Iridium-Catalyzed Preparation of Silylboranes by Silane Borylation and Their Use in the Catalytic Borylation of Arenes

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Silylboranes are versatile reagents for transition metal-catalyzed reactions of unsaturated organic molecules. These reagents are typically prepared by the addition of a silyl lithium species to a boron electrophile. However, the need to generate anionic silane reagents limits the scope of silylboranes that can be readily obtained. Here, we describe the synthesis of trialkylsilylboranes by the borylation of silanes catalyzed by iridium complexes. The reaction of trialkylhydrosilanes with B_2pin_2 catalyzed by the combination of $[Ir(OMe)cod]_2$ and 4,4′-di-*tert*-butylbipyridine forms trialkylsilylboronic esters. In addition, we show that these trialkylsilylboranes serve as boron sources for the iridium-catalyzed borylation of aryl C−H bonds. In contrast to diboron reagents, the silylboranes react with methylarenes at both the aryl and methyl C−H bonds.

Introduction

Transition metal-catalyzed reactions of silylboranes have gained significant attention in recent years.[1,2] Silylboranes undergo metal-catalyzed additions to the unsaturated C−C bond in substrates such as alkynes,[3−9] alkenes,[10,11] 1,3-dienes,[12−14] allenes,[15−19] and alkylidenes,[20,21] and the resulting difunctionalized products possess orthogonal functionality for the diverse reaction manifolds of organoboron[22] and organosilicon[23,24] compounds. Considering the utility of silylborane reagents, improved methods for their preparation would contribute to their utility.

The most commonly employed method for the preparation of silylboranes involves the addition of silyllithium reagents to boron electrophiles, such as haloboranes,[25,26] trialkyborates, or pinacolborane (HBpin).[27] A significant limitation of these methods is the need for silyl-metal reagents. Although aryl-substituted silyl lithium reagents can be prepared from the corresponding chlorosilanes, trialkylsilyl lithium reagents must be prepared from disilanes, and few disilanes are commercially available.[28] In addition to these general methods, Berry has reported a tantalum-mediated formation of Si−B bonds,[29] and Smith has described an isolated example of a rhodium-catalyzed coupling of *N*-trimethylsilylpyrrole with HBpin.[30]

Our group has described catalytic methods for the direct C−H borylation of alkanes[31−34] and, in collaboration with Ishiyama and Miyaura, the direct C−H borylation of arenes[35,36] using

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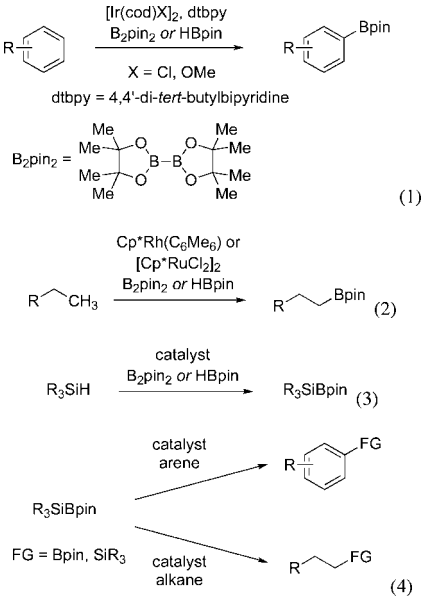
bis(pinacolato)diboron (B_2pin_2) or pinacolborane (HBpin), which are both commercially available in bulk quantities, as the boron source (eqs 1 and 2). We considered that a similar functionalization of Si−H bonds could convert hydrosilanes into silylboranes (eq 3). Furthermore, we wished to explore the reactivity of silylboranes toward metal-catalyzed C−H functionalization and to determine whether the borane or silane would be found in the functionalized product (eq 4).



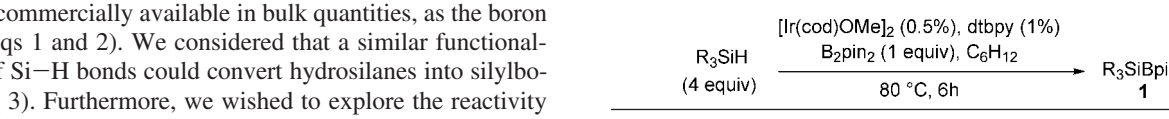
Herein, we describe the borylation of the Si−H bonds in trialkylsilanes to provide trialkylsilyl(pinancolato)borane products. In addition, we demonstrate that silylboranes participate in iridium-catalyzed borylation of arenes to form arylboronic esters and silane as byproduct (eq 4, right). In some cases, the use of $R_3SiBpin$ provides contrasting regioselectivity to that observed when using B_2pin_2 as the boron source.

Results and Discussion

1. Discovery and Scope of the Borylation of Trialkylsilane Si−H Bonds. Initial studies were conducted to identify potential catalysts for the coupling of triethylsilane with B_2pin_2. Complexes previously reported to catalyze the borylation of aliphatic C−H bonds, $[Cp^*RuCl_2]_2$ and $Cp^*Rh(C_6Me_6)$,[31−34] did not lead to the formation of silylborane products. However, the combination of $[Ir(cod)OMe]_2$ and 4,4′-di-*tert*-butylbipyridine (dtbpy), which catalyzes the borylation of arene C−H bonds,[35,36] afforded $Et_3SiBpin$ (**1a**) in good yield. Under optimized reaction conditions, B_2pin_2 reacted with Et_3SiH (4 equiv) in the presence of $[Ir(cod)OMe]_2$ (0.5%) and dtbpy (1%) in cyclohexane solvent to give **1a** in 58% yield after chromatographic purification (entry 1, Table 1). When the reaction was repeated with HBpin in place of B_2pin_2, no silylborane was observed (entry 2). Several trialkylhydrosilanes also reacted to form silylborane products in good yields (entries 3−6), although the sterically hindered *i*-Pr_3SiH did not react (entry 7). In general, reactions of hydrosilanes bearing longer alkyl chains occurred to higher conversions and gave higher isolated yields.

In contrast to the borylation of trialkyl hydrosilanes, the attempted borylation of alkoxy- and dialkylamino-substituted hydrosilanes, as well as dihydrosilanes, resulted in no reaction.

