Journal of Organometallic Chemistry 842 (2017) 54–58

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Palladium-catalyzed cross-coupling of aryl chlorides with O, N-chelate stabilized diarylborinates

Nan Zhang [a], Chen Wang [a], Gang Zou [a, *], Jie Tang [b, **]

[a] School of Chemistry & Molecular Engineering, East China University of Science & Technology, 130 Meilong Rd, Shanghai, China
[b] Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, Shanghai Key Laboratory of Green Chemistry and Chemical Processes, SCME, East China Normal University, 3663 North Zhongshan Rd Shanghai, China

ARTICLE INFO

Article history:
Received 20 March 2017
Received in revised form
1 May 2017
Accepted 4 May 2017
Available online 6 May 2017

Keywords:
Cross-coupling
Diarylborinate
O, N-Chelate
Palladium
N-Heterocyclic carbene

ABSTRACT

A series of O, N-chelated diarylborinates have been prepared and tested as arylboron counterpart alternative to oxygen-labile diarylborinic acids in palladium catalyzed Suzuki coupling of aryl chlorides. 3-Dimethylaminopropyl diarylborinates (**B-5a**), featuring a six-membered O, N-chelated boron ring that was confirmed by single crystal X-ray diffraction, displayed a delicately balanced stability and reactivity. Their cross-coupling with structurally various aryl chlorides could be effected as efficiently as that of the parent diarylborinic acids by using 0.1~1mol% $Pd(OAc)_2$/IPr/$P(OPh)_3$ as catalyst system, to provide the corresponding biaryls in good to excellent yields.

1. Introduction

Four-coordinate diarylborinates, in particular those bearing an intramolecular B-N coordinate bond, are much more stable than the corresponding three-coordinate ones [1]. In fact, the former, as stable derivatives of diarylborinic acids, has been increasingly found in pharmaceutical reagents [2] and advanced materials [3] while the later has been proposed as active intermediates in borinic acid catalyzed processes, e.g. aldol condensation [4], Mannich-type reaction [5] and amidation [6]. More recently, the parent five-membered O, N-chelated diarylborinate, 2-aminoethyl diphenylborinate (2-APB), has been identified as a universal blocker of transient receptor potential channels [7]. We have recently reported that diarylborinic acids could be used as a cost-effective aryl source in palladium and nickel catalyzed cross-coupling reactions with aryl (pseudo)halides [8], carboxylic acids [9] and amides [10]. However, the coordinatively unsaturated diarylborinic acids are sometimes oxygen-labile and prone to dehydration and protodeboronation, complicating their long-term storage, stoichiometry and applications as arylation reagents. Inspired by the great successes achieved by Burke et al. [11] in finely tuning the stability and reactivities of arylboronates via coordinative, electronic and steric properties of boron center, we anticipate that it should be possible to develop storage-stable and easy-to-handle diarylborinates to replace diarylborinic acids as arylation reagents in transition metal-catalyzed cross-couplings. Herein, we report palladium catalyzed cross-coupling of aryl chlorides, which are the least reactive but most practical aryl halides due to their low cost and wide availability, with a series of O, N-chelate stabilized diarylborinates, among them 3-dimethylaminopropyl diarylborinates performed as efficiently as diarylborinic acids.

2. Results and discussion

The cross-coupling of 4-acetylchlorobenzene (**Cl-1**) with 2-aminoethyl diphenylborinate (2-APB, **B-1**) was tested at first under the conditions that we had developed for *N*,*N*'-bis(2,6-diisopropylphenyl) imidazol-2-ylidene (IPr) palladium-catalyzed cross-coupling of aryl halides with free diarylborinic acids, 0.1mol % $Pd(OAc)_2$/IPr/$P(OPh)_3$ (1/1/2, mol/mol) in the presence of 2equiv. $K_3PO_4.3H_2O$ in *t*BuOH at 80 °C by using a slightly excess aryl source (B/Cl = 0.55 mol/mol, 1.1equiv. with respect to phenyl group) [8b]. The desired cross-coupling product, 4-acetylbiphenyl (**P-1**), was

* Corresponding author.
** Corresponding author.
E-mail addresses: zougang@ecust.edu.cn (G. Zou), jtang@chem.ecnu.edu.cn (J. Tang).

