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Palladium-Catalyzed Amidation of Aryl Halides Using 2-Dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl as Ligands

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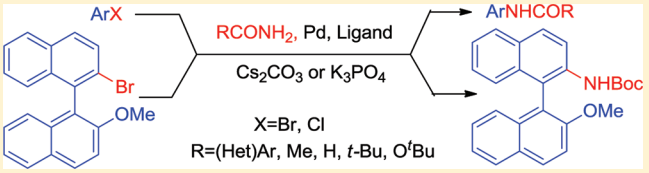
Supporting Information

ABSTRACT: Palladium-catalyzed intermolecular C−N bond-forming reactions between aryl halides and amides are described using 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl, which is both bulky and electron-rich, as the ligand. A variety of amides, including aliphatic and aromatic primary amides, lactams, and carbamates, were viable substrates for the amidation, which exhibited good functional group compatibility. By tuning the substituents at the 2,2′-position of 1,1′-binaphthyl of the ligand, the palladium-catalyzed amidation of bulky aryl halides was realized and this coupling reaction was used to synthesize 2-amino-2′-methoxy-1,1′-binaphthyl in high yield.



INTRODUCTION

N-Arylamides are key structural motifs for many natural products as well as important intermediates for primary arylamines.[1] As a more efficient and facile method, the transition metal-catalyzed coupling reaction of aryl halides or pseudo halides and amides has been attractive for many years.[2] Since Shakespeare's first report on Pd-catalyzed amide arylation,[3] many Pd-based catalytic systems have been developed for the coupling of amides with aryl sulfonates,[4] aryl bromides,[5] and more recently, aryl chlorides,[6] which proved to be useful to synthetic chemists.[7] However, relative to the amination reaction,[8] less efficient or general Pd-based catalytic systems were developed for the amidation of aryl halides, which was more difficult because: 1) the amides are less nucleophilic due to their electron-withdrawing carbonyl groups; 2) the amidates tend to bind with palladium in a κ^2-fashion, and the resultant metal−ligand bond was expected to inhibit the reactions.[9] Recently, studies revealed that bidentate phosphine and monodentate biarylphosphine ligands bearing a substituent *ortho* to the phosphorus can promote the catalytic amidation of aryl halides through inhibiting the formation of the κ^2-amidate complex by the steric hindrance.[5b,6a] 2-Dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl, the monodentate phosphines with a binaphthyl skeleton and an tunable alkoxy group at the adjacent position of phosphorus atom, incline to form hemilabile coordination with the palladium center,[10] which may inhibit the formation of a κ^2-amidate complex and thus promote the reductive elimination of the palladium complex with an amidate ligand. Herein, we report the efficiency of 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl as ligands in palladium-catalyzed amidation of aryl halides.

RESULTS AND DISCUSSION

We have reported a concise synthesis of a series of 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl as the bulky and electron-rich ligands and their high activity in Pd-catalyzed amination reactions.[11] For example, the coupling of bromobenzene with aniline employing $Pd(dba)_2$/2-di-*tert*-butyl phosphino-2′-isopropoxy-1,1′-binaphthyl (**L1**) system gave diphenylamine in good yield even at room temperature. We initiated our investigation by examining the coupling reaction of bromobenzene and benzamide with $Pd(dba)_2$/2-di-*tert*-butyl phosphino-2′-isopropoxy-1,1′-binaphthyl as the catalyst, *t*-BuONa as the base and toluene as the solvent at room temperature. Unfortunately, no product was detected. Increasing the reaction temperature to 100 °C, only a trace amount of product was observed. However, the coupling reaction occurred in 78% yield when the solvent was switched to *tert*-BuOH (Table 1, entry 2). We then examined the effects of solvents, bases, Pd sources and ligands in the coupling reaction at 100 °C (bath temperature). The results are summarized in Table 1. We found that *t*-BuOH was the best among the tested solvents (Table 1, entries 1−7); K_3PO_4, *t*-BuONa, KOH were found to be less effective than Cs_2CO_3 as a base (Table 1, entries 2−4 and 7); and $Pd(dba)_2$ was superior to $Pd(OAc)_2$ as the Pd source (Table 1, entry 8). When using $Pd(dba)_2$ as a precatalyst, **L1** as a ligand, Cs_2CO_3 as a base, and *t*-BuOH as a solvent, the amidation of bromobenzene gave a 95% yield (Table 1, entry 4). Consequently, the structure of 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl can promote the palladium-catalyzed amidations. Next, other ligands of monodentate phosphines with a heteroatom at the adjacent position of phosphorus atom were explored. When the substituent of

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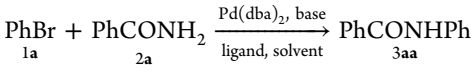
Table 1. Optimization of Reaction Conditions for the Amidation of Bromobenzene with Benzamide[a]



entry	ligand	base	solvent	yield[b] (%)
1	**L1**	*t*-BuONa	toluene	trace
2	**L1**	*t*-BuONa	*t*-BuOH	78
3	**L1**	K_3PO_4	*t*-BuOH	64
4	**L1**	Cs_2CO_3	*t*-BuOH	95
5	**L1**	Cs_2CO_3	1,4-dioxane	25
6	**L1**	Cs_2CO_3	toluene	15
7	**L1**	KOH	*t*-BuOH	75
8	**L1**	Cs_2CO_3	*t*-BuOH	0[c]
9	**L2**	Cs_2CO_3	*t*-BuOH	22
10	**L3**	Cs_2CO_3	*t*-BuOH	46
11	**L4**	Cs_2CO_3	*t*-BuOH	36

