HETEROCYCLES, Vol. 85, No. 8, 2012, pp. 1795 - 1819. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 28th February, 2012, Accepted, 10th April, 2012, Published online, 16th April, 2012
DOI: 10.3987/REV-12-736

TRANSITION-METAL-CATALYZED BORYLATION OF ORGANIC HALIDES WITH HYDROBORANES

Miki Murata*

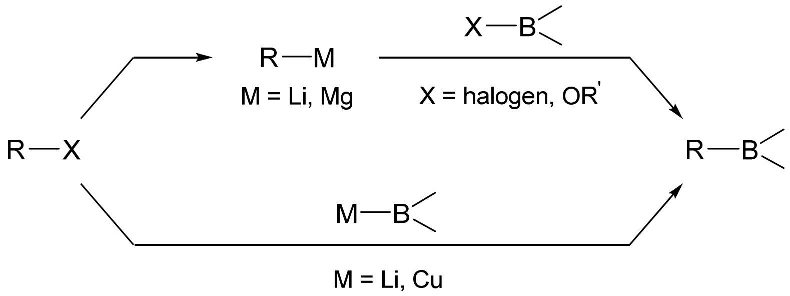
Department of Materials Science and Engineering, Kitami Institute of Technology,
165 Koencho, Kitami 090-8507, Japan
E-mail: muratamk@mail.kitami-it.ac.jp

Abstract – Metal-catalyzed cross-coupling reaction of B–H compounds provides a direct method for conversion of C–X bonds to C–B bonds. Dialkoxyboranes are excellent boron sources in the borylation of aryl, 1-alkenyl, allyl or benzyl halides or pseudohalides. These reactions tolerate large number of functional groups and proceeds with excellent yields, thereby allowing the simple, convenient, and elegant preparation of functionalized C–B compounds.

CONTENTS

1. INTRODUCTION

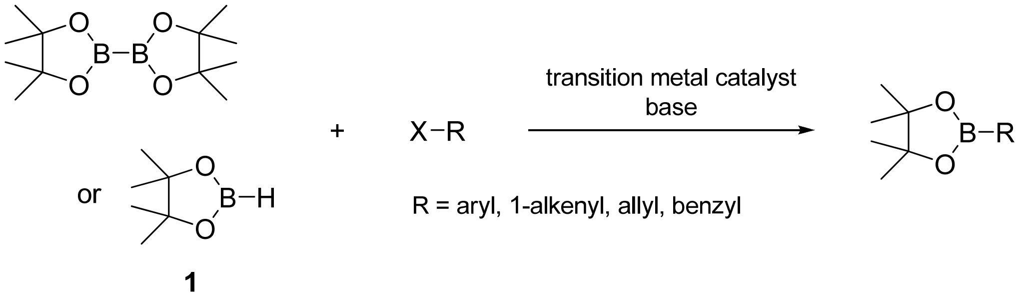
Organoboron compounds are an important class of organometallics, which can be widely used as versatile building blocks in modern organic chemistry.[1-3] Among many methods available to prepare this class of compounds, representative synthetic route to organoboron compounds from organic electrophiles is illustrated in Scheme 1.



Scheme 1. C–B Bond Formation from C–X Bond

The most common method for the preparation of boronic acids and esters is based on the reaction of boron halides or alkoxides with carbon nucleophiles including organolithiums or Grignard reagents derived from the corresponding organic halides R–X.[1] Although this traditional transmetalation protocol is still common for large scale synthesis of simple boronates, the use of such reactive organometallics R–M is inefficient in terms of step-economy because of the protection of electrophilic or protic functional groups. Since boronic acid and their esters are playing the crucial role for the construction of complex molecules, carbon–boron bond-forming reaction is demanded to tolerate the presence of a diverse and adequate number of functionalities. Another approach is based on direct construction of C–B bonds from organic electrophiles R–X with anionic boron species such as B–Li[4] and B–Cu.[5]

While a palladium-catalyzed coupling reaction of organic electrophiles with mild boron nucleophiles should be an alternative route to a wide range of functionalized boronates, the lack of boron nucleophiles has nevertheless limited the catalytic carbon–boron bond-forming reaction. However, at the end of 20th century, two reports on boron nucleophiles for palladium-catalyzed coupling opened the door to the catalytic borylation of organic electrophiles R–X (Scheme 2). On one hand, Ishiyama and Miyaura reported on the palladium-catalyzed borylation with bis(pinacolato)diboron.[6] This remarkable discovery is now called “Miyaura borylation”.[7] On the other, we demonstrated pinacolborane (**1**) acts as a boron source in the coupling with organic electrophiles in the presence of a palladium catalyst and a tertiary amine.[8] Transition metal-catalyzed cross-coupling reaction of tetra(alkoxo)diborons or dialkoxyboranes provides a simple, elegant and direct method for preparation of functionalized boronates from organic electrophiles. The advantage of pinacolborane (**1**) over bis(pinacolato)diboron is more economically profitable. Additionally, the borylation using dialkoxyborane is an atom-economical method; thus, the reaction is recommended for large-scale preparation of organoboronates. In this review, we will focus on the catalytic borylation of organic electrophiles with dialkoxyboranes. Miyaura borylation has been reviewed elsewhere.[7]



Scheme 2. Transition Metal-Catalyzed Borylation of Organic Electrophiles

Another method of the catalytic C–B bond formation is the borylation of C–H bonds of hydrocarbons.[9] During the past decade, much attention has been focused on the C–H borylation using bis(pinacolato)diboron or pinacolborane (**1**) as a boron source, and numerous catalyst systems were reported in the literature for these transformations. The borylation of ubiquitous C–H bonds is the most straightforward and atom-economical route; however, this is still a little problematic with regard to the control of regioselectivity. The catalytic C–H borylation has been reviewed elsewhere,[9] and will not be covered by the present review.

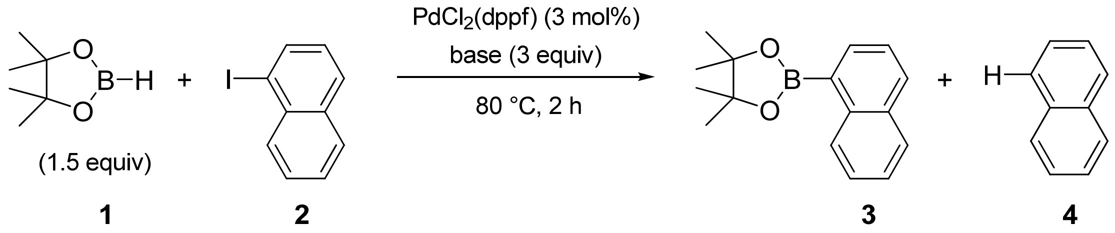
2. BORYLATION OF ARYL ELECTROPHILES

In 1997, we reported the preparation of pinacol arylboronates from the corresponding aryl halides by palladium-catalyzed cross-coupling with pinacolborane (**1**) in the presence of Et_3N (Table 1).[8] To the best of our knowledge, this is the first example of the catalytic borylation of C–X bonds using B–H compounds. Dialkoxyboranes are now recognized as atom-economical and cost-effective alternatives to the catalytic borylation of aryl electrophiles.

2-1 REACTION CONDITIONS

As shown in Table 1, 1-iodonaphthalene **2** undergo the borylation with **1** in the presence of 3 mol% of $PdCl_2$(dppf) and 3 equiv of tertiary amines.[8] The reaction often suffers from arene byproduct **4** by partially reduction of C–X bonds. The choice of base is critical for the selective borylation, that is, Et_3N plays a crucial role in not only preventing the formation of undesired dehalogenated arenes but also facilitating the borylation. Hunig's base promoted an increase in dehalogenation. In the presence of other bases, such as pyridine, DBU, and KOAc, the formation of byproduct **4** predominated over that of desired boronate **3**. Although the use of DMF caused both a low yield and selectivity, the yields are not significantly influenced by the choice of solvent. In 2003, Zaidlewicz has described that the use of ionic liquids as the reaction medium for the borylation of aryl iodides with **1** is advantageous over conventional solvents.[10]

Table 1. Effects of Bases and Solvents on the Borylation of 1-Iodonaphthalene[8]

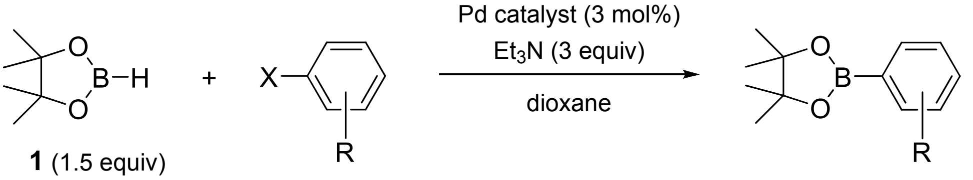


base	solvent	yield / %	
		3	**4**
Et_3N	dioxane	89	6
iPr_2NEt	dioxane	64	29
pyridine	dioxane	12	47
DBU	dioxane	3	36
KOAc	dioxane	6	82
Et_3N	toluene	79	7
Et_3N	CH_2ClCH_2Cl	81	7
Et_3N	MeCN	83	8
Et_3N	DMF	27	23

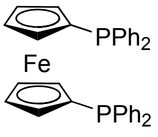
2-1-1. ELECTROPHILES AND CATALYSTS

2-1-1-1. Aryl Iodides and Perfluoroalkanesulfonates. In our first report, $PdCl_2$(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene, **5**) and $PdCl_2(PPh_3)_2$ were recommended for the reaction of aryl iodides and triflates.[8] Representative results are shown in Table 2. Generally, aryl iodides exhibited higher reactivity than aryl bromides or fluoroalkanesulfonates in the present reaction. Even at elevated temperatures, pinacolborane (**1**) is inert to much reducible functionality due to low reducing ability.[9] Consequently, the present reaction tolerates various functional groups such as carbonyl, cyano, and nitro groups. However, the dehalogenation of C–X bonds was not completely suppressed, and small amount of arene byproducts (ca. 10%) was observed in most instances. The differences in the yields and on the selectivity among aryl iodides possessing electron-donating or -withdrawing groups were not particularly large under these conditions. Although higher reaction temperature was required, the conditions for aryl iodides using $PdCl_2$(dppf) in dioxane facilitate the borylation of aryl fluoroalkanesulfonates, such as aryl triflates (X = OSO_2CF_3, OTf) and nonaflates (X = $OSO_2(CF_2)_3CF_3$, ONf), bearing either electron-donating or -withdrawing groups.

