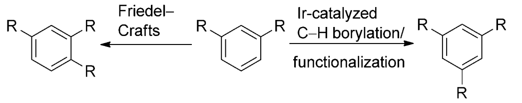
Arene Alkylation

DOI: 10.1002/anie.201208203

Sterically Controlled Alkylation of Arenes through Iridium-Catalyzed C–H Borylation**

*Daniel W. Robbins and John F. Hartwig**

Alkylarenes are conventionally prepared by electrophilic aromatic substitution with carbon electrophiles (Friedel–Crafts reactions), but these methods have many limitations. First, arenes containing electron-withdrawing groups are much less reactive than those containing electron-donating groups. Second, the electrophiles often undergo rearrangements, limiting the utility for the synthesis of linear alkylarenes. Third, the electronic effects prevent formation of products containing alkyl groups located *meta* to electron-donating groups [Eq. (1)].[1]



(1)

The site-selectivity for the formation of C–C bonds at aromatic systems can be altered by transition-metal-catalyzed C–H bond functionalization. However, transition-metal-catalyzed alkylation of aromatic C–H bonds has typically been limited to reactions that are either intramolecular or occur at positions ortho to a directing group.[2]

Iridium-catalyzed borylation could provide a method for the alkylation of arenes with alternative selectivity. The site-selectivity of iridium-catalyzed C–H borylation is predominantly controlled by steric factors [Eq. (1)].[3] Therefore, a sterically controlled arene alkylation could be envisioned to occur by the combination of C–H borylation, followed by alkylation of the resulting arylboronate ester. However, methods to form sp^3 carbon–aryl linkages with the products of the C–H borylation are not known.[4] The pinacolboronate esters formed by C–H borylation are significantly less reactive than other aryl boron species such as aryl boronic acids, for which coupling reactions with alkyl halides are known.[4a,5]

Herein, we report the discovery of a one-pot method for the *meta*-selective allylation, benzylation, and alkylation of arenes through Ir-catalyzed C–H borylation, followed by Pd- and Ni-catalyzed coupling of the resulting arylboronate ester with allyl, benzyl, and unactivated alkyl electrophiles, including secondary alkyl electrophiles. This transformation is a surrogate for *meta*-selective Friedel–Crafts arene alkylation with site-selectivity controlled by steric effects.

Our efforts to develop the alkylation of arenes by the combination of C–H borylation and cross-coupling began with a survey of existing systems reported for the coupling of alkyl halides with organoboron species. Palladium catalysts are less effective for the coupling of alkyl halides than for the coupling of aryl halides because of the slow oxidative addition of alkyl halides and β-hydride elimination from the alkylpalladium intermediate formed from oxidative addition. To address these limitations, iron,[6] nickel,[7] and copper[8] catalysts have been developed for the Suzuki coupling of alkyl halides or pseudohalides.

However, the current iron-catalyzed Suzuki coupling of alkyl halides with aryl boronate esters requires complexation of the aryl boronate with an alkyl lithium reagent, limiting the operational simplicity and functional-group tolerance of this method. The current copper-catalyzed alkylation of pinacol-substituted arylboronates is limited to a single example, and this reaction of an alkyl tosylate occurred in modest yield. The existing nickel-catalyzed Suzuki couplings of alkyl halides are limited to reactions of boronic acids or 9-BBN-derivatives. Because transmetallation has been proposed to be the rate-limiting step in nickel-catalyzed cross-coupling with alkyl halides, it was unclear whether the less-reactive pinacol boronate esters would participate in this transformation.[9]

To identify a system that couples alkyl halides with aryl pinacolboronates, we initially examined various copper and nickel catalysts for the reaction of phenyl pinacol boronate with 1-iodooctane or 1-octyl *p*-toluenesulfonate (Table 1). The highest yield of 1-phenyloctane was obtained from reactions conducted in the presence of $NiBr_2$(dme) (dme = dimethoxyethane) as the precatalyst with *trans-N,N'*-dimethylcyclohexane-1,2-diamine (**L4**) as the ancillary ligand.[10] This reaction, catalyzed by $NiBr_2$(dme), **L4**, and KO*t*Bu base in 2-butanol and dioxane, formed 1-octylbenzene in 68% yield after 18 h at 60°C (Table 1).

