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Rapid Access to Highly Functionalized Alkylboronates *via* NiH-Catalyzed Remote Hydroarylation of Boron-Containing Alkenes

Yao Zhang, Bo Han, and Shaolin Zhu*

Abstract: The direct and selective functionalization of relatively simple and readily accessible precursors to produce highly functionalized alkylboronates is a synthetically useful process. Here we report a NiH-catalyzed remote hydroarylation process that can, through a synergistic combination of chainwalking and subsequent cross-coupling, introduce an aryl group into the adjacent carbon of alkylboronates under mild conditions. By means of a preliminary experiment with moderate enantioselectivity, it was shown that the asymmetric version could be realized.

Alkylboronates are a privileged scaffold in materials science and drug discovery, they are also valuable and versatile precursors for the construction of structurally complex molecules.[1] Recently, there have been advances in stereospecific transformation of alkylboronates to forge C–C, C–O, C–N, and C–X bonds.[2] Accordingly, efficient, selective and sustainable methods to introduce a boryl moiety have been developed to access these functionalized alkylboronates (Figure 1a, left).[3] Introduction of a functional group into a boron-containing substrate *via* catalytic functional group transformation offers a complementary route to these valuable and densely functionalized boronates (Figure 1a, right).[4] In contrast, the direct and selective sp^3 C–H functionalization of easily accessible alkylboronates remains a significant unexplored challenge.

The recently reported remote functionalization through the synergistic combination of chainwalking and cross-coupling chemistry provides a mild and efficient strategy for the rapid assembly of structurally complex molecules from easily prepared alkenes and a wide variety of commercially available cross-coupling partners.[5-9] With the low cost, sustainability, and nickel cross-coupling chemistry[10], migratory cross-coupling catalyzed by nickel hydride[11] has led to the discovery and development of a variety of unique and valuable transformations.[9] In this type of reaction, nickel plays two roles, catalyzing the processes of chainwalking and of cross-coupling. We recently questioned whether this generic strategy could be used to gain rapid access to a valuable class of α-functionalized alkylboronates from easily accessible unsaturated alkylboronates and commercially available cross-coupling partners (Figure 1b). It was envisioned that the NiH species generated *in situ* would promote a rapid chainwalking process, accessing various alkylnickel species along the alkylchain prior to a selective cross-coupling with an aryl halide. Ideally, with a suitable ligand, such a migratory arylation process could take place at the adjacent α-carbon of the alkylboronate to deliver the corresponding α-aryl alkylboronate in a chemo- and regioselective manner from an alkene whose double bond is in an arbitrary position. In this communication we describe the successful execution of this reaction under exceptionally mild conditions.

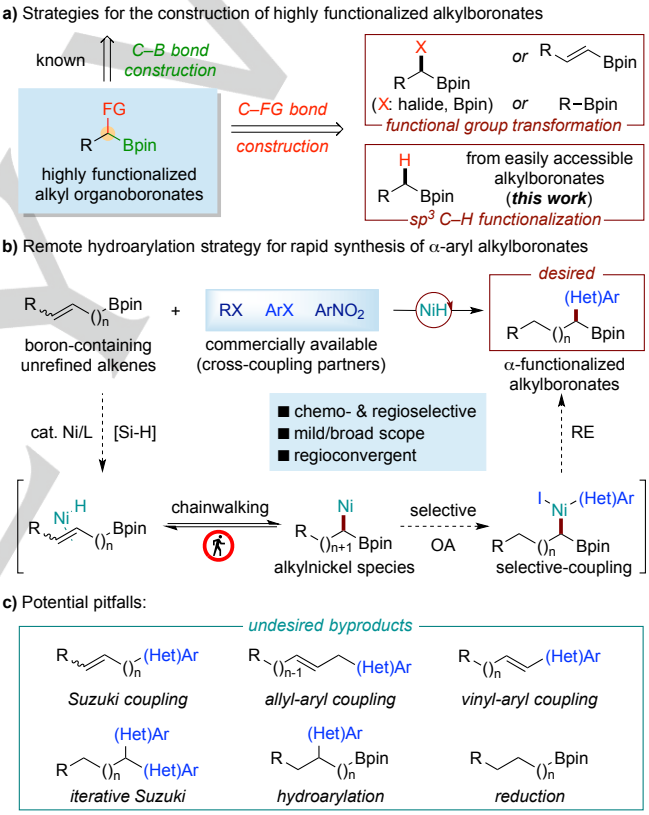

Figure 1. Design plan: access to highly functionalized alkylboronates by functionalization of readily accessible precursors.

