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Ammonia Coupling

Nickel-Catalyzed Amination of Aryl Chlorides with Ammonia or Ammonium Salts**

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Abstract: *The nickel-catalyzed amination of aryl chlorides to form primary arylamines occurs with ammonia or ammonium sulfate and a well-defined single-component nickel(0) precatalyst containing a Josiphos ligand and an* η^2*-bound benzonitrile ligand. This system also catalyzes the coupling of aryl chlorides with gaseous amines in the form of their hydrochloride salts.*

The transition-metal-catalyzed amination of aryl halides is a valuable tool for the construction of arylamines.[1] Many palladium catalysts have been developed for the amination of aryl electrophiles with a wide variety of amines. However, there are few catalysts based on cost-effective and earth-abundant metals for the amination of aryl electrophiles, and little mechanistic information has been gained about the coupling reactions of amines catalyzed by first-row metals. Copper-catalyzed aminations of aryl halides are typically limited to sterically unhindered aryl iodides and activated aryl bromides.[2] Nickel catalysts for amination reactions have been reported, but the scope of the reaction, until recently,[3,4] was limited to secondary alkyl[5–19] and aryl[5,8,9,11,13–20] amines.

The development of a nickel catalyst for the coupling of aryl electrophiles with primary amines and ammonia is a long-standing challenge. Nickel-catalyzed coupling reactions of aryl chlorides with primary alkylamines occurred, until recently, in low yields with unactivated substrates.[5,18] Our report of a catalyst for the coupling of unactivated aryl chlorides with primary alkylamines demonstrated the value of single-component catalysts to achieve high reactivity and selectivity.[3] Despite the progress on the development of first-row transition-metal catalysts for C–N coupling reactions, few studies have been published on the amination of aryl electrophiles with ammonia catalyzed by nickel. Concurrent with the work we report here,[21] Stradiotto and co-workers reported a Josiphos-ligated nickel catalyst for the coupling of aryl chlorides with ammonia.[4]

The development of the nickel-catalyzed coupling of ammonia poses several challenges. First, ammonia binds tightly to transition metals,[22,23] often causing catalyst deactivation. Ammonia is neither strongly basic nor acidic, disfavoring proton exchanges to and from the reagent, and the strong N–H bond disfavors oxidative addition of the N–H bond of ammonia. In addition, the physical properties of ammonia create challenges for conducting coupling reactions conveniently. Because it is a corrosive gas, specialized equipment is required to run reactions at high pressures. Finally, the aniline formed during the reaction can act as a nucleophile for subsequent amination reactions to form diarylamines. Herein, we report a series of Ni-catalyzed monoarylations of ammonia with aryl electrophiles. These studies show the value of using a single-component catalyst for high activity and for generating clear mechanistic information. Our mechanistic studies strongly imply that the process occurs by shuttling between Ni^0 and arylnickel(II) halide intermediates.

The palladium-catalyzed amination of aryl electrophiles with ammonia has been reported,[24–32] and the mechanism has been studied.[33] These studies showed that the steric bulk of the ligand is crucial to favor the binding of ammonia over the binding of aniline. Nickel complexes of bidentate ligands are known to add aryl chlorides.[3,34] Based on this information, we investigated the coupling of chlorobenzene **1** with ammonia (added to the reaction as a dioxane solution), catalyzed by $[Ni(cod)_2]$ and a variety of bidentate phosphine ligands (Table 1). We began our evaluation of the ligands by studying catalysts containing common chelating bisphosphines, such as BINAP (Table 1, entry 1), Xantphos (entry 2), and dppf (entry 3). Because BINAP-ligated nickel complexes catalyzed the amination of aryl chlorides with primary alkylamines,[3] the primary arylamines formed from the coupling of ammonia might be expected to react competitively with ammonia. Indeed, the reaction of chlorobenzene with ammonia, catalyzed by a BINAP-ligated nickel complex, occurred in low yield with low selectivity for the primary amine **2** over the diarylamine **2′** (Table 1, entry 1).

However, reactions catalyzed by nickel complexes that were bound by ligands of the Josiphos family occurred with high conversions of the aryl chloride, high yields of anilines, and varying selectivities. The nickel catalyst ligated by the same Josiphos ligand as in a Pd catalyst for the coupling of aryl halides with ammonia[24,27] gave high selectivity for the primary amine. However, the conversion and yield were low (Table 1, entry 8). Fortunately, reactions conducted with the smaller Josiphos ligand **L5** occurred with both high yields and high selectivity (Table 1, entry 9).

