Room-Temperature Palladium-Catalyzed Amination of Aryl Bromides and Chlorides and Extended Scope of Aromatic C−N Bond Formation with a Commercial Ligand

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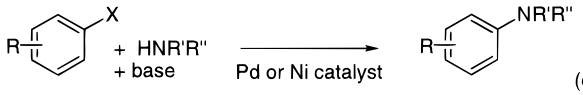
The reactions of aryl bromides with amines occurs at room temperature when using Pd(0) and P(*t*-Bu)$_3$ in a 1:1 ratio, and the reactions of aryl chlorides occur at room temperature or 70 °C. The arylation of indoles and the new arylation of carbamates also occur when using P(*t*-Bu)$_3$ as ligand.

The palladium-catalyzed amination of aryl halides[1−6] (eq 2) has become an important method for the synthesis of arylamines found in pharmaceuticals,[7,8] materials with important electronic properties,[9−21] and ligands for early metal catalysts.[22] Because of the importance of this synthetic method, there has been extensive effort to find catalysts that provide high turnover numbers,[23,24] fast reaction rates,[25,26] high functional group compatibility,[27] and increased scope of the aromatic C−N bond formation. Workers at Tosoh Co. reported that P(*t*-Bu)$_3$ provided high turnover numbers for the formation of arylpiperazines with excess ligand at 120 °C.[23] Our group has shown that a sterically hindered alkylphosphine prepared in one step allows for room-temperature amination of aryl halides and that another commercially available, sterically hindered alkylphosphine allows for the reaction of aryl chlorides with primary alkylamines under mild conditions.[25] Buchwald's group has recently reported that a P,N ligand containing a biphenyl backbone, which is prepared in three steps, generates a catalyst that leads to examples of room-temperature amination chemistry with aryl bromides and room-temperature Suzuki chemistry.[26]



(eq. 1)

In this paper, we show that conditions can be found for the amination of aryl bromides with arylamines and with secondary alkylamines at room temperature using commercially available P(*t*-Bu)$_3$. Moreover, this ligand allows for similar aminations to be conducted with unactivated aryl chlorides at 70 °C and in one case room temperature. In addition, aryl halides react with *tert*-butylcarbamate to provide Boc-protected anilines in the presence of P(*t*-Bu)$_3$ and Pd(dba)$_2$, and they react with azoles such as indole and pyrrole under mild conditions to provide *N*-arylazoles in high yield. Thus, many of the examples of mild amination reported previously with new ligands can be conducted with the simple commercially available P(*t*-Bu)$_3$ if certain procedures are followed. Our adoption of these procedures, which simply use a 1:1 ratio of ligand to palladium in most cases, stemmed from preliminary kinetic studies on the amination of *p*-tolyl bromide with *N*-methylbenzylamine using preformed Pd[P(*t*-Bu)$_3$]$_2$ as catalyst. We found that this reaction occurred rapidly at room temperature, in contrast to the elevated temperatures necessary for the reaction using a 4:1 ratio of P(*t*-Bu)$_3$ and Pd(OAc)$_2$.

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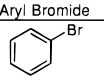
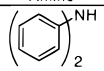
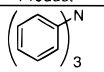
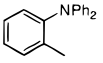
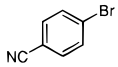
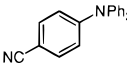
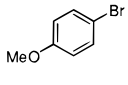
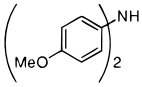
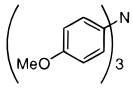
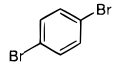
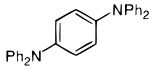
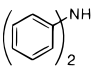
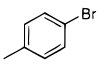
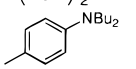
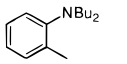
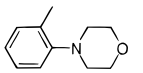
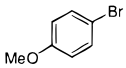
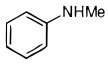
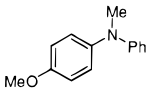
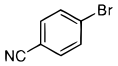
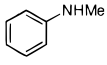
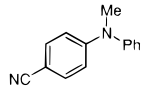
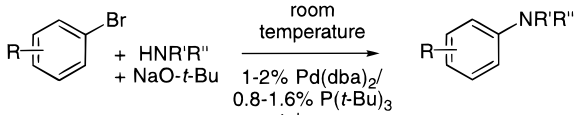
Table 1. Room-Temperature Reactions of Aryl Bromides with Amines Catalyzed by Pd(0)/P(*t*-Bu)$_3$

Entry	Aryl Bromide	Amine	Product	Cond.[a]	Yield[b]
1				1 % Pd 1 h	91 %
2				1 % Pd 4 h	97 %
3				1 % Pd 1 h	97 %
4				1 % Pd 1 h	94 %
5				1 % Pd 1 h	85 %
6				1 % Pd 1 h	87 %
7		HNBu$_2$		1 % Pd 4 h	90 %
8		HNBu$_2$		2 % Pd[c] 6 h	81 %
9				1 % Pd[c] 6 h	96 %
10				1 % Pd 6 h	99 %
11				1 % Pd 5 h	95 %

[a] Reactions run with 1 mmol of aryl halide in 1−2 mL of toluene solvent at room temperature. Pd(dba)$_2$ was used in combination with 0.8 equiv of ligand/Pd. [b]Isolated yields are an average of at least two runs. [c]Pd(OAc)$_2$ was used in place of Pd(dba)$_2$.