While the above strategy can be viewed as an attractive approach to highly functionalized alkylboronates, there are many potential pitfalls (Figure 1c). First, a Ni-catalyzed Suzuki reaction is possible because both starting materials and products are organoboronates. Second, a chainwalking process could potentially lead to the formation of isomeric products due to the similar reactivities of the alkylmetal intermediates. Third, alkenes and aryl iodides could be reduced by nickel hydride. Achieving the requisite chemo- and regioselectivity is a major unexplored challenge.

Aware of these possible pitfalls, our investigation began with examination of the remote hydroarylation[12] of homoallyl-

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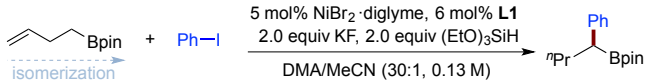
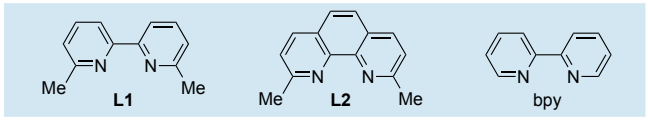
boronic acid pinacol ester (**1a**) with iodobenzene (**2a**). After extensive examination of nickel sources, ligands, silanes, bases, solvents, and additives, the desired α-aryl alkylboronate (**3a**) was obtained at 30 °C in 70% isolated yield. The reaction manifested excellent regioselectivity [regioisomeric ratio, rr (α-aryl product : all other isomers) = 97:3] (Table 1, entry 1). Use of other nickel sources such as NiI_2 gave diminished yields (entry 2). Evaluation of other ligands showed that use of a similar ligand, neocuproine (**L2**) led to a significantly lower yield (entry 3) and replacement of **L1** with the parent bipyridine (bpy) produced no desired arylation product (entry 4). Polymethylhydrosiloxane (PMHS) was shown to be a less effective silane (entry 5) and replacement of KF by CsF led to diminished yield (entry 6). The reactivity could however be improved by the addition of KI as an additive (entry 1 vs entry 7) and acetonitrile as co-solvent (entry 1 vs entry 8). Finally, bromobenzene was found to be considerably less reactive than iodobenzene (entry 9).

Table 1: Variation of reaction parameters.



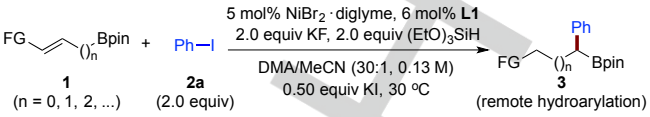
Entry	Variation from standard conditions	Yield (%)[a]	rr[b]
1	none	87(70)	97:3
2	NiI_2, instead of $NiBr_2$·diglyme	27	98:2
3	**L2**, instead of **L1**	25	95:5
4	bpy, instead of **L1**	trace	–
5	PMHS, instead of $(EtO)_3SiH$	35	93:7
6	CsF, instead of KF	47	95:5
7	w/o KI	78	92:8
8	w/o MeCN	36	95:5
9	PhBr, instead of PhI	39	96:4

