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Efficient catalytic aryl amination of bromoarenes using 3-iminophosphine palladium(II) chloride

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ABSTRACT

While pursuing the development of new hydroamination catalysts, a 3-iminophosphine palladium(II) chloride complex [**(3IP)PdCl$_2$**] was synthesized that has subsequently proven to be an effective pre-catalyst for the aryl amination of bromoarenes. This **(3IP)PdCl$_2$** complex has been utilized in the catalytic aryl amination of both bromobenzene and bromopyridine derivatives, specifically yielding excellent activity in coupling reactions involving bromobenzene, 4-bromotoluene, and 2-bromopyridine. Using a standard set of catalytic conditions, many alkyl and aryl amines have been investigated as coupling partners in the aryl amination of bromoarenes. In general, secondary alkyl amines and *ortho*-substituted anilines proved to be the best substrates for this reaction, commonly giving quantitative conversion to products, while primary amines and other anilines gave only poor to moderate results. Catalytic screening data, product yields, and full characterization of isolated products are included.

1. Introduction

Throughout the past few decades, transition metal catalysis, especially organometallic catalysis, has proven useful in the construction of molecules with a wide range of applications, including specialized materials, pharmaceuticals, and natural-products syntheses [1–3]. The significance of the advances in this field have been broadly recognized, as evidenced by the recent Nobel prizes awarded in carbon–carbon bond formation via metathesis catalysis [4–6] and palladium coupling chemistry [7–9]. Continued investigation in modern catalysis commonly focuses on the formation of carbon–nitrogen bonds, as these moieties are crucial to the function of many biologically relevant compounds. Catalytic hydroamination [10–14] and aryl amination reactions [15–18] represent atom-efficient, low cost methods for the production of new C–N bonds, and as a result the development of new catalysts for each of these reactions remains at the forefront of modern organometallic research.

Catalytic aryl amination reactions (often referred to as Buchwald–Hartwig coupling when palladium is employed) were first developed over a decade ago [19–22]. Aryl amination catalysis is a useful method for conversion of an aryl halide or pseudohalide into an aryl amine with loss of one equivalent of the corresponding acid. This reaction has been studied in great detail by numerous research groups with many studies targeting the use of palladium complexes in this chemistry [23–33]. Palladium is often favored for this chemistry because its complexes have displayed good tolerance to a wide range of substrate functional groups, while also having useful catalytic activity for many complementary cross-coupling reactions [34]. This leads to the obvious hope that aryl amination catalysis can be utilized in tandem with other cross-coupling reactions in order to effectively carry out multiple catalytic transformations in one pot with a single catalyst, thus converting simple substrates to more complicated organic molecules with reduced waste and lower energy consumption.

Over the past several years, research in the Schmidt group has focused on the development of a new class of palladium complexes supported by 3-iminophosphine (3IP) ligands [35–39]. In general, these ligands have demonstrated a preferred binding mode in which the strongly donating phosphine and the much weaker imine nitrogen donor atom are chelated to a single metal center. To date, most of the studies have targeted complexes of the form **[(3IP)Pd(allyl)][OTf]** (Fig. 1A) since these species have proven to be very effective catalysts for the hydroamination of alkynes [38], 1,3-dienes [37,38], and allenes [36,37]. In addition to catalytic experiments, stoichiometric reactions have shown that the weakly bound imine nitrogen donor atom in the chloride complex, **(3IP)PdCl$_2$** (Fig. 1B), is readily displaced from the metal center, even by simple ligands such as amines [39], leading us to conclude that 3IP ligands could serve as useful hemilabile ligands in late-transition metal

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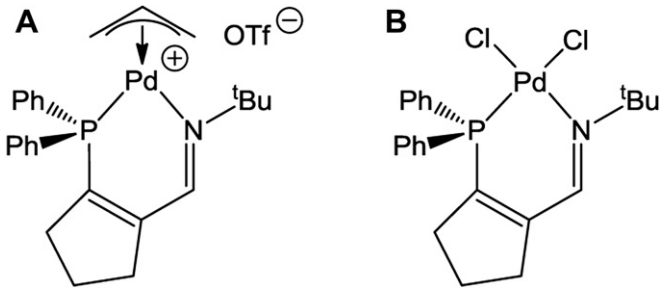


Fig. 1. Palladium catalysts based on the 3-iminophosphine ligand.

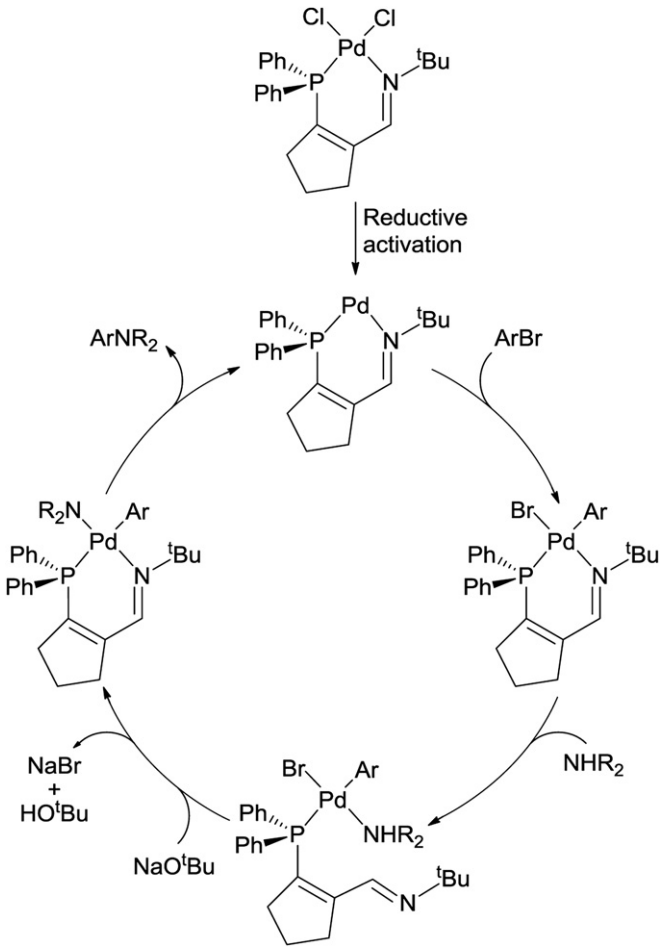
chemistry. Though totally unreactive in hydroamination chemistry, we speculated that 3-iminophosphine palladium(II) halide complexes might prove to be effective in aryl amination catalysis where amine binding occurs prior to deprotonation under catalytic reaction conditions. Thus, herein we describe our successful application of the **(3IP)PdCl$_2$** catalyst system in the aryl amination of bromoarenes, including bromobenzene, 4-bromotoluene, and 4-bromoanisole, as well as 2- and 3-bromopyridine.