http://dx.doi.org/10.1016/j.jorganchem.2017.05.013
0022-328X/

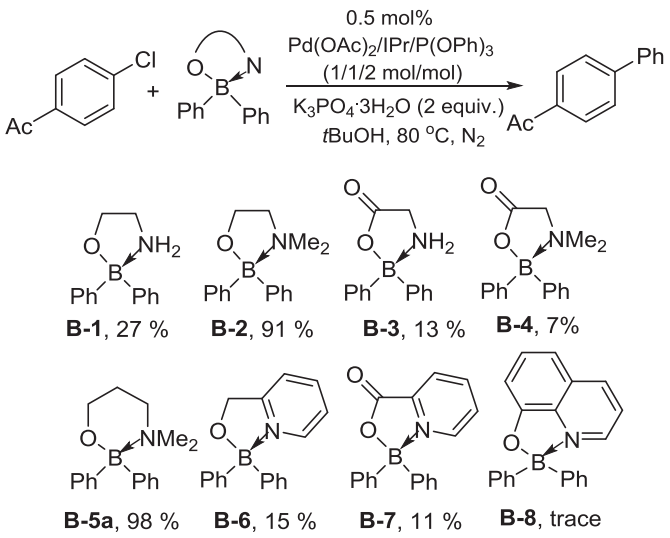
obtained in a low but promising yield (27%) (Scheme 1). Encouraged by the preliminary result, a couple of five/six-membered, O, N-chelate stabilized diarylborinates (**B-2**~**B-8**) [1b,12-15] were prepared by reaction of diarylborinic acids with representative N-containing alcohols or acids, e.g. dimethylaminoethanol, glycine, dimethyl glycine, pyridin-2-ylmethanol, picolinic acid, 3-(dimethylamino)propanol and quinolin-8-ol. Resonances at 4.45–11.92 ppm in ^{11}B NMR spectra of these diarylborinates are consistent with the O, N-chelated four-coordinate boron center [1b,2c]. The characteristic absorption of B-N (1350-1310cm-^{1}) in IR spectra also confirmed the formation of O, N-chelated four-coordinate boron center in these diarylborinates [16].

Reactivities of these diarylborinates in the model cross-coupling reaction were investigated. The biaryl product **P-1** could be obtained in 91% and 98% yields, respectively, with 2-dimethylaminoethyl diphenylborinate (**B-2**) and 3-dimethylaminopropyl diphenylborinate (**B-5a**) as the aryl source in the model reaction while the analogues **B-2**~**B4** and **B-6**~**B-8** performed poorly.

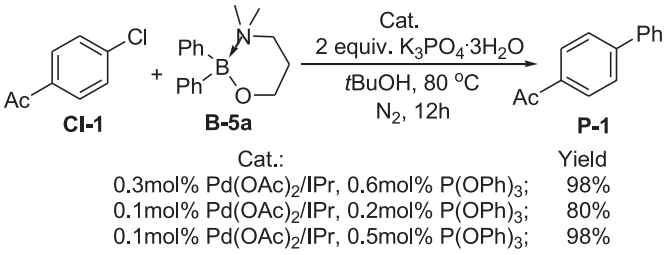
In fact, excellent yields for **P-1** could still be obtained when the catalyst loading was reduced to 0.3mol% or even 0.1mol% provided that $P(OPh)_3$ was increased to 5equiv. (0.5mol%) with respect to Pd/IPr (0.1mol%) (Scheme 2). The high reactivity of the six-membered O, N-chelated diphenylborinate (**B-5a**) may be attributed to the steric hindrance and/or the so-called through-bond interactions [1b].

Crystal structure of the most reactive diphenylborinate **B-5a** was determined and confirmed the presence of the six-membered N, O-chelate stabilized boron center (Fig. 1). The N→B coordinate bond distance is 1.7095(17)Å in **B-5a** is significantly longer than previously reported data for the related five/six-membered O, N-chelated diphenylborinates **B-1**, **B-2** and 3-aminopropyl diphenylborinate where the bond lengths range from 1.61 to 1.65 Å while the B-O (1.4542(16)Å) bond length is in the normal range from 1.35 to 1.48 Å [1b,17]. The B-C_{Ph} bond lengths (1.6425(18) and 1.6265(18) Å) are slightly longer than those in **B-1** (1.620 and 1.613 Å), **B-2** (1.627 and 1.614 Å) and 3-aminopropyl diphenylborinate (1.620 and 1.626 Å). The angles around the tetra-coordinated boron atom are between 102.9(9)° and 113.8(10)° closed to tetrahedral angle values.