[a]Reaction conditions: bromobenzene (1.0 mmol), benzamide (1.2 mmol), base (1.5 mmol), $Pd(dba)_2$ (2 mmol %), ligand (3 mmol %), solvent (4.0 mL), 100 °C (bath temperature), 20 h. [b]Isolated yields (average of two runs). [c]$Pd(OAc)_2$ (2 mmol %) as palladium source.

phosphorus was *tert*-butyl group, the ligands showed some catalytic activity for the reaction. As a result, when di-*tert*-butylbiarylphosphine (**L4**) was used as a ligand, the coupling product was obtained in 36% of yield. However, ditert-butyl(2′,4′,6′-triisopropyl-[1,1′-biphenyl]-2-yl)phosphine, the similar bulky biaryl monophosphine, was reported to be less active for the amidation of bromobenzene.[6a] In these P, X-type ligands, monodentate phosphines with a heteroatom at the adjacent position of phosphorus atom, the hemilabile coordination of the heteroatom with the palladium center has been confirmed by the X-ray crystallographic study.[4g,10c] Therefore, the activity of these ligands for amidation may be attributed to the hemilabile coordination of the oxygen atom with the palladium center to inhibit the formation of the κ^2-amidate complex. Furthermore, the catalytic activity decreased with a decrease of the steric hindrance of the ligands. When 2-di(*tert*-butyl)phosphino-2′-methoxy-1,1′-binaphthyl (**L2**) was used as a ligand, the yield of the amidation was reduced to 22% (Table 1, entry 9). When the dialkylphosphino group of the ligands was changed from di(*tert*-butyl)phosphino to di(cyclohexyl)phosphine group, such as **L5-L8,** no amidation products were detected. This is in accordance with the report that the bulky steric hindrance of the ligands facilitates the reductive elimination during the C−N bond forming step.[8,11,12] Therefore, to actualize the Pd-catalyzed amidation reactions, the ligand should have enough steric hindrance to promote the reductive elimination and meanwhile, to inhibit the κ^2-binding mode of the amides. Xantphos, a fairly general and efficient ligand for amidation reactions of aryl iodide and bromide when 1,4-dioxane or THF was used as solvent,[5a,b] was inactive for the intermolecular coupling of bromobenzene and the primary amides under our reaction conditions.

The scope of the palladium-catalyzed amidation of bromobenzene was subsequently explored using $Pd(dba)_2$ as precatalyst, **L1** as the ligand, Cs_2CO_3 as the base, and *t*-BuOH as the solvent at 100 °C (bath temperature). The results are listed in Table 2. A variety of primary amides, both aliphatic and aromatic, and lactam participated in the coupling reactions in good to excellent yields. A number of functional groups, such as fluoro, methoxy, and heteroaromatic, were tolerated under such reaction conditions. Of particular interest, an amide

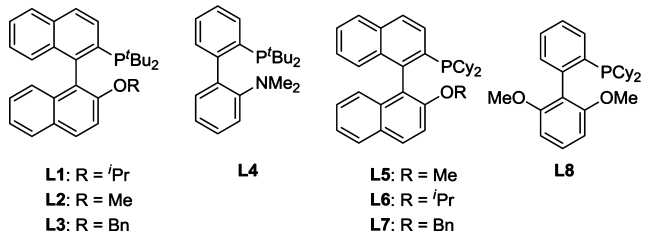
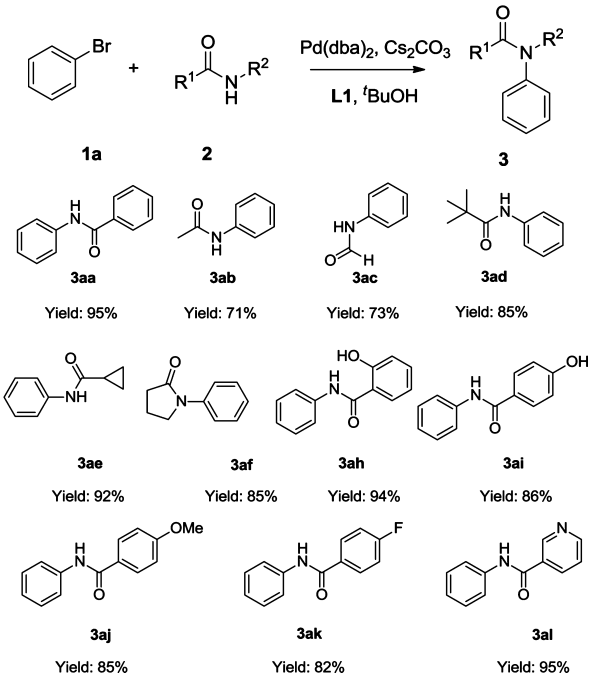


Figure 1. Ligands surveyed in optimization.

Table 2. Pd-catalyzed Amidation of Aryl Bromides[a]



[a]Reaction conditions: ArBr (1.0 mmol), amide (1.2 mmol), base (1.5 mmol), $Pd(dba)_2$ (2 mmol %), **L1** (3 mmol %), *t*-BuOH (4.0 mL), 100 °C (bath temperature), 20 h; isolated yields (average of two runs).

containing a free hydroxy group was converted to the desired amidation product in high yield, and no ether product was detected; amide containing a pyridine moiety was also a good coupling partner in this reaction. When the substituents of benzamide were changed from electron-donating group (hydroxy, methoxy) to electron-withdrawing group (fluoro), the yield of the arylation reaction did not vary remarkably.

