Zinc-Catalyzed Dual C–X and C–H Borylation of Aryl Halides

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Abstract: *The zinc-catalyzed combined C–X and C–H borylation of aryl halides is described using B_2pin_2 (pin = $OCMe_2CMe_2O$) to produce the corresponding 1,2-diborylarenes, under mild conditions. Catalytic C–H bond activation occurred ortho to the halide groups, if such a site is available, or meta to the halide if the ortho position is already substituted, representing a novel use of a group XII catalyst for C–H borylation. This transformation does not proceed via a free aryne intermediate, but a radical process seems to be involved.*

Arylboronic acids and arylboronates are widely used as versatile building blocks in organic synthesis, being important synthetic intermediates for transition-metal catalyzed C−C and C−heteroatom bond-forming reactions.[1] Traditional methods for their synthesis are based on the reaction of aryl Grignard or lithium reagents with boron electrophiles.[2] More recently, transition metal-catalyzed borylation of aryl halides[3] and the direct C–H borylation of arenes[4-6] have become increasingly important from the viewpoint of efficiency and functional-group compatibility. The most efficient catalysts for C–H borylation of arenes are based on precious metals such as Rh or Ir.[4-7] Similarly, aryl halide borylation typically utilizes Pd or Ni catalysts,[3a,b] although inexpensive, abundant and environmentally more acceptable Cu,[8a-e] Fe[8f] or even Zn[9] now represent attractive alternatives to the commonly used expensive and toxic noble metals. However, the development of zinc catalysis is still in its infancy.[9-11]

We recently reported an efficient catalytic system using $ZnBr_2$ and IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) for the cross-coupling of aryl- and heteroaryl halides with diboron reagents.[11] We have now found that the combination of $ZnCl_2$ and 4,4′-di-tert-butyl-2,2′-bipyridine (dtbpy; **L1**) borylates not only the C–X bond of halobenzenes, but also a C–H bond *ortho* to the halide group, yielding valuable 1,2-bis(Bpin)benzenes[12,13] along with the monoborylated products (Table 1). Classical methods for the preparation of 1,2-disubstituted arenes necessitate availability of the appropriate dihaloarenes.[12,14] Recently, Yoshida reported that the Pt or Cu catalyzed diboration of the highly reactive C−C triple bond of arynes at elevated temperatures (Pt catalyst at 80 °C, Cu catalyst at 100 °C), yielded 1,2-diborylarenes.[13] This route entails preparing the appropriate *ortho*-(trimethylsilyl)aryl triflate derivative from a suitable precursor.[15] Our novel Zn-catalyzed diborylation of aryl halides *via* both C–X and C–H activation under mild conditions represents a new type of catalytic process.

Using **1a** as the substrate, we screened a range of conditions, zinc sources, ligands, bases and solvents to assess the scope and limitations of this diborylation reaction (Table 1; see Tables S1-S7 for details). Diborylated product **1c** was obtained in the highest yield using 1.5 equivalents of B_2pin_2 and MeOK in the presence of $ZnCl_2$ as the catalyst and **L1** (dtbpy) as the ligand at ambient temperature in MTBE (methyl-*tert*-butylether), with complete conversion after 8 h (entry 1), while $ZnBr_2$ and ZnI_2 provided the product in lower yields (entries 2 and 3). $ZnEt_2$[9b] yielded predominantly the monoborylation product **1b**, and $Zn(OAc)_2$ showed very low catalytic activity (entries 4 and 5). In the absence of a Zn source, the borylation reaction does not occur at either the C–X or the C–H bond (entry 6) in this solvent.[3d]

The choice of ligand is crucial for this unusual diborylation reaction. Several substituted 2,2′-bipyridine and 1,10′-phenanthroline ligands were investigated (**L2**, **L4**-**L8**), which provided lower yields than **L1** and **L3** (entries 7-14). The 5,5′-di-Me-bpy (**L3**) ligand displayed comparable reactivity to **L1** when used in combination with 2 equivalents of B_2pin_2 and MeOK (entry 9). Ligand is essential for this catalytic process; no borylated products were observed when the ligand was omitted (entry 15). Next, the effects of base were examined (entries 16-19). The replacement of MeOK by Cs_2CO_3 or *t*BuOK resulted in limited or no reaction, whereas MeONa was only somewhat less effective than MeOK (entries 16-18). There was no reaction in the absence of a base (entry 19).

