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Highly efficient nickel/phosphine catalyzed cross-couplings of diarylborinic acids with aryl tosylates and sulfamates

KE HaiHua, CHEN XiaoFeng, FENG YuanYuan & ZOU Gang*

Department of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China

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Highly efficient cross-couplings of diarylborinic acids with aryl tosylates and sulfamates are reported for construction of biaryls using a tri(4-methoxyphenyl)phosphine-supported nickel catalyst system: $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ in the presence of $K_3PO_4·3H_2O$ in toluene. A variety of unsymmetrical biaryls could be obtained in good to excellent yields with 1.5–3 mol% or 3–5 mol% catalyst loadings for aryl sulfamates and tosylates, respectively. In sharp contrast to the conventional nickel-catalyzed Suzuki coupling with arylboronic acids, arylsulfamates unexpectedly displayed a higher reactivity than the corresponding tosylates in coupling with diarylborinic acids catalyzed by the nickel/phosphine catalyst system.

nickel, phosphine, cross-coupling, diarylborinic acid, aryl tosylate, aryl sulfamate

1 Introduction

Because of the friendly properties of organoboronic acids (e.g. non-toxicity, air/moisture-stability, and tolerance of a variety of functional groups [1]), Suzuki coupling has become more popular in organic synthesis than other cross-coupling reactions that use air- and moisture-sensitive or toxic organometallic reagents [2]. Although they have not attracted attention until the seminal report by Percec *et al.* [3] in 1995, nickel catalysts have recently been found to display several advantages in Suzuki coupling over the well-known palladium catalysts [4]. For example, nickel catalysts are not only cost-effective but also active to many aryl C–O-based electrophiles, which in Suzuki coupling are conventionally challengeable to palladium catalysts, such as sulfonates [3, 4d), 5], esters [4d), 5d), 6], sulfamates [4d), 5h)–j), 7], carbamates [4d), 7, 8], phosphates [9], ethers [10], and even phenolates [11]. Fu group [12] effectively achieved Suzuki coupling of alkyl electrophiles by taking advantage of nickel-based catalysts. High-order arylborons, e.g. diarylborinic acids (Ar_2BOH), triarylboranes (Ar_3B), and tetraarylborates ($[Ar_4B]^-$), have not been widely applied in Suzuki coupling [13], although they have higher atom economy and could be more economically prepared under non-cryogenic conditions than arylboronic acids [1, 14]. One possible issue that has hampered the palladium-catalyzed Suzuki coupling of high-order arylborons is their stronger reduction than arylboronic acids [15], which could lead to deactivation of catalysts through reduction of the Pd(II) intermediates in the catalytic cycle. The better reduction-resisting property of Ni(II) species than the corresponding Pd(II) ones gives nickel catalysts better potential for cross-couplings of reductive high-order organoborons. We recently achieved an efficient cross-coupling of diarylborinic acids with aryl chlorides with a nickel catalyst supported by an electron-rich but sterically undemanding tri(4-methoxyphenyl)phosphine ligand, $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ [16]. Although industry has produced large-scale yields of many arylchlorides, these compounds are still far less available than the naturally abundant phenols [17]. Therefore, development of nickel-catalyzed cross-coupling of phenol derivatives with high-order organoborons, such as diarylborinic acids, is important. As a part of our

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Dedicated to Professor Qian Changtao on the occasion of his 80th birthday.
*Corresponding author (email: zougang@ecust.edu.cn)

ongoing efforts to develop arylation methodology using high-order arylborons, we report efficient cross-couplings of diarylborinic acids with aryl tosylates and sulfamates, catalyzed by the $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ catalyst system.

