now, versatile catalytic systems based on Pd(II) complexes have been reported,[2] in which much attention was mainly focused on developing 'universal' (robust, highly efficient, readily prepared and tolerating broad substrate scopes) catalysts for the transformation. In contrast with bulky tertiary monophosphines,[3] *N*-heterocyclic carbenes (NHCs) represent a type of air, heat and moisture stable as well as environmental friendly ligands, which also exhibit much potential in Pd-catalyzed cross-coupling reactions.[2b,4] Since the first NHC was reported,[5] the design, synthesis, and catalytic application of novel NHCs have become a very active and intriguing research field.[6,7]

Influenced by the 'flexible steric bulky' concept proposed by Glorius,[8] recently, Organ and co-workers developed a series of pyridine stabilized NHC–Pd complexes **1** (Fig. 1), which demonstrated high activity toward several C–C and C–N formation reactions, such as Suzuki–Miyaura cross-coupling reactions, aminations, and etc.[2b] By increasing steric bulky environment around Pd center, the metal–metal exchange and the reductive elimination steps did speed up, which enhanced the catalytic activity and improved yields. As the catalytic active species, Pd(0) species played the crucial role in coupling process and the stability of the Pd(0)–carbon bond is considered as another key issue to influence the catalytic efficiency. Therefore, tuning σ-donor property of NHC may offer us another optional strategy to create more robust and active Pd–NHC complexes with steady metal–carbon bonds.

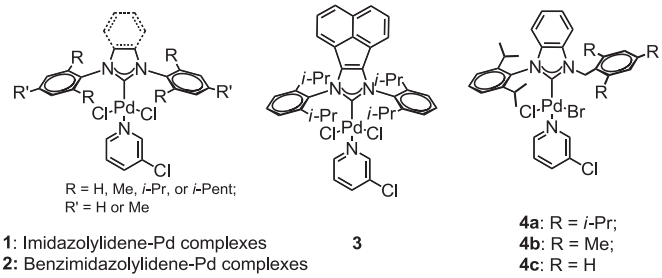


**Fig. 1.** A selection of palladium–NHC complexes.

Along with our recent research on the synthesis of metal complexes and their potential applications in catalysis and soft matter aspects,[9,10] we notified that the less intensive studied ylidenes derived from benzimidazolium salts behave differently, which may be attributed to their stronger σ-donor and weaker π-acceptor

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properties.[11] Therefore, pyridine stabilized benzimidazolylidene palladium complexes **2** were proposed to verify our hypothesis: besides the 'flexible steric bulky' environment around the catalytic center, σ-donor property of NHC ligands is another vital factor to impact on the efficiency of the catalyst.[11] Due to the steric hindrance between *i*-Pr groups and benzene ring, steric bulky NHC–Pd complex **2**, unfortunately, is hardly accessible, even after various attempts.[12] Alternatively, another two kinds of ylidenes derived from other π-extended arylimidazolium salts or unsymmetrical benzimidazolium salts with benzyl type substitutions were selected to study the influence of catalytic activity by tuning the σ-donor property of NHC ligands (Fig. 1). To our delight, the Pd–NHC complex **3** with a large π-extended acenaphthoimidazolium ring revealed extremely high catalytic activity in several cross-coupling reactions even with a catalyst loading as low as 0.075 mol %.[13] In order to further confirm the concept and gain direct insight into the relationship between σ-donor property and the steric environment around Pd center, in this article, we synthesized novel complexes **4a**–**c**, and explored their structure properties and catalytic potentials toward amination reactions.

## 2. Results and discussion

By heating with $PdCl_2$ and $K_2CO_3$ in neat 3-chloropyridine at 80 °C, robust Pd–NHC complexes **4a**–**c** were synthesized in good yields from the corresponding unsymmetrical benzimidazolium salts **5a**–**c** (Fig. 2), which were readily accessible in excellent yields by the N-alkylation of the 2,6-diisopropyl-phenyl-benzimidazole

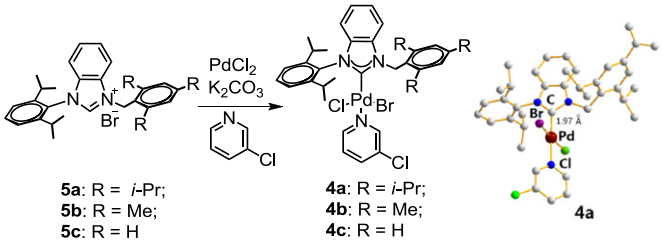
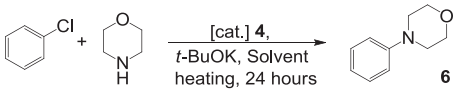



**Fig. 2.** Synthesis and structure of Pd–NHCs **4a**–**c**.

with the corresponding substituted benzyl bromides (see Supplementary data). By slow diffusion of petroleum ether into the solution of complexes **4a**–**c** in dichloromethane, yellow needle crystals were obtained, which were suitable for single crystal diffraction analysis. The molecular structure of complex **4a** was depicted in Fig. 2 (for **4b**–**c**, see Supplementary data). In contrasted with their imidazol-2-ylidene and acenaphtho-imidazol-2-ylidene analogs (**1** and **3**), the space around the Pd centers of complexes **4a**–**c** is less congested, which may be aroused by the less bulky methylene group attached to the benzimidazole ring. Whereas, the methylene linker also offered another flexible means for substrates easily approaching the Pd center, which is also a strategy to increase the activity of the catalyst. Due to the size of substituted groups (*i*-Pr, Me, and H) of the benzyl rings, the steric environment of complex **4a** is much more congested than what observed in complexes **4b** and **4c**, and which may assist the reductive elimination step and concomitant regeneration Pd(0) to accelerate cross-coupling reactions. From X-ray analysis, the bond distance of Pd–$_N$C$_N$ in the complex **4a** is 1.972(4) Å, which is longer than what we observed in the complex **3**[13] and indicate the σ-donor property of the benzene ring is worse than that of the acenaphtho-ring. To our surprise, the bond distance of Pd–$_N$C$_N$ in the complex **4b** is shortest among three complexes (**4a**–**c**), which is 1.945(5) Å and may be influenced by the appropriate steric effect of Mes group.