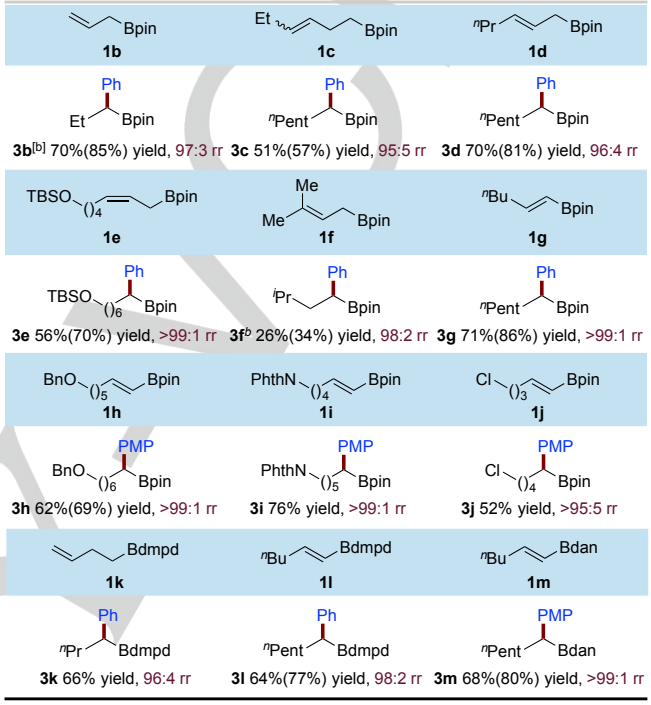


[a] Yields determined by GC using *n*-dodecane as the internal standard, the yield in parentheses is the isolated yield and is an average of two runs (0.20 mmol scale). [b] Ratio of the arylation at adjacent carbon of boronate to the sum of all other isomers as determined by GC analysis. PMHS, polymethylhydrosiloxane.

Under the optimal conditions, a variety of unactivated terminal (**1a**, **1b**, and **1k**) and internal (**1c**–**1f**) alkenes, as well as activated alkenyl boronic esters (**1g**–**1j**, **1l**, and **1m**) successfully underwent the desired migratory arylation, delivering the α-aryl alkylboronates in good yields and with excellent regioselectivity (Table 2). As expected, both *E* (**1d**, **1g**–**1j**, **1l**, and **1m**) and *Z* (**1e**) alkenes, as well as *E*/*Z* mixtures (**1c**) were accommodated well, and high selectivity for arylation at the adjacent carbon position of alkylboronate was observed, regardless of the position of the C=C bond in the starting material (compare **1c**, **1d**, and **1g**). The current reaction conditions could also be used with a more sterically hindered trisubstituted alkene (**1f**) to form the migratory product (**3f**), albeit in diminished yield. Notably, even with a heteroatomic substituent at the other terminus of the alkyl chain, including ethers (**1e**, **1h**), a phthaloyl amide (**1i**), and an alkyl chloride (**1j**), arylation at the α-carbon of the alkylboronate was still observed.

Table 2: Scope of the alkene component.[a]



