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## Synthesis of Secondary and Tertiary Alkylboranes via Formal Hydroboration of Terminal and 1,1-Disubstituted Alkenes

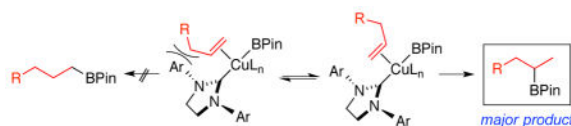
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### Abstract

Copper-catalyzed functionalization of terminal or 1,1-disubstituted alkenes with *bis*(pinacolato)diboron and methanol provides formal hydroboration products with exceptional regiocontrol favoring the branched isomer. Through pairing this procedure with photocatalytic cross couplings using iridium and nickel co-catalysis, an effective, highly regioselective procedure for the hydroarylation of terminal alkenes is provided.

### Graphical Abstract



The hydroboration of simple terminal alkenes is a transformation of fundamental importance in synthesis, and the hydroboration/oxidation sequence serves as the introduction to anti-Markovnikov regioselectivity in most introductory organic chemistry courses.<sup>1</sup> Despite the long history of this process, a general approach to reversing the regioselectivity of hydroborations of simple alkenes bearing aliphatic substituents has remained elusive. Coupled with oxidation of the resulting organoborane, this outcome would provide an equivalent process to the acid-catalyzed hydration of alkenes with accompanying advantages in scope and functional group tolerance. Additionally, we envisioned that other processes such as metal-catalyzed cross-coupling, when paired with a reversal of regiochemistry in hydroborations, would provide a useful and simple method for the synthesis of tertiary carbon frameworks through the two-step branch-selective reductive union of alkenes and  $sp^2$ -carbon electrophiles. Considering the tremendous recent advances in cross-couplings of secondary organoboranes,<sup>2–5</sup> the development of more efficient methods for accessing the requisite branched organoboranes could find immediate utility.

Most catalytic hydroboration methods provide the linear alkylborane product, often with efficiencies that greatly exceed the direct thermal addition of boranes to alkenes.<sup>6</sup> The direct

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Supporting Information

Synthetic details and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

access to branched boranes from the hydroboration of terminal olefins is typically accompanied by chain walking<sup>7</sup> that often leads to terminal or benzylic boranes. Advances in reversing the regiochemical outcome of hydroborations are often accomplished through the installation of directing groups, which can override normally expected preferences based on the alkene substitution pattern.<sup>8</sup> More recent advances illustrated that subtle remote electronic biases can also be used as a handle for regiocontrol.<sup>9</sup> Alkenes such as styrenes provide an electronic bias for the development of catalyst-substrate interactions that enable regioselectivity reversals, with notable illustrations in directly accessing benzylic boranes from the rhodium-catalyzed hydroboration of styrenes.<sup>10</sup> The copper-catalyzed addition of bis(pinacolato)diboron ( $B_2Pin_2$ ) in the presence of methanol has been utilized by Hoveyda as a formal hydroboration of terminal alkynes with regio reversal compared with traditional strategies,<sup>11</sup> whereas styrenes afforded the terminal borane product.<sup>11b</sup> The procedure, which involves borylmatalation followed by protonation of the resulting Cu-C bond, provides considerable utility as a means to access the more hindered alkenylborane products. Secondary alkylboranes, such as those that potentially could be made by a branch-selective hydroboration of terminal alkenes, are typically accessed by methods such as addition of organolithium or organomagnesium reagents to boron electrophiles,<sup>12</sup> conversion of alkyl halides to alkylboranes,<sup>13</sup> hydrogenations of vinylboranes,<sup>14</sup> or variations of the Matteson rearrangement, which has proven to be immensely useful in asymmetric versions (Scheme 1).<sup>15</sup> Impressive cascade functionalizations of terminal alkenes have enabled preparation of secondary alkylboranes in tandem with arylation or alkenylation of the terminal alkene carbon,<sup>16</sup> and reports of aminoboration and carboboration were recently disclosed.<sup>17</sup> Furthermore a recent approach from Ito described the formal hydroboration of terminal alkenes via a process catalyzed by copper phosphine complexes.<sup>18</sup> While these methods have enabled many impressive advances in the synthesis and application of secondary alkylboranes, a more general approach to the hydroboration of a variety of terminal and 1,1-disubstituted alkenes to provide a regiochemical outcome opposite that of classical thermal additions of borohydrides to alkenes would provide an important entry to branched alkylboranes for utilization in synthesis. The development of a highly regio- and branch-selective hydroboration process using a copper-NHC catalyst is described herein, and the method utility with photocatalytic cross-couplings<sup>3</sup> is demonstrated.