2 Experimental

2.1 General information

All reactions were carried out under a N_2 atmosphere unless otherwise stated. Commercially available chemicals were used as received. Nickel complexes $Ni(PCy_3)_2Cl_2$ [5j)], $Ni(dppm)Cl_2$ [18], $Ni(dppe)Cl_2$ [18], $Ni(dppp)Cl_2$ [18], $Ni(dppb)Cl_2$ [18], $Ni(dppf)Cl_2$ [19], $Ni(PPh_3)_2Cl_2$ [20], and $Ni[(4\text{-}MeOC_6H_4)_3P]_2Cl_2$ [20]; aryl sulfamates [4d)], aryl tosylates [5b)], and diarylborinic acids [13f)] were prepared according to previously reported procedures. Chemical shifts in NMR are reported in ppm (δ) relative to the internal standard of tetramethylsilane (TMS). The signals observed are described as s (singlet), d (doublet), t (triplet), dd (double doublet), and m (multiplets). The number of protons (n) for a given resonance is indicated as nH. Coupling constants are reported as J in Hz. The high-resolution mass spectra (HRMS) were performed on an electron ionization mass spectrometer (Agilent, USA) with a quadrupole analyzer. The known compounds were identified by their spectral data of ^1H NMR and ^{13}C NMR. Characterization of the new compound **3hf** and spectra can be seen in the Supporting Information online.

2.2 General procedure for cross-couplings of aryl tosylates and sulfamates

Cross-coupling of diarylborinic acids with aryl tosylates

To a 10 mL flask were added aryl tosylate (2.0 mmol), diarylborinic acid (1.3 mmol), 3–5 mol% $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$ (0.06–0.1 mmol), $P(4\text{-}MeOC_6H_4)_3$ (0.12–0.2 mmol), $K_3PO_4\cdot 3H_2O$ (5.2 mmol), and toluene (5 mL). The mixture was stirred at 110 °C for a given time or monitored by TLC until the starting material was completely consumed. The reaction mixture was diluted with CH_2Cl_2 (15 mL). The organic layer was separated and washed with H_2O (2 × 10 mL), followed by drying over Na_2SO_4, and filtering and removal of solvents under reduced pressure to give the crude product. The pure product was obtained by column chromatography on silica gel with EtOAc/petroleum ether.

Cross-coupling of diarylborinic acids with aryl dimethylsulfamates

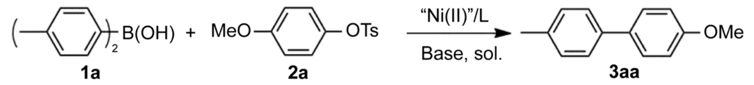
A procedure similar to the cross-coupling of aryl tosylates was adopted with aryl dimethylsulfamates but using 1.5–3 mol% catalyst loadings.

3 Results and discussion

3.1 Cross-coupling of diarylborinic acids with aryl tosylates

Among the phenol derivatives that could serve as aryl sources in arylation reactions, aryl tosylates are the most attractive because of their ready availability, low cost, high stability and good crystallization property. Cross-coupling of bis(p-tolyl)borinic acid (**1a**) with 4-methoxyphenyl tosylate (**2a**) was chosen as model reaction to screen reaction conditions considering that electron-rich aryl electrophiles are generally difficult in Suzuki coupling (Table 1). The desired product **3aa** could be obtained in 51% yield with 3 mol% $NiCl_2(PPh_3)_2/2PPh_3$ as catalyst system in the presence of $K_3PO_4\cdot 3H_2O$ in toluene at 110 °C in 10 h. Surprisingly, a couple of nickel/phosphine catalyst systems that have been reported to be more efficient in Suzuki coupling of aryl tosylates with arylboronic acids, e.g. $Ni(PCy_3)_2Cl_2$ [5e), 5j)], $Ni(dppe)Cl_2$ [5c)], $Ni(dppf)Cl_2$ [3, 21], and $Ni(dppp)Cl_2$ [22] showed no advantage over the simple $NiCl_2(PPh_3)_2/2PPh_3$ or even no activity in the model reaction (Table 1, entries 1–7). However, the yield of **3aa** could be increased to 65% under otherwise identical conditions by using the electron-rich but sterically undemanding phosphine-supported nickel catalyst system $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ (Table 1, entry 8). No further reaction was detected after prolonging the reaction time from 10 to 16 h, which implies the deactivation of the nickel/phoshphine catalyst. An inspection of the related reports on nickel-catalyzed cross-coupling of arylboronic acids indicated that the reaction of aryl tosylates appeared to be not only more difficult than halides but also much more sensitive to a change in reaction conditions [4, 5], e.g. base and solvent, etc. Aside from toluene, dioxane has proven to be another suitable solvent for nickel-catalyzed Suzuki coupling of aryl tosylates, especially when K_3PO_4 or K_2CO_3 was used as base [4f)]. However, when the model reaction was run in dioxane at 100 °C, a significantly lower yield (37%) was obtained under otherwise identical conditions (Table 1, entry 9). It was reported that a bidentate phosphine-supported nickel chloride, $Ni(dppp)Cl_2$, could serve as single-component catalyst precursor and displayed high efficiencies in cross-coupling of arylboronic acids with aryl tosylates in dioxane [22]. However, no reaction was detected for the cross-coupling of diarylborinic acid **1a** with tosylate **2a** using 3 mol% $Ni(dppp)Cl_2$ either with K_2CO_3 or K_3PO_4 in dioxane (Table 1, entries 10 and 12). When 3 mol% extra free phosphine ligand (dppp) was used along with 3 mol% $Ni(dppp)Cl_2$, the cross-coupling did take place with $K_3PO_4\cdot 3H_2O$ as base, but it gave **3aa** in just 34% yield. Finally, an acceptable yield (82%) for **3aa** was obtained in the model reaction with 5 mol% $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ in toluene (Table 1, entry 15).

