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Synthesis of a class of binaphthyl monophosphine ligands with a naphthofuran skeleton and their applications in Suzuki-Miyaura coupling reactions

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Abstract: A series of new monophosphine ligands containing a naphthofuran skeleton have been prepared, characterized and evaluated in the palladium-catalyzed Suzuki-Miyaura coupling reactions. Using $Pd_2(dba)_3$-**L6** as the catalyst the reactions were performed with high catalytic activity under mild reaction conditions and the desired coupling products were obtained in good to excellent yields. The new catalyst system also showed broad substrate adaptability and practicality for gram-scale production.

Introduction

In 1979, Akira Suzuki and co-workers firstly reported Pd-catalyzed cross-coupling between an organoboron compound and an organic halide.[1,2] Nowadays, this kind of reaction named after words for Suzuki-Miyaura coupling reaction has become one of the most efficient and powerful methods for the construction of organic biaryl frameworks under mild reaction conditions because of broad functional group tolerance of this transformation. Besides, organoboron reagents and aryl halides can be easily obtained via various ways and they all exhibit low toxicities and high stabilities towards air and moisture.[3-12] Ligand structure is a key factor in this reaction, this is based on two effects: 1) the ligands can increase catalyst stability by preventing cyclometalation and promoting the formation of Pd(0); 2) the lone pairs of the hetero atom such as N or O might coordinate with [Pd] or increase electron density to the ligand, and this will help to stabilize intermediate [Pd] complexes.[10, 13, 14, 15] In 1998, Buchwald and co-workers reported an amino

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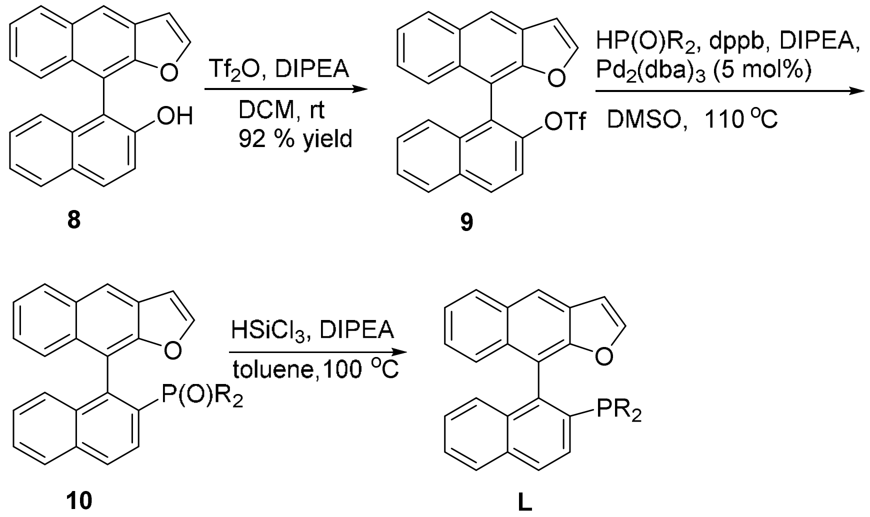
phosphine ligands for Suzuki coupling of aryl chlorides at room-temperature.[16] Since than, a series of bulkily substituted diphenyl monophosphine ligands haves been prepared and used for Suzuki coupling.[17-29]

Although many of efficient phosphine ligands had been developed over the past 35 years,[17-44] the influence of their steric structure and electronic property on the reaction performance need to be further explored for the diversity of substrate and reaction. Most recently, we developed a series of new biphenyl monophosine ligands with a chiral-bridged chain.[45, 46] The lone pair electrons of the alkoxy oxygen and amino nitrogen atoms might interact with the Pd center and increase the electron density, which could be beneficial to stabilize the intermediate complexes of ligand and Pd.[13, 14, 15, 18, 21, 47-52] Based on this viewpoint, continuing efforts in developing new biaryl phosphine ligands proceed in our laboratory. Herein, we report the progress in preparation of a class of binaphthyl monophosphine ligands containing a naphthofuran skeleton and their applications in Suzuki-Miyaura coupling reactions.