Efforts to access branched alkylboranes from terminal alkenes began with exploration of hydroborations using HBPIn, with Ni, Pd, Pt, Co, and Rh catalysts and the *N*-heterocyclic carbene ligands IMes, SIMes, IPr, and SIPr (Table 1, entries 1–7, selected data). In all cases, the terminal alkylborane product was favored, with Co- and Rh-catalyzed processes most strongly favoring the linear products, and no more than 21% of the desired branched products being observed in any case. We next examined additions using  $B_2Pin_2$  with methanol using Cu(I) catalysts given the success seen in regiochemistry reversals involving terminal alkynes from Hoveyda with similar catalyst systems.<sup>11</sup> The combination of CuCl with IMes provided a nearly 2:1 ratio of regioisomers favoring branched isomer **1a** (Table 1, entry 8), whereas the use of SIPr provided excellent regioselectivities favoring **1a**, albeit in modest yield (Table 1, entry 9). A solvent screen illustrated that  $CH_3CN$  provided superior conversions compared with THF and other common solvents, and a variety of Cu(I) and Cu(II) precatalysts were therefore examined in  $CH_3CN$  for yield optimization (Table 1,

entries 10–13). In cases where Cu(II) precatalysts are effective, it is likely that Cu(I) species generated under the reaction conditions are functioning as the active catalyst.<sup>19</sup> Among the cases explored, the use of the preformed complex Cu(Cl)IPr with B<sub>2</sub>Pin<sub>2</sub>/MeOH (Table 1, entry 11) provided an optimum outcome in terms of conversion, regioselectivity, and reproducibility across various substrate classes, and this protocol was thus selected for further study.

A range of simple terminal olefins were examined in the regioselective formation of branched alkylborane products. Using either 4-phenyl-1-butene or 1-octene, excellent yields and regioselectivities favoring the branched isomer were observed (compounds **2–3**, Scheme 2). Branching at the allylic position was tolerated (compound **4**, Scheme 2). Other tolerated functional groups included benzyl ethers, silyl ethers, unprotected hydroxyls, pivalate esters, and bromoarenes (compounds **5–9**, Scheme 2). Allylbenzene was a highly effective substrate, and no isomerization to the styrene or to the corresponding benzylic borane product was noted (compound **10**, Scheme 2). Notably, compound **10** was previously prepared in highly en-antioselective fashion from prop-1-en-1-ylbenzene via Cu-NHC catalyzed hydroboration.<sup>20</sup> Examination of similar chiral NHC's in the current procedure using allylbenzene as substrate led to poor enantioselectivities (see Supporting Information for details). Therefore, the current procedure will be most useful for non-styrenyl substrates in comparison to this alternative method that is highly effective for styrene hydroborations. As additional examples, allylsilanes were tolerated in the procedure, leading to 1,2-*bis*-metalated products (compound **11**, Scheme 2). Indoles were also tolerated to afford products borylated at the  $\beta$ - or  $\gamma$ -positions of the *N*-alkyl chain (compounds **12–13**, Scheme 2). To explore selectivity among different olefin classes, hydroboration of a substrate possessing both a trisubstituted alkene and a monosubstituted alkene afforded complete selectivity for the terminal alkene (compound **14**, Scheme 2). Similarly, complete selectivity was seen for hydroboration of the terminal alkene when a 1,1-disubstituted alkene was present (compound **15**, Scheme 2). While alkenes that possess two or more substituents were generally unreactive, 1,1-disubstituted alkenes could be converted to tertiary borane products under modified conditions (compounds **16–17**, Scheme 2).<sup>21</sup>

In analogy with other reports of copper-catalyzed additions of B<sub>2</sub>Pin<sub>2</sub> and methanol to alkynes and styrenes,<sup>11,17</sup> the mechanism of the process likely involves addition of a copper borane intermediate to the terminal alkene as the regiochemistry-determining step as depicted in the **18** to **19** conversion (Scheme 3). Formation of the linear borane is disfavored as ligand size increases (compare Table 1, entries 8 and 9) due to developing steric interactions experienced in complex **20a**.<sup>22</sup> Alternatively, complex **20b**, which leads to the observed branched product, avoids steric interactions between the ligand and alkene substituent. Following the sterically preferred formation of **19**, protonation of the metal-copper bond produces the desired product along with the formation of a copper methoxide species, which is converted to the reactive Cu-BPin complex by the reaction with B<sub>2</sub>Pin<sub>2</sub>.