Table 1 Optimization of the nickel-catalyzed cross-coupling of bis(4-tolyl)borinic acid (**1a**) with 4-methoxyphenyl tosylate (**2a**) [a)]

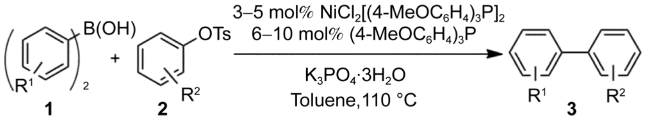


Entry	"Ni(II)" (mol%)	Extra L (mol%)	Base	Sol.	*T* (°C)	Yield (%) [b)]
1	$Ni(PPh_3)_2Cl_2$ (3)	PPh_3 (6)	$K_3PO_4·3H_2O$	toluene	110	51
2	$Ni(PCy_3)_2Cl_2$ (3)	PCy_3 (6)	$K_3PO_4·3H_2O$	toluene	110	N.R.
3	$Ni(dppf)Cl_2$ (3)	dppf (3)	$K_3PO_4·3H_2O$	toluene	110	56
4	$Ni(dppp)Cl_2$ (3)	dppp (3)	$K_3PO_4·3H_2O$	toluene	110	37
5	$Ni(dppe)Cl_2$ (3)	dppe (3)	$K_3PO_4·3H_2O$	toluene	110	34
6	$Ni(dppb)Cl_2$ (3)	dppb (3)	$K_3PO_4·3H_2O$	toluene	110	53
7	$Ni(dppm)Cl_2$ (3)	dppm (3)	$K_3PO_4·3H_2O$	toluene	110	10
8	$Ni[(4-MeOC_6H_4)_3P]_2Cl_2$ (3)	$(4-MeOC_6H_4)_3P$ (6)	$K_3PO_4·3H_2O$	toluene	110	65
9	$Ni[(4-MeOC_6H_4)_3P]_2Cl_2$ (3)	$(4-MeOC_6H_4)_3P$ (6)	$K_3PO_4·3H_2O$	dioxane	100	37
10	$Ni(dppp)Cl_2$ (3)	–	K_2CO_3	dioxane	100	N.R.
11	$Ni(dppp)Cl_2$ (3)	dppp (3)	K_2CO_3	dioxane	100	N.R.
12	$Ni(dppp)Cl_2$ (3)	–	K_3PO_4	dioxane	100	N.R.
13	$Ni(dppp)Cl_2$ (3)	dppp (3)	$K_3PO_4·3H_2O$	dioxane	100	34
14	$Ni(PPh_3)_2Cl_2$ (5)	PPh_3 (10)	$K_3PO_4·3H_2O$	toluene	110	60
15	$Ni[(4-MeOC_6H_4)_3P]_2Cl_2$ (5)	$(4-MeOC_6H_4)_3P$ (10)	$K_3PO_4·3H_2O$	toluene	110	82

a) Reaction conditions: **1a** (1.3 mmol), **2a** (2 mmol), base (5.2 mmol), sol. (5 mL), N_2, 10 h; b) isolated yields.