As a class of useful compounds, aryl amines have diverse applications in chemistry, pharmaceutical, and material science,[14] it is a very active and intriguing research field to develop 'universal' protocol to synthesize them. Although, palladium catalyzed amination reactions constitute as a powerful protocol for its high selectivity, mild conditions, and broad substrate scopes, the efficient catalyst is still rare especially for sluggish chloroarenes and especially for bulky substrates, nowadays which is still considered as a challenging task. Therefore, the amination of a variety of chloroarenes was selected to explore the catalytic activities of Pd–NHC **4a**–**c**. Initially, the amination of chlorobenzene with morpholine was picked as a model reaction to optimize the various reaction conditions (Table 1). In the presence of *t*-BuOK and 2 mol % Pd–NHC complex **4a**, the reactions proceeded well and similar

**Table 1**
Condition screening and optimization[a]



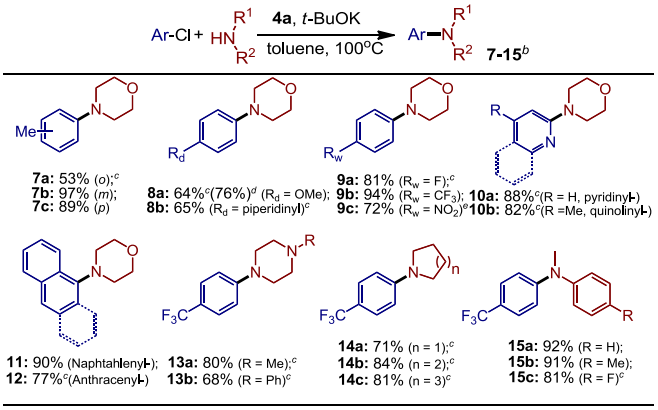

| Entry | [Cat.] | (mol %) | Solvent | *T* (°C) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | **4a** | 2 | Dioxane | 80 | 90 |
| 2 | **4a** | 2 | THF | 80 | 85 |
| 3 | **4a** | 2 | DME | 80 | 91 |
| 4 | **4a** | 2 | DME | 80 | 66[c] |
| 5 | **4a** | 2 | Toluene | 80 | 93 |
| 6 | **4a** | 1 | Toluene | 80 | 84 |
| 7 | **4a** | 1 | Toluene | 100 | 98 |
| 8 | **4b** | 1 | Toluene | 100 | 82 |
| 9 | **4c** | 1 | Toluene | 100 | 60 |
| 10 | **4a** | 0.5 | Toluene | 100 | 88 |
| 11 | **4a** | 0.1 | Toluene | 100 | 20 |
| 12 | \ | \ | Toluene | 100 | 10 |

[a] 1 mmol scale for 24 h.
[b] Isolated yield.
[c] With *t*-BuONa as a base.

isolated yields of product **6** were obtained when dioxane, DME and THF were applied (85–91%, entries 1–3, Table 1). When *t*-BuONa was used instead in DME, only a 66% yield was observed (entry 4, Table 1). Other inorganic and organic bases, such as KOH, $Cs_2CO_3$, $Et_3N$, and DBU all fell out in unsatisfied yields (<46%, see Supplementary data), which additionally confirmed that the choice of base is critical for the transformation.[2b,15] The best result (93%, entry 5, Table 1) was obtained with nonpolar solvent toluene under the identical reaction conditions with *t*-BuOK as base. Further reducing the catalyst loading to 1 mol %, only an 84% yield was presented (entry 6, Table 1). To our delight, upon increasing the reaction temperature to 100 °C, the amination reaction went along well and resulted in an excellent isolated yield (98%, entry 7, Table 1). When less bulky Pd–NHC precatalysts **4b** and **4c** were applied, slightly low yields were revealed (82% and 60%, entries 8 and 9, Table 1). Further decreasing the catalyst loading to 0.5 and 0.1 mol %, 88% and 20% isolated yields were still observed (entries 10 and 11, Table 1) and suppressed the blank test (entry 12, Table 1). In order to directly compare the catalytic activity of complex **4a** with other pioneering catalysts, the catalysts **1** and their allylic analog as well as Buchwald's bulky tertiary monophosphines were involved the model reaction, and all revealed less effective activities than complex **4a** under the optimal reaction condition (see Supplementary data).

With the optimized reaction condition in hand, the substrate scope with various amines was then explored. As shown in Table 2, the protocol well tolerates diverse electronic and steric substituents on both sides of the reacting partners, as well as for heterocyclic substrates. When morpholine was utilized as a nucleophile,

**Table 2**
Amination of chloroarenes with secondary amines[a]



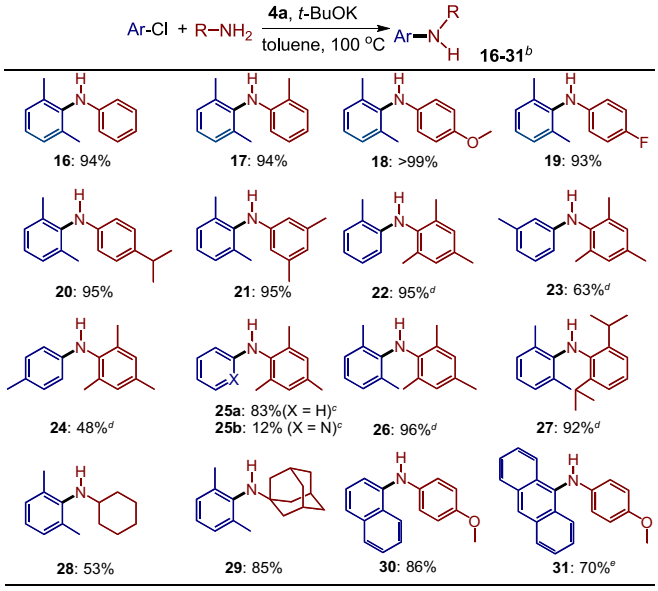

[a] 1 mol % **4a**, 1 mmol scale for 24 h.
[b] Isolated yield.
[c] With 2 mol % **4a**.
[d] With 5 mol % **4a**.
[e] $Cs_2CO_3$ with 2 mol % **4a**.