Results and Discussion

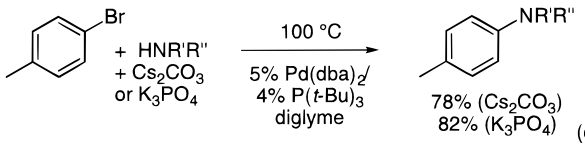
Room-Temperature Amination of Aryl Bromides and Mild Amination of Aryl Chlorides. The room-temperature amination of aryl bromides with arylamines and secondary alkylamines is summarized in eq 2, and specific examples are provided in Table 1. In most cases,



(eq. 2)

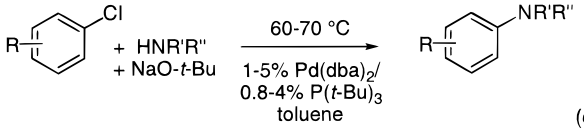
the use of Pd(dba)$_2$ led to faster reactions than the use of Pd(OAc)$_2$. However, in the singular case of reacting ortho-substituted aryl bromides with secondary amines, reactions initiated with Pd(OAc)$_2$ were faster. In all cases, the room-temperature chemistry was achieved by using 0.8 equiv of ligand/ Pd(dba)$_2$. The use of 4 equiv of ligand, or even 2 equiv in most cases, led to reactions that occurred only at elevated temperatures.

When 0.8 equiv of ligand was used, 1−2 mol % of catalyst led to complete conversion of the aryl bromide within hours. Reactions with diarylamines were the fastest, occurring within 15 min in some cases. Reactions of aniline with aryl bromides also occurred within hours at room temperature. In this case, small amounts of triarylamine were observed. Thus, catalysts bearing this ligand are remarkably efficient for the synthesis of diarylamines, but they are not suitable for the formation of polyanilines that would be free of cross-links directly from haloanilines. Reactions with secondary alkyl amines were the slowest, but the use of 1−2 mol % catalyst allowed room-temperature reactions to occur with unactivated aryl bromides within 6 h. Reaction between primary alkylamines and unhindered aryl halides was the one class of reaction that was not amenable to this room-temperature chemistry.



(eq. 3)

Systems with enolizable hydrogens, nitro groups, or labile esters are incompatible with the strongly basic NaO-*t*-Bu. Thus, Buchwald and Wolfe previously reported conditions using Cs_2CO_3 or K_3PO_4 for the amination of activated aryl bromides with BINAP as ligand and conditions involving the use of the commercially available but expensive ligand of Kumada and Hayashi for the reaction of unactivated aryl halides with secondary amines in the presence of Cs_2CO_3 or K_3PO_4 base.[26,27] Equation 3 shows that this class of reaction can be conducted under similar conditions when using 0.8 equiv of P(*t*-Bu)$_3$/Pd(dba)$_2$ as catalyst.



(eq. 4)

Finally, the use of aryl chlorides rather than bromides or iodides in cross-coupling chemistry has been actively pursued because of the low cost of these reagents.[26,28−42] P(*t*-Bu)$_3$ complexes of palladium have allowed for the palladium-catalyzed arylation of ketones and malonates at room temperature[26,43] and for Suzuki and Heck chemistry to be conducted with chlorides at mild temperatures.[35,36] Our optimized conditions for aromatic amination allow for the formation of dialkylanilines, diarylamines, or triarylamines from aryl chlorides at 70 °C with 1−5 mol % catalyst in yields that are similar to those observed at room temperature with bromides. The reaction of activated aryl chlorides with secondary amines occurred at room temperature. Remarkably, the reaction

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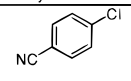
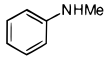
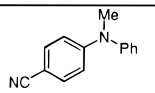
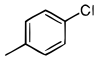
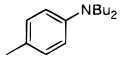
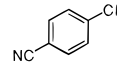
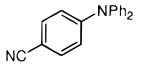
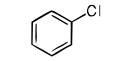
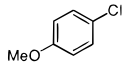
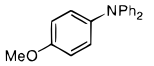
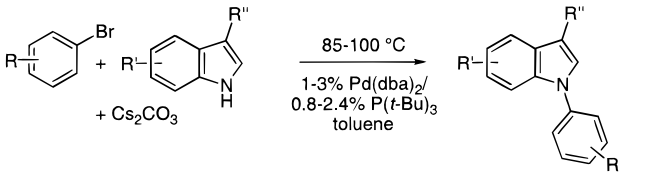
Table 2. Reactions of Aryl Chlorides with Amines Catalyzed by Pd(0)/P(*t*-Bu)$_3$