Having identified conditions for the coupling of aryl pinacolboronate esters with primary alkyl halides, we developed a one-pot procedure for the alkylation of arenes. Reactions of 1,3-disubstituted arenes with bis(pinacolato)diboron (B_2pin_2) in the presence of a catalyst formed in situ from the combination of [{Ir(cod)OMe}$_2$] (cod = 1,5-cyclooctadiene) and 4,4'-di-*tert*-butylbipyridine (dtbpy) in THF at

---

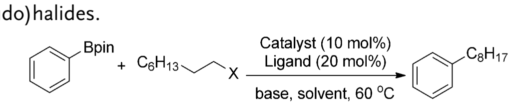
[*] D. W. Robbins, Prof. J. F. Hartwig[+]
Department of Chemistry, University of Illinois
Urbana-Champaign, Urbana, IL 61801 (USA)
E-mail: jhartwig@berkeley.edu

[+] Current address: University of California, Department of Chemistry, 718 Latimer Hall, Berkeley, CA 94720 (USA)

[**] We thank the NSF (CHE-0910641) for support, Johnson-Matthey for a gift of iridium, and Allychem for a gift of B_2pin_2. We also thank the American Chemical Society Division of Organic Chemistry (sponsored by Boehringer Ingelheim) for fellowship support (D.W.R.).

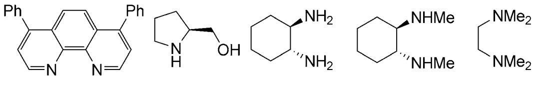
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208203.

Table 1: Effect of conditions on the coupling of PhBpin with alkyl (pseudo)halides.

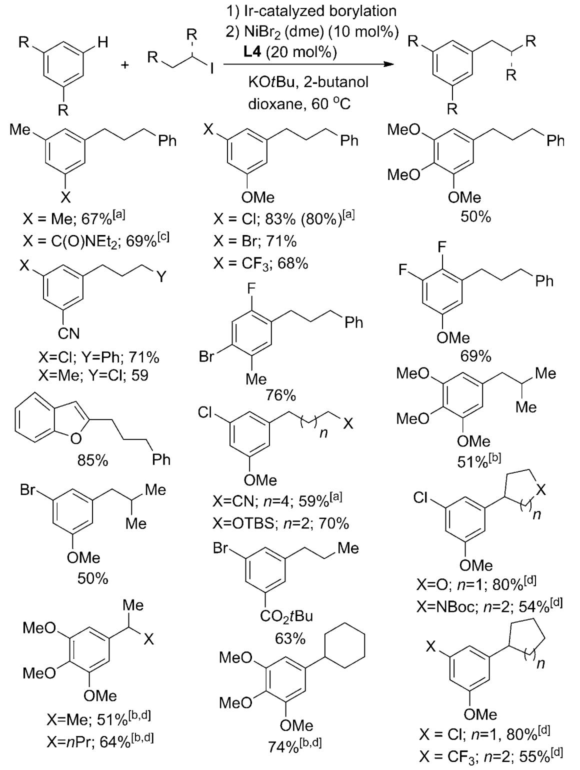


Entry	Catalyst[a]	Ligand	X	Yield [%][b]
1	CuI	none	OTs	44
2	CuI	PPh_3	OTs	57
3[c]	CuI	1,10-phen	OTs	32
4	$NiCl_2$(dme)	**L1**	I	44
5	$NiCl_2$(dme)	**L2**	I	26
6	$NiCl_2$(dme)	**L3**	I	44
7	$NiCl_2$(dme)	**L4**	I	58
8	$NiCl_2$(dme)	**L5**	I	27
9	**$NiBr_2$(dme)**	**L4**	**I**	**68**
10	$NiBr_2$(dme)	**L4**	Br	55
11[d]	**$NiBr_2$(dme)**	**L4**	**Br**	**69**

[a] Cu-catalyzed reactions conducted with LiO*t*Bu (2 equiv); Ni-catalyzed reactions conducted with KO*t*Bu (1.2 equiv) and 2-butanol (2 equiv). [b] Yield determined by GC with an internal standard. [c] 10 mol% ligand used. [d] NaI (1 equiv) added. 1,10-phen = 1,10-phenanthroline, Ts = *p*-toluenesulfonyl.



