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This work may now be cited as: *Chin. J. Chem.* **2021**, *39,* 10.1002/cjoc.202100115.

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ISSN 1001-604X • CN 31-1547/O6
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Report

Cite this paper: *Chin. J. Chem.* **2021**, *39*, XXX—XXX. **DOI: 10.1002/cjoc.202100XXX**

Photoinduced NaI-Promoted Radical Borylation of Alkyl Halides and Pseudohalides

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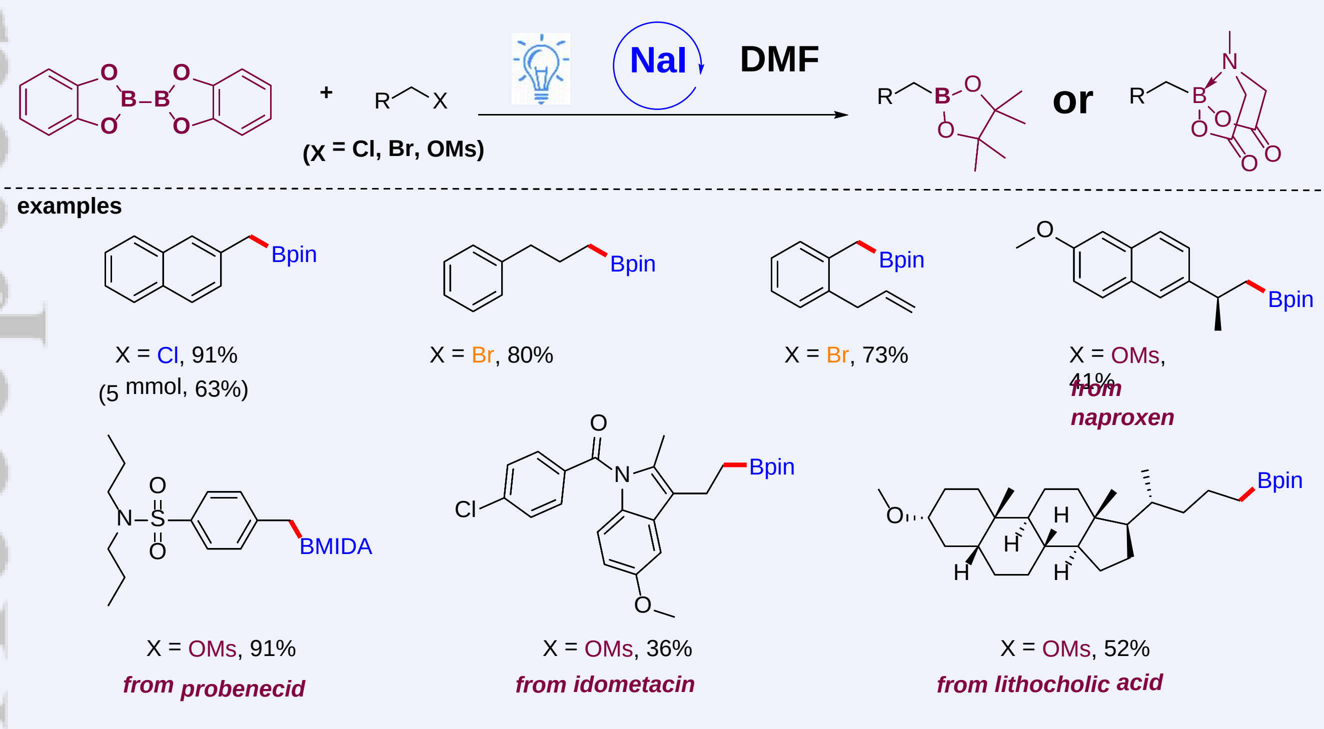
Keywords

Alkylboronate | Borylation | Radical | Metal-catalyst free | Aliphatic halide

Main observation and conclusion

A method for photoinduced NaI-promoted radical borylation of aliphatic halides and pseudohalides with bis(catecholato)diboron (B_2cat_2) as the boron source is introduced. The borylation reaction is operationally simple and shows high functional group tolerance and broad substrate scope. Preliminary mechanistic studies suggest that the reaction proceeds through S_N2-based radical-generation strategy.