Entry	Aryl Chloride	Amine	Product	Cond.[a]	Yield[b]
1				1 % Pd RT 12 h	90 %
2		$HNBu_2$		1 % Pd 70 °C 12 h	88 %
3		$HNPh_2$		1 % Pd RT 5.5 h	89 %
4		H_2NPh	$HNPh_2$	5 % Pd, RT 25 h	75 %
5		$HNPh_2$		5 % Pd 70 °C 16 h	97 %

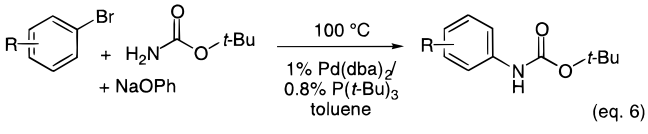
[a] Reactions run with 1 mmol of aryl halide in 1−2 mL of toluene solvent. $Pd(dba)_2$ was used in combination with 0.8 equiv of ligand/Pd. [b]Isolated yields are an average of at least two runs.

of aniline with even the unactivated phenyl chloride occurred at room temperature and was complete in 1 day when 5 mol % of palladium was used. As for aryl bromides, reaction of primary alkylamines with unhindered aryl chlorides was the one class of reaction that was not amenable to chemistry with this ligand system. This reaction is currently best conducted with ligands developed at Novartis using procedures reported by our group previously.[25]

Extended Scope of C−N Bond Formation. The reductive elimination to form arylamines, ethers, and sulfides is sensitive to the nucleophilicity of the heteroatom bound to palladium.[44−47] For example, the reductive elimination of *N*-arylazoles is slow,[48] and the reductive elimination of *N*-arylcarbamates has not been observed. However, we recently observed directly that sterically hindered alkylphosphines accelerated reductive elimination of aryl ethers.[49] Thus, it seemed likely that optimized conditions with P(*t*-Bu)$_3$ as ligand might increase the scope of aromatic C−N bond formation to examples that are hampered by slow reductive elimination. This potential was realized as shown in eqs 5 and 6 and Tables 3 and 4.



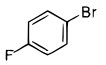
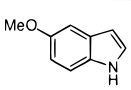
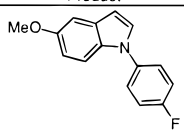
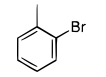
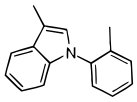
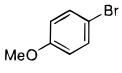
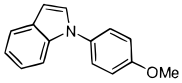
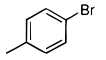
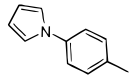
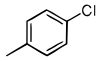
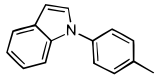
(eq. 5)



(eq. 6)

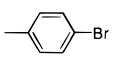
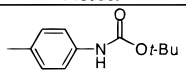
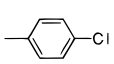
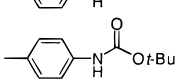
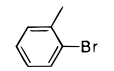
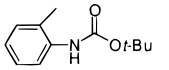
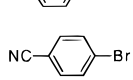
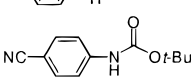
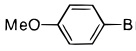
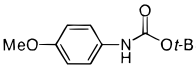
The catalyst system involving P(*t*-Bu)$_3$ as ligand allows for much milder arylation of azoles than the combination

Table 3. Reactions of Aryl Halides with Azoles Catalyzed by Pd(0)/P(*t*-Bu)$_3$

Entry	Aryl Halide	Azole	Product	Cond.[a]	Yield[b]
1				4 % Pd 12 h	72 %
2				3 % Pd 12 h	88 %
4				3 % Pd 6 h	83 %
5				3 % Pd 6 h	77 %
6				5 % Pd 12 h	64 %

[a] Reactions were run with 1 mmol of azole in 1−2 mL of toluene solvent at 100 °C. $Pd(dba)_2$ was used in combination with 0.8−1.0 equiv of ligand/Pd. [b]Isolated yields are an average of at least two runs.

Table 4. Reactions of Aryl Halides with *tert*-Butyl Carbamate Catalyzed by Pd(0)/2P(*t*-Bu)$_3$

Entry	Aryl Halide	Product	Cond.[a]	Yield[b]
1			2.5 % Pd 2 h	80 %
2			4 % Pd 24 h	59 %
3			2.5 % Pd 2 h	86 %
4			2.5 % Pd 1.5 h	83 %
5			4 % Pd 4 h	62 %

[a] Reactions run with 1 mmol of aryl halide and 1.5 mmol *tert*-butyl carbamate in 3 mL of toluene solvent at 100 °C. $Pd(dba)_2$ was used in combination with 2.0 equiv of ligand/Pd. [b]Isolated yields are an average of at least two runs.

of $Pd(OAc)_2$ and DPPF we reported previously.[48] The reaction between indole or pyrrole and unhindered aryl halides, either activated or unactivated, occurred at 100 °C after 12 h. The use of Cs_2CO_3 as base, rather than NaO-*t*-Bu, was crucial to the success of this reaction. Perhaps a high concentration of azolyl anion leads to palladium ate complexes as we described previously.[48] When reacted with simple indoles, hindered aryl halides such as 2-bromotoluene generated two isomeric products and one product from the addition of two aryl groups. We assigned these materials to the products of arylation at the nitrogen, at the C3-position and both sites. Thus, reaction of 2-bromotoluene with 3-methylindole occurred cleanly to give the N-arylation product in high yield.