Scope and limitation of the palladium-catalyzed cross-coupling of aryl chlorides with 3-dimethylaminopropyl diarylborinates have



Scheme 1. The coupling of 4-acetylchlorobenzene with O, N-chelate stabilized diarylborinates.



Cat.:	Yield
0.3mol% $Pd(OAc)_2$/IPr, 0.6mol% $P(OPh)_3$;	98%
0.1mol% $Pd(OAc)_2$/IPr, 0.2mol% $P(OPh)_3$;	80%
0.1mol% $Pd(OAc)_2$/IPr, 0.5mol% $P(OPh)_3$;	98%

Scheme 2. The coupling of 4-acetylchlorobenzene with **B-5a.**

been explored (Table 1). Similar to the reaction of free diarylboronic acids, a large electronic effect was observed from aryl chlorides. For example, aryl chlorides bearing an electron-deficient benzene ring reacted smoothly with **B-5a** to give biaryl products in excellent yields (Entries 1–9).

However, reaction of electron-rich 4-(benzyloxy)phenyl chloride (**Cl-11**) with **B-5a** became rather sluggish under the model reaction conditions to offer biaryl **P-11** in just 11% yield although the high yields could be restored in the reaction of electron-rich aryl chlorides by using 1mol% catalyst loading under the otherwise identical conditions (Entries 10–19). Obviously, steric hindrance from a small ortho-substituent in these electron-deficient aryl chlorides could be overcome since the yields of biaryl products just slightly decreased compared with those with a substituent at para- or meta-positions. Compared with electron-deficient ones, steric hindrance of electron-rich aryl chlorides affected their coupling remarkably. For example, *o*-tolylchloride and *o*-methoxylphenyl chloride reacted to give biaryl products 2-methylbiphenyl (**P-13**, 72%) and 2-phenylanisole (**P-16**, 62%), in significantly lower yields than their para-isomers (Entries 12 and 15). The yield further decreased to 42% in the reaction of 2,6-dimethylphenyl chloride (Entry 13).

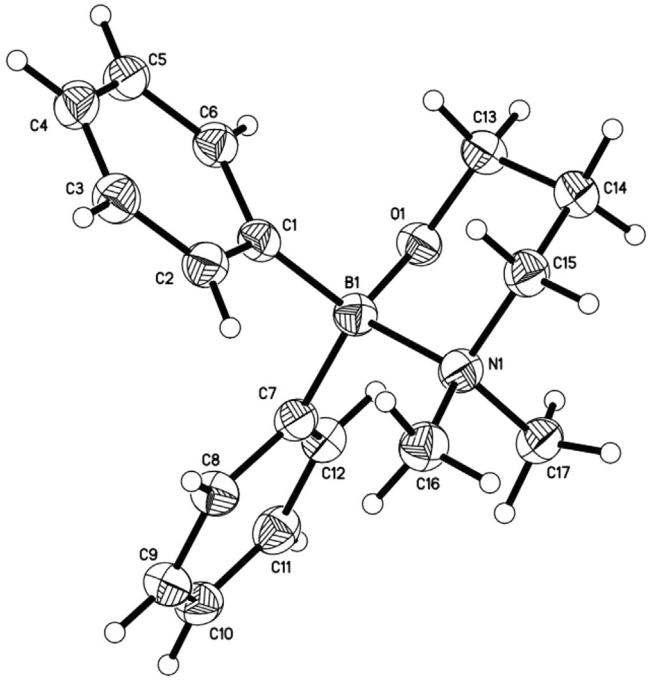
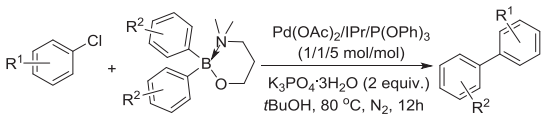


Fig. 1. An ORTEP view of the molecular structure of **B-5a**. B(1)-O(1) 1.4542(16)Å, B(1)-N(1) 1.7095(17)Å, B(1)-C(1) 1.6425(18)Å, B(1)-C(7) 1.6265(18)Å; O(1)-B(1)-C(7) 108.84(10)°, O(1)-B(1)-C(1) 112.19(10)°, C(7)-B(1)-C(1) 110.97(10)°, O(1)-B(1)-N(1) 102.86(9)°, C(7)-B(1)-N(1) 107.80(10)°, C(1)-B(1)-N(1) 113.76(10)°.

