Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Gorlos-Phos for palladium-catalyzed borylation of aryl chlorides†

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 3604

Received 8th February 2014,
Accepted 20th March 2014

DOI: 10.1039/c4ob00293h

www.rsc.org/obc

Pengbin Li, Chunling Fu and Shengming Ma*

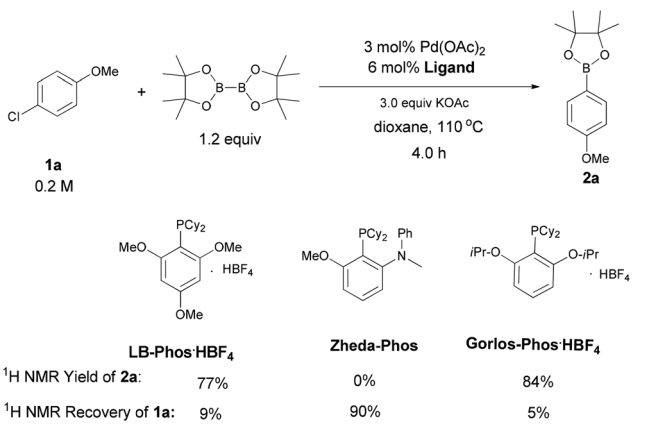
Using a readily available form of the mono-phosphine ligand, **Gorlos-Phos·HBF$_4$**, Pd-catalyzed borylation of aryl chlorides afforded aryl boronates in high yields. A variety of functional groups are well compatible with this palladium catalyzed borylation reaction.

Introduction

Aryl boronic acids and their derivatives play important roles in organic synthesis, especially in metal-catalyzed cross-coupling reactions, due to their air-stability, low-toxicity and functional group compatibility.[1] When an aryl lithium or Grignard reagent was used for preparation of aryl boronic derivatives, the harsh conditions limited the scope seriously. On one hand, the development of transition metal-catalyzed borylation of aryl halides and direct C–H activation borylation reaction in the last decade provides an efficient alternative to aryl boronic derivatives with various functional groups.[2] On the other hand, the huge demand for various aryl boronic derivatives requires a highly efficient, yet cheap enough synthetic protocol and obviously aryl chlorides are ideal substrates for the borylation reaction, which show great advantages in terms of atom-economy, cost, and availability.[3] The sterically bulky and electron-rich phosphine ligands are the key to the success of C–Cl activation reaction.[4] Some notable phosphine ligands in borylation of aryl chlorides are listed as follows: the pioneering work on Pd-catalyzed borylation of aryl chlorides was reported by Miyaura and coworkers in 2001 with PCy_3 as a ligand;[5] in 2007, Buchwald and coworkers reported a method using SPhos or XPhos as a ligand with 1 mol% loading of [Pd_2dba_3] in 10 min to 5 h;[6] in 2010, Molander reported a direct route to aryl boronic acid by Pd-catalyzed borylation of aryl chlorides with tetrahydroxydiboron using XPhos as a ligand giving facile access to diverse boronic acids;[7,8] it is impressive that Sawamura's silica-supported phosphine silica-SMAP is efficient in borylation of sterically demanding aryl chlorides;[9] Kwong's indole-based phosphine PPh_2-Andole-Phos is the only efficient ligand bearing a –PPh_2 moiety instead of dialkylphosphino for the borylation reaction of aryl chlorides.[10] Thus, development of practical and highly efficient readily available ligands for such a transformation is still highly desirable. Recently we have developed readily available mono-phosphines **LB-Phos**, **Zheda-Phos**, and **Gorlos-Phos**.[11] They have been proven to be efficient in the palladium-catalyzed C–Cl bond based Suzuki coupling reactions,[11a–c] amination reactions,[11d] and α-arylation of acetone.[11e] In this paper, we wish to report the application of those phosphines in C–Cl activation-based borylation reaction.

Results and discussion

Using *p*-chloroanisole (**1a**) and B_2pin_2 as the model substrates for the catalyzed-borylation reaction, we first screened these above mentioned phosphines developed by our group. $Pd(OAc)_2$/**LB-Phos·HBF$_4$** did catalyze the borylation reaction of **1a** using KOAc (2.0 equiv.) as the base with 77% yield of **2a** and 9% recovery of **1a**. While **Zheda-phos** was used instead, 90% recovery of **1a** was achieved. Interestingly, the readily available **Gorlos-Phos·HBF$_4$** [11d] gave a better result with 84% yield of **2a**, though still 5% of **1a** was recovered (Scheme 1).



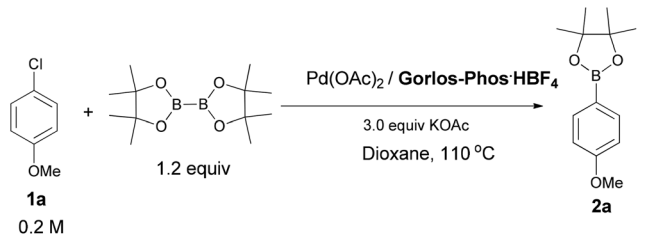
Scheme 1

Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, P. R. China.
E-mail: masm@mail.sioc.ac.cn; Fax: (+86)21-6416-7510

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ob00293h

Reducing the loading of **Gorlos-Phos·HBF$_4$** would decrease the yield of **2a** sharply to 49% (Table 1, entry 1). In contrast, further optimizing the ratio of Pd(OAc)$_2$/**Gorlos-Phos·HBF$_4$** to 1/4 could reduce the loading of Pd(OAc)$_2$ to 1 mol% (Table 1, entries 2 and 3). Strong bases like K_2CO_3 and K_3PO_4 would lead to the formation of a symmetric biaryl compound as a byproduct (Table 1, entries 4 and 5). Finally, we found that improving the concentration of **1a** from 0.2 M to 0.5 M would shorten the reaction time to 2.5 h and improve the yield of **2a** to 98% (Table 1, entry 6). Compared to DMSO and toluene, dioxane is a better solvent (Table 1, entries 6–8).