As *tert*-butyloxycarbonyl (Boc) is a readily removable amine-protecting group, Pd-catalyzed coupling of *tert*-butyl carbamates with aryl halides can directly deliver primary amines in a conveniently protected form. Nevertheless, there are currently only a few catalytic systems which are effective in using *tert*-butyl carbamate as the ammonia equivalent in Pd-catalyzed amidation. Xantphos is frequently encountered as a ligand to effect this conversion of aryl bromides, especially the activated aryl bromides[5,7,13] Tri(*tert*-butyl)phosphine[14] and X-phos[15] are also effective ligands for the coupling reactions of aryl bromides; however, employing sodium phenoxide or sodium *tert*-butoxide as a base was crucial for the success of the reaction, which led to a narrow functional group tolerability of the catalytic system. Recently, Zou reported that high loading (9%) of X-phos may actualize the coupling of aryl chlorides and heteroaryl halides with *tert*-butyl carbamate in moderate yields.[15b] Encouraged by our results, the coupling reaction of

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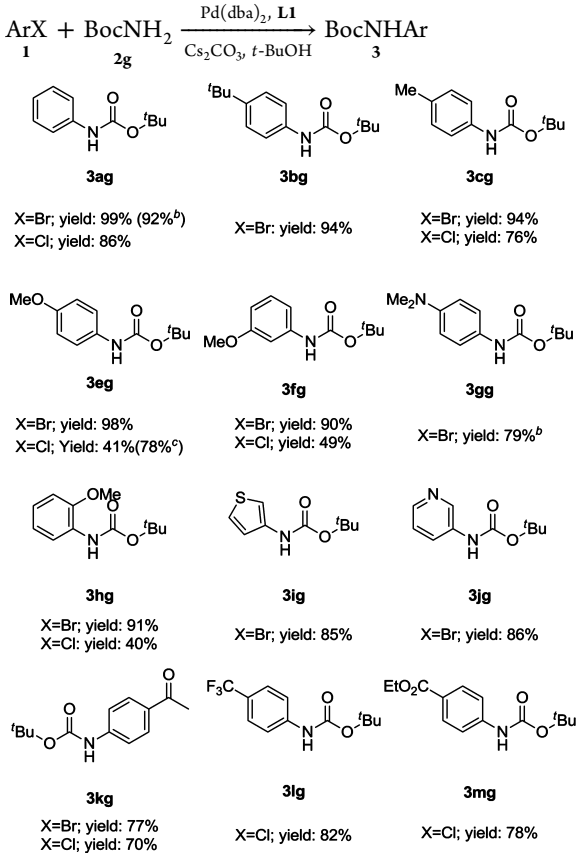
tert-butyl carbamate and aryl bromide was explored with our catalytic system. To our delight, under the optimized conditions, a quantitative yield of the product was obtained with bromobenzene as substrate. Even when the milder base, K_3PO_4, was employed and toluene was used as the solvent, the yield showed only a slight decrease. We then examined the scope of the coupling reaction of inactivated aryl halides with *tert*-butyl carbamate. The results were given in Table 3. The

Table 3. Pd-Catalyzed the Coupling Reaction of *tert*-Butyl Carbamate with Aryl Halides[a]



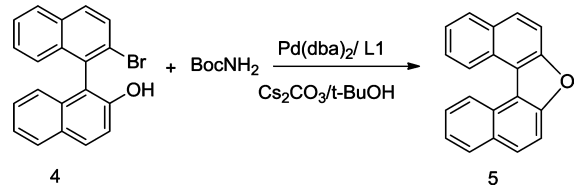
[a]Reaction conditions: ArX (1.0 mmol), *tert*-butyl carbamate (1.2 mmol), Cs_2CO_3 (1.5 mmol), $Pd(dba)_2$ (2 mmol %), **L1** (3 mmol %), *t*-BuOH (4.0 mL), 100 °C (bath temperature), 20 h; isolated yields are an average of two runs. [b]K_3PO_4 as the base, toluene as the solvent. [c]$Pd(dba)_2$ (4 mmol %) and **L1** (6 mmol %).

catalyst system, $Pd(dba)_2$/**L1**, allowed for the use of *tert*-butyl carbamate to form Boc-protected anilines from inactivated aryl halides in moderate to excellent yields. The reaction was insensitive to the electronic and steric effect of the functional groups on the aryl bromides. Both electron-neutral and electron-rich aryl bromides worked well, providing the corresponding *N*-Boc-anilines in excellent yields. *o*-Methoxybromobenzene was also reacted with *tert*-butyl carbamate in 91% of yield. Furthermore, heteroaryl bromides also worked well under the reaction conditions.

The good results with aryl bromides and hetero bromides prompted us to extend the amidation to aryl chlorides, which are generally the most attractive substrates for cross-coupling reactions as they are less expensive and more readily available. However, the yields of products were strongly affected by the electronic effect of aryl chlorides. Aryl chlorides bearing electron-withdrawing groups (such as trifluoromethyl, acetyl, or ester group) gave higher yields than those with electron-donating groups. Different from the high efficiency of the catalytic system in the amination of inactivated aryl chlorides,[11] the lower reactivity of aryl chlorides in the amidation may be due to the lower nucleophilicity of the amide and the poor dissociation of chloride from Pd(II) complexes, as reported that transmetalation is the rate-limiting step in the Pd-catalyzed amidation when the monodentate biaryldialkyl phosphine was used as ligand.[6a,16] The yields of the reaction of the inactivated aryl chlorides could be increased when more catalyst was loaded. In the case of coupling reaction of *p*-methoxychlorobenzene, the yields increased from 41% to 78% as the $Pd(bda)_2$ loading was increased from 2% to 4% and the ligand londing was increased from 3% to 6%. In addition, for aryl halides bearing a base-sensitive functional group, the conversion was also accomplished in moderate yields.