L1 **L2** **L3** **L4** **L5**



Scheme 1. Scope of the alkylation with unactivated alkyl electrophiles. [a] Alkylation conducted with alkyl bromide and NaI. [b] Borylation conducted with [{Ir(cod)OMe}$_2$] (0.5 mol%) and dtbpy (1.0 mol%). [c] Borylation conducted with [{Ir(cod)OMe}$_2$] (1.0 mol%) and dtbpy (2.0 mol%). [d] Alkylation conducted with **L1**. Boc = *tert*-butoxycarbonyl.

80 °C,[11] followed by addition of the nickel catalyst, KO*t*Bu, 2-butanol, and dioxane to the crude arylboronate ester and heating at 60 °C, gave the *meta*-alkylation product in good yield.[12]

The scope of the *meta*-selective alkylation with unactivated alkyl halides in the presence of the iridium and nickel catalysts is shown in Scheme 1. Arenes containing a variety of substituents reacted, including those containing ethers, esters, nitriles, amides, and trifluoromethyl groups. The coupling of an alkyl halide occurred in preference to the coupling of an aryl halide. The reaction with benzofuran occurred at the 2-position in good yield, thus providing a method for the alkylation of five-membered ring heteroarenes at the less electron-rich position. The pinacolboronates generated by the iridium-catalyzed borylation *ortho* to fluorine also coupled with alkyl iodides in good yield, despite the propensity of the corresponding boronic acids to undergo protodeborylation in other Suzuki coupling processes.[13]

The examples in Scheme 1 also reveal the range of alkyl halides that undergo this arene alkylation process. Alkyl halides containing a TBS-protected (TBS = *tert*-butyldimethylsilyl) alcohol and a nitrile coupled in acceptable yield. Alkyl iodides containing a branch point at the position β to the halogen also coupled in good yield. Primary alkyl bromides also coupled with pinacol boronates in good yield when the reactions were conducted with added NaI to initiate halogen exchange, followed by coupling of the alkyl iodide generated in situ with the aryl pinacol boronate ester. In each case, no rearrangement, which would be observed for a true Friedel–Crafts reaction, occurred.

The sterically controlled, *meta*-selective alkylations of arenes also occurred with secondary alkyl halides. With the nickel catalyst bearing diamine **L4** as the ancillary ligand, only trace amounts of the product from the coupling of phenyl pinacolboronate ester with iodocyclohexane was observed. However, the same reaction catalyzed by $NiBr_2$(dme) with bathophenanthroline (**L1**) as the ancillary ligand occurred in 67% yield. Moreover, these conditions were compatible with the one-pot protocol involving borylation of the arene and coupling of the arylboronate with a secondary alkyl halide.

As shown by examples in Scheme 1, cyclic and acyclic secondary alkyl iodides and bromides coupled in good yield with several arenes generated by the C–H borylation chemistry. The alkylation of arenes possessing methoxy, chloro, and trifluoromethyl groups with iodocyclopentanes and cyclohexanes occurred regioselectively. The alkylation of 3-chloroanisole with 3-iodotetrahydrofuran and an iodopiperidine derivative occurred without any rearrangement of the alkyl group during the coupling process. Even the reaction of the acyclic 2-bromopentane occurred without rearrangement. The primary side products from the alkylation reaction were those from protodehalogenation of the alkyl halide.

The success of this combination of C–H borylation and the coupling of alkylhalides led us to extend this strategy to the allylation and benzylation of arenes with steric control. Few examples of the catalytic direct allylation of arenes have been published,[14] and the known direct benzylation of aromatic and heteroaromatic C–H bonds have required either acidic C–H bonds or a directing group.[15] If methods for the allylation and benzylation of pinacolate-substituted arylboronate esters could be identified, then a method for the allylation and benzylation of arenes with stereocontrol would result.