2. Results and discussion

2.1. General considerations

Due to the broad investigation of catalytic aryl amination over the past decade, a consensus mechanism for this reaction has emerged [18]. The mechanism typically begins with a Pd(0) or Pd(II) precatalyst that enters the catalytic cycle via ligand dissociation or a reductive process, respectively. This activation step generates a coordinatively unsaturated Pd(0) complex in situ, usually ligated by a bulky phosphine or *N*-heterocyclic carbene ligand. The aryl halide substrate then undergoes oxidative addition, followed by coordination of the amine reactant. This coordinated amine is subsequently deprotonated by an external base, often NaO^{t}Bu, which is added to the reaction in stoichiometric or greater amounts. The resulting transient highly reactive (aryl)Pd(II) amido complex then rapidly undergoes reductive elimination, producing the product aryl amine while regenerating the putative Pd(0) complex to complete the catalytic cycle. The overall balanced reaction for aryl amination is given in Equation (1). Based on the known hemilability of the 3IP ligands [39], a proposed catalytic cycle employing them is shown in Scheme 1 and serves as the basis for the catalytic aryl amination experiments described herein. As with many other aryl amination catalysts, the Pd(II) precursor undergoes a reductive activation process in situ prior to entering the catalytic cycle. We note that the hemilabile nitrogen atom of the weakly chelating 3IP ligand is likely to help prevent decomposition of the highly reactive catalytic intermediates, but can be readily displaced by the reactant amine [39], allowing for productive catalysis. Although many of the different members of the 3IP ligand family are likely to be effective for aryl amination catalysis, this report focuses only on the originally published version of the 3IP ligand (Fig. 1B) because our previously reported stoichiometric experiments were also limited to this ligand derivative. Our main goal in the current contribution has been to investigate the utility of the 3IP ligand set in catalytic aryl amination and to determine the effective substrate scope amenable to this catalysis.

$$\underset{\text{Aryl Halide}}{\text{Ar}-\text{X}} + \underset{\text{Amine}}{\text{HNRR}'} \xrightarrow[\substack{110\ ^\circ\text{C}\\ \text{Toluene}\\ \text{NaO}^t\text{Bu}\\ -\text{HO}^t\text{Bu}\\ -\text{NaX}}]{\text{Cat.(1 mol\%)}} \text{Ar}-\text{NR}R' \qquad (1)$$

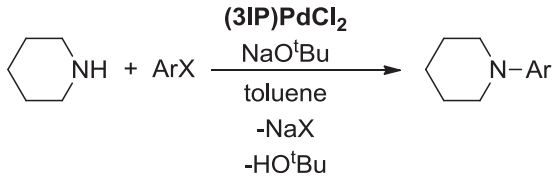


Scheme 1. Proposed catalytic cycle for aryl amination mediated by 3-iminophosphine palladium complexes.

Our first attempt at aryl amination involved the reaction of bromobenzene with piperidine, catalyzed by **(3IP)PdCl$_2$** (1 mol%). This reaction proceeded steadily at 110 °C reaching completion in less than 4 h (see supporting information; Table S1). After screening several additional amines, it was found that for the less reactive substrates, significant product formation was still occurring after 4 h. Ultimately, a reaction time of 22 h proved ideal for the reaction since after this period, reaction rates dropped off dramatically even for those substrates that had not reached quantitative conversion (see supporting information; Table S2). This is probably due to slow catalyst decomposition under the reaction conditions, especially given the elevated temperature necessary for these reactions. Thus, for the complete substrate investigation reported in this manuscript, standardized experimental conditions were chosen to be catalyst loading (1 mol%), aryl halide (1.0 mmol), amine (1.2 mmol), toluene (2 mL), NaO^{t}Bu (1.4 mmol), temperature (110 °C), and time (22 h), unless otherwise noted.

In order to undertake a thorough investigation of aryl amination substrate scope utilizing the **(3IP)PdCl$_2$** complex, it was first necessary to choose appropriate aryl halides for this reaction. To accomplish this, piperidine was reacted with a variety of aryl halides under the standard catalytic conditions (Table 1). Of the eight substrates tested, five of them proved to be quite amenable to this catalysis: bromobenzene, iodobenzene, 4-bromotoluene, 2-bromopyridine, and 3-bromopyridine. Chlorobenzene did not proceed efficiently, which is likely caused by the more difficult oxidative addition step due to the stronger bond strength of the C–

Table 1
Investigation of aryl halide scope.[a]



Entry	Aryl halide	Conversion[b] (%)
1	C_6H_5Cl	40
2	C_6H_5I	99
3	C_6H_5Br	99
4	*p*-MeC_6H_4Br	99
5	*p*-$MeOC_6H_4Br$	38
6	3-Bromopyridine	99
7	2-Bromopyridine	99
8	1-Bromonaphthalene	49

[a] Conditions: aryl halide (1.0 mmol); piperidine (1.2 mmol); NaO^tBu (1.4 mmol); **(3IP)PdCl$_2$** (1 mol%); toluene (2 mL); 110 °C; 22 h; Teflon-sealed 8-mL vial.
[b] Conversion determined by gas chromatography.

Cl bond. Less effective catalysis was also observed with 4-bromoanisole and 1-bromonaphthalene. The electron donating methoxy group in 4-bromoanisole (due to its mesomeric effect) seems to impede catalysis significantly, most likely due to its more difficult oxidative addition. Additionally, the low solubility of 1-bromonaphthalene made it a poor substrate. Given these results, we decided to proceed with a full substrate study using five haloarene derivatives, specifically bromobenzene, 4-bromotoluene, 4-bromoanisole, 2-bromopyridine, and 3-bromopyridine. The 4-bromoanisole was chosen despite its poor reactivity in order to provide a useful contrast to the other two phenyl-based species. Additionally, the pyridines were chosen due to the effectiveness observed in this simple screening experiment.

In order to thoroughly investigate **(3IP)PdCl$_2$** in catalytic aryl amination, a set of thirty-five amines was first dried and transferred to the glove box. All catalytic aryl amination experiments were set up under anhydrous and anaerobic conditions and were run in Teflon-sealed vials. Product distribution and conversions were determined via gas chromatography. Given the large number of different products investigated, calibration curves were not utilized in the GC analysis, meaning that for those reactions giving moderate yields, the reported conversion should be viewed as an approximation of the actual value. Reaction products were then isolated using column chromatography and their identities further confirmed by NMR spectroscopy and high-resolution mass spectrometry. For discussion herein, the array of available amines has been separated into two portions: alkyl amines (both primary and secondary) and aniline derivatives. Due to differences in reactivity, the results have been further separated into two groups of bromoarenes: phenyl and pyridyl derivatives. Thus, the catalytic results can be readily discussed in four groups, as given in Tables 2–5. Finally, the results presented herein represent primarily those amines that exhibited moderate to excellent yield in these reactions. Complete details of additional reactions tested with this catalyst can be found in the supporting information file.