Recent advances in Suzuki couplings can benefit from the facile entry to the secondary alkylboranes provided by this procedure.<sup>2,3</sup> For example, the nickel-catalyzed photocatalytic cross-coupling procedure recently developed by Molander,<sup>3b</sup> when paired with the above developments, provides a convenient and versatile method for the direct conversion of

terminal alkenes to tertiary branched motifs. Alkyl(BPin) derivatives accessed by the catalytic, regiocontrolled addition of  $B_2Pin_2$  with methanol to terminal alkenes (Scheme 4) are readily converted to the corresponding trifluoroborate derivatives,<sup>3a,23</sup> while maintaining the versatile functional group tolerance of the hydroboration procedure (Scheme 4). The resulting functionalized trifluoroborate derivatives then directly participate in nickel-catalyzed cross-couplings in the presence of iridium photocatalysts following the Molander protocol. Both electron-rich and electron-deficient bromoarenes participate in the sequence (**21–22**, Scheme 4). Notably, the functional group tolerance demonstrated in the synthesis of branched alkyl-boranes is carried through the trifluoroborate synthesis/photocatalytic cross-coupling sequence to provide the preservation of sensitive functional groups such as free alcohols, esters, and indoles (**23–25**, Scheme 4).

In summary, the regiodivergent hydroboration of a broad range of simple terminal alkenes may now be readily accomplished.<sup>24</sup> While a range of thermal or catalyzed additions of boranes provides access to linear alkylboranes according to previous reports, the copper-catalyzed addition of  $B_2Pin_2$  with methanol reported herein provides highly regioselective access to the isomeric branched alkylboranes. This procedure complements previous methods for accessing secondary alkylborane structures, and the utilization of the products obtained in nickel-catalyzed photocatalytic cross-couplings provides a branch-selective strategy for the reductive cross-coupling of alkenes and aryl bromides. Further exploration of asymmetric versions of the formal hydroboration is in progress, and utilization of the racemic organoboranes will be possible with emerging developments in stereoconvergent cross-couplings.<sup>3</sup>