The derivative of 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) is an important organocatalyst and chiral ligand of the transition-metal-catalyzed reaction, which can be typically synthesized by the oxidative coupling of the 2-naphthylamine with 2-naphthol.[17] Buchwald's group reported a palladium-catalyzed amination reaction of a binaphthyl triflate derivative with diphenylmethanimine to give the product.[18] However, it was claimed that the use of benzophenone imine did not provide a convenient deprotective transformation to aniline.[15a] The good activity of our catalyst system promoted us to synthesize the derivative of NOBIN by the coupling reaction of aryl bromides with *tert*-butyl carbamate. Because a free phenol group on the aromatic ring (Table 2, entry 7) was compatible under the Pd-catalyzed amidation conditions, we tried to synthesize NOBIN by direct coupling reaction between *tert*-butyl carbamate and 2-bromo-2′-hydoxy-1,1′-binaphthyl (**4**), which can be easily obtained by our reported method.[19] However, under the optimized conditions, only intramolecular coupling product (**5**, Scheme 1) was formed by the reductive

Scheme 1. Coupling Reaction of 2-Bromo-2′-hydroxy-1,1′-binaphthyl and *tert*-Butyl Carbamate



elimination of the Pd−O bond, which is generally difficult to carry out.[20] The result may be due to the bulky steric hindrance of aryl bromide (**4**) and the stability of the five-membered ring of the product. The hydroxyl group methylated product (**6**) was examined for the reaction with *tert*-butyl carbamate. When **L1** was used as the ligand, the coupling reaction occurred in very low yield under previously optimized reaction conditions, probably because the bulkier steric hindrance of **6** hindered the coupling reaction. Several other ligands of 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl were screened, and to our delight, **L5** gave the best result, and the desired product (**7**) was obtained in 91% yield. This result demonstrated further that the proper steric hindrance of ligand can promote the reductive elimination in the amidation of aryl bromide. Finally, a derivative of NOBIN, 2′-menthoxy-1,1′-binaphthyl-2-amine

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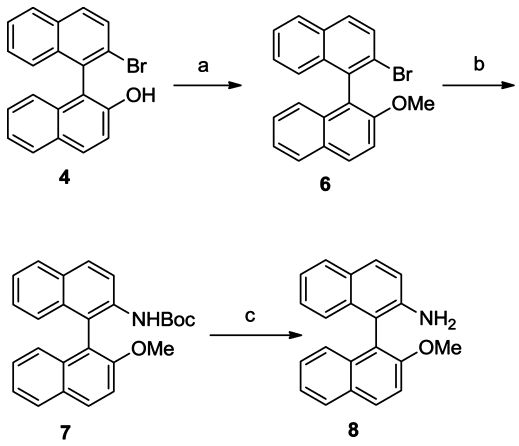
(8) can be prepared in 71% total yield from binaphthofuran through a four-step transformation (Scheme 2).

Scheme 2. Synthetic Approach of 2′-Methoxy-1,1′-binaphthyl-2-amine (8)



a, MeI/K_2CO_3, 99%; b, $BocNH_2$, $Pd(dba)_2$/ **L5**, Cs_2CO_3/t-BuOH, 91%; c, 2*N* HCl 97%.

CONCLUSION

In conclusion, we have reported a Pd-catalyzed coupling reaction between inactivated aryl halides and amides or *tert*-butyl carbamate using the bulky and electron-rich 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl as ligands (**L1**, **L5**) under optimized conditions, providing an easy method for the synthesis of protected primary amines. The catalytic activity of these ligands can be attributed to the hemilabile coordination of the oxygen atom with the palladium center to inhibit the formation of the κ^2-amidate complex and to the fact that proper steric hindrance can promote the reductive elimination. Furthermore, because the substituents on the phosphino and oxygen group are easily to be tuned, the ligands of 2-dialkylphosphino-2′-alkoxyl-1,1′-binaphthyl can be employed for a wider range of the amidation reactions of various substrates. The efficient coupling reaction of 2-bromo-2′-methoxy- 1,1′-binaphthyl and commercially available *tert*-butyl carbamate offered a facile synthetic method for the NOBIN derivatives.

EXPERIMENTAL SECTION

Experimental Procedures for the Amidation of Aryl Halides Using 2-Dialkylphosphino-2′-alkoxy-1,1′-binaphthyl as Ligands. An oven-dried Schlenk tube was evacuated and backfilled with nitrogen. The Schlenk tube was charged with $Pd(dba)_2$ (11.4 mg, 0.02 mmol), **L1** (13.6 mg, 0.03 mmol), amide (1.2 mmol), and base (1.5 mmol) and capped with a rubber septum. The Schlenk tube was evacuated and backfilled with nitrogen three times. To the Schlenk tube were added aryl halide (1.0 mmol) and solvent (4.0 mL). The septum was replaced with a Teflon screw cap, and the mixture was heated to 100 °C with stirring for 20 h. Then reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate, filtered through Celite, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel.

N-Phenylbenzamide (**3aa**).[21] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:5) to give the compound as a white solid (159.6 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.88 (m, 3H), 7.64 (d, J = 8.8 Hz, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 6.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 138.2, 135.3, 132.1, 129.4, 129.1, 127.3, 124.9, 120.6.

Acetanilide (**3ab**).[21] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:2) to give the compound as a white solid (95.9 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 138.0, 126.7, 124.1, 120.1, 24.2.