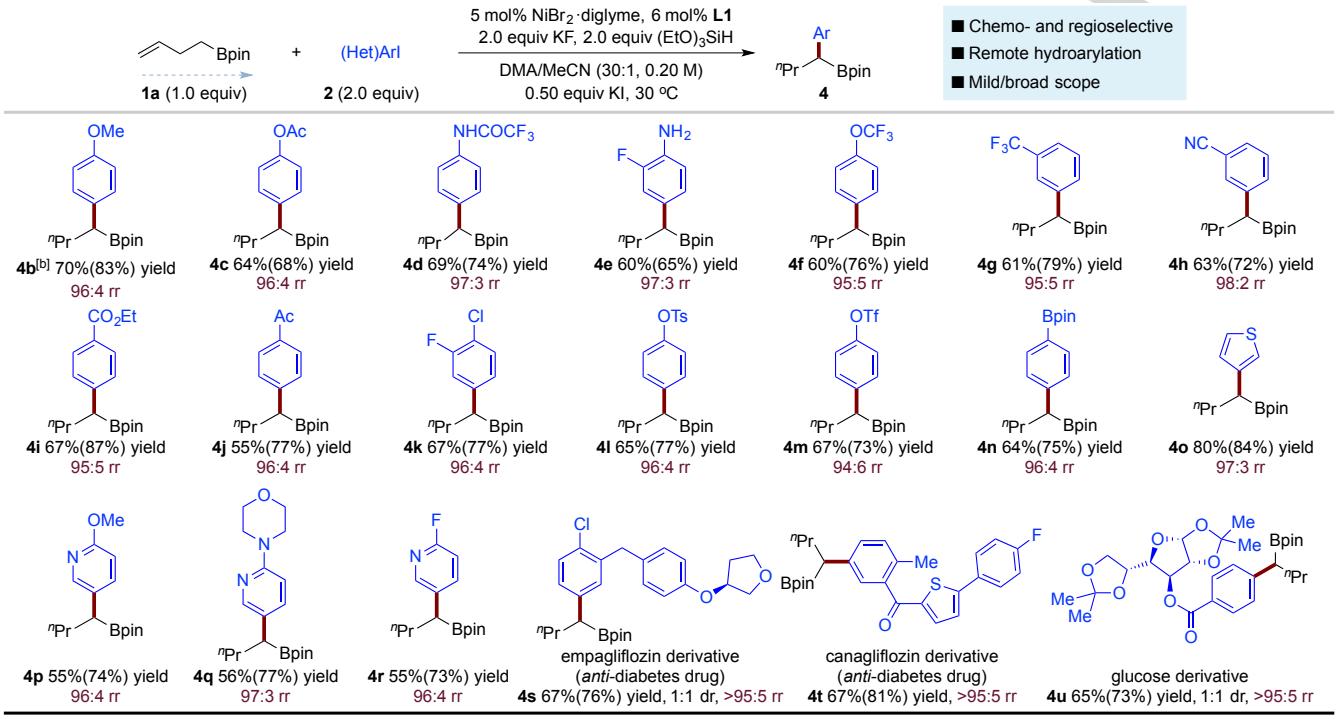


[a] Under each product is the percentage yield, crude ^{1}H NMR yield, and the regioisomeric ratio (rr). Yield refers to isolated yield (0.20 mmol scale, average of two runs), yields in parentheses refer to the crude ^{1}H NMR yield (1,1,2,2-tetrachloroethane as internal standard). rr represents the ratio of the arylation at adjacent carbon of boronate to the sum of all other isomers as determined by GC analysis, ratios reported as >95:5 were determined by crude ^{1}H NMR analysis. [b] 35 °C. Phth, phthaloyl.

A subsequent survey of aryl iodides revealed that a range of aryl- and heteroaryl groups could be used. As depicted in Table 3, several electron-rich (**2b**–**2e**) and electron-poor (**2f**–**2n**) aryl iodides were shown to be acceptable substrates. A variety of functional groups were readily accommodated, including ethers (**2b**, **2f**, **2p**, **2q**, **2s**, and **2u**), esters (**2c**, **2i**, and **2u**), an amide (**2d**), anilines (**2e**, **2q**), a nitrile (**2h**), ketones (**2j**, **2t**), and an acetal (**2u**). Of particular interest is that potential coupling motifs, including aryl fluorides (**2e**, **2k**, **2r**, and **2t**), an aryl chloride (**2k**), an aryl tosylate (**2l**), an aryl triflate (**2m**), and a boronic ester (**2n**) remained intact and were available for subsequent chemical modification. A series of heterocycles frequently found in medicinally relevant targets including thiophenes (**2o**, **2t**) and pyridines (**2p**, **2q**, and **2r**) were well tolerated. This valuable transformation could therefore be used for the late-stage functionalization of pharmaceutically relevant and structurally complex intermediates (**2s**-**2u**). Aryl iodides

derived from commercially available pharmaceuticals, such as empagliflozin (**2s**) and canagliflozin (**2t**) successfully underwent this migratory cross-coupling. Carbohydrate compounds such as the glucose derivative (**2u**) also readily underwent the targeted migratory arylation successfully.

Table 3: Scope of aryl iodide coupling partner.[a]