Table 2. $PdCl_2$(dppf)-Catalyzed Borylation of Aryl Electrophiles with Pinacolborane[8]



X	R	catalyst	conditions	yield / %
I	4-OMe	$PdCl_2$(dppf)	80 °C, 1 h	77
I	4-Me	$PdCl_2$(dppf)	80 °C, 1 h	79
I	2-Me	$PdCl_2$(dppf)	80 °C, 5 h	78
I	4-Cl	$PdCl_2$(dppf)	80 °C, 3 h	83
I	4-CO_2Et	$PdCl_2$(dppf)	80 °C, 2 h	79
I	4-COMe	$PdCl_2$(dppf)	80 °C, 4 h	74
I	4-CN	$PdCl_2$(dppf)	80 °C, 4 h	73
I	4-NO_2	$PdCl_2$(dppf)	80 °C, 4 h	84
Br	4-NMe_2	$PdCl_2(PPh_3)_2$	100 °C, 2 h	79
OTf	H	$PdCl_2$(dppf)	100 °C, 4 h	93
OTf	4-CO_2Et	$PdCl_2$(dppf)	100 °C, 2 h	77
ONf	4-OMe	$PdCl_2$(dppf)	100 °C, 4 h	74

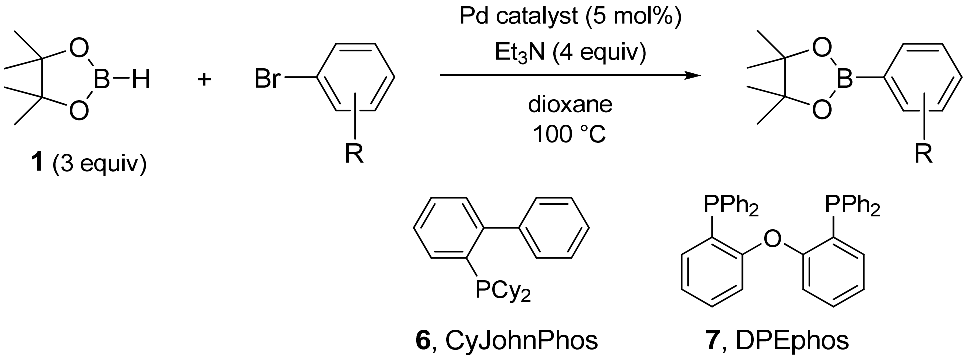


5, dppf

Under these conditions, the reactivity of aryl bromides was not favorable when compared with that of aryl iodides or triflates. The borylation of less-hindered electron-rich aryl bromides proceeded at 100 °C by using the $PdCl_2(PPh_3)_2$ catalyst; however, the presence of electron-withdrawing substituents remarkably decreased the yield and the product selectivity of arylboronates.

2-1-1-2. Electron-Rich Aryl Bromides. Under the conditions using $PdCl_2$(dppf) catalyst, *ortho*-substituted aryl bromides were also problematic. In 2000, Baudoin described that the borylation of *ortho*-substituted aryl iodides and bromides can be readily accomplished by using a catalyst system based on CyJohnPhos (**6**).[11] In 2004, Colobert reported that DPEphos (**7**) as a supporting ligand can be employed for the borylation of *para*- and *ortho*-substituted aryl bromides.[12] Table 3 compares three catalyst systems. Whereas the scope of the aryl halides in the palladium-catalyzed borylation has been improved, these catalyst systems still have some drawbacks; e.g., the reactions of electron-deficient or *ortho,ortho'*-disubstituted bromides produced only poor yields due to the formation of considerable amount of dehalogenated arene byproducts.

Table 3. Effect of Ligands on the Borylation of Aryl Bromides



1 (3 equiv)

6, CyJohnPhos

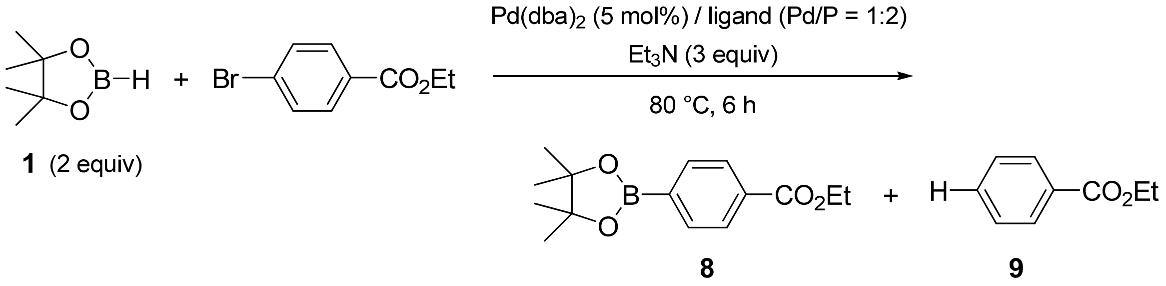
7, DPEphos

R	yield (%) / time (h)			ref.
	$PdCl_2(dppf)$	$Pd(OAc)_2$ + 20% **6**	$Pd(OAc)_2$ + 10% **7**	
2-NH_2	48 / 4	81 / 1	39 / 20	[11, 12]
2-OMe		59 / 1	78 / 4	[11, 12]
4-OMe	77 / 3		99 / 4	[8, 12]
2-NO_2		20 / 3	<3 / 20	[11, 12]
4-NO_2			<1 / 20	[12]
2,6-Me_2	<5 / 6	51 / 0.5		[11]
2,4,6-Me_3			25 / 20	[12]

2-1-1-3. Electron-Deficient Aryl Bromides and Aryl Chlorides. In 2006, we found that the use of tBuDPEphos (**10**)[13] or dtbpf (**12**) as a ligand has overcome many limitations of the above catalyst systems.[14] That is, the selective borylation of electron-deficient or *ortho*,*ortho'*-disubstituted bromides and that of electron-rich chlorides have been achieved by using the combination of $Pd(dba)_2$ and **10**. As shown in Table 4, the use of electron-rich and sterically-hindered bidentate phosphine **10** or **12** effectively suppressed the formation of dehalogenated arene byproduct **9**.

The substrate scope was significantly broad, and a variety of functional groups, such as ester and ketone carbonyl, cyano, and nitro groups, were tolerated under these conditions (Table 5). However, the reaction of electron-deficient chlorides has remained a challenging task; i.e., the presence of electron-withdrawing substituents remarkably increases the yield of dehalogenated arene byproducts. In 2010, we found that electron-deficient chlorides undergo the selective borylation using a catalyst system based on **10** with the aid of 2 equiv of Bu_4NI.[15] The addition of an iodide anion source improved the product selectivity on the borylation of aryl chlorides; although we still have no definitive explanation for the role of halide ion. Bu_4NBr or Bu_4NCl was less effective. To the best of our knowledge, this catalyst system based on **10** has the widest substrate scope of any reported to date.

Table 4. Effect of Ligands on the Borylation of Electron-Deficient Aryl Bromides[14]



ligand	yield / %	
	8	**9**
7	0	46
10	84	16
11	15	62
5	0	40
12	75	15
13	11	80
6	0	0
14	6	44

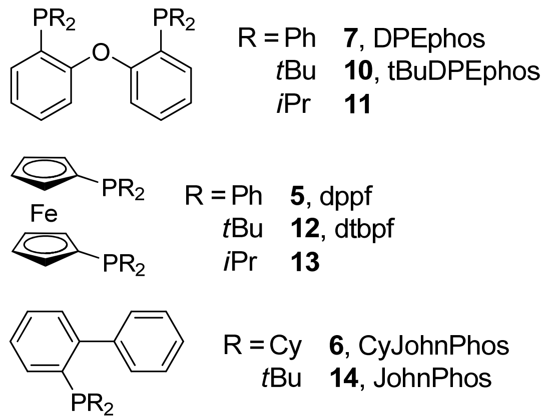
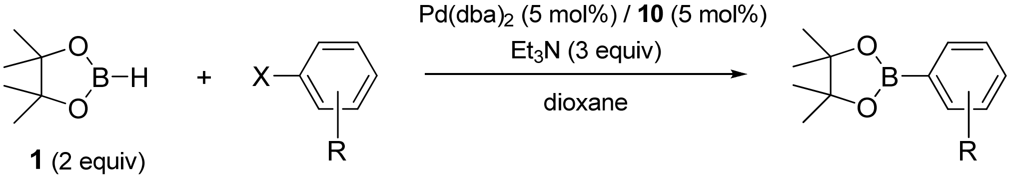
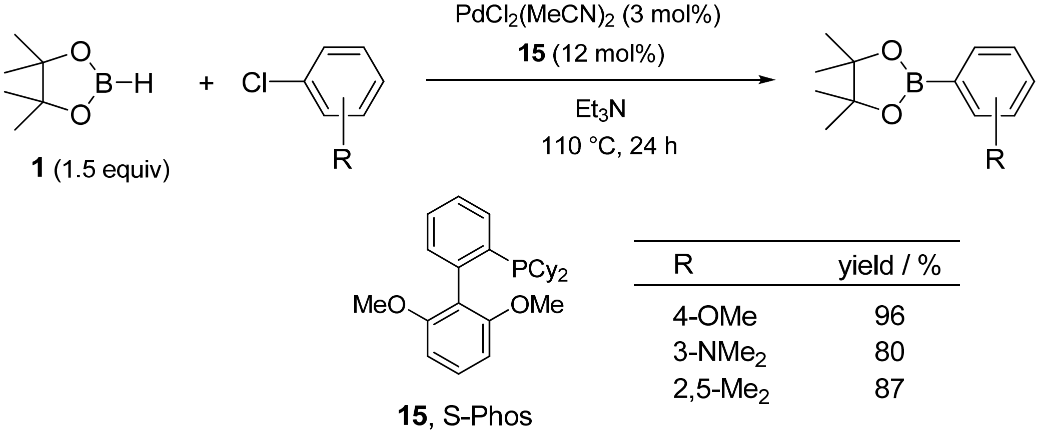


Table 5. Borylation of Aryl Bromides and Chlorides[14,15]



X	R	additive	conditions	yield / %
Br	4-OMe		100 °C, 6 h	91
Br	4-CO_2Et		80 °C, 6 h	84
Br	4-COMe		80 °C, 6 h	78
Br	3-CN		80 °C, 6 h	79
Br	4-NO_2		80 °C, 2 h	76
Br	2,6-Me_2		100 °C, 6 h	82
Br	2,4,6-$i\text{Pr}_3$		100 °C, 6 h	72
Cl	4-NHMe		120 °C, 24 h	81
Cl	4-CF_3	Bu_4NI	100 °C, 24 h	84
Cl	4-COMe	Bu_4NI	100 °C, 24 h	87
Cl	3-COPh	Bu_4NI	100 °C, 24 h	70
Cl	4-CN	Bu_4NI	100 °C, 24 h	80

Baudoin first introduced Buchwald's biarylphosphine ligands[16] into the borylation with pinacolborane (**1**), as already mentioned.[11] In 2008, the positive role of biarylphosphines in the catalytic borylation was described again by Buchwald.[17] The use of S-Phos (**15**) allows high efficiency and relatively low catalyst loadings for the borylation of aryl bromides and electron-rich chlorides, provided that Et_3N was used as solvent for the reaction of aryl chlorides (Scheme 3). However, they provided no example of the borylation of aryl chlorides possessing electron-withdrawing groups on the aromatic rings.