The possible involvement of copper, nickel or palladium contamination in the catalyst was eliminated by the observation that copper[8a-e] and nickel[3a] salts provided trace or very small amounts of **1b** and no **1c** (entries 20 and 21), and $Pd(OAc)_2$ provided a low yield of monoborylation product **1b** and no diborylation product **1c** under the standard reaction conditions (entry 22). The reaction is moderately sensitive to air,[16] but very sensitive to moisture; after addition of 2 equiv of water, no significant amount of the arylboronic esters were formed (entry 23).

Further screening of metal salts, ligands and bases identified the two best catalyst systems. System A comprises $ZnCl_2$, **L1**, and 1.5 equiv of B_2pin_2 and MeOK in MTBE (entry 1), and system B comprises $ZnBr_2$, **L3**, and 2 equiv of B_2pin_2 and MeOK in MTBE (entry 9).

With optimized reaction conditions in hand, we examined the substrate scope of the diborylation reaction (Table 2). Substituted aryl halides underwent diborylation reactions exclusively at the position *ortho* to the halide group, irrespective of the electronic nature of the substituent. Aryl halides possessing electron-donating substituents, such as *p*-methyl, 3,5-di-methyl, *p*-methoxy and *p*-*N*,*N*-dimethylamino groups (**2a**-**5a**) are well tolerated, providing 1,2-diborylarenes in moderate yields. Aryl bromides (**6a** and **7a**) are less reactive, the yields of the bis(boronate) being lower even at higher temperature. An

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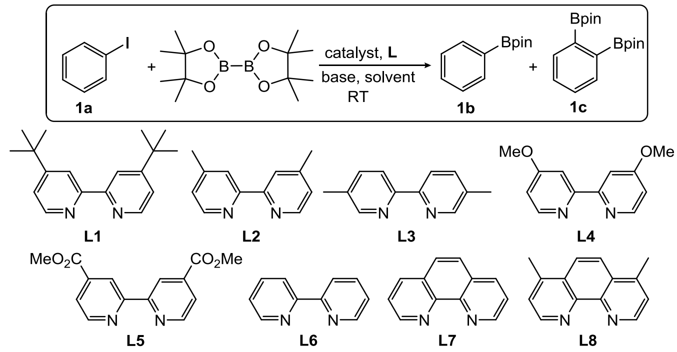
electron-withdrawing CF_3 group (**8a**) at the *para* position yielded diborylation product (**8c**) in lower yield, along with mainly monoborylation product **8b**. The sterically congested, *ortho*-tolyl derivative (**10a**) was diborylated in 34% yield.

Table 1: Optimization of the reaction conditions for the zinc-catalyzed borylation of iodobenzene, **1a**.[a]