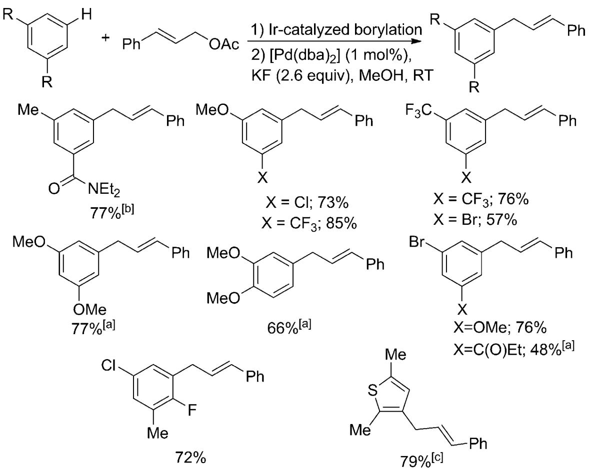
Several methods for the coupling of organoboranes with allylic acetates, alcohols, and halides catalyzed by phosphine-ligated palladium complexes have been developed.[16] After surveying previously reported reaction conditions for the allylation of electron-rich and electron-deficient, pinacol-substituted arylboronate esters with cinnamyl acetate, we found that $[Pd(dba)_2]$ (dba = dibenzylideneacetone) with KF as an additive and no added ligand in MeOH solvent at room temperature provided the *meta*-allylation products of aryl pinacolboronate esters in good yield.[17]

Several methods for the Pd-catalyzed coupling of organometallic reagents with benzylic electrophiles, including halides and phosphates, have also been developed.[18] After examining catalysts formed from the combination of several common phosphine ligands with $[Pd(dba)_2]$, we found that catalysts containing phosphine ligands gave higher yields for the coupling of the aryl boronate esters with benzylic halides than did ligandless catalysts. The simple catalyst formed in situ from the combination of $[Pd(dba)_2]$ and PPh_3 with Na_2CO_3 in a mixture of THF and H_2O at 100 °C provided good yields of the product from the coupling of electron-rich and electron-deficient pinacol-substituted aryl boronate esters with 4-methylbenzyl bromide.

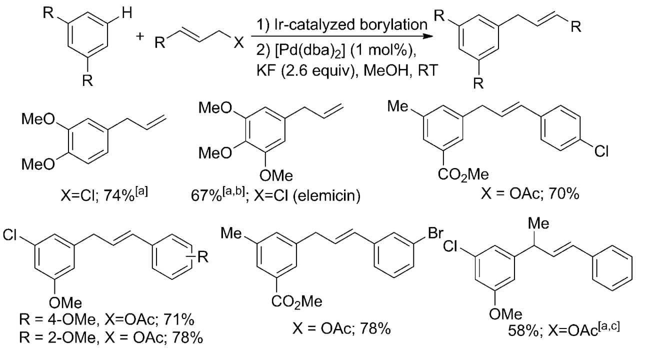
With these methods for the coupling of aryl pinacolboronate esters with cinnamyl acetate and 4-methylbenzyl bromide, we developed the one-pot *meta*-allylation and *meta*-benzylation of arenes. Reactions of 1,3-disubstituted arenes with B_2pin_2 in the presence of a catalyst formed in situ from the combination of $[\{Ir(cod)OMe\}_2]$ and dtbpy in THF at 80 °C,[11] followed by addition of the appropriate Pd catalyst, the allylic or benzylic electrophile, the additive, and solvent gave good yield of the *meta*-allylation or *meta*-benzylation product.

The scope of the *meta*-allylation of 1,2-, and 1,3-substituted arenes with cinnamyl acetate is summarized in Scheme 2. These reactions formed the *meta*-allylation products in good yield from electron-rich and electron-deficient arenes and tolerated a variety of functional groups, including aryl fluorides, chlorides, and bromides, as well as esters, amides, ethers, and trifluoromethyl groups. Ketones on the arene did not undergo reduction of the carbonyl group. Tetrasubstituted arenes were also synthesized from 1,2,4-trisubstituted arenes by borylation *ortho* to a fluorine substituent on the arene. Site-selective allylation was performed on a thiophene derivative in good yield with cinnamyl chloride as the allylic electrophile in place of cinnamyl acetate.

This allylation process occurred with a series of allyl electrophiles (Scheme 3). The conversion of arenes to allylarenes occurred with substituted cinnamyl acetates, as well as allyl chloride itself. Cinnamyl electrophiles that underwent this process include those containing electron-donating groups, electron-withdrawing groups, and *ortho*-substituents. Cinnamyl acetates containing chloride and bromide substituents reacted without cleavage of the aromatic carbon–halogen bond. The reaction with the parent allyl chloride occurred in good yield. Allylbenzenes, the products of these reactions, are known to undergo olefin cross metathesis to generate 1,2-disubstituted olefins.[19] Moreover, one allylarene, elemicin,[20] is a natural product studied for its antibacterial activity[21] and was prepared by a one-pot borylation–allylation sequence in 67 % yield.