8 **9** **10** **L**

10a: R = Ph, 71% yield
10b: R = 4-MeC_6H_4, 75% yield
10c: R = 3,5-$Me_2C_6H_3$, 69% yield
10d: R = 3,5-$^tBu_2C_6H_3$, 63% yield
10e: R = 3,5-$^tBu_2$-4-$MeOC_6H_2$, 61% yield
10f: R = Cy, 51% yield

L1: R = Ph, 83% yield
L2: R = 4-MeC_6H_4, 85% yield
L3: R = 3,5-$Me_2C_6H_3$, 79% yield
L4: R = 3,5-$^tBu_2C_6H_3$, 89% yield
L5: R = 3,5-$^tBu_2$-4-$MeOC_6H_2$, 87% yield
L6: R = Cy, 74% yield

Scheme 1. Synthesis of ligands **L1**-**L6**

Results and discussion

The synthetic protocol was shown in Scheme 1. Compound **8** was synthesized from BINOL as

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showed in detail in the supporting information. Then the target ligands were readily prepared in high yields from compound **8** in 3 steps. Treatment of **8** with trifluoromethanesulfonic anhydride in the presence of DIPEA afforded **9** quantitatively. Catalytic introduction of $R_2P(O)$- moisty to compound **9** was carried out by using $R_2P(O)H$ in dppb, 5 mol% of $Pd_2(dba)_3$ and DIPEA in an anhydrous DMSO system. The corresponding product **10** were provided in 51~75 % yields. Other Pd source or similar diphosphine ligands such as $Pd(OAc)_2$ or dppp or dppf only gave **10** in low yields. The desired binaphthyl monophosphine ligands with a naphthofuran skeleton (**L1**-**L6**) were finally afforded in 79~89% yields by reduction of **10** in the presence of DIPEA and $HSiCl_3$ in toluene.

After acquiring ligands **L1**-**L6** successfully, they were applied to palladium-catalyzed Suzuki-Miyaura coupling reaction. As shown in table 1, cross-coupling of 1-bromo-2-methoxynaphthalene and naphthalen-1-ylboronic acid was chosen as the model reaction. With $Pd_2(dba)_3$-**L6** as the catalyst, K_3PO_4 as the base, various solvents including toluene, THF, dioxane and DMF were examined at 80 ^{o}C under N_2 for 0.5 h (table 1, entries 1-4). Interestingly, the solvent polarity was found to have great impact on the yield of the reaction, and only 82 % yield was obtained using DMF as the solvent (table 1, entry 4). In contrast, toluene showed the best performance with a 99% yield given (table 1, entry 1). Encouraged by the results, the base optimization was then carried out. $K_3PO_4$was found to be the best one. Changing K_3PO_4 to Cs_2CO_3, KF, KHF_2 or K_2CO_3, the yields decreased significantly (table 1, entries 5-8). Using $Pd(OAc)_2$ or $PdCl_2$ instead of $Pd_2(dba)_3$, the desired product was only obtained in 89 % and 81 % yield, respectively (table 1,entries 9-10). This displays the superiority of $Pd_2(dba)_3$ as the palladium source. On the basis of these results, different ligands (**L1**-**L5**) were further screened (table 1, entries 11-15), and **L6** was the best one among all of the ligands. In order to further investigate the effectiveness of **L6**-$Pd_2(dba)_3$, the amount of palladium was reduced to 0.5 mol% and substrate **A** was increased to 0.4 mmol. There was a light yield decrease after a reaction time of 6 hours (table 1, entry 16). In addition, catalytic activity of **L6** in low temperature (40 ^{o}C, 60 ^{o}C) and [Pd]/**L** ratio (1:0.5) were also tested. Product **AB** was given in 54 %, 71 % and 79 % yields respectively, along with a lot of starting material retained. This implies that 80 ^{o}C and the ratio of 1:1 are the appropriate choice for the reaction temperature and [Pd]/L ratio in our catalyst system. Given the above results, the optimal reaction conditions were the combination of $Pd_2(dba)_3$ (1.0 mol%), **L6** (2.0 mol%), K_3PO_4, toluene, 80 ^{o}C and nitrogen atmosphere. As control, only a

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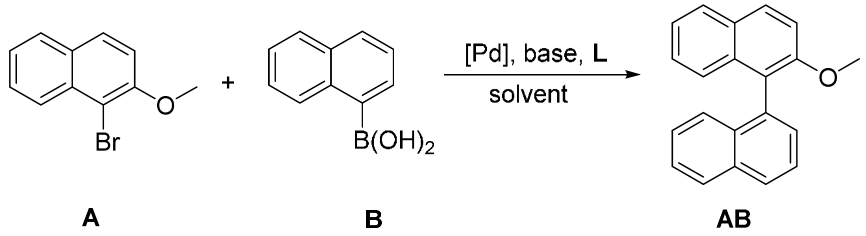
moderate yield was obtained for the reaction when Cy-MOP was employed as the ligand (81 % vs 99% yield, table 1, entry 17 vs entry 1). This clearly demonstrates the efficacy of introduction of the naphthofuran moiety.

