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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Transition-Metal-Free Stereospecific Cross-Coupling with Alkenylboronic Acids as Nucleophiles

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Supporting Information

ABSTRACT: We herein report a transition-metal-free cross-coupling between secondary alkyl halides/mesylates and aryl/alkenylboronic acid, providing expedited access to a series of nonchiral/chiral coupling products in moderate to good yields. Stereospecific S_N2-type coupling is developed for the first time with alkenylboronic acids as pure nucleophiles, offering an attractive alternative to the stereospecific transition-metal-catalyzed $C(sp^2)-C(sp^3)$ cross-coupling.

Due to the continuing advances in transition-metal catalysis, cross-coupling, in particular $C(sp^2)-C(sp^2)$ Suzuki–Miyaura coupling, is noted for its unprecedented broad scope and applications in organic synthesis.[1] In contrast, $C(sp^2)-C(sp^3)$ cross-coupling[2] remains relatively underdeveloped due to issues related to β-hydride elimination. A few enantioselective aryl/alkenyl–alkyl couplings[3,4] have appeared with the employment of chiral transition-metal catalysts (Figure 1). Alternatively, enantiospecific aryl/alkenyl–alkyl couplings are accomplished by employing chiral reagents such as chiral secondary alkyl organometallic reagents[5] or chiral secondary alkyl electrophiles with a considerable amount of transition metal catalysts (mostly 5–10 mol %).[6] The traditional S_N2 reactions using lithium or Grignard reagents often require cryogenic reaction conditions and usually suffer from poor functional group compatibility. An attractive alternative would be a transition-metal-free enantiospecific $C(sp^2)-C(sp^3)$ cross-coupling[7] with stable, nontoxic, and environmentally friendly aryl/alkenylboronic acids as nucleophiles. Herein we report for the first time a stereospecific transition-metal-free cross-coupling between chiral secondary benzylic mesylates and alkenylboronic acids that have led to a series of chiral coupling products with functionalities in excellent stereochemical fidelity.

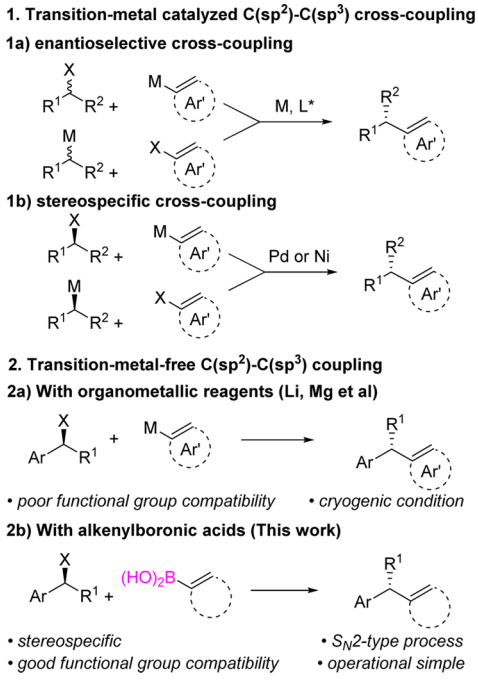


Figure 1. Asymmetric $C(sp^2)-C(sp^3)$ cross-coupling.

Due to relatively low nucleophilicity, aryl/alkenylboronic acids are less reported as pure nucleophiles, but more rather as coupling reagents in transition-metal catalyzed Suzuki–Miyaura cross-coupling reactions.[1] One of most known examples of aryl/alkenylboronic acids as pure nucleophiles is the Petasis borono-Mannich reaction,[8] where the addition of an aryl/alkenylboronic acid or equivalent to a C=N π bond takes place. Accordingly, the nucleophilic addition of aryl/alkenylboronic acids or equivalents to π systems such as C=N, C=O, and C=C double bonds are most reported,[7b,9] whereas little study is available on nucleophilic substitution of aryl/alkenylboronic acids to tetravalent (sp^3) carbons.