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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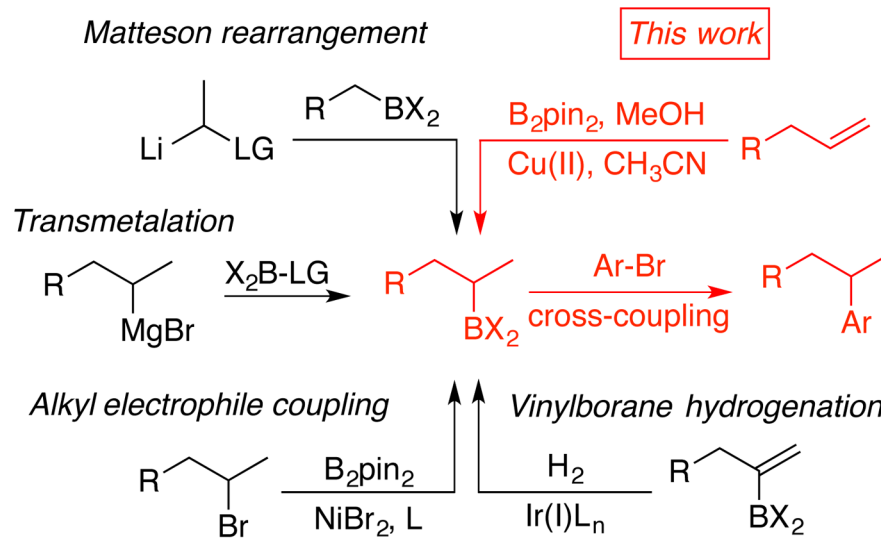
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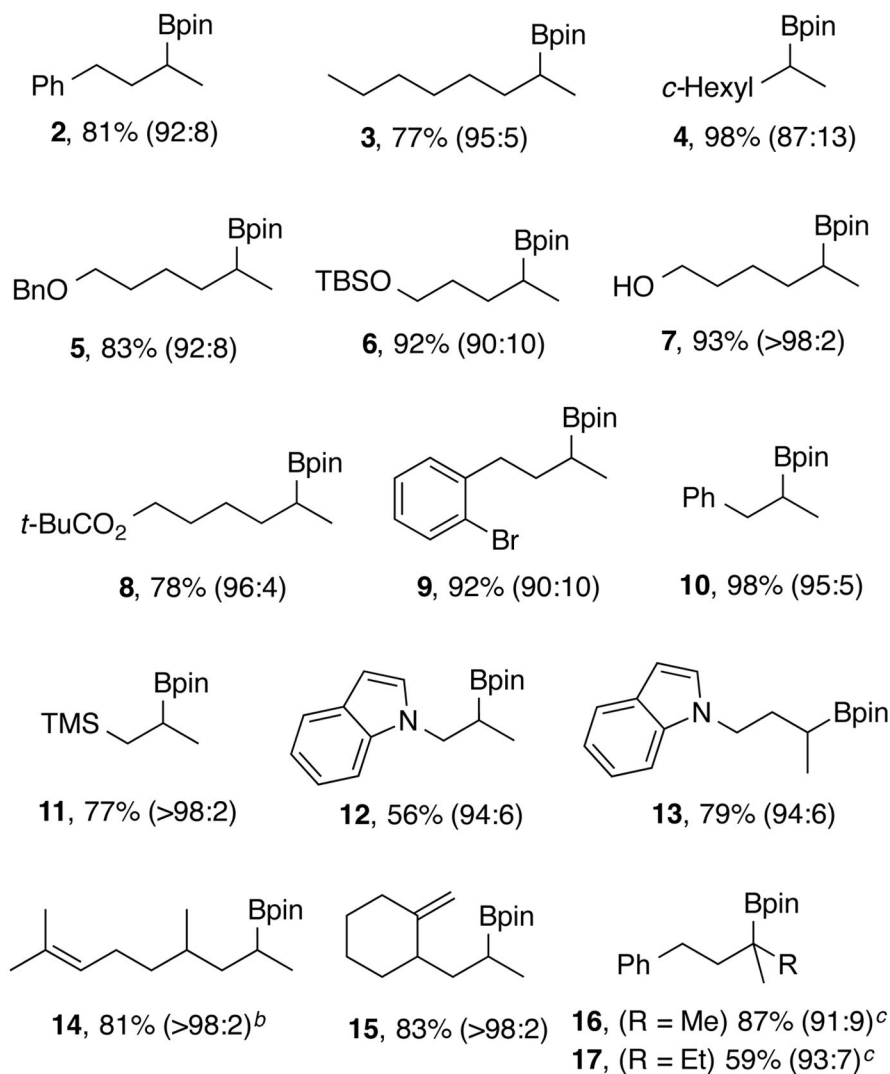
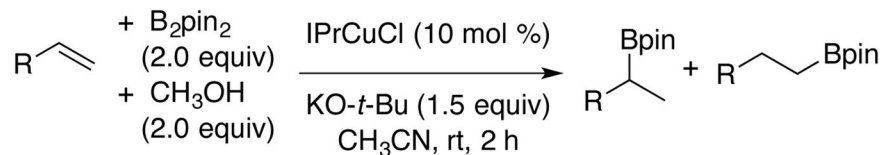
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**Scheme 1.**  
Approaches to Secondary Alkyl-boranes.