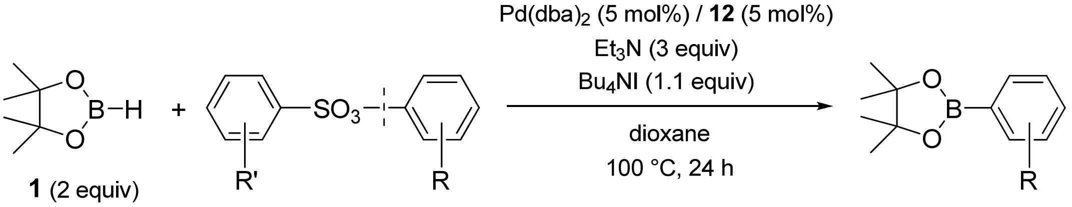


R	yield / %
4-OMe	96
3-NMe_2	80
2,5-Me_2	87

Scheme 3. Borylation of Electron-Rich Aryl Chlorides[17]

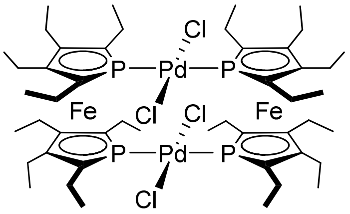
2-1-1-4. Aryl Arenesulfonates. Aryl arenesulfonates are relatively unreactive compared to the corresponding aryl halide and triflate counterparts; however, they undergo the borylation with **1** in the presence of 5 mol% of $Pd(dba)_2$ and dtbpf (**12**) and 1.1 equiv of Bu_4NI.[18] Unlike the reaction of aryl halides, tBuDPEphos (**10**) did not promote the selective borylation with **1**. As shown in Table 6, electron-deficient aryl benzenesulfonates were efficiently converted to the corresponding boronates. In contrast to the electron-deficient substrates, an electron-neutral aryl sulfonate, phenyl benzenesulfonate, did not have enough reactivity. We found, however, phenyl 4-trifluoromethylbenzenesulfonate participated in the present palladium-catalyzed borylation.

Table 6. Borylation of Aryl Arenesulfonates with Pinacolborane[18]

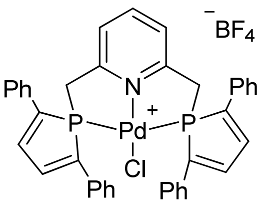


R	R'	yield / %
4-CN	H	77
3-COMe	H	71
4-COPh	H	71
4-CF_3	4-Me	83
H	H	24
H	4-CF_3	80
4-OMe	4-CF_3	74

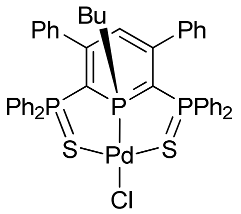
2-1-1-5. Other Catalyst Systems. Floch reported that palladium complexes with phosphorus heterocycle ligands **16**–**18** exhibit remarkable potential as catalysts for the borylation with pinacolborane (**1**).[19] TONs exceed classical catalysts by a few orders of magnitude (3000–100000) and impressively underline the catalytic activity of these catalysts.



16



17

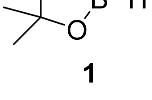


18

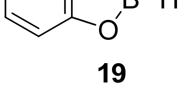
Additionally, it has been reported that $\mathrm{NiCl_2(dppp)}$[20] and CuI[21] catalyze the cross-coupling of aryl halides with **1**. It is interesting to note that CuI allowed the substitutional borylation of aryl iodides to proceed at room temperature, although it required more reactive sodium hydride as a base. Furthermore, there are several reports focusing on an improved catalyst system for specific targets. Christophersen reported that $\mathrm{Pd(P}\mathit{t}\mathrm{Bu_3)_2}$ catalyzes the borylation of 2,3-substituted bromothiophenes under the mild conditions, which tolerates even formyl group.[22] Westcott recommended $\mathrm{PdCl_2(}\mathit{t}\mathrm{Bu_2PCl)_2}$ for the borylation of iodoaniline derivatives.[23] The Miller group described that palladium black was the ideal catalyst for the large scale preparation of functionalized arylboronates in their drug synthesis.[24]

2-1-2. HYDROBORANES

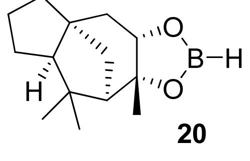
Our and other groups successfully introduced several cyclic dialkoxyboranes, such as catecholborane (**19**),[8] **20**,[25] 4,4,6-trimethyl-1,3,2-dioxaborinane (**21**),[15,18,26-28] and 5,5-dimethyl-1,3,2-dioxaborinane (neopentylglycolborane, **22**),[29,30,31] to participate in the catalytic borylation of aryl halides. (Diisopropyl)aminoborane (**23**) is also an efficient boron source in the palladium-catalyzed borylation affording aryl(dialkylamino)boranes.[32,33] Among the hydroboranes, pinacolborane (**1**) has become one of the most popular borylation reagents, predominantly because of the high stability, availability from



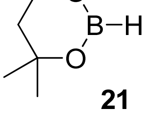
1



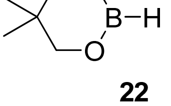
19



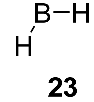
20



21

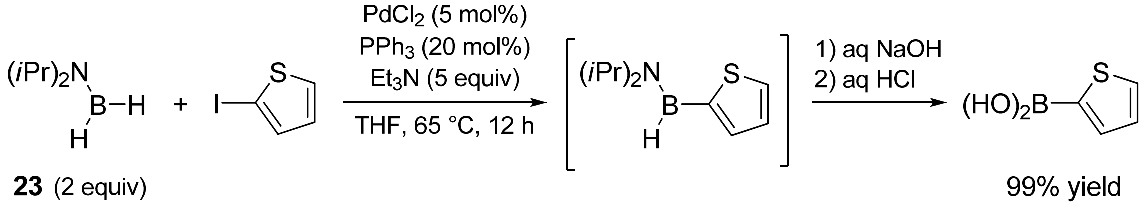


22



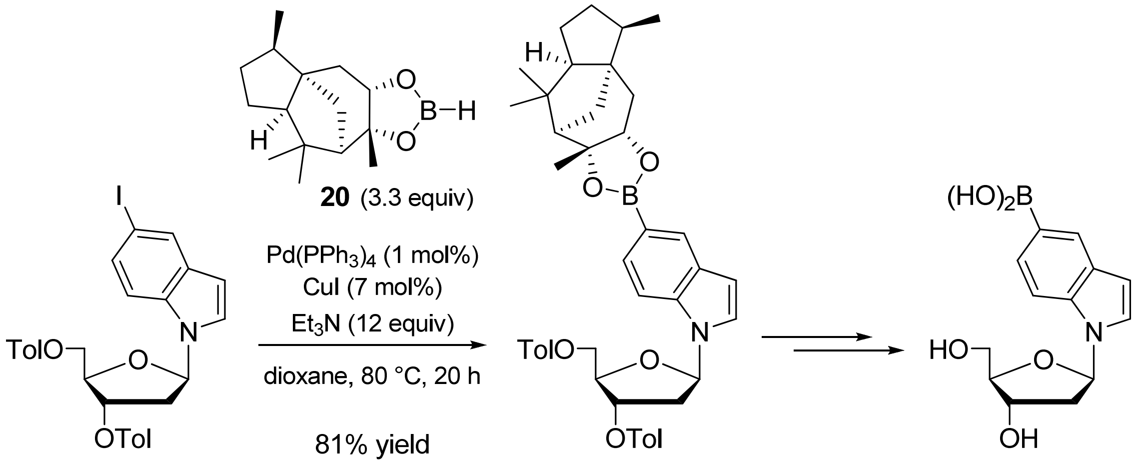
23

commercially source, and functional group compatibility.[34] While the arylboronates synthesized by dialkoxyboranes **1**, **21**, or **22** are generally stable to air, water and chromatography, they can be directly employed in the Suzuki–Miyaura cross-coupling reaction.[1-3] Additionally, they can be transformed into the corresponding boronic acids by several methods, but deprotection protocols have not always been trouble-free.[25,35] On the other hand, monomeric aminoborane **23** has been recommended for the synthesis of arylboronic acids via the borylation followed by simple hydrolysis procedure (Scheme 4).[33]



Scheme 4. Synthesis of Boronic Acids via Borylation with (Diisopropyl)aminoborane[33]

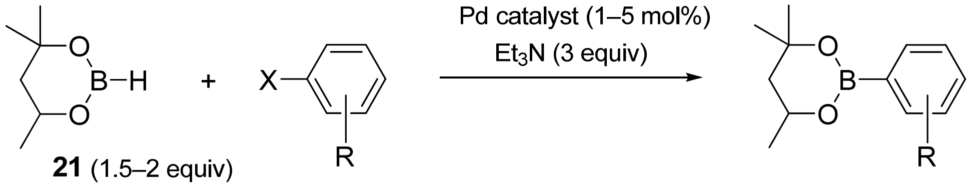
20 has been introduced for similar propose by Morin (Scheme 5).[25] The borylation with **20** has been achieved by using catalytic amounts of Pd(PPh_3)$_4$ and CuI.



Scheme 5. Synthesis of Boronic Acids via Borylation with Cedranediolborane[25]

2-1-2-1. 4,4,6-Trimethyl-1,3,2-dioxaborinane. In 2007, we demonstrated that 4,4,6-trimethyl-1,3,2-dioxaborinane (**21**), which is easily accessible, much less expensive, and more conveniently prepared, is an alternative for the borylation of aryl halides (Table 7).[26] It is remarkable that **21** also tolerates various functional groups such as ester, ketone and nitrile functionalities. The palladium complex coordinated with tBuDPEphos (**10**) can catalyze the reaction of aryl iodides even in the presence of the electron-withdrawing or *ortho* substituent to afford the corresponding hexylene glycol boronates in high yields.[26] The Chavant group has achieved the borylation of aryl electrophiles by using PPh_3[27] or CyJohnPhos (**6**) ligand[28] after our intervention, but these conditions result in somewhat low yields when aryl halides possesses electron-withdrawing groups. We have also achieved the coupling of electron-deficient aryl chlorides[15] and that of aryl benzensulfonates[18] with the aid of tetrabutylammonium halides. $NiCl_2$(dppp) has been recommended for electron-deficient aryl chlorides, but the $Pd(dba)_2$/**10** catalyst system was not suitable.