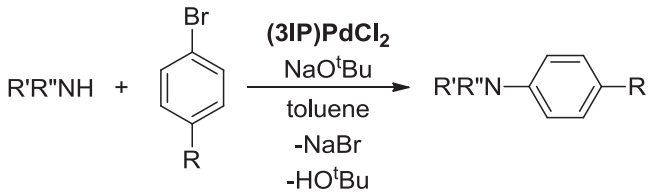
2.2. Aryl amination of bromophenyl derivatives

Three bromophenyl derivatives were used in catalytic aryl amination reactions with a wide range of primary and secondary alkyl amines (Table 2). Several primary amines underwent catalytic aryl amination with good to excellent yields (Table 2, entries 1–4), although generally speaking, the secondary amines proved to be better substrates (Table 2, entries 5–15). In fact, many of the cyclic secondary amines gave virtually quantitative yield under the standard reaction conditions (Table 2, entries 10–15). Even tetrahydroquinoline and tetrahydroisoquinoline proved to be very effective substrates for aryl amination of bromobenzene and 4-bromotoluene (Table 2, entries 14–15). Some of the more volatile amines gave reduced catalytic conversion, which we attribute to their vaporization under the reaction conditions, causing them to reside primarily in the headspace during catalysis and hindering their reactivity significantly. Similar to the initial screening experiments, bromobenzene and 4-bromotoluene were much more reactive than 4-bromoanisole. Small amounts of demethoxylation products were observed in the coupling reactions involving 4-bromoanisole, which seemed to be coupled to catalyst decomposition. This side reaction may explain the poor catalytic results using 4-bromoanisole throughout this report. Overall, catalytic aryl amination proved to be quite effective for bromobenzene and 4-bromotoluene with good to excellent conversion for most substrates tested. For those amines that provided poor yields (see supporting information; Table S3) two main features were present: large steric bulk or readily available side reactions. For example, diisopropylamine gave poor yield due to its size, while *N*-methylaniline and indoline derivatives reacted poorly due to competing C–H bond reactivity at their β-carbon positions. These side reactions included β-hydride elimination, deprotonation and coupling of the β-carbon atoms, and dehydrogenation chemistry (in the case of indoline derivatives). Thiomorpholine was also a poor substrate, an effect that can be attributed to irreversible deactivation of the catalyst upon binding of the sulfur to the palladium center.

In continued screening experiments, a wide scope of anilines was investigated in the aryl amination of the three bromobenzene derivatives. Although representative anilines with *ortho*, *meta*, and *para* substituents were each tested (see supporting information; Table S4), it was readily apparent that only those with *ortho* substituents were particularly effective in catalytic aryl amination (Table 3). Unsubstituted aniline ($PhNH_2$) was completely unreactive in most cases, while *meta*-and *para*-substituted anilines provided poor yields (<25%) in all cases. In contrast, *ortho*-substituted anilines proved to be good to excellent substrates for the aryl amination of bromobenzene and 4-bromotoluene and even worked in limited instances with 4-bromoanisole (Table 3). Unlike the reactions with alkyl amines, 4-bromoanisole showed no evidence of demethoxylation during screening with anilines, making some aryl amination reactions with this difficult substrate possible. Based on the results in Table 3, it is clear that substrates with alkyl groups in both *ortho* positions were more effective than their mono-substituted analogs. Furthermore, the larger alkyl groups gave better yields than smaller ones in every case. These reactivity trends are especially evident in the catalytic results using 4-bromoanisole. Overall, the aryl amination reactions involving anilines show that higher yields are obtained as aniline steric bulk increases. This is consistent with a rate-limiting reductive elimination step, although we cannot rule out the possibility of catalyst decomposition in the reactions involving *meta*- or *para*-substituted anilines. For those reactions involving anilines of similar steric bulk, differences in product yields correlated well to the trends in electronic parameters previously established by Hartwig [40].

Overall, the **(3IP)PdCl$_2$** catalytic system worked very well in the aryl amination of bromobenzene derivatives. Clearly, bromobenzene and 4-bromotoluene exhibited superior reactivity to that of 4-bromoanisole throughout this portion of the study, but there were cases where 4-bromoanisole underwent successful aryl amination reactions. This system was quite effective utilizing most alkyl amines and worked very well with *ortho*-substituted anilines.

Table 2
Aryl amination of alkyl amines using bromobenzene derivatives.[a]



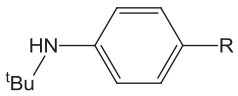
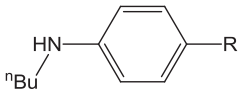
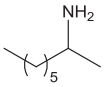
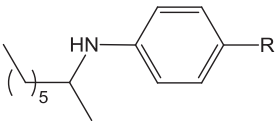
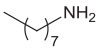
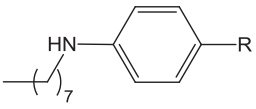
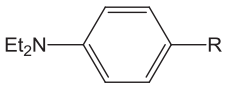
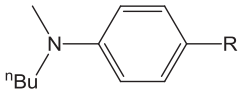
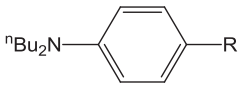
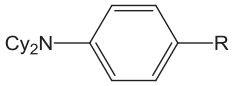
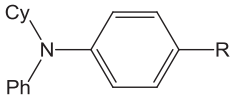
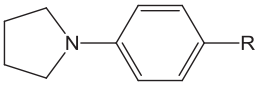
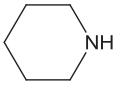
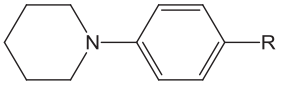
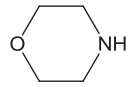
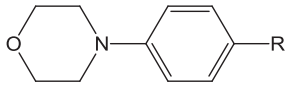
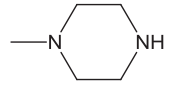
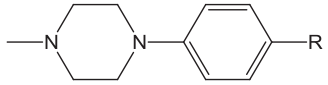
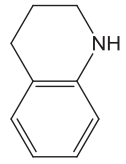
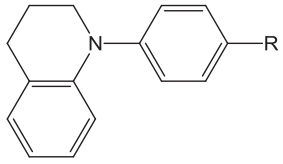
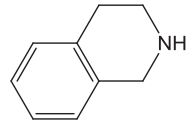
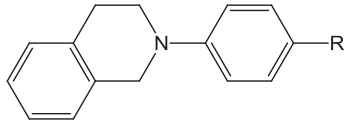
Entry	Amine	Product	Conversion[b] (%; R = H)	Conversion[b] (%; R = Me)	Conversion[b] (%; R = OMe)
1	$^{t}BuNH_2$[c]		36	26	13
2	$^{n}BuNH_2$		99	71	0
3			44	44	30
4			81	10	18
5	Et_2NH[c]		50	75	0
6	$^{n}BuMeNH$		64	12	6
7	$^{n}Bu_2NH$		99	99	13
8	Cy_2NH		99	99	12
9	CyNHPh		99	99	3
10			81	48	4
11			99	99	38

Table 2 (*continued*)

Entry	Amine	Product	Conversion[b] (%; R = H)	Conversion[b] (%; R = Me)	Conversion[b] (%; R = OMe)
12			99	99	56
13			99	99	8
14			99	99	64
15			99	99	53

[a] Conditions: aryl bromide (1.0 mmol); amine (1.2 mmol); NaO^{t}Bu (1.4 mmol); **(3IP)PdCl$_2$** (1 mol%); toluene (2 mL); 110 °C; 22 h; Teflon-sealed 8-mL vial.
[b] Conversion determined by gas chromatography.
[c] Toluene (8 mL).

Furthermore, several previously uncharacterized aryl amination products were synthesized.