Considering that electron-rich 4-methoxyphenyl tosylate (**2a**) represents electronically deactivated electrophiles in Suzuki coupling, one could reasonably expect that electron-neutral and -deficient aryl tosylates would react more efficiently with diarylborinic acids using the $Ni[P(4-MeOC_6H_4)_3]_2Cl_2/2P(4-MeOC_6H_4)_3$ catalyst system. Therefore, the scope of the nickel/phosphine-catalyzed Suzuki coupling of aryl tosylates with diarylborinic acids was explored under optimal conditions (Table 2). In fact, high yields could be obtained for the corresponding cross-coupling products (**3ab**, 88%, and **3ad**, 90%) in the reactions of *p*-tolyl (**2b**) and phenyl (**2d**) tosylates. Electron-deficient aryl tosylates such as 4-acetylphenyl (**2f**), 4-ethoxycarbonylphenyl (**2g**), and 4-formylphenyl (**2h**) tosylates reacted faster than the electron-neutral or -rich analogues, even with a lower catalyst loading (3 mol%) to give cross-coupling products in excellent yields (Table 2, entries 5–7). Even aryl tosylates with a small *ortho*-substituent, *o*-methyl (**2c**) and *o*-methoxy (**2e**), still reacted smoothly (Table 2, entries 2 and 4). Structural effects of diarylborinic acids on the nickel/phosphine-catalyzed cross-coupling with aryl tosylates were also briefly investigated. Diarylborinic acids bearing an electron-donating (MeO, **1c**) or withdrawing (F, **1d**) group at the *para*-position of aromatic ring reacted with 4-acetylphenyl tosylate (**2f**) similarly to those with a neutral group (Me, **1a**, and H, **1b**) to provide the corresponding products **3cf** and **3df** in excellent yields (Table 2, entries 9 and 10). A small steric effect of some *ortho*-substitutents, such as methyl (**1e**), ethyl (**1f**), methoxy (**1g**), and isopropoxy (**1h**), was observed for diarylborinic acids.

Table 2 Scope of the nickel-catalyzed cross-coupling of aryl tosylates with diarylborinic acids [a)]



Entry	R^1 (**1**)	R^2 (**2**)	Cat. (mol%)	*T* (h)	Yield (%) [b)]
1	4-Me (**1a**)	4-Me (**2b**)	5	10	88 (**3ab**)
2	4-Me (**1a**)	2-Me (**2c**)	5	10	83 (**3ac**)
3	4-Me (**1a**)	H (**2d**)	5	10	90 (**3ad**)
4	4-Me (**1a**)	2-OMe (**2e**)	5	10	85 (**3ae**)
5	4-Me (**1a**)	4-Ac (**2f**)	3	6	98 (**3af**)
6	4-Me (**1a**)	$4-CO_2Et$ (**2g**)	3	6	93 (**3ag**)
7	4-Me (**1a**)	4-CHO (**2h**)	3	6	96 (**3ah**)
8 [c)]	H (**1b**)	4-Ac (**2f**)	3	6	91 (**3bf**)
9	4-OMe (**1c**)	4-Ac (**2f**)	3	6	95 (**3cf**)
10	4-F (**1d**)	4-Ac (**2f**)	3	6	90 (**3df**)
11	2-Me (**1e**)	4-Ac (**2f**)	3	6	88 (**3ef**)
12	2-Et (**1f**)	4-Ac (**2f**)	3	10	85 (**3ff**)
13	2-OMe (**1g**)	4-Ac (**2f**)	3	6	90 (**3gf**)
14	$2-O^iPr$ (**1h**)	4-Ac (**2f**)	3	6	92 (**3hf**)
15	2-Me (**1e**)	4-OMe (**2a**)	5	10	65 (**3ea**)
16	2-Me (**1e**)	2-OMe (**2e**)	5	10	62 (**3ee**)

a) Reaction conditions: diarylborinic acid (1.3 mmol), aryltosylate (2 mmol), $K_3PO_4·3H_2O$ (5.2 mmol), toluene (5 mL), N_2, 110 °C; b) isolated yields; c) 0.65 mmol of diphenylborinic anhydride was used.