Table 7. Borylation of Aryl Electrophiles with 4,4,6-Trimethyl-1,3,2-dioxaborinane



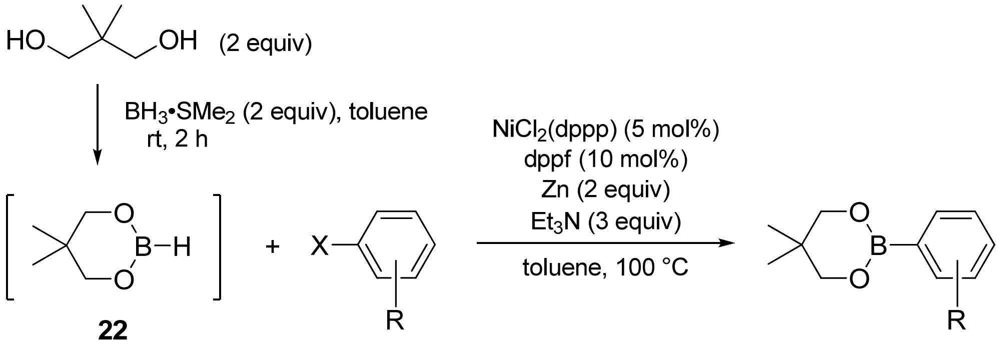
X	R	catalyst	conditions	yield / %	ref.
I	4-OMe	$PdCl_2(MeCN)_2$/**10**	80 °C, 16 h	86	[26]
I	4-CO_2Et	$PdCl_2(MeCN)_2$/**10**	80 °C, 16 h	78	[26]
I	4-COMe	$PdCl_2(MeCN)_2$/**10**	80 °C, 16 h	80	[26]
I	3-CN	$PdCl_2(MeCN)_2$/**10**	80 °C, 16 h	86	[26]
I	4-NO_2	$PdCl_2(MeCN)_2$/**10**	80 °C, 16 h	77	[26]
I	2,4,6-Me_3	$PdCl_2(MeCN)_2$/**10**	80 °C, 16 h	88	[26]
Br	4-OMe	$PdCl_2(PPh_3)_2$	80 °C, 6 h	73	[27]
Br	4-NMe_2	$PdCl_2(PPh_3)_2$	80 °C, 6 h	84	[27]
Br	H	$PdCl_2(PPh_3)_2$	80 °C, 16 h	82	[27]
OTf	4-Me	$Pd_2(dba)_3$/**6**	80 °C, 6 h	82	[28]
OTf	4-COMe	$Pd_2(dba)_3$/**6**	80 °C, 16 h	73	[28]
Cl	4-OMe	$Pd_2(dba)_3$/**6**	100 °C, 16 h	90	[28]
Cl	4-CO_2Et	$NiCl_2$(dppp)	100 °C, 24 h[a]	86	[15]
Cl	4-CF_3	$NiCl_2$(dppp)	100 °C, 24 h[a]	77	[15]
OSO_2Ph	4-CN	$Pd(dba)_2$/**12**	100 °C, 24 h[b]	70	[18]

[a] 2 equiv of Bu_4NBr. [b] 1.1 equiv of Bu_4NI.

2-1-2-2. 5,5-Dimethyl-1,3,2-dioxaborinane.

Borylation of aryl electrophiles 5,5-dimethyl-1,3,2-dioxaborinane (**22**) with has been energetically developed by the group of Percec. 5,5-Dimethyl-1,3,2-dioxaborinane (**22**), which can be conveniently prepared in situ from much less expensive neopentyl glycol and borane dimethylsulfide complex, is found to be an effective boron source in the nickel-catalyzed coupling of aryl halides. The use of $PdCl_2$(dppf) with in situ-prepared **22** was ineffective due to the palladium catalyst poisoning in the presence of dimethylsulfide from borane dimethylsulfide complex. The combination of $NiCl_2$(dppp) and additional dppp ligand was originally used as a catalyst system, but this catalyst has a limited substrate scope as only less hindered aryl iodides and bromides were efficiently converted to the corresponding boronates.[29] Percec has found that the mixed-ligand catalyst system $NiCl_2$(dppp)/dppf[30] and the addition of Zn powder as a reductant[31] greatly improved the reactivity and the substrate scope (Table 8).

Table 8. Borylation of Aryl Electrophiles with in Situ-Prepared 5,5-Dimethyl-1,3,2-dioxaborinane[31]



X	R	time / h	yield / %
I	4-OMe	0.5	95
I	2-OMe	1	96
I	2-CO_2Me	0.5	81
Br	2-Me	1	85
Br	2-CO_2Me	6	87
Br	2,6-F_2	1	73
Cl	4-CO_2Me	1	79
Cl	2-CF_3	4	91
Cl	4-OMe	1	91
OMs	4-CN	2	88
OTs	3-CO_2Me	1	84

2-2 CATALYTIC CYCLE

The accepted mechanism of the palladium-catalyzed borylation is illustrated in Figure 1. This catalytic cycle was theoretically proposed using DFT methods by Marder and Lin.[36] First, oxidative addition of an aryl halide to Pd(0) species **24** generates an arylpalladium(II) halide **25**. After displacement of the halide ligand on **25** with Et_3N to form a cationic arylpalladium(II) species **26**, σ-bond metathesis between the Pd–aryl bond of **26** and the B–H bond of **1** through a transition state **27**, in which the boron atom is pointing toward the aryl ligand, affords the desired borylation product and a palladium(II) hydride **28**. The energy profiles suggest that the B–C bond-forming metathesis is rate-determining step. This cationic pathway is favored over the neutral one which should involve ligand dissociation. Finally, deprotonation of **28** regenerates the Pd(0) active species **24** with the aid of Et_3N. Thus, Et_3N plays a dual role, assisting the formation of the cationic palladium(II) **26** as well as reducing **28** to Pd(0). A transition state **29**, in which the hydride is pointing toward the aryl ligand, would account for the undesirable dehalogenation, but the activation barrier is higher than the formation of transition state **27**.

This B–C bond-forming reaction using **1** differs from many cross-coupling reactions in that electron-donating substituents on the aryl halide substrates promote their catalytic borylations. Our experiments showed that the neutral arylpalladium(II) halide **25** underwent predominantly the aryl–H bond formation with pinacolborane (**1**),[8] suggesting that in this B–C bond-forming reaction the formation of cationic arylpalladium(II) species **26** should be a key step. The electron-withdrawing substituents would prevent the formation of **26**. The use of electron-rich and bulky ligands, such as tBuDPEphos (**10**), dtbpf (**12**), and Buchwald's biarylphosphine ligands (**6** and **15**), would assist the dissociation of the halide anion on arylpalladium(II) halide **25**, and the cationic species **26** would be stabilized. The addition of Bu_4NI would prevent arylpalladium(II) halide **25** from reacting with hydroboranes **1**, and thus the product selectivity would increase. The order of an inhibiting effect on the transmetalation between Pd(II) and boron reagents by additional halide ions has been reported to be as follows: $I^- > Br^- > Cl^-$.[37]

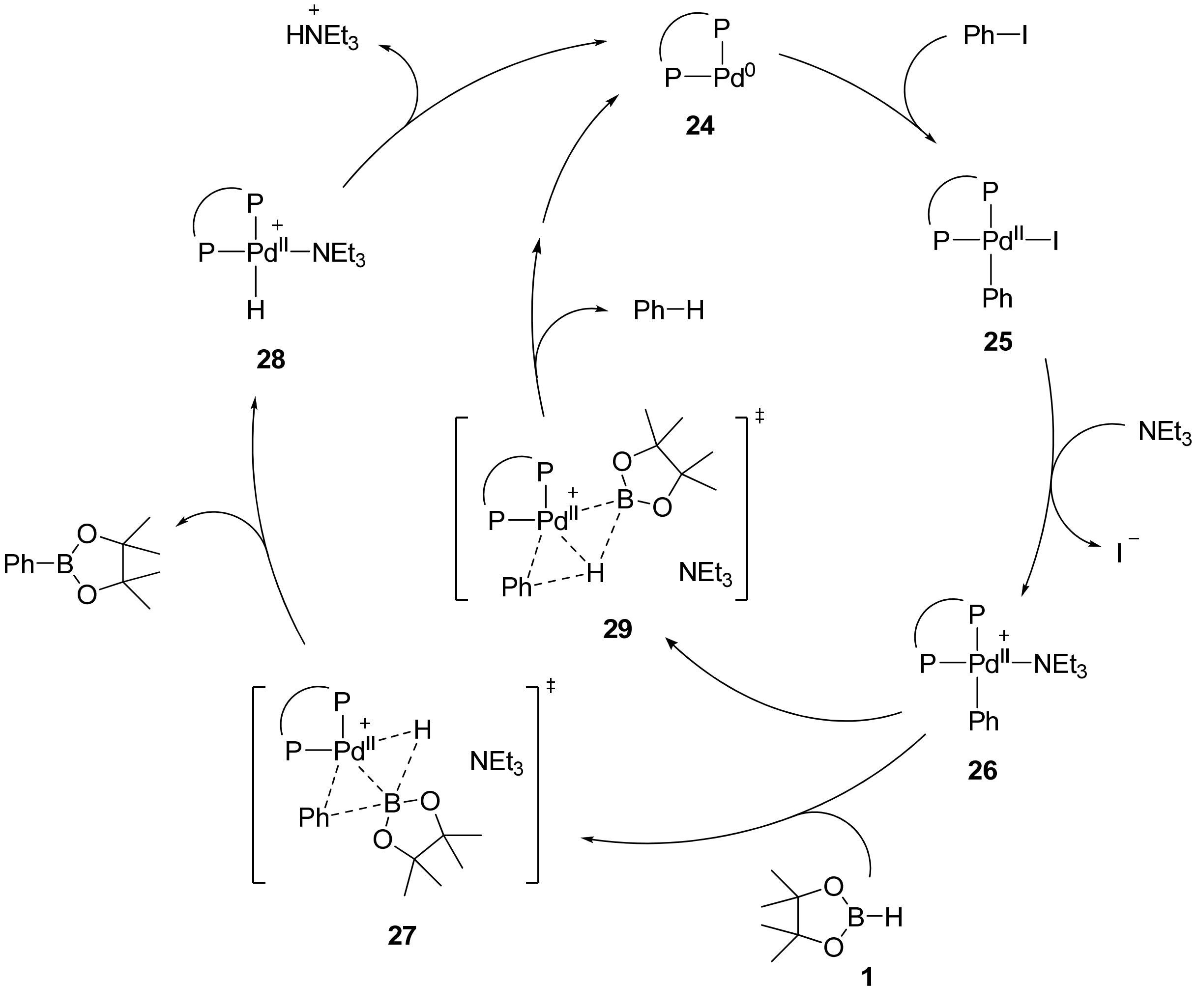


Figure 1. Catalytic Cycle for Borylation of Aryl Electrophiles with Pinacolborane[36]

2-3 SYNTHESIS OF ARYLBORONATES

Arylboronates have become a useful building block in the construction of complex aromatic compounds through Suzuki–Miyaura cross-coupling.[2] Therefore, the application of the catalytic borylation began to appear rapidly, and a large number of functionalized aryl- and heteroarylboronates have been synthesized via the palladium-catalyzed borylation with pinacolborane (**1**). Representative examples are selected in Figure 2. In most cases, arylboronates thus obtained has been used for the synthesis of functionalized biaryls including natural compounds and biologically active molecules via Suzuki–Miyaura coupling.