We have previously shown that benzonitrile stabilizes the Ni^0 intermediate in the catalytic system, and the benzonitrile-ligated nickel complex readily undergoes oxidative addition of aryl chlorides.[3] To avoid the presence of cyclooctadiene in

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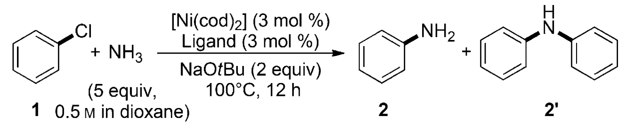
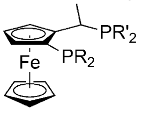
Table 1: Evaluation of nickel precursors and ligands for the amination of chlorobenzene with ammonia.[a]



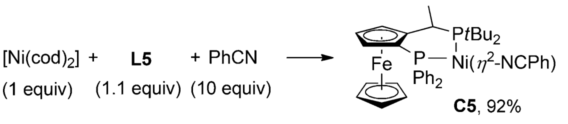
Entry	Ligand	Conv. [%]	Yield [%]	2:2'
1	BINAP	78	39	5:1
2	Xantphos	0	–	–
3	dppf	0	–	–
4	dtbpe	71	46	4:1
5	**L1**	100	67	32:1
6	**L2**	100	43	2:1
7	**L3**	100	41	2:1
8	**L4**	28	11	>50:1
9[b]	**L5**	82	67	>50:1
10[b]	–[c]	100	80	>50:1

[a] Reactions were performed with 0.10 mmol of chlorobenzene. Conversion, yield, and selectivity were determined by GC analysis using dodecane as an internal standard. [b] Reaction time: 3 h. [c] Preformed catalyst [(**L5**)Ni(η^2-NCPh)] (**C5**) used instead of in situ prepared catalysts. cod = 1,5-cyclooctadiene, Cy = cyclohexyl. BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, Xantphos = 4,5-bis(diphenylphosphino)-9,9'-dimethylxanthene, dppf = 1,1'-bis(diphenylphosphino)ferrocene, dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane



L1 R = Cy, R' = Cy
L2 R = Cy, R' = Ph
L3 R = Ph, R' = Cy
L4 R = Cy, R' = *t*Bu
L5 R = Ph, R' = *t*Bu

the reaction mixture, we prepared a single-component nickel(0) precursor containing **L5** and benzonitrile. The substitution of **L5** for cyclooctadiene in [Ni(cod)$_2$] requires heating, but this ligand substitution occurs quickly at ambient temperature in the presence of benzonitrile. The combination of [Ni(cod)$_2$], **L5**, and excess benzonitrile generated complex **C5**, which contains the Josiphos ligand and a side-bound benzonitrile [Eq. (1)].



(1)

The structure of this complex is shown in Figure 1. The η^2-bound benzonitrile ligand stabilizes Ni^0 through back-bonding into the C≡N π* orbital. The C≡N bond in **C5** is longer than a typical C≡N bond of a nitrile, (1.225(2) Å, average C≡N bond length:[35] 1.136 Å), and the C–C≡N bond axis is bent (136.4(2)°). These properties are indicative of strong π-backbonding from the nickel into the nitrile π-bond (Figure 1).

The source of ammonia for the reactions summarized in Table 1 is a commercially available solution of NH$_3$ in dioxane. Inexpensive ammonium salts are also potential sources of NH$_3$ for the coupling process, and we recently reported palladium-catalyzed reactions of aryl halides with ammonium salts as precursors to ammonia.[36] Because of the practical advantages of developing C–N coupling reactions with ammonium salts in place of ammonia solutions, we investigated the potential to use ammonium salts in the Ni-catalyzed amination. We investigated ammonium chloride, acetate, and sulfate as sources of ammonia. For reactions catalyzed by **C5**, only those conducted with ammonium sulfate gave comparable yields and selectivities to reactions conducted with ammonia in dioxane. Furthermore, because the solvent is not limited to the commercially available solution of ammonia in dioxane when conducting reactions with ammonium salts, a range of solvents were explored. Reactions conducted in ethereal solvents occurred in the highest yields, and 2-Me-THF was selected for both its green-chemistry properties and elevated boiling point, compared to other ethers.[37,38]

