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Efficient phosphine ligands for the one-pot palladium-catalyzed borylation/Suzuki–Miyaura cross-coupling reaction†

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We report the synthesis of 2-(anthracen-9-yl)-1*H*-inden-3-yl dicyclohexylphosphine and its use in palladium-catalyzed borylation/Suzuki–Miyaura cross-coupling reaction to prepare a variety of symmetrical and unsymmetrical biaryl compounds in excellent yield.

Introduction

The Suzuki–Miyaura cross-coupling of boronic acids with organic halides is one of the most widely applied methods in modern synthetic organic chemistry.[1] Since the first report of the palladium-catalyzed cross-coupling reaction between an aryl halide and an arylboronic acid by Suzuki and Miyaura in 1981,[2] it has emerged as a synthetic method that tolerates a wide range of functional groups providing reliable and efficient access to structurally diverse biaryl motifs.[3] It is for these reasons that it remains one of the most important methods of choice for C–C bond formation in both industrial and academic groups. Fueled by the commercial availability of numerous organic halides and boronic acids, and the constant development of improved catalyst systems,[4] intense research efforts continue in this area.

With all of the advances, the Suzuki–Miyaura cross-coupling reaction still suffers a major limitation in that it relies upon the direct use of boronic acids. Although many boronic acids are commercially available, they can be very expensive and decompose upon storage over time, often resulting in the need to use at least 1.2 equiv. (with regard to the organic halide) in a typical Suzuki–Miyaura cross-coupling reaction.[5] In addition, when boronic acid is not commercially available, its synthesis is required, adding additional, often lengthy, steps to the synthetic process.[6]

Over the last two decades, progress has been made to circumvent some of the limitations of the Suzuki–Miyaura cross-coupling reaction with the advent of the one-pot borylation/Suzuki–Miyaura cross-coupling reaction. The first system was reported by Miyaura in 1997,[6d] which involved converting an aryl triflate *in situ* into a boronate ester followed by the addition of a second aryl triflate along with the palladium catalyst and a base. Since then, the development of one-pot, catalytic C–H or C–X borylation/Suzuki–Miyaura coupling processes have allowed the preparation of unsymmetrical biaryl compounds.[7,8] This protocol has been applied to the syntheses of pharmaceuticals.[9] However, a high catalyst loading (5–10 mol%) and the addition of a second portion of the palladium catalyst are necessary. In 2007, Buchwald reported that $Pd_2(dba)_3$ and XPhos actively combine to efficiently catalyze the one-pot borylation/Suzuki–Miyaura coupling reaction without the need to add a second portion of the catalyst prior to conducting the Suzuki–Miyaura coupling reaction.[10] In this process, an excess amount of the phosphine ligand (P/Pd, 4 : 1) was required. Recently, Buchwald demonstrated an efficient synthesis of biaryl compounds from aryl halides using a lithiation/borylation/Suzuki–Miyaura coupling sequence under continuous-flow conditions.[11] In addition, the groups of Molander,[12] Kwong,[13] Zhang,[14] Wu,[15] and others have reported their progress. Despite these advances, many limitations remain. These include: (1) high catalyst loading is employed or a second loading of the catalyst is often required to facilitate the Suzuki–Miyaura coupling reaction in the second step, and (2) heteroaryl halides, which are important for medicinal chemistry applications, react slowly with a narrow scope and often require a higher catalyst loading when compared with aryl halides.

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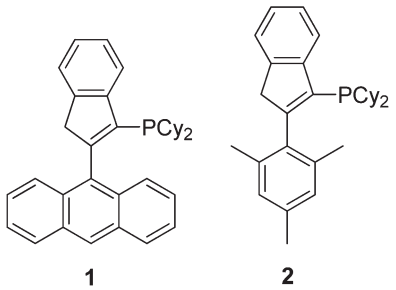


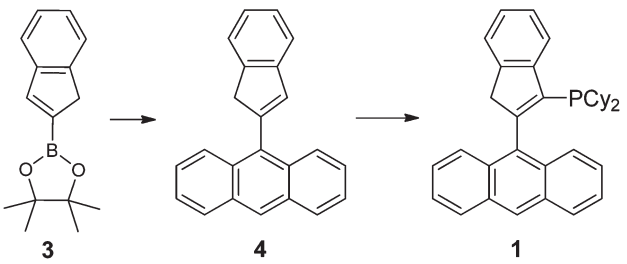
Scheme 1 Ligands used in this study.

