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Visible-Light-Mediated Alkenylation of Alkyl Boronic Acids without an External Lewis Base as an Activator

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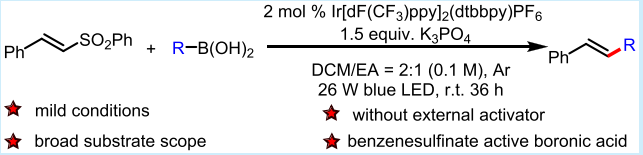
ABSTRACT: Herein we report a protocol for the direct visible-light-mediated alkenylation of alkyl boronic acids at room temperature without an external Lewis base as an activator, and we propose a mechanism involving benzenesulfinate activation of the alkyl boronic acids. The protocol permits the efficient functionalization of a broad range of cyclic and acyclic primary and secondary alkyl boronic acids with various alkenyl sulfones. We demonstrated its utility by preparing or functionalizing several pharmaceuticals and natural products.



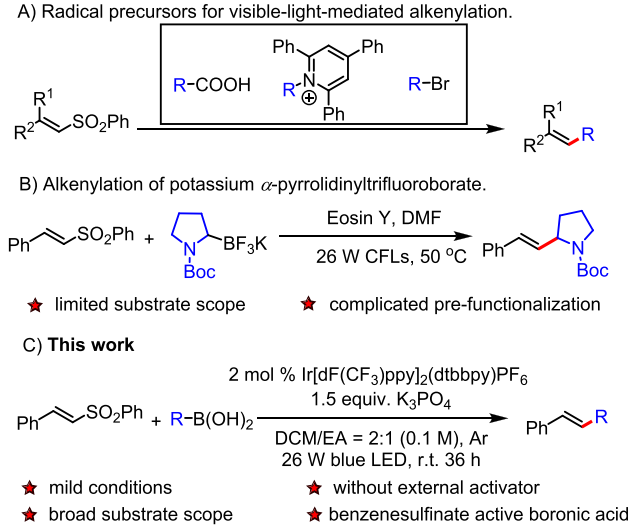
Because of their versatility, alkenes are widely used in synthetic chemistry and materials science.[1] Consequently, tremendous research effort has been devoted to developing methods for alkene synthesis, such as Heck-type,[2] Wittig-type,[3] and Corey−Winter-type reactions[4] as well as many others.[5] Of the known methods, the transition-metal-catalyzed cross-coupling of alkenes with preactivated/functionalized alkanes is the best, most straightforward tool for the synthesis of these compounds with predictable chemo- and regioselectivity.[5] Nevertheless, the currently available methods have some drawbacks, such as requiring the use of organometallic reagents (which are usually sensitive to water and air), strong oxidants, or high temperatures.[6]

With the rapidly increasing interest in the use of photoredox catalysis in organic chemistry,[7] photoredox alkenylation reactions have begun to emerge in recent years.[8] For example, visible-light-mediated alkenylation reactions that use alkenyl sulfones as radical acceptors and aliphatic carboxylic acids,[8a] alkyl bromides,[9] or Katritzky pyridinium salts[10] as radical precursors have been reported (Scheme 1A). In addition, the use of vinyl potassium trifluoroborates[11] and alkenylboronic acids[12] instead of vinyl sulfones has been reported. Although these reactions are operationally simpler and use fewer oxidants than previously reported methods, most of them have a limited substrate scope, and some of them require high temperature.

In 2016, Molander and coworkers[13] described a protocol for visible-light-mediated alkenylation that utilizes potassium α-pyrrolidinyltrifluoroborate as an alkyl radical source in reactions involving alkenyl sulfones (Scheme 1B); however, the preparation of these alkyl fluoroborate salts needed three harsh steps, and the substrate scope was limited in potassium α-pyrrolidinyltrifluoroborate.