Table 1 Borylation reaction of *p*-chloroanisole (**1a**)[a]

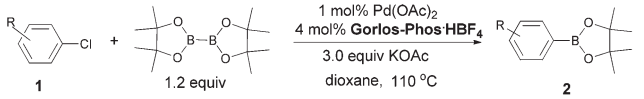


Entry	Pd/ligand/ (mol%/mol%)	Time/h	Yield of **2a**[b]/%	Recovery of **1a**[b]/%
1	3/4.5	5.0	49	32
2	1/3	9.5	81	8
3	1/4	17	91	8
4[c]	1/4	17	71	—
5[d]	1/4	17	62	—
6[e]	1/4	2.5	98	—
7[f]	1/4	2.5	18	67
8[g]	1/4	2.5	61	11

[a] Reaction conditions: aryl chloride (0.4–1.0 mmol, 0.2 M), B_2pin_2 (1.2 equiv.), Pd(OAc)$_2$ (1 mol%), Gorlos-Phos·HBF$_4$ (4 mol%), and KOAc (3.0 equiv.) in dioxane at 110 °C. [b] Determined by ^{1}H-NMR analysis. [c] 3.0 equiv. of K_2CO_3 were used as the base here and 29% yield of 4,4′-dimethoxybiphenyl was detected. [d] 3.0 equiv. of K_3PO_4 were used as the base here and 37% yield of 4,4′-dimethoxybiphenyl was detected. [e] The concentration of **1a** was 0.5 M here. [f] DMSO was used as a solvent here. [g] Toluene was used as a solvent instead here.

With the optimized conditions in hand (Table 1, entry 6), we explored the scope of aryl chlorides in the borylation reaction. The Pd(OAc)$_2$/**Gorlos-Phos·HBF$_4$** system demonstrated very high activity on borylation reaction of differently substituted aryl chlorides. Electron-donating group-substituted aryl chlorides such as *p*-chloroanisole, *m*-chloroanisole, 1-chloronaphthalene, and *p*-chloro-*tert*-butylbenzene could be transformed into the corresponding borate products smoothly within 1.0–2.5 h with excellent yields (Table 2, entries 1–2 and 4–5). It took 7.5 h for complete conversion with *o*-chlorotoluene probably due to its steric factor (Table 2, entry 3). The equivalent of B_2pin_2 could be reduced to 1.02 equivalents without any drop in the yield but with a longer reaction time (Table 2, entries 6–7). The borylation reaction of the electron-deficient 4-chlorophenyl methylsulfone and 4-chloronitrobenzene could be completed within 1.0 h to afford borate products in yields of 89% and 92% (Table 2, entries 8 and 9). Base sensitive functional groups, such as –COMe, –CHO, –COOMe, –CONH$_2$, –NHCOMe, and –OH, were well tolerated under this set of mild reaction conditions (Table 2, entries 10–15). And even *p*-chlorobenzoic acid could be directly transformed into borate with a yield of 74% in 3.0 h (Table 2, entry 16).

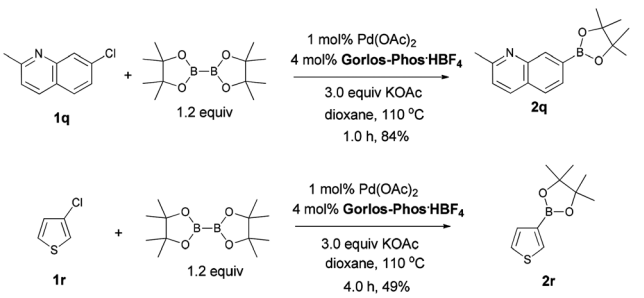
Table 2 Borylation reaction of aryl chlorides with B_2pin_2[a]



Entry	**1**	Time/h	Yield of **2**[b]/%
1	4-MeOC$_6$H$_4$ (**1a**)	2.5	90 (**2a**)
2	3-MeOC$_6$H$_4$ (**1b**)	1.0	91 (**2b**)
3	2-MeC$_6$H$_4$ (**1c**)	7.5	82 (**2c**)
4	1-Naphthyl (**1d**)	2.0	92 (**2d**)
5	4-*t*BuC$_6$H$_4$ (**1e**)	2.5	80 (**2e**)
6[c]	4-MeCOC$_6$H$_4$ (**1f**)	5.0	81 (**2f**)
7[c]	4-NCC$_6$H$_4$ (**1g**)	3.0	87 (**2g**)
8	4-MeSO$_2$C$_6$H$_4$ (**1h**)	1.0	89 (**2h**)
9	4-O$_2$NC$_6$H$_4$ (**1i**)	1.0	92 (**2i**)
10	3-MeCOC$_6$H$_4$ (**1j**)	1.0	88 (**2j**)
11	2-OCHC$_6$H$_4$ (**1k**)	1.0	89 (**2k**)
12	4-MeO$_2$CCH$_2$OC$_6$H$_4$ (**1l**)	1.5	79 (**2l**)
13	4-H$_2$NCOC$_6$H$_4$ (**1m**)	1.5	81 (**2m**)
14	4-MeCONHC$_6$H$_4$ (**1n**)	1.0	92 (**2n**)
15	4-HOC$_6$H$_4$ (**1o**)	2.5	76 (**2o**)
16	4-HOOCC$_6$H$_4$ (**1p**)	3.0	74 (**2p**)

