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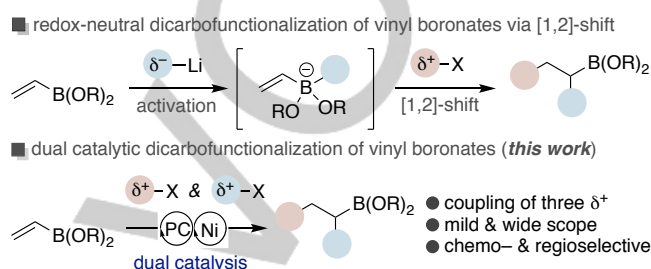
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## Site-Selective 1,2-Dicarbonylation of Vinyl Boronates via Dual Catalysis

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**Abstract:** A modular, site-selective 1,2-dicarbonylation of vinyl boronates with organic halides via dual catalysis is described. This protocol occurs under mild conditions and is characterized by its excellent chemo- & regioselectivity, thus unlocking a complementary new technique for preparing densely functionalized alkyl boron architectures from simple and accessible precursors.

The tunable reactivity, ease of handling and stability of organoboron compounds make them ideal synthons with which to build up molecular complexity.<sup>[1]</sup> Conventional approaches for their synthesis include transmetalation events from well-defined, stoichiometric organometallic reagents and electrophilic boron precursors,<sup>[2]</sup> hydroboration of unsaturated bonds<sup>[3]</sup> or transition-metal catalyzed borylation reactions of polarized C–(pseudo)halide bonds with bisboron reagents,<sup>[4]</sup> among others.<sup>[5]</sup> Recent elegant disclosures have shown the viability of accessing organoboranes via boron-ate complexes – generated from stoichiometric organolithium reagents – inducing a [1,2]-shift that forges two C–C bonds via one- or two-electron events (Scheme 1, *top*)<sup>[6]</sup>.<sup>[7]</sup> Despite the advances realized, several challenges remain to be addressed. Among these, a complementary method for triggering a catalytic 1,2-dicarbonylation with simple electrophilic partners that obviates the need for stoichiometric organometallics while enabling a rapid, reliable and modular access to organoboron skeletons would constitute a worthwhile endeavor for chemical invention.<sup>[8]</sup>



**Scheme 1.** Regioselective 1,2-Dicarbonylation of Vinyl Boronates.

As part of our interest in cross-electrophile coupling reactions and site-selective functionalization of olefins,<sup>[9]</sup> we recently questioned whether it would be possible to design a catalytic reaction that would allow the incorporation of two different electrophilic partners into readily accessible vinyl boranes in a 1,2-fashion with total control of the regioselectivity pattern.<sup>[10]</sup> In line with the elegant work of Nevado and Chu,<sup>[8c,g]</sup> we hypothesized that a dual catalytic approach might be suited for our purposes. Specifically, we propose that nucleophilic alkyl radicals – generated upon SET from an electron donor – might undergo regioselective addition to a vinyl boronate en route to **I**, the stability of which is dictated by the effective delocalization of the radical through the vacant p orbital of the boron atom (Scheme 2).<sup>[11]</sup> Concurrently, oxidative addition of an organic halide to Ni(0)L<sub>n</sub> would result in an electrophilic Ni(II) entity **II**. Polarity-matched recombination of **I** with **II** might result in Ni(III) species **III**, setting the stage for a reductive elimination en route to the targeted product and a Ni(I) intermediate. We anticipated that catalytic turnover might be achieved via SET reduction, thus recovering back the competent Ni(0)L<sub>n</sub> species. This strategy bore considerable risk and might seem counterintuitive at first sight, as finding catalysts able to perform a site-selective reductive 1,2-dicarbonylation event with two distinct electrophilic partner might be hampered by (a) undesired reductive cross-coupling between two electrophilic counterparts (**VI**) and/or (b) competitive formation of **IV** & **V** depending on the relative rate of SET and/or oxidative addition. If successful, however, the ability to trigger such a multicomponent reaction with an exquisite control of the site-selectivity would not only expand the range of technologies to access alkyl organoboron reagents, but also open up new strategic approaches in the realm of cross-electrophile coupling events.<sup>[12]</sup> Herein, we report the successful realization of this platform by merging photocatalysis and nickel catalysis (Scheme 1, *bottom*).<sup>[13]</sup> Our protocol is characterized by its mild conditions, and excellent chemo- and regioselectivity profile in the absence of stoichiometric organometallics, thus leading to a new