N-phenylformamide (**3ac**).[22] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:3) to give the compound as a white solid (88.4 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66−8.71 (m, 1H), 8.36 (d, J = 1.6 Hz, 0.4H), 7.76 (br, 0.4H), 7.54 (d, J = 8.8 Hz, 1H), 7.30−7.38 (m, 2H), 7.08−7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 159.2, 136.7, 129.7, 129.0, 125.2, 124.8, 120.0, 118.8.

N-Phenylpivalamide (**3ad**).[23] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:25) to give the title compounds as a white solid (151.2 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d. J = 8.8 Hz, 2H), 7.32 (t, J = 8.4 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 138.0, 128.9, 124.1, 120.0, 39.5, 27.6.

N-Phenylcyclopropanecarboxamide (**3ae**).[24] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:2) to give the compound as a white solid (147.9 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 2H), 7.73 (br, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 6.8 Hz, 1H), 1.50 (br, 1H), 1.07−1.11 (m, 2H), 0.82−0.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 138.2, 120.7, 123.9, 120.0, 15.3, 7.7.

1-Phenylpyrrolidin-2-one (**3af**).[5a] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:3) to give the title compounds as a white solid (136.6 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 8.4 Hz, 2H), 7.14 (t, J = 8.4 Hz, 1H), 3.87 (t, J = 7.2 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H), 2.14−2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 139.2, 128.5, 124.2, 119.7, 48.5, 32.5, 17.7.

tert-Butyl Phenylcarbamate (**3ag**).[25] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (191.0 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.45 (br, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.3, 128.9, 122.9, 118.5, 80.4, 28.3.

2-Hydroxy-N-phenylbenzamide (**3ah**).[26] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the title compounds as a white solid (200.1 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.0 (s, 1 H), 7.93 (br, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 6.8 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.93 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 161.6, 136.5, 134.6, 129.1, 125.6, 125.3, 121.3, 119.0, 118.8, 114.6.

4-Hydroxy-N-phenylbenzamide (**3ai**).[27] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:5) to give the title compounds as a white solid (183.2 mg, 86%): ^{1}H NMR (400 MHz, DMSO) δ 10.06 (s, 1H), 9.95 (br, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.73 (dd, J = 8.8 Hz, 1.2 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ 165.1, 160.5, 139.5, 129.7, 128.5, 125.5, 123.3, 120.3, 114.9.

4-methoxy-N-phenylbenzamide (**3aj**).[6a] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:5) to give the compound as a white solid (192.8 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.74 (br, 1H), 7.63 (dd, J = 8.8 Hz, 1.2 Hz, 2H), 7.37 (t, J = 8.8 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 164.9, 161.9, 139.4, 129.6, 128.5, 127.0, 123.4, 120.3, 113.6, 55.4.

4-Fluoro-N-phenylbenzamide (**3ak**).[28] The crude material was purified by column chromatography on silica gel (eluting with ethyl

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acetate/hexanes 1:10) to give the compound as a white solid (176.8 mg, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.91 (m, 2H), 7.76 (br, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.8 Hz, 2H), 7.16 (t, J = 8.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 165.3, 164.4, 162.8, 139.1, 131.4, 130.4, 128.6, 123.7, 120.4, 115.4, 115.2.

*N-phenylnicotinamide (**3al**).*[29] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:2) to give the compound as a white solid (153.0 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.91 (s, 1H), 8.47 (d, J = 1.2 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.12−7.18 (m, 2H), 7.00 (dt, J = 8.8 Hz, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 151.7, 148.0, 137.6, 135.4, 130.7, 128.8, 124.8, 123.4, 120.8.

*tert-Butyl-4-tert-butylphenylcarbamate (**3bg**).*[30] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:30) to give compound as a white solid (233.2 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.32 (m, 4H), 6.41 (br, 1H), 1.51 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1552.9, 145.9, 135.7, 125.7, 118.4, 80.3, 34.2, 31.4, 28.3.

*tert-Butyl p-Tolylcarbamate (**3cg**).*[27] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:30) to give the compound as a white solid (203.2 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.40 (br, 1H), 2.29 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 135.7, 132.4, 129.4, 118.7, 80.2, 28.3, 20.6.

*tert-Butyl 4-Methoxyphenylcarbamate (**3eg**).*[30] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (218.6 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.27 (m, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.33 (br, 1H), 3.78 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 153.2, 131.4, 120.5, 120.3, 114.0, 80.0, 55.3, 28.3.

*tert-Butyl 3-methoxyphenylcarbamate (**3fg**).*[30] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (200.3 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 8.4 Hz, 1H), 7.10 (s, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.58 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.48 (br, 1H), 3.80 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 152.7, 139.6, 129.5, 110.7, 108.8, 104.0, 80.4, 55.1, 28.3.

*tert-Butyl 4-(Dimethylamino)phenylcarbamate (**3gg**).*[30] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:15) to give the compound as a white solid (185.2 mg, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 9.2 Hz, 2H), 6.26 (br, 1H), 2.89 (s, 6H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 147.2, 126.5, 120.7, 120.6, 113.6, 79.8, 41.1, 28.3.

*tert-Butyl 2-Methoxyphenylcarbamate (**3hg**).*[31] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:50) to give the compounds a white solid (202.3 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 6.8 Hz, 1H), 7.08 (s, 1H), 6.92−6.99 (m, 2H), 6.85 (dt, J = 6.8 Hz, 1.2 Hz, 1H), 3.86 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 147.4, 128.0, 122.2, 121.0, 118.0, 109.9, 80.1, 55.5, 28.3.