Table 1. Iridium-Catalyzed Hydrosilane Borylation



entry	R_3SiH	product	yield (%)[a]
1	Et_3SiH	**1a**	58 (76)
2[b]	Et_3SiH	**1a**	0
3	*n*-Pr_3SiH	**1b**	66 (71)
4	*n*-Bu_3SiH	**1c**	71 (84)
5	*n*-$(pentyl)_3SiH$	**1d**	70 (90)
6[c]	*t*-$BuMe_2SiH$	**1e**	41 (61)
7	*i*-Pr_3SiH	**1f**	0

[a] Yield based on 1 equiv of boron per B_2pin_2. Yield in parentheses is GC yield. [b] HBpin (1 equiv) used in place of B_2pin_2. [c] 1% $[Ir(cod)OMe]_2$ and 2% dtbpy used.

Furthermore, attempted borylations of aryl-functionalized hydrosilanes did not form the silylborane products, due to the lability of the Ar−Si bond under the reaction conditions.[37,38]

Arene C−H Bond Functionalization with Borylsilanes. Having developed the borylation of alkylhydrosilane Si−H bonds, we explored the reactivity of silylboranes toward arene C−H bond functionalization (eq 4). Substrates containing only aryl C−H bonds were studied first. Accordingly, $Et_3SiBpin$ (**1a**, 1 equiv) was combined with $[Ir(cod)OMe]_2$ (1%) and dtbpy (2%) in neat benzene (10 equiv) and heated at 80 °C. This reaction gave the aryl boronic ester **2** in 91% yield (entry 1, Table 2), along with triethylsilane. No products from arene silylation were observed. In addition to benzene, a range of electron-rich and -deficient arenes were successfully borylated when using **1a** as the boron source. Monosubstituted arenes provided mixtures of *meta*- and *para*-substituted products in excellent yields (entries 2 and 3). Likewise, reactions of 1,3-disubstituted arenes and symmetrically 1,2-disubstituted arenes formed single products with high conversions of the silylborane (entries 4−8). The yields and regioselectivities for reactions of these substrates are comparable to those reported previously for the iridium-catalyzed borylation of arenes with B_2pin_2 (eq 1).[35,36]

Despite the initial similarity of arene borylations conducted with $Et_3SiBpin$ and with B_2pin_2, significant differences in the reactivity of methylarenes with $Et_3SiBpin$ and B_2pin_2 were observed. The reactions of silylborane **1a** with methylarenes are summarized in Table 3. The reaction of silborane **1a** with toluene under the standard reaction conditions formed a mixture of three isomeric boronic esters in a combined 92% yield (entry 1, Table 3). The major product (**10a**) resulted from catalytic borylation at the benzylic position.[39] Similarly, the reaction of electron-rich *m*-xylene with silborane **1a** afforded products resulting from benzylic and aryl C−H bond functionalization in a 9:1 ratio and 86% yield (entry 2). The opposite preference for formation of the two regioisomers was observed in the reaction of **1a** with the more electron-deficient 3-chlorotoluene. This reaction led to preferential functionalization at the mutually *meta*-aryl C−H bond over the benzylic C−H bonds, but significant amounts of benzylboronic ester product were still formed (entry 3). The formation of benzyl-substituted products in these examples stands in contrast with the essentially exclusive aryl C−H functionalization that is observed when B_2pin_2 is employed as the boron source for arene borylation in the presence of this iridium catalyst.[36,40,41]

Other substrates underwent exclusive benzylic C−H borylation. Mesitylene, a substrate that has not been reported to

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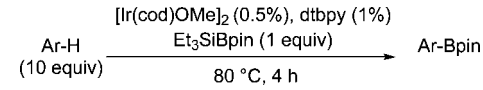
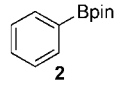
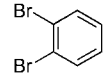
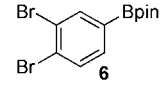
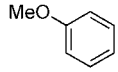
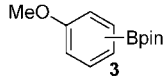
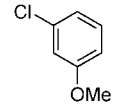
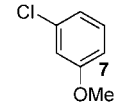
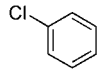
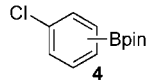
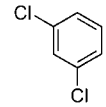
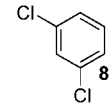
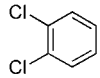
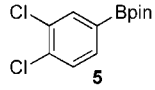
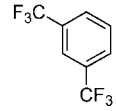
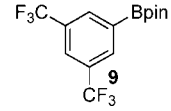
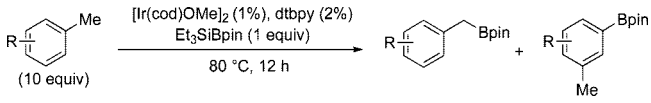
Table 2. Catalytic Borylation of Arenes with $Et_3SiBpin$

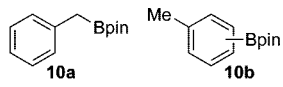
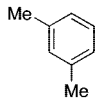
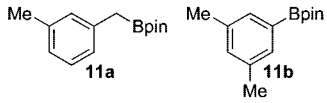
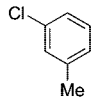
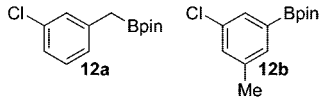
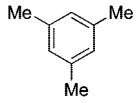
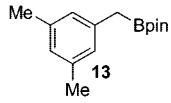
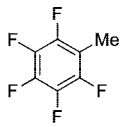
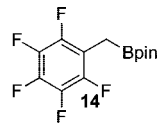
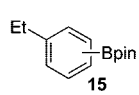


entry	Ar-H	product	yield%[a] (m:p)[b]	entry	Ar-H	product	yield%[a] (m:p)
1[c]		 **2**	91	5		 **6**	86
2[c]		 **3**	90 70:30	6		 **7**	99
3		 **4**	100 18:19	7		 **8**	96
4		 **5**	89	8		 **9**	88

[a] Yield determined by GC. [b] *Meta*:*para* isomer ratios determined by ^{1}H NMR. [c] 1% $[Ir(cod)OMe]_2$ and 2% dtbpy were used over a 12 h reaction time.