Finally, an optimized catalyst system allows for the use of a convenient ammonia equivalent, *tert*-butylcarbamate, to form Boc-protected anilines from aryl halides. In this case, the use of NaOPh as base was crucial to the success of this reaction. We reported the synthesis of

(44) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860.
(45) Barañano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937−2938.
(46) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232−8245.
(47) Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504.
(48) Mann, G.; Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 827−828.
(49) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3715−6.

palladium phenoxide intermediates in the formation of aryl ethers,[49] and it was the clean reaction of these compounds with carbamates[50] that led to our use of this base. Reactions that employed Cs_2CO_3 or NaO-*t*-Bu as base for the coupling of *tert*-butylcarbamate with aryl bromides gave low conversions. In contrast to the C−N bond formations described above, the use of a 2:1 ratio of ligand/palladium was optimal, presumably because the rate for oxidative addition is less important than other steps of the cycle in dictating the kinetics of this process. For these reactions, toluene proved to be the most effective solvent.

Conclusions

In general, we have shown that the use of P(*t*-Bu)$_3$ as ligand in a 0.8:1 ratio with Pd(dba)$_2$ allows for all the room temperature aminations reported previously with new ligands and for an increase in the scope of nitrogen substrates that react with aryl halides. The reason for the rate acceleration with low ligand/palladium ratios is complex and under investigation. It is likely that the reaction rates are inverse first order in phosphine and a ratio that is less than 2:1 ensures a low concentration of free phosphine. The original observation that led to this study, the room-temperature amination when using preformed Pd[P(*t*-Bu)$_3$]$_2$, suggests that a 2:1 ratio would be optimal. However, loss of palladium during the reaction as either insoluble material or as complexes containing only one phosphine ligand will generate free phosphine and will lead to rate decreases. Perhaps this explains the benefits of a ratio that is substantially less than 2:1. Pd(dba)$_2$ does not catalyze these reactions.

Experimental Section

General Methods. All reactions were assembled in the drybox in sealed reaction vessels and were reacted either at room temperature or were heated in an oil bath. Toluene solvent was distilled from sodium/benzophenone ketyl. Diethylene glycol dimethyl ether was purchased in anhydrous grade from Aldrich and was used in the drybox. Palladium bis(dibenzylideneacetone) was prepared according to literature procedures,[52] and the palladium content was determined by elemental analysis. Sodium *tert*-butoxide and cesium carbonate were purchased from Aldrich and were used in a drybox. Sodium phenoxide was prepared by deprotonation of phenol with sodium hydride in THF followed by precipitation with pentane. All amines were used as received and were *not* degassed prior to use.

General Prodecure for the Reaction of Amines with Aryl Halides. In a drybox, aryl halide (1.00−1.10 mmol), amine (1.00 mmol), Pd(dba)$_2$ or Pd(OAc)$_2$ (0.01−0.02 mmol), tri-*tert*-butylphosphine (1.6−3.2 mg, 0.008−0.016 mmol, 0.8 eq/Pd), and sodium *tert*-butoxide (144 mg, 1.50 mmol) were weighed directly into a screw cap vial. A stir bar was added followed by 1.0−2.0 mL of toluene to give a purple mixture. The vial was removed from the drybox, and the mixture was stirred at room temperature. The reaction was monitored by thin-layer chromatography or GC. After complete consumption of starting materials, the resulting thick brown suspension was adsorbed onto silica gel and purified by flash chromatography.

Triphenylamine.[53] The above general procedure was followed using bromobenzene (171 mg, 1.10 mmol) and diphenylamine (169 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 1 h, the reaction mixture was adsorbed onto silica gel and chromatographed using 5% ethyl acetate/hexanes to give 236 mg (91%) of triphenylamine as a white solid: ^{1}H NMR (500 MHz, C_6D_6) δ 7.17−6.99 (m, 12 H), 6.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 148.4, 129.5, 124.6, 122.9.

***N*-(2-Tolyl)diphenylamine.**[54] The above general procedure was followed using 2-bromotoluene (188 mg, 1.10 mmol) and diphenylamine (169 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.5 mL of toluene. After 4 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 2.5% ethyl acetate/hexanes to give 247 mg (95%) of *N*-(2-tolyl)diphenylamine as a colorless oil that crystallized to a white solid: ^{1}H NMR (500 MHz, C_6D_6) δ 7.05−6.96 (m, 12 H), 6.78 (tt, J = 7.25, 1.30 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 148.0, 146.0, 136.6, 132.0, 129.9, 129.4, 127.7, 126.1, 122.0, 121.8, 18.7.

***N*-(4-Cyanophenyl)diphenylamine.**[54] The above general procedure was followed using 4-bromobenzonitrile (188 mg, 1.03 mmol) and diphenylamine (169 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.5 mL of toluene. After 1 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 50% toluene/hexanes to give 263 mg (97%) of *N*-(4-cyanophenyl)diphenylamine as a white solid: ^{1}H NMR (500 MHz, C_6D_6) δ 6.97 (t, J = 8 Hz, 4H), 6.92 (d, J = 8.9 Hz, 2H), 6.86−6.83 (m, 6H), 6.56 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.3, 146.6, 133.2, 129.9, 126.1, 124.9, 120.5, 119.4, 104.0.