*tert-Butyl Thiophene-3-ylcarbamate (**3ig**).*[32] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (168.2 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 5.6 Hz, 2.4 Hz, 2H), 6.90 (d, J = 4.0 Hz, 1 H), 6.66 (br, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 136.1, 124.5, 120.7, 107.3, 80.4, 28.3.

*tert-Butyl Pyridin-3-ylcarbamate (**3jg**).*[30] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:3) to give the title compounds as a white solid (166.7 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 2.4 Hz, 1H), 8.29 (d, J = 4.8 Hz, 1H), 7.99 (br, 1H), 7.24 (dd, J = 8.0 Hz, 4.4 Hz, 1H), 6.88 (br, 1H), 1.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 143.8, 140.1, 135.6, 125.7, 123.6, 80.9, 28.2.

*tert-Butyl 4-Acetylphenylcarbamate (**3 kg**).*[33] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (180.0 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.75 (br, 1H), 2.56 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 152.3, 143.2, 131.5, 129.7, 117.4, 81.0, 28.1, 26.2.

*tert-Butyl 4-Trifluoromethylphenylcarbamate (**3lg**).*[34] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (214.4 mg, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.85 (br, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 141.5, 126.2 (q, J = 28.0 Hz), 125.6, 124.8, 124.6, 122.9, 117.9, 81.2, 28.2.

*Ethyl 4- (tert-Butoxycarbonylamino)benzoate (**3mg**).*[35] The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:10) to give the compound as a white solid (207.0 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.69 (br, 1H), 4.35 (q, J = 6.8 Hz, 2H), 1.53 (s, 9H), 1.38 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 152.3, 142.6, 130.7, 124.5, 117.3, 81.0, 60.7, 28.1, 14.3.

Synthesis of 2′-Methoxy-1,1′-binaphthyl-2-amine. *2′-Bromo-1,1′-binaphthalen-2-ol (**4**).*[19] To a suspension of lithium chip (2.4 g, 340.0 mmol) in Et_2O (80 mL) was added dropwise a solution of binaphthofuran **6** (5.4 g, 20.0 mmol) in toluene (70 mL), and the mixture was stirred at room temperature for 3 h to achieve complete conversion of the starting material. After removal of excess lithium by filtration, the mixture of Et_2O (20 mL) and 1,1,2,2-tetrabromoethane (6.9 g, 20.0 mmol) was added dropwise to the solution cooled to −30 to −40 °C, and then the mixture was stirred for 2 h at room temperature. The reaction mixture was acidified with 1 M HCl solution to pH < 5, and the two layers were separated; the aqueous phase was extracted with EtOAc (2 × 30 mL), and the combined organic fractions were washed with brine (60 mL). The organic phase was dried over Na_2SO_4 and evaporated to give a crude product, which was purified by flash chromatography eluting with hexane/EtOAc (20:1). The title compound was obtained as a white solid (5.6 g, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.96 (m, 5H), 7.54 (td, J = 6.8 Hz, 1.6 Hz, 1H), 7.31−7.36 (m, 3H), 7.24−7.28 (m, 2H), 6.96 (d, J = 8.0 Hz, 1H), 4.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 134.1, 132.9, 132.7, 131.8, 130.5, 130.4, 130.3, 129.0, 128.3, 128.2, 127.8, 126.9, 126.7, 126.0, 124.7, 124.2, 123.6, 118.2, 117.6.

*2′-Bromo-2-methoxy-1,1′-binaphthalenyl (**6**).*[36] Methyl iodide (2.6 g, 18.0 mmol) and potassium carbonate (2.5 g, 18.0 mmol) were added to a stirred solution of **6** (2.1 g, 6.0 mmol) in acetone under nitrogen. The mixture was stirred overnight. The mixture was filtered, and the filtrate was evaporated to yield the product as a white solid (2.2 g, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 9.2 Hz, 1H), 7.89 (dd, J = 8.0 Hz, 3.6 Hz, 2H), 7.81 (s, 2H), 7.44−7.48 (m, 2H), 7.34 (td, J = 8.0 Hz, 1.2 Hz, 1H), 7.22−7.28 (m, 2H), 7.17 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 134.9, 134.1, 133.1, 132.4, 130.1, 130.0, 129.1, 129.0, 128.0, 126.9, 126.8, 126.3, 126.0, 124.1, 123.7, 123.3, 122.1, 113.8, 56.7.

*tert-Butyl 2′-Methoxy-1,1′-binaphthyl-2-ylcarbamate (**7**).* 2′-Bromo-2-methoxy-1,1′-binaphthalenyl (**6**, 1.1 g, 3.0 mmol), *tert*-butyl carbamate (421.9 mg, 3.6 mmol), $Pd(dba)_2$ (34.2 mg, 60.0 μmmol), **L5** (40.8 mg, 90.0 μmol), and Cs_2CO_3 (1.5 g, 4.5 mmol) in *t*-BuOH (8.0 mL) were added to a Schlenk tube fitted with a septum. The septum was replaced with a Teflon screw cap, and the mixture was heated to 100 °C with stirring for 20 h. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate, filtered through Celite, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes 1:15) to give the title compounds as a white solid (1.1 g, 91%): mp 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 9.2 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 9.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H) 7.46 (d, J = 8.8 Hz, 1H), 7.33 (qd, J = 8.0 Hz, 1.2 Hz, 2H), 7.22 (td, J = 8.0 Hz, 1.2 Hz, 1H), 7.16 (td, J = 8.4 Hz, 1.2 Hz, 1H), 7.06 (d, J = 8.6 Hz,

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1H), 6.97 (d, J = 8.0 Hz, 1H), 6.20 (br, 1H), 3.75 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 153.1, 134.9, 133.7, 133.0, 130.7, 130.3, 129.3, 128.5, 128.0, 127.1, 126.1, 125.4, 125.0, 124.2, 124.0, 119.9, 117.3, 113.8, 80.3, 56.5, 28.2; IR (neat, cm^{-1}) 3409, 3056, 2976, 2933, 1719, 1598, 1505, 1454, 1427, 1367, 1263, 1155, 1073, 956, 813; HRMS-ESI (collected on an UPLC and Q-TOF MS spectrometer) calcd for $C_{26}H_{25}NO_3$ 399.1834, found 399.1830.