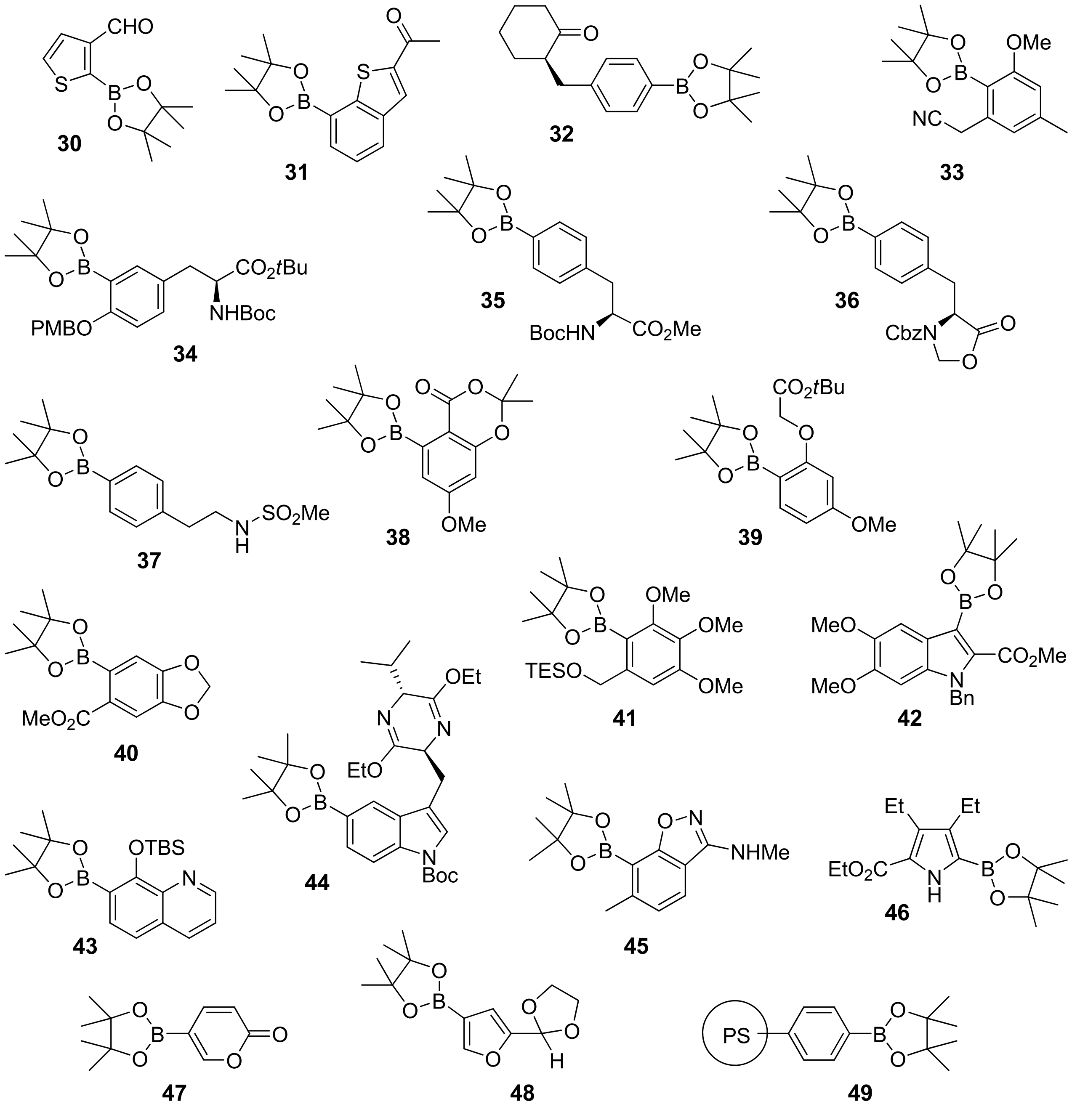


Figure 2. Examples of Functionalized Arylboronates via the Borylation with Pinacolborane

As shown in Figure 2, the reaction with **1** tolerates various functional groups; e.g., aldehyde (**30**[22]) and ketone carbonyl (**31**[38] and **32**[39]), nitrile (**33**[40]), amino acid (**34**,[41] **35**[42] and **36**[43]) and sulfonamide functionalities (**37**[24]). Interestingly, Spino has described that **32** could be obtained without racemization.

Substituents at the *ortho* positions (**38**,[44] **39**,[45,46] **40**[47] and **41**[48]) are also tolerated. These conditions also offer the synthesis of functionalized heteroarylboronates containing sulphur, nitrogen (**42**,[49] **43**,[50] **44**,[51] **45**[52] and **46**[53]) and/or oxygen atoms (**47**[54] and **48**[55]). The borylation of polymer-supported aryl halides has been achieved (**49**[39]). The substrate scope of the palladium-catalyzed borylation with **1** seems to be similar to that of the Miyaura borylation using B–B reagents,[7] except that the examples of substrates possessing pyridine moieties or aldehyde carbonyl group (e.g., **43** and **30**) are still rare. Although the difference in the substrate scope between two borylation methods is undefined, in some cases shown in Figure 2 (e.g., **38**, **42** and **46**), **1** was a much more efficient borylation agent as compared to bis(pinacolato)diboron.[44,49,53]

The reaction also offers an easy access to building blocks for the construction of teraryl frameworks in functional molecules. Figure 3 presents selected examples of the palladium-catalyzed double-borylation of diharoarenes. With an excess of **1**, arylene-bridged bis-boronates (**50**,[56] **51**,[57] **52**,[58] **53**,[59] **54**,[45,60] **55**[61] and **56**[62]) were obtained in moderate to high yields. As shown in Figure 3, the borylation tolerates various arylene cores including porphyrin (**50**), carbazole (**51**), pyrrole (**52**), phenothiazine (**53**) and thiophen rings (**55**).

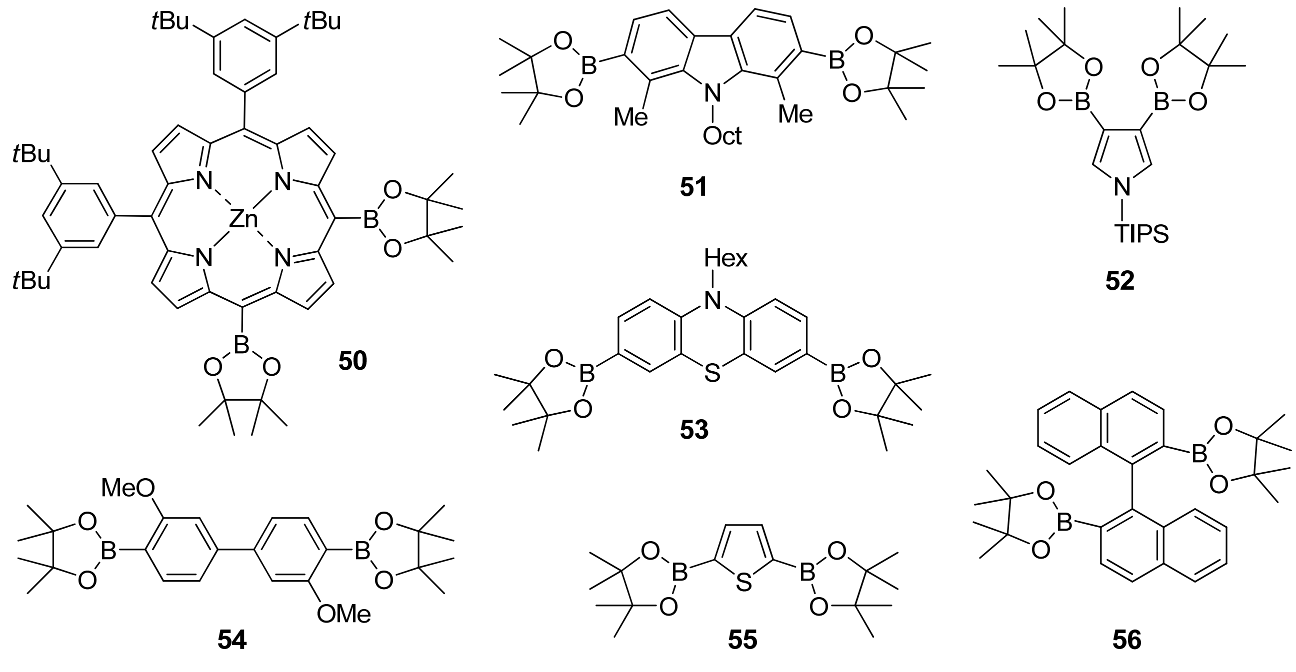
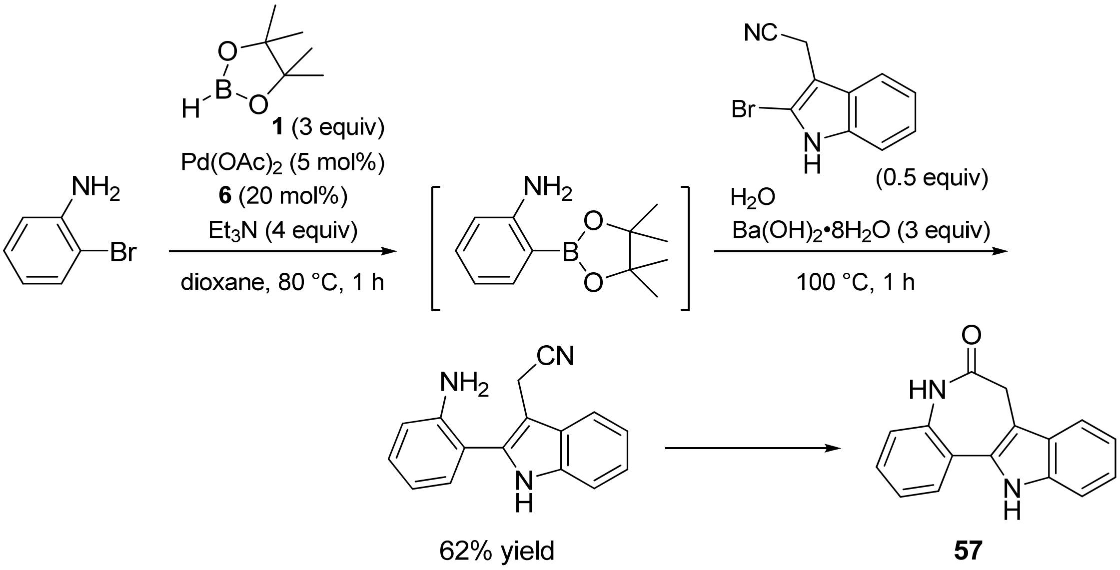