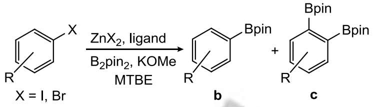


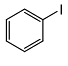
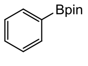
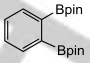
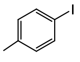
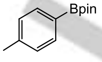
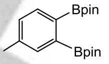
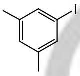
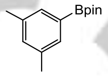
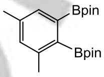
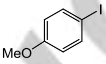
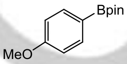
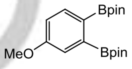
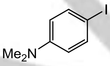
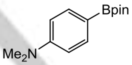
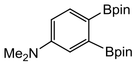
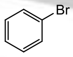
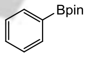
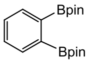
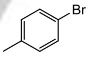
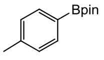
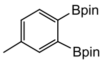
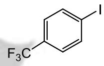
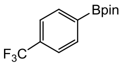
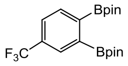
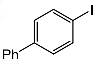
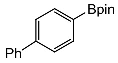
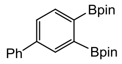
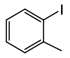
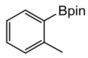
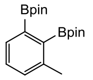
Entry	Catalyst	Ligand	Base	Solvent [2 mL]	Product Yield [%][b] **1b**	**1c**
1	$ZnCl_2$	**L1**	MeOK	MTBE	56	37[c]
2	$ZnBr_2$	**L1**	MeOK	MTBE	45	20
3	ZnI_2	**L1**	MeOK	MTBE	43	27
4	$ZnEt_2$	**L1**	MeOK	MTBE	84	9
5	$Zn(OAc)_2$	**L1**	MeOK	MTBE	10	0
6	-	**L1**	MeOK	MTBE	0	0
7	$ZnCl_2$	**L2**	MeOK	MTBE	30	15
8	$ZnCl_2$	**L3**	MeOK	MTBE	56	24
9	$ZnBr_2$	**L3**	MeOK	MTBE	50	35[c-e]
10	$ZnCl_2$	**L4**	MeOK	MTBE	trace	0
11	$ZnCl_2$	**L5**	MeOK	MTBE	trace	0
12	$ZnCl_2$	**L6**	MeOK	MTBE	35	14
13	$ZnCl_2$	**L7**	MeOK	MTBE	trace	0
14	$ZnCl_2$	**L8**	MeOK	MTBE	5	0
15	$ZnCl_2$	-	MeOK	MTBE	0	0
16	$ZnCl_2$	**L1**	Cs_2CO_3	MTBE	7	0
17	$ZnCl_2$	**L1**	*t*BuOK	MTBE	trace	0
18	$ZnCl_2$	**L1**	MeONa	MTBE	25	17
19	$ZnCl_2$	**L1**	-	MTBE	0	0
20[f]	CuI	**L1**	MeOK	MTBE	trace	0
21[g]	$NiBr_2$	**L1**	MeOK	MTBE	3	0
22[h]	$Pd(OAc)_2$	**L1**	MeOK	MTBE	26	0
23[i]	$ZnCl_2$	**L1**	MeOK	MTBE	trace	0

[a] Reaction conditions: C_6H_5I, **1a** (0.5 mmol, 1 equiv), catalyst (10 mol%), ligand (20 mol%), base (1.5 equiv), B_2pin_2 (1.5 equiv), MTBE (2 mL), at room temperature unless otherwise stated. [b] The yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two runs. [c] Complete conversion was observed, determined by GC-MS analysis (see Table S8). [d] The reaction was performed using 2 equiv of B_2pin_2 and 2 equiv of MeOK. [e] The reaction was performed at 50 °C. [f] 2 mol% of CuI catalyst was used. [g] 2 mol% of anhydrous $NiBr_2$ used. A similar result was obtained with $NiCl_2$. [h] 2 mol% of $Pd(OAc)_2$ catalyst was used. [i] 18 µL (1 mmol) of water was added.

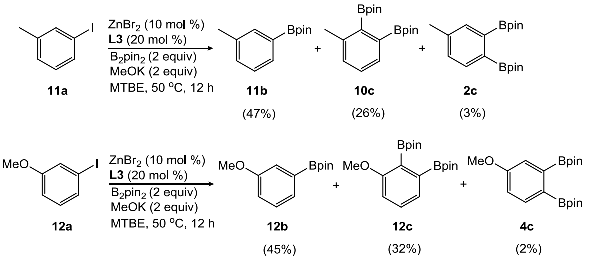
In the absence of a combination of directing groups and specific catalysts[5] the regioselectivity of the Rh or Ir-catalyzed C–H borylation of arenes is primarily controlled by steric effects[6] and, consequently, the reactions typically occur at unhindered sites.[4-7] To study the steric effect of substituents in our zinc-catalyzed reaction, we investigated the diborylation of *meta*-substituted aryl halides (Scheme 1). Significantly, the zinc-catalyzed diborylation of **11a** occurred preferentially at the more hindered site, *ortho* to the substituent, yielding 1,2-bis(Bpin)-3-methylbenzene (**10c**), accompanied by a small amount of 1,2-bis(Bpin)-4-methylbenzene (**2c**). A similar result was observed for the corresponding 1-iodo-3-methoxybenzene **12a**, providing further evidence that the regioselectivity of the C–H borylation is not dominated by steric effects of the substituents.

Table 2: Screening of aryl halides for the zinc catalyzed diborylation reaction.