Table 1
Scope of the palladium-catalyzed cross-coupling of aryl halides with 3-dimethylaminopropyl diarylborinates.[a]



Entry	R^1	R^2	Cat (%)	Yield (%)[b]
1	*o*-Ac(**Cl-2**)	H(**B-5a**)	0.1	83(**P-2**)
2	*m*-Ac(**Cl-3**)	H(**B-5a**)	0.1	99(**P-3**)
3	*o*-CN(**Cl-4**)	H(**B-5a**)	0.1	92(**P-4**)
4	*m*-CN(**Cl-5**)	H(**B-5a**)	0.1	96(**P-5**)
5	*p*-CN(**Cl-6**)	H(**B-5a**)	0.1	95(**P-6**)
6	*p*-CO_2Me(**Cl-7**)	H(**B-5a**)	0.1	97(**P-7**)
7	*p*-CHO(**Cl-8**)	H(**B-5a**)	0.1	87(**P-8**)
8	*p*-NO_2(**Cl-9**)	H(**B-5a**)	0.1	90(**P-9**)
9	*o*-NO_2(**Cl-10**)	H(**B-5a**)	0.1	87(**P-10**)
10	*p*-OBn(**Cl-11**)	H(**B-5a**)	1	98(11)[c] (**P-11**)
11	*p*-Me(**Cl-12**)	H(**B-5a**)	1	97(**P-12**)
12	*o*-Me(**Cl-13**)	H(**B-5a**)	1	72(**P-13**)
13	*2,6*-Me_2(**Cl-14**)	H(**B-5a**)	1	42(**P-14**)
14	*p*-OMe(**Cl-15**)	H(**B-5a**)	1	95(**P-15**)
15	*o*-OMe(**Cl-16**)	H(**B-5a**)	1	62(**P-16**)
16	*p*-NH_2(**Cl-17**)	H(**B-5a**)	1	91(**P-17**)
17	*o*-NH_2(**Cl-18**)	H(**B-5a**)	1	85(**P-18**)
18	2-Cl-Py(**Cl-19**)	H(**B-5a**)	1	83 (**P-19**)
19	3-Cl-Py(**Cl-20**)	H(**B-5a**)	1	85 (**P-20**)
20	*p*-Ac(**Cl-1**)	*p*-Me(**B-5b**)	0.1	91(**P-21**)
21	*p*-Ac(**Cl-1**)	*p*-F(**B-5f**)	0.1	80(**P-22**)
22	*p*-Ac(**Cl-1**)	*p*-OMe(**B-5j**)	0.1	93(**P-23**)
23	*p*-OBn(**Cl-11**)	*p*-Me(**B-5b**)	1	99(**P-24**)
24	*p*-OBn(**Cl-11**)	*m*-Me(**B-5c**)	1	95(**P-25**)
25	*p*-OBn(**Cl-11**)	*o*-Me(**B-5d**)	1	96(**P-26**)
26	*p*-OBn(**Cl-11**)	*m*-F(**B-5e**)	1	82(**P-27**)
27	*p*-OBn(**Cl-11**)	*p*-F(**B-5f**)	1	88(**P-28**)
28	*p*-OBn(**Cl-11**)	*o*-Et(**B-5g**)	1	92(**P-29**)
29	*p*-OBn(**Cl-11**)	*p*-CF_3(**B-5h**)	1	70(**P-30**)
30	*p*-OBn(**Cl-11**)	*o*-OMe(**B-5i**)	1	94(**P-31**)
31	*p*-OBn(**Cl-11**)	*p*-OMe(**B-5j**)	1	94(**P-32**)

[a] Reaction conditions: aryl chloride 1 mmol; diarylborinate 0.55 mmol; $K_3PO_4 \cdot 3H_2O$, 2 mmol (2equiv.); *t*BuOH, 5 mL.
[b] Isolated yields.
[c] 0.1mol% cat used.