Table 1: Pd-catalyzed Suzuki-Miyaura coupling of 1-bromo-2-methoxynaphthalene and naphthalen-1-ylboronic acid[a].



Entry	[Pd]	Base	L	Solvent	Yield (%)[b]
1	$Pd_2(dba)_3$	K_3PO_4	**L6**	toluene	99
2	$Pd_2(dba)_3$	K_3PO_4	**L6**	THF	95
3	$Pd_2(dba)_3$	K_3PO_4	**L6**	dioxane	93
4	$Pd_2(dba)_3$	K_3PO_4	**L6**	DMF	82
5	$Pd_2(dba)_3$	Cs_2CO_3	**L6**	toluene	90
6	$Pd_2(dba)_3$	KF	**L6**	toluene	81
7	$Pd_2(dba)_3$	KHF_2	**L6**	toluene	83
8	$Pd_2(dba)_3$	K_2CO_3	**L6**	toluene	79
9	$Pd(OAc)_2$	K_3PO_4	**L6**	toluene	89
10	$PdCl_2$	K_3PO_4	**L6**	toluene	81
11	$Pd_2(dba)_3$	K_3PO_4	**L1**	toluene	94
12	$Pd_2(dba)_3$	K_3PO_4	**L2**	toluene	95
13	$Pd_2(dba)_3$	K_3PO_4	**L3**	toluene	97
14	$Pd_2(dba)_3$	K_3PO_4	**L4**	toluene	96
15	$Pd_2(dba)_3$	K_3PO_4	**L5**	toluene	96
16	$Pd_2(dba)_3$	K_3PO_4	**L6**	toluene	92[c]
17	$Pd_2(dba)_3$	K_3PO_4	**Cy-MOP**	toluene	81

[a] Reaction conditions: 0.2 mmol of **A**, 0.4 mmol of **B**, 0.6 mmol of base, [Pd] (2 mol%), **L** (2 mol%), solvent (4.0 mL), 0.5 h, 80 ^{o}C; [b] Determined by isolated yield; [c] 0.4 mmol of **A**, [Pd] (0.5 mol%), **L** (0.5 mol%), 6 h.

With the optimized reaction conditions in hand, we next turned our attention to the scope and limitations of this reaction using a variety of boronic acids with 1-bromo-2-methoxynaphthalene (table 2). It was found that aryl boronic acids with *ortho*-substituted groups such as -OMe, -OEt, -Ph, -F, or -Cl reacted with **A** quickly to give the corresponding desired products in excellent yields (table 2, entries 1-5). It is worth noting that the yields are also very high for aryl boronic

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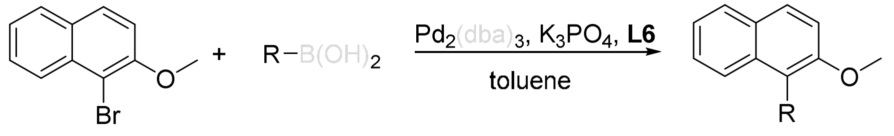
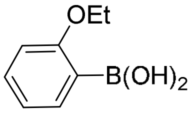
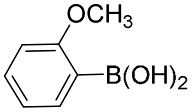
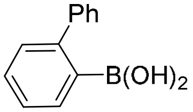
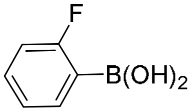
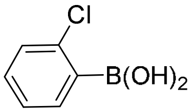
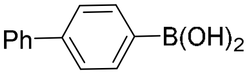
acids possessing strong electron-withdrawing groups such as 4-OCF_3, 4-CF_3 and 3-COOMe substituents (table 2, entries 11, 12 and 14). Generally, alkyl-substituted aromatic derivatives are important substructure in organic synthesis. Especially for arylcyclo propanes, they play an important role in pharmaceutically active molecules.[53-57] Gratifyingly, reaction with alkylboronic acids bearing cyclopropyl or *n*-butyl group still gave the desired products in good yields (table 2, entries 15 and 16, **AB$_{15}$** and **AB$_{16}$**), and the obtained results are better than those using phosphine adducts of cyclopalladated ferrocenylimine as the catalyst.[57] Further reducing the [Pd]/**A** ratio from 1.0 mol% to 0.1 mol%, the conversion decreased obviously, but moderate yield was still obtained (table 2, entry 2). When pyridylboronic acids were used as the substrate under the above-mentioned general conditions, the reactions just only acquired low yields. Employing *i*-PrOH instead of toluene as the solvent, however, 82% and 91% yields for the target products (**AB$_{17}$** and **AB$_{18}$**) were obtained satisfactorily (table 2, entries 17 and 18).