Table 3. Catalytic Borylation of Alkyl-Substituted Arenes with $Et_3SiBpin$



entry	Ar-H	product(s)	yield%[a] (b:m:p)[b]
1		 **10a** **10b**	92 48:33:19
2		 **11a** **11b**	86 89:11
3[c]		 **12a** **12b**	72 40:60
4		 **13**	95
5		 **14**	79
6		 **15**	71% 0:70:30

[a] Yield determined by GC. [b] Benzyl:*meta*:*para* isomer ratios determined by ^{1}H NMR. [c] 0.5% $[Ir(cod)OMe]_2$ and 1% dtbpy were used over a 4 h reaction time.

undergo aryl C−H bond borylation, reacted with **1a** to give benzylboronic ester **13** in excellent yield (entry 4). Furthermore, 2,3,4,5,6-pentafluorotoluene underwent clean borylation of the benzylic C−H bond (entry 5). This result indicates that the benzylic C−H functionalization of alkylarenes can occur through direct cleavage of the benzylic C−H bonds without initial reaction with an aromatic C−H bond. In contrast with the borylation of toluene, the borylation of ethylbenzene formed arylboronic esters (**15**) without evidence for any benzylic functionalization (entry 6).

Mechanistic Considerations. The unexpected formation of benzylboronic esters in the presence of reactive aryl C−H bonds led us to consider how the mechanism would be altered by the use of a silylborane in place of B_2pin_2. Previous studies on the mechanism of arene borylation have demonstrated that the C−H bond cleavage step occurs after dissociation of the alkene ligand in the trisboryl complex **16** (eq 5, left).[36,42] These studies have also shown that the resting state of reactions initiated with $[Ir(cod)OMe]_2$, dtbpy, B_2pin_2, and coe is the version of complex **16** in which the alkene ligand is coe. In the absence of added coe the olefin ligand in **16** can be cod, coe from reduction of the cod, or a borylated derivative of cod. By analogy, the combination of $[Ir(cod)OMe]_2$/dtbpy and $Et_3SiBpin$ could generate the related complex **17**, and mixed silyl boryl complex **17** could react with distinct selectivity for reaction with benzylic and aromatic C−H bonds. Although the silyl ligand of **17** would alter the electronic properties of the metal center, the steric differences between trisboryl complex **16** and the mixed silyl boryl complex **17** seem more pronounced.

To probe the dependence of ligand size on the regioselectivity of borylation, catalytic reactions between *m*-xylene and three boron sources (XBpin, X = pinB, *t*-$BuMe_2Si$, and Bu_3Si) in addition to $Et_3SiBpin$ were conducted (entries 1−4, Table 4). While the reaction with B_2pin_2 solely formed products resulting

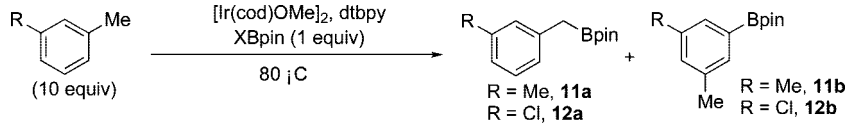
(39) Catalytic benzylic borylation has been previously noted. See: (a) Ishiyama, T.; Ishida, K.; Takagi, J.; Miyaura, N. *Chem. Lett.* **2001**, 1082–1083. (b) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2168–2171.

(40) Takagi, J.; Sato, K.; Hartwig, J. F.; Ishiyama, T.; Miyaura, N. *Tetrahedron Lett.* **2002**, *43*, 5649–5651.

(41) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. *Chem. Commun.* **2003**, 2924–2925.

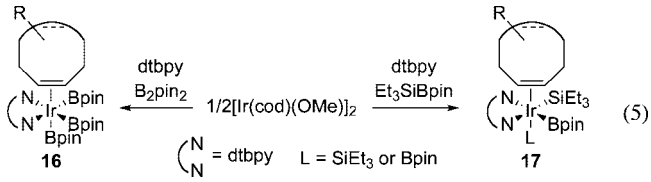
(42) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263–14278.

Table 4. Regioselectivity Dependence of Regioselectivity on Boron Source



entry	R	boron reagent	$[Ir(cod)OMe]_2$, %	dtbpy, %	time, h	yield, %[a] (**a**:**b**)[b]
1	Me	B_2pin_2	1	2	12	83 (0:1)
2	Me	*t*-$BuMe_2SiBpin$	1	2	12	75 (70:30)
3	Me	$Et_3SiBpin$	1	2	12	86 (89:11)
4	Me	*n*-$Bu_3SiBpin$	1	2	12	65 (93:7)
5	Cl	B_2pin_2	0.5	1	4	102 (0:1)
6	Cl	*t*-$BuMe_2SiBpin$	0.5	1	4	98 (10:90)
7	Cl	$Et_3SiBpin$	0.5	1	4	72 (40:60)
8	Cl	*n*-$Bu_3SiBpin$	0.5	1	4	87 (60:40)

[a] Yield determined by GC. [b] **12a**:**12b** isomer ratios determined by ^1H NMR.



(5)

from aryl C−H functionalization, the reactions of *t*-$BuMe_2$-SiBpin, $Et_3SiBpin$, and *n*-$Bu_3SiBpin$ gave a mixture of benzyl- and aryl-functionalized products in 70:30, 89:11, and 93:7 ratios, respectively. For reactions of B_2pin_2, $Et_3SiBpin$, and $Bu_3SiBpin$, there is a good correlation between the size of the X group and the selectivity for benzylic C−H functionalization over aryl C−H functionalization (X = pinB < Et_3Si < *n*-Bu_3Si). The same trend in selectivity was observed for the catalytic borylation of 3-chlorotoluene (entries 5−8). The selectivity from reactions of *t*-$BuMe_2SiBpin$ did not fit these trends, if one considers the cone angle of *t*-$BuMe_2Si$ to be larger than that of Et_3Si, as based on Tolman's parameters for phosphines.[43] However, conformations of unsymmetrical substituents can render them less hindered than would be expected from the calculated angles.[44]

In addition to these steric effects on selectivity, the reactions in Table 3 reveal the effect of arene electronics on regioselectivity; the more electron-rich *m*-xylene forms more product from benzylic functionalization than does the more electron-deficient 3-chlorotoluene. This trend fits with the slower rate of functionalization of C−H bonds in electron-rich arenes than those of electron-poor arenes.[42]

Conclusion

We have demonstrated that $[Ir(cod)OMe]_2$ and dtbpy generates a catalyst for the borylation of the Si−H bonds in trialkylhydrosilanes to give silylborane products. Although the reaction scope is limited to trialkylsilanes possessing modest steric properties, this reaction provides access to materials that would be more challenging to obtain by the more typical reaction of silyl lithium reagents with boranes. In addition, we have shown that silylboranes can serve as reagents for the catalytic borylation of arenes. In contrast to reactions of B_2pin_2 with methylarenes, the reactions of silylboranes with methylarenes occurred with competitive aryl and benzyl C−H bond functionalization. The ratio of benzyl to aryl C−H functionalization varied with arene electronics as well as the size of the silyl group; reactions with more hindered silylboranes formed more of the product from benzylic borylation. Future efforts will probe for the presence of silyl intermediates on the catalytic reaction pathway and for a method to control the regioselectivity of arene C−H functionalization in a synthetically valuable fashion by judicious choice of boron source.