For example, the reactions of bis(*o*-tolyl)borinic acid (**1e**) and bis(2-ethylphenyl)borinic acid (**1f**) with 4-acetylphenyltosylate (**2f**) gave products **3ef** (88%) and **3ff** (85%) in slightly lower yields than those of **1a**–**d** with a *para*-substituent (Table 2, entries 5, 11, and 12). Similar to the corresponding reaction of aryl chlorides [16], we observed a maller steric effect of *ortho*-alkoxy groups than alkyl ones in diarylborinic acids on the nickel/phosphine-catalyzed cross-coupling reaction. For example, the reactions of bis(2-methoxyphenyl)borinic acid (**1g**) and bis(2-isopropoxyphenyl)borinic acid (**1h**) with 4-acetylphenyltosylate (**2f**) gave the products **3gf** (90%) and **3hf** (92%), in slightly higher yields than bis(*o*-tolyl)borinic acid (**1e**) and bis(2-ethylphenyl)borinic acid (**1f**) (Table 2, entries 11–14). However, due to the accumulative effects of steric hindrance and electronic deactivation from aryl tosylates and diarylborinic acids, the cross-coupling of bis(*o*-tolyl)borinic acid (**1e**) with 2- and 4-methoxyphenyl tosylates (**2a**) and (**2e**) gave the desired products (**3ea**, 65%) and (**3ee**, 62%) in significantly lower yields than those of bis(*p*-tolyl)borinic acid **1a** (Table 2, entries 15 and 16).

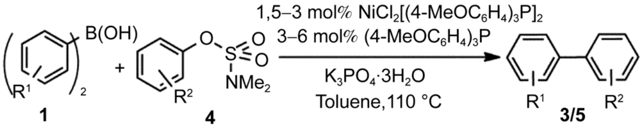
3.2 Cross-coupling of diarylborinic acids with aryl sulfamates

Aryl sulfamates are generally more stable and tolerable than aryl tosylates to harsh conditions. As a result, a sulfamate group can direct the introduction of substituents to the aromatic ring in addition to a leaving group. This ability has attracted increasing interest to the development of efficient cross-couplings by taking advantage of aryl sulfamates as electrophiles. The first Suzuki coupling of aryl sulfamates with arylboronic acids was reported by Grag *et al.* [7a)] in 2009, using 5–10 mol% $NiCl_2(PCy_3)_2$ in the presence of 4.5 equiv. K_3PO_4 in toluene. Han *et al.* [22] reported that $NiCl_2$(dppp) could catalyze Suzuki coupling of aryl sulfamates more efficiently in dioxane. Recently, Percec *et al.* [4d)] conducted a comprehensive study on the nickel-catalyzed Suzuki coupling of C–O based electrophiles, including aryl sulfamates with respect to catalyst precursors, solvents, bases, and structure of arylboronic acid derivatives. However, no report has been made on cross-coupling of aryl sulfamates with diarylborinic acids. We therefore investigated the cross-coupling of aryl dimethylsulfamates catalyzed by our $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ catalyst system, adopting the conditions for aryl tosylates (Table 3). Surprisingly, aryl sulfamates appeared to be more reactive than the corresponding tosylates in the nickel/phosphine-catalyzed cross-coupling with diarylborinic acids. Reaction of bis(*p*-tolyl)borinic acid (**1a**) with electron- neutral and -rich aryl sulfamates such as phenyl (**4a**), *p*-tolyl (**4b**), *o*-tolyl (**4c**), 4-methoxyphenyl (**4d**) and 2-methoxyphenyl (**4e**) dimethylsulfamates afforded diaryls **3ad**, **3ab**, **3ac**, **3aa**, and **3ae** in 85%–97% yields with a 3 mol% catalyst-loading (Table 3, entries 1–5), whereas the corresponding reaction of tosylates required a 5 mol% catalyst-loading to give comparable or even lower yields (83%–90%) under otherwise identical conditions (Table 2, entries 1–4). For electron-deficient arylsulfamates such as 4-acetylphenyl (**4f**), 4-ethoxycarbonylphenyl (**4g**), and 4-formylphenyl (**4h**) dimethylsulfamates, a 1.5 mol% catalyst-loading proved enough to complete their coupling with bis(*p*-tolyl)borinic acid **1a** in 6–8 h, which afforded the biaryls **3af**, **3ag**, and **3ah** in excellent yields (93%–96%). Similar to the reaction of aryl tosylates, electronic effects from diarylborinic acids appeared to be negligible (Table 3, entries 9–11). However, a remarkable steric effect was observed in the nickel/phosphine-catalyzed coupling of diarylborinic acids with aryl sulfamates. The product yields in reaction of phenyl dimethylsulfamate (**4a**) with bis(*o*-tolyl)borinic acid (**1e**) and bis(2-ethylphenyl)borinic acid (**1f**) decreased significantly to 84% and 33%, respectively, from 97% in the reaction with bis(*p*-tolyl)borinic acid (**1a**). Similarly, a good yield of **5ga** (87%) was obtained in the reaction of bis(2-methoxyphenyl)borinic acid (**1g**) with **4a** whereas the corresponding reaction of sterically demanding bis(2-isopropoxyphenyl)borinic acid (**1h**) gave **5ha** in only 42% yield (Table 3, entries 12–15). A slightly smaller steric effect of *ortho*-alkoxy groups than alkyl ones in diarylborinic acids was also observed, but to much less extent than those in the reactions of aryl chlorides and tosylates.