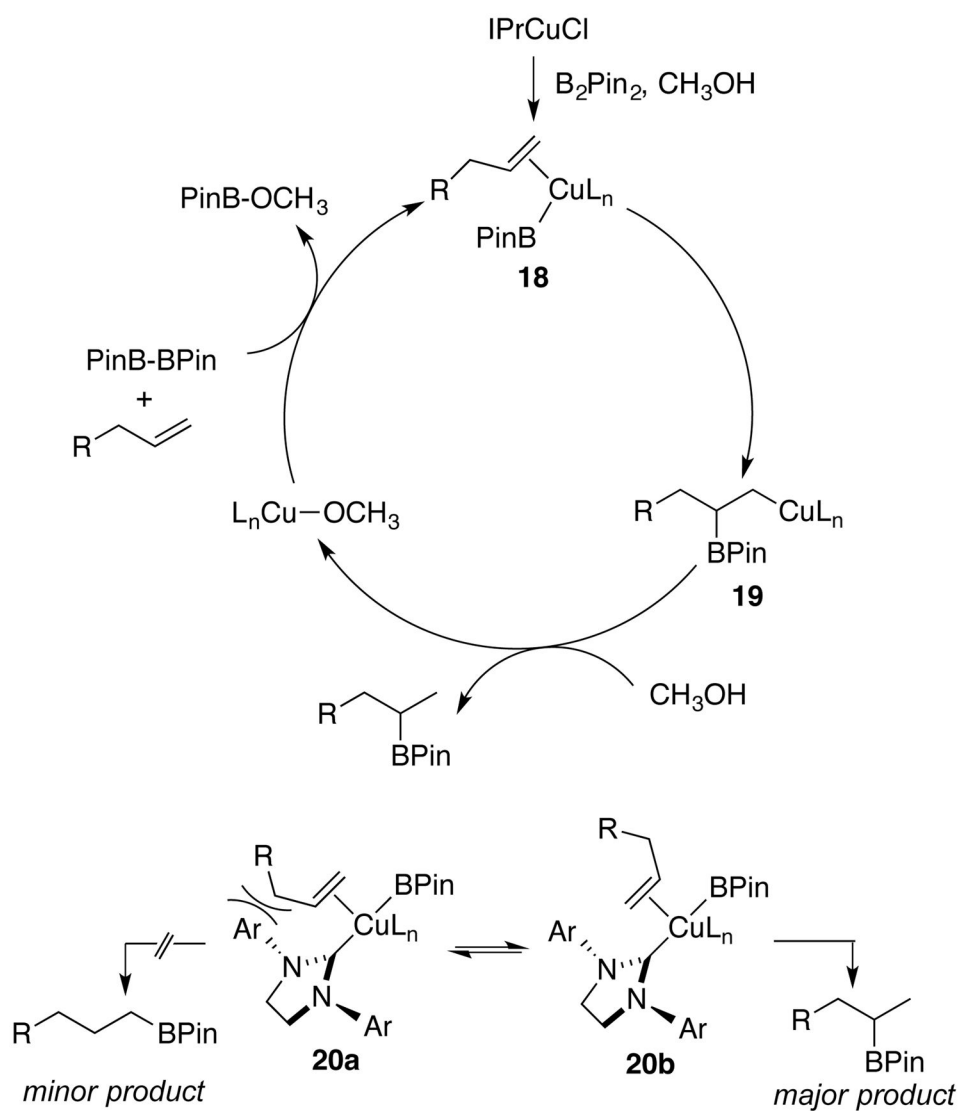


**Scheme 2.**Scope of Branched Alkylborane Synthesis.<sup>a</sup><sup>a</sup>B<sub>2</sub>Pin<sub>2</sub> = bis(pinacolato)diboron; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

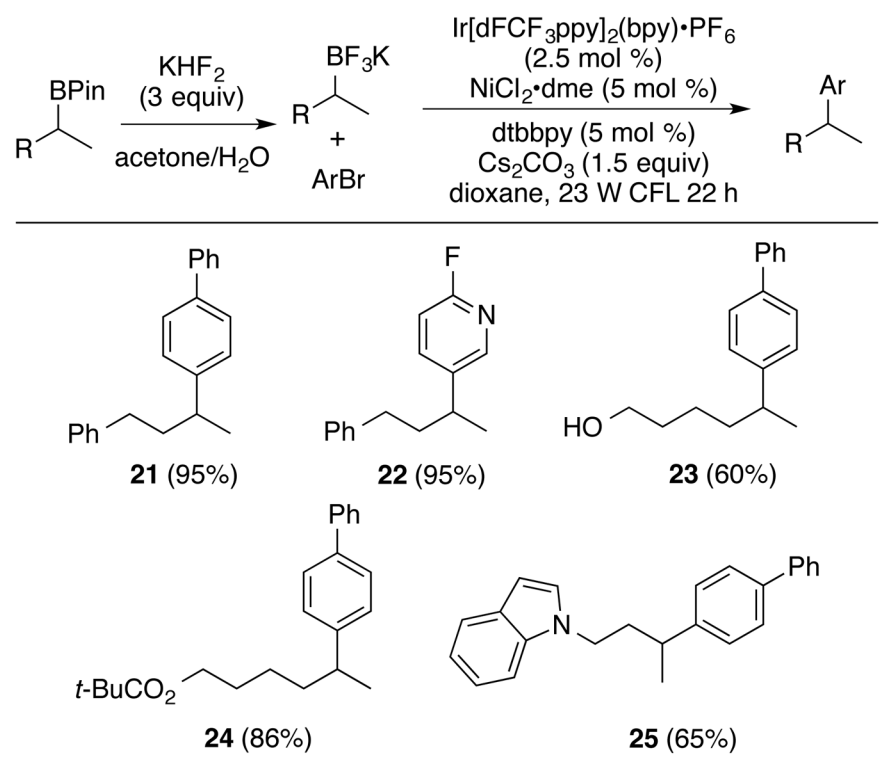
Regioselectivity ratios were determined on crude reaction mixtures. Isolated yields are