a variety of (hetero)-chloroarenes was inspected, which all resulted in good to excellent isolated yields (Table 2). The relative position of substituents impacted the coupling efficiency; *p*-chlorotoluene resulted in a slightly lower yield than its *m*-analog (**7b** vs **7c**, 97% vs 89%); but even with 2 mol % Pd–NHC complex **4a**, only a 53% yield of **7a** was observed with the *o*-isomer. In the presence of 2.0 mol % catalyst, similar moderate yields were obtained with *p*-chloroanisole and *p*-piperidylchlorobenzene (**8a** and **8b**, 64% and 65%). Further increasing the catalyst loading to 5.0 mol %, the yield was enhanced to 76%, which revealed that strong electron-donating group slightly hampered the coupling process. To our delight, electron-deficient, heterocyclic, and even bulky chloroarenes all gave out good to excellent yields (**9**–**11**, 72–94%) indicating the broad protocol applicability. With nitro group substituted chloroarene, even weak base $Cs_2CO_3$ accelerated the amination reaction of 4-chloronitro-benzene (**9c**, 72%). For sterically congested substrate like 9-chloroanthracene, the amination also operated well to produce **12** in a 77% yield.

In consideration of broad applications of fluorine containing aromatic compounds in pharmaceuticals, pesticides, and functional materials,[16] *p*-chlorotrifluoromethylbenzene was selected for the further substrate scope study. At first, *N*-methylpiperazine and *N*-phenylpiperazine were selected as nucleophiles instead of morpholine and resulted in 80% and 68% yields, respectively (**13a** and **13b**). The ring size of cyclic amines affected coupling reactions slightly; pyrrolidine, piperidine, and azepane all resulted in similar good yields (71–84%, **14a**–**c**). Besides cyclic alkylamines, several anilines with different electronic substituents were also involved, and resulted in 92%, 91%, and 81% yields, respectively (**15a**–**c**).

Due to their sluggish properties in the Pd-catalyzed amination reactions, primary amines were regarded as rather poor substrates in the previous reports, even with precatalysts like **1**.[2] Recently, we revealed that Pd–NHC complex **3** exhibited high activity toward amination of a variety of chloroarenes with primary amines.[13] Therefore, we would like to further evaluate the capability of the new catalytic system of catalyst **4a** with various primary amines (Table 3). To our delight, under optimal conditions, the amination by aniline proceeded very well and afforded compound **16** in a 94% yield. The identical yield of compound **17** was achieved with *o*-toluidine, indicating an inconspicuous stereo-electronic effect for the protocol. Good to quantitative isolated yields (83–>99%) were also observed with products **18**–**31**, which further confirmed the general capability of the catalyst **4a**. The amination by anilines with electron-donating groups are slightly more efficient than those with electron-deficient groups (95–>99% vs 93%, **18**, **20** and **21** vs **19**). Spectacularly, satirically more hindered substrates, such as 2,4,6-trimethylaniline and 2,6-diisopropyl-aniline, were also well tolerated and resulted in similar yields (48–96%, **22**–**27**) even with a catalyst loading down to 1 mol %. Furthermore, aliphatic primary amines were also involved; again bulky amine resulted in a better yield (85% vs 53%, **29** vs **28**). Other steric bulkier substrates also were exploited and good isolated yields (**30** and **31**, 86% and 70%) were obtained.

**Table 3**
Amination of chloroarenes with primary amines[a]




[a] 1 mmol scale for 24 h, 5 mol % **4a**.
[b] Isolated yield.
[c] with 2 mol % **4a**.
[d] with 1 mol % **4a**.
[e] with 9-bromoanthracene as a substrate.

## 3. Conclusion

In summary, a series of pyridine stabilized Pd–NHC catalysts **4a**–**c** were developed and complex **4a** exhibited high activity in the amination of various (hetero)-aryl chlorides. Besides various secondary amines, a wide range of primary anilines and aliphatic amines were also well tolerated. Although, in comparison with previous reported Pd–NHC catalysts, the steric environment around Pd center is less congested, by alternating the σ-donor properties of benzimidazoles and flexibility of methylene group in Pd–NHC **4a**–**c**, the catalytic activity of the catalyst is also enhanced. Further studies on the potential application of Pd–NHC complexes **4a**–**c** in other related cross-coupling reactions are under investigation in our laboratory.

## 4. Experimental section

### 4.1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Dry *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and dimethyl-sulfoxide (DMSO) were purchased from Alfa Aesar and Acros, stored over 4 Å molecular sieves and handled under $N_2$. Anhydrous methanol

(MeOH) and *tert*-butanol (*t*-BuOH) were distilled from anhydrous calcium chloride prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone prior to use. 1,2-Dimethoxy-ethane (DME), 1,4-dioxane, and toluene were distilled from calcium hydride prior to use. *t*-BuOK was purchased from Acros. $^1$H, $^{13}$C NMR were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. GC–MS spectra were recorded on a Bruker micrOTOF II instrument.

### 4.2. Synthesis of 1-(benzyl)-3-(2,6-diisopropylphenyl)-3*H*-benzimidazolium bromide salts (5a–c)

According to the literature,[17] to the solution of 1-(2,6-diisopropylphenyl)-1*H*-benzimidazole (2.43 g, 8.7 mmol) in 20 mL EtOAc, 2-(bromomethyl)-1,3,5-triisopropylbenzene (2.53 g, 8.7 mmol) was added, the resulting mixture was stirred at room temperature for 24 h, then at 60 °C for another 12 h until the reaction was completed (monitored by TLC). After cooling to the room temperature, the mixture was filtered and washed with $Et_2O$ to afford the salt **5a** as a white solid 4.28 g.

*4.2.1. (Compound **5a**).* Yield: 86%, $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=10.89 (s, 1H), 7.63 (t, $J$=10.6 Hz, 1H), 7.56–7.47 (m, 2H), 7.42 (t, $J$=10.4 Hz, 3H), 7.18 (d, $J$=10.6 Hz, 1H), 7.13 (s, 2H), 6.48 (s, 2H), 3.32 (sept, $J$=8.8 Hz, 2H), 2.94 (sept, $J$=9.4 Hz, 1H), 2.15 (sept, $J$=9.0 Hz, 2H), 1.28 (t, $J$=8.2 Hz, 12H), 1.18 (d, $J$=8.8 Hz, 12H), 1.03 (d, $J$=9.2 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=151.20, 148.83, 146.14, 141.79, 133.37, 132.20, 131.16, 127.93, 127.70, 127.05, 124.99, 122.15, 122.04, 115.48, 112.77, 47.12, 34.14, 29.91, 28.73, 24.53, 24.20, 23.86, 23.72.

