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Efficient palladium-catalyzed Suzuki cross-coupling reaction with β-ketoamine ligands

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ABSTRACT

A series of β-ketoamine ligands with different steric and electronic substituents on the backbone and with aniline moieties have been synthesized and characterized. In the presence of $PdCl_2$, catalytic studies indicated that they are effective ligands for Suzuki cross-coupling of various aryl bromides with phenylboronic acid, under aerobic conditions.

Palladium-catalyzed reactions, such as C—C bond formation, have attracted significant interest over the past few decades [1,2]. Specifically, the Suzuki cross-coupling reaction of aryl halides with organoboron reagents is becoming one of the most important and reliable methods for the construction of biaryls, which are present in a wide range of natural products, pharmaceuticals, agrochemicals and functional polymer materials [3–10]. Like other types of palladium-catalyzed coupling reactions, the Suzuki coupling reaction is also highly dependent on the nature of the ligand structure. Bulky, electron-rich phosphine ligands are outstanding in the palladium-catalyzed Suzuki cross-coupling reaction, resulting from their superior donor capability and stabilization effects [11–14]. Though these catalysts exhibited excellent catalytic properties, most phosphines are highly toxic and are air- and moisture-sensitive, and therefore require oxygen-free handling to minimize ligand oxidation. These drawbacks place a significant limitation on their synthetic applications. However, the development of phosphine-free ligands has seriously challenged this situation. Recently, the use of N-heterocyclic carbenes (NHCs) in Suzuki cross-couplings has gained much popularity for both superior σ-donating properties and easily variable steric substituents, which allow for the stabilization of the active metal center and the enhancement of the catalytic activity [15,16]. NHCs/palladium complexes are quite stable, but the ligand can be sensitive to oxygen. Therefore, additional research on new ligands that are moisture- and air-stable is needed.

In contrast, phosphine-free ligands, such as tridentate [17–20] and bidentate [21–41] ligands containing N, O and S atoms, are typically inexpensive, easily prepared and moisture- and air-stable. Among them, β-ketoamine ligands, previously used as excellent candidates for olefin and ε-caprolactone polymerization [42,43], have recently been applied to Suzuki cross-coupling [38–41]. Hong and coworkers found that β-ketoamine ligands derived from acetylacetone exhibited moderate activity toward aryl bromides [38]. Recently, Jin and coworkers developed a series of β-ketoamine palladium complexes with triphenylphosphine as an ancillary ligand that showed high activity toward both aryl and heteroaryl chlorides [39–41]. Nevertheless, the β-ketoamine palladium complexes developed were exclusively based on acetylacetone. Considering that both the backbone and the amines have profound effects on the catalytic properties of the palladium complexes, herein we present a simple and efficient preparation of a series of novel β-ketoamines complexes with aryl backbones and substituted aniline moieties generated in situ. Furthermore, conditions are described that easily provide the desired products in moderate to high yields under aerobic conditions, with great tolerance for a broad range of functional groups on the aryl bromides.

As shown in Scheme 1, the target β-ketoamine ligands with various steric and electronic substituents were prepared according to a previously reported protocol [44–48], with some modifications. At first, the enaminones were synthesized from the starting material, acetophenone, and then were reacted with 1.2 equiv of aniline in refluxing ethanol or glacial acetic acid. After recrystallization from methanol, β-ketoamine ligands (**L1**–**5**) were obtained in moderate to high yields [49].

The catalytic activity of **L1**–**5** in Suzuki cross-coupling reactions was then evaluated. In an effort to understand how the ligands would promote this coupling reaction most efficiently, a reaction in which Na_2CO_3 was used as a base and ethanol/water was a cosolvent in the

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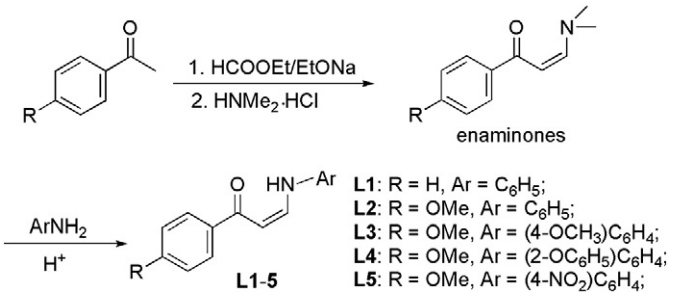


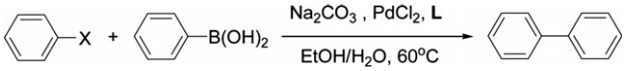
Scheme 1. Synthetic route of the Ligand **L1**–**5**.

reaction of phenylboronic acid with bromobenzene, at 60 °C, within 3 min, and under aerobic conditions, was examined. As shown in Table 1, the data revealed that the β-ketoamines were effective ligands for palladium-catalyzed Suzuki cross-coupling. For a comparison, in the absence of ligands, only 45% yield of biphenyl was produced in the presence of 0.5 mol% of $PdCl_2$ (entry 1, Table 1). However, when adding the ligands, the yield of product increased dramatically, to a range of 77–91% (entries 2–5, Table 1), indicating that the catalysts were formed in situ.