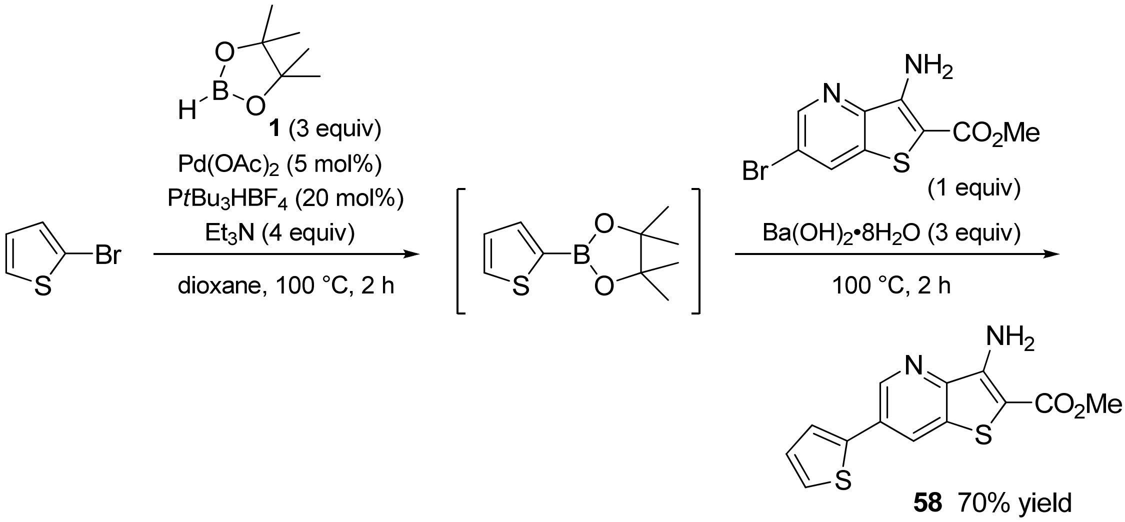
Figure 3. Examples of Bis(boryl)arenes via the Double-Borylation

The palladium-catalyzed, stepwise, one-pot borylation/Suzuki coupling (BSC) procedure was pioneered by the work of Baudoin in 2000,[10] and it has been applied to the concise synthesis of functionalized biaryls. In most of the reports about the BSC procedure using **1**, the first catalyst for the borylation works on the next Suzuki coupling. For examples, Pd(OAc)$_2$/ CyJohnPhos (**6**) catalyzes both the borylation of 2-bromoaniline derivatives and Suzuki coupling with *ortho*-substituted aryl halides.[11,63,64] In 2002, Baudoin reported the synthesis of paullone (**57**) (Scheme 6).[64]



Scheme 6. Synthesis of Biologically Active Biphenyl Lactam[64]

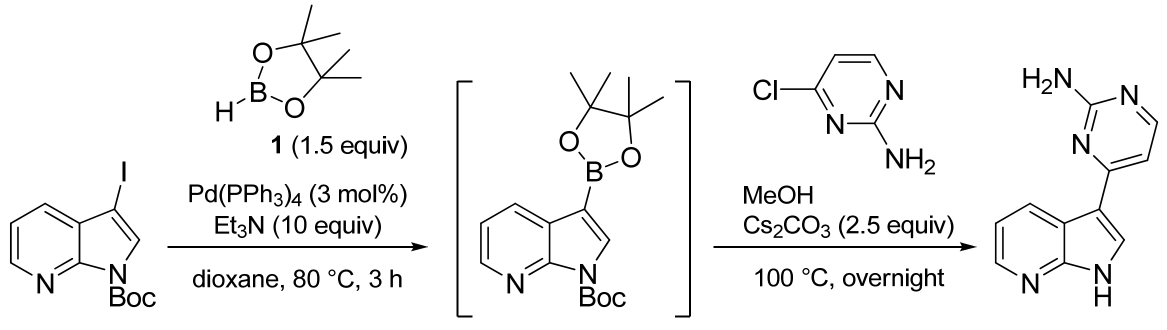
Another application of BSC procedure is the preparation of heterobiaryls. Queiroz showed that tri-*t*-butylphosphonium tetrafluoroborate (*t*Bu$_3$PHBF$_4$), a *t*Bu$_3$P ligand precursor,[65] was the efficient supporting ligand in the synthesis of 6-(thien-2-yl)thieno[3,2-b]pyridine (**58**) through the one-pot, two-step procedure (Scheme 7).[66]



Scheme 7. Synthesis of 6-(Thien-2-yl)thieno[3,2-b]pyridine[66]

In 2011, Müller reported the synthesis of various 3-(hetero)aryl substituted indoles, 7-azaindoles, and pyrroles.[67] The *N*-Boc protected azaindolyl iodide **59** was borylated with **1** and a catalytic amount of

$Pd(PPh_3)_4$, and then the coupling with 4-chloropyrimidin-2-amine took place without further addition of palladium complexes to afford meriolin 1 (**60**) (Scheme 8).



59

60 meriolin 1

Scheme 8. Synthesis of Biologically Active 2-Amino-4-(7-azaindol-3-yl)pyrimidines[67]

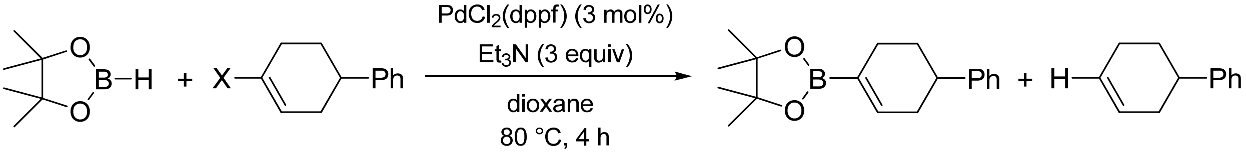
3. BORYLATION OF OTHER ELECTROPHILES

The catalytic borylation with pinacolborane (**1**) has been extended to other organic electrophiles, such as 1-alkenyl, benzyl, and allyl halides. In either case, tertiary amines play a crucial role in the selective borylation.

3-1. VINYL HALIDES AND TRIFLATES

Hydroboration of 1-alkynes is a method of choice for the syntheses of 1-alkenylboronates.[1,3] However, the protocol is inapplicable to the synthesis of cyclic 1-alkenylboronates. Such boronates can be conveniently synthesized from the corresponding 1-alkenyl electrophiles by the palladium-catalyzed coupling with boron nucleophiles. In 2000, we reported that the use of a mixed-ligand catalyst system

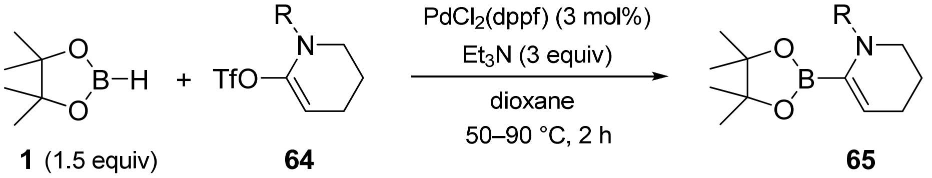
Table 9. Effect of Co-Ligands on the Borylation of 1-Alkenyl Electrophiles[68]



1 (1.5 equiv) **61** **62** **63**

X	co-ligand	yield / %	
		62	**63**
OTf	none	47	14
OTf	12 mol% $AsPh_3$	83	7
OTf	6 mol% PPh_3	51	14
OTf	3 mol% dppf	53	11
I	12 mol% $AsPh_3$	82	14

$PdCl_2$(dppf)/$AsPh_3$ achieved the borylation of cyclic 1-alkenyl iodides and triflates **61** with pinacolborane (**1**) (Table 9).[68] The absence of $AsPh_3$ caused the catalyst decomposition during the reaction, resulting in low conversion. In addition, the use of excess phosphine ligand, such as dppf and PPh_3, in place of $AsPh_3$ rather retarded the reaction. But then, Occhiato described that the presence of $AsPh_3$ as an additional ligand was unnecessary in the borylation of lactam-derived 1-alkenyl triflates **64** (Scheme 9).[69] **1** showed a greater reactivity than bis(pinacolato)diboron toward **64**.

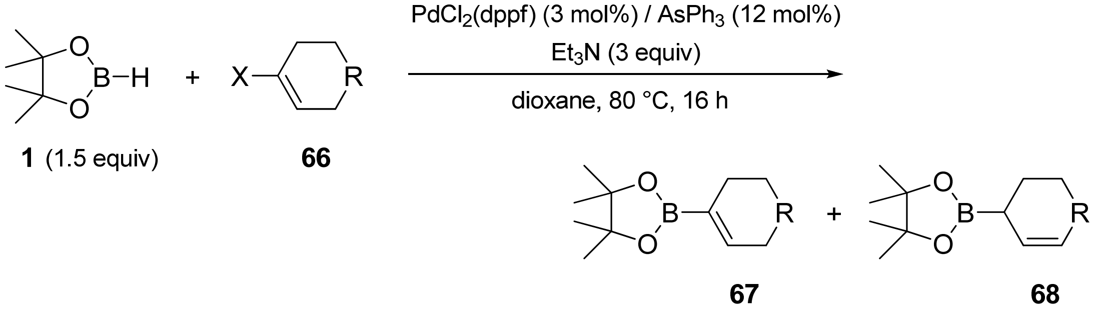


R = Cbz (83% yield), Boc (67% yield), Ts (95% yield)

Scheme 9. Preparation of Tetrahydropyridine-2-boronic Acid Pinacol Esters[69]

Under these conditions, some cyclic 1-alkenyl halides partly undergo positional isomerization of C–C double bonds to afford an inseparable mixture of the desired 1-alkenylboronates **67** and allylic byproducts **68** (Table 10).[68] Interestingly, the borylation of **66** including an allyl ether moiety afforded the allyl boronate **68** as a major product due to the n–π conjugation.