Entry	Aryl-X	Arylboronates (yield [%])		ArH [%][a]
1	 **1a**	 **1b** (56)[b,c]	 **1c** (37)[b,c]	[5]
2	 **2a**	 **2b** (50)[c,d]	 **2c** (34)[c,d]	[8]
3	 **3a**	 **3b** (52)[b,e,f]	 **3c** (28)[b,e-h]	[8]
4	 **4a**	 **4b** (48)[d-f]	 **4c** (37)[d-g]	[6]
5	 **5a**	 **5b** (39)[d-f]	 **5c** (28)[d-g]	[21]
6	 **6a**	 **1b** (53)[b,c,f]	 **1c** (18)[b,c,f]	[11]
7	 **7a**	 **2b** (45)[c,d,f]	 **2c** (11)[c,d,f]	[12]
8	 **8a**	 **8b** (64)[d-f]	 **8c** (12)[d-f]	[6]
9	 **9a**	 **9b** (52)[d-f]	 **9c** (19)[d-g]	[15]
10	 **10a**	 **10b** (40)[c,d,f]	 **10c** (34)[c,d,f]	[9]

[a] Approximate ArH yields were estimated by GC-MS analysis. [b] Reaction conditions (A): aryl halide (0.5 mmol, 1 equiv), B_2pin_2 (1.5 equiv), $ZnCl_2$ (10 mol%), Ligand: **L1** (20 mol%), MeOK (1.5 equiv), MTBE (2 mL), at room temperature unless otherwise stated. [c] Yields were determined by GC-MS analysis *vs.* a calibrated internal standard and are averages of two experiments. [d] Reaction conditions (B): aryl halide (0.5 mmol, 1 equiv), B_2pin_2 (2 equiv), $ZnBr_2$ (10 mol%), Ligand: **L3** (20 mol%), MeOK (2 equiv), MTBE (2 mL), at room temperature unless otherwise stated. [e] Yield was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [f] The reaction was performed at 50 °C for 12 h. [g] GC-MS analysis of the crude reaction mixture revealed the presence of a small amount of one more isomer of the diborylation product. [h] The structure of **3c** was confirmed by single-crystal X-ray diffraction (see Figure S7).



Scheme 1. Borylation of 1-iodo-3-methylbenzene, **11a** and 1-iodo-3-methoxybenzene, **12a** (the structure of **12c** was confirmed by single-crystal X-ray diffraction; see Figure S8).

The mechanism of this Zn-catalyzed diborylation of aryl halides is not immediately obvious. To probe the possibility of a two-step process, in which the C–X borylation product subsequently undergoes *ortho*-C–H borylation, we monitored the reaction of **2a** by GC-MS analysis. As shown in Figure S1, the monoborylated product **2b** and diborylated product **2c** formed in maximum yields of 50% and 34%, respectively, within 8 h. The roughly similar shapes of time dependence of formation of the two products indicates that both the products are formed simultaneously under the standard reaction conditions, so a two-step process is unlikely. Indeed, the isolated monoborylated product **2b**, which would arise from initial C–X borylation, did not undergo a second (C–H) borylation reaction under the standard conditions. We do note that there is an induction period for the formation of both products.

Addition of anthracene, 9,10-dimethylanthracene, 1,3-diphenylisobenzofuran and 2,5-dimethylfuran as benzyne traps did not generate Diels-Alder adducts, indicating that our diborylation reaction does not generate a free benzyne intermediate resulting from base-promoted dehydrohalogenation. However, careful analysis of the crude reaction mixture with added anthracene revealed the formation of a small amount of 9-phenyl-9,10-dihydroanthracene,[17] suggesting the possibility of a radical mechanism (Scheme S1). Furthermore, no *vic*-diborylbenzene **1c** was observed *via* GC-MS analysis when benzyne, generated *in situ* from 2-(trimethylsilyl)phenyl triflate and KF/[18]crown-6, was reacted with B_2pin_2 in the presence of $ZnCl_2$ and **L1** as the ligand.[9b,13]

The borylation of sterically congested iodomesitylene **13a**, substituted at both *ortho* positions, afforded the unexpected 1,3-diborylarene product **13c**, confirmed by X-ray diffraction (Figure 1). It is significant that in the case of **13a**, the C–H activation took place at a remote aryl C–H bond rather than a weaker benzylic C–H bond (c.f. **2a**, **3a**, **7a** and **10a**). The formation of **13c** further excluded the possibility of an aryne intermediate.