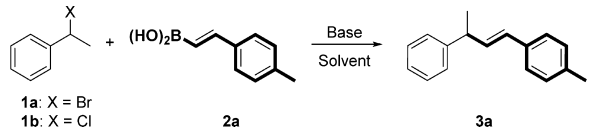
To the best of our knowledge, only reactions of aryl/alkenylboronic acids with terminal allyl bromides were studied[10] and no reports are available on nucleophilic substitution between secondary alkyl halides/pseudohalides and aryl/alkenylboronic acids under transition-metal-free conditions. We herein report the transition-metal-free cross-coupling between secondary benzylic halides/mesylates and aryl/alkenylboronic acids. Stereospecific S_N2-type couplings between chiral functionalized secondary benzylic mesylates and alkenylboronic acids are observed for the first time, offering an attractive alternative to the stereospecific transition-metal-catalyzed $C(sp^2)-C(sp^3)$ cross-coupling.

We chose to study the cross-coupling between 1-bromoethylbenzene (**1a**) and (*E*)-(4-methylstyryl)boronic acid (**2a**) under metal-free conditions (Table 1). The reactions were initially performed in toluene at 80 °C for 4 h. To our delight, the desired coupling product was formed in 32% yield with KOH as the base (entry 1). Screening of different bases (entries 1–8) revealed

Received: June 17, 2016
Published: August 12, 2016

DOI: 10.1021/jacs.6b06285
J. Am. Chem. Soc. 2016, 138, 10774–10777

Table 1. Metal-Free Cross-Coupling between 1-Haloethylbenzene (1a/b) and (*E*)-(4-Methylstyryl)boronic Acid (2a)



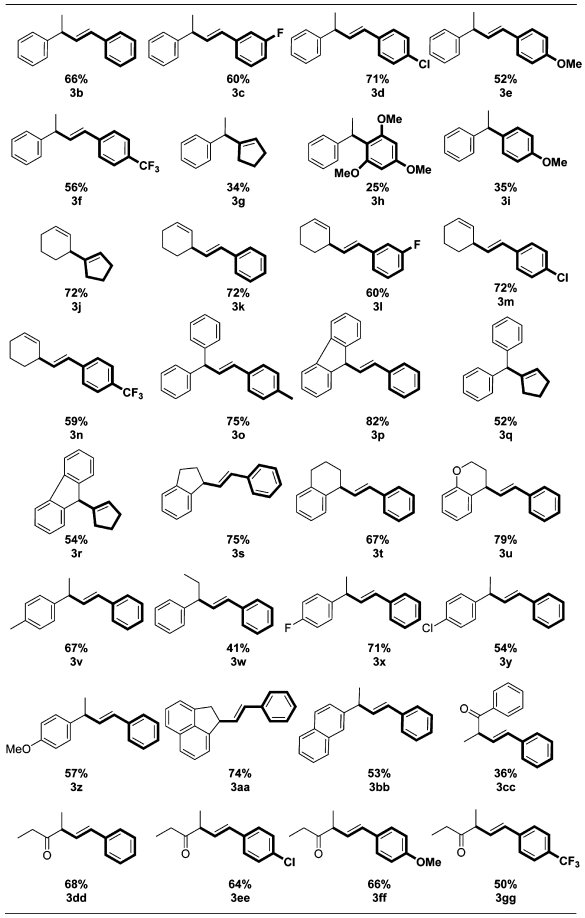
entry[a]	X	base	solvent	*T* (°C)	yield (%)[b]
1	Br	KOH	toluene	80	32
2	Br	NaO*t*Bu	toluene	80	24
3	Br	KF	toluene	80	0
4	Br	$NaHCO_3$	toluene	80	1
5	Br	K_2CO_3	toluene	80	31
6	Br	Cs_2CO_3	toluene	80	46
7	Br	Et_3N	toluene	80	0
8	Br	K_3PO_4	toluene	80	73
9	Br	K_3PO_4	THF	80	19
10	Br	K_3PO_4	dioxane	80	24
11	Br	K_3PO_4	DCE	80	57
12	Br	K_3PO_4	cyclohexane	80	31
13	Br	K_3PO_4	DMF	80	17
14	Br	K_3PO_4	toluene	110	50
15	Br	K_3PO_4	toluene	50	59
16	Br	K_3PO_4	toluene	rt	14
17[c]	Br	K_3PO_4	toluene	80	5
18	Cl	K_3PO_4	toluene	80	35