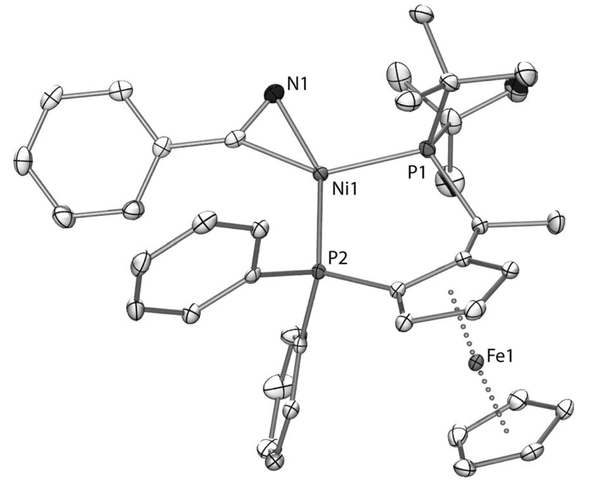
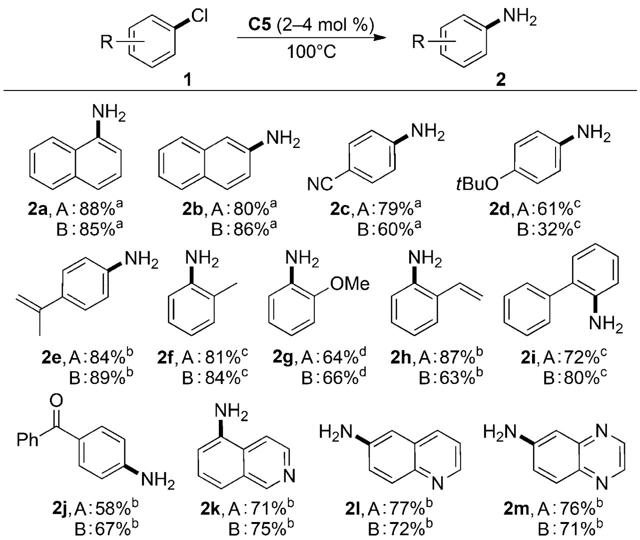


Figure 1. ORTEP structure of [(**L5**)Ni(η^2-NCPh)] (**C5**). Ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity.

The scope of aryl chlorides that couple with ammonia or ammonium sulfate is shown in Scheme 1. Aryl chlorides containing *ortho* substituents (**1f**, **1g**, **1h**, **1i**), electron-withdrawing groups (**1c**, **1j**), and electron-donating groups (**1d**, **1g**) underwent the transformation in moderate to high yields. Heteroaryl chlorides (**1k**, **1l**, **1m**) also underwent this transformation in high yields. Nitriles (**1c**), styrenes (**1e, 1h**), and non-enolizable ketones (**1j**) were tolerated by the reaction conditions. In general, the yields of reactions conducted with ammonia are similar to the yields of reactions conducted with ammonium sulfate.

Based on the finding that $(NH_4)_2SO_4$ is a practical source of ammonia in transition-metal-catalyzed coupling reactions, we investigated the reaction of aryl chlorides with ammonium salts of gaseous amines. Although methylamine is a primary aliphatic amine, the coupling of methylamine hydrochloride with aryl chlorides catalyzed by [(BINAP)Ni(η^2-NCPh)], our previously reported catalyst for the coupling of aryl chlorides with primary aliphatic amines,[3] occurred in low yields.

However, reactions of aryl chlorides with methylamine hydrochloride catalyzed by **C5** in toluene occurred in high yields (Scheme 2). The scope of aryl chlorides that undergo this transformation is similar to that for the coupling reactions with ammonia or ammonium sulfate. In addition, the catalyst loadings for reactions of aryl chlorides with ammonia or ammonium sulfate are similar to those for reactions of aryl chlorides with methylamine hydrochloride.



Scheme 1. Nickel-catalyzed amination of aryl chlorides with ammonia or ammonium sulfate. Reactions were performed with 0.60 mmol of the aryl chloride. Conditions A: 5 equiv NH_3, 1.5 equiv NaO*t*Bu, 1,4-dioxane, 3 h; Conditions B: 1.5 equiv $(NH_4)_2SO_4$, 4.5 equiv NaO*t*Bu, 2-Me-THF, 7 h. Yields of isolated products are given. [a] 2 mol% **C5**. [b] 3 mol% **C5**. [c] 4 mol% **C5**.