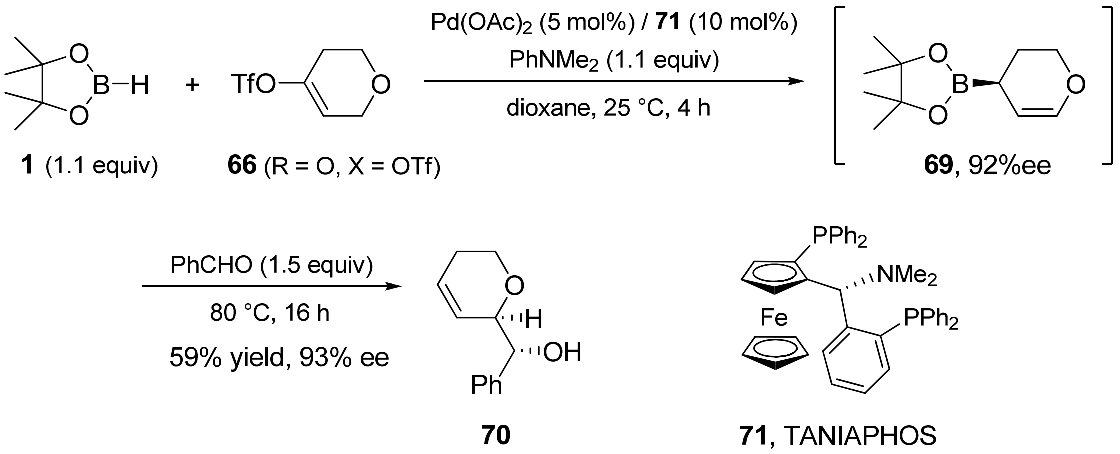
Table 10. Borylation of Representative 1-Alkenyl Electrophiles[68]



R	X	total yield (**67**+**68**) / %	product ratio / %	
			67	**68**
CH*t*Bu	OTf	86	90	10
CH_2	I	77	95	5
	OTf	84	92	8
$(CH_2)_2$	OTf	74	90	10
O	OTf	72	19	81

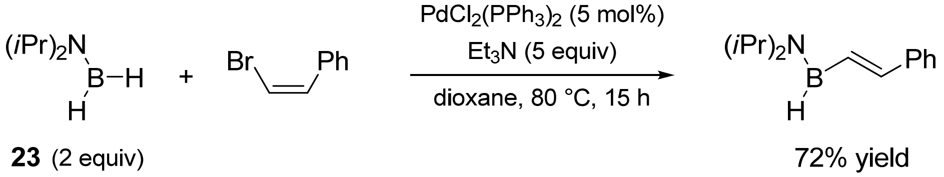
As shown in Scheme 10, heterocyclic 1-alkenyl triflate **66** (R = O, X = OTf) can be product-selectively and asymmetrically transformed to allylboronate **69** by treatment with 5 mol% of $Pd(OAc)_2$, 10 mol% of

TANIAPHOS (**71**), and 1.1 equiv of $PhNMe_2$.[70] The borylation and subsequent allylboration gave moderate yield of homoallylalcohol **70** with high enantiomeric excess.



Scheme 10. Enantioselective Preparation of Heterocyclic Allylic Boronates[70]

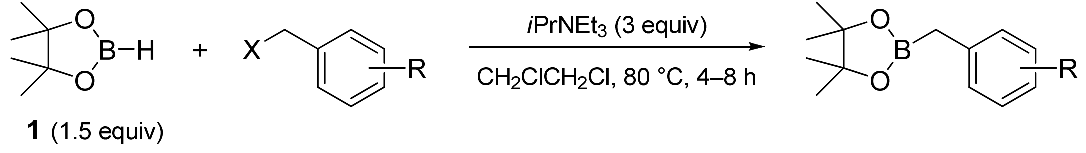
The borylation of acyclic 1-alkenyl halides with **1** suffers from low yields and isomerization of C–C double bonds, resulting in a complex mixture of several byproducts. In the case of acyclic (*Z*)-alkenyl halides with **1** or (diisopropylamino)borane (**23**), the complete isomerization of the starting geometry occurred to give (*E*)-alkenylboron compounds (Scheme 11).[68,71]



Scheme 11. Borylation of (Z)-1-alkenyl halide with (Diisopropyl)aminoborane[71]

3-2 BENZYL HALIDES

Benzyl chlorides and bromides can be coupled with pinacolborane (**1**) in the presence of a catalytic



X = Cl R = H (96% yield), 3-Me (73% yield), 4-CO_2Me (83% yield), 4-CN (70% yield)
X = Br R = H (79% yield), 4-Br (72% yield)

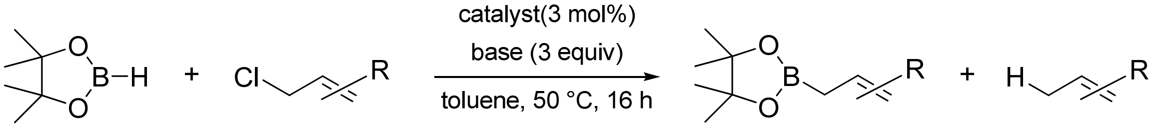
Scheme 12. Synthesis of Benzylboronates via Palladium-Catalyzed Borylation[72] amount of $PdCl_2(PPh_3)_2$ to afford the corresponding benzylboronates in high yields (Scheme 12).[72] *i*Pr_2NEt was more effective base for the palladium-catalyzed borylation of benzyl halides than Et_3N.

In 2010, Duñach described that a catalytic amount of Mg(0) permitted the reductive coupling between benzyl bromides and **1**.[73] The borylation takes place via an organomagnesium species generated in situ. The DFT study showed that **1** acts both as an electrophile and as a reducing agent to regenerate the Grignard reagents.

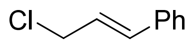
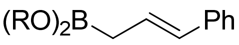
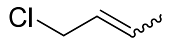
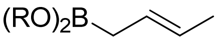
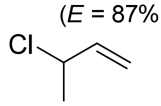
3-3 ALLYL HALIDES

Unlike the coupling between most organic electrophiles and pinacolborane (**1**), palladium catalysts did not promote the borylation of allylic halides. In 2000, we reported that the use of a platinum catalyst $Pt(dba)_2/AsPh_3$ achieved the selective borylation of allylic halides with **1** (Table 11).[74] The presence of Et_3N plays a key role in facilitating the B–C bond formation. Although the starting crotyl chloride was a mixture of (*E*)- and (*Z*)-isomers, the borylation of such aliphatic allyl electrophiles proceeded regio- and stereoselectively to give (*E*)-crotylboronates exclusively. Also, 3-chloro-1-butene afforded the same product, suggesting a process via π-allyl platinum species.

Table 11. Platinum-Catalyzed Borylation of Allyl Chlorides[74]



1 (1.5 equiv) **72** **73**

substrate	catalyst	base	product **72**	yield / %	
				72	**73**
	$Pt(dba)_2/4AsPh_3$	Et_3N		72	27
	$Pd(dba)_2/4AsPh_3$	Et_3N	(*E* = >99%)	0	68
	$Ni(cod)_2/4AsPh_3$	Et_3N		0	0
	$Pt(dba)_2/4AsPh_3$	pyridine		0	50
	$Pt(dba)_2/4AsPh_3$	KOAc		9	69
 (*E* = 87%)	$Pt(dba)_2/4AsPh_3$	Et_3N	 (*E* = >99%)	67	
	$Pt(dba)_2/4AsPh_3$	Et_3N		78	

4. CONCLUSION

As illustrated in this review, dialkoxyboranes has offered the transition metal-catalyzed borylation of organic electrophiles, such as aryl, 1-alkenyl, benzyl and allyl (pseudo)halides. Pinacolborane, 4,4,6-trimethyl-1,3,2-dioxaborinane, 5,5-dimethyl-1,3,2-dioxaborinane, etc., were introduced to use in the catalytic borylation, and dialkoxyboranes are now recognized as atom-economical and cost-effective boron sources. While numerous catalyst systems and solvents have been reported in the literature for the selective borylation, the use of tertiary amines is essential in either case. The substrate scope of the catalytic borylation is significantly broad and includes organic electrophiles possessing diverse functional groups.

ACKNOWLEDGEMENTS

The author sincerely thanks all co-workers involved in our own studies referred to in this review for their invaluable contributions. Our work has been supported in part by Grants-in-Aid from MEXT and JSPS. BASF Corporation is gratefully acknowledged for a generous donation of pinacolborane.

REFERENCES

1. 'Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine', ed. by D. G. Hall, Wiley-VCH, Weinheim, 2005.
2. A. Suzuki and H. C. Brown, 'Organic Syntheses via Boranes: Volume 3 Suzuki Coupling', Aldrich Chemical Co., Milwaukee, 2003.
3. D. S. Matteson, 'Stereodirected Synthesis with Organoboranes', Springer-Verlag, Berlin, 1995.
4. M. Yamashita, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 983.
5. H. Ito, S. Ito, Y. Sasaki, K. Matsuura, and M. Sawamura, *Pure Appl. Chem.*, 2008, **80**, 1039.
6. T. Ishiyama, M. Murata, and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508.
7. T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2000, **611**, 392; T. Ishiyama and N. Miyaura, *Chem. Rec.*, 2004, **3**, 271.
8. M. Murata, S. Watanabe, and Y. Masuda, *J. Org. Chem.*, 1997, **62**, 6458; M. Murata, T. Oyama, S. Watanabe, and Y. Masuda, *J. Org. Chem.*, 2000, **65**, 164.
9. I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890; T. Ishiyama and N. Miyaura, *Pure Appl. Chem.*, 2006, **78**, 1369.
10. A. Wolan and M. Zaidlewicz, *Org. Biomol. Chem.*, 2003, **1**, 3274.
11. O. Baudoin, D. Guénard, and F. Guéritte, *J. Org. Chem.*, 2000, **65**, 9268.
12. P. E. Broutin, I. Čerňa, M. Campaniello, F. Leroux, and F. Colobert, *Org. Lett.*, 2004, **6**, 4419.
13. M. A. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, and P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, 2002, 2308.
14. M. Murata, T. Sambommatsu, S. Watanabe, and Y. Masuda, *Synlett*, 2006, 1867.
15. M. Murata, T. Sambommatsu, T. Oda, S. Watanabe, and Y. Masuda, *Heterocycles*, 2010, **80**, 213.