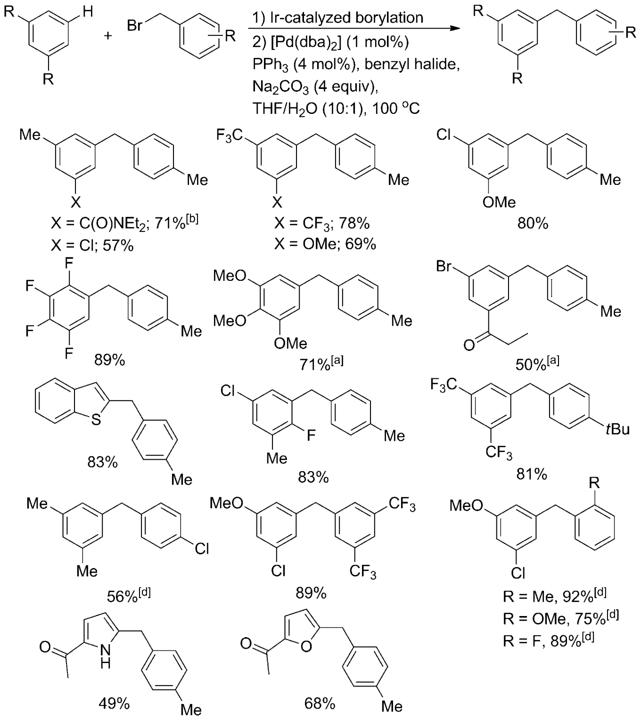


Scheme 2. Scope of the allylation of 1,3-disubstituted arenes with cinnamyl acetate. [a] Borylation conducted with $[\{Ir(cod)OMe\}_2]$ (0.5 mol %) and dtbpy (1.0 mol %). [b] Borylation conducted with $[\{Ir(cod)OMe\}_2]$ (1.0 mol %) and dtbpy (2.0 mol %). [c] Allylation conducted with cinnamyl chloride.



Scheme 3. Scope of the allylation with various allylic electrophiles. [a] Allylation conducted with $[Pd(dba)_2]$ (2 mol %). [b] Borylation conducted with $[\{Ir(cod)OMe\}_2]$ (0.5 mol %) and dtbpy (1.0 mol %). [c] 14:1 mixture of linear/branched isomers.

The scope of the *meta*-benzylation is summarized in Scheme 4. These examples also include reactions of electron-rich and electron-deficient arenes containing a variety of functional groups. Benzylation of benzothiophene occurred at the C2 position, whereas the uncatalyzed benzylation of five-membered ring heterocycles is known to occur at C3.[22] Thus, this approach to arene alkylation leads to site selectivity that is orthogonal to that of the alkylation of heteroarenes mediated by Lewis acids. The *meta*-selective borylation and benzylation was performed with a variety of benzyl halides. Similar yields were obtained when benzylic bromides and



Scheme 4. Scope of the benzylation of 1,3-disubstituted arenes with benzylic bromides and chlorides. [a] Borylation conducted with [{Ir(cod)OMe}$_2$] (0.5 mol%) and dtbpy (1.0 mol%). [b] Borylation conducted with [{Ir(cod)OMe}$_2$] (1.0 mol%) and dtbpy (2.0 mol%). [c] Benzylation conducted with a benzyl chloride.

benzylic chlorides were used as the alkyl electrophile. Benzylic halides containing electron-donating groups, electron-withdrawing groups, and *ortho*-substituents all reacted in good yield.

In conclusion, a method for the site-selective alkylation, allylation, and benzylation of arenes through Ir-catalyzed borylation and Ni- or Pd-catalyzed coupling has been developed. The method is effective with various allylic, benzylic, primary alkyl, and secondary alkyl electrophiles. This approach to arene alkylation gives products with site-selectivity that is complementary to that of Friedel–Crafts alkylation, C–H functionalization methods controlled by directing groups, or C–H functionalization methods in which the site-selectivity is governed by electronic effects.