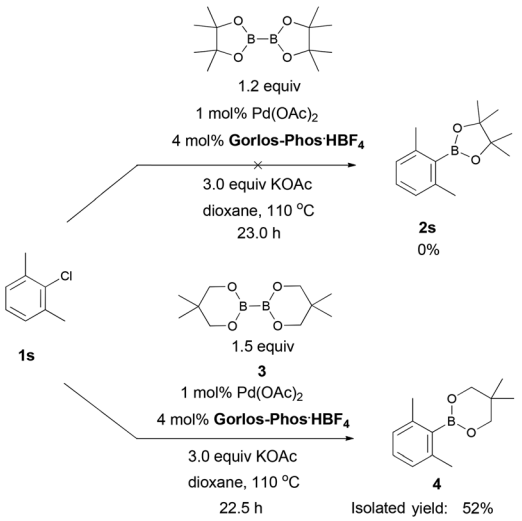
[a] Reaction conditions: aryl chloride (1.0 mmol), B_2pin_2 (1.2 mmol), Pd(OAc)$_2$ (0.01 mmol), Gorlos-Phos·HBF$_4$ (0.04 mmol), and KOAc (3.0 mmol) in 2.0 mL of dioxane at 110 °C. [b] Isolated yield. [c] 1.02 equiv. of B_2pin_2 were used.

It is noted that the borylation of heteroaryl chlorides such as 7-chloro-2-methylquinoline and 3-thienyl chloride also occurred smoothly to produce **2q**[12] and **2r**[5] in 84% and 49% yields (Scheme 2).



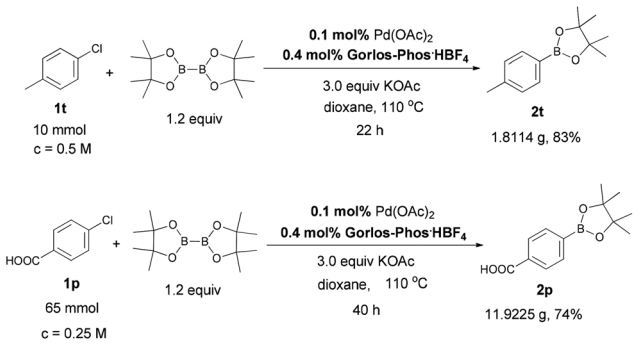
Scheme 2 Borylation reaction of heteroaryl chlorides with B_2pin_2.

It is found that the highly sterically hindered substrate, 2-chloro-*m*-xylene **1s**, is hard to convert when B_2pin_2 was used as a boron source. Luckily, the application of commercially available less steric demanding bis(neophentylglycolato)-diboron **3**[13] afforded borate **4** in 52% yield (Scheme 3).



Scheme 3 Palladium-catalyzed borylation of the highly steric hindered substrate **1s**.

In order to show the practicality, a 10 mmol scale reaction of 4-chlorotoluene **1t** was conducted. The loading of the Pd-catalyst could be reduced further to 0.1 mol% affording **2t** in 83% yield in 22 h; product **2p** (~12 g) could be easily obtained by simple recrystallization right after the borylation with a yield of 74% (see also entry 16 of Table 2, Scheme 4).



Scheme 4 1 g scale and 10 g scale reactions.

Conclusions

In summary, we have developed the Pd-catalyzed borylation reaction of a variety of electron-rich and electron-deficient group-substituted aryl chlorides under mild conditions using the readily available **Gorlos-phos**, affording aryl boronates with much synthetically active functionality. Even the steric demanding 2,6-disubstituted aryl chlorides and heteroaryl chlorides work. Further studies in this area are being conducted by our group.

Experimental

General information

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on the instrument operated at 300 and 75 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) with the residual peak of $CHCl_3$ at 7.260 ppm or TMS at 0.000 ppm as the internal standard. Infrared spectra were recorded for thin films of pure samples on sodium chloride plates for liquid samples or in the form of KBr discs for solid samples. Mass and HRMS spectra were recorded in EI mode. Thin layer chromatography was performed on pre-coated glass-back plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (10–40 μm). Commercially available aryl chlorides, B_2pin_2, and KOAc were used directly. Dioxane and toluene used in the experiment were refluxed in the presence of sodium using diphenyl ketone as an indicator and distilled right before use. DMSO was refluxed in the presence of CaH_2 overnight and distilled right before use. CH_2Br_2 was used as the internal standard for ^{1}H NMR analysis (Tables 1 and 2).