Although the performance of nickel catalysts in Suzuki coupling has appeared to be sensitive to reaction conditions in slightly previous reports [4, 5], nickel catalysts supported by a bidentate phosphine have shown consistent performance, especially under a few privileged conditions such as dioxane or toluene in the presence of K_3PO_4. Therefore, we further investigated the catalytic activities of nickel catalysts supported by a couple of common bidentate phosphines in the model reaction (Scheme 1), such as 1,1-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino) ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), and 1,1′-bis(diphenylphosphino)ferrocene (dppf).

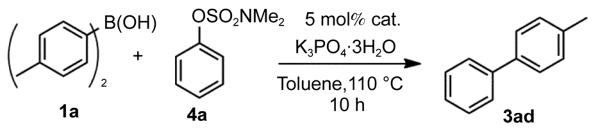
With the bidentate phosphines having a small bite angle [23] such as dppm (71°), dppe (82°), and dppp (91°), the

Table 3 Scope of the nickel-catalyzed cross-coupling of aryl sulfamates with diarylborinic acids a)



Entry	R^1 (**1**)	R^2 (**4**)	Cat. (mol%)	*T* (h)	Yield (%) b)
1	4-Me (**1a**)	H (**4a**)	3	10	97 (**3ad**)
2	4-Me (**1a**)	4-Me (**4b**)	3	10	95 (**3ab**)
3	4-Me (**1a**)	2-Me (**4c**)	3	10	85 (**3ac**)
4	4-Me (**1a**)	4-OMe (**4d**)	3	10	90 (**3aa**)
5	4-Me (**1a**)	2-OMe (**4e**)	3	10	91 (**3ae**)
6	4-Me (**1a**)	4-Ac (**4f**)	1.5	6	93 (**3af**)
7	4-Me (**1a**)	4-CO_2Et (**4g**)	1.5	8	96 (**3ag**)
8	4-Me (**1a**)	4-CHO (**4h**)	1.5	6	96 (**3ah**)
9 c)	H (**1b**)	H (**4a**)	3	6	97 (**5ba**)
10	4-OMe (**1c**)	H (**4a**)	3	6	97 (**5ca**)
11	4-F (**1d**)	H (**4a**)	3	10	94 (**5da**)
12	2-Me (**1e**)	H (**4a**)	3	10	84 (**5ea**)
13	2-Et (**1f**)	H (**4a**)	3	10	33 (**5fa**)
14	2-OMe (**1g**)	H (**4a**)	3	10	87 (**5ga**)
15	2-O^{i}Pr (**1h**)	H (**4a**)	3	10	42 (**5ha**)

a) Reaction conditions: diarylborinic acid (1.3 mmol), arylsulfamate (2 mmol), $K_3PO_4\cdot 3H_2O$ (5.2 mmol), toluene (5 mL), N_2, 110 °C; b) isolated yields; c) 0.65 mmol of diphenylborinic anhydride was used.