*4.2.2. (Compound **5b**).* Yield: 85%, $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=11.53 (s, 1H), 7.63 (t, $J$=7.8 Hz, 1H), 7.54–7.45 (m, 2H), 7.41 (d, $J$=8.0 Hz, 2H), 7.27 (t, $J$=4.0 Hz, 1H), 7.19 (d, $J$=8.0 Hz, 1H), 6.94 (s, 2H), 6.47 (s, 2H), 2.41 (s, 6H), 2.31 (s, 3H), 2.17 (sept, $J$=6.8 Hz, 2H), 1.27 (d, $J$=6.8 Hz, 6H), 1.05 (d, $J$=6.8 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=146.07, 142.95, 142.84, 139.29, 139.60, 133.23, 132.10, 130.63, 130.02, 127.85, 127.71, 127.00, 125.35, 124.88, 114.58, 112.82, 48.43, 28.74, 24.71, 23.45, 20.83, 20.05.

*4.2.3. (Compound **5c**).* Yield: 72%. $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=11.64 (s, 1H), 7.82 (d, $J$=8.0 Hz, 1H), 7.66–7.55 (m, 5H), 7.41–7.34 (m, 5H), 7.30 (d, $J$=8.4 Hz, 1H), 6.39 (s, 2H), 2.14 (sept, $J$=6.4 Hz, 2H), 1.27 (d, $J$=6.8 Hz, 6H), 1.03 (d, $J$=6.8 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=146.05, 142.77, 133.22, 132.95, 132.01, 130.45, 129.03, 128.83, 128.20, 127.89, 127.69, 127.12, 124.80, 114.34, 112.78, 50.98, 28.66, 24.60, 23.39.

### 4.3. Synthesis of pyridine-stabilized palladium–NHC complexes (4a–c)

According to the similar literature,[12] 3-chloropyridine (10.0 mL) was added to a Schlenk tube containing $PdCl_2$ (532 mg, 3.0 mmol), **5a** (1.73 g, 3.0 mmol), $K_2CO_3$ (2.07 g, 15.0 mmol) and a stirrer bar. The reaction mixture was heated with vigorous stirring for 16 h at 80 °C. After cooling to room temperature, the reaction mixture was diluted with $CH_2Cl_2$ and passed through a short pad of silica gel covered with a pad of Celite eluting with $CH_2Cl_2$ until the product was completely recovered. Most of the $CH_2Cl_2$ was removed (rotary evaporator), and the 3-chloropyridine was then distilled (under water aspirator vacuum) and saved for reuse. Pure complex **4a** was isolated after triturating with pentane, decanting of the supernatant and drying in high vacuum to afford 2.31 g solid.

*4.3.1. (Compound **4a**).* Yield: 93%. $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=8.92 (s, 1H), 8.81 (s, 1H), 7.66 (s, 1H), 7.58 (t, $J$=7.2 Hz, 1H), 7.42 (d, $J$=3.6 Hz, 2H), 7.24–7.20 (m, 1H), 6.99–6.98 (m, 1H), 6.91–6.80 (m, 2H), 6.59–6.54 (m, 2H), 6.46–6.25 (m, 1H), 3.64–3.57 (m, 2H), 3.98–2.94 (m, 1H), 2.92–2.79 (m, 2H), 1.42 (d, $J$=3.5 Hz, 6H), 1.33–1.00 (m, 18H), 0.83 (d, $J$=4.4 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=163.45, 151.59, 151.04, 150.60, 150.32, 150.05, 149.26, 148.07, 137.77, 134.02, 132.37, 131.50, 130.72, 125.29, 124.66, 123.05, 122.21, 121.74, 112.30, 50.37, 34.30, 29.78, 28.58, 28.48, 25.90, 24.58, 24.45, 24.04.

*4.3.2. (Compound **4b**).* Yield: 63%. $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=8.88 (d, $J$=5.6 Hz, 1H), 8.77 (t, $J$=4.4 Hz, 1H), 7.69 (d, $J$=8.0 Hz, 1H), 7.59 (t, $J$=7.8 Hz, 1H), 7.42 (d, $J$=8.0 Hz, 2H), 7.24–7.21 (m, 1H), 7.08–7.03 (m, 1H), 7.00–6.92 (m, 3H), 6.86 (t, $J$=7.2 Hz, 1H), 6.61–6.51 (m, 1H), 6.46–6.43 (m, 2H), 2.90–2.74 (m, 2H), 2.40 (s, 6H), 2.35 (s, 3H), 1.41 (d, $J$=6.4 Hz, 6H), 0.87 (t, $J$=6.4 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=163.71, 151.50, 150.97, 150.49, 150.26, 149.96, 148.82, 148.03, 147.46, 138.50, 137.71, 135.79, 133.60, 132.26, 131.39, 130.70, 129.70, 127.70, 124.62, 124.30, 123.41, 122.47, 112.34, 111.55, 51.81, 28.65, 25.94, 24.44, 24.07, 21.04, 20.82.

*4.3.3. (Compound **4c**).* Yield: 73%. $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=8.88 (s, 1H), 8.87 (d, $J$=4.0 Hz, 1H), 7.67 (d, $J$=6.8 Hz, 3H), 7.61 (t, $J$=7.6 Hz, 1H), 7.43 (t, $J$=7.6 Hz, 4H), 7.36 (t, $J$=7.6 Hz, 1H), 7.23–7.12 (m, 4H), 6.92–6.88 (m, 1H), 6.45–6.43 (m, 2H), 2.93–2.76 (m, 2H), 1.42 (d, $J$=6.4 Hz, 6H), 0.90–0.88 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=164.63, 151.65, 151.11, 150.66, 150.38, 150.12, 149.39, 148.30, 137.96, 135.21, 133.51, 132.44, 131.42, 130.95, 129.11, 128.36, 128.18, 124.82, 123.72, 123.02, 112.66, 111.77, 54.65, 28.75, 26.28, 24.68, 24.23.