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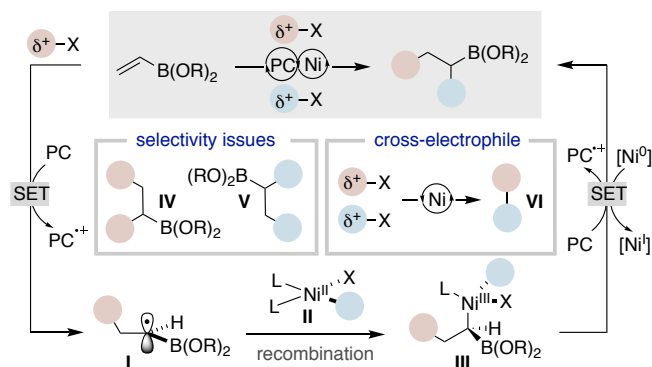
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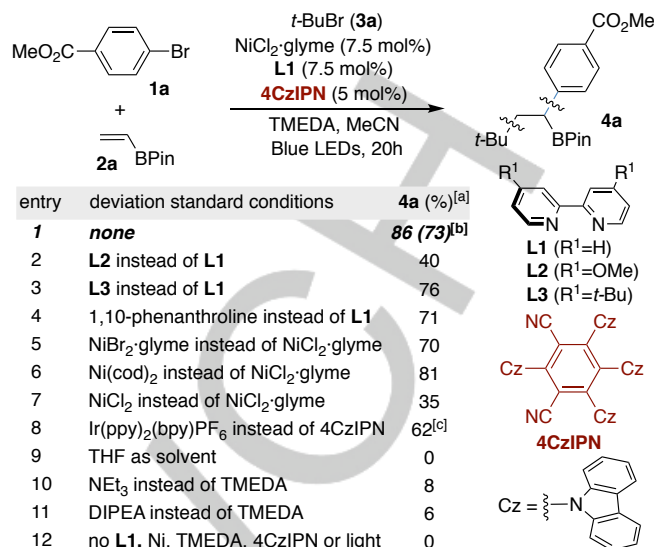
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retrosynthetic disconnection for accessing densely functionalized alkyl boron reagents from three distinct electrophilic partners.<sup>[14]</sup>



**Scheme 2.** Mechanistic Rationale.

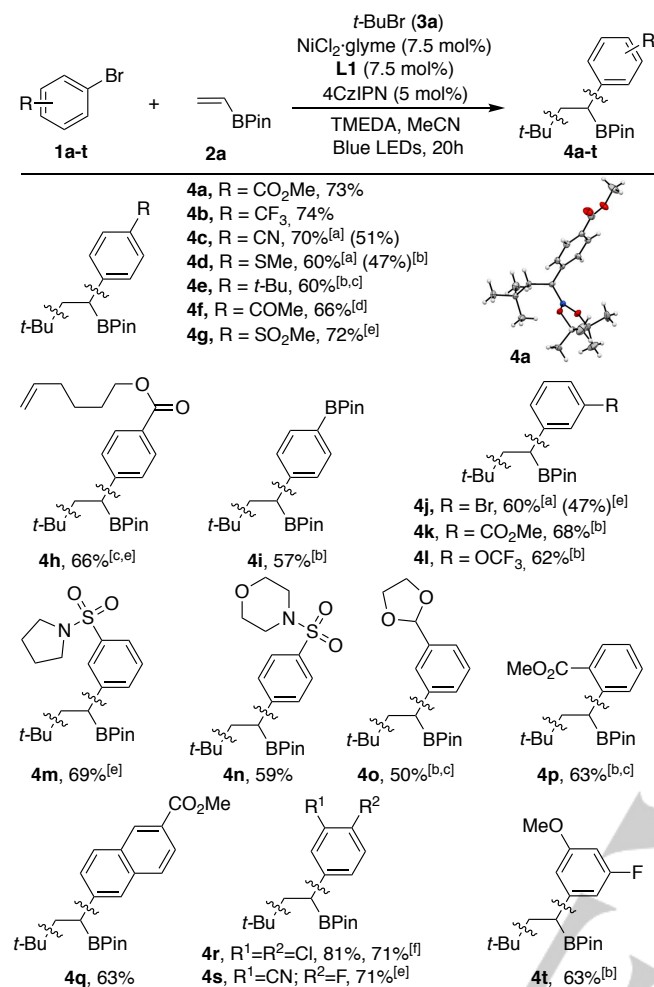
Our investigations began by reacting **1a** with methyl 4-bromobenzoate (**3a**) and vinyl boronate **2a** (Scheme 3). After some experimentation,<sup>[15]</sup> the best results were accomplished with NiCl<sub>2</sub>·glyme (7.5 mol%), **L1** (7.5 mol%), 4CzIPN as photosensitizer (5 mol%) and TMEDA as electron donor under irradiation from blue light-emitting diodes (LEDs), affording **4a** in 73% isolated yield as single regioisomer (entry 1). In contrast to the known literature data on cross-electrophile coupling reactions, the substitution pattern at the ligand backbone did not play a significant role on reactivity or regioselectivity (entries 2–4).<sup>[12]</sup> A significant erosion in yield was observed when using NiCl<sub>2</sub> as the nickel source (entry 7), while comparable yields were observed with Ni(COD)<sub>2</sub> (entry 6). Notably, Ir(ppy)<sub>2</sub>(bpy)PF<sub>6</sub> (E<sub>red</sub> [Ir<sup>III</sup>/Ir<sup>I</sup>] = -1.38 V vs SCE in MeCN) could be employed as photocatalyst instead of 4CzIPN (E<sub>red</sub> = -1.21 V vs SCE in MeCN), albeit in slightly lower yields (entry 8). Interestingly, the nature of the electron donor and the solvent markedly influenced the reactivity profile; indeed, trace amounts of **4a**, if any, were obtained with Et<sub>3</sub>N, DIPEA or THF (entries 9–11). As anticipated, control experiments revealed that all of the reaction parameters were crucial for the multicomponent reaction to occur (entry 12).<sup>[16]</sup> It is worth noting that under these reaction conditions, no reductive cross-coupling between the two electrophilic counterparts (**VI**),<sup>[17]</sup> Heck-type products or competitive Suzuki-Miyaura coupling of **2a** with **1a** were observed in the crude mixtures.<sup>[18]</sup>