The electronic and steric influence of 3-dimethylaminopropyl diarylborinates on their cross-coupling with aryl halides were also investigated. The steric influence from a small ortho-substituent on the benzene ring of diarylborinates **B-5** was negligible. For example, diarylborinates bearing an ortho-methyl (**B-5d**), ethyl (**B-5g**) and methoxyl (**B-5i**) group reacted with 4-(benzyloxy) phenyl chloride (**Cl-11**) similarly to their para-isomers (Entries 23, 25, 28, 30 and 31), giving the corresponding biaryl products **P-26, P-29** and **P-31** in comparable yields. Although electronically various diarylborinates (**B-5**) could react smoothly with both electron-rich (**Cl-11**) and -deficient (**Cl-1**) aryl chlorides to offer biaryls **P-21~23** and **P-24~P-32** in good to excellent yields (Entries 20–31), a larger electronic effect was observed from the diarylborinates in reaction with electron-rich aryl chlorides compared with the free diarylborinic acids, which displayed a negligible electronic influence on their coupling with aryl chlorides under similar conditions [8b]. For example, the electron-deficient diarylborinates (**B-5e, B-5f** and **B-5h**) reacted with **Cl-11** to give biaryls in obviously lower yields (70–88%) than the electron-neutral and -rich analogues (**B-5b, B-5c** and **B-5j**) (94–99%) (Entries 26, 27, 29 vs 23, 24, 31).

3. Conclusion

In summary, a series of O, N-chelated diarylborinates with typical N-containing alcohol or acid ligands have been prepared and fully characterized by spectroscopy including ^{11}B NMR and single crystal X-ray diffraction, aiming to develop an easy-to-handle and storage-stable alternative to free diarylborinic acids in palladium-catalyzed Suzuki coupling of aryl chlorides. Although a slightly larger electronic effect of diarylborinates was observed 3-dimethylaminopropyl diarylborinates, in which the six-membered O, N-chelate-stabilized boron ring appeared to be crucial to delicately balance their stability and reactivity, performed comparably to diarylborinic acids in cross-coupling with a wide range of aryl chlorides. A variety of biaryls could be obtained in good to excellent yields via the cross-coupling of 3-dimethylaminopropyl diarylborinates with aryl chlorides catalyzed by 0.1~1mol% $Pd(OAc)_2/IPr/P(OPh)_3$. These results clearly indicated that diarylborinates with well-balanced stability and reactivity could be effected by carefully tuning the structure of the chelate ligand.

4. Experimental section

General information: All reactions were carried out under nitrogen by using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were used as received. Diarylboronic acids [8b], O, N-chelated diarylborinates [12,13,18] and IPr·HCl [19], were prepared according to previously reported procedures. Column chromatograph was performed on 200–300 mesh silica gal. ^1H, ^{13}C and ^{11}B NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at ambient temperature. 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), q (quartet), dd (double doublet), m (multiplets). The number of protons (n) for a given resonance is indicated as nH. Coupling constants are reported as J in Hz. The organic compounds were identified by ^1H and ^{13}C NMR (see Supporting Information) [8a,8b,20–27]. All new compounds were further characterized by HRMS.

4.1. Synthesis of O, N-chelated diarylborinates

General procedure **A**: Diarylboronic acid (10 mmol) in EtOAc (20 mL) was added ethanolamine (0.61 g, 10 mmol). The mixture was stirred at room temperature for 2 h. Precipitates were collected by filtration and dried to give O, N-chelated diarylborinates **(B-1**, **B-2** and **B-4~B-8)**.

Procedure for **B-3**: To a solution of the diarylboronic acid (10 mmol) in EtOH (20 mL) was added glycine (0.75 g, 10 mmol) in H_2O (5 mL). The mixture was stirred for 4 h at reflux before cooling down to room temperature. Precipitates were collected by filtration and dried in vacuum to give **B-3**.

4.1.1. 3-((Bis(4-methylphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (*B-5b*)

White solid (2.83 g, 96% yield), mp 104–105 °C, ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.39 (d, $J = 8.0$ Hz, 4H), 7.01 (d, $J = 7.6$ Hz, 4H), 3.74 (t, $J = 5.6$ Hz, 2H), 3.00 (t, $J = 5.6$ Hz, 2H), 2.43 (s, 6H), 2.24 (s, 6H), 1.78–1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 135.1, 133.3, 128.0, 126.8, 60.2, 58.5, 46.1, 24.6, 20.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 14.38. HRMS (EI) m/z $[M]^+$ calcd for $C_{19}H_{26}BNO$ 295.2107, found 295.2104. IR (KBr) ν (N→B) 1310 cm^{-1}.