### 4.4. General procedure for Pd-catalyzed amination[12]

To a 50 mL Schlenk tube containing base (1.5 mmol) and pre-catalyst **4a** (1 mol %, 0.0083 g) purged with $N_2$ (three times), amine (1.2 mmol) was added via syringe, and the resulted mixture was allowed to stir at room temperature for 2–3 min. Solvent (1 mL) was then injected via syringe followed by the aryl chloride (1.0 mmol). If the aryl chloride was a solid, it was introduced into the vial prior to purging with $N_2$. At this time, the reaction was stirred for 24 h at 100 °C. After cooling to the room temperature, the reaction mixture was concentrated in vacuo and directly purified via silica gel flash chromatography.

*4.4.1. 4-Phenylmorpholine (**6**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.32–7.27 (m, 2H), 6.93 (d, $J$=8.4 Hz, 2H), 6.89 (t, $J$=7.2 Hz, 1H), 3.87 (t, $J$=4.8 Hz, 4H), 3.17 (t, $J$=4.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=151.11, 139.03, 119.86, 115.54, 66.78, 49.18; GC–MS: $t_R$=12.517 min, $m/z$=163.1 $[M]^+$, 163.1, 132.0, 77.0, 51.0.

*4.4.2. 4-(o-Tolyl)morpholine (**7a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.20 (t, $J$=7.2 Hz, 2H), 7.04 (d, $J$=7.2 Hz, 1H), 7.01 (d, $J$=7.2 Hz, 1H), 3.86 (t, $J$=4.4 Hz, 4H), 2.92 (t, $J$=4.4 Hz, 4H), 2.33 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=151.20, 132.53, 131.09, 126.59, 123.33, 118.87, 67.38, 52.17, 17.79; GC–MS: $t_R$=12.528 min, $m/z$=177.1 $[M]^+$, 177.1, 132.0, 91.1, 65.0.

*4.4.3. 4-(m-tolyl)morpholine (**7b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.22 (t, $J$=7.2 Hz, 1H), 6.79–6.77 (m, 3H), 3.89 (m, 4H), 3.18 (m, 4H), 2.38 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=151.22, 138.68, 128.87, 120.80, 116.38, 112.72, 66.81, 49.30, 21.64.

*4.4.4. 4-(p-Tolyl)morpholine (**7c**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.09 (d, $J$=8.4 Hz, 2H), 6.84 (d, $J$=8.0 Hz, 2H), 3.86 (t, $J$=4.8 Hz, 4H), 3.11 (t, $J$=4.8 Hz, 4H), 2.28 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz,

298 K): δ=149.02, 129.51, 129.22, 115.82, 66.75, 49.68, 20.25; GC–MS: $t_R$=13.381 min, *m*/*z*=177.1 $[M]^+$, 177.1, 146.1, 91.1, 65.0.

*4.4.5. 4-(4-Methoxyphenyl)morpholine (**8a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=6.90–6.84 (m, 4H), 3.85 (t, *J*=4.6 Hz, 4H), 3.77 (s, 3H), 3.05 (t, *J*=4.6 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=153.84, 145.52, 117.67, 114.37, 66.91, 55.36, 50.63.

*4.4.6. 4-(4-(Piperidin-1-yl)phenyl)morpholine (**8b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=6.94–6.86 (m, 4H), 3.85 (t, *J*=4.2 Hz, 4H), 3.06–3.02 (m, 8H), 1.72 (t, *J*=4.2 Hz, 4H), 1.58–1.52 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=146.52, 144.77, 118.02, 117.01, 66.84, 51.66, 50.33, 25.88, 24.03.

*4.4.7. 4-(4-Fluorophenyl)morpholine (**9a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=6.98 (d, *J*=8.4 Hz, 2H), 6.92 (d, *J*=8.8 Hz, 2H), 3.86 (t, *J*=4.8 Hz, 4H), 3.08 (t, *J*=4.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=158.37, 155.99, 147.83, 117.35, 115.49, 66.79, 50.19; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−124.12; GC–MS: $t_R$=11.216 min, *m*/*z*=181.0 $[M]^+$, 181.0, 109.0, 95.0, 75.0.

*4.4.8. 4-(4-(Trifluoromethyl)phenyl)morpholine (**9b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.50 (d, *J*=8.8 Hz, 2H), 6.92 (d, *J*=8.8 Hz, 2H), 3.86 (t, *J*=4.8 Hz, 4H), 3.23 (t, *J*=4.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=153.29, 126.31, 126.00, 123.31, 120.89, 120.57, 114.16, 66.49, 47.97; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−61.28; GC–MS: $t_R$=16.757 min, *m*/*z*=231.1 $[M]^+$, 231.1, 173.1, 145.0.

*4.4.9. 4-(4-Nitrophenyl)morpholine (**9c**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=8.14 (d, *J*=9.6 Hz, 2H), 6.83 (d, *J*=9.6 Hz, 2H), 3.86 (t, *J*=4.8 Hz, 4H), 3.37 (t, *J*=4.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=154.87, 138.69, 125.74, 112.47, 66.21, 46.92; GC–MS: $t_R$=17.403 min, *m*/*z*=208.1 $[M]^+$, 207.9, 149.9, 119.9, 77.0, 51.0.

*4.4.10. 4-(Pyridin-2-yl)morpholine (**10a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=8.19 (d, *J*=4.0 Hz, 1H), 7.49 (t, *J*=8.8 Hz, 1H), 7.01 (t, *J*=7.2 Hz, 2H), 3.82 (t, *J*=4.8 Hz, 4H), 3.49 (t, *J*=4.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=159.39, 147.73, 137.35, 113.63, 106.78, 66.54, 45.40; GC–MS: $t_R$=12.728 min, *m*/*z*=164.0 $[M]^+$, 164.0, 133.0, 119.0, 107.0, 51.0.

*4.4.11. 4-(4-methylquinolin-2-yl)morpholine (**10b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.73–7.68 (m, 2H), 7.50 (dt, *J*=1.6 Hz, *J*=8.4 Hz, 1H), 7.20 (dt, *J*=1.2 Hz, *J*=8.2 Hz, 1H), 6.68 (s, 1H), 3.75 (t, *J*=4.8 Hz, 4H), 3.60 (t, *J*=4.8 Hz, 4H), 2.50 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=157.00, 147.37, 144.83, 128.98, 126.90, 123.31, 123.18, 122.06, 109.26, 66.52, 45.16, 18.87.