We speculated that readily available alkyl boronic acids could serve as an alternative radical source.[14] Because alkyl boronic acids have high oxidation potentials (E_{red} = +2.5 V vs SCE for secondary boronic acids), they cannot efficiently quench the excited states of metal or organic photocatalysts to generate alkyl radicals,[15] and their synthetic utility has therefore been limited. However, it is worth noting that Ley and coworkers[16] overcame this problem by using a Lewis base to decrease the oxidation potentials of alkyl boronic acids so that they could efficiently quench excited-state photocatalysts. Chen and coworkers[17] used hypervalent iodine activated

Scheme 1. Photoredox-Mediated Alkenylation Reactions



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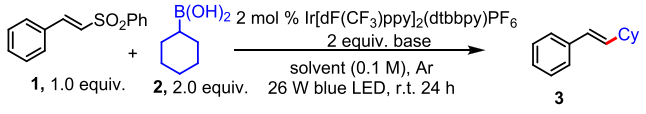
boronic acids as an alkyl radical source. We hypothesized that benzenesulfinates, which can be obtained from alkenyl sulfones, could effectively activate boronic acids and thus avoid the need for an additional Lewis base. Herein we now report that we have indeed succeeded in developing a protocol for mild, visible-light-mediated alkenylation reactions of a wide array of boronic acids directly, without the need for an external activator (Scheme 1C).

To optimize the reaction conditions, we used phenyl *trans*-styryl sulfone (**1**, 1.0 equiv) and cyclohexylboronic acid (**2**, 2.0 equiv) as model substrates (Table 1). First, several different

Table 1. Optimization of Conditions[a]



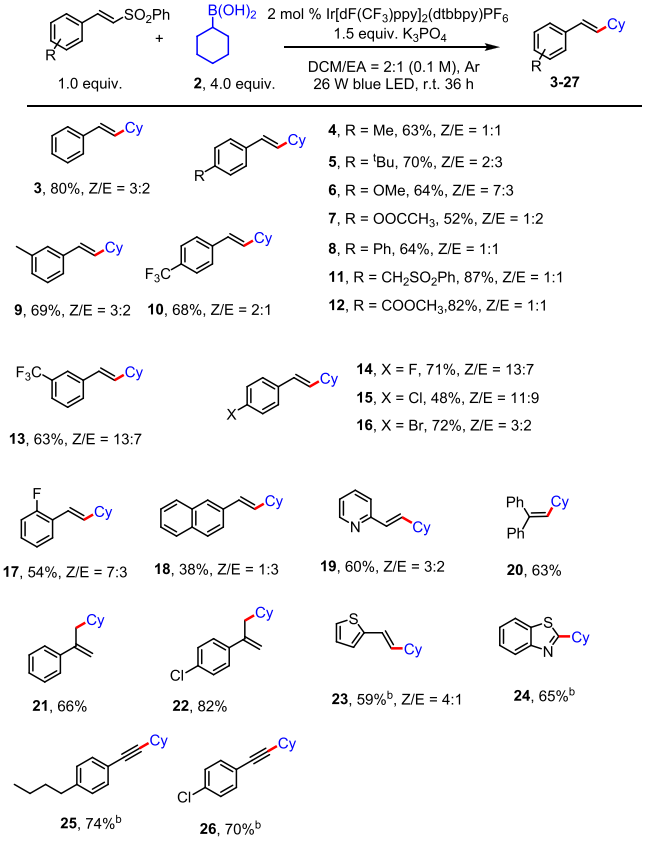
entry	solvent	base	yield (%)[b]
1	DCM	K_2HPO_4	44
2	DCM/EA = 2:1	K_2HPO_4	51
3	DCM/EA = 2:1	K_2HPO_4	57
4	DCM/EA = 2:1	K_2CO_3	60
5	DCM/EA = 2:1	K_3PO_4	67
6[c]	DCM/EA = 2:1	K_3PO_4	75
7[c,d]	DCM/EA = 2:1	K_3PO_4	89 (80[e])
8[c,d,f]	DCM/EA = 2:1 (0.13 M)	K_3PO_4	78
9[c,d,g]	DCM/EA = 2:1 (0.2 M)	K_3PO_4	62
10[c,d,h]	DCM/EA = 2:1	K_3PO_4	NR
11[c,d,i]	DCM/EA = 2:1	K_3PO_4	NR
12[c,d,j]	DCM/EA = 2:1	no base	trace
13[c,d,k]	DCM/EA = 2:1	K_3PO_4	42

[a]Reaction conditions, unless otherwise noted: **1** (0.2 mmol), **2** (0.4 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.004 mmol), base (0.4 mmol), solvent (2 mL), rt, Ar atmosphere, 24 h. [b]Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. NR = no reaction. [c]**2** (4 equiv., 0.8 mmol), 36 h. [d]Base (1.5 equiv., 0.3 mmol). [e]Isolated yield. [f]Solvent (1.5 mL, 0.13 M). [g]Solvent (1 mL, 0.2 M). [h]No photocatalyst. [i]No light. [j]No base. [k]Air atmosphere.