2.3. Aryl amination of bromopyridines

Since both 2- and 3-bromopyridine proved to be quite reactive in our initial aryl amination screening with piperidine, these two substrates were tested with the full scope of amines. Both were found to undergo catalytic aryl amination with a broad range of alkyl amines to give moderate to excellent yields (Table 4). Other than *n*-octylamine, the primary amines were poor substrates for this reaction (Table 4, entries 1–3), while many of the secondary amines proceeded to give virtually quantitative yield (Table 4, entries 4–14). In nearly every case, 2-bromopyridine outperformed 3-bromopyridine. In fact, only the most reactive substrates provided high yields when using 3-bromopyridine, as seen with di-*n*-butylamine, pyrrolidine, piperidine, and the tetrahydroquinolines. Most of the other amines gave moderate to no yield when utilizing 3-bromopyridine. On the other hand, 2-bromopyridine proved to be a very useful substrate for aryl amination, producing good to excellent yield with many amines. Comparing the data for bromobenzene with that of 2-bromopyridine, it is clear that both are excellent substrates for this reaction with only slight differences between their product yields. In general, the same amine reactivity trends noted for the bromobenzene derivatives (see Section 2.2) were observed in the bromopyridine coupling reactions.

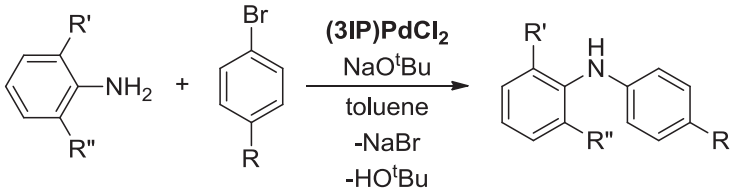
Finally, we applied the full range of anilines in catalytic aryl amination of 2- and 3-bromopyridines. Aryl amination of 3-bromopyridine with the various anilines did not proceed in most cases, and in the rare instance that catalysis was observed, only poor to moderate yield was achieved (see supporting information; Table S7). We attribute this to the likely coordination of the basic pyridine nitrogen to the palladium center effectively blocking the catalysis. On the other hand, 2-bromopyridine was quite effective in aryl amination with a wide range of aniline derivatives (Table 5), resulting in modest yields throughout these experiments. Coordination of the 2-bromopyridine nitrogen to the metal center is not likely to block catalysis, but more likely precedes oxidative addition of the carbon–bromine bond due to their relative positions on the pyridine ring. Unlike the bromobenzene derivatives, 2-bromopyridine underwent coupling with unsubstituted aniline, as well as *meta*- and *para*-substituted anilines, giving modest yields of the respective products. Strangely though, virtually no conversion was observed in coupling reactions with 2,6-disubstituted anilines. It is possible that these disubstituted species are too sterically bulky to effectively couple with 2-bromopyridine. This reduced reactivity with the 2,6-substituted derivatives was unexpected, but proved to be reproducible over multiple catalytic attempts. Overall, the aryl amination reactions between anilines and both bromopyridines gave only poor to modest yields, making them less effective reaction partners for **(3IP)PdCl$_2$** catalyzed aryl amination.

3. Conclusions

It has been shown that **(3IP)PdCl$_2$** functions well as a precatalyst for the coupling of bromoarenes and various amines. It was especially effective in the aryl amination of bromobenzene, 4-bromotoluene, and 2-bromopyridine. Although this catalyst system proved to have relatively broad substrate scope, it showed only moderate catalytic efficiency in terms of product yield, reaction time, and reaction temperature.

Overall, the aryl amination catalyst reported herein demonstrates the versatility of 3-iminophosphine ligated palladium species. Our previous reports have shown that cationic palladium complexes of this ligand set are quite effective in catalytic hydroamination reactions. Current efforts in our research group involve the combination of these two catalytic reactions (hydroamination and aryl amination) in order to effectively carry out multi-component one-pot coupling reactions for the synthesis of highly functionalized organic species, as Ackermann has recently demonstrated in an efficient indole synthesis [41]. Additionally, we aim to continue improving the 3-iminophosphine ligand

Table 3
Aryl amination of anilines using bromobenzene derivatives.[a]



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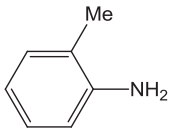
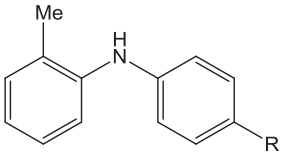
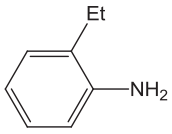
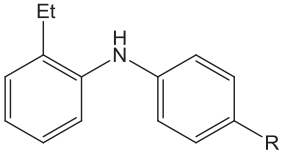
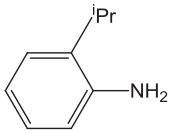
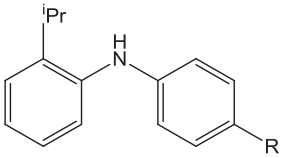
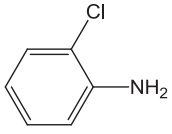
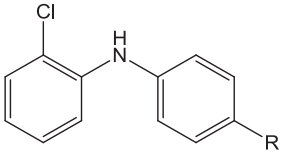
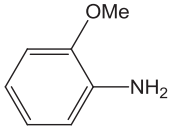
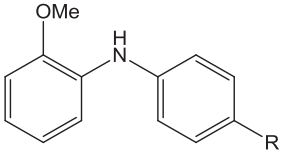
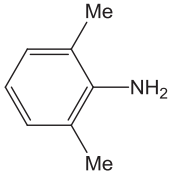
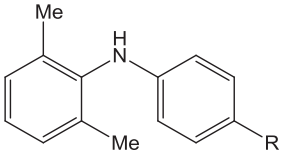
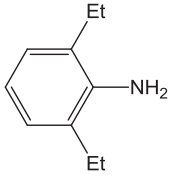
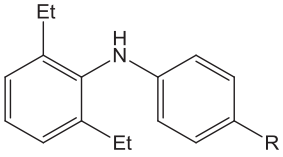
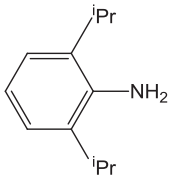
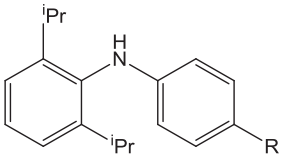
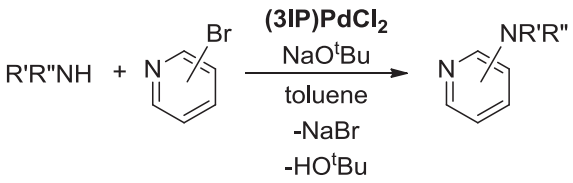
1			42	20	5
2			82	47	29
3			99	99	81
4			23	39	5
5			61	60	0
6			75	50	13
7			99	99	70
8			99	99	99

[a] Conditions: aryl bromide (1.0 mmol); aniline (1.2 mmol); NaO^{t}Bu (1.4 mmol); **(3IP)PdCl$_2$** (1 mol%); toluene (2 mL); 110 °C; 22 h; Teflon-sealed 8-mL vial.
[b] Conversion determined by gas chromatography.