We have developed a series of 2-aryl indenyl phosphine ligands and have demonstrated their high reactivity in the Suzuki–Miyaura coupling reaction, Buchwald–Hartwig amination reaction, dehydrogenation reactions and hydration reactions.[16] Herein we report the application of 2-aryl indenyl phosphine ligands **1** and **2**[16c] (Scheme 1) in the one-pot, palladium-catalyzed borylation/Suzuki–Miyaura cross-coupling reaction. Excellent reactivity has been achieved on a series of aryl halide and heteroaryl halide substrates.

Results and discussion

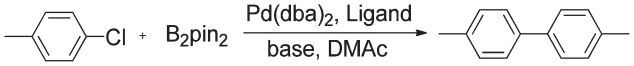
The synthesis of **1** was accomplished in three steps from indenyl boronic ester **3**, which could be prepared on a kilogram scale from 2-bromo-1*H*-indene. The palladium-catalyzed Suzuki–Miyaura coupling of **3** with 9-bromoanthracene provided **4** in 87% yield.[17] Then, straightforward deprotonation of **4** using *n*BuLi and trapping of the lithiated intermediate with dicyclohexyl phosphine chloride (Cy_2PCl) afforded the monophosphine ligand **1** in 68% yield (Scheme 2). Ligand **1** was found to be stable under air.

To test the effectiveness of this new ligand **1**, we initially investigated the one-pot reaction of 4-chlorotoluene with bis(pinacolato)diboron to establish the feasibility of our strategy and to optimize the reaction conditions (Table 1). First, the reaction was conducted without any base and/or phosphine ligand and no product was obtained (Table 1, entries 1–3). Then 2.0 mol% $Pd(dba)_2$, 4.0 mol% phosphine ligand **1** and 3.0 equivalent KOAc were used and a 12% yield of the symmetrical biaryl product was observed (Table 1, entry 4). The use of the base was found to be crucial for a high yield. Strong bases such as Cs_2CO_3, $CsOH{\cdot}H_2O$ and *t*BuONa provided moderate yields (Table 1, entries 5–7), while the weak base $K_3PO_4{\cdot}3H_2O$ proved to be the most efficient and gave an 81% yield (GC yield is 91%) (Table 1, entry 8). A scanning of commercially available palladium precursors revealed that $Pd(dba)_2$ was the best choice (Table 1, entries 8–10). In addition to ligand **1**, the use of ligand **2** was examined for comparison with moderate conversions being observed in this reaction (Table 1, entry 11).



Scheme 2 Synthesis of ligand **1**.

Table 1 Optimization of the reaction conditions[a]

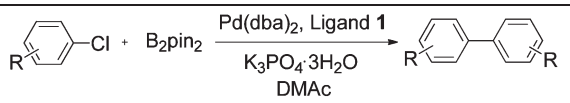


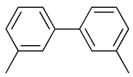
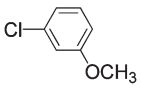
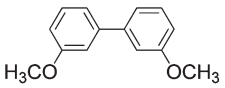
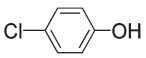
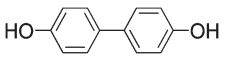
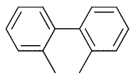
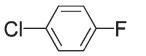
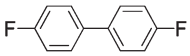
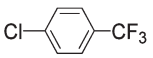
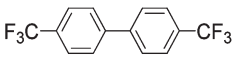
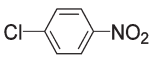
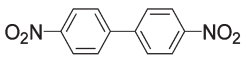
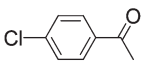
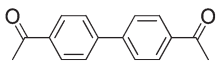
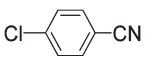
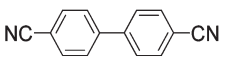
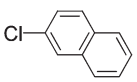
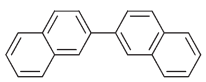
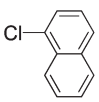
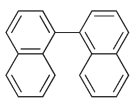
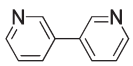
Entry	Pd precursor	Ligand	Base	Yield[b] (%)
1	$Pd(dba)_2$	—	—	0
2	$Pd(dba)_2$	**1**	—	0
3	$Pd(dba)_2$	—	KOAc	0
4	$Pd(dba)_2$	**1**	KOAc	12
5	$Pd(dba)_2$	**1**	Cs_2CO_3	40
6	$Pd(dba)_2$	**1**	$CsOH{\cdot}H_2O$	44
7	$Pd(dba)_2$	**1**	*t*BuONa	36
8	$Pd(dba)_2$	**1**	$K_3PO_4{\cdot}3H_2O$	81 (91)[c]
9	$Pd(OAc)_2$	**1**	$K_3PO_4{\cdot}3H_2O$	47
10	$PdCl_2$	**1**	$K_3PO_4{\cdot}3H_2O$	44
11	$Pd(dba)_2$	**2**	$K_3PO_4{\cdot}3H_2O$	58