*4.4.12. 4-(Naphthalen-1-yl)morpholine (**11**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=8.35–8.28 (m, 1H), 7.92–7.85 (m, 1H), 7.65–7.43 (m, 4H), 7.12 (d, *J*=7.2 Hz, 1H), 4.02 (t, *J*=4.8 Hz, 4H), 3.14 (t, *J*=4.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=149.19, 134.58, 128.56, 128.26, 125.64, 125.21, 123.53, 123.19, 114.46, 114.37, 67.17, 53.22.

*4.4.13. 4-(Anthracen-9-yl)morpholine (**12**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=8.56 (d, *J*=8.8 Hz, 2H), 8.34 (s, 1H), 8.03 (d, *J*=8.0 Hz, 2H), 7.53–7.46 (m, 4H), 4.06 (t, *J*=4.2 Hz, 4H), 3.54 (t, *J*=4.2 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=143.37, 132.49, 130.44, 128.95, 125.30, 125.23, 125.06, 124.48, 68.41, 51.60; GC–MS: $t_R$=19.658 min, *m*/*z*=263.1 $[M]^+$, 263.0, 204.0, 176.0, 88.0.

*4.4.14. 1-Methyl-4-(4-(trifluoromethyl)phenyl)piperazine (**13a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.47 (d, *J*=8.4 Hz, 2H), 6.92 (d, *J*=8.4 Hz, 2H), 3.29 (t, *J*=4.4 Hz, 4H), 2.56 (t, *J*=4.4 Hz, 4H), 2.35 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=153.20, 126.28, 123.36, 120.45, 120.12, 114.39, 54.71, 47.80, 46.01; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−61.18; GC–MS: $t_R$=17.769 min, *m*/*z*=244.1 $[M]^+$, 244.0, 173.0, 145.0, 71.0.

*4.4.15. 1-Phenyl-4-(4-(trifluoromethyl)phenyl)piperazine (**13b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.56 (d, *J*=8.0 Hz, 2H), 7.36 (t, *J*=7.0 Hz, 2H), 7.04–6.95 (m, 5H), 3.46 (t, *J*=3.2 Hz, 4H), 3.38 (t, *J*=2.8 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=153.16, 150.99, 129.21, 126.40, 123.37, 120.85, 120.53, 120.25, 116.35, 114.68, 49.11, 48.07; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−61.12; GC–MS: $t_R$=27.955 min, *m*/*z*=306.1 $[M]^+$, 305.9, 172.9, 90.9, 76.9.

*4.4.16. 1-(4-(Trifluoromethyl)phenyl)pyrrolidine (**14a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.43 (d, *J*=8.8 Hz, 2H), 6.54 (d, *J*=8.8 Hz, 2H), 3.32 (t, *J*=6.6 Hz, 4H), 2.03 (q, *J*=3.2 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=149.74, 126.35, 124.04, 116.68, 116.35, 110.80, 47.45, 25.39; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−60.42; GC–MS: $t_R$=16.202 min, *m*/*z*=215.1 $[M]^+$, 214.0, 158.9, 144.9.

*4.4.17. 1-(4-(Trifluoromethyl)phenyl)piperidine (**14b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.46 (d, *J*=8.4 Hz, 2H), 6.92 (d, *J*=8.4 Hz, 2H), 3.27 (t, *J*=4.8 Hz, 4H), 1.69–1.63 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=153.79, 126.28, 123.56, 119.60, 119.28, 114.52, 49.23, 25.38, 24.23; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−61.06; GC–MS: $t_R$=16.379 min, *m*/*z*=229.1 $[M]^+$, 228.1, 210.1, 188.0, 172.0, 145.0.

*4.4.18. 1-(4-(Trifluoromethyl)phenyl)azepane (**14c**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.41 (d, *J*=8.8 Hz, 2H), 6.68 (d, *J*=8.8 Hz, 2H), 3.48 (t, *J*=5.8 Hz, 4H), 1.80–1.78 (m, 4H), 1.56–1.53 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=150.93, 126.51, 123.96, 116.56, 116.25, 110.29, 49.15, 27.29, 26.87; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−60.51; GC–MS: $t_R$=19.280 min, *m*/*z*=243.1 $[M]^+$, 243.1, 214.1, 172.0, 159.0, 145.0.

*4.4.19. N-Methyl-N-phenyl-4-(trifluoromethyl)aniline (**15a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.46–7.39 (m, 4H), 7.23–7.19 (m, 3H), 6.87 (d, *J*=8.8 Hz, 2H), 3.37 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=151.48, 147.70, 129.77, 126.18, 125.28, 124.94, 123.55, 119.98, 119.66, 114.75, 40.09; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−60.99; GC–MS: $t_R$=18.868 min, *m*/*z*=250.1 $[M]^+$, 251.2, 167.1, 145.0, 77.0.

*4.4.20. N,4-Dimethyl-N-(4-(trifluoromethyl)phenyl)aniline (**15b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.43 (d, *J*=8.8 Hz, 2H), 7.23 (d, *J*=8.0 Hz), 7.12 (d, *J*=8.4 Hz, 2H), 6.80 (d, *J*=8.8Hz, 2H), 3.34 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=151.66, 145.10, 135.17, 130.45, 126.10, 125.89, 123.64, 119.12, 113.78, 40.16, 20.91; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−60.91; GC–MS: $t_R$=20.453 min, *m*/*z*=265.1 $[M]^+$, 265.1, 145.0, 91.1.

*4.4.21. 4-Fluoro-N-methyl-N-(4-(trifluoromethyl)-phenyl)-aniline (**15c**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.41 (d, *J*=8.8 Hz, 2H), 7.18–7.15 (m, 2H), 7.12–7.08 (m, 2H), 6.75 (d, *J*=8.8 Hz, 2H), 3.31 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=161.50, 159.06, 151.59, 143.73, 127.87, 126.25, 126.15, 123.58, 119.68, 119.36, 116.62, 113.85, 113.78, 40.23; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): δ=−60.99, −116.34; GC–MS: $t_R$=18.879 min, *m*/*z*=269.1 $[M]^+$, 269.1, 185.1, 145.0, 95.0.