Table 4
Aryl amination of alkyl amines using bromopyridines.[a]



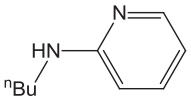
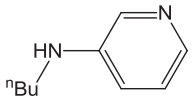
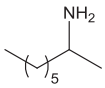
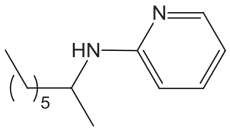
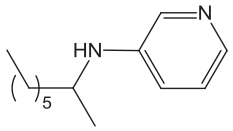
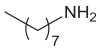
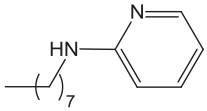
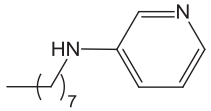
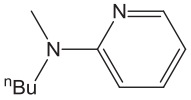
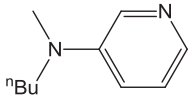
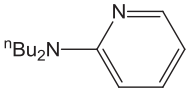
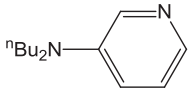
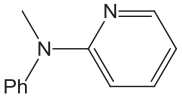
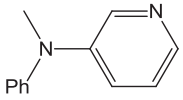
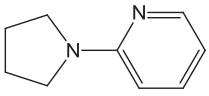
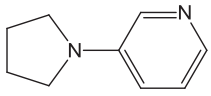
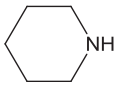
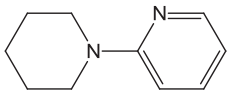
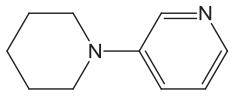
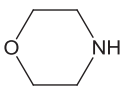
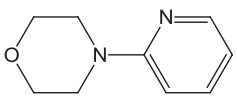
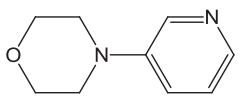
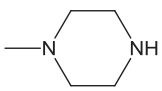
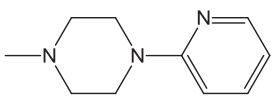
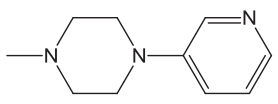
Entry	Amine	Product	Conversion[b] (%)	Product	Conversion[b] (%)
1	$^{n}BuNH_2$		4		42
2			33		64
3			98		13
4	$^{n}BuMeNH$		48		30
5	$^{n}Bu_2NH$		42		99
6	PhMeNH		83		69
7			99		94
8			99		99
9			99		16
10			96		6

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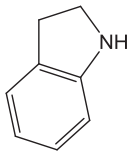
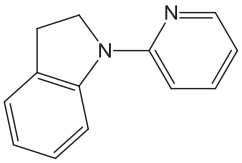
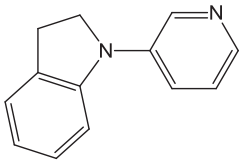
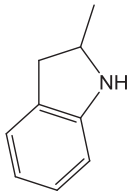
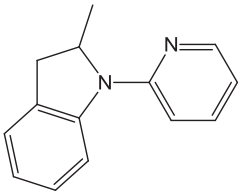
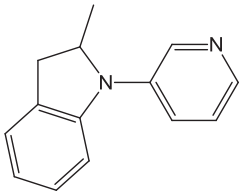
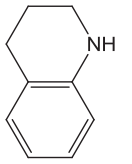
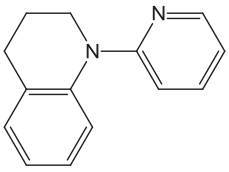
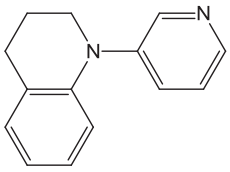
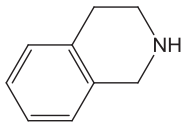
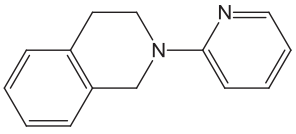
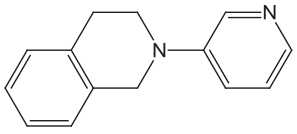
Table 4 (*continued*)

Entry	Amine	Product	Conversion[b] (%)	Product	Conversion[b] (%)
11			99		18
12			64		0
13			99		99
14			99		99

[a] Conditions: 2- or 3-bromopyridine (1.0 mmol); amine (1.2 mmol); NaO^{t}Bu (1.4 mmol); **(3IP)PdCl$_2$** (1 mol%); toluene (2 mL); 110 °C; 22 h; Teflon-sealed 8-mL vial.
[b] Conversion determined by gas chromatography.

framework and broadening the scope of reactivity amenable to these palladium-based catalysts.

4. Experimental

4.1. General methods and instrumentation

Unless otherwise specified, all reagents and solvents were purchased from commercial sources and used as received. Each liquid amine and aryl halide was vacuum distilled after drying over CaH_2 for several days. Solid amines were dissolved in CH_2Cl_2, stirred over CaH_2 for several days, filtered, and solvent removed under vacuum. Toluene was passed through columns of activated alumina and 4 Å molecular sieves and sparged with nitrogen. **(3IP)PdCl$_2$** was synthesized as previously reported [38]. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories. Gas chromatography was performed on a Varian CP-3800 gas chromatograph equipped with an FID detector. Silica gel (Sorbent Technologies; porosity = 60 Å; particle size = 40–63 mm) was used as received. All ^{1}H and ^{13}C NMR data were obtained on a 600 MHz Inova NMR or a 400 MHz VXRS NMR spectrometer at ambient temperature at 599.9 MHz for ^{1}H NMR and 150.8 MHz for ^{13}C NMR or 399.9 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR spectroscopy, respectively. ^{1}H NMR shifts are reported relative to $CHCl_3$ (7.26 ppm) or C_6D_5H (7.16 ppm), and ^{13}C NMR shifts are given relative to $CDCl_3$ (77.3 ppm) or C_6D_6 (128.1 ppm). Unless otherwise noted, all coupling constants reflect H–H J-coupling. High-resolution mass spectrometry, using electrospray ionization, was performed at the University of Illinois Mass Spectrometry Laboratory, Urbana, IL.

4.2. Catalysis

4.2.1. Aryl amination general procedures

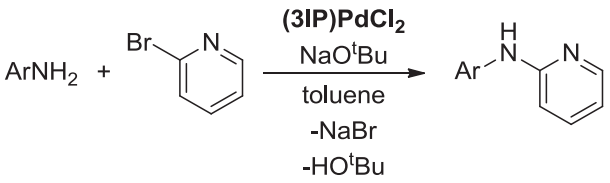
Under a nitrogen atmosphere, an 8-mL vial was charged with NaO^{t}Bu (135 mg, 1.40 mmol), toluene (2 mL), aryl halide (1.0 mmol), amine (1.2 mmol) and **(3IP)PdCl$_2$** (5.6 mg, 11 μmol, 1.1 mol%). For the lower boiling amines (as noted in the data tables), 8 mL of toluene was used in order to minimize headspace within the vial. The reaction mixture was stirred and heated at 110 °C for 22 h. An aliquot of the resulting mixture was diluted with diethyl ether (1.8 mL), filtered through an alumina column and analyzed by gas chromatography. Bulk products were then isolated via column chromatography (silica; 10% ethyl acetate in pentane, unless otherwise noted) and further characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as high-resolution mass spectrometry.