Experimental Section

Reagents and Methods. All reactions, unless otherwise noted, were performed in oven-dried 20 mL vials. Organic solutions were concentrated either under high vacuum or by rotary evaporation. Flash column chromatography was performed employing 230−400 mesh silica gel. Thin-layer chromatography was performed using glass plates precoated to a depth of 0.25 mm with 230−400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Compounds were visualized using iodine followed by ceric ammonium molybdate stain. Anhydrous cyclohexane was purchased from commercial sources. Arene and hydrosilane reagents were degassed prior to use. All other reagents were obtained from commercial sources and used without further purification. Proton, carbon-13, and fluorine-19 nuclear magnetic resonance (^1H NMR, ^{13}C NMR, ^{19}F NMR) spectra were recorded on a Varian 500, a Varian VXR 500, or a Varian Inova 500 NMR spectrometer. Boron-11 nuclear magnetic resonance (^{11}B) spectra were recorded on a Varian Unity Inova 300 or a Varian Unity Inova 600 NMR spectrometer. Silicon-29 nuclear magnetic resonance (^{29}Si) spectra were recorded on a Varian Inova 600 NMR spectrometer. ^1H chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual protium in the NMR solvent ($\delta = 7.26$ ppm). ^{13}C NMR chemical shifts are expressed in parts per million (δ scale) downfield from trimethylsilane and are referenced to the ^{13}C resonance of $CDCl_3$ ($\delta = 77.00$ ppm). In the ^{13}C NMR spectra of arylboronic esters, the carbon attached to boron was not observed. ^{11}B, ^{19}F, and ^{29}Si NMR chemical shifts are expressed in parts per million (δ scale) and are referenced to external stardards: C_6F_6 in $CDCl_3$ at $\delta = -163.0$ ppm, $BF_3 \cdot OEt_2$ at $\delta = 0.0$ ppm, and $SiMe_4$ at $\delta = 0.0$ ppm. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet and/or multiple resonances), integration, coupling constant in hertz (Hz). GC/MS traces were acquired on an Agilent Technologies 6890N Network GC system with an Alltech EC-1 column and an attached Agilent Technologies 5973 Network mass selective detector. GC traces were acquired on a Hewlett-Packard 5890 Series II GC system with a DB-1701 column and a FID detector. *n*-Dodecane was used as an internal standard for the integration of GC peaks. Elemental analyses were conducted by Robertson Microlit Larboratories. High-resolution mass spectroscopy (HRMS) was conducted by the University of Illinois at Urbana−Champaign Mass Spectrometry Laboratory.

(43) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.
(44) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *128*, 89–116.

General Procedure for Silane Borylation. Inside a nitrogen-filled glovebox, an oven-dried vial was charged with $[Ir(cod)OMe]_2$ (3.3 mg, 0.0050 mmol), dtbpy (2.7 mg, 0.010 mmol), B_2pin_2 or HBpin, C_6H_{12} (1.0 mL), *n*-dodecane (20 μL, 0.088 mmol), and silane. The resulting dark brown solution was heated at 80 °C outside the glovebox. After 6 h, the reaction was cooled to room temperature. GC analysis was used to determine the yield of **1** by integration against the *n*-dodecane standard. The crude reaction mixture was concentrated under high vacuum. Purified product was obtained by silica gel chromatography, using a hexane/ethyl acetate gradient, 0%, to 2%, to 5% ethyl acetate.

Borylation of Triethylsilane. The reaction of B_2pin_2 (254 mg, 1.00 mmol) with triethylsilane (640 μL, 4.01 mmol) gave **1a** (76% by GC analysis). Purification on silica gel gave **1a** (140.0 mg, 58%) as a colorless oil. $R_f = 0.56$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 12H, Bpin-CH_3), 0.96 (t, 9H, $J = 7.9$ Hz, $CH_2C\underline{H}_3$), 0.59 (q, 6H, $J = 7.9$ Hz, $C\underline{H}_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 82.86, 25.00, 8.32, 2.91; ^{11}B NMR ($CDCl_3$) δ 34.9; ^{29}Si NMR (neat) δ −13.0; GC/MS (EI) *m/z* (% relative intensity) $[M - Me]^+$ 227 (2), $[M - Et]^+$ 213 (28), 199 (5), 184 (6), 129 (7), 115 (10), 103 (19), 84 (100), 69 (34), 55 (16). Anal. Calcd for $C_{12}H_{27}BO_2Si$: C, 59.50; H, 11.23. Found: C, 59.28; H, 11.51.

Attempted Borylation of Triethylsilane with HBpin in Place of B_2pin_2. The reaction of HBpin (145 μL, 1.00 mmol) with triethylsilane (640 μL, 4.01 mmol) resulted in no formation of silylborane product by GC and GC/MS analysis.

Borylation of Tri-*n*-propylsilane. The reaction of B_2pin_2 (253 mg, 0.995 mmol) with tri-*n*-propylsilane (835 μL, 4.00 mmol) gave **1b** (71% by GC analysis). Purification on silica gel gave **1b** (188.2 mg, 66%) as a colorless oil. $R_f = 0.64$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 1.36 (m, 6H, $CH_2C\underline{H}_2CH_3$), 1.22 (s, 12H, Bpin-CH_3), 0.95 (t, 9H, $J = 7.3$ Hz, $CH_2CH_2C\underline{H}_3$), 0.57 (m, 6H, $C\underline{H}_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 82.85, 24.96, 18.42, 18.31, 14.60; ^{11}B NMR ($CDCl_3$) δ 35.1; GC/MS (EI) *m/z* (% relative intensity) $[M - Me]^+$ 269 (1), $[M - Pr]^+$ 241 (21), 199 (8), 159 (9), 115 (14), 84 (100), 69 (28), 55 (13). Anal. Calcd for $C_{15}H_{33}BO_2Si$: C, 63.37; H, 11.70. Found: C, 63.61; H, 11.98.