Comprehensive Graphic Content



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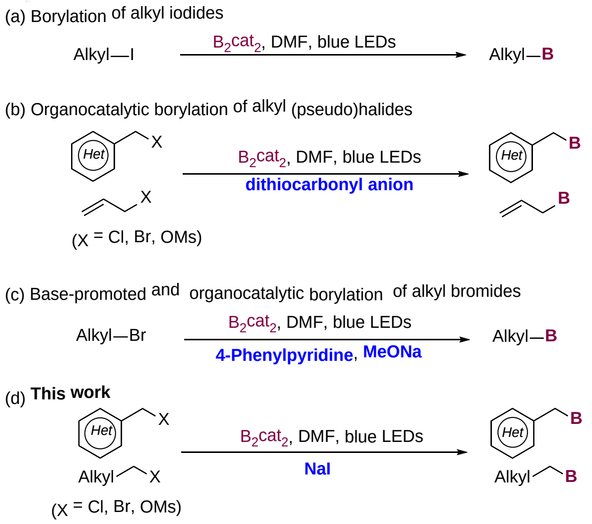
Background and Originality Content

Alkylboronates are versatile synthetic building blocks due to the fact that the C-B bond is readily transformed into a great variety of useful functional groups.[1] Therefore, the construction of alkylboronates is the subject of substantial synthetic efforts.[2]

Classical approaches to prepare alkylboronates include hydroboration of alkenes[3] and electrophilic substitution of suitable boron compounds with organometallic reagents.[4] Organohalides are commercially abundant, with diverse structures and stable properties. They are commonly used as raw materials in organic synthesis.[5] In the past several years, numerous novel strategies for constructing C-B bonds from alkyl halides with diboron reagents have emerged. Significant progress on transition-metal-catalyzed borylation of alkyl halides has been achieved by Marder,[6] Liu,[7] Ito,[8] Fu[9] and Cook[10] and many others.[11] However, these highly efficient methods inevitably use transition-metals, ligands and bases. Recently, photoinduced radical borylation reaction has become a powerful platform for the synthesis of alkylboronates.[12] For example, in 2018, Studer group reported a radical borylation of alkyl iodides with B_2cat_2 (bis(catecholato)diboron) as the boron source (Scheme 1a).[13] Subsequently, Melchiorre et al. reported a visible-light-mediated organocatalytic system for the synthesis of alkylboronates (Scheme 1b).[14] In addition, the base-promoted radical borylations of alkyl halides were developed by Mo[15] and Jiao (Scheme 1c),[16] respectively. Despite the clear improvement, these methods still require highly reactive and unstable iodide derivatives or benzylic and allylic compounds, while the transition-metal-free borylation of alkyl chlorides or pseudohalides are rarely reported. Therefore, simple and reliable synthetic routes for the synthesis of alkylboronates from less reactive alkyl halides or pseudohalides, especially alkyl chlorides in the absence of transition-metal catalysts are still worth exploring.

Herein, we report a visible-light-mediated catalytic system for the synthesis of alkylboronic acid derivatives from alkyl chlorides, bromides and mesylates with commercially accessible bis(catecholato)diboron as the boron source. This strategy demonstrated good functional group tolerance for rapid access to various alkylboronates.

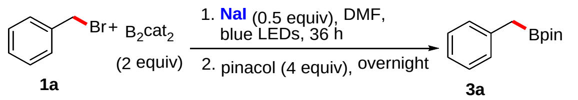
Scheme 1 Photoinduced borylation of alkyl (pseudo)halides



Results and Discussion

We evaluated the conditions for this borylation reaction and found out that in the presence of 50 mol% NaI and B_2cat_2 (2 equiv) in DMF (0.2 M) at ambient temperature under irradiation of blue LEDs, alkylboronate **3a** was obtained in 90% yield from benzyl bromide (**1a**) (Table 1, entry 1). Control experiments established that in the absence of light irradiation or NaI, the reaction proceeded in low yields (entries 2 and 3). In the absence of light irradiation and NaI, only trace amounts of the borylation product 3a were observed (entry 4). Switching the solvent from DMF to the DMA slightly lowered the reaction efficiency (entry 5), while further solvent screening (MeCN, CH_2Cl_2) did not lead to the desired product **3a** (entries 6 and 7). Other boron sources were evaluated as well, such as B_2pin_2 (bis(pinacolato)diboron) and $B_2(OH)_2$ ((dihydroxyboranyl)boronic acid), both of them did not render any product formation under the identical conditions (entries 8 and 9).