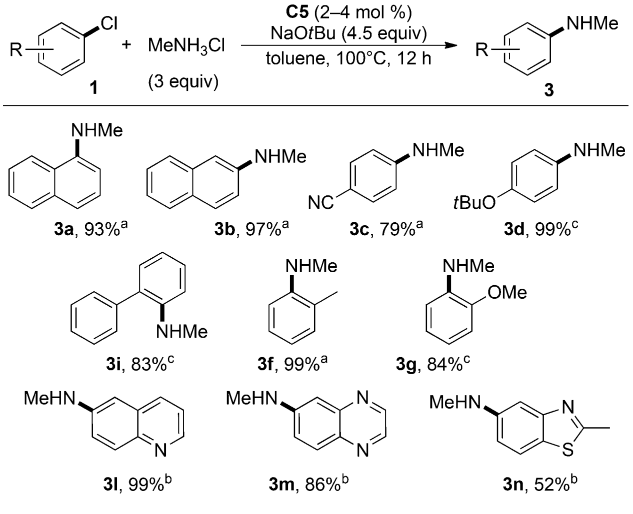
In addition to methylamine hydrochloride, ethylamine hydrochloride couples with aryl chlorides to form the corresponding *N*-ethylanilines. However, neither the reactions catalyzed by **C5** nor those catalyzed by [(BINAP)Ni(η^2-NCPh)] occurred to full conversion of *p*-chlorotoluene to *N*-ethyl-*p*-toluidine (up to 70%) under conditions with various solvents, temperatures, and reagent stoichiometries.

Therefore, we re-examined ligands for this reaction in which the nucleophile is larger than ammonia but is smaller than most primary alkylamines. We investigated ligands that we anticipated would promote the oxidative addition of aryl chlorides but would be less sterically bulky than those that promote the selective coupling of ammonia and methylamine. The results summarized in Table 1 include two examples (Table 1, entries 6 and 7) in which the reactions proceeded to full conversion, but occurred with poor selectivity. These results suggest that the catalyst in these examples would be less sterically bulky than **C5** and catalyze the coupling of ethylamine hydrochloride. Indeed, nickel bound by the Josiphos ligands **L2** and **L3**, both of which contain one cyclohexyl group and one phenyl group, catalyzed the amination of aryl chlorides with ethylamine hydrochloride with full conversion of the aryl chloride. We prepared single-component catalysts from both these ligands, [Ni(cod)$_2$], and benzonitrile. Both complexes catalyzed the coupling of ethylamine hydrochloride in high yields, but the reactions catalyzed by [(**L2**)Ni(η^2-NCPh)] (**C2**) led to the secondary amine product in higher yields than the reactions catalyzed by [(**L3**)Ni(η^2-NCPh)] (**C3**).

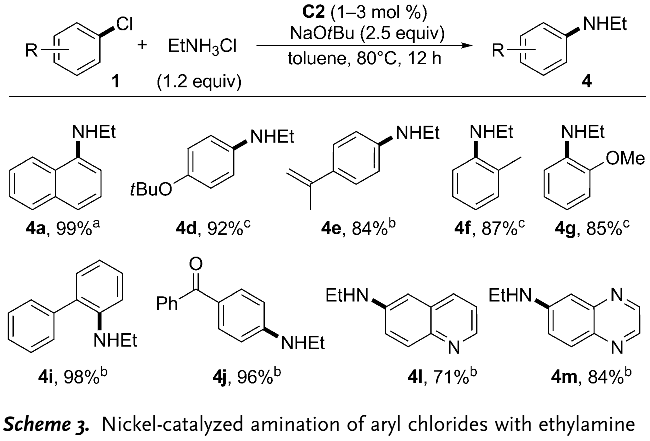
Examples of the coupling of $EtNH_3Cl$ with chloroarenes are summarized in Scheme 3. The reactions of aryl chlorides with $EtNH_3Cl$ catalyzed by **C2** occurred to full conversion with lower catalyst loadings (1–3 mol%) and at a lower temperature (80 °C) than the analogous coupling reactions with ammonia, ammonium sulfate, or methylamine hydrochloride (2–4 mol%, 100 °C). The scope of the couplings of $EtNH_3Cl$ is similar to that of ammonia and $MeNH_3Cl$.