Borylation of Tri-*n*-butylsilane. The reaction of B_2pin_2 (254 mg, 1.00 mmol) with tri-*n*-butylsilane (1.03 mL, 4.00 mmol) gave **1c** (84% by GC analysis). Purification on silica gel gave **1c** (250.5 mg, 77%) as a colorless oil. $R_f = 0.70$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 1.31 (m, 12H, $CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.22 (s, 12H, Bpin-$CH_3$), 0.87 (t, 9H, $J = 7.2$ Hz, $CH_2CH_2CH_2C\underline{H}_3$); 0.59 (m, 6H, $C\underline{H}_2CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 82.84, 27.04, 26.61, 24.94, 13.83, 11.44; ^{11}B NMR ($CDCl_3$) δ 35.2; GC/MS (EI) *m/z* (% relative intensity) $[M - Me]^+$ 311 (1), $[M - Bu]^+$ 269 (22), 213 (18), 187 (6), 129 (18), 101 (18), 84 (100), 69 (20), 55 (13). Anal. Calcd for $C_{18}H_{39}BO_2Si$: C, 66.24; H, 12.04. Found: C, 66.31; H, 12.10.

Borylation of Tri-*n*-pentylsilane. The reaction of B_2pin_2 (255 mg, 1.00 mmol) with tri-*n*-pentylsilane (1.23 mL, 4.01 mmol) gave **1d** (95% by GC analysis). Purification on silica gel gave **1d** (258.3 mg, 70%) as a pale pink oil. $R_f = 0.76$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 1.29 (m, 18H, $CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$), 1.22 (s, 12H, Bpin-$CH_3$), 0.86 (m, 9H, $CH_2CH_2CH_2CH_2C\underline{H}_3$), 0.58 (m, 6H, $C\underline{H}_2CH_2CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 82.83, 35.84, 24.96, 24.39, 22.33, 14.00, 11.66; ^{11}B NMR ($CDCl_3$) δ 35.2; GC/MS (EI) *m/z* (% relative intensity) $[M - Me]^+$ 353 (0.4), $[M - pentyl]^+$ 297 (10), 227 (15), 143 (12), 115 (10), 101 (11), 84 (100), 69 (20), 55 (10). Anal. Calcd for $C_{21}H_{45}BO_2Si$: C, 68.45; H, 12.31. Found: C, 68.21; H, 12.20.

Borylation of *tert*-Butyldimethylsilane. The reaction of B_2pin_2 (253 mg, 1.00 mmol) with *tert*-butyldimethylsilane (665 μL, 4.01 mmol) gave **1e** (61% by GC analysis). Purification on silica gel gave **1e** (99.3 mg, 41%) as a white solid. $R_f = 0.57$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 12H, Bpin-CH_3), 0.91 (s, 9H, $C(CH_3)_3$), 0.01 (s, 6H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 82.94, 26.98, 24.99, 16.20, −6.46; ^{11}B NMR ($CDCl_3$) δ 34.8; GC/MS (EI) *m/z* (% relative intensity) M^+ 242 (1), $[M - Me]^+$ 227 (4) $[M - tBu]^+$ 185 (97), 101 (49), 83 (100), 69 (35), 55 (34); Anal. Calcd for $C_{12}H_{27}BO_2Si$: C, 59.50; H, 11.23. Found C, 59.23; H, 10.98.

Attempted Borylation of Tri-isopropylsilane. The reaction of B_2pin_2 (253 mg, 1.00 mmol) with tri-isopropylsilane (820 μL, 4.00 mmol) resulted in no formation of silylborane product by GC and GC/MS analysis.

General Procedure for Arene Borylation with Silylboranes. Inside a nitrogen-filled glovebox, an oven-dried 20 mL vial was charged with $[Ir(cod)OMe]_2$, dtbpy, arene, *n*-dodecane (20 μL, 0.088 mmol), and silylborane. The resulting dark brown solution was heated at 80 °C outside the glovebox. After heating, the reaction was cooled to room temperature. GC analysis was used to determine the yields of borylated products by integration against the *n*-dodecane standard. Purified product was obtained by chromatography on a short plug of silica gel, using a hexane/diethyl ether gradient, 0 to 5% diethyl ether.

Borylation of Benzene with $Et_3SiBpin$. The reaction of $[Ir(cod)OMe]_2$ (6.6 mg, 0.010 mmol), dtbpy (5.2 mg, 0.019 mmol), benzene (895 μL, 10.0 mmol), and **1a** (270 μL, 0.992 mmol) gave **2** (91% by GC analysis) after 12 h. Purification on silica gel gave **2** (116.4 mg, 58%) as a pale pink oil. The spectroscopic characterization of arylboronic ester **2** has been previously described.[36]

Borylation of Anisole with $Et_3SiBpin$. The reaction of $[Ir(cod)OMe]_2$ (6.5 mg, 0.0098 mmol), dtbpy (6.0 mg, 0.022 mmol), anisole (1.09 mL, 10.0 mmol), and **1a** (270 μL, 0.992 mmol) gave **3** (90% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed *meta*- and *para*-borylated products in a 4.3:1 ratio. Purification on silica gel gave **3** (148.4 mg, 64%) as a pale pink oil, in a 3.8:1 ratio of *meta*:*para*-substituted products. The spectroscopic characterization of both isomers of arylboronic ester **3** has been previously described.[36]

Borylation of Chlorobenzene with $Et_3SiBpin$. The reaction of $[Ir(cod)OMe]_2$ (3.4 mg, 0.0051 mmol), dtbpy (2.6 mg, 0.0097 mmol), chlorobenzene (1.02 mL, 10.0 mmol), and **1a** (270 μL, 0.992 mmol) gave **4** (93% by GC analysis) after 4 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed *meta*- and *para*-borylated products in a 4.4:1 ratio. Purification on silica gel gave **4** (152.4 mg, 65%) as a pale pink oil, in a 3.3:1 ratio of *meta*:*para*-substituted products. **4**, *meta*-isomer: $R_f = 0.51$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, 1H, $J = 2.0$ Hz, Ar-H), 7.66 (td, 1H, $J = 1.1$, 7.2 Hz, Ar-H), 7.42 (ddd, 1H, $J = 1.3$, 2.3, 8.0 Hz, Ar-H), 7.30 (t, 1H, $J = 7.6$ Hz, Ar-H), 1.34 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 134.50, 133.96, 132.61, 131.21, 129.14, 84.06, 24.79; ^{11}B NMR ($CDCl_3$) δ 30.3; GC/MS (EI) *m/z* (% relative intensity) M^+ 238 (36), $[M - Me]^+$ (77), 152(100), 139 (95). **4**, *para*-isomer: $R_f = 0.51$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.72 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.34 (d, 2H, $J = 8.3$ Hz, Ar-H), 1.34 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 137.46, 136.08, 127.94, 83.94, 24.65; ^{11}B NMR ($CDCl_3$) δ 30.3; GC/MS (EI) *m/z* (% relative intensity) M^+ 238 (36), $[M - Me]^+$ (77), 152(100), 139 (95). **4**, mixture of isomers: HRMS (EI) *m/z* calcd for $C_{12}H_{16}BClO_2$ M^+ 238.0931, found 238.0931. Anal. Calcd for $C_{12}H_{16}BClO_2$: C, 60.43; H, 6.76; N, 0.00. Found: C, 60.72; H, 7.09; N, <0.02.