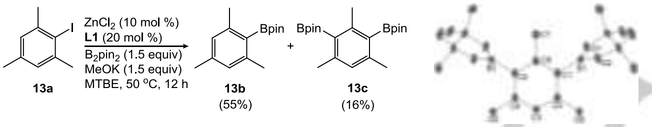
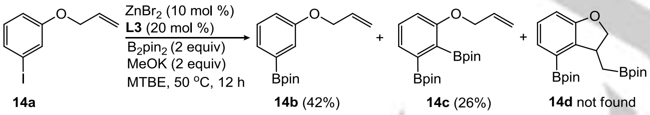
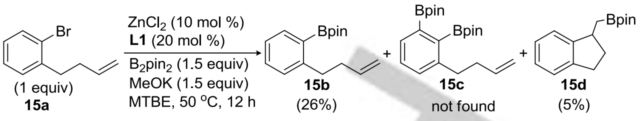


Figure 1. Borylation of 1-iodo-2,4,6-trimethylbenzene, **13a**, along with the molecular structure of **13c**, see Figure S9 for details.



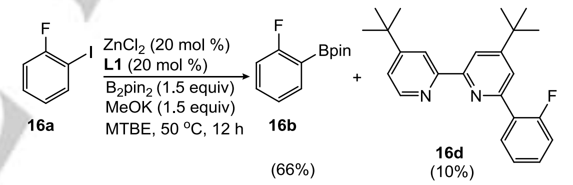
Scheme 2. Borylation of 1-(allyloxy)-3-iodobenzene, **14a**

When the reaction was performed in the presence of 1 equiv of the radical inhibitor 9,10-dihydroanthracene, the desired products were obtained in lower yields (**1b**: 26%; **1c**: 18%); increasing the radical inhibitor to 7 equiv shuts down the reaction almost completely (4% of **1b** and no **1c** by GC-MS) and a similar result was obtained using 3 equiv of TEMPO as the inhibitor. Thus, it seemed that the borylation reaction might involve one-electron processes. A radical-clock experiment using substrate **14a** under the standard conditions afforded the major acyclic mono and diborylation products **14b** and **14c** in 42 and 26% yields, respectively, and no 5-*exo*-trig cyclization product **14d** was detected (Scheme 2; a trace amount of one more isomeric diborylation product was also observed by GC-MS analysis). However, an experiment using 1-bromo-2-(but-3-en-1-yl)benzene (Scheme 3) gave monoborylated product **15b**, along with cyclized (borylmethyl)indane **15d**; no diborylation product **15c** was detected by GC-MS (small amounts of hydrodehalogenation byproducts 4-phenyl-1-butene and 1-methylindane were also observed). Formation of cyclized product **15d** supports the possibility of a radical mechanism.



Scheme 3. Borylation of 1-bromo-2-(but-3-en-1-yl)benzene, **15a**

Itami and co-workers reported a transition-metal-free *t*BuOK-promoted coupling of electron-deficient nitrogen heterocycles with aryl iodides.[18a] Recently, Jutand and Lei *et al.* reported that the interaction between 1,10-phenanthroline (Phen) and *t*BuOK generates the 1,10-phenanthroline radical anion, $Phen^{\bullet-}$ and the $tBuO^{\bullet}$ radical.[18b] Further, Phen serves as a relay for the reduction of phenyl bromide to the phenyl radical *via* $Phen^{\bullet-}$. Echegoyen *et al.* reported $[Ru(bpy)_3]^0$, formed by reductive electrocrystallization of $[Ru(bpy)_3](PF_6)_2$, and the crystal structure provides evidence that the extra electrons reside on the bpy ligands.[18c] Interestingly, the borylation of 2-fluoroiodobenzene afforded monoborylated product **16b**, along with the arylated dtbpy product **16d;** no diborylated product was observed by GC-MS (Scheme 4). The formation of coupling product **16d** suggested the possibility of dtbpy reduction followed by attack at the aryl iodide. In the absence of a Zn source, neither the borylation nor arylation occured (see Table S9), suggesting the intermediacy of a Zn-dtbpy complex. Running the reaction with **1a** under standard conditions, but in the dark (Table S7, entry 9), had no effect on the conversion or product distribution; therefore the borylations are not triggered by a photoexcited state.