The above general procedure was followed using 4-chlorobenzonitrile (138 mg, 1.00 mmol) and diphenylamine (169 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 2.0 mL of toluene. After 5.5 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 50% toluene/hexanes to give 242 mg (90%) of *N*-(4-cyanophenyl)diphenylamine as a white solid.

Tri(4-methoxyphenyl)amine.[55] The above general procedure was followed using 4-bromoanisole (187 mg, 1.00 mmol) and di(4-methoxyphenyl)amine (229 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.5 mL of toluene. After 1 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 5% ethyl acetate/hexanes to give 321 mg (96%) of tri(4-methoxyphenyl)amine as a white solid: ^{1}H NMR (500 MHz, C_6D_6) δ 7.08 (d, J = 10 Hz, 6 H), 6.73 (d, J = 10 Hz, 6H), 3.31 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.7, 142.6, 125.3, 115.0, 55.0.

***N,N,N′,N′*-Tetraphenyl-1,4-phenylenediamine.**[53] The above general procedure was followed using 1,4-dibromobenzene (130 mg, 0.55 mmol) and diphenylamine (169 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.5 mL of toluene. After 1 h, the reaction mixture was adsorbed onto silica gel and chromatographed using 30% toluene/hexanes to give 200 mg (97%) of *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine as a white solid. This solid was recrystallized from ethy acetate to afford 168 mg (81%): ^{1}H NMR (500 MHz, C_6D_6) δ 7.10 (d, J = 7.5 Hz, 8H), 7.03 (t, J = 8 Hz, 8H), 6.95 (s, 4H), 6.81 (t, J = 7.2 Hz, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 148.4, 143.4, 129.6, 125.8, 124.2, 122.8.

Diphenylamine. The above general procedure was followed using bromobenzene (157 mg, 1.00 mmol) and aniline (93 mg, 1.00 mmol) with 1 mol % Pd(dba)$_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.5 mL of toluene. After 1 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 5% ethyl acetate/hexanes to give 145 mg (86%) of diphenylamine as a gray solid: ^{1}H NMR (500 MHz, C_6D_6) δ 7.11−7.08 (m, 4H), 6.85−6.80 (m, 6H), 4.97 (br s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 143.6, 129.5, 121.1, 118.2. In addition, 21 mg (8%) of triphenylamine was isolated.

The above general procedure was followed using chlorobenzene (135 mg, 1.20 mmol) and aniline (93 mg, 1.00 mmol) with 5 mol % Pd(dba)$_2$ and 4 mol % tri-*tert*-butylphosphine in 2.0 mL of toluene. After 25 h, the reaction mixture was adsorbed

(50) Hartwig, J. F. Unpublished results.
(51) This ligand is commercially available from Strem.
(52) Ukai, T.; Kawazura, H.; Ishii, Y.; Bounet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(53) Paine, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1496−1502.
(54) Nelson, R. F.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 3925−3930.
(55) Walters, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999−6002.

onto silica gel and chromatographed with 2.5% ethyl acetate/hexanes to give 126 mg (75%) of diphenylamine as an off-white solid.

***N*-(4-Methoxyphenyl)diphenylamine.**[53] The above general procedure was followed using 4-chloroanisole (127 mg, 1.00 mmol) and diphenylamine (169 mg, 1.00 mmol) with 5 mol % $Pd(dba)_2$ and 4 mol % tri-*tert*-butylphosphine in 2.0 mL of toluene. After 16 h at 70 °C, the reaction mixture was adsorbed onto silica gel and chromatographed with 2% ethyl acetate/hexanes to give 267 mg (97%) of *N*-(4-methoxyphenyl)-diphenylamine as a white solid: ^{1}H NMR (500 MHz, C_6D_6) δ 7.10−6.99 (m, 10 H), 6.81 (t, J = 7 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 3.28 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 156.8, 148.8, 141.2, 129.4, 127.7, 123.4, 122.2, 115.2, 54.94.

***N*-(2-Methylphenyl)morpholine.**[56] The above general procedure was followed using 2-bromotoluene (171 mg, 1.10 mmol) and morpholine (87 mg, 1.00 mmol) with 1 mol % $Pd(OAc)_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 6 h, the reaction mixture was adsorbed onto silica gel and chromatographed using 5% ethyl acetate/hexanes to give 179 mg (>99%) of *N*-(2-methylphenyl)morpholine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d J = 7.4 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 3.86 (t, J = 4.5 Hz, 4H), 2.92 (t, J = 4.5 Hz, 4H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 132.7, 131.2, 126.7, 123.5, 119.0, 67.5, 52.4, 17.8.