Cat.:	Bite angle (°) (bidentate phosphine)	Yield (%)
$NiCl_2$(dppm)/dppm	71.53	6
$NiCl_2$(dppe)/dppe	82.55	35
$NiCl_2$(dppp)/dppp	91.56	38
$NiCl_2$(dppp)	91.56	7
$NiCl_2$(dppb)/dppb	97.07	63
$NiCl_2$(dppf)/dppf	98.74	72

Scheme 1 The performance of bidentate phosphine-supported nickel catalysts in cross-coupling of aryl sulfamates with diarylborinic acids.

model reaction occurred to give the product **3ad** in only trace (6%) or low yields (35%–38%), even with a 5 mol% nickel/phosphine catalyst loading. A 1 mol% $NiCl_2$(dppp) alone has showed a high catalytic efficiency in the conventional Suzuki coupling of arylboronic acids with aryl sulfamates in dioxane [22]. However, the reaction of bis(*p*-tolyl)-borinic acid (**1a**) with phenyl sulfamate (**4a**) occurred rather sluggishly and gave the product **3ad** in only trace (7%) yield with 5 mol% $NiCl_2$(dppp), under previously reported conditions: 4 equiv. K_3PO_4 in dioxane at 110 °C for 10 h. The nickel catalysts supported by the bidentate phosphines with a larger bite angle, dppb (97°) and dppf (98°), performed better than those with smaller ones. Unfortunately, the yields of **3ad** increased just to 63% and 72% in the reactions catalyzed by 5 mol% $NiCl_2$(dppb)/dppb and $NiCl_2$-(dppf)/dppf, respectively, which were still significantly lower than those obtained with 3 mol% $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ under otherwise identical conditions.

4 Conclusions

General and efficient nickel/phosphine-catalyzed cross-couplings of diarylborinic acids with aryl tosylates and sulfamates were effected by using the tri(4-methoxyphenyl)-phosphine-supported nickel-catalyst system $Ni[P(4\text{-}MeOC_6H_4)_3]_2Cl_2/2P(4\text{-}MeOC_6H_4)_3$ in the presence of $K_3PO_4·3H_2O$ in toluene. The coupling of diarylborinic acids with activated aryl tosylates gave biaryl products in excellent yields with a 3 mol% catalyst-loading with respect to nickel. For the reaction of deactivated aryl tosylates, excellent yields were obtained just by increasing the catalyst loading to 5 mol% under otherwise identical conditions. Only small electronic and steric effects from diarylborinic acids were observed. Interestingly, the aryl sulfamates displayed a higher reactivity than tosylates in the nickel/phosphine-catalyzed cross-coupling with diraylborinic acids. Both electronically activated and deactivated aryl sulfamates were readily coupled with sterically undemanding diarylborinic acids using 1.5 mol% and 3 mol% catalyst loadings, respectively, although a large steric effect from the diarylborinic acid counterpart was observed in the nickel/phosphine-catalyzed cross-coupling with aryl sulfamates.

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ZOU Gang obtained a BSc degree from Anhui Normal University in 1992 and his MSc and PhD degrees from Shanghai Institute of Organic Chemistry (SIOC) in 1995 and 1998, respectively, under the supervision of professor Changtao Qian. After postdoctoral experience at University of Miami and UT Southwestern Medical Center at Dallas, he joined the faculty of East China Normal University in 2001 and moved to East China University of Science and Technology as a full professor of chemistry in 2006. He has co-authored about 60 publications in peer-reviewed journals, 15 patents, and received 1st class award from the Science & Technology Commission of Shanghai Municipality in 2003 and the 2011 Applied Organometallic Chemistry Best Publication Award from John Wiley & Sons Ltd. His research interests include transition metal catalysis, green chemistry and organic process research & development.