[a] Reaction conditions: 2.4 mmol 4-chlorotoluene, 1.0 mmol bis(pinacolato)diboron, 0.02 mmol Pd source, 0.04 mmol ligand, 3.0 mmol base, 2.0 mL DMAc, 100 °C, 20 h. [b] Isolated yield. [c] GC yield.

Under the optimized reaction conditions (Table 1, entry 8), a wide range of aryl chlorides reacted smoothly to provide symmetrical biaryl products (Table 2). For example, 3-chlorotoluene was directly converted into the symmetrical biaryl product in high yield (Table 2, entry 1). Borylation/Suzuki–Miyaura cross-coupling reactions of substrates bearing electron-donating substituents such as $-OCH_3$ and –OH occurred smoothly, providing high yields of the expected products (Table 2, entries 2 and 3). The reaction of the relatively hindered 2-chlorotoluene gave the desired product in moderate yield (Table 2, entry 4). Aryl chlorides bearing electron-withdrawing groups such as –F, $-CF_3$, $-NO_2$ and $-COCH_3$ at the *para* position also permit the borylation/Suzuki–Miyaura cross-coupling reaction, giving the required products in good yields (Table 2, entries 5–8). Moreover, the base-sensitive –CN group was tolerated using our catalytic system and the corresponding symmetrical biaryl product was obtained in a near-quantitative yield (Table 2, entry 9). In addition, 2-chloronaphthalene and 3-chloronaphthalene underwent the desired reaction, giving the symmetrical binaphthalenes in moderate yield (Table 2, entries 10 and 11). To further extend the scope of the reaction using our catalytic system, we investigated the reaction of 3-chloropyridine; fortunately, the desired 3,3′-bipyridine was obtained in 76% yield (Table 2, entry 12).

Table 2 Palladium-catalyzed one-pot preparation of symmetrical biaryl compounds[a]



Entry	Substrate	Product	Yield[b] (%)
1			90
2			95
3			90
4			72
5			82
6			84
7			88
8			81
9			97
10			70
11			72
12			76

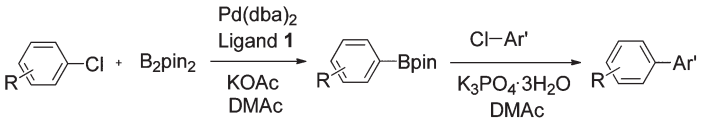
[a] Reaction conditions: 2.4 mmol aryl chlorides or heteroaryl chlorides, 1.0 mmol bis(pinacolato)diboron, 2.0 mmol% $Pd(dba)_2$, 4.0 mmol% ligand **1**, 3.0 mmol $K_3PO_4{\cdot}3H_2O$, 2.0 mL DMAc, 100 °C, 20 h. [b] Isolated yield.