Among the β-ketoamines investigated, **L1**, with a phenyl backbone and an aniline group, showed moderate efficiency and yielding the coupling product at 77% (entry 2, Table 1). **L2**, with an anisole backbone, was found to be a more efficient ligand and afforded the coupling product in 81% yield (entry 3, Table 1). These results suggested that the increase in the electron-donating properties of the backbone positively affected catalytic ability. Significantly, **L4** (where a sterically-demanding and electron-donating phenyloxyl group was substituted on the *ortho* aniline moiety) exhibited the highest activity. In this case, the conversion of the biphenyl product reached 91%. Comparatively, **L5**, with an electron-withdrawing nitro group on the *para* position of the aniline, was less active under the same conditions (78% yield). These results could be ascribed to the increase in electron-donating ability of both the backbone and the aniline moieties of the ligand, leading to an increase in the rate of oxidative addition and the stabilization of the palladium species. Moreover, the steric hindrance on the ligands could further facilitate reductive elimination and facilitate cross-coupling [12].

With the preliminary results of the cross-coupling reaction in hand, we performed optimization studies to determine how solvents, bases, and temperature influenced the coupling reaction (Table 2). Initially, the reactions were carried out in different solvents at a reaction temperature of 60 °C, and the polarity of the solvent had a profound effect. For instance, the nonpolar solvent toluene gave a poor yield (33%), whereas the polar solvents, such as *N*, *N*-dimethylformamide

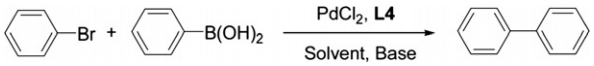
Table 1
Screening of the ligands on Suzuki cross-coupling reaction.



Entry	X	Ligand	Pd (mol%)[a]	t (min)	Yield (%)[b]
1	Br	None	0.5	3	45
2	Br	**L1**	0.5	3	77
3	Br	**L2**	0.5	3	81
4	Br	**L3**	0.5	3	83
5	Br	**L4**	0.5	3	91
6	Br	**L5**	0.5	3	78

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (2.0 mmol), EtOH/H_2O (3 ml: 3 ml), at a temperature of 60 °C.
[a] The molar ratio of Ligand and Pd is 1:1.
[b] Yield of biphenyl, determined by GC.

Table 2
Conditions optimization in Suzuki cross-coupling reaction.



Entry	Solvent	Base	T(°C)	Pd (mo1%)[a]	t (h)	Yield (%)[b]
1	Toluene	Na_2CO_3	60	0.5	6	33
2	DMF	Na_2CO_3	60	0.5	6	67
3	Acetone	Na_2CO_3	60	0.5	6	72
4	EtOH	Na_2CO_3	60	0.5	6	73
5	H_2O	NaCO3	60	0.5	6	92
6[c]	Toluene/H_2O	Na_2CO_3	60	0.5	6	85
7[c]	DMF/H_2O	Na_2CO_3	60	0.5	6	93
8[c]	Acetone/H_2O	Na_2CO_3	60	0.2	2	95
9[c]	EtOH/H_2O	Na_2CO_3	60	0.1	1	99
10[c]	EtOH/H_2O	Na_2CO_3	25	0.5	0.5	67
11[c]	EtOH/H_2O	Na_2CO_3	25	0.5	1	88
12[c]	EtOH/H_2O	Na_2CO_3	25	0.5	2	94
13[c]	EtOH/H_2O	K_3PO_4	25	0.5	2	68
14[c]	EtOH/H_2O	K_2CO_3	25	0.5	2	99
15[c]	EtOH/H_2O	KF	25	0.5	2	62
16[c]	EtOH/H_2O	KOH	25	0.5	2	81
17[c]	EtOH/H_2O	NaOH	25	0.5	2	98
18[c]	EtOH/H_2O	NaOMe	25	0.5	2	86
19[c]	EtOH/H_2O	NaOAc	25	0.5	2	52

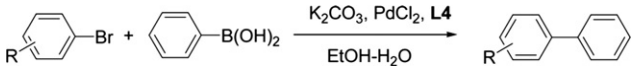
Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), Base (2.0 mmol), solvent (6 ml).
[a] The molar ratio of Ligand and Pd is 1:1.
[b] Yield of biphenyl, determined by GC.
[c] The mixture of cosolvent ratio (3 ml:3 ml).