*4.1.2. 3-((Bis(3-methylphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5c**)*

White solid (2.86 g, 97% yield), mp 132–134 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.42 (s, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 3.82 (t, J = 5.6 Hz, 2H), 3.09 (t, J = 6.0 Hz, 2H), 2.53 (s, 6H), 2.31 (s, 6H), 1.86–1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 136.2, 135.0, 131.4, 127.7, 127.0, 61.1, 59.5, 47.1, 25.6, 21.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 11.27. HRMS (EI) m/z $[M]^+$ calcd for $C_{19}H_{26}BNO$ 295.2107, found 295.2106. IR (KBr) ν (N→B) 1310 cm^{-1}.

*4.1.3. 3-((Bis(2-methylphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5d**)*

Yellow liquid (2.78 g, 94% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.33 (d, J = 7.6 Hz, 2H), 7.29–7.25 (m, 2H), 7.14 (t, J = 8.0 Hz, 4H), 3.84 (s, 2H), 2.44 (s, 2H), 2.37 (s, 6H), 2.16 (s, 6H), 1.74 (t, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 141.9, 134.1, 129.8, 129.5, 124.9, 64.4, 58.3, 45.1, 28.3, 22.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 11.67. HRMS (EI) m/z $[M]^+$ calcd for $C_{19}H_{26}BNO$ 295.2107, found 295.2104. IR (KBr) ν (N→B) 1340 cm^{-1}.

*4.1.4. 3-((Bis(3-fluorophenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5e**)*

White solid (2.94 g, 97% yield), mp 130–131 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.27–7.16 (m, 6H), 6.87–6.82 (m, 2H), 3.82 (t, J = 5.6 Hz, 2H), 3.22 (t, J = 6.0 Hz, 2H), 2.60 (s, 6H), 1.92–1.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 162.5 (d, J = 242.9 Hz), 129.3 (d, J = 2.2 Hz), 128.4 (d, J = 7.1 Hz), 120.1 (d, J = 18.0 Hz), 112.6 (d, J = 21.0 Hz), 60.25, 59.9, 47.9, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 6.34. HRMS (EI) m/z $[M]^+$ calcd for $C_{17}H_{20}BF_2NO$ 303.1606, found 303.1608. IR (KBr) ν (N→B) 1310 cm^{-1}.

*4.1.5. 3-((Bis(4-fluorophenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5f**)*

White solid (2.97 g, 98% yield), mp 122–123 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.49 (q, J = 6.4 Hz, 4H), 6.94 (t, J = 8.8 Hz, 4H), 3.77 (t, J = 5.6 Hz, 2H), 3.06 (t, J = 6.0 Hz, 2H), 2.54 (s, 6H), 1.88–1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 161.9 (d, J = 240.0 Hz), 135.5 (d, J = 6.8 Hz), 113.7 (d, J = 18.9 Hz), 60.4, 59.7, 47.8, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 8.87. HRMS (EI) m/z $[M]^+$ calcd for $C_{17}H_{20}BF_2NO$ 303.1606, found 303.1605. IR (KBr) ν (N→B) 1310 cm^{-1}.

*4.1.6. 3-((Bis(2-ethylphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5g**)*

Yellow liquid (3.17 g, 98% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.33–7.28 (m, 4H), 7.19 (d, J = 7.2 Hz, 2H), 7.12 (t, J = 7.6 Hz, 2H), 3.85 (s, 2H), 2.73 (q, J = 7.2 Hz, 4H), 2.42 (t, J = 7.2 Hz, 2H), 2.14 (s, 6H), 1.77–1.71 (m, 2H), 1.15 (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.4, 134.3, 129.5, 128.3, 128.2, 124.9, 64.4, 58.9, 45.3, 29.1, 28.3, 16.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 9.99. HRMS (ESI) m/z $[M+1]^+$ calcd for $C_{21}H_{31}BNO$ 324.2499, found 324.2499. IR (KBr) ν (N→B) 1330 cm^{-1}.

*4.1.7. 3-((Bis(4-trifluoromethylphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5h**)*

Yellow liquid (3.87 g, 96% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.60 (d, J = 8.0 Hz, 4H), 7.45 (d, J = 8.0 Hz, 4H), 3.78 (t, J = 4.8 Hz, 2H), 3.16 (s, 2H), 2.59 (s, 6H), 1.91–1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 134.9, 133.6, 127.7 (q, J = 31.5 Hz), 124.9 (q, J = 270.0 Hz), 123.4 (q, J = 3.5 Hz), 60.8, 59.7, 45.5, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 5.79. HRMS (EI) m/z $[M]^+$ calcd for $C_{19}H_{20}BF_6NO$ 403.1542, found 403.1543. IR (KBr) ν (N→B) 1330 cm^{-1}.