given. <sup>b</sup>Diastereomeric ratio (1:1). <sup>c</sup>Reaction was conducted in CH<sub>2</sub>Cl<sub>2</sub> using NaO-*t*-Bu at rt.





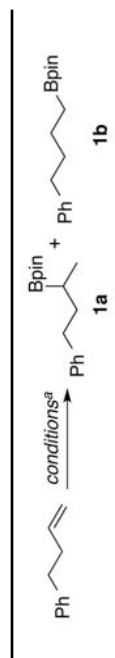
**Scheme 3.**  
Mechanism of Secondary Alkylborane Formation.

**Scheme 4.**Photocatalytic Cross-Couplings of Branched Trifluoroalkylboranes.<sup>a</sup>

<sup>a</sup>Isolated yields for the photocatalytic cross-coupling step are provided in the Table. Details for the synthesis of the RBF<sub>3</sub> salts are provided in the Supporting Information. dFCF<sub>3</sub>ppy = 2-(2,4-difluorophenyl)-5-(trifluoromethyl) pyridine; dme = dimethoxyethane; dtbbpy = 4,4'-di-*tert*-butyl-2-2'-bipyridine.

Table 1

## Optimization of Branched Alkylborane Synthesis.



entry	catalyst	ligand <sup>b</sup>	reagent	solvent	1a : 1b (yield, %) <sup>c</sup>
1	Pd <sub>2</sub> dba <sub>3</sub>	IMes	HBPin	THF	17:83 (62)
2	Pd <sub>2</sub> dba <sub>3</sub>	SIPr	HBPin	THF	21:79 (47)
3	Ni(cod) <sub>2</sub>	IMes	HBPin	THF	21:79 (14)
4	Ni(cod) <sub>2</sub>	SIPr	HBPin	THF	13:87 (<5)
5	PtCl <sub>2</sub>	SIPr	HBPin	THF	7:93 (74)
6	CoBr <sub>2</sub>	SIPr	HBPin	THF	<2:98 (62)
7	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	SIPr	HBPin	THF	<2:98 (33)
8	CuCl	IMes	B <sub>2</sub> Pin <sub>2</sub>	THF	67:33 (3)
9	CuCl	SIPr	B <sub>2</sub> Pin <sub>2</sub>	THF	79:21 (48)
10	CuCl	SIPr	B <sub>2</sub> Pin <sub>2</sub>	CH <sub>3</sub> CN	95:5 (52)
11	Cu(Cl)IPr	—	B <sub>2</sub> Pin <sub>2</sub>	CH <sub>3</sub> CN	92:8 (81) <sup>d</sup>
12 <sup>d</sup>	Cu(OAc) <sub>2</sub>	SIPr	B <sub>2</sub> Pin <sub>2</sub>	CH <sub>3</sub> CN	93:7 (62)
13 <sup>e</sup>	CuBr <sub>2</sub>	SIPr	B <sub>2</sub> Pin <sub>2</sub>	CH <sub>3</sub> CN	96:4 (78)

<sup>a</sup> All experiments were conducted at rt for 2 h at 0.2 M under nitrogen atmosphere. Experiments with B<sub>2</sub>Pin<sub>2</sub> also used CH<sub>3</sub>OH (2 equiv). B<sub>2</sub>Pin<sub>2</sub> = bis(pinacolato)diboron.

<sup>b</sup> Ligand HCl salts were used with KO-*t*-Bu; IMes•HCl = 1,3-bis(mesityl)imidazolium chloride; SIPr•HCl = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

<sup>c</sup> With the exception of entry 11, NMR yields are shown, using 1,3,5-trimethoxybenzene as internal standard. Regioselectivity ratios were determined on crude reaction mixtures.

<sup>d</sup> Isolated yield is given.