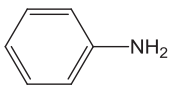
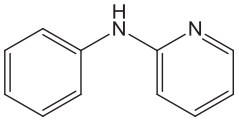
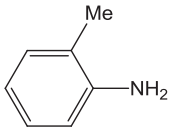
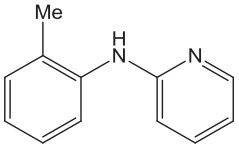
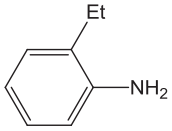
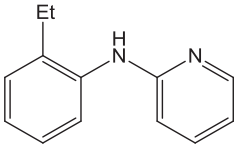
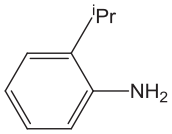
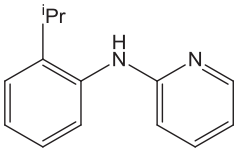
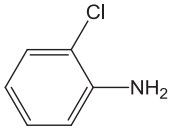
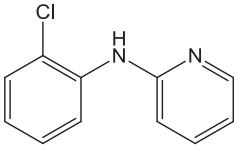
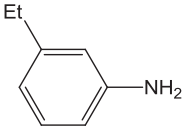
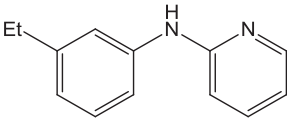
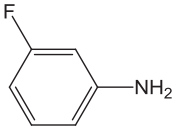
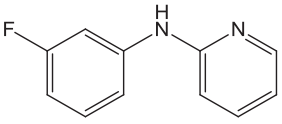
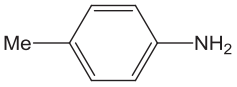
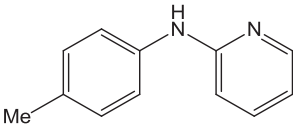
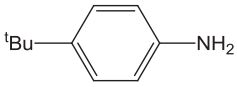
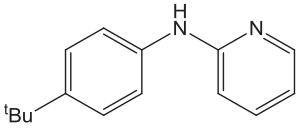
4.2.2. Aryl amination products

The following aryl amination products were identified by comparison to published NMR data: *N*-phenylpiperidine (Table 1, entries 1–3; Table 2, entry 11H) [42]; *N*-(4-methylphenyl)piperidine (Table 1, entry 4; Table 2, entry 11Me) [43]; *N*-(4-methoxyphenyl)piperidine (Table 1, entry 5; Table 2, entry 11MeO) [44]; *N*-(3-pyridyl)piperidine (Table 1, entry 6; Table 4, entry 8b) [43]; *N*-(2-pyridyl)piperidine (Table 1, entry 7; Table 4, entry 8a) [43]; *N*-(1-naphthyl)piperidine (Table 1, entry 8) [29].

N-(tert-butyl)aniline (Table 2, entry 1H) [45]; *N*-(tert-butyl)-4-methylaniline (Table 2, entry 1Me) [46]; *N*-(tert-butyl)-4-methoxyaniline (Table 2, entry 1MeO) [47]; *N*-(n-butyl)aniline (Table 2, entry 2H) [48]; *N*-(n-butyl)-4-methylaniline (Table 2, entry 2Me) [48]; *N*-phenyl-2-aminooctane (Table 2, entry 3H) [49]; *N*-(4-methylphenyl)-2-aminooctane (Table 2, entry 3Me) [49]; *N*-(4-

Table 5
Aryl amination of anilines using 2-bromopyridine.[a]



Entry	Aniline	Product	Conversion[b] (%)
1			45
2			32
3			52
4			55
5			48
6			52
7			28
8			45
9			55

[a] Conditions: 2-bromopyridine (1.0 mmol); aniline (1.2 mmol); NaO^{t}Bu (1.4 mmol); **(3IP)PdCl$_2$** (1 mol%); toluene (2 mL); 110 °C; 22 h; Teflon-sealed 8-mL vial.
[b] Conversion determined by gas chromatography.

methoxyphenyl)-2-aminooctane (Table 2, entry 3MeO) [49]; *N*-(phenyl)octylamine (Table 2, entry 4H) [50]; *N*-(4-methylphenyl) octylamine (Table 2, entry 4Me) [51]; *N*-(4-methoxyphenyl)octylamine (Table 2, entry 4MeO) [52]; *N*,*N*-diethylaniline (Table 2, entry 5H) [53]; *N*,*N*-diethyl-4-methylaniline (Table 2, entry 5Me) [54]; *N*-butyl,*N*-methylaniline (Table 2, entry 6H) [55]; *N*-butyl,*N*-methyl-4-methylaniline (Table 2, entry 6Me) [56]; *N*-butyl,*N*-methyl-4-methoxyaniline (Table 2, entry 6MeO) [56]; *N*,*N*-di-*n*-butylaniline (Table 2, entry 7H) [52]; *N*,*N*-di-*n*-butyl-4-methylaniline (Table 2, entry 7Me) [57]; *N*,*N*-di-*n*-butyl-4-methoxyaniline (Table 2, entry 7MeO) [55]; *N*,*N*-dicyclohexylaniline (Table 2, entry 8H) [53]; cyclohexyldiphenylamine (Table 2, entry 9H) [58]; *N*-phenylpyrrolidine (Table 2, entry 10H) [48]; *N*-(4-methylphenyl)pyrrolidine (Table 2, entry 10Me) [43]; *N*-(4-methoxyphenyl)pyrrolidine (Table 2, entry 10MeO) [43]; *N*-phenylmorpholine (Table 2, entry 12H) [48]; *N*-(4-methylphenyl)morpholine (Table 2, entry 12Me) [52]; *N*-(4-methoxyphenyl)morpholine (Table 2, entry 12MeO) [59]; *N*-methyl,*N*′-phenylpiperazine (Table 2, entry 13H) [60]; *N*-methyl,*N*′-(4-methylphenyl)piperazine (Table 2, entry 13Me) [61]; *N*-methyl,*N*′-(4-methoxyphenyl)piperazine (Table 2, entry 13MeO) [60]; *N*-phenyltetrahydroquinoline (Table 2, entry 14H) [62]; *N*-(4-methylphenyl) tetrahydroquinoline (Table 2, entry 14Me) [63]; *N*-(4-methoxyphenyl) tetrahydroquinoline (Table 2, entry 14MeO) [64]; *N*-phenyltetrahydroisoquinoline (Table 2, entry 15H) [65]; *N*-(4-methylphenyl) tetrahydroisoquinoline (Table 2, entry 15Me) [66]; *N*-(4-methoxyphenyl)tetrahydroisoquinoline (Table 2, entry 15MeO) [65].

N-(phenyl)-2-methylaniline (Table 3, entry 1H) [61]; *N*-(4-methylphenyl)-2-methylaniline (Table 3, entry 1Me) [52]; *N*-(4-methoxyphenyl)-2-methylaniline (Table 3, entry 1MeO) [59]; *N*-(phenyl)-2-ethylaniline (Table 3, entry 2H) [59]; *N*-(phenyl)-2-isopropylaniline (Table 3, entry 3H) [67]; *N*-(4-methylphenyl)-2-isopropylaniline (Table 3, entry 3Me) [68]; *N*-(phenyl)-2-chloroaniline (Table 3, entry 4H) [69]; *N*-(4-methylphenyl)-2-chloroaniline (Table 3, entry 4Me) [70]; *N*-(4-methoxyphenyl)-2-chloroaniline (Table 3, entry 4MeO) [70]; *N*-(phenyl)-2-methoxyaniline (Table 3, entry 5H) [59]; *N*-(4-methylphenyl)-2-methoxyaniline (Table 3, entry 5Me) [71]; *N*-(phenyl)-2,6-dimethylaniline (Table 3, entry 6H) [72]; *N*-(4-methylphenyl)-2,6-dimethylaniline (Table 3, entry 6Me) [52]; *N*-(4-methoxyphenyl)-2,6-dimethylaniline (Table 3, entry 6MeO) [59]; *N*-(phenyl)-2,6-diethylaniline (Table 3, entry 7H) [73]; *N*-(phenyl)-2,6-diisopropylaniline (Table 3, entry 8H) [59]; *N*-(4-methylphenyl)-2,6-diisopropylaniline (Table 3, entry 8Me) [74]; *N*-(4-methoxyphenyl)-2,6-diisopropylaniline (Table 3, entry 8MeO) [72].