Table 2: Suzuki-Miyauracoupling reactions using different boronic acids[a].



A **B$_n$** **AB$_n$**

Entry	Boronic acid	[Pd] (mol%)	Time (h)	Yield of AB$_n$ (%)[b]
1		1	0.5	99
2		1	0.5	99(79 [c])
3		1	0.5	99
4		1	0.5	96
5		1	0.5	98
6		1	0.5	96

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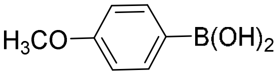
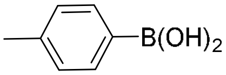
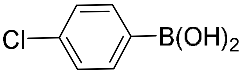
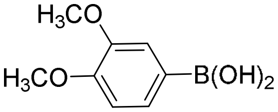
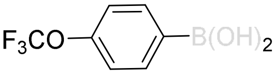
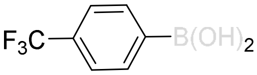
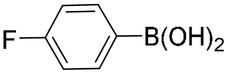
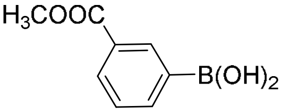
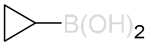
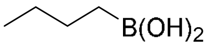
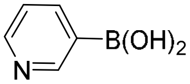
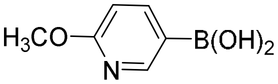
7		1	0.5	99
8		1	0.5	99
9		1	0.5	98
10		1	0.5	97
11		1	0.5	97
12		1	0.5	98
13		1	0.5	97
14		1	0.5	96
15		1	1	89
16		1	1	93
17		2	6	82[d]
18		2	6	91[d]

[a] Reaction conditions: 0.2 mmol of **A**, 0.4 mmol of $\mathbf{B_n}$, 0.6mmol of K_3PO_4, **L6** (1 equiv. of [Pd]), toluene (4.0 mL), 80 ^{o}C; [b] Determined by isolated yield; [c] gram scale, 4.3 mmol of **A**, 0.1 mol% of [Pd], 0.1 mol% of **L6**, 36 h. [d] *i*-PrOH (4.0 mL) as the solvent.

The substrate scope of the reaction was further extended to various aryl halides, and the results are summarized in table 3. A variety of functional groups such as -CHO, -CH_2CN, -NH_2, -NO_2 and heterocyclic groups were tolerated under the reaction conditions. To our delight, the reactions proceeded fluently in high yields even for bulky substrates with substituents at 2- or 6-position of the aryl halides (table 3, entries 2 *vs* 3 and 5 *vs* 6). In addition, substrates with electron-withdrawing substituents on the aromatic ring (table 3, entries 4 and 11) and hetero aryl halides (table 3, entries 13 and 14) were also tested in this reaction. The desired products were given in good to excellent yields, but 2 mol% of the Pd catalyst and 3 hours of reaction time were