Typical procedure

(1) Synthesis of 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a).[5] To a flame-dried and nitrogen filled Schlenk vessel were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.0 mg, 0.04 mmol), KOAc (294.7 mg, 3.0 mmol), and bis(pinacolato)diboron (305.9 mg, 1.2 mmol). The Schlenk vessel was evacuated and backfilled with nitrogen two times. Then **1a** (141.8 mg, 1.0 mmol) and 2.0 mL of dioxane were added (if the aryl chloride is a solid, it should be added before evacuation). The vessel was heated at 110 °C with a preheated oil bath. After 2.5 h, the reaction was complete as monitored by GC. The reaction mixture was diluted with 10 mL of ethyl acetate and filtered through a short column of silica gel (eluent: 2 × 10 mL of ethyl acetate). Evaporation and purification by chromatography (eluent: petroleum ether–ethyl acetate = 10/1) on a short silica gel column (10 cm, ∅ 2 cm) afforded **2a** (209.9 mg, 90%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.7 Hz, 2H, ArH), 6.91 (d, J = 8.4 Hz, 2H, ArH), 3.82 (s, 3H, OCH_3), 1.34 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 136.5, 113.3, 83.8, 55.0, 24.8; IR (neat) ν (cm^{-1}) 2978, 2934, 2838, 1605, 1570, 1518, 1466, 1410, 1397, 1362, 1318, 1278, 1248, 1214, 1175, 1144, 1092, 1031, 1011; MS (70 eV, EI) m/z (%): 235 (M^+ + 1, 13.01), 234 (M^+, 95.13), 134 (100).

The following compounds were prepared by this procedure.

(2) 2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b).[5] The reaction of **1b** (143.6 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (305.8 mg, 1.2 mmol), and KOAc (295.3 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2b** (214.2 mg, 91%) as a liquid (eluent: petroleum ether–ethyl acetate = 10/1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 1H, ArH), 7.37–7.22 (m, 2H, ArH), 7.05–6.97 (m, 1H, ArH), 3.83 (s, 3H, ArCH3), 1.34 (s, 12H, 4 ×

CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 128.9, 127.1, 118.7, 117.9, 83.8, 55.2, 24.8; IR (neat) ν (cm^{-1}) 2978, 2935, 2834, 1599, 1576, 1491, 1450, 1424, 1386, 1356, 1317, 1270, 1240, 1227, 1145, 1102, 1073, 1046; MS (70 eV, EI) *m*/*z* (%): 235 (M^+ + 1, 5.72), 234 (M+, 39.61), 134 (100).

(3) 4,4,5,5-Tetramethyl-2-*o*-tolyl-1,3,2-dioxaborolane (2c).[5] The reaction of **1c** (125.8 mg, 1.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (305.5 mg, 1.2 mmol), and KOAc (295.6 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2c** (177.1 mg, 82%) as a liquid (eluent: petroleum ether–ethyl acetate = 10/1): ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.9 Hz, 1H, ArH), 7.22 (t, *J* = 7.2 Hz, 2H, ArH), 7.12–6.97 (m, 2H, ArH), 2.45 (s, 3H, $ArCH_3$), 1.24 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 135.8, 130.8, 129.7, 124.7, 83.3, 24.8, 22.2; IR (neat) ν (cm^{-1}) 3053, 2978, 2930, 1601, 1566, 1490, 1441, 1424, 1381, 1347, 1312, 1265, 1146, 1124, 1110, 1073, 1043; MS (70 eV, EI) *m*/*z* (%): 219 (M^+ + 1, 6.10), 218 (M^+, 46.98), 161 (100).

(4) 4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (2d).[5] The reaction of **1d** (162.3 mg, 1.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (305.1 mg, 1.2 mmol), and KOAc (294.3 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2d**[5] (232.4 mg, 92%) as a solid (eluent: petroleum ether–ethyl acetate = 20/1): m.p. 56–57 °C (*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.4 Hz, 1H, ArH), 8.11 (d, *J* = 6.3 Hz, 1H, ArH), 7.96 (d, *J* = 8.4 Hz, 1H, ArH), 7.85 (d, *J* = 8.4 Hz, 1H, ArH), 7.63–7.39 (m, 3H, ArH), 1.44 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 135.6, 133.2, 131.6, 128.4, 128.3, 126.3, 125.5, 124.9, 83.7, 24.9; IR (KBr) ν (cm^{-1}) 3043, 2978, 2929, 1577, 1508, 1463, 1436, 1414, 1405, 1371, 1339, 1298, 1257, 1207, 1147, 1135, 1111, 1059, 1023, 1006; MS (70 eV, EI) *m*/*z* (%): 255 (M^+ + 1, 14.99), 254 (M^+, 90.06), 154 (100).

(5) 2-(4-*t*-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e).[14] The reaction of **1e** (169.3 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (304.4 mg, 1.2 mmol), and KOAc (294.6 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2e** (208.8 mg, 80%) as a solid (eluent: petroleum ether–ethyl acetate = 10/1): m.p. 137–138 °C (*n*-hexane) ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.4 Hz, 2H, ArH), 1.34 (s, 12H, 4 × CH_3), 1.33(s, 9H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8; IR (KBr) ν (cm^{-1}) 2968, 2868, 1612, 1472, 1400, 1364, 1326, 1270, 1212, 1144, 1118, 1084, 1021. MS (70 eV, EI) *m*/*z* (%): 261 (M^+ + 1, 2.50), 260 (M^+, 15.36), 245 (100).

(6) 1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)-ethanone (2f).[10] The reaction of **1f** (154.6 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (260.2 mg, 1.02 mmol), and KOAc (296.3 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2f** (200.3 mg, 81%) as a solid (eluent: petroleum ether–ethyl acetate = 10/1): m.p. 63–64 °C (*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H, ArH), 7.88 (d, *J* = 7.8 Hz, 2H, ArH), 2.61 (s, 3H, CH_3), 1.35 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 138.9, 134.9, 127.3, 84.2, 26.7, 24.8; IR (KBr) ν (cm^{-1}) 2990, 2932, 1682, 1560, 1508, 1398, 1360, 1326, 1267, 1212, 1144, 1107, 1094, 1066, 1017; MS (70 eV, EI) *m*/*z* (%): 247 (M^+ + 1, 3.91), 246 (M^+, 24.84), 231 (100).