*4.4.22. 2,6-Dimethyl-N-phenylaniline (**16**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.14–7.07 (m, 5H), 6.71 (t, *J*=6.8 Hz, 1H), 6.47 (d, *J*=7.6 Hz, 2H), 5.09 (br s, 1H), 2.18 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=146.19, 138.14, 135.84, 129.16, 128.47, 125.68, 118.08, 113.41, 18.28.

*4.4.23. 2,6-Dimethyl-N-(o-tolyl)aniline (**17**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=7.28–7.22 (m, 4H), 7.15–7.05 (m, 1H), 6.88–6.80 (m, 1H), 6.33–6.25 (m, 1H), 5.04 (br s, 1H), 2.46 (s, 3H), 2.33 (s, 6H);

$^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=114.05, 138.67, 135.46, 130.18, 128.48, 126.86, 125.48, 122.32, 118.03, 111.64, 18.16, 17.58.

*4.4.24. N-(4-Methoxyphenyl)-2,6-dimethylaniline (**18**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.13–7.03 (m, 3H), 6.77 (d, $J$=8.8 Hz, 2H), 6.51 (d, $J$=8.8 Hz, 2H), 5.03 (br s, 1H), 3.76 (s, 3H), 2.21 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=152.66, 140.06, 139.20, 134.83, 128.53, 124.97, 115.20, 114.65, 55.61, 18.31.

*4.4.25. N-(4-Fluorophenyl)-2,6-dimethylaniline (**19**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.10–7.03 (m, 3H), 6.83 (t, $J$=7.8 Hz, 2H), 6.41 (t, $J$=4.1 Hz, 2H), 5.05 (br s, 1H), 2.17 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=157.38, 155.04, 142.45, 138.51, 135.45, 128.61, 125.61, 115.60, 114.43, 18.23; $^{19}$F NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=−126.83.

*4.4.26. N-(4-Isopropylphenyl)-2,6-dimethylaniline (**20**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.08–6.98 (m, 5H), 6.42 (d, $J$=7.2 Hz, 2H), 5.03 (br s, 1H), 2.78 (m, 1H), 2.18 (s, 6H), 1.19 (d, $J$=6.8 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=143.99, 138.70, 138.61, 135.40, 128.45, 126.95, 125.29, 113.66, 33.08, 24.16, 18.37.

*4.4.27. N-(3,5-Dimethylphenyl)-2,6-dimethylaniline (**21**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.12–7.03 (m, 3H), 6.39 (s, 1H), 6.12 (s, 2H), 5.03 (br s, 1H), 2.21–2.15 (m, 12H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=146.16, 138.80, 138.37, 135.76, 128.42, 125.48, 120.18, 111.34, 21.40, 18.36.

*4.4.28. 2,4,6-Trimethyl-N-(o-tolyl)aniline (**22**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.13 (d, $J$=7.2 Hz, 1H), 6.99–6.96 (m, 3H), 6.69 (t, $J$=7.4 Hz, 1H), 6.15 (d, $J$=8.0 Hz, 1H), 4.87 (br s, 1H), 2.33–2.32 (m, 6H), 2.16 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=144.02, 135.93, 135.53, 135.05, 130.12, 129.15, 126.88, 121.94, 117.67, 111.29, 20.84, 18.02, 17.52; GC–MS: $t_R$=22.130 min, $m/z$=225.2 $[M]^+$, 225.2, 208.1, 194.1, 121.1.

*4.4.29. 2,4,6-Trimethyl-N-(m-tolyl)aniline (**23**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.16 (t, $J$=7.6 Hz, 1H), 7.08 (s, 2H), 6.69 (d, $J$=7.6 Hz, 1H), 6.46–6.41 (m, 2H), 5.14 (br s, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 2.32 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=146.56, 138.91, 135.85, 135.56, 135.17, 129.11, 129.01, 118.76, 113.86, 110.32, 21.51, 20.85, 18.19.

*4.4.30. 2,4,6-Trimethyl-N-(p-tolyl)aniline (**24**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.10–7.07 (m, 4H), 6.55 (d, $J$=8.0 Hz, 2H), 5.11 (br s, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.31 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=144.20, 135.89, 135.57, 134.95, 129.66, 129.12, 126.96, 113.35, 20.83, 20.37, 18.16.

*4.4.31. 2,4,6-Trimethyl-N-phenylaniline (**25a**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.13 (t, $J$=7.6 Hz, 2H), 6.93 (s, 2H), 6.71 (t, $J$=7.0 Hz, 1H), 6.47 (d, $J$=7.6 Hz, 2H), 5.06 (br s, 1H), 2.29 (s, 3H), 2.16 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=146.60, 135.92, 135.48, 135.34, 129.17, 117.82, 113.20, 20.88, 18.20.

*4.4.32. N-mesitylpyridin-2-amine (**25b**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K):δ=8.12 (dd, $J$=0.8 Hz, $J$=4.8 Hz, 1H), 7.34 (dt, $J$=1.6 Hz, $J$=7.2 Hz, 1H), 6.95 (s, 2H), 6.62–6.59 (m, 1H), 6.25 (br s, 1H), 6.00 (d, $J$=8.4 Hz, 1H), 2.31 (s, 3H), 2.19 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=158.02, 148.36, 137.75, 136.55, 136.35, 133.73, 129.28, 113.36, 105.55, 20.90, 18.22.

*4.4.33. N-(2,6-Dimethylphenyl)-2,4,6-trimethylaniline (**26**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=6.97 (d, $J$=7.6 Hz, 2H), 6.81–6.78 (m, 3H), 4.71 (br s, 1H), 2.25 (s, 3H), 1.99–1.95 (m, 12H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=142.14, 138.94, 131.43, 130.40, 129.17, 128.74, 128.34, 120.91, 20.55, 19.06, 18.96; GC–MS: $t_R$=16.270 min, $m/z$=239.1 $[M]^+$, 239.1, 222.1, 208.1, 132.0, 120.0.

*4.4.34. N-(2,6-Diisopropylphenyl)-2,6-dimethylaniline (**27**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.18–7.11 (m, 3H), 6.95 (d, $J$=7.6 Hz, 2H), 6.74 (t, $J$=7.4 Hz, 1H), 4.81 (br s, 1H), 3.20–3.13 (m, 2H), 1.99 (s, 6H), 1.13 (d, $J$=6.8 Hz, 12H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=144.07, 143.08, 138.74, 129.48, 125.57, 124.81, 123.20, 119.59, 28.00, 23.44, 19.31; GC–MS: $t_R$=16.556 min, $m/z$=281.2 $[M]^+$, 281.3, 236.2, 208.1, 196.1.