Reactions catalyzed by nickel complexes have been proposed to occur through one- or two-electron pathways.[39,40] To investigate the mechanism of these coupling reactions, we conducted stoichiometric experiments with our new nickel complexes. First, we conducted the oxidative addition of aryl chlorides to nickel complex **C5**, resulting in complex **C5A**. The oxidative addition of the activated aryl chloride occurred in a high yield [Eq. (2)], while the oxidative additions of electron-neutral and electron-rich aryl chlorides were slow and occurred in low yields.

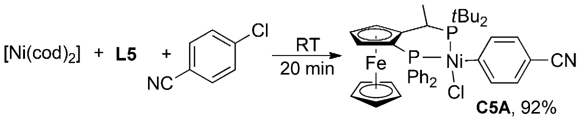
Although the oxidative addition of electron-neutral and electron-rich haloarenes to the Ni^0 species that contain **L5** was slow, the oxidative addition of electron-neutral, electron-rich, and *ortho*-substituted aryl chlorides to [(**L2**)Ni(η^2-NCPh)]



Scheme 2. Nickel-catalyzed amination of aryl chlorides with methylamine hydrochloride. Reactions were performed with 0.60 mmol of the aryl chloride. Yields of isolated products are given. [a] 2 mol% **C5**. [b] 3 mol% **C5**. [c] 4 mol% **C5**.

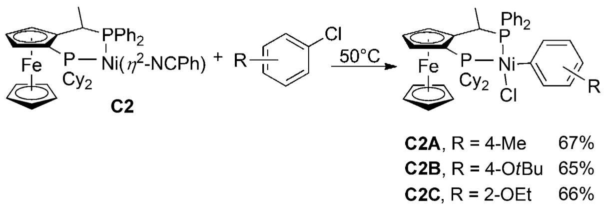


Scheme 3. Nickel-catalyzed amination of aryl chlorides with ethylamine hydrochloride. Reactions were performed with 0.60 mmol of the aryl chloride. Yields of isolated products are given. [a] 1 mol% **C2**. [b] 2 mol% **C2**. [c] 3 mol% **C2**.



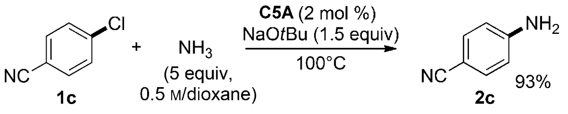
(2)

(**C2**) occurred cleanly to give the corresponding bisphosphine-ligated arylnickel chloride complexes [Eq. (3)].



(3)

The catalytic activity of the bisphosphine-ligated arylnickel chloride complexes was evaluated by conducting the coupling reaction of chlorobenzonitrile with ammonia under the standard conditions with 2 mol% of **C5A** as catalyst.[41] Compared with $\mathrm{Ni^0}$ nitrile complex **C5**, the arylnickel(II) chloride complex **C5A** was found to be an equally active catalyst for the amination of 4-chlorobenzonitrile with ammonia [Eq. (4)]. However, complexes **C2A–C** do not contain a benzonitrile moiety, and not all reactions catalyzed by these complexes occurred to full conversion. Yet, reactions catalyzed by **C2B** and **C2C** occurred to full conversion in the presence of 8 mol% of added benzonitrile (Table 2, entries 2 and 3). These results imply that the $\mathrm{Ni^{II}}$ complexes are catalytically active for the amination reaction and that benzonitrile acts as a ligand for the $\mathrm{Ni^0}$ species to improve activity or stability of this intermediate.[3]



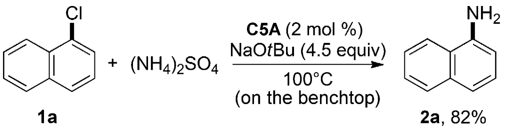
(4)

Many $\mathrm{Ni^{II}}$ complexes are stable in air. To test whether the aryl $\mathrm{Ni^{II}}$ halide complex would be a valuable, air-stable catalyst precursor for these amination reactions, we conducted the coupling reaction of 1-chloronaphthalene (**1a**) with ammonium sulfate catalyzed by complex **C5A** using standard Schlenk techniques with the catalyst weighed on the benchtop. Complex **C5A** was chosen as the catalyst because it contains a benzonitrile functional group to stabilize $\mathrm{Ni^0}$ intermediates. This reaction gave isolated 2-aminonaphthalene (**2a**) in 82% yield [Eq. (5)].