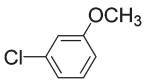
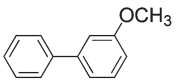
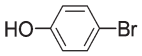
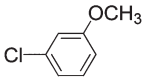
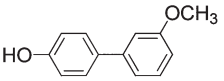
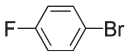
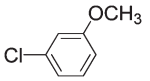
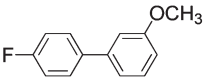
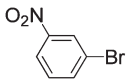
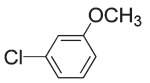
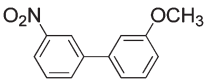
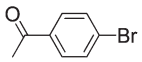
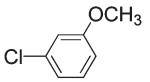
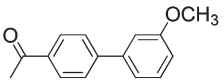
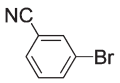
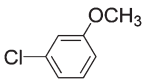
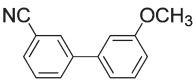
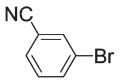
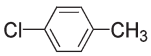
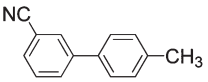
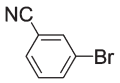
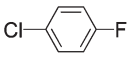
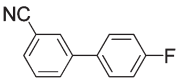
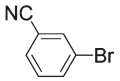
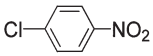
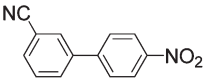
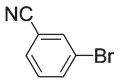
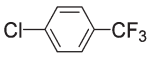
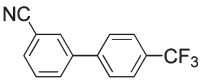
To further extend the scope of our catalytic system, we carried out reactions towards the direct synthesis of unsymmetrical biaryl compounds. In this endeavor, a catalytic system based upon $Pd(dba)_2$ and ligand **1** proved to be effective for borylation as well as the subsequent Suzuki–Miyaura cross-coupling reaction. In this process, aryl bromides were subjected to the Pd-catalyzed borylation conditions with the addition of the second aryl chloride and $K_3PO_4{\cdot}3H_2O$. No workup was performed or catalyst added prior to conducting the second reaction in the sequence (Table 3). For example, bromobenzene was subject to the Suzuki–Miyaura cross-coupling reaction after the borylation reaction; the resulting boronic ester could smoothly couple with 3-chloroanisole and give the desired product in 96% yield (Table 3, entry 1). Aryl bromides bearing electron-donating and electron-withdrawing groups such as –OH, –F, and $–NO_2$ were also tolerated in the borylation and subsequent cross-coupling reaction with aryl chloride and afforded the corresponding products in high yields (Table 3, entries 2–4). It is noteworthy that this protocol avoids the α-arylation reaction of ketones with aryl boronate esters, and no reduction of ketones as previously observed in the aryl halide borylation of ketones was observed when they were employed in the second step (Table 3, entry 5).[18] In addition, aryl bromide bearing the base-sensitive –CN group was tolerated in our catalytic system (Table 3, entries 6–10). Moreover, aryl chlorides with both electron-donating and electron-withdrawing groups could be employed in the second step while maintaining good to excellent yields of the unsymmetrical biaryl products (Table 3, entries 6–10).

Heterocyclic compounds are of particular interest in the pharmaceutical industry.[19] The application of heterocyclic compounds in cross-coupling reactions still remains a synthetic challenge,[20] because the ligating ability of the heteroatoms present can lead to catalyst deactivation. In addition, the electronic properties at certain positions in the heterocycle can be unfavorable for the elementary reactions required for these catalytic processes.[21] We next turned our attention to exploring the scope of heteroaryl halides. As few heteroaryls performed exceptionally well under the general borylation conditions, we focused on their use as coupling partners in the second step. As outlined in Table 4, all heteroaryl chlorides undergo efficient cross-coupling reactions. For example, 3-chloropyridine and 2-chloropyridine provided good to excellent yields (Table 4, entries 1–3). 2-Chlorothiophene coupled smoothly and provided a moderate yield over two steps (Table 4, entry 4). 4-Chlorobenzonitrile was also tolerated in the borylation reaction and subsequent cross-coupling reaction with heteroaryl chlorides such as 2-chloropyridine, 3-chloropyridine, 2-chloropyrazine and 2-chloroquinoxaline, to afford the desired heteroaryl products in good yield (Table 4, entries 5–8). In addition, 3-chloropyridine was tolerated in the borylation reaction and subsequent reaction with 2-chloroquinoxaline to give the corresponding heteroaryl product in 51% yield (Table 4, entry 9).

To carry out an economical large-scale synthesis of fine chemicals, a low loading catalyst is needed. To further study the efficiency of our catalytic system, we then studied the TON (turnover number) of our catalytic system at low loading. For example, carrying out the one-pot reaction of 3-chloropyridine with bis(pinacolato)diboron at a palladium loading of 0.2 mol% led to an yield of 27% after 20 h (Table 5, entry 1). This corresponds to a TON of 135.