[a]Unless otherwise specified, all reactions were performed in the selected solvent (10 mL) under nitrogen at 80 °C for 4 h with **1a** or **1b** (1 mmol), **2a** (1.5 mmol) with base (2 equiv). [b]Isolated yields. [c]Pinacol boronate of **2a** was employed as the reagent.

that strong inorganic bases promoted this reaction, and an organic base such as triethylamine was ineffective. Potassium phosphate led to a good coupling yield (73%, entry 8). Solvent screening (entries 8−13) showed polar solvents such as THF, DCE, dioxane, and DMF were detrimental to the yields (entries 9−13). This could be due to the severe elimination side reaction of **1a** in a polar solvent. The coupling was sluggish at rt (entry 16), but proceeded at both 50 and 110 °C to provide moderate yields (entries 14−15). The boronic acid form of **2a** was important for the reactivity since its pinacol boronate under similar conditions offered only a 5% yield (entry 17). 1-Chlorethylbenzene was also applicable to this protocol to provide the product in 35% yield (entry 18).

We then looked into the substrate scope of this metal-free cross-coupling reaction. As shown in Table 2, a variety of coupling products were synthesized in moderate to good yields between secondary benzylic bromides and phenyl/styrylboronic acids under metal-free conditions. A series of substituted styrylboronic acids were reacted with 1-bromoethylbenzene (**1a**) to form coupling products **3b−i** in good yields. Cyclopentenylboronic acid was also applicable. Electron-rich arylboronic acids such as 2,4,6-$(MeO)_3C_6H_2B(OH)_2$ and 4-$MeOC_6H_4B(OH)_2$ were also employed to form the 1,1-diarylethane derivatives **3h−i** albeit in low yields. A secondary allyl bromide 3-bromocyclohex-1-ene was also employed to couple with various alkenylboronic acids to provide coupling products **3j−n** in 59−72% yields. Diphenylmethyl bromide and 9-bromofluorene were also adaptable to provide corresponding coupling products **3o−r** in 52−82% yields. Cyclic secondary benzyl bromides were also successfully employed to couple with styrylboronic acid to give products **3s−u** in good yields. Various

Table 2. Cross-Coupling between Secondary Bromides and Alkenyl/Arylboronic Acids[a]



[a]Unless otherwise specified, all reactions were performed in toluene (10 mL) under nitrogen at 80 °C for 4 h with bromide (1 mmol), alkenyl/arylbronic acid (1.5 mmol), with K_3PO_4 (2 equiv) as the base. Isolated yields.

substituted benzyl bromides with different electronic properties were applicable to react with styrylboronic acid, leading to coupling products **3v−3bb** in moderate to good yields. Interestingly, α-bromo ketones were also able to react with various substituted styrylboronic acids to form the coupling products **3cc−gg** in acceptable yields.

To understand whether a radical process was involved (Figure 2), the reaction of **1a** and (*E*)-styrylboronic acid (**2b**) was performed in the presence of TEMPO and the coupling product **3b** was obtained in 68% yield, indicating that the reaction was unlikely to proceed through a radical pathway. A series of deuterium-labeling experiments showed that the deuterium at the benzylic position was well preserved during the reaction course and in the deuterated coupling product **5**, excluding the possibility of deprotonation of the benzylic proton during the reaction. The observation of a secondary kinetic isotope effect (1.2) indicated an S_N2-type reaction process. Finally, an enantiomerically enriched bromide (*R*)-**1a** (88% ee) was employed to react with boronic acid **2b** and the coupling product (*R*)-**3b** was isolated in 70% yield and 64% ee with an inverse configuration, further supporting the S_N2-type coupling process. The slight erosion of ee in (*R*)-**3b** was likely due to the prone-to-racemization nature of (*R*)-**1a**.[11]