*2′-Methoxy-1,1′-binaphthyl-2-amine (**8**).*[37] *tert*-Butyl 2′-methoxy-1,1′-binaphthyl-2-ylcarbamate (1.0 g) was added at room temperature to a solution of 2.0 N HCl in 1,4-dioxane (10.0 mL) and the mixture stirred for 5 h. Then 1,4-dioxane was removed under reduced pressure. The residue was added to a saturated solution of sodium bicarbonate (10.0 mL), the solution was extracted with diethyl ether (3 × 20 mL), the organic layers were combined, and the mixture was dried over Na_2SO_4. The mixture was filtered, and the filtrate was evaporated to yield the product (0.7 g, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 9.2 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.77−7.81(m, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.35−7.37 (m, 1H), 7.13−7.28 (m, 5H), 6.96−6.98 (m, 1H), 3.79 (s, 3H), 1.58 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.0, 134.1, 133.6, 129.9, 129.5, 128.9, 128.1, 128.0, 127.9, 126.9, 126.2, 124.9, 124.2, 123.9, 122.1, 118.8, 118.1, 114.3, 113.7, 56.8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR data of compounds **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Masse, C. E.; Yang, M.; Solomon, J.; Panek, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 4123. (b) Evano, G.; Schaus, J. V.; Panek, J. S. *Org. Lett.* **2004**, *6*, 525. (c) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (d) Satyanarayana, K.; Srinivivas, K.; Himabindu, V.; Reddy, G. M. *Org. Process Res. Dev.* **2007**, *11*, 842.

(2) For reviews, see: Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400. (b) Kunz, K.; Scholz, U.; Ganzer, D. *Synlett* **2003**, 2428. (c) Ma, D.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450. (d) Jiang, L.; Buchwald, S. L. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004. (e) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338.

(3) Shakespeare, W. C. *Tetrahedron Lett.* **1999**, *40*, 2035.

(4) (a) Imbriglio, J. E.; DiRocco, D.; Raghavan, S.; Ball, R. G.; Tsou, N.; Mosley, R. T.; Tata, J. R.; Colletti, S. L. *Tetrahedron Lett.* **2008**, *49*, 4897. (b) Klapars, A.; Campos, K. R.; Chen, C.; Volante, R. P. *Org. Lett.* **2005**, *7*, 1185. (c) Willis, M. C.; Brace, G. N.; Holmes, I. P. *Synthesis* **2005**, 3229. (d) Wallace, D. J.; Klauber, D. J.; Chen, C.; Volante, R. P. *Org. Lett.* **2003**, *5*, 4749. (e) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653. (f) Dooleweerdt, K.; Fors, B. P.; Buchwald, S. L. *Org. Lett.* **2010**, *12*, 2350. (g) Hicks, J. D.; Hyde, A. M.; Cuezva, A. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 16720.

(5) (a) Yin, J.; Buchwald, S. L. *Org. Lett.* **2000**, *2*, 1101. (b) Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 6043. (c) McLaughlin, M.; Palucki, M.; Davies, I. W. *Org. Lett.* **2006**, *8*, 3311. (d) Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 7734. (e) Dallas, A. S.; Gothelf, K. V. *J. Org. Chem.* **2005**, *70*, 3321.

(6) (a) Ikawa, T.; Barder, T. E.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 13001. (b) Shen, Q.; Shekhar, S.; Stambuli, J. P.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1371. (c) Ghosh, A.; Sieser, J. E.; Riou, M.; Cai, W.; Rivera-Ruiz, L. *Org. Lett.* **2003**, *5*, 2207. (d) Fors, B. P.; Dooleweerdt, K.; Zeng, Q.; Buchwald, S. L. *Tetrahedron* **2009**, *65*, 6576. (e) Vimolratana, M.; Simard, J. L.; Brown, S. P. *Tetrahedron Lett.* **2011**, *52*, 1020.

(7) (a) Barfoot, C.; Brooks, G.; Brown, P.; Dabbs, S.; Davies, D. T.; Giordano, I.; Hennessy, A.; Jones, G.; Markwell, R.; Miles, T.; Pearson, N.; Smethurst, C. A. *Tetrahedron Lett.* **2010**, *51*, 2685. (b) Nodwell, M.; Pereira, A.; Riffell, J. L.; Zimmerman, C.; Patrick, B. O.; Roberge, M.; Anderson, R. J. *J. Org. Chem.* **2009**, *74*, 995. (c) Bringmann, G.; Gulder, T.; Reichert, M.; Meyer, F. *Org. Lett.* **2006**, *8*, 1037. (d) Shi, F.; Smith, M. R., III; Maleczka, R. E. *Org. Lett.* **2006**, *8*, 1411. (e) Kuwahara, A.; Nakano, K.; Nozaki, K. *J. Org. Chem.* **2005**, *70*, 413. (f) Willis, M. C.; Brace, G. N.; Holmes, I. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 403.