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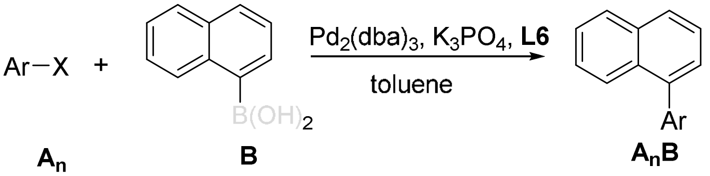
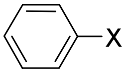
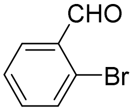
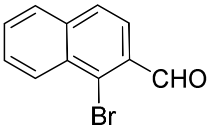
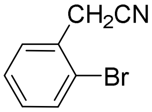
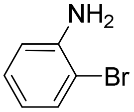
needed for the reaction of bromobenzene with an *ortho*-acetonitrile substituent (table 3, entry 4). Even for the substrate with a bulky benzyloxy substituent and a strong electron-withdrawing aldehyde group at the *ortho*-position, the reaction activity and yield were still good enough (table 3, entry12). Particularly noteworthy is the coupling of aryl chloride, which is generally difficult due to the low reactivity.[13, 18, 58, 59, 60] Delightedly, our catalyst system successfully provided the desired products in good yields. For bulky 2,6-dimethylchlorobenzene the coupling yield reached 80% (table 3, entries 1, 7, 15 and 17). Coupling of 4-chloronitrobenzene gave product $\mathbf{A_{15}B}$ up to 95% yield, this result is better than that using (2-mesitylindenyl)dicyclohexylphosphine/Pd(OAc)$_2$ as the catalyst (table 3, entry 15, 95% *vs* 85%).[61] Moreover, our catalyst system can also be used for the synthesis of some complicated compounds. For example, cross-coupling of an indole derivative and 1-naphthylboronic acid successfully provided the desired product $\mathbf{A_{16}B}$ in 94% yield (table 3, entry 16).

Table 3. Suzuki-Miyaura coupling reactions using different aryl halide [a]



Entry	Aryl halide	[Pd] (mol%)	Time (h)	Yield of A_nB (%)^b
1	 X = Br X = Cl	1	0.5 4	99 89^c
2		1	0.5	99
3		1	0.5	99
4		2	3	87
5		1	0.5	92

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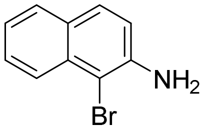
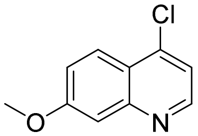
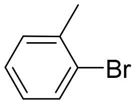
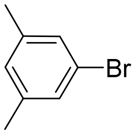
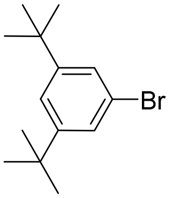
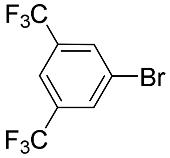
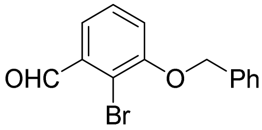
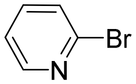
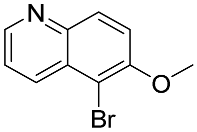
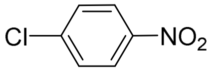
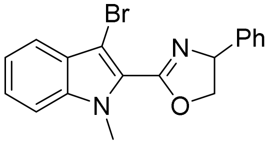
6		1	0.5	94
7		1	8	78
8		1	0.5	99
9		1	0.5	99
10		1	0.5	99
11		1	0.5	95
12		1	2	85
13		1	1	93
14		1	1	95
15		1	4	95
16		1	1	94

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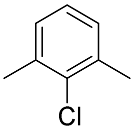
17		1	12	80

^{a} Reaction conditions: 0.2 mmol of $\mathbf{A_n}$, 0.4 mmol of **B**, 0.6 mmol of K_3PO_4, **L6** (1 equiv. of [Pd]), toluene (4.0 mL), 80 ^{o}C; ^{b} Determined by isolated yield; $^{c}\mathbf{A_n}$ is chlorobenzene, 100 ^{o}C.

Conclusions

A series of novel binaphthyl monophosphine ligands with a naphthofuran skeleton **L1**-**L6** were successfully developed and applied to palladium-catalyzed Suzuki-Miyaura coupling reactions with high catalytic activity and good to excellent yields. Extensive substrate structure adapt ability in both aryl halides and boronic acids and high functional group tolerance were also displayed. The introduction of naphthofuran skeleton with more rigidity and higher electron density gave the ligands better performance than the parent MOP in the catalytic reactions.

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The **L6**-Pd$_2$(dba)$_3$ showed excellent activity in the Suzuki-Miyaura reaction of sterically hindered and electron-rich aryl halide with aryl boronic acids.