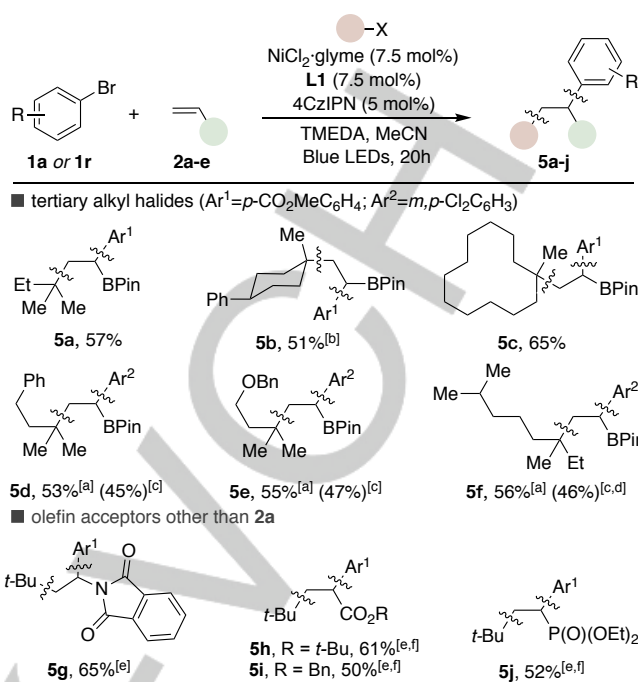
**Scheme 3.** Optimization of the Reaction Conditions. **1a** (0.40 mmol), **2a** (0.2 mmol), **3a** (0.50 mmol), 4CzIPN (5 mol%), NiCl<sub>2</sub>·glyme (7.5 mol%), **L1** (7.5 mol%), TMEDA (0.6 mmol) in acetonitrile (3 mL) at 30 °C under irradiation of blue LEDs with a fan for 20 hours. [a] <sup>1</sup>H NMR yields were determined by using CH<sub>2</sub>Br<sub>2</sub> as internal standard. [b] Isolated yield, average of two independent runs. [c] [Ir] (2 mol%) was used. TMEDA = N,N,N',N'-tetramethylethylenediamine; B<sub>2</sub>Pin<sub>2</sub> = bis(pinacolato)diboron; DIPEA = N,N-diisopropylethylamine.