Borylation of 1,2-Dichlorobenzene with $Et_3SiBpin$. The reaction of $[Ir(cod)OMe]_2$ (3.3 mg, 0.0050 mmol), dtbpy (2.7 mg, 0.010 mmol), 1,2-dichlorobenzene (1.13 mL, 10.0 mmol), and **1a** (270 μL, 0.992 mmol) gave **5** (89% by GC analysis) after 4 h. Purification on silica gel gave **5** (135.6 mg, 50%) as a pale pink oil. The spectroscopic characterization of arylboronic ester **5** has been previously described.[36]

Borylation of 1,2-Dibromobenzene with $Et_3SiBpin$. The reaction of $[Ir(cod)OMe]_2$ (3.2 mg, 0.0048 mmol), dtbpy (2.9 mg, 0.011 mmol), 1,2-bromobenzene (1.21 mL, 10.0 mmol), and **1a** (270 μL,

0.992 mmol) gave **6** (86% by GC analysis) after 4 h. Purification on silica gel gave **6** (229.8 mg, 64%) as a colorless oil. $R_f = 0.44$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, 1H, $J = 1.4$ Hz, Ar-H), 7.62 (d, 1H, $J = 7.9$ Hz, Ar-H), 7.54 (dd, 1H, $J = 1.4$, 7.9 Hz, Ar-H), 1.34 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 139.62, 134.38, 133.20, 128.12, 124.60, 84.28, 24.79; ^{11}B NMR ($CDCl_3$) δ 29.92; GC/MS (EI) *m/z* (% relative intensity) M^+ 362 (53), $[M - Me]^+$ 347 (100), 276 (87), 263 (54); HRMS (EI) *m/z* calcd for $C_{12}H_{15}BBr_2O_2$ M^+ 359.9532, found 359.9533.

Borylation of 3-Chloroanisole with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (3.6 mg, 0.0054 mmol), dtbpy (2.6 mg, 0.0097 mmol), 3-chloroanisole (1.22 mL, 9.96 mmol), and **1a** (270 μL, 0.992 mmol) gave **7** (99% by GC analysis) after 4 h. Purification of silica gel gave **7** (140.5 mg, 53%) as a pale orange oil. $R_f =$ 0.37 in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.37 (dd, 1H, J = 0.7, 2.0 Hz, Ar-H), 7.19 (dd, 1H, $J = 0.6$, 2.5 Hz), 6.98 (t, 1H, $J = 2.2$ Hz, Ar-H), 3.82 (s, 3H, OCH_3), 1.34 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 159.82, 134.52, 126.79, 117.66, 117.35, 84.12, 55.45, 24.78; ^{11}B NMR ($CDCl_3$) δ 30.1; GC/MS (EI) *m/z* (% relative intensity) M^+ 268 (78), $[M - Me]^+$ 253 (46), 182 (100), 168 (78); HRMS (EI) *m/z* calcd for $C_{13}H_{18}BClO_3$ M^+ 268.1038, found 268.1036. Anal. Calcd for $C_{13}H_{18}BClO_3$: C, 58.14; H, 6.76; N, 0.00. Found: C, 58.25; H, 6.42; N, <0.02.

Borylation of 1,3-Dichlorobenzene with Et$_3$SiBpin. The reaction of $Ir(cod)OMe]_2$ (3.2 mg, 0.0048 mmol), dtbpy (2.8 mg, 0.010 mmol), 1,3-dichlorobenzene (1.14 mL, 9.99 mmol), and **1a** (270 μL, 0.992 mmol) gave **8** (96% by GC analysis) after 4 h. Purification of silica gel gave **8** (150.3 mg, 56%) as a pale pink oil. $R_f = 0.46$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.65 (d, 1H, $J = 2.1$ Hz, Ar-H), 7.43 (t, 1H, $J = 2.0$ Hz, Ar-H), 1.34 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 134.7, 132.7, 131.06, 84.48, 24.81; ^{11}B NMR ($CDCl_3$) δ 29.8; GC/MS (EI) *m/z* (% relative intensity) M^+ 272 (44), $[M - Me]^+$ 257 (82), 186 (100), 173 (52); HRMS (EI) *m/z* calcd for $C_{12}H_{15}BCl_2O_2$ M^+ 272.0542, found 272.0542.

Borylation of 1,3-Bis(trifluoromethyl)benzne with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$(3.6 mg, 0.0054 mmol), dtbpy (2.7 mg, 0.010 mmol), 1,3-bis(trifluoromethyl)benzene (1.55 mL, 9.98 mmol), and **1a** (270 μL, 0.992 mmol) gave **9** (88% by GC analysis) after 4 h. Purification of silica gel gave **9** (181.4 mg, 54%) as a white solid. The spectroscopic characterization of arylboronic ester **9** has been previously described.[45]

Borylation of Toluene with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (6.5 mg, 0.0098 mmol), dtbpy (5.6 mg, 0.021 mmol), toluene (1.06 mL, 9.95 mmol), and **1a** (270 μL, 0.992 mmol) gave **10** (92% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl-, *meta*-, and *para*-borylated products in a 2.6:1.8:1 ratio. Purification of silica gel gave **10** (140.0 mg, 65%) as a colorless oil, in a 2.7:2.0:1 ratio of benzyl: *meta*:*para*-substituted products. The spectroscopic characterization of benzylboronic ester **10a**[46] and both isomers of arylboronic ester **10b**[36] has been previously described.