***N*-(4-Methoxyphenyl)-*N*-methylaniline.**[42] The above general procedure was followed using 4-bromoanisole (187 mg, 1.00 mmol) and *N*-methylaniline (107 mg, 1.00 mmol) with 1 mol % $Pd(dba)_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 6 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 5% ethyl acetate/hexanes to give 218 mg (>99%) of *N*-(4-methoxyphenyl)-*N*-methylaniline: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.9, 7.0 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.80 (t, J = 7.0 Hz, 1H), 3.83 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 149.8, 142.4, 128.9, 126.1, 118.5, 115.9, 114.8, 55.5, 40.4.

***N*-(4-Cyanophenyl)-*N*-methylaniline.**[57] The above general procedure was followed using 4-bromobenzonitrile (187 mg, 1.00 mmol) and *N*-methylaniline (107 mg, 1.00 mmol) with 1 mol % $Pd(dba)_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 6 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 10% ethyl acetate/hexanes to give 201 mg (97%) of *N*-(4-cyanophenyl)-*N*-methylaniline: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.42 (m, 4H), 7.27 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.3 Hz, 2H), 6.73 (d, J = 9.0 Hz, 2H), 3.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 146.8, 133.1, 130.1, 126.4, 126.2, 120.2, 114.0, 99.4, 40.1.

The above general procedure was followed using 4-chlorobenzonitrile (137 mg, 1.00 mmol) and *N*-methylaniline (107 mg, 1.00 mmol) with 1 mol % $Pd(dba)_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 12 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 10% ethyl acetate/hexanes to give 191 mg (92%) of *N*-(4-cyanophenyl)-*N*-methylaniline.

***N*,*N*-Dibutyl-*p*-toluidine.**[58] The above general procedure was followed using 4-bromotoluene (171 mg, 1.00 mmol) and dibutylamine (129 mg, 1.00 mmol) with 1 mol % $Pd(dba)_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 4 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 2% ethyl acetate/hexanes to give 207 mg (95%) of *N*,*N*-dibutyl-*p*-toluidine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, J = 8.7 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 3.23 (t, J = 7.6 Hz, 4H), 2.24 (s, 3H), 1.58−1.52 (m, 4H), 1.34 (sept, J = 7.4 Hz, 4H), 0.95 (t, J = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 129.7, 124.5, 112.5, 51.1, 29.6, 20.5, 20.2, 14.0.

The above general procedure was followed using 4-chlorotoluene (126 mg, 1.00 mmol) and dibutylamine (129 mg, 1.00 mmol) with 1 mol % $Pd(dba)_2$ and 0.8 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 4 h at 70 °C, the reaction mixture was adsorbed onto silica gel and chromatographed with 2% ethyl acetate/hexanes to give 196 mg (90%) of *N*,*N*-dibutyl-*p*-toluidine.

***N*,*N*-Dibutyl-*p*-toluidine Using Cs_2CO_3 or K_3PO_4 as Base.** The above general procedure was followed using 4-bromotoluene (171 mg, 1.00 mmol) and dibutylamine (162 mg, 1.25 mmol) with 5 mol % $Pd(dba)_2$, 4 mol % tri-*tert*-butylphosphine, and cesium carbonate (489 mg, 1.50 mmol) or K_3PO_4 (318 mg, 1.50 mmol) in 1.0 mL of diglyme. After 12 h at 100 °C, the reaction mixture was adsorbed onto silica gel and chromatographed with 2% ethyl acetate/hexanes to give 179 mg (82%) of *N*,*N*-dibutyl-*p*-toluidine.

***N*,*N*-Dibutyl-*o*-toluidine.**[59] The above general procedure was followed using 2-bromotoluene (171 mg, 1.00 mmol) and dibutylamine (129 mg, 1.00 mmol) with 2 mol % $Pd(OAc)_2$ and 1.6 mol % tri-*tert*-butylphosphine in 1.0 mL of toluene. After 6 h, the reaction mixture was adsorbed onto silica gel and chromatographed with 2% ethyl acetate/hexanes to give 181 mg (83%) of *N*,*N*-dibutyl-*o*-toluidine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 6.97 (t, J = 7.8 Hz, 1H), 2.91 (t, J = 7.5 Hz, 4H), 2.30 (s, 3H), 1.41−1.37 (m, 4H), 1.27 (sept, J = 7.3 Hz, 4H), 0.87 (t, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 135.0, 130.9, 126.0, 123.1, 122.3, 53.9, 29.6, 20.5, 18.3, 14.0.

General Procedure for Reaction of Azoles with Aryl Halides. In a drybox, aryl halide (1.00−1.20 mmol), azole (1.00 mmol), $Pd(dba)_2$ (17−23 mg, 0.03−0.04 mmol, 3−4 mol %), tri-*tert*-butylphosphine (4.8−8.1 mg, 0.024−0.040 mmol, 0.8−1.0 equiv/Pd), and cesium carbonate (489−554 mg, 1.50−1.70 mmol) were weighed directly into a 1 dram screw cap vial. A stir bar was added followed by 1.0−2.0 mL of toluene. The vial was removed from the drybox, and the mixture was stirred as rapidly as possible with a magnetic stir plate at 100 °C. The reaction was monitored by GC, and after the consumption of starting materials, the reaction mixture was adsorbed onto silica gel and purified by chromatography.