With these results in hand, we investigated the generality of our 1,2-difunctionalization of **2a**. As shown in Scheme 4, a host of aryl halides could be utilized in the targeted reaction.<sup>[19]</sup> Importantly, similar results were obtained regardless of the electronic and steric properties of the substituents on the arene partner. Note, however, that the addition of LiCl was required in some cases to reach high conversion to products. Particularly noteworthy was the chemoselectivity profile of our protocol, as esters (**4a**, **4h**, **4k**, **4p**, **4q**), nitriles (**4c**, **4s**), alkenes (**4h**), sulfonamides (**4m**, **4n**), sulfones (**4g**), acetals (**4o**) and ketones (**4f**) were all well tolerated. Equally interesting was the possibility to tolerate aryl boronic esters (**4i**) and aryl halides (**4j**, **4r**, **4s**, **4t**), leaving ample room for further derivatization via classical redox-neutral cross-coupling reactions.<sup>[20]</sup> Notably, this reaction can be executed on a gram scale, affording **4r** without significant erosion in yield. Encouraged by these findings, we wondered whether our 1,2-difunctionalization protocol could be extended to alkyl halides and alkenes other than **2a** and **3a**, respectively. As shown in Scheme 5, this turned out to be the case and a variety of tertiary alkyl bromides bearing different groups on the side-chain could be used as coupling partners (**5a–5f**).<sup>[18],[19]</sup> Notably, olefins end-capped with phthalimides (**5g**), esters (**5h**, **5i**) and phosphonates (**5j**) could be utilized as counterparts in lieu of **2a**, albeit in slightly lower yields.<sup>[21]</sup>

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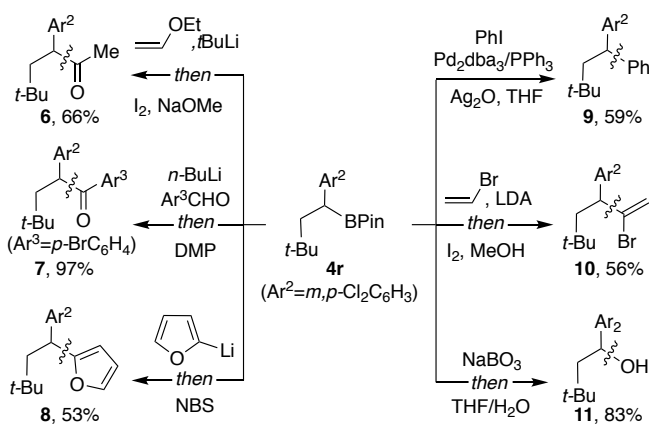


**Scheme 4.** Scope of aryl bromides. As Scheme 3, entry 1; Yields of isolated products, average of at least two independent runs. [a] NMR yields using 1,1-dibromomethane as internal standard. [b] Ir(ppy)<sub>2</sub>bpyPF<sub>6</sub> (2 mol%), Ni(COD)<sub>2</sub> (7.5 mol%), L3 (7.5 mol%), LiCl (0.5–0.6 mmol). [c] Isolated yield upon oxidation with NaBO<sub>3</sub>. [d] Isolated yield of the corresponding BF<sub>3</sub>K salts upon exposure to KHF<sub>2</sub>. [e] Ni(COD)<sub>2</sub> (7.5 mol%), L3 (7.5 mol%). [f] 1r (5.0 mmol) were used.



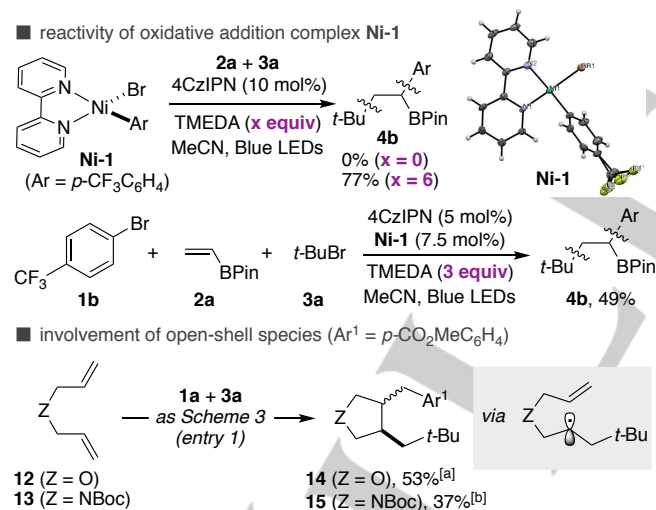
**Scheme 5.** Scope of tertiary bromides and substituted alkenes. [a] As Scheme 1, entry 1; Yields of isolated product are illustrated in parentheses, average of at least two independent runs. [b] dr = 2.8:1. [c] Ni(COD)<sub>2</sub> (7.5 mol%), L3 (7.5 mol%). [d] dr = 1:1. [e] 3a (0.6 mmol) and L3 (7.5 mol%) was used instead of L1 for 36 h. [f] Isolated yield.