Experimental Section

General Procedure for Alkylation of Arenes with Primary Alkyl Halides: Inside a glove box, [{Ir(cod)OMe}$_2$] (2.5 mg, 0.0038 mmol, 0.0038 equiv), dtbpy (2.0 mg, 0.0075 mmol, 0.0075 equiv), B$_2$pin$_2$ (229 mg, 0.900 mmol, 0.900 equiv), arene (1.50 mmol, 1.50 equiv), and THF (3 mL) were added to a dry vial with a magnetic stir bar. The vial was sealed and heated at 80 °C for 18 h. The reaction mixture was cooled to room temperature, and the volatile materials were removed under vacuum. NiBr$_2$(dme) (30.9 mg, 0.100 mmol, 0.100 equiv), *trans-N,N'*-dimethylcyclohexane-1,2-diamine (28.5 mg, 0.200 mmol, 0.200 equiv), an alkyl halide (1.00 mmol, 1.00 equiv), KO*t*Bu (135 mg, 1.20 mmol, 1.20 equiv), 2-butanol (149 mg, 2.00 mmol, 2.00 equiv) and 1,4-dioxane (2 mL) were added consecutively to the reaction mixture. The reaction mixture was stirred at 60 °C for 15 h. The reaction mixture was then cooled to room temperature, filtered through silica gel (which was then washed with EtOAc), and concentrated under vacuum. The residue was then purified by column chromatography to give the product.

Received: October 11, 2012
Published online: December 11, 2012

Keywords: alkylation · arenes · iridium · nickel · palladium

---

[1] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry. Part B: Reactions and Synthesis*, 5th ed., Springer, New York, **2007**.

[2] a) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; b) P. Ren, I. Salihu, R. Scopelliti, X. Hu, *Org. Lett.* **2012**, *14*, 1748; c) O. Vechorkin, V. Proust, X. Hu, *Angew. Chem.* **2010**, *122*, 3125; *Angew. Chem. Int. Ed.* **2010**, *49*, 3061.

[3] I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890.

[4] a) J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, M. R. Smith, *Science* **2002**, *295*, 305; b) G. A. Chotana, V. A. Kallepalli, R. E. Maleczka, Jr., M. R. Smith III, *Tetrahedron* **2008**, *64*, 6103; c) P. Harrisson, J. Morris, T. B. Marder, P. G. Steel, *Org. Lett.* **2009**, *11*, 3586; d) T. Ishiyama, Y. Nobuta, J. F. Hartwig, N. Miyaura, *Chem. Commun.* **2003**, 2924.

[5] a) J. M. Murphy, X. Liao, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 15434; b) J. M. Murphy, C. C. Tzschucke, J. F. Hartwig, *Org. Lett.* **2007**, *9*, 757; c) C. C. Tzschucke, J. M. Murphy, J. F. Hartwig, *Org. Lett.* **2007**, *9*, 761; d) R. E. Maleczka, Jr., F. Shi, D. Holmes, M. R. Smith, *J. Am. Chem. Soc.* **2003**, *125*, 7792; e) C. W. Liskey, X. Liao, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 11389; f) N. D. Litvinas, P. S. Fier, J. F. Hartwig, *Angew. Chem.* **2012**, *124*, 551; *Angew. Chem. Int. Ed.* **2012**, *51*, 536; g) T. Liu, X. Shao, Y. Wu, Q. Shen, *Angew. Chem.* **2012**, *124*, 555; *Angew. Chem. Int. Ed.* **2012**, *51*, 540.

[6] T. Hatakeyama, T. Hashimoto, Y. Kondo, Y. Fujiwara, H. Seike, H. Takaya, Y. Tamada, T. Ono, M. Nakamura, *J. Am. Chem. Soc.* **2010**, *132*, 10674.

[7] a) F. González-Bobes, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 5360; b) Z. Lu, G. C. Fu, *Angew. Chem.* **2010**, *122*, 6826; *Angew. Chem. Int. Ed.* **2010**, *49*, 6676; c) G. A. Molander, O. A. Argintaru, I. Aron, S. D. Dreher, *Org. Lett.* **2010**, *12*, 5783; d) B. Saito, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 9602; e) J. Zhou, G. C. Fu, *J. Am. Chem. Soc.* **2004**, *126*, 1340.

[8] C.-T. Yang, Z.-Q. Zhang, Y.-C. Liu, L. Liu, *Angew. Chem.* **2011**, *123*, 3990; *Angew. Chem. Int. Ed.* **2011**, *50*, 3904.

[9] a) X. Hu, *Chem. Sci.* **2011**, *2*, 1867; b) Z. Li, Y.-Y. Jiang, Y. Fu, *Chem. Eur. J.* **2012**, *18*, 4345.