*4.4.35. N-Cyclohexyl-2,6-dimethylaniline (**28**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.02 (d, $J$=7.6 Hz, 2H), 6.83 (t, $J$=7.6 Hz, 1H), 3.04–2.97 (m, 1H), 2.92 (br s, 1H), 2.31 (s, 6H), 2.05–1.98 (m, 2H), 1.81–1.76 (m, 2H), 1.69–1.64 (m, 1H), 1.35–1.11 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=145.08, 128.92, 128.67, 121.03, 56.13, 34.94, 25.94, 25.54, 18.98.

*4.4.36. N-(2,6-dimethylphenyl)adamantan-1-amine (**29**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.10–7.04 (m, 2H), 6.98–6.92 (m, 1H), 2.70 (br s, 1H), 2.42 (s, 6H), 2.15–2.05 (m, 3H), 1.86–1.80 (m, 6H), 1.70–1.62 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=142.95, 134.61, 128.24, 122.86, 55.41, 44.27, 36.33, 30.01, 20.57.

*4.4.37. N-(4-Methoxyphenyl)naphthalen-1-amine (**30**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta$=7.96 (d, $J$=8.0 Hz, 1H), 7.82 (d, $J$=5.2 Hz, 1H), 7.47–7.41 (m, 3H), 7.30 (t, $J$=8.0 Hz, 1H), 7.08 (d, $J$=7.6 Hz, 1H), 7.02 (d, $J$=8.8 Hz, 2H), 6.85 (d, $J$=8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta$=155.01, 140.84, 136.83, 134.56, 128.53, 126.12, 125.95, 125.28, 121.78, 121.03, 120.84, 114.71, 111.64, 55.54.

*4.4.38. N-(4-methoxyphenyl)anthracen-9-amine (**31**).* $^1$H NMR ($CDCl_3$, 400 MHz, 298 K): δ=8.34 (s, 1H), 8.18 (d, $J$=8.4 Hz, 2H), 8.04 (d, $J$=8.4 Hz, 2H), 7.49–7.41 (m, 4H), 6.73 (d, $J$=8.8 Hz, 2H), 6.56 (d, $J$ =8.8Hz, 2H), 5.92 (br s, 1H), 3.72 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, 298 K): δ=152.80, 141.98, 132.26, 128.75, 128.60, 125.69, 125.39, 124.65, 123.76, 115.32, 114.79, 55.66.

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## Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.11.003.

## References and notes

1. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004.
2. (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461; (b) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 3314; (c) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151.
3. Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27.
4. Díez-González, S.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.
5. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
6. For selected examples, see: (a) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. *Chem. Rev.* **2011**, *111*, 2705; (b) Nair, V.; Menon, R. S.; Biju, A. T.; Sinu, C. R.; Paul, R. R.; Josea, A.; Sreekumar, V. *Chem. Soc. Rev.* **2011**, *40*, 5336; (c) Bierenstiel, M.; Cross, E. D. *Coord. Chem. Rev.* **2011**, *255*, 574; (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
7. (a) Wu, L.; Falivene, L.; Drinkel, E.; Grant, S.; Linden, A.; Cavallo, L.; Dorta, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2870; (b) Wu, L.; Drinkel, E.; Gaggia, F.; Capolicchio, S.; Linden, A.; Falivene, L.; Cavallo, L.; Dorta, R. *Chem.—Eur. J.* **2011**, *17*, 12886.
8. Wurtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523.

9. (a) Tu, T.; Fang, W.; Bao, X.; Li, X.; Dötz, K. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 6601; (b) Tu, T.; Bao, X.; Assenmacher, W.; Peterlik, H.; Daniels, J.; Dötz, K. H. *Chem.—Eur. J.* **2009**, *15*, 1853; (c) Tu, T.; Assenmacher, W.; Peterlik, H.; Schnakenburg, G.; Dötz, K. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 7127; (d) Tu, T.; Assenmacher, W.; Peterlik, H.; Weisbarth, R.; Nieger, M.; Dötz, K. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 6368.
10. (a) Wang, Z.; Feng, X.; Fang, W.; Tu, T. *Synlett* **2011**, 951; (b) Tu, T.; Feng, X.; Wang, Z.; Liu, X. *Dalton Trans.* **2010**, 10598; (c) Tu, T.; Mao, H.; Herbert, C.; Xu, M.; Dötz, K. H. *Chem. Commun.* **2010**, 7796; (d) Tu, T.; Malineni, J.; Bao, X.; Dötz, K. H. *Adv. Synth. Catal.* **2009**, *351*, 1029; (e) Tu, T.; Malineni, J.; Dötz, K. H. *Adv. Synth. Catal.* **2008**, *350*, 1791.
11. (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122; (b) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988; (c) Kühl, O. *Chem. Soc. Rev.* **2007**, *36*, 592; (d) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348; (e) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 541; (f) Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem.—Eur. J.* **1999**, *5*, 1931.
12. During this paper in the hand of referees, an unexpected synthesis of benzimidazolium salts (the precursor of complex **2**, R=Me, R′=Me) through dihydrophenazines en route was reported, more detail see: *Adv. Synth. Catal.* **2012**, *354*, 1356.
13. Tu, T.; Fang, W.; Jiang, J. *Chem. Commun.* **2011**, 12358.
14. (a) Suwanprasop, S.; Nhujak, T.; Roengsumran, S.; Petsom, A. *Ind. Eng. Chem. Res.* **2004**, *43*, 4973; (b) *Amines: Synthesis, Properties and Application*; Lawrence, S. A., Ed.; Cambridge University: Cambridge, 2004; (c) *Industrial Organic Chemistry*; Weissermel, K., Arpe, H.-J., Eds.; Wiley-VCH: Weinheim, Germany, 1997.
15. Schlummer, B.; Scholz, U. *Adv. Synth. Catal.* **2004**, *346*, 1599.
16. (a) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320; (b) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119 and references therein.
17. Hirano, K.; Biju, A. T.; Glorius, F. *J. Org. Chem.* **2009**, *74*, 9570.