Table 2: Evaluation of the catalytic activity of [(**L2**)Ni(Ar)(Cl)] complexes.

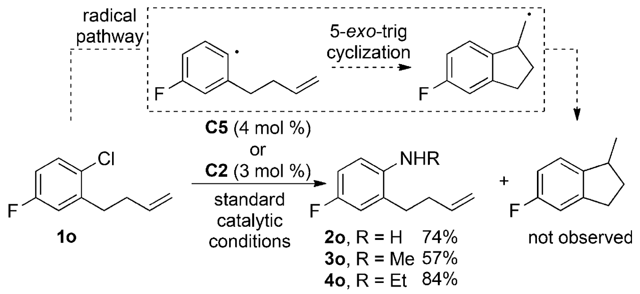
$$\text{Ar–Cl} + \underset{(1.2\ \text{equiv})}{\text{EtNH}_3\text{Cl}} \xrightarrow[\text{toluene, 80°C}]{[(\textbf{L2})\text{Ni(Ar)(Cl)}]\ \ \text{NaO}t\text{Bu (2.5 equiv)}} \text{Ar–NHEt}$$

Entry	Ar	Catalyst	Yield [%]	Additive
1	4-Me-C_6H_4	**C2A** (2 mol%)	82	–
2	4-O*t*Bu-C_6H_4	**C2B** (3 mol%)	95	PhCN (8 mol%)
3	2-OEt-C_6H_4	**C2C** (2 mol%)	84	PhCN (8 mol%)



(5)

To probe for the potential intermediacy of aryl radicals in the catalytic process, we conducted the coupling of a substrate (**1p**) that would rapidly undergo cyclization if an aryl radical were generated (Scheme 4). The coupling of this substrate with ammonium sulfate, methylamine hydrochloride, and ethylamine hydrochloride was conducted under standard catalytic conditions. In all cases, no cyclized product was observed by GC-MS analysis of the crude reaction mixture. Thus, it is unlikely that free aryl radicals are formed during the catalytic reaction. Together with the kinetic competence of the arylnickel(II) halide intermediates, these data imply that the reaction occurs by a catalytic cycle involving $\mathrm{Ni^0}$ and arylnickel(II) halide intermediates.



Scheme 4. Radical clock experiments.

In conclusion, we reported new $\mathrm{Ni^0}$ complexes containing a bisphosphine ligand and a side-bound benzonitrile ligand that catalyze the coupling of aryl electrophiles with ammonia with moderate catalyst loadings at short reaction times. We also demonstrated that ammonium sulfate can be used in place of ammonia to effect the same transformation, as can ammonium salts of the gaseous amines methylamine and ethylamine in the form of their easily handled hydrochloride salts. Preliminary mechanistic studies suggest that bisphosphine-ligated arylnickel(II) chloride complexes are intermediates in this transformation, and the lack of cyclization with a substrate that probes for aryl intermediates suggests that free aryl radicals are not formed during the course of the reaction. Further mechanistic analysis of these reactions will be the subject of future work.

Experimental Section

General procedure for the amination of aryl chlorides with ammonia: The aryl chloride (0.6 mmol), **C5** (0.012–0.024 mmol), NaO*t*Bu

(0.9 mmol), and the solution of ammonia in dioxane (0.5 M, 6 mL) were placed into a 25 mL round-bottom flask. The mixture was stirred at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL), filtered through a pad of Celite, and concentrated. The product was purified by extraction with aqueous acid or flash column chromatography.

General procedure for the amination of aryl chlorides with ammonium salts: The aryl chloride (0.6 mmol), **C2** or **C5** (0.012–0.024 mmol), NaO*t*Bu (1.5–2.7 mmol), the ammonium salt (0.9 mmol $(NH_4)_2SO_4$, 1.8 mmol $MeNH_3Cl$, 0.72 mmol $EtNH_3Cl$), and solvent (3 mL, 2-Me-THF or toluene) were placed into a 20 mL scintillation vial. The mixture was stirred at 80–100 °C for 7–12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL), filtered through a pad of Celite, and concentrated. The product was purified by flash column chromatography.

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