(7) 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo-nitrile (2g).[5] The reaction of **1g** (137.8 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.3 mg, 0.04 mmol), B_2pin_2 (259.4 mg, 1.02 mmol), and KOAc (295.3 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2g** (200.6 mg, 87%) as a solid (eluent: petroleum ether–ethyl acetate = 10/1): m.p. 94–95 °C (*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H, ArH), 7.64 (d, *J* = 8.1 Hz, 2H, ArH), 1.35 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 131.0, 118.8, 114.4, 84.4, 24.8; IR (KBr) ν (cm^{-1}) 3003, 2976, 2932, 2228, 1611, 1508, 1399, 1359, 1334, 1272, 1210, 1143, 1089, 1021; MS (70 eV, EI) *m*/*z* (%): 230 (M^+ + 1, 2.01), 229 (M^+, 13.99), 143 (100).

(8) 4,4,5,5-Tetramethyl-2-(4-(methylsulfonyl)phenyl)-1,3,2-dioxaborolane (2h).[15] The reaction of **1h** (191.0 mg, 1.0 mmol), $Pd(OAc)_2$ (2.1 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (303.5 mg, 1.2 mmol), and KOAc (296.7 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2h** (252.3 mg, 89%) as a solid (eluent: petroleum ether–ethyl acetate = 20/1): m.p. 160–161 °C (*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H, ArH), 7.91 (d, *J* = 8.1 Hz, 2H, ArH), 3.03 (s, 3H, CH_3), 1.34 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 135.5, 126.2, 84.5, 44.3, 24.8; IR (KBr) ν (cm^{-1}) 2977, 2932, 1605, 1492, 1396, 1362, 1333, 1301, 1271, 1156, 1143, 1095, 1079; MS (70 eV, EI) *m*/*z* (%): 283 (M^+ + 1, 2.69), 282 (M^+, 13.13), 196 (100).

(9) 4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (2i).[5] The reaction of **1i** (156.0 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (304.7 mg, 1.2 mmol), and KOAc (294.6 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2i** (226.4 mg, 92%) as a solid (eluent: petroleum ether–ethyl acetate = 10/1): m.p. 107–108 °C (*n*-hexane–ethyl ether); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H, ArH), 7.95 (d, *J* = 8.1 Hz, 2H, ArH), 1.36 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 135.6, 122.4, 84.6, 24.8; IR (KBr) ν (cm^{-1}) 2991, 2976, 2933, 1599, 1520, 1397, 1363, 1350, 1307, 1276, 1147, 1088, 1012; MS (70 eV, EI) *m*/*z* (%): 250 (M^+ + 1, 1.13), 249 (M^+, 7.99), 234 (100).

(10) 1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)-ethanone (2j).[14] The reaction of **1j** (155.7 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (306.4 mg, 1.2 mmol), and KOAc (295.6 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2j** (217.0 mg, 88%) as a liquid (eluent: petroleum ether–ethyl acetate = 10/1): ^1H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H, ArH), 8.03 (d, *J* = 8.1 Hz, 1H, ArH), 7.97 (d, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.7 Hz, 1H, ArH), 2.61 (s, 3H, CH_3), 1.34 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 139.4, 136.5, 134.8, 130.8, 128.0, 84.1, 26.7, 24.8; IR (neat) ν (cm^{-1}) 2974, 2929, 1687, 1599, 1485, 1417, 1358, 1324,

1275, 1250, 1144, 1072; MS (70 eV, EI) *m*/*z* (%): 247 (M^+ + 1, 3.26), 246 (M^+, 17.15), 231 (100).

(11) 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2k).[16] The reaction of **1k** (139.9 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.0 mg, 0.04 mmol), B_2pin_2 (304.7 mg, 1.2 mmol), and KOAc (294.8 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2k** (204.3 mg, 89%) as a liquid (eluent: petroleum ether–ethyl acetate = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H, CHO), 7.99–7.91 (m, 1H, ArH), 7.89–7.78 (m, 1H, ArH), 7.64–7.47 (m, 2H, ArH), 1.38 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 141.2, 135.4, 132.9, 130.7, 127.8, 84.3, 24.8; IR (neat) ν (cm^{-1}) 2975, 2932, 1697, 1593, 1567, 1489, 1441, 1380, 1347, 1325, 1258, 1202, 1144, 1111, 1068, 1036; MS (70 eV, EI) *m*/*z* (%):217 ($M^+ - CH_3$, 10.61), 174 (100).

(12) Methyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenoxy)acetate (2l). The reaction of **1l** (200.6 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (305.3 mg, 1.2 mmol), and KOAc (295.9 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2l** (229.7 mg, 79%) as a liquid (eluent: petroleum ether–ethyl acetate = 10/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.7 Hz, 2H, ArH), 6.89 (d, *J* = 8.7 Hz, ArH), 4.66 (s, 2H, CH_2), 3.79 (s, 3H, CH_3), 1.32 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 160.2, 136.6, 113.8, 83.6, 64.9, 52.2, 24.8; IR (neat) ν (cm^{-1}) 2978, 1759, 1604, 1573, 1515, 1437, 1394, 1361, 1317, 1291, 1205, 1142, 1093, 1079, 1012; MS (70 eV, EI) *m*/*z* (%): 293 (M^+ + 1, 11.81), 292 (M^+, 62.87), 133 (100). HRMS Cacld for $C_{15}H_{21}BO_5$ (M^+): 292.1482, Found 292.1481.