DOI: 10.1021/jacs.6b06285
J. Am. Chem. Soc. 2016, 138, 10774−10777

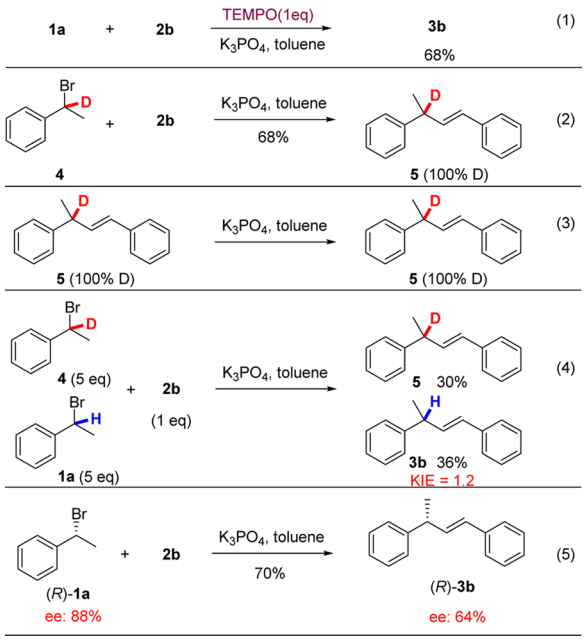


Figure 2. Mechanistic studies.

A plausible mechanism was proposed for this transition-metal-free coupling process (Figure 3). Under basic conditions,

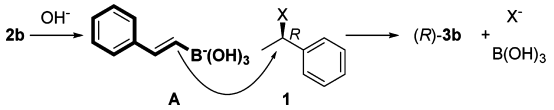
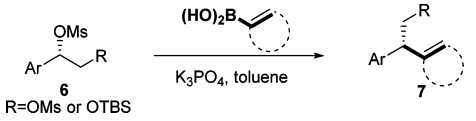


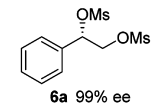
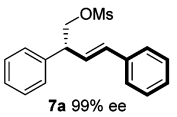
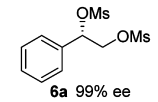
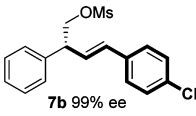
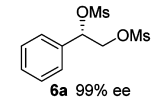
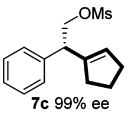
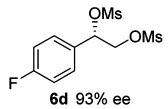
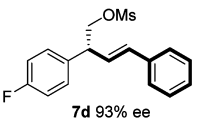
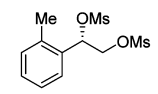
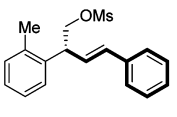
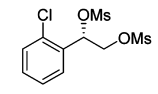
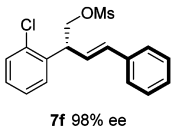
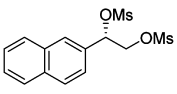
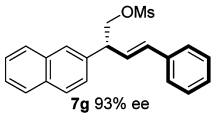
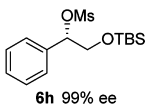
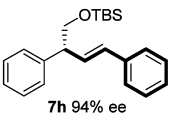
Figure 3. A proposed mechanism.

hydroxyl ions coordinate with alkenylboronic acids **2b** to form the species **A**, whose anionic nature leads to enhanced nucleophilicity at the olefinic carbon. Nucleophilic attack of **A** to the chiral secondary benzyl halide **1** forms the desired coupling product (*R*)-**3b** with an inverted stereochemical outcome. Noteworthy is the active nature of the secondary benzyl/allyl halide or α-bromo ketone[12] which allows for the first time the successful S_N2-type attack of a weakly nucleophilic aryl/alkenylboronic acid.