Scheme 4. Borylation of 2-fluoroiodobenzene, **16a**

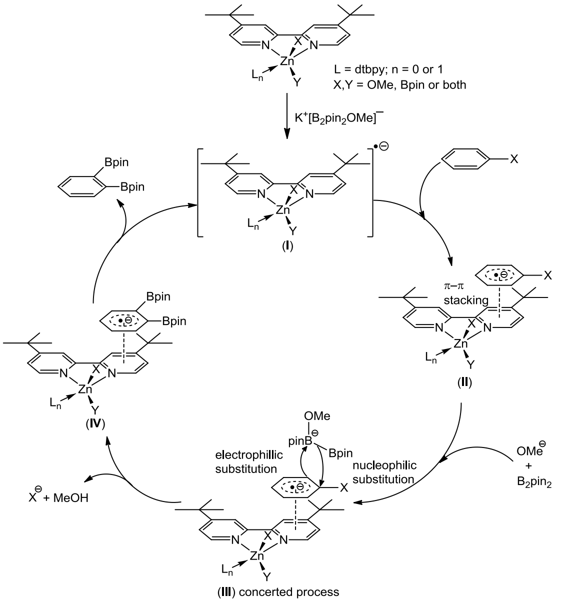


Figure 2. A plausible mechanism of pathway (B).

We propose two plausible, independent pathways: (A) to give monoborylated products *via* metathesis between a (dtbpy)Zn(II)-boryl and ArX,[8b,11] and (B) (Figure 2) to give diborylated products. In pathway (B), MeOK reacts with B_2pin_2 to generate the adduct $K^+[B_2pin_2OMe]^-$,[19a,b] which may reduce a $(dtbpy)_nZn(II)XY$ complex (n = 1 or 2; X,Y = OMe, Bpin or both) to produce a Zn(II)-stabilized $[dtbpy]^{\bullet-}$ radical. This could pass the electron to ArX forming $ArX^{\bullet-}$ (**II**) which reacts with $K^+[B_2pin_2OMe]^-$ (either step-wise or concerted (**III**)) giving diborylated arene and regenerating the $[Zn\text{-}dtbpy]^{\bullet-}$ radical anion. The regioselectivity shown in Scheme 1 can be explained by a concerted mode, in which $ArX^{\bullet-}$ undergoes nucleophilic substitution (releasing X^-) which in turn promotes the electrophillic substitution (**III**).[19c] For the formation of **13c**, the regioselectivity can be explained by a fast step-wise addition process.

We have discovered a novel process which yields 1,2-diborylarenes *via* Zn-catalyzed C–X and C–H activation of aryl halides, under mild conditions. Preliminary investigations show that the C–X/C–H diborylation reaction does not involve a free aryne, but one-electron processes seem to be involved.

Acknowledgements

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Keywords: boronate esters • C–H activation • cross-coupling • homogeneous catalysis • nitrogen heterocycles

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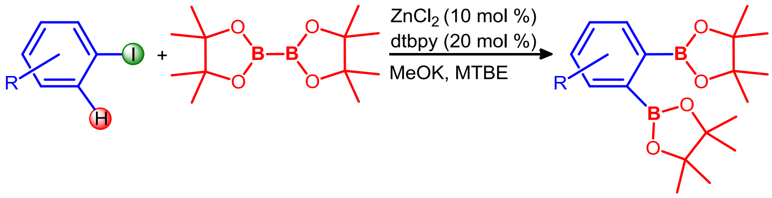
COMMUNICATION



Two B or not two B: A novel catalytic system based on a Zn(II)-dtbpy precursor has been developed for the preparation of 1,2-diborylarenes, which represents a new type of catalytic process for diborylation of aryl halides *via* both C–X and C–H activation.

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Zinc-Catalyzed Dual C–X and C–H Borylation of Aryl Halides