solvents were screened with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as the photocatalyst and K_2HPO_4 as the base under irradiation with a 26 W blue LED for 24 h at room temperature (entries 1−3). We were pleased to find that the desired product **3** could be obtained in 57% yield from the reaction in 2:1 (v/v) dichloromethane/ethyl acetate. When we varied the base, we discovered that K_3PO_4 gave a slightly higher yield than K_2HPO_4 and K_2CO_3 (compare entries 3−5). When we increased the amount of **2** from 2.0 to 4.0 equiv and the reaction time from 24 to 36 h, the yield further increased to 75% (entry 6). Simultaneously reducing the amount of base from 2 to 1.5 equiv afforded the highest yield (89% by NMR, 80% isolated; entry 7). Increasing the concentration of the reactants (entries 8 and 9) was detrimental. Control experiments showed that the reaction failed to proceed in the absence of light, base, or photocatalyst (entries 10−12). Under air, **3** was obtained in 42% yield (entry 13). Then, we screened the photocatalyst. The desired product **3** was obtained in excellent yield when 2 mol % of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was used as the photocatalyst. (See the SI.) Then, the light source was screened. All light sources could provide products in excellent yield (see the SI), and the yield would increase slightly when we used 450 nm light.

With the optimized conditions in hand, we explored the scope of the reaction with respect to the alkenyl sulfone (Scheme 2). Reactions between cyclohexylboronic acid and

Scheme 2. Scope of the Reaction with Respect to the Alkenyl Sulfone[a]



[a]Reactions were performed on a 0.2 mmol scale, and isolated yields are given. [b]Reactions were performed under 450 nm LED irradiation.

various sulfones with electron-donating or electron-withdrawing substituents all gave moderate yields (52−87%) of the desired products (**4**−**9** and **10**−**13**, respectively). Fluorinated and brominated sulfones (**14** and **16**) gave higher yields than a chlorinated sulfone (**15**), and para substitution (**14**) resulted in a higher yield than ortho substitution (**17**). Naphthyl, pyridyl, and 1,1-disubstituted alkenyl compounds were also suitable, affording the desired products **18**−**20** in moderate yields (38−63%). In addition, we were delighted to find that ((2-phenylallyl)sulfonyl)benzene and 1-chloro-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene could also be used as radical acceptors; when they were subjected to the alkenylation conditions, the desired products **21** and **22** were obtained in moderate yields. We continued to explore other vinyl compounds, such as thiophene (**23**) and benzothiazole (**24**), all of which were obtained in moderate yields (59 and 65%). We were pleasantly surprised to find that when we used alkynyl sulfone as a free-radical acceptor, the products (**25** and **26**) were still obtained in moderate yields (74 and 70%). As for Z/E geometry,[18] unfortunately, in our reaction system, we could not increase its ratio. (See the SI.)

Next we explored the scope of the reaction with respect to the alkyl boronic acid by using methyl (*E*)-4-(2-(phenylsulfonyl)vinyl)benzoate or (*E*)-4-(2-(phenylsulfonyl)-

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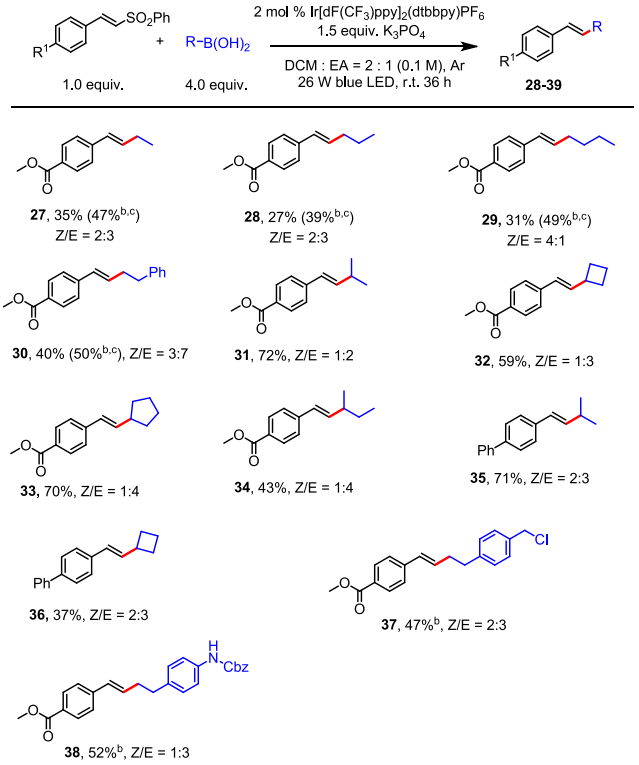
vinyl)-1,1′-biphenyl as the alkenyl sulfone (Scheme 3). We found that a wide range of primary alkyl boronic acids reacted