In order to develop a racemization-free coupling process, a stable chiral secondary benzyl halide/pseudohalide is required. While simple chiral 1-haloethylbenzene is prone to racemization and 1-phenylethyl mesylate is too unstable for isolation at rt,[11] we were pleased to learn that some functionalized benzylic mesylates **6a–h** were relative stable solids free of racemization.[14] We envisioned that chiral 1-arylethan-1,2-diyl dimesylates **6a–g** could be suitable substrates for S_N2-type attack of an alkenylboronic acid. Thus, the transition-metal-free cross-coupling between compounds **6a–g** and alkenylboronic acids were studied. As shown in Table 3, the coupling proceeded smoothly to provide a series of chiral coupling products **7a–g** containing terminal mesylates in good yields and excellent chemo- and regioselectivity. A cyclic alkenylboronic acid was also applicable (entry 3).[15] Only the benzylic mesylates were active for the coupling reaction under the reaction conditions, demonstrating the excellent functional group compatibility of the coupling. The terminal mesylates were opt for further derivatizations. The chiral products **7a–g** with inverted stereochemistry and excellent stereochemical fidelity further verified its

Table 3. Stereospecific Transition-Metal-Free Cross-Coupling between Chiral Benzylic Mesylate 6 and Alkenylboronic Acids[a]



Entry	Substrates	Product	Yield (%)
1	 **6a** 99% ee	 **7a** 99% ee	72%
2	 **6a** 99% ee	 **7b** 99% ee	58%
3[b]	 **6a** 99% ee	 **7c** 99% ee	65%
4	 **6d** 93% ee	 **7d** 93% ee	75%
5	 **6e** 90% ee	 **7e** 90% ee	70%
6	 **6f** 98% ee	 **7f** 98% ee	55%
7	 **6g** 96% ee	 **7g** 93% ee	66%
8[b]	 **6h** 99% ee	 **7h** 94% ee	68%

[a]Unless otherwise specified, all reactions were performed in toluene (10 mL) under nitrogen at 50 °C for 2 h with mesylate **6** (1 mmol), alkenylboronic acid (1.5 mmol), and K_3PO_4 (2 equiv) as the base; isolated yields, enantiomeric excesses were determined by chiral HPLC. Compound **6a** was prepared from corresponding commercially available chiral diol by dimesylation. Compounds **6d–g** were prepared from corresponding olefins by Sharpless dihydroxylation with AD-mix-α as the reagent. The absolute configuration of **7a** was determined by conversion to (*R*)-**3b** by treatment with LAH and comparison of its optical rotation to the reported data.[13] The absolute configuration of **7b–h** was assigned by analogy. [b]T = 12 h.

S_N2-type coupling process. A chiral benzylic mesylate **6h** with a terminal OTBS group was also employed to form the coupling product **7h** in 68% yield and 94% ee.

In conclusion, we have developed for the first time the transition-metal-free cross-coupling between secondary benzyl/allyl halides/mesylates and aryl/alkenylboronic acids in moderate to good yields. Mechanistic studies have revealed its S_N2-type process. Stereospecific couplings between chiral functionalized

DOI: 10.1021/jacs.6b06285
J. Am. Chem. Soc. 2016, 138, 10774–10777

benzylic mesylates and alkenylboronic acids are developed, providing a series of chiral coupling products with functionalities in good yields as well as excellent regio- and chemoselectivities with great functional group compatibility. The discovery and application of alkenylboronic acids as pure nucleophiles for S_N2-type reaction not only offers an attractive alternative to the stereospecific transition-metal-catalyzed $C(sp^2)-C(sp^3)$ cross-couplings but also enriches the nucleophile repertoire for nucleophilic substitution.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06285.

Full experimental details, characterization data, NMR spectra of **3a**−**gg**, **6a**−**h**, **7a**−**h**, derivatization of **7a**, chiral separation methods and HPLC trace of **6a**−**h** and **7a**−**h** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by NSFC-21432007, 21272254, 21572246.

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DOI: 10.1021/jacs.6b06285
J. Am. Chem. Soc. 2016, 138, 10774−10777