(13) 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzamide (2m).[17] The reaction of **1m** (155.4 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (305.4 mg, 1.2 mmol), and KOAc (296.7 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2m** (200.7 mg, 81%) as a solid (eluent: petroleum ether–ethyl acetate = 5/1 (300 mL), then petroleum ether–ethyl acetate = 1/1): m.p. 178–180 °C (ethyl acetate–dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H, ArH), 7.78 (d, *J* = 8.1 Hz, 2H, ArH), 6.76 (s, 1H, one proton of NH_2), 6.55 (s, 1H, one proton of NH_2), 1.32 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 135.6, 134.8, 126.4, 84.1, 24.8; IR (KBr) ν (cm^{-1}) 3484, 3411, 3352, 3289, 3188, 2985, 2938, 1671, 1604, 1555, 1510, 1358, 1328, 1273, 1211, 1168, 1143, 1111, 1086, 1018; MS (70 eV, EI) *m*/*z* (%): 248 (M^+ + 1, 3.40), 247 (M^+, 21.44), 148 (100).

(14) *N*-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)-acetamide (2n).[8d] The reaction of **1n** (170.6 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (304.7 mg, 1.2 mmol), and KOAc (294.8 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2n** (261.1 mg) as a solid after chromatographic separation (eluent: petroleum ether–ethyl acetate = 5/1, then petroleum ether–ethyl acetate–dichloromethane = 5/1/1). The impurity in this product was removed by washing with 10 mL *n*-hexane to afford 240.5 mg (92%) of the pure product **2n**: m.p. 157–158 °C (*n*-hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (bs, 1H, NH), 7.74 (d, *J* = 8.1 Hz, 2H, ArH), 7.53 (d, *J* = 7.8 Hz, 2H, ArH), 2.15 (s, 3H, CH_3), 1.32 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 140.7, 135.7, 118.6, 83.7, 24.8, 24.6; IR (KBr) ν (cm^{-1}) 3312, 3271, 3183, 3108, 3057, 2979, 2931, 1673, 1598, 1535, 1400, 1360, 1321, 1290, 1258, 1141, 1092, 1019; MS (70 eV, EI) *m*/*z* (%): 262 (M^+ + 1, 9.55), 261 (M^+, 65.57), 119 (100).

(15) 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (2o).[6] The reaction of **1o** (127.7 mg, 0.99 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (305.9 mg, 1.2 mmol), and KOAc (297.1 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2o** (166.0 mg, 76%) as a solid (eluent: petroleum ether–ethyl acetate = 10/1): m.p. 109–110 °C (*n*-hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H, ArH), 6.82 (d, *J* = 8.4 Hz, 2H, ArH), 5.85–5.53 (bs, 1H, OH), 1.34 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 136.8, 114.9, 83.7, 24.8; IR (KBr) ν (cm^{-1}) 3319, 2985, 2941, 1608, 1579, 1430, 1401, 1393, 1383, 1373, 1360, 1309, 1273, 1263, 1218, 1170, 1141, 1096, 1080; MS (70 eV, EI) *m*/*z* (%): 221 (M^+ + 1, 5.04), 220 (M^+, 32.19), 121 (100).

(16) 2-Methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (2q).[12] The reaction of **1q** (177.1 mg, 1.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), B_2pin_2 (302.9 mg, 1.2 mmol), and KOAc (296.6 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2q** (225.3 mg, 84%) as a solid (eluent: petroleum ether–ethyl acetate–pyridine = 5/1/0.05): m.p. 105–107 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H, ArH), 7.99 (d, *J* = 8.1 Hz, 2H, ArH), 7.83 (d, *J* = 8.1 Hz, 1H, ArH), 7.73 (d, *J* = 8.1 Hz, 1H, ArH), 7.26 (d, *J* = 8.7 Hz, 1H, ArH), 2.73 (s, 3H, CH_3), 1.37 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 147.2, 136.6, 135.8, 130.1, 128.1, 126.5, 122.6, 83.9, 25.3, 24.8; IR (KBr) ν (cm^{-1}) 3051, 2979, 2929, 1604, 1554, 1508, 1449, 1409, 1382, 1356, 1329, 1296, 1273, 1216, 1166, 1143, 1131, 1113, 1075; MS (70 eV, EI) *m*/*z* (%): 270 (M^+ + 1, 8.97), 269 (M^+, 57.26), 268 (100).

(17) 4,4,5,5-Tetramethyl-2-(thien-3-yl)-1,3,2-dioxaborolane (2r).[5] The reaction of **1r** (118.9 mg, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), B_2pin_2 (304.2 mg, 1.2 mmol), and KOAc (296.7 mg, 3.0 mmol) in 2.0 mL of dioxane at 110 °C under nitrogen afforded **2r** (102.2 mg, 49%) as a solid (eluent: petroleum ether–ethyl acetate = 20/1): m.p. 76–78 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J_1 = 2.7 Hz, J_2 = 0.9 Hz, 1H, ArH), 7.41 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, ArH), 7.7.34 (dd, J_1 = 4.8 Hz, J_2 = 2.7 Hz, 1H, ArH), 1.34 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 132.0, 125.3, 83.6, 24.8; IR (KBr) ν (cm^{-1}) 3083, 2980, 2929, 1519, 1412, 1389, 1372, 1341, 1312, 1264, 1211, 1200, 1166, 1139, 1111, 1089; MS (70 eV, EI) *m*/*z* (%): 211 (M^+ + 1, 5.6), 210 (M^+, 43.19), 124 (100).