Scheme 3. Scope of the Reaction with Respect to the Alkyl Boronic Acid[a]

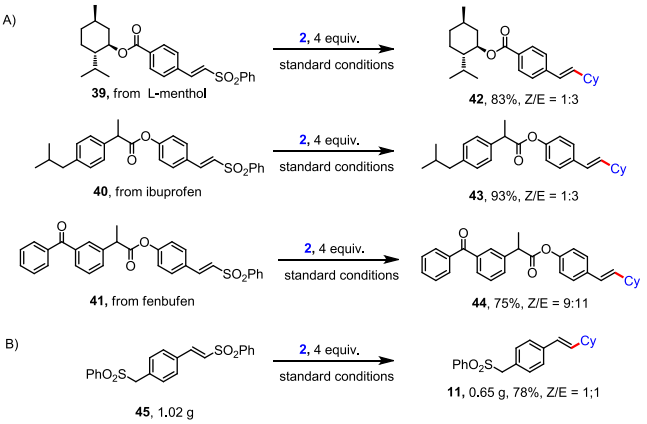


[a]Reactions were performed on a 0.2 mmol scale, and isolated yields are given. [b]Reactions were performed under 450 nm LED irradiation. [c]t = 48 h, Yields were determined by ^{1}H NMR spectroscopy with dibromomethane as an internal standard.

with methyl (*E*)-4-(2-(phenylsulfonyl)vinyl)benzoate to afford alkenylated products (**27**−**30**) in 27−40% yields. Owing to the lower nucleophilicity and stability of primary radicals, the alkenylation of primary alkyl boronic acids is much more challenging than the alkylation of secondary and tertiary compounds.[19] Therefore, we tested some secondary boronic acids in our alkenylation reaction under the standard conditions and found that they afforded the corresponding alkenylated products (**31**−**36**) in much higher yields than those obtained from the primary alkyl boronic acids. We were pleasantly surprised to find that when we used more complex boronic acids, the products (**37** and **38**) could be obtained in moderate yields (47 and 52%). When we used a 450 nm light source and extended the reaction time to 48 h, the yield of the reaction was slightly improved (see the SI), but for tertiary boronic acid, the yield was extremely poor.[20]

Next, we subjected some natural products and drug molecules to the standard alkenylation conditions to test the utility of the protocol for functionalized molecules. We were pleased to find that L-menthol-, ibuprofen-, and fenbufen-derived (**39**−**41**) alkenylation products (**42**−**44**) could be obtained in excellent yields (Scheme 4A). In addition, a gram-scale reaction between **45** and **2** under the standard conditions gave the corresponding alkenylated product (**11**) in 78% yield (Scheme 4B).

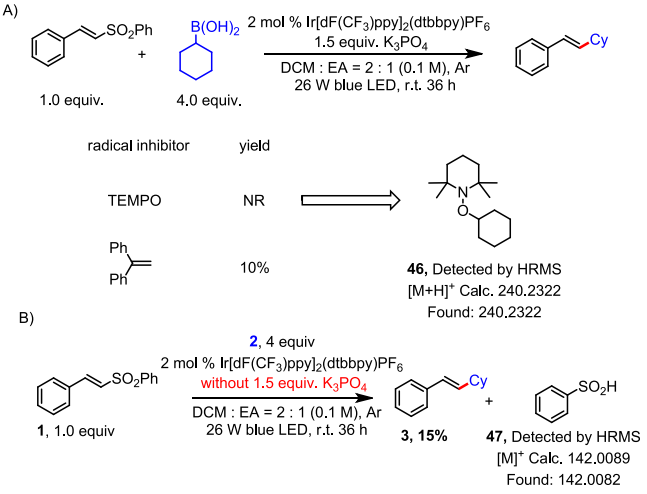
Scheme 4. Applications of the Alkenylation Protocol: (A) Alkenylation of Natural Products and Drug Molecules and (B) Gram-Scale Experiment[a]



[a]Reactions were performed on a 0.2 mmol scale, and isolated yields are given.