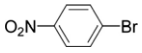
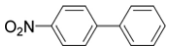
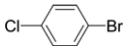
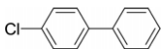
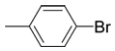
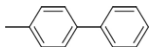
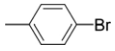
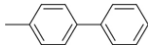
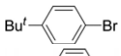
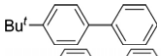
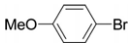
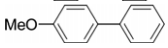
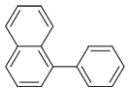
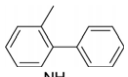
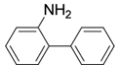
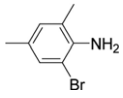
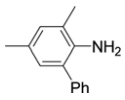
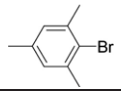
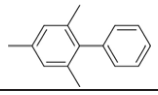
(DMF), acetone and ethanol, provided the product in moderate yield (entries 2–4, Table 2). Notably, the coupling reaction in pure water gave a satisfactory yield of 92% without tetrabutylammonium bromide (TBAB). Recently, the use of water as an environmentally friendly solvent has received considerable attention for green chemistry [50]. Moreover, reaction activities were dramatically improved using organic/water cosolvents (entries 6–9, Table 2). For instance, the biphenyl product obtained in toluene/water resulted in a good yield (85%), and a nearly quantitative conversion was obtained from the reactions in ethanol/water and acetone/water. These observations suggested that the cosolvent system played an important role in the solubility of the reagents (such as inorganic bases) and the easier reduction of Pd^{2+} to Pd(0), facilitating entry into the catalytic cycle [51]. Although both ethanol/water and acetone/water solvent systems provided excellent yields for the model reaction, ethanol/water was chosen for further study because it was readily available, inexpensive and had a higher efficiency.

Based on the earlier results of the ethanol/water system, different conditions were tested to optimize the reaction. As seen in Table 2, excellent yields of the cross-coupling reaction were achieved at room temperature within 2 h (entries 10–12), which further supported the high efficiency of the β-ketoamines. Moreover, the base usually plays an important role in Suzuki cross-coupling reactions because the addition of bases exerts a remarkable accelerating effect on the transmetalation between Ar–Pd–X and organoboronic acids [3,5]. Thus, several bases have been screened for their influence on the catalytic system. The investigation suggested that K_2CO_3, with a mild basicity, was the best choice. Notably, Na_2CO_3, which is usually an effective base for Suzuki cross-couplings, proved to be less active. Other bases, including K_3PO_4, KF, KOH, NaOMe, and NaOAc, gave inferior results and showed slow reaction rates compared to K_2CO_3 (entries 13–19, Table 2). Although NaOH also worked, it was not chosen because of its much stronger basicity. K_2CO_3 was thus found to be the most effective base and was used in all subsequent reactions.

The improvement of the catalytic activity encouraged us to examine the cross-coupling reactions of aryl bromide substrates as well. As shown in Table 3, using K_2CO_3 as a base and ethanol/water as

Table 3
Suzuki cross-coupling reaction of aryl halides with phenylboronic acid under aerobic conditions.



Entry	Aryl bromide	Product	T (°C)	Pd (mol%)	t (h)	Yield (%)[c]
1			25	0.01	0.05	92
2			25	0.5	6	98
3			25	1	6	31
4			60	1	6	96
5			60	1	6	96
6			60	1	6	97
7			60	1	6	99
8			60	1	16	93
9			60	1	16	97
10			60	1	24	90
11			60	1	16	63
12			60	1	24	95

Reaction conditions: aryl bromides (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), EtOH/H_2O (6 ml). [a]The molar ratio of Ligand and Pd is 1:1. [b]Yield of product determined by GC. [c]The reaction carried out under the nitrogen protection.