***N*-(4-Fluorophenyl)-5-methoxyindole.**[60] The above general procedure was followed using 4-flouorobromobenzene (210 mg, 1.20 mmol), 5-methoxyindole (147 mg, 1.00 mmol), 4 mol %$Pd(dba)_2$, 4 mol % tri-*tert*-butylphosphine, and cesium carbonate (1.70 mmol) in 1.0 mL of toluene. After 12 h at 100 °C, the reaction mixture was adsorbed onto silica gel and chromatographed with 5% ethyl acetate/hexanes to give 212 mg (88%) of *N*-(4-fluorophenyl)-5-methoxyindole. Recrystallization from 5% ethyl acetate/hexanes gave 174 mg (72%) of pure product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49−7.39 (m, 3H), 7.28 (d, J = 3.2 Hz, 1H), 7.22 (t, J = 8.6 Hz, 1H), 7.18 (d, J = 2.3 Hz, 1H), 6.93 (dd, J = 9.0, 1.6 Hz, 1H), 6.64 (d, J = 3.1 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (76 Mz, $CDCl_3$) δ 160.9 (d, J = 244.0 Hz)154.4, 136.0, 131.3, 129.7, 128.4, 125.76 (d, J = 8.5 Hz), 116.38 (d, J = 23 Hz), 112.6, 11.0, 103.2, 102.7, 55.76.

***N*-(2-Methylphenyl)-3-methylindole.** The above general procedure was followed using 2-bromotoluene (205 mg, 1.20 mmol), 3-methylindole (131 mg, 1.00 mmol), 3 mol % $Pd(dba)_2$, 2.4 mol % tri-*tert*-butylphosphine, and cesium carbonate (1.70 mmol) in 1.0 mL of toluene. After 12 h at 100 °C, the reaction mixture was adsorbed onto silica gel and chromatographed with 5% ethyl acetate/hexanes to give 195 mg (88%) of *N*-(2-methylphenyl)-3-methylindole: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (m, 1H), 7.46 (m, 2H), 7.40 (m, 2H), 7.28 (m, 2H), 7.15 (m, 1H), 7.06 (s, 1H), 2.53 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (76 MHz, $CDCl_3$) δ 138.4, 137.1, 135.7, 131.1, 128.6, 128.1, 127.8, 126.6, 126.2, 121.9, 119.3, 118.9, 111.6, 110.4, 17.7, 9.6. HRMS(EI): m/z calcd for $C_{16}H_{15}N$ 221.1204, obsd 221.1202.

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***N*-(4-Methoxyphenyl)indole.**[61] The above general procedure was followed using bromoanisole (138 μL, 1.10 mmol) and indole (119 mg, 1.02 mmol) with 3 mol % $Pd(dba)_2$, 3 mol % tri-*tert*-butylphosphine, and cesium carbonate (1.70 mmol) in 2 mL of toluene. After 6 h at 100 °C, the reaction mixture was adsorbed onto silica gel and flash chromatographed with 5% ethyl acetate/hexanes to give 163 mg (72%) of product as a colorless oil that was pure by ^{1}H NMR. Recrystallization from ethanol gave a white, crystalline solid: mp 59.5−60.5 °C (lit.[61] mp 57−58 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.84 Hz, 1H), 7.52 (d, J = 7.93 Hz, 1H), 7.45 (d, J = 7.80 Hz, 2H), 7.32 (d, J = 3.4 Hz, 2H), 7.26 (t, J = 6.90 Hz, 1H), 7.21 (t, J = 7.40 Hz, 1H), 7.08 (d, J = 8.01 Hz, 2H), 6.71 (d, J = 3.11 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 136.3, 132.8, 128.9, 128.2, 125.9, 122.1, 121.0, 120.0, 114.7, 110.3, 102.8, 55.5.

***N*-(4-Methylphenyl)pyrrole.**[62] The above general procedure was followed using bromotoluene (135 μL, 1.10 mmol) and pyrrole (69 μL, 1.00 mmol) with 3 mol % $Pd(dba)_2$, 3 mol % tri-*tert*-butylphosphine, and cesium carbonate (1.70 mmol) in 2.0 mL of toluene. After being heated at 100 °C for 6 h, the reaction mixture was loaded on silica gel and flash chromatographed with 2.5% ethyl acetate/hexanes to give 135 mg (86%) of product as a pinkish solid that was pure by ^{1}H NMR. Recrystallization from ethanol gave a colorless, crystalline solid: mp 81.5−83 °C (lit.[62] mp 82−83 °C);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 8.15 Hz, 2H), 7.23 (d, J = 8.44 Hz, 2H), 7.08 (brs, 2H), 6.36 (brs, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 135.3, 130.0, 120.5, 119.4, 110.0, 20.8.