(18) Synthesis of 2-(2,6-dimethylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (4).[18] The reaction of $Pd(OAc)_2$ (2.1 mg,

0.01 mmol), Gorlos-Phos·HBF_4 (19.2 mg, 0.04 mmol), KOAc (292.3 mg, 3.0 mmol), bis(neophentyl glycolato)diboron (338.2 mg, 1.5 mmol), **1s** (140.9 mg, 1.0 mmol), and 2.0 mL of dioxane afforeded **4** (113.3 mg, 52%) as a solid (petroleum ether–ethyl acetate = 10/1). m.p. 47–49 °C (*n*-hexane): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (t, J = 7.5 Hz, 1H, ArH), 6.96 (d, J = 7.2 Hz, 2H, ArH), 3.81 (s, 4H, 2 × CH_2), 2.41 (s, 6H, 2 × CH_3), 1.12 (s, 6H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 128.4, 126.3, 72.2, 31.6, 22.2; IR (KBr) ν (cm^{-1}) 3051, 3012, 2967, 2929, 2872, 1596, 1476, 1457, 1414, 1376, 1327, 1297, 1249, 1219, 1129, 1091, 1029; MS (70 eV, EI) m/z (%): 219 (M^+ + 1, 16.23), 218 (M^+, 100).

(19) 10 mmol scale reaction of 1t – synthesis of 4,4,5,5-tetramethyl-2-*p*-tolyl-1,3,2-dioxaborolane (2t).[5] The reaction of $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.1 mg, 0.04 mmol), KOAc (2.9380 g, 30.0 mmol), B_2pin_2 (3.047 g, 12.0 mmol), **1t** (1.2679 g, 10.0 mmol) and 20 mL of dioxane afforded **2t** (1.8114 mg, 83%) as a liquid (eluent: petroleum ether–ethyl acetate = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H, ArH), 7.21 (d, J = 8.1 Hz, 2H, ArH), 2.39 (s, 3H, CH_3), 1.36 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 134.8, 128.4, 83.5, 24.8, 21.7; IR (neat) ν (cm^{-1}) 3047, 2978, 2926, 1614, 1518, 1481, 1465, 1446, 1398, 1360, 1318, 1304, 1266, 1213, 1183, 1145, 1106, 1089; MS (70 eV, EI) m/z (%): 219 (M^+ + 1, 4.78), 218 (M^+, 33.83), 119 (100).

Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoic acid (2p).[19] To a flame-dried and nitrogen filled Schlenk vessel were added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Gorlos-Phos·HBF_4 (19.0 mg, 0.04 mmol), KOAc (295.6 mg, 3.0 mmol), B_2pin_2 (305.6 mg, 1.2 mmol), and **1p** (156.1 mg, 1.0 mmol). The Schlenk vessel was evacuated and backfilled with nitrogen two times. Then 2.0 mL of dioxane were added. The vessel was heated with a preheated oil bath at 110 °C. After 3.0 h, the reaction was complete as monitored by TLC. The reaction mixture was quenched with 10 mL of H_2O, extracted with ethyl acetate (10 mL × 3), washed with 20 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation and purification by chromatography (eluent: petroleum ether–ethyl acetate = 10/1) on a short silica gel column (10 cm, ∅ 2 cm) afforded **2p** (182.8 mg, 74%) as a solid: m.p. 227–228 °C (*n*-hexane–ethyl acetate); ^{1}H NMR (300 MHz, CDCl3) δ 10.9 (bs, 1H, COOH), 8.10 (d, J = 8.1 Hz, 2H, ArH), 7.91 (d, J = 8.1 Hz, 2H, ArH), 1.37 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 134.8, 131.5, 129.2, 84.3, 24.9; IR (KBr) ν (cm^{-1}) 2982, 2667, 2542, 1686, 1560, 1510, 1425, 1400, 1362, 1329, 1270, 1145, 1126, 1088, 1018; MS (70 eV, EI) m/z (%): 248 (M^+, 23.34), 149 (100).

65 mmol scale reaction of 1p. To a flame-dried and nitrogen filled 500 mL Schlenk vessel were added $Pd(OAc)_2$ (14.7 mg, 0.066 mmol), Gorlos-Phos·HBF_4 (124.3 mg, 0.260 mmol), KOAc (19.1170 g, 195.1 mmol), bis(pinacolato) diboron (19.8142 g, 78.0 mmol), and **1p** (10.1814 g, 65 mmol). The Schlenk vessel was evacuated and backfilled with nitrogen two times. Then 260 mL of dioxane were added. The resulting mixture was stirred vigorously and heated with a preheated oil bath at 110 °C. After 40 h, the reaction was complete as monitored by TLC. The resulting mixture was quenched with 100 mL of H_2O, extracted with ethyl acetate (100 mL × 3), washed with 100 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation and purification by recrystallization three times (*n*-hexane and ethyl acetate) afforded **2p** (5.7863 g + 5.0512 g + 1.0850 g = 11.9225 g, 74%) as a solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.61 (bs, 1H, COOH) 8.10 (d, J = 8.1 Hz, 2H, ArH), 7.91 (d, J = 8.1 Hz, 2H, ArH), 1.37 (s, 12H, 4 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 134.7, 131.4, 129.2, 84.2, 24.8.

Acknowledgements

Financial support from the National Natural Science Foundation of China (21172192) and the National Basic Research Program of China (2011CB808700) are greatly appreciated. Shengming Ma is a Qiu Shi Adjunct Professor at Zhejiang University. We thank Bukeyan Miao in our group for reproducing the results of **2i**, **2o** and **2r**.