Borylation of *meta*-Xylene with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (6.5 mg, 0.0098 mmol), dtbpy (5.9 mg, 0.022 mmol), *meta*-xylene (1.22 mL, 9.97 mmol), and **1a** (270 μL, 0.992 mmol) gave **11** (86% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl- and *meta*-borylated products in a 8:1 ratio. Purification on silica gel gave **11** (163.9 mg, 71%) as a pale pink oil, in a 7:1 ratio of benzyl: *meta*-substituted products. The spectroscopic characterization of benzylboronic ester **11a**[46] and arylboronic ester **11b**[36] has been previously described.

Borylation of 3-Chlorotoluene with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (3.2 mg, 0.0048 mmol), dtbpy (2.7 mg, 0.010 mmol), 3-chlorotoluene (1.18 mL, 9.99 mmol), and **1a** gave **12** (88% by GC analysis) after 4 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl- and *meta*-borylated products in a 1:1.5 ratio. Purification on silica gel gave **12** (180.4 mg, 72%) as a pale pink oil, in a 1:1.7 ratio of benzyl: *meta*-substituted products. **12a**: $R_f = 0.35$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.18 (m, 1H, Ar-H), 7.16 (t, 1H, $J = 7.8$ Hz, Ar-H), 7.10 (m, 1H, Ar-H), 7.06 (m, 1H, Ar-H), 2.27 (s, 2H, CH_2-Bpin), 1.24 (s, 12H, Bpin-CH_3), 1.24 (t, 3H, $J = 7.5$ Hz, $CH_2\underline{CH_3}$); ^{13}C NMR ($CDCl_3$) δ 133.86, 133.77, 129.56, 129.01, 127.15, 125.02, 83.54, 24.65, 19.64 (br s); ^{11}B NMR ($CDCl_3$) δ 32.4; GC/MS (EI) *m/z* (% relative intensity) M^+ 252 (48), $[M - Me]^+$ 237 (31), 166 (71), 152 (74), 117 (63), 83 (100), 59 (29). **12b**: $R_f =$ 0.46 in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.59 (m, 1H, Ar-H), 7.49 (m, 1H, Ar-H), 7.25 (m, 1H, Ar-H), 2.33 (s, 3H, Ar-CH_3), 1.34 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 140.73, 139.19, 133.37, 131.83, 131.48, 84.02, 24.79, 20.91; ^{11}B NMR (C_6D_6) δ 30.4; GC/MS (EI) *m/z* (% relative intensity) M^+ 252 (32), $[M - Me]^+$ 237 (39), 166 (100), 153 (85), 117 (37); HRMS (EI) *m/z* calcd for $C_{13}H_{18}BClO_2$ M^+ 252.1088, found 252.1089. Anal. Calcd for $C_{13}H_{18}BClO_2$: C, 61.83; H, 7.18; N, 0.00. Found: C, 61.83; H, 7.01; N, <0.02.

Borylation of 1,3,5-Trimethylbenzene with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (6.6 mg, 0.010 mmol), dtbpy (5.3 mg, 0.020 mmol), 1,3,5-trimethylbenzene (1.39 mL, 9.99 mmol), and **1a** (270 μL, 0.992 mmol) gave **13** (95% by GC analysis) after 12 h. Purification of silica gel gave **13** (186.5 mg, 78%) as a pale yellow oil. $R_f = 0.40$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 6.80 (s, 2H, Ar-H), 6.76 (s, 1H, Ar-H), 2.26 (s, 6H, Ar-CH_3), 2.21 (s, 2H, CH_2-Bpin), 1.24 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 138.28, 137.55, 126.80, 126.52, 83.30, 24.66, 21.23, 19.74 (br s); ^{11}B NMR ($CDCl_3$) δ 32.8; GC/MS (EI) *m/z* (% relative intensity) M^+ 246 (89), $[M - Me]^+$ 231 (27), 160 (42), 146 (100), 131 (22), 119 (62), 105 (29), 83 (28); HRMS (EI) *m/z* calcd for $C_{15}H_{23}BO_2$ M^+ 246.1791, found 246.1793. Anal. Calcd for $C_{15}H_{23}BO_2$: C, 73.19; H, 9.42; N, 0.00. Found: C, 73.44; H, 9.68; N, <0.02.

Borylation of 2,3,4,5,6-Pentafluorotoluene with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (6.6 mg, 0.010 mmol), dtbpy (5.4 mg, 0.020 mmol), 2,3,4,5,6-pentafluorotoluene (1.26 mL, 9.96 mmol), and **1a** (270 μL, 0.992 mmol) gave **14** (79% by GC analysis) after 12 h. Purification of silica gel gave **14** (194.4 mg, 64%) as a pale pink oil. $R_f = 0.21$ (compound streaks on TLC plate) in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 2.25 (br s, 2H, CH_2), 1.24 (s, 12H, Bpin-CH_3); ^{13}C NMR ($CDCl_3$) δ 144.82 (d of m, $J = 243.5$ Hz), 138.86 (ttd, $J = 4.8$, 13.7, 250.2 Hz), 137.37 (d of m, $J = 248.6$ Hz), 112.71 (dt, $J = 3.7$, 19.6 Hz), 84.17, 24.54, 6.02 (br s), 0.97; ^{11}B NMR ($CDCl_3$) δ 32.2; ^{19}F NMR ($CDCl_3$) δ −144.4 (dd, $J =$ 8.8, 22.9 Hz), −161.1 (t, $J = 21.0$ Hz), −165.0 (dt, $J = 7.7$, 21.3 Hz); GC/MS (EI) *m/z* (% relative intensity) M^+ 308 (7), $[M - Me]^+$ 293 (56), 235 (19), 208 (30), 202 (57), 189 (23), 181 (34), 85 (100), 59 (50); HRMS (EI) *m/z* calcd for $C_{13}H_{14}BF_5O_2$ $(M - H)^+$ 308.1007, found 308.1008.