16. D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2011, **2**, 27; R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461.
17. K. L. Billingsley and S. L. Buchwald, *J. Org. Chem.*, 2008, **73**, 5589.
18. M. Murata, T. Oda, Y. Sogabe, H. Tone, T. Namikoshi, and S. Watanabe, *Chem. Lett.*, 2011, **40**, 962.
19. M. Melaimi, C. Thoumazet, L. Ricard, and P. Le Floch, *J. Organomet. Chem.*, 2004, **689**, 2988; M. Doux, N. Mézailles, M. Melaimi, L. Ricard, and P. Le Floch, *Chem. Commun.*, 2002, 1566; M. Melaimi, F. Mathey, and P. Le Floch, *J. Organomet. Chem.*, 2001, **640**, 197.
20. A. B. Morgan, J. L. Jurs, and J. M. Tour, *J. Appl. Polym. Sci.*, 2000, **76**, 1257.
21. W. Zhu and D. Ma, *Org. Lett.*, 2006, **8**, 261.
22. C. Christophersen, M. Begtrup, S. Ebdrup, H. Petersen, and P. Vedsø, *J. Org. Chem.*, 2003, **68**, 9513.
23. S. L. Wheaton, S. M. H. Kabir, H. Zhang, C. M. Vogels, A. Decken, and S. A. Westcott, *Cent. Eur. J. Chem.*, 2010, **8**, 725.
24. W. D. Miller, A. H. Fray, J. T. Quatroche, and C. D. Sturgill, *Org. Process Res. Dev.*, 2007, **11**, 359.
25. Y. L. Song and C. Morin, *Synlett*, 2001, 266.
26. M. Murata, T. Oda, S. Watanabe, and Y. Masuda, *Synthesis*, 2007, 351.
27. N. PraveenGanesh and P. Y. Chavant, *Eur. J. Org. Chem.*, 2008, 4690.
28. N. PraveenGanesh, E. Demory, C. Gamon, V. Blandin, and P. Y. Chavant, *Synlett*, 2010, 2403.
29. B. M. Rosen, C. Huang, and V. Percec, *Org. Lett.*, 2008, **10**, 2597; D. A. Wilson, C. J. Wilson, B. M. Rosen, and V. Percec, *Org. Lett.*, 2008, **10**, 4879.
30. C. Moldoveanu, D. A. Wilson, C. J. Wilson, P. Corcoran, B. M. Rosen, and V. Percec, *Org. Lett.*, 2009, **11**, 4974; 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.
31. 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. 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.
32. L. Euzenat, D. Horhant, Y. Ribourdouille, C. Duriez, G. Alcaraz, and M. Vaultier, *Chem. Commun.*, 2003, **9**, 2280.
33. D. Haddenham, C. L. Bailey, C. Vu, G. Nepomuceno, S. Eagon, L. Pasumansky, and B. Singaram, *Tetrahedron*, 2011, **67**, 576.
34. C. E. Tucker, J. Davidson, and P. Knochel, *J. Org. Chem.*, 1992, **57**, 3482.
35. A. K. L. Yuen and C. A. Hutton, *Tetrahedron Lett.*, 2005, **46**, 7899; S. J. Coutts, J. Adams, D.

Krolikowski, and R. J. Snow, *Tetrahedron Lett.*, 1994, **35**, 5109; H. Nakamura, M. Fujiwara, and Y. Yamamoto, *J. Org. Chem.*, 1998, **63**, 7529; C. P. Decicco, Y. Song, and D. A. Evans, *Org. Lett.*, 2001, **3**, 1029; T. E. Pennington, C. Kardiman, and C. A. Hutton, *Tetrahedron Lett.*, 2004, **45**, 6657; C. Malan and C. Morin, *J. Org. Chem.*, 1998, **63**, 8019.

36. K. C. Lam, T. B. Marder, and Z. Lin, *Organometallics*, 2010, **29**, 1849.
37. T. Kinzel, Y. Zhang, and S. L. Buchwald, *J. Am. Chem. Soc.*, 2010, **132**, 14073.
38. P. Y. Michellys, J. D'Arrigo, T. A. Grese, D. S. Karanewsky, M. D. Leibowitz, D. A. Mais, C. M. Mapes, A. Reifel-Miller, D. Rungta, and M. F. Boehm, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 1593.
39. C. Spino, V. G. Gund, and C. Nadeau, *J. Comb. Chem.*, 2005, **7**, 345.
40. W. Liu, M. Buck, N. Chen, M. Shang, N. J. Taylor, J. Asoud, X. Wu, B. B. Hasinoff, and G. I. Dmitrienko, *Org. Lett.*, 2007, **9**, 2915.
41. C. Poriel, M. Lachia, C. Wilson, J. R. Davies, and C. J. Moody, *J. Org. Chem.*, 2007, **72**, 2978.
42. S. Iimura and W. Wu, *Tetrahedron Lett.*, 2010, **51**, 1353.
43. H. Nakamura, M. Fujiwara, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 231.
44. M. Altemöller, T. Gehring, J. Cudaj, J. Podlech, H. Goesmann, C. Feldmann, and A. Rothenberger, *Eur. J. Org. Chem.*, 2009, 2130; M. Altemöller, J. Podlech, and D. Fenske, *Eur. J. Org. Chem.*, 2006, 1678.
45. F. Mora, D. H. Tran, N. Oudry, G. Hopfgartner, D. Jeannerat, N. Sakai, and S. Matile, *Chem.–Eur. J.*, 2008, **14**, 1947.
46. N. Sakai, A. L. Sisson, S. Bhosale, A. Fürstenberg, N. Banerji, E. Vauthey, and S. Matile, *Org. Biomol. Chem.*, 2007, **5**, 2560; Y. Baudry, D. Ronan, D. Jeannerat, and S. Matile, *Helv. Chim. Acta*, 2004, **87**, 2181; D. Ronan, Y. Baudry, D. Jeannerat, and S. Matile, *Org. Lett.*, 2004, **6**, 885.
47. U. V. Mentzel, D. Tanner, and J. E. Tønder, *J. Org. Chem.*, 2006, **71**, 5807.
48. O. Baudoin, A. Décor, M. Cesario, and F. Guéritte, *Synlett*, 2003, 2009; A. Joncour, A. Décor, J. M. Liu, M. E. Tran Huu Dau, and O. Baudoin, *Chem.–Eur. J.*, 2007, **13**, 5450.
49. H. A. Duong, S. Chua, P. B. Huleatt, and C. L. L. Chai, *J. Org. Chem.*, 2008, **73**, 9177.
50. F. Babudri, A. Cardone, C. T. Cioffi, G. M. Farinola, F. Naso, and R. Ragni, *Synthesis*, 2006, 1325.
51. M. Okada, I. Sato, S. J. Cho, Y. Suzuki, M. Ojika, D. Dubnau, and Y. Sakagami, *Biosci. Biotechnol. Biochem.*, 2004, **68**, 2374.
52. L. H. Pettus, R. P. Wurz, S. Xu, B. Herberich, B. Henkle, Q. Liu, H. J. McBride, S. Mu, M. H. Plant, C. J. M. Saris, L. Sherman, L. M. Wong, S. Chmait, M. R. Lee, C. Mohr, F. Hsieh, and A. S. Tasker, *J. Med. Chem.*, 2010, **53**, 2973.
53. J. i. Setsune, M. Toda, K. Watanabe, P. K. Panda, and T. Yoshida, *Tetrahedron Lett.*, 2006, **47**, 7541.

54. E. C. Gravett, P. J. Hilton, K. Jones, and F. Romero, *Tetrahedron Lett.*, 2001, **42**, 9081; E. C. Gravett, P. J. Hilton, K. Jones, and J. M. Péron, *Synlett*, 2003, 253.

55. O. Ilovich and J. Deutsch, *J. Heterocycl. Chem.*, 2005, **42**, 1409.

56. L. A. Fendt, M. Stöhr, N. Wintjes, M. Enache, T. A. Jung, and F. Diederich, *Chem.–Eur. J.*, 2009, **15**, 11139.

57. J. Bouchard, S. Wakim, and M. Leclerc, *J. Org. Chem.*, 2004, **69**, 5705.

58. M. G. Banwell, T. E. Goodwin, S. Ng, J. A. Smith, and D. J. Wong, *Eur. J. Org. Chem.*, 2006, 3043; M. G. Banwell, A. M. Bray, A. J. Edwards, and D. J. Wong, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1340.

59. C. S. Krämer, T. J. Zimmermann, M. Sailer, and T. J. J. Müller, *Synthesis*, 2002, 1163; C. S. Krämer, K. Zeitler, and T. J. J. Müller, *Tetrahedron Lett.*, 2001, **42**, 8619.

60. N. Sakai, D. Gerard, and S. Matile, *J. Am. Chem. Soc.*, 2001, **123**, 2517.

61. M. S. Montaudo, G. Adamus, and M. Kowalczuk, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 2360.

62. H. Brath, M. Dubovská, M. Juríček, P. Kasák, and M. Putala, *Collect. Czech. Chem. Commun.*, 2004, **69**, 1517.

63. O. Baudoin, F. Claveau, S. Thoret, A. Herrbach, D. Guénard, and F. Guéritte, *Bioorg. Med. Chem.*, 2002, **10**, 3395; M. J. R. P. Queiroz, E. M. S. Castanheira, T. C. T. Lopes, Y. K. Cruz, and G. Kirsch, *J. Photochem. Photobiol. A*, 2007, **190**, 45; H. Fuwa, Y. Okamura, Y. Morohashi, T. Tomita, T. Iwatsubo, T. Kan, T. Fukuyama, and H. Natsugari, *Tetrahedron Lett.*, 2004, **45**, 2323.

64. O. Baudoin, M. Cesario, D. Guénard, and F. Guéritte, *J. Org. Chem.*, 2002, **67**, 1199.

65. M. R. Netherton and G. C. Fu, *Org. Lett.*, 2001, **3**, 4295.

66. M. J. R. P. Queiroz, R. C. Calhelha, L. A. Vale-Silva, E. Pinto, R. T. Lima, and M. H. Vasconcelos, *Eur. J. Med. Chem.*, 2010, **45**, 5628.

67. E. Merkul, E. Schäfer, and T. J. J. Müller, *Org. Biomol. Chem.*, 2011, **9**, 3139.

68. M. Murata, T. Oyama, S. Watanabe, and Y. Masuda, *Synthesis*, 2000, 778.

69. E. G. Occhiato, F. Lo Galbo, and A. Guarna, *J. Org. Chem.*, 2005, **70**, 7324.

70. S. Lessard, F. Peng, and D. G. Hall, *J. Am. Chem. Soc.*, 2009, **131**, 9612.

71. L. Euzénat, D. Horhant, C. Brielles, G. Alcaraz, and M. Vaultier, *J. Organomet. Chem.*, 2005, **690**, 2721.

72. M. Murata, T. Oyama, S. Watanabe, and Y. Masuda, *Synth. Commun.*, 2002, **32**, 2513.

73. C. Pintaric, S. Olivero, Y. Gimbert, P. Y. Chavant, and E. Duñach, *J. Am. Chem. Soc.*, 2010, **132**, 11825.

74. M. Murata, S. Watanabe, and Y. Masuda, *Tetrahedron Lett.*, 2000, **41**, 5877.

Miki Murata was born in Hokkaido, Japan in 1971. He received his B.Sc. from Kitami Institute of Technology (1993) and M.Sc. from Hokkaido University (1995). In 1995 he started his academic career as a Research Associate at Kitami Institute of Technology (Professor Yuzuru Masuda) and was promoted to Associate Professor in 2004. In 2000 he received his Ph.D. degree from Hokkaido University under the supervision of Professor Norio Miyaura. In 2002–2003 he was a visiting scholar with Professor Stephen L. Buchwald at Massachusetts Institute of Technology. His current research interests are mainly in the field of metal-catalyzed C–B and C–Si bond-forming reactions.