[10] This ligand was used previously for the coupling of alkyl halides with 1-alkyl-BBN derivatives; see Ref. [13d].

[11] T. Ishiyama, J. Takagi, J. F. Hartwig, N. Miyaura, *Angew. Chem.* **2002**, *114*, 3182; *Angew. Chem. Int. Ed.* **2002**, *41*, 3056.

[12] Ir-catalyzed borylation of electron-deficient arenes and heteroarenes in high yield can be conducted at lower temperatures.

[13] a) T. Kinzel, Y. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.* **2010**, *132*, 14073; b) D. W. Robbins, J. F. Hartwig, *Org. Lett.* **2012**, *14*, 4266.

[14] a) S. Fan, F. Chen, X. Zhang, *Angew. Chem.* **2011**, *123*, 6040; *Angew. Chem. Int. Ed.* **2011**, *50*, 5918; b) Y.-B. Yu, S. Fan, X. Zhang, *Chem. Eur. J.* **2012**, *18*, 14643; c) R. Hayashi, G. R. Cook, *Org. Lett.* **2007**, *9*, 1311; d) G. Onodera, H. Imajima, M. Yamanashi, Y. Nishibayashi, M. Hidai, S. Uemura, *Organometallics* **2004**, *23*, 5841.

[15] a) L. Ackermann, P. Novák, *Org. Lett.* **2009**, *11*, 4966; b) D. Lapointe, K. Fagnou, *Org. Lett.* **2009**, *11*, 4160; c) T. Mukai, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 1360.

[16] a) F. C. Pigge, *Synthesis* **2010**, 1745; b) T. Nishikata, B. H. Lipshutz, *J. Am. Chem. Soc.* **2009**, *131*, 12103; c) H. Tsukamoto, M. Sato, Y. Kondo, *Chem. Commun.* **2004**, 1200; d) T. Mino, K. Kajiwara, Y. Shirae, M. Sakamoto, T. Fujita, *Synlett* **2008**, 2711; e) N. Miyaura, K. Yamada, H. Suginome, A. Suzuki, *J. Am. Chem. Soc.* **1985**, *107*, 972; f) G. W. Kabalka, E. Dadush, M. Al-Masum, *Tetrahedron Lett.* **2006**, *47*, 7459; g) M. Moreno-Manas, F. Pajuelo, R. Pleixats, *J. Org. Chem.* **1995**, *60*, 2396.

[17] G. Ortar, *Tetrahedron Lett.* **2003**, *44*, 4311.

[18] a) R. Kuwano, M. Yokogi, *Org. Lett.* **2005**, *7*, 945; b) L. Chahen, H. Doucet, M. Santelli, *Synlett* **2003**, 1668; c) B. P. Bandgar, S. V. Bettigeri, J. Phopase, *Tetrahedron Lett.* **2004**, *45*, 6959; d) M. J. Burns, I. J. S. Fairlamb, A. R. Kapdi, P. Sehnal, R. J. K. Taylor, *Org. Lett.* **2007**, *9*, 5397; e) G. A. Molander, M. D. Elia, *J. Org. Chem.* **2006**, *71*, 9198; f) S. M. Nobre, A. L. Monteiro, *Tetrahedron Lett.* **2004**, *45*, 8225.

[19] G. C. Vougioukalakis, R. H. Grubbs, *J. Am. Chem. Soc.* **2008**, *130*, 2234.

[20] D. C. Gerbino, S. D. Mandolesi, H.-G. Schmalz, J. C. Podesta, *Eur. J. Org. Chem.* **2009**, 3964.

[21] P.-G. Rossi, L. Bao, A. Luciani, J. Panighi, J.-M. Desjobert, J. Costa, J. Casanova, J.-M. Bolla, L. Berti, *J. Agric. Food Chem.* **2007**, *55*, 7332.

[22] a) M. Bandini, A. Melloni, S. Tommasi, A. Umani-Ronchi, *Synlett* **2005**, 1199; b) A. Croisy, J. Mispelter, J.-M. Lhoste, F. Zajdela, P. Jacquignon, *J. Heterocycl. Chem.* **1984**, *21*, 353; c) P. D. Clark, K. Clarke, D. F. Ewing, R. M. Scrowston, *J. Chem. Soc. Perkin Trans. 1* **1980**, 677.