***N*-(4-Methylphenyl)indole.**[59] The above general procedure was followed using 4-chlorotoluene (126 mg, 1.00 mmol), indole (117 mg, 1.00 mmol), 4 mol % $Pd(dba)_2$, 4 mol % tri-*tert*-butylphosphine, and cesium carbonate (1.50 equiv) in 1.0 mL of toluene. After 12 h at 100 °C, the reaction mixture was adsorbed onto silica gel and chromatographed with 10% ethyl acetate/hexanes to give 137 mg (66%) of *N*-(4-methylphenyl)-indole: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.34−7.33 (m, 3H), 7.23 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 136.4, 136.1, 130.2, 129.3, 128.2, 124.4, 122.3, 121.2, 120.3, 110.6, 103.3, 21.1.

General Procedure for Carbamate Arylation. In a drybox, a small round-bottom flask was charged with $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 2.5 mol %), *t*-Bu_3P (10.1 mg, 0.050 mmol), sodium phenoxide (174 mg, 1.50 mmol), aryl halide (1.00 mmol), and *tert*-butyl carbamate (176 mg, 1.50 mmol). Toluene (3 mL) was added to give a thick suspension. The flask was sealed with a septum, removed from the drybox, and placed in an oil bath preheated to 100 °C. The reaction was vigorously stirred until the aryl halide was completely consumed as judged by GC analysis. The reaction was then worked up as described below. The pure product was obtained by flash chromatography.

***t*-Butyl *N*-(4-Tolyl)carbamate.**[63] The above general procedure was followed using 4-bromotoluene (123 μL, 1.00 mmol). After 2 h, the toluene was removed under reduced pressure and the residue loaded on silica gel. The crude material was flash chromatographed eluting with 1:1 CH_2Cl_2/hexanes (150 mL) and then 70:30 CH_2Cl_2/hexanes. A pale yellow oil that crystallized upon standing was isolated (177 mg, 85%). Recrystallization from hexanes gave colorless needles: mp 92−92.5 °C (lit.[63] mp 91−93 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (br d, 8.3 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 6.41 (br s, 1H), 2.30 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 135.7, 132.5, 129.4, 118.7, 80.3, 28.3, 20.7; FTIR (KBr disk) 3356, 1699, 1529, 1240, 1157 cm^{-1}.

The above general procedure was followed using 4-chlorotoluene (118 μL, 1.00 mmol), 4 mol % $Pd(dba)_2$, and 8 mol % tri-*tert*-butylphosphine. After 24 h, *tert*-butyl *N*-(4-tolyl)carbamate was isolated as described above to give 122 mg (59% yield) of product.

***t*-Butyl *N*-(2-Tolyl)carbamate.**[64] The above general procedure was followed using 2-bromotoluene (120 μL, 1.00 mmol). After 2 h, the toluene was removed under reduced pressure and the residue loaded on silica gel. The crude material was flash chromatographed eluting with 1:1 CH_2Cl_2/hexanes. A pale yellow oil that crystallized upon standing was isolated (178 mg, 86%). Recrystallization from hexanes gave colorless needles: mp 82−83 °C (lit.[64] mp 82 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (br s, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.4 Hz, 1H), 6.99 (t, J = 8.3 Hz, 1H), 6.27 (br s, 1H), 2.26 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 136.4, 130.3, 127.3, 126.8, 123.7, 121.1, 80.4, 28.3, 17.6; FTIR (KBr disk) 3261, 1696, 1510, 1371, 1155 cm^{-1}.

***t*-Butyl *N*-(4-Cyanophenyl)carbamate.** The above general procedure was followed using 4-bromobenzonitrile (186 mg, 1.02 mmol). After 1.5 h, the reaction was diluted with CH_2Cl_2 and extracted with 10% NaOH solution to remove phenol, which coelutes with the product. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was flash chromatographed eluting with 70:30 CH_2Cl_2/hexanes (200 mL) and then CH_2Cl_2. A pale yellow solid was isolated (193 mg, 87%). Recrystallization from toluene/hexanes gave colorless needles: mp 120−120.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 6.74 (br s, 1H), 1.53 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 142.6, 133.2, 119, 118.1, 105.8, 81.7, 28.2; FTIR (KBr disk) 3368, 2226, 1692, 1510, 1239, 1151 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.05; H, 6.47; N, 12.83. Found: C, 65.80; H, 6.43; N, 12.77.

***tert*-Butyl *N*-(4-Methoxyphenyl)carbamate.**[65] The above general procedure was followed using 4-bromoanisole (123 μL, 0.98 mmol), 4 mol % $Pd(dba)_2$, and 8 mol % tri-*tert*-butylphosphine. Upon completion of the reaction, the reaction was diluted with CH_2Cl_2 and extracted with 10% NaOH solution to remove phenol which coelutes with the product. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was flash chromatographed eluting with 70:30 CH_2Cl_2/hexanes. A pale yellow, waxy solid was isolated (145 mg, 66%). Recrystallization from hexanes gave colorless needles: mp 92.5−93 °C (lit.[65] mp 92−94 °C); ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.28 (br s, 2H), 6.84 (d, J = 9.4 Hz, 2H), 6.36 (br s, 1H), 3.79 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 153.1, 131.4, 120.4, 114.0, 80.1, 55.4, 28.3; FTIR (KBr disk) 3365, 1694, 1522, 1246, 1161 cm^{-1}.

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