Borylation of Ethylbenzene with Et$_3$SiBpin. The reaction of $[Ir(cod)OMe]_2$ (6.6 mg, 0.010 mmol), dtbpy (5.6 mg, 0.021 mmol), ethylbenzene (1.22 mL, 9.96 mmol), and **1a** (270 μL, 0.992 mmol) gave **15** (71% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed *meta*- and para-borylated products in a 2.3:1 ratio. Purification on silica gel gave **15** (138.0 mg, 60%) as a pale pink oil, in a 2.4:1 ratio of *meta*: *para*-substituted products. **15**, *meta*-isomer: $R_f = 0.38$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.65 (s, 1H, Ar-H), 7.63 (m, 1H, Ar-H), 7.30 (m, 1H, Ar-H), 2.65 (q, 2H, $J = 7.6$ Hz, $C\underline{H_2}CH_3$), 1.35 (s, 12H, Bpin-CH_3), 1.24 (t, 3H, $J = 7.5$ Hz, $CH_2C\underline{H_3}$); ^{13}C NMR ($CDCl_3$) δ 143.43, 134.19, 132.06, 130.83, 127.72, 83.63, 28.77, 24.80, 15.71; ^{11}B NMR ($CDCl_3$) δ 30.7; GC/MS (EI) *m/z*

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(% relative intensity) M^+ 232 (47), $[M - Me]^+$ 217 (57), 146 (100), 133 (100), 117 (38). **15**, *para*-isomer: $R_f = 0.43$ in 5% EtOAc in hexane; ^{1}H NMR ($CDCl_3$) δ 7.74 (d, 1H, $J = 8.0$ Hz, Ar-H), 7.21 (d, 1H, $J = 7.9$ Hz, Ar-H), 2.66 (q, 2H, $J = 7.6$ Hz, $C\underline{H}_2CH_3$), 1.34 (s, 12H, Bpin-CH_3), 1.23 (t, 3H, $J = 7.5$ Hz, $CH_2C\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 147.66, 134.86, 127.29, 83.53, 29.06, 24.80, 15.44; ^{11}B NMR ($CDCl_3$) δ 30.7; GC/MS (EI) *m*/*z* (% relative intensity) M^+ 232 (41), $[M - Me]^+$ 217 (53), 146 (80), 133 (100), 117 (31). **15**, mixture of isomers: HRMS (EI) *m*/*z* calcd for $C_{14}H_{21}BO_2$ M^+ 232.1635, found 232.1638. Anal. Calcd for $C_{14}H_{21}BO_2$: C, 72.44; H, 9.12; N, 0.00. Found: C, 72.16; H, 9.38; N, <0.02.

Borylation of *m*-Xylene with B_2pin_2. The reaction of [Ir(cod)OMe]$_2$ (6.7 mg, 0.010 mmol), dtbpy (5.6 mg, 0.021 mmol), B_2pin_2 (254 mg, 1.00 mmol), and *m*-xylene (1.22 mL, 9.97 mmol) gave **11b** (83% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed **11b** as the only isomeric product. Purification of silica gel gave **11b** (352.1 mg, 76%) as a pale pink oil.

Borylation of *m*-xylene with *t*-BuMe$_2$SiBpin. The reaction of [Ir(cod)OMe]$_2$ (6.4 mg, 0.0097 mmol), dtbpy (5.4 mg, 0.020 mmol), *m*-xylene (1.22 mL, 9.97 mmol), and **1e** (201 mg, 0.829 mmol) gave **11** (75% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl- and *meta*-borylated products in a 2.3:1 ratio. Purification on silica gel gave **11** (143.2 mg, 74%) as a pale pink oil, in a 2.1:1 ratio of benzyl:*meta*-substituted products.

Borylation of *m*-Xylene with *n*-Bu$_3$SiBpin. The reaction of [Ir(cod)OMe]$_2$ (6.8 mg, 0.010 mmol), dtbpy (5.6 mg, 0.021 mmol), *m*-xylene (1.22 mL, 9.97 mmol), and **1c** (375 μL, 1.01 mmol) gave **11** (65% by GC analysis) after 12 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl- and *meta*-borylated products in a 13.3:1 ratio. Purification on silica gel gave **11** (142.2 mg, 61%) as a pale pink oil, in a 11.3:1 ratio of benzyl:*meta*-substituted products.

Borylation of 3-Chlorotoluene with B_2pin_2. The reaction of [Ir(cod)OMe]$_2$ (3.3 mg, 0.0050 mmol), dtbpy (2.8 mg, 0.010 mmol), B_2pin_2 (253 mg, 1.00 mmol), and 3-chlorotoluene (1.18 mL, 9.99 mmol) gave **12b** (102% by GC analysis) after 4 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed **12b** as the only isomeric product. Purification on silica gel gave **12b** (348.2 mg, 69%) as a white solid.

Borylation of 3-Chlorotoluene with *t*-BuMe$_2$SiBpin. The reaction of [Ir(cod)OMe]$_2$ (3.4 mg, 0.0051 mmol), dtbpy (2.8 mg, 0.010 mmol), 3-chlorotoluene (1.18 mL, 9.99 mmol), and **1e** (243 mg, 1.00 mmol) gave **12** (98% by GC analysis) after 4 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl- and *meta*-borylated products in a 1:9.3 ratio. Purification on silica gel gave **12** (163.4 mg, 65%) as a pale pink oil, in a 1:6.2 ratio of benzyl:*meta*-substituted products.

Borylation of 3-Chlorotoluene with *n*-Bu$_3$SiBpin. The reaction of [Ir(cod)OMe]$_2$ (3.4 mg, 0.0051 mmol), dtbpy (2.6 mg, 0.0097 mmol), 3-chlorotoluene (1.18 mL, 9.99 mmol), and **1c** (375 μL, 1.01 mmol) gave **12** (87% by GC analysis) after 4 h. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy showed benzyl- and *meta*-borylated products in a 1.5:1 ratio. Purification on silica gel gave **12** (158.7 mg, 62%) as a pale pink oil, in a 1.1:1 ratio of benzyl:*meta*-substituted products.

Borylation of 3-Chlorotoluene with Et$_3$SiBpin. Evaluation of Ratio of Benzylic vs Aryl C−H Functionalization over Time. Inside a nitrogen-filled glovebox, an oven-dried 20 mL vial was charged with [Ir(cod)OMe]$_2$ (3.3 mg, 0.0050 mmol), dtbpy (2.7 mg, 0.010 mmol), 3-chlorotoluene (1.18 mL, 9.99 mmol), *n*-dodecane (20 μL, 0.088 mfmol), and **1a** (270 μL, 0.992 mmol). The resulting dark brown solution was heated at 80 °C inside the glovebox. Reaction aliquots (5 μL) were removed at 10 min intervals and diluted with diethyl ether (1.5 mL) for subsequent GC analysis. After 120 min, GC analysis indicated complete conversion of 3-chlorotoluene to **12a** and **12b**, in a 1:1.6 ratio.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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