Notes and references

1 D. G. Hall, *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, Wiley-VCH, Weinheim, Germany, 2nd edn, 2011, vol. 1 and 2.
2 For a review on the transition metal-catalyzed borylation of aryl halides, see: (*a*) W. K. Chow, O. Y. Yuen, P. Y. Choy, C. M. So, C. P. Lau, W. T. Wong and F. Y. Kwong, *RSC Adv.*, 2013, **3**, 12518. For the recent reviews on the transition metal-catalyzed borylation reaction by C–H activation, see: (*b*) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890; (*c*) J. F. Hartwig, *Acc. Chem. Res.*, 2012, **45**, 864.
3 V. V. Grushin and H. Alper, *Chem. Rev.*, 1994, **94**, 1047.
4 For the reviews, see: (*a*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176; (*b*) D. S. Surry and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2008, **47**, 6338; (*c*) R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461.
5 T. Ishiyama, K. Ishida and N. Miyaura, *Tetrahedron*, 2001, **57**, 9813.
6 K. L. Billingsley, T. E. Barder and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2007, **46**, 5359.
7 (*a*) G. A. Molander, S. L. J. Trice and S. D. Dreher, *J. Am. Chem. Soc.*, 2010, **132**, 17701; (*b*) G. A. Molander, S. L. J. Trice, S. M. Kennedy, S. D. Dreher and M. T. Tudge, *J. Am. Chem. Soc.*, 2012, **134**, 11667.
8 For selected samples of Ni catalyzed borylation reaction of aryl chlorides, see: (*a*) B. M. Rosen, C. Huang and V. Percec, *Org. Lett.*, 2008, **10**, 2597; (*b*) C. Moldoveanu, D. A. Wilson, C. J. Wilson, P. Leowanawat, A. M. Resmerita, C. Liu, B. M. Rosen and V. Percec, *J. Org. Chem.*, 2010, **75**, 5438; (*c*) P. Leowanawat, A. M. Resmerita, C. Moldoveanu, C. Liu, N. Zhang, D. A. Wilson, L. M. Hoang, B. M. Rosen and V. Percec, *J. Org. Chem.*, 2010, **75**, 7822;

(*d*) T. Yamamoto, T. Morita, J. Takagi and T. Yamakawa, *Org. Lett.*, 2011, **13**, 5766; (*e*) A. S. Dudnik and G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 10693; (*f*) G. A. Molander, L. N. Cavalcanti and C. García-García, *J. Org. Chem.*, 2013, **78**, 6427. For Ni catalyzed borylation of aryl mesylates, tosylates, or carbamates, see: (*g*) D. A. Wilson, C. J. Wilson, C. Moldoveanu, A. M. Resmerita, P. Corcoran, L. M. Hoang, B. M. Rosen and V. Percec, *J. Am. Chem. Soc.*, 2010, **132**, 1800; (*h*) K. Huang, D. G. Yu, S. F. Zheng, Z. H. Wu and Z. J. Shi, *Chem. – Eur. J.*, 2011, **17**, 786.

9 S. Kawamorita, H. Ohmiya, T. Iwai and M. Sawamura, *Angew. Chem., Int. Ed.*, 2011, **50**, 8363.

10 (*a*) W. K. Chow, O. Y. Yuen, C. M. So, W. T. Wong and F. Y. Kwong, *J. Org. Chem.*, 2012, **77**, 3543; (*b*) T. Iwai, T. Harada, R. Tanaka and M. Sawamura, *Chem. Lett.*, 2014, DOI: 10.1246/cl.131161.

11 (*a*) B. Lü, C. Fu and S. Ma, *Tetrahedron Lett.*, 2010, **51**, 1284; (*b*) B. Lü, C. Fu and S. Ma, *Chem. – Eur. J.*, 2010, **16**, 6434; (*c*) P. Li, B. Lü, C. Fu and S. Ma, *Org. Biomol. Chem.*, 2013, **11**, 98; (*d*) B. Lü, P. Li, C. Fu, L. Xue, Z. Lin and S. Ma, *Adv. Synth. Catal.*, 2011, **353**, 100; (*e*) P. Li, B. Lü, C. Fu and S. Ma, *Adv. Synth. Catal.*, 2013, **355**, 1255. Patents filed (CN201210146220.6 and PCT/CN2012/078129), 2012.

12 P. Zhang, M. Zou, A. L. Rodriguez, P. J. Conn and A. H. Newman, *Bioorg. Med. Chem.*, 2010, **18**, 3026.

13 H. Fang, G. Kaur, J. Yan and B. Wang, *Tetrahedron Lett.*, 2005, **46**, 1671.

14 C. Zhu and M. Yamane, *Org. Lett.*, 2012, **14**, 4560.

15 Y. Yamamoto, *Adv. Synth. Catal.*, 2010, **352**, 478.

16 F. Wienhold, D. Claes, K. Graczyk and W. Maison, *Synthesis*, 2011, 4059.

17 F. Mo, Y. Jiang, D. Qiu, Y. Zhang and J. Wang, *Angew. Chem., Int. Ed.*, 2010, **49**, 1846.

18 M. Schnürch, M. Holzweber, M. D. Mihovilovic and P. Stanetty, *Green Chem.*, 2007, **9**, 139.

19 D. Qiu, L. Jin, Z. Zheng, H. Meng, F. Mo, X. Wang, Y. Zhang and J. Wang, *J. Org. Chem.*, 2013, **78**, 1923.