N-(2-pyridyl)-*n*-butylamine (Table 4, entry 1a) [48]; *N*-(3-pyridyl)-*n*-butylamine (Table 4, entry 1b) [48]; *N*-(2-pyridyl)-2-aminooctane (Table 4, entry 2a) [75]; *N*-(2-pyridyl)-*n*-octylamine (Table 4, entry 3a) [52]; *N*-(3-pyridyl)-*n*-octylamine (Table 4, entry 3b) [52]; *N*-(2-pyridyl),*N*-methyl-*n*-butylamine (Table 4, entry 4a) [43]; *N*-(3-pyridyl),*N*-methyl-*n*-butylamine (Table 4, entry 4b) [43]; *N*-(2-pyridyl)-di-*n*-butylamine (Table 4, entry 5a) [76]; *N*-(3-pyridyl)-di-*n*-butylamine (Table 4, entry 5b) [57]; *N*-(2-pyridyl),*N*-methyl-aniline (Table 4, entry 6a) [52]; *N*-(3-pyridyl),*N*-methyl-aniline (Table 4, entry 6b) [57]; *N*-(2-pyridyl)pyrrolidine (Table 4, entry 7a) [43]; *N*-(3-pyridyl) pyrrolidine (Table 4, entry 7b) [43]; *N*-(2-pyridyl)morpholine (Table 4, entry 9a) [59]; *N*-(3-pyridyl)morpholine (Table 4, entry 9b) [52]; *N*-(2-pyridyl),*N*′-methylpiperazine (Table 4, entry 10a) [77]; *N*-(3-pyridyl),*N*′-methylpiperazine (Table 4, entry 10b) [78]; *N*-(2-pyridyl) indoline (Table 4, entry 11a) [79]; *N*-(3-pyridyl)indoline (Table 4, entry 11b) [62]; *N*-(2-pyridyl)tetrahydroquinoline (Table 4, entry 13a) [79]; *N*-(2-pyridyl)tetrahydroisoquinoline (Table 4, 14a) [77].

N-(2-pyridyl)aniline (Table 5, entry 1) [52]; *N*-(2-pyridyl)-2-methyl-aniline (Table 5, entry 2) [80]; *N*-(2-pyridyl)-2-ethyl-aniline (Table 5, entry 3) [81]; *N*-(2-pyridyl)-2-isopropyl-aniline (Table 5, entry 4) [82]; *N*-(2-pyridyl)-2-chloro-aniline (Table 5, entry 5) [83]; *N*-(2-pyridyl)-3-fluoro-aniline (Table 5, entry 7) [83]; *N*-(2-pyridyl)-4-methyl-aniline (Table 5, entry 8) [52]; *N*-(2-pyridyl)-4-tert-butyl-aniline (Table 5, entry 9) [80].

4.2.2.1. N,N-di-cyclohexyl-4-methylaniline (Table 2, entry 8Me). Purified by column chromatography (toluene with a dichloromethane gradient). ^{1}H NMR ($CDCl_3$) δ 1.71–1.76 (m, 4H), 1.81–1.86 (m, 4H), 2.03–2.06 (m, 2H), 2.30–2.38 (m, 4H), 2.34 (s, 3H), 2.41–2.47 (m, 4H), 2.50–2.53 (m, 2H), 2.97–2.99 (m, 2H), 7.17 (d, ^3J = 8.4 Hz, 2H), 7.20 (d, ^3J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.29, 26.29, 28.55, 38.99, 39.05, 126.48, 130.04, 137.19, 138.41.

4.2.2.2. N-cyclohexyl,N-phenyl-4-methylaniline (Table 2, entry 9Me). ^{1}H NMR ($CDCl_3$) δ 1.79–1.85 (m, 2H), 1.98–2.23 (m, 4H), 2.24–2.29 (m, 1H), 2.33 (s, 3H), 2.44–2.60 (m, 3H), 3.55–3.60 (m, 1H), 7.00 (t, ^3J = 7.6 Hz, 1H), 7.03 (d, ^3J = 8.4 Hz, 2H), 7.16 (d, ^3J = 8.4 Hz, 2H), 7.19 (d, ^3J = 7.6 Hz, 2H), 7.21 (t, ^3J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.31, 25.58, 28.04, 35.31, 39.29, 42.41, 57.24, 128.56, 128.70, 128.94, 129.32, 133.85, 135.90, 136.70, 137.54, 140.48, 147.67; $HRMS_{calc}$: 266.1909 for $C_{19}H_{24}N$ $[M + H]^+$; $HRMS_{meas}$: 266.1910.

4.2.2.3. N-(4-methylphenyl)-2-ethylaniline (Table 3, entry 2Me). ^{1}H NMR (C_6D_6) δ 1.15 (t, ^3J = 7.6 Hz, 3H), 2.15 (s, 3H), 2.32 (q, ^3J = 7.6 Hz, 2H), 4.92 (s, 1H), 6.77 (d, ^3J = 8.0 Hz, 2H), 6.93 (t, ^3J = 8.0 Hz, 1H), 6.94 (d, ^3J = 8.0 Hz, 2H), 7.05 (t, ^3J = 8.0 Hz, 1H), 7.10 (d, ^3J = 8.0 Hz, 1H), 7.22 (d, ^3J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (C_6D_6) δ 13.79, 20.58, 24.34, 118.36, 119.55, 122.25, 126.95, 129.01, 129.80, 129.99, 134.14, 141.68, 142.28; $HRMS_{calc}$: 212.1439 for $C_{15}H_{18}N$ $[M + H]^+$; $HRMS_{meas}$: 212.1444.

4.2.2.4. N-(4-methoxyphenyl)-2-ethylaniline (Table 3, entry 2MeO). ^{1}H NMR (C_6D_6) δ 1.08 (t, ^3J = 7.6 Hz, 3H), 2.31 (q, ^3J = 7.6 Hz, 2H), 3.34 (s, 3H), 4.87 (s, 1H), 6.75 (d, ^3J = 8.8 Hz, 2H), 6.82 (d, ^3J = 8.8 Hz, 2H), 6.90 (t, ^3J = 7.2 Hz, 1H), 7.07 (t, ^3J = 7.2 Hz, 1H), 7.10 (d, ^3J = 7.2 Hz, 1H), 7.12 (d, ^3J = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (C_6D_6) δ 14.39, 23.09, 31.99, 115.03, 117.26, 121.14, 122.14, 127.14, 129.01, 132.14, 137.39, 143.24, 155.60; $HRMS_{calc}$: 228.1388 for $C_{15}H_{18}NO$ $[M + H]^+$; $HRMS_{meas}$: 228.1389.