Having explored the substrate scope and the utility of the reaction, we turned our attention to its mechanism (Scheme 5). First, we found that the reaction of **1** and **2** was prevented

Scheme 5. Mechanistic Experiments: (A) Free-Radical Inhibition Experiment and (B) Control Experiment[a]



[a]Reactions were performed on a 0.2 mmol scale. Yields were determined by ^{1}H NMR spectroscopy with dibromomethane as an internal standard.

when a radical scavenger such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (butylated hydroxytoluene) was present in the reaction mixture (Scheme 5A). Furthermore, the radical trapping product 1-(cyclohexyloxy)-2,2,6,6-tetramethyl-piperidine (**46**) was detected by high-resolution mass spectrometry. This experiment clearly points to a radical pathway. A light/dark experiment showed that **3** formed only under light irradiation (see the SI), indicating that light was essential for product formation and that any chain-propagation process was short-lived. To determine whether the benzene-sulfinate derived from the alkenyl sulfone could effectively activate the boronic acid, we measured the ^{1}H NMR spectra of mixtures of phenethylboronic acid and benzenesulfinate at various concentrations in DMSO-d_6, and we observed that

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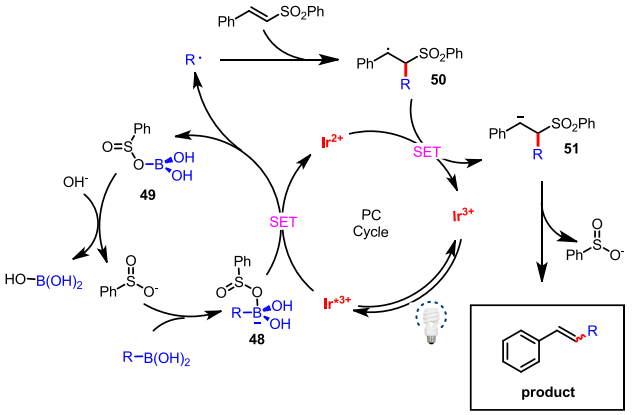
gradually increasing the total concentration of benzenesulfinate in the NMR tube shielded the phenethylboronic acid α-CH_2 signal. (See the SI.) In addition, we performed cyclic voltammetry measurements to study the effect of the benzenesulfinate on the oxidation potential of cyclohexylboronic acid. When we added benzenesulfinate and cyclohexylboronic acid to acetonitrile, we detected a new, low-potential oxidation peak (see the SI). We also studied the emission quenching experiments. (See the SI.) Therefore, we assumed that the oxidation potential of cyclopentane boronic acid was markedly reduced by the coordination of benzenesulfinate.

To explore the role of the base, we did a control experiment. We found that in the absence of base, we detected the formation of benzenesulfonic acid in the reaction system (Scheme 5B), and the fluorescence quenching experiment proved that the mixture of base and boronic acid could not quench the photocatalyst. The solubility of benzenesulfinate in our reaction solvent is very poor. Therefore, we think that if there is no base and our reaction system is acidic and benzenesulfinate will capture hydrogen protons, then the ability to activate boronic acid by benzenesulfinate will be significantly reduced.

On the basis of our experimental observations and literature reports,[8−12,17] we proposed the mechanism depicted in Scheme 6.[21] First, the Ir^{3+} photocatalyst is excited by visible

Scheme 6. Proposed Mechanism



light; then, the excited state is quenched by benzenesulfinate-activated alkyl boronic acid **48** to form a nucleophilic alkyl radical and species **49**, along with a highly reducible Ir^{2+} species. Then, the alkyl radical adds to the alkenyl sulfone to afford benzyl radical **50**. Single-electron reduction of **50** by Ir^{2+} generates benzyl anion **51**, and the subsequent departure of a sulfone group gives the product and completes the photoredox cycle. Attack of solvent-derived water on **49** completes the benzenesulfinate activation cycle.

In conclusion, we have developed a mild protocol for visible-light-mediated alkenylation reactions of alkyl boronic acids without the need for an external Lewis base as an activator, and we propose that the reactions proceed via a mechanism involving benzenesulfinate-activated alkyl boronic acids. The mildness of the protocol makes it suitable for the late-stage functionalization of natural products and drug molecules. Our findings offer a new route to active alkyl boronic acids, leading to the generation of alkyl radicals under mild photoredox conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00399.

Experimental procedure and characterization for all new compounds, copies of NMR spectra, and cyclic voltammograms (PDF)

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Notes

The authors declare no competing financial interest.

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