(8) For reviews, see: (a) Yang, B. H.; Buchwald, S, L. *J. Organomet. Chem.* **1999**, *576*, 125. (b) Beller, M; Zapf, A; Magerlein, W. *Chem. Eng. Technol.* **2001**, *24*, 575. (c) Muci, A. R.; Buchwald, S, L. *Top. Curr. Chem.* **2002**, *219*, 131. (d) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534. (e) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27. (f) Schlummer, B.; Scholz, U. *Adv. Synth. Catal.* **2004**, *346*, 1599. (g) Hartwig, J. F. *Nature* **2008**, *455*, 314.

(9) Fujita, K.-I.; Yamashita, M.; Puuschman, F.; Alvarez-Falcon, M. M.; Invarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 9044.

(10) (a) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722. (b) Bei, X.; Uno, T.; Norris, J.; Turner, H. W.; Weinberg, W. H.; Guram, A. S. *Organomatallics* **1999**, *18*, 1840. (c) Lundgren, R. J.; Peters, B. D.; Alsabeh, P. G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4071.

(11) Xie, X.; Zhang, T. Y.; Zhang, Z. *J. Org. Chem.* **2006**, *71*, 6522.

(12) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978.

(13) (a) Yang, B. H.; Buchwald, S. L. *Org. Lett.* **1999**, *1*, 35. (b) Trabanco, A. A.; Vega, J. A.; Fernández, M. A. *J. Org. Chem.* **2007**, *72*, 8146.

(14) Hartwig, J. F.; Kawatsura, M.; Hauck, S. L.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575.

(15) (a) Bhagwanth, S.; Waterson, A. G.; Adjabeng, G. M.; Hornberger, K. R. *J. Org. Chem.* **2009**, *74*, 4634. (b) Qin, L.; Cui, H.; Zou, D.; Li, J.; Wu, Y.; Zhu, Z.; Wu, Y. *Tetrahedron Lett.* **2010**, *51*, 4445.

(16) Biscoe, M. R.; Barder, T. E.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7232.

(17) (a) Smrčina, M.; Lorenc, M.; Hanuš, V.; Kočovský, P. *Synlett* **1991**, 231. (b) Vyskočil, Š.; Jaracz, S.; Smrčina, M.; Štícha, M.; Hanuš, V.; Polášek, M.; Kočovský, P. *J. Org. Chem.* **1998**, *63*, 7727. (c) Ding, K. *Chem. Commun.* **2008**, 909. (d) Körber, K.; Tang, W.; Hu, X.; Zhang, X. *Tetrahedron Lett.* **2002**, *43*, 7163. (e) Ding, K.; Xu, Q.; Wang, Y.; Liu, J.; Yu, Z.; Du, B.; Wu, Y.; Koshima, H.; Matsuura, T. *Chem. Commun.* **1997**, 693. (f) Hu, X.; Chen, H.; Zhang, X. *Angew. Chem., Int. Ed.* **1999**, *38*, 3518. (g) Singer, R. A.; Brock, J. R.; Carreira, E. M. *Helv. Chim. Acta* **2003**, *86*, 1040.

(18) Singer, R. A.; Buchwald, S. L. *Tetrahedron Lett.* **1999**, *40*, 1095.

(19) Xie, X.; Ding, L.; Ni, G.; Zhang, Z.; Gao, J. *Chin. J. Chem.* **2010**, *28*, 1630.

(20) (a) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936. (b) Bäckvall, J.-E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369.

(21) Ramalingan, C.; Park, Y. T. *J. Org. Chem.* **2007**, *72*, 4536.

(22) Hosseini-Sarvari, M.; Sharghi, H. *J. Org. Chem.* **2006**, *71*, 6652.

(23) Jiang, H.; Liu, B.; Li, Y.; Wang, A.; Huang, H. *Org. Lett.* **2011**, *13*, 1028.

(24) Yang, Y.; Shi, M. *J. Org. Chem.* **2005**, *70*, 8645.

(25) Chankeshwara, S. V.; Chakraborti, A. K. *Org. Lett.* **2006**, *8*, 3259.

(26) Lin, G.; Wang, Q.; Jiang, Q.; Jiang, Q.; Jiang, Y. *J. Org. Chem.* **2007**, *72*, 9947.

(27) Chakraborti, A. K.; Sharma, L.; Nayak, M. K. *J. Org. Chem.* **2002**, *67*, 6406.
(28) Salvadori, J.; Balducci, E.; Zara, S.; Petricci, E.; Taddei, M. *J. Org. Chem.* **2010**, *75*, 1841.
(29) Lv, X.; Bao, W. *J. Org. Chem.* **2007**, *72*, 3863.
(30) Bhagwanth, S.; Waterson, A. G.; Adjabeng, G. M.; Hornberger, K. R. *J. Org. Chem.* **2009**, *74*, 4634.
(31) Kondo, Y.; Kojima, S.; Sakamoto, T. *J. Org. Chem.* **1997**, *62*, 6507.
(32) Crawford, K. R.; Padwa, A. *Tetrahedron Lett.* **2002**, *43*, 7365.
(33) Chankeshwara, S. V.; Chakraborti, A. K. *Tetrahedron Lett.* **2006**, *47*, 1087.
(34) Swenson, R. E.; Sowin, T. J.; Zhang, H. Q. *J. Org. Chem.* **2002**, *67*, 9182.
(35) Frank, K. E.; Aubé, J. *J. Org. Chem.* **2000**, *65*, 655.
(36) Clayden, J.; Kubinski, P. M.; Sammiceli, F.; Helliwell, M.; Diorazio, L. *Tetrahedron* **2004**, *60*, 4387.
(37) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954.