*4.1.8. 3-((Bis(2-methoxyphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5i**)*

Yellow liquid (3.21 g, 98% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.31–7.25 (m, 4H), 6.95–6.87 (m, 4H), 5.67 (s, 2H), 3.96 (t, J = 6.4 Hz, 2H), 3.83 (s, 6H), 3.76 (s, 6H), 3.08–3.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 136.4, 129.4, 120.9, 113.8, 109.7, 58.8, 55.2, 55.1, 45.4, 27.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 13.31. HRMS (ESI) m/z $[M+1]^+$ calcd for $C_{19}H_{26}BNO_3$ 328.2084, found 328.2084. IR (KBr) ν (N→B) 1330 cm^{-1}.

*4.1.9. 3-((Bis(4-methoxyphenyl)boranyl)oxy)-N,N-dimethylpropan-1-amine (**B-5j**)*

White solid (3.11 g, 95% yield), mp 114–115 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.52 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 3.83 (t, J = 5.6 Hz, 2H), 3.79 (s, 6H), 3.02 (t, J = 5.6 Hz, 2H), 2.48 (s, 6H), 1.85–1.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 159.5, 135.9, 129.5, 112.8, 55.1, 55.0, 46.5, 26.5, 18.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ(ppm): 12.86. HRMS (EI) m/z $[M]^+$ calcd for $C_{19}H_{26}BNO_3$ 327.2006, found 327.2012. IR (KBr) ν (N→B) 1310 cm^{-1}.

4.2. General procedure for Suzuki coupling reaction of aryl chlorides with O, N-chelated diarylborinates

Under a N_2 atmosphere, to a 10 mL dry flask were added aryl chloride (1.0 mmol), O, N-chelated diarylborinates (0.55 mmol), $Pd(OAc)_2$ (0.1~1 mol%), IPr·Cl (0.1~1 mol%), $P(OPh)_3$ (0.5~5 mol%), K_3PO_4. H_2O (2 mmol), and *t*BuOH (5 mL). The mixture was stirred at 80 °C for a given time or monitored by TLC until the starting material was completely consumed. The reaction mixture was diluted with EtOAc (15 mL), followed by washing with H_2O (2 × 10 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give crude product, which was purified by column chromatography on silica gel to afford product.

*4.2.1. 4-Benzyloxy-3′-fluorobiphenyl (**P-27**)*

White solid (228 mg, 82% yield), mp 103–104 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.51–7.48 (m, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.41–7.30 (m, 5H), 7.25–7.21 (m, 1H), 7.04 (m, 2H), 7.00–6.95 (m, 1H), 5,10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 161.3 (d, J = 244 Hz), 158.8, 143.1 (d, J = 7.6 Hz), 136.9, 132.7 (d, J = 2.4 Hz), 130.2 (d, J = 8.4 Hz), 128.7, 128.2, 128.1, 127.5, 122.3 (d, J = 2.7 Hz), 115.3, 113.7 (d, J = 9.2 Hz), 113.4 (d, J = 8.6 Hz), 70.1. HRMS (EI) m/z $[M]^+$ calcd for $C_{19}H_{15}FO$ 278.1107, found 278.1108.

4.3. X-ray crystallographic data

The X-ray diffraction measurements of compound **B-5a** was carried out using SC-XRD D8 VENTURE area-detector diffractometer and using CuKα radiation (λ = 1.54178 Å). The structure was solved by SHELXT followed by successive refinements using the φ -ω scans method on F2 using SHELXL-2014.

*4.4. Crystal data of **B-5a***

$C_{17}H_{22}BNO$, M = 267.17, Monoclinic, a = 9.1048(2), b = 23.7982(6), c = 7.2326(2) Å, β = 112.1410(10)°, V = 1451.58(6) Å^3, Space group $P2_1/n$, Z = 4, D_{calc} = 1.223 Mg/m^3. Crystal size 0.05 × 0.04 × 0.03 mm^3, θ_{max} = 66.68°, 11623 reflections measured, 2555 unique (R_{int} = 0.0220), μ = 0.568 mm^{-1}. The final R1 and wR2 were 0.0414 and 0.1210 (I > 2\ σ(I)), for 183 parameters.

Acknowledgements

We are grateful for financial support provided by the National Natural Science Foundation of China (21472041) and National Key

Technology R&D Program, the Ministry of Science and Technology of China (2015BAK44B00).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.05.013.

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