The utility of our method is further illustrated in Scheme 6. As expected, an array of different derivatizations of **4r** were within reach by using the boronic ester motif as a divergence point. As initially anticipated, a canonical oxidation with NaBO<sub>3</sub> cleanly delivered **11** in good yields.<sup>[22]</sup> Likewise, a series of C–C bond-forming reactions could easily be conducted via C–B bond-cleavage in **4r**, including Pd-catalyzed Suzuki–Miyaura protocols (**9**),<sup>[23]</sup> or the incorporation of heterocycles (**8**),<sup>[24]</sup> vinyl halides (**10**)<sup>[25]</sup> or ketone backbones (**6**)(**7**)<sup>[26],[27]</sup> in one-pot procedures. Taken together, the data shown in Schemes 4–6 serves as a testament to the prospective impact of our 1,2-difunctionalization protocol.



**Scheme 6.** Synthetic Applicability

The efficiency of our 1,2-dicarbofunctionalization prompted us to conduct preliminary mechanistic studies. As expected, Stern-Volmer luminescence studies revealed that the excited state of 4CzIPN was quenched by TMEDA.<sup>[15]</sup> This experiment supported the notion that a reductive quenching photocatalytic cycle is occurring, whereby a transient carbon-centered radical is generated via single-electron transfer (SET) from the reduced photocatalyst to a tertiary alkyl halide, with TMEDA serving as sacrificial electron donor. In line with this notion, the formation of **4a** was inhibited in the presence of 1,4-cyclohexadiene, TEMPO or 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as spin-trapping reagents.<sup>[15]</sup> The intermediacy of open-shell species was further corroborated by exclusively forming five-membered **14** and **15** from the corresponding dienes under our optimized reaction conditions (Scheme 7, *bottom*).<sup>[28]</sup> In addition, **Ni-1**<sup>[15],[29]</sup> – easily obtained upon exposure of 4-trifluoromethyl bromobenzene to Ni(COD)<sub>2</sub> and **L1** in THF – was shown to be catalytically competent in the reaction, leading to **4b** in comparable yield to that shown in Scheme 3 (Scheme 7, *middle*). More importantly, stoichiometric experiments with **Ni-1** revealed that **4b** could only be obtained in the presence of TMEDA (Scheme 7, *top pathway*). Taken together, our data are consistent with the rationale depicted in Scheme 2, with an in situ generated tertiary alkyl radical adding across a vinyl boronate in a regioselective manner prior to recombination with an oxidative addition species, with turnover effected by an intertwined scenario with a photochemical event that recovers back the competent Ni(0)**L1** species upon SET reduction.



**Scheme 7.** Preliminary Mechanistic Experiments. [a] dr = 4:1. [b] dr = 1.2:1.

In summary, we have developed a modular chemo- and regioselective 1,2-difunctionalization of simple vinyl boronates with readily available organic halides via a dual catalytic platform. In a formal sense, our protocol serves as a testament to the viability of conducting a reductive cross-coupling of three different electrophilic partners in a synergistic manner. Further studies into related processes, including the design of an asymmetric variant, are currently ongoing in our laboratories.

## Acknowledgements

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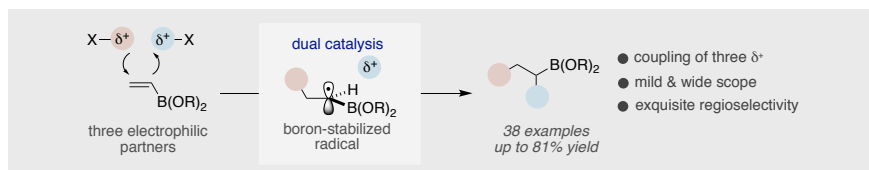
**Keywords:** radical • dicarbofunctionalization • dual catalysis • Ni catalysis

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## COMMUNICATION



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**Site-Selective 1,2-Dicarbonylation of Vinyl Boronates via Dual Catalysis**

A modular, site-selective 1,2-dicarbonylation of vinyl boronates with readily available organic halides was developed by a dual catalysis approach. This protocol is characterized by mild conditions, excellent chemo- and regioselectivity in the absence of stoichiometric organometallic reagents, thus unlocking a new pathway for preparing densely functionalized alkyl boron fragments from three distinct, yet widely available, electrophilic partners.