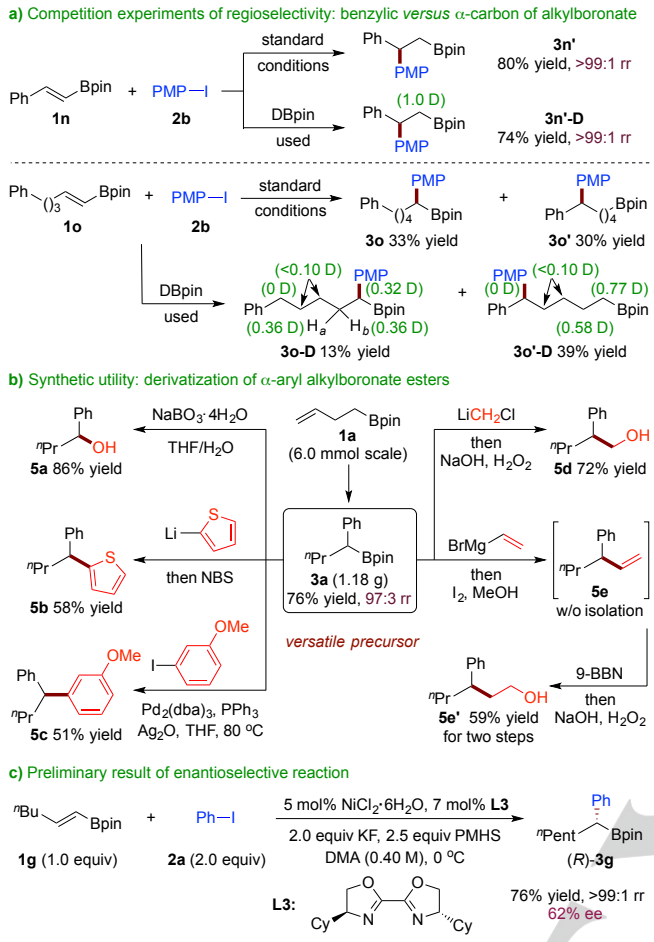


[a] Yield and rr are as defined in Table 2. [b] DMA/MeCN (0.13 M).

The regioselectivity could also be switched to other positions. Competition experiments were carried out to compare the site-selectivity of the benzylic position and the adjacent α-carbon of alkylboronate (Scheme 1a). In general, under the current conditions, arylation takes place at the benzylic position rather than the adjacent α-carbon of the boronate. In the case of the β-boronic ester substituted styrene (**1k**), arylation at the benzylic position to produce exclusively the β-aryl substituted boronate product (**3k'**) was observed. In case of an alkenyl boronate with a remote aryl group in the alkyl chain (**1l**), products arylated at both α-carbon of the boronate (**3l**) and the benzylic position (**3l'**) were obtained as a 1:1 mixture. In contrast to the highly regiospecific insertion of NiH into a styrenic intermediate, isotope labeling experiments indicate that the insertion of NiH into β-alkyl substituted alkenyl boronate is nonregiospecific and reversible.

The robustness and synthetic utility of this catalytic system were further demonstrated by the gram-scale synthesis and subsequent derivatization of the products (Scheme 1b). With the reaction on a gram scale, **3a** was obtained in 76% isolated yield. As noted at the outset, α-functionalized alkylboronates are versatile synthetic intermediates which can be converted into a wide range of other valuable compounds through facile transformations. As illustrated in Scheme 1b, a wide array of functional groups could, using known protocols be introduced smoothly into the benzylic position of **3a** in good yields (**5a**–**5e**).

The current transformation can be realized in an enantioselective fashion using a suitable chiral ligand. In a preliminary experiment (Scheme 1c), with a simple chiral (*S*,*S*)-Cy-Biox ligand **L3**, (*R*)-**3g** was obtained with moderate enantioselectivity (62% ee) and good isolated yield (76%).



Scheme 1. Competition experiments, synthetic utility, and preliminary result of enantioselective conversion.

In summary, based on the NiH-catalyzed remote hydrofunctionalization platform, we have established a practical and efficient remote hydroarylation process forming α-functionalized alkylboronates, from simple boron-containing olefins and commercially available cross-coupling partners. With the mild conditions used, excellent chemo- and regioselectivity was observed for a wide range of both alkene and aryl iodide partners. Further studies on the catalytic asymmetric version of the current transformation based on ligand design are in progress.

Acknowledgements

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Keywords: arylation • C–H activation • isomerization • nickel • regioselectivity

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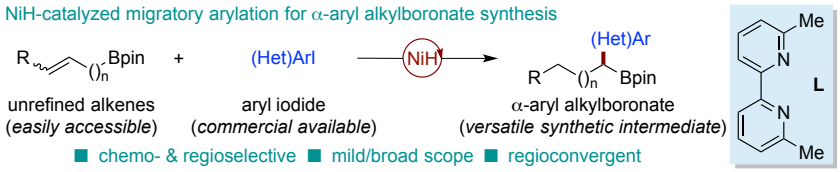

Highly functionalized alkylboronates are versatile synthetic intermediates which are widely used for further derivatization. Using a NiH-catalyzed remote hydrofunctionalization strategy, a migratory arylation process is reported and permits the facile conversion of easily accessible boron-containing olefins and aryl iodides to α-aryl alkylboronates.

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