Table 3 Palladium-catalyzed one-pot two-step preparation of unsymmetrical biaryl compounds[a]



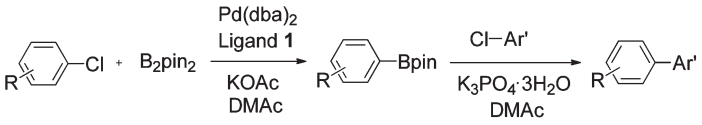
Entry	Ar–X	Ar'Cl	Product	Yield[b] (%)
1				96
2				88
3				82
4				81
5				93
6				95
7				88
8				82
9				88
10				89

[a] Reaction conditions: 1.2 mmol the first aryl bromides, 1.0 mmol the second aryl chlorides, 1.2 mmol bis(pinacolato)diboron, 2.0 mmol% $Pd(dba)_2$, 4.0 mmol% ligand **1**, 3.0 mmol KOAc, 3.0 mmol $K_3PO_4{\cdot}3H_2O$, 2.0 mL DMAc, 100 °C. [b] Isolated yield.

Conclusion

In summary, a novel, efficient and air-stable anthracenyl substituted indenyl phosphine ligand **1** was synthesized in high yield and used to generate a very active and broadly useful Pd catalyst system for the borylation/Suzuki–Miyaura cross-coupling reaction. With the Pd/**1** catalyst system, a range of aryl chlorides bearing various functional groups can be converted into symmetrical biaryl compounds. A direct synthesis of unsymmetrical biaryls from aryl chlorides or aryl bromides using a one-pot, two-step procedure can also be successfully accomplished using this catalyst system without an excess amount of ligand and the addition of a catalyst in the second step. Such methodology tolerated not only a number of functional groups, but also was applied successfully to a range of heteroaryl chlorides.

Table 4 Use of heteroaryl chlorides as electrophiles in the palladium-catalyzed one-pot two-step preparation of unsymmetrical biaryl compounds[a]



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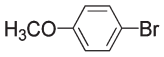
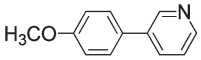
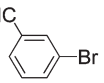
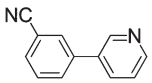
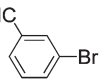
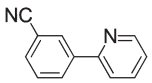
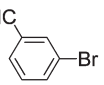
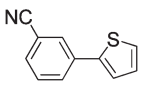
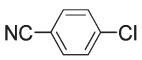
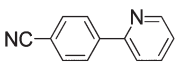
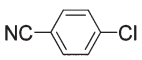
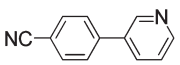
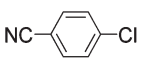
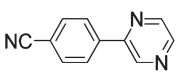
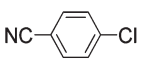
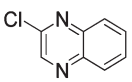
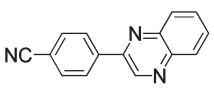
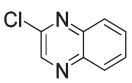
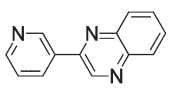
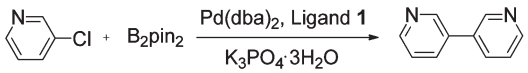
1				87
2				92
3				94
4				65
5				81
6				89
7				88
8				91
9				51

[a] Reaction conditions: 1.2 mmol of aryl halides, 1.0 mmol of heteroaryl chlorides, 1.2 mmol of bis(pinacolato)diboron, 2 mmol% $Pd(dba)_2$, 4 mmol% $\mathbf{L_1}$, 3.0 mmol KOAc, 3.0 mmol of $K_3PO_4{\cdot}3H_2O$, 2.0 mL DMAc, 100 °C. [b] Isolated yield.

Table 5 Palladium-catalyzed one-pot preparation of symmetrical heteroaryl compounds using ultra-low loading of the catalyst[a]



Entry	Mol% Pd	Yield[b] (%)	TON
1	0.2	27	135
2	0.02	<5	—

[a] Reaction conditions: 2.4 mmol 3-chloropyridine, 1.0 mmol bis-(pinacolato)diboron, $Pd(dba)_2$/ligand **1** = 1 : 2, 3.0 mmol $K_3PO_4{\cdot}3H_2O$, 2.0 mL DMAc, 100 °C, 20 h. [b] Isolated yield.

Acknowledgements

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