the solvent, high catalytic activity was observed in the coupling of activated bromides with phenylboronic acid at room temperature (entries 1–2, Table 3). Conversely, increasing electron density on the aryl bromides lowered the activity at low reaction temperatures. For instance, when the electronically deactivated 4-methylbromide was employed at room temperature, only a 31% yield was obtained after 6 h (entry 3, Table 3). In contrast, an excellent conversion (96%) was found at the elevated reaction temperature of 60 °C. Similar results were also observed for 4-tertbutylbromide, 4-bromoanisole and naphthylbromide (entries 5–7, Table 3). Substrates with *ortho*-methyl and *ortho*-amino substituents, which retard both the oxidative addition and transmetalation processes, were proven less active in other catalytic systems [20,23], but could achieve high yield with prolonged reaction time in this study (entries 8–10, Table 3). Significantly, the sterically hindered substrate 2,4,6-trimethybromombenzene afforded a satisfactory yield (95%) (entry 12, Table 3). However, the catalytic system was less effective with substrates such as aryl chlorides, even under harsh conditions.

In summary, a series of β-ketoamine ligands with different steric and electronic substituents were synthesized and characterized. The ligands were complexed to $PdCl_2$ in situ and were successfully employed in Suzuki cross-coupling reactions, under aerobic conditions. Catalytic studies revealed that **L4**, with a sterically demanding and electron-donating structure, was most efficient and enabled the coupling of a wide variety of aryl bromides with phenylboronic acid in high yields. Additional studies focused on the coupling of aryl chlorides using β-ketoamine ligands are currently underway.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.01.044.

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[49] The β-ketoamine ligands **L1**–**3** were synthesized by the following procedures. A solution of enaminone (10 mmol) and the related substituted aniline (12 mmol) were dissolved in ethanol (20 ml), with the formic acid as catalyst. The mixture was heated under reflux for 6 hours. As for **L4**–**5**, the reaction carried out in the presence of 20 ml glacial acetic acid instead of ethanol. After recrystallization from the methanol, the crystals were obtained. **L1**–**2** have been well characterized by the literatures, however, the analysis data of **L3** and **L5** was absent. **L3**: yellow crystals in 92% yield; ^{1}H NMR ($CDCl_3$, 500 MHz): 12.11 (d, J= 12.6 Hz, 1H, NH), 7.92 (d, J= 8.4 Hz, 2H, Ar-H), 7.40 (m, 1H, CH=), 7.02 (m, 2H, Ar-H), 6.95 (m, 2H, Ar-H), 6.89 (m, 2H, Ar-H), 5.94 (d, J= 10 Hz, 1H, CH=), 3.81 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3).^{13}C NMR ($CDCl_3$, 125 MHz): 189.65, 162.33, 156.20, 145.27, 134.01, 132.11, 129.21, 117.76, 114.99, 113.62, 92.61, 55.89, 55.39. *Anal.* Calc. for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 71.95; H, 6.10; N, 4.87. **L4**: flavo-green crystals in 73% yield; ^{1}H NMR ($CDCl_3$, 500 MHz): 12.22 (d, J=12 Hz, 1H, NH), 7.94 (d, J=9 Hz, 2H, Ar-H), 7.55 (m, 1H, CH=), 7.39 (m, 2H, Ar-H), 7.29 (m, H, Ar-H), 7.15 (m, 2H, Ar-H), 7.14 (m, 2H, Ar-H), 7.00-6.90 (m, 4H, Ar-H), 6.05 (d, J= 9 Hz, 1H, CH=), 3.89 (s, 3H, OCH_3).^{13}C NMR ($CDCl_3$, 125 MHz): 190.12, 162.59, 156.69, 146.46, 143.15, 132.34, 132.30, 130.00, 129.63, 124.09, 124.03, 123.32, 119.51, 118.86, 114.52, 113.76, 94.58, 55.58. *Anal.* Calc. For $C_{22}H_{19}NO_3$: C, 76.50; H, 5.54; N, 4.06; Found: C, 76.34; H, 5.62; N, 4.01. **L5**: yellow crystals in 61% yield; ^{1}H NMR ($CDCl_3$, 500 MHz): 12.24 (d, J=12 Hz, 1H, NH), 8.24 (d, J=7 Hz, 2H, Ar-H), 7.95 (m, 1H, CH=), 7.48 (m, 2H, Ar-H), 7.13 (m, 2H, Ar-H), 6.97 (m, 2H, Ar-H), 6.16 (d, J=8 Hz, 1H, CH=), 3.89 (s, 3H, OCH_3).^{13}C NMR ($CDCl_3$, 125 MHz): 191.45, 162.67, 145.50, 142.16, 141.13, 130.74, 129.27, 129.27, 125.61, 114.57, 113.40, 96.34, 55.01. *Anal.* Calc. For $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39; Found: C, 64.35; H, 4.64; N, 9.33.
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