4.2.2.5. N-(4-methoxyphenyl)-2-isopropylaniline (Table 3, entry 3MeO). ^{1}H NMR ($CDCl_3$) δ 1.28 (d, ^3J = 6.8 Hz, 6H), 3.10 (sept, ^3J = 6.8 Hz, 1H), 3.80 (s, 3H), 5.30 (s, 1H), 6.85 (d, ^3J = 8.4 Hz, 2H), 6.95 (t, ^3J = 7.6 Hz, 1H), 6.96 (d, ^3J = 8.4 Hz, 2H), 7.05 (d, ^3J = 7.6 Hz, 1H), 7.09 (t, ^3J = 7.6 Hz, 1H), 7.27 (d, ^3J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.95, 27.63, 55.76, 114.81, 117.96, 121.15, 121.34, 125.85, 126.54, 137.23, 137.56, 141.80, 154.74; $HRMS_{calc}$: 242.1545 for $C_{16}H_{20}NO$ $[M + H]^+$; $HRMS_{meas}$: 242.1543.

4.2.2.6. N-(4-methylphenyl)-2,6-diethylaniline (Table 3, entry 7Me). ^{1}H NMR ($CDCl_3$) δ 1.14 (t, ^3J = 7.6 Hz, 6H), 2.23 (s, 3H), 2.57 (q, ^3J = 7.6 Hz, 4H), 5.06 (s, 1H), 6.40 (d, ^3J = 8.4 Hz, 2H), 6.94 (d, ^3J = 8.4 Hz, 2H), 7.16 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.88, 20.64, 24.87, 113.60, 126.41, 126.80, 127.32, 129.89, 137.50, 142.20, 145.07; $HRMS_{calc}$: 240.1752 for $C_{17}H_{22}N$ $[M + H]^+$; $HRMS_{meas}$: 240.1755.

4.2.2.7. N-(4-methoxyphenyl)-2,6-diethylaniline (Table 3, entry 7MeO). ^{1}H NMR ($CDCl_3$) δ 1.14 (t, ^3J = 7.6 Hz, 6H), 2.56 (q, ^3J = 7.6 Hz, 4H), 3.73 (s, 3H), 5.00 (s, 1H), 6.46 (d, ^3J = 8.8 Hz, 2H), 6.73 (d, ^3J = 8.8 Hz, 2H), 7.15 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.81, 24.81, 55.81, 114.78, 114.90, 126.00, 126.78, 137.99, 141.33, 141.64, 152.58; $HRMS_{calc}$: 256.1701 for $C_{17}H_{22}NO$ $[M + H]^+$; $HRMS_{meas}$: 256.1703.

4.2.2.8. N-(3-pyridyl)-2-aminooctane (Table 4, entry 2b). Purified by column chromatography (80% pentane; 10% ethyl acetate; 10% triethylamine). ^{1}H NMR (C_6D_6) δ 0.81 (d, ^3J = 6.4 Hz, 3H), 0.91 (t,

^3J = 7.2 Hz, 3H), 1.21 (m, 10H), 2.76 (d, ^3J = 7.2 Hz, 1H), 3.04 (m, 1H), 6.41 (dd, ^3J = 8.0 Hz, ^4J = 2.4 Hz, 1H), 6.77 (dd, ^3J = 8.0 Hz, ^{3}J = 4.8 Hz, 1H), 8.08 (d, ^4J = 2.4 Hz, 1H), 8.17 (d, ^3J = 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 14.31, 20.37, 22.99, 26.28, 29.62, 32.14, 37.02, 47.99, 117.82, 123.65, 137.30, 138.80, 143.76; $HRMS_{calc}$: 207.1861 for $C_{13}H_{23}N_2$ $[M + H]^+$; $HRMS_{meas}$: 207.1853.

4.2.2.9. N-(2-pyridyl)-2-methylindoline (Table 4, entry 12a). ^{1}H NMR (C_6D_6) δ 1.36 (d, ^3J = 6.4 Hz, 3H), 2.71 (dd, ^2J = 15.6 Hz, ^3J = 2.4 Hz, 1H), 3.44 (dd, ^2J = 15.6 Hz, ^3J = 9.2 Hz, 1H), 4.67 (m, 1H), 6.76 (dd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, 1H), 6.90 (t, ^3J = 7.6 Hz, 1H), 6.93 (d, ^3J = 7.6 Hz, 1H), 7.20 (t, ^3J = 7.6 Hz, 1H), 7.22 (d, ^3J = 7.6 Hz, 1H), 7.56 (td, ^3J = 7.6 Hz, ^4J = 2.0 Hz, 1H), 8.03 (d, ^3J = 7.6 Hz, 1H), 8.35 (dd, ^3J = 4.8 Hz, ^4J = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 19.93, 36.42, 56.56, 109.11, 113.93, 114.41, 120.71, 125.11, 127.25, 130.56, 137.28, 143.95, 148.22, 154.97; $HRMS_{calc}$: 211.1235 for $C_{14}H_{15}N_2$ $[M + H]^+$; $HRMS_{meas}$: 211.1240.

4.2.2.10. N-(3-pyridyl)tetrahydroquinoline (Table 4, entry 13b). ^{1}H NMR ($CDCl_3$) δ 2.05 (m, 2H), 2.85 (t, ^3J = 6.4 Hz, 2H), 3.64 (t, ^3J = 6.4 Hz, 2H), 6.79 (t, ^3J = 4.8 Hz, 1H), 6.80 (d, ^3J = 7.6 Hz, 1H), 6.97 (t, ^3J = 7.6 Hz, 1H), 7.08 (d, ^3J = 7.6 Hz, 1H), 7.25 (t, ^3J = 4.8 Hz, 1H), 7.56 (d, ^3J = 4.8 Hz, 1H), 8.28 (d, ^3J = 4.8 Hz, 1H), 8.54 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 22.95, 27.62, 50.45, 116.44, 120.04, 124.04, 126.26, 126.72, 129.29, 129.73, 130.62, 143.03, 143.28, 145.07; $HRMS_{calc}$: 211.1235 for $C_{14}H_{15}N_2$ $[M + H]^+$; $HRMS_{meas}$: 211.1228.

4.2.2.11. N-(2-pyridyl)-3-ethyl-aniline (Table 5, entry 6). ^{1}H NMR ($CDCl_3$) δ 1.25 (t, ^3J = 7.6 Hz, 3H), 2.65 (q, ^3J = 7.6 Hz, 2H), 6.51 (s, 1H), 6.73 (dd, ^3J = 7.2 Hz, ^3J = 4.8 Hz, 1H), 6.88 (d, ^3J = 8.0 Hz, 1H), 6.90 (d, ^3J = 7.2 Hz, 1H), 7.13 (s, 1H), 7.15 (d, ^3J = 8.0 Hz, 1H), 7.25 (t, ^3J = 8.0 Hz, 1H), 7.49 (td, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 8.20 (dd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 15.71, 29.02, 108.20, 115.07, 117.89, 120.13, 122.71, 129.32, 137.81, 140.44, 145.76, 148.58, 156.14; $HRMS_{calc}$: 199.1235 for $C_{13}H_{15}N_2$ $[M + H]^+$; $HRMS_{meas}$: 199.1232.

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Appendix A. Supplementary material

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