Table 1 Optimization studies[a]



1a **3a**

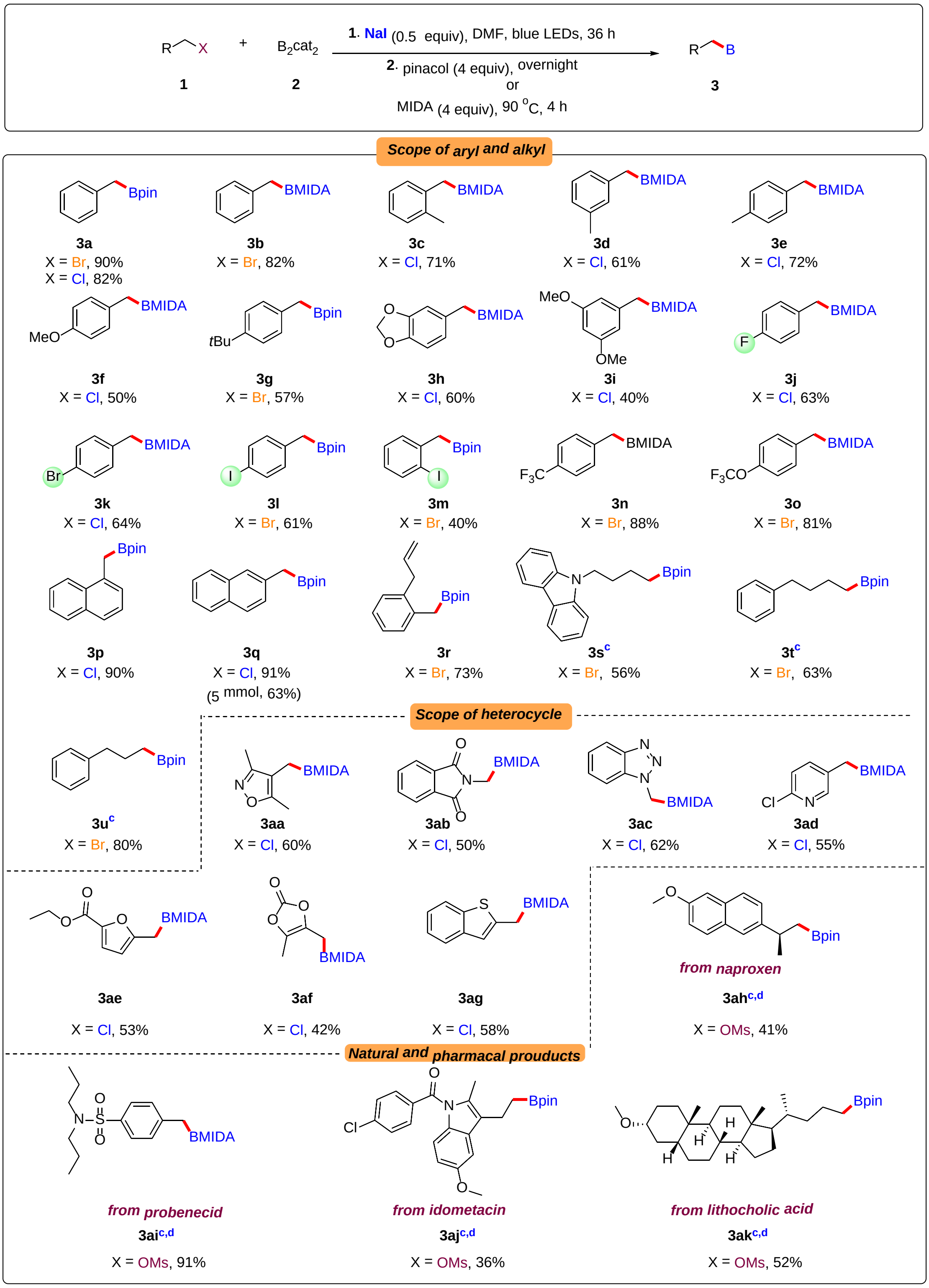
Entry	Deviation from the standard conditions	Yield of **3a** (%)[b]
1	none	90
2	dark	28
3	no NaI	34
4	dark and no NaI	5
5	DMA instead of DMF	85
6	MeCN instead of DMF	NR
7	CH_2Cl_2 instead of DMF	NR
8	B_2pin_2 instead of B_2cat_2	NR
9	$B_2(OH)_2$ instead of DMF	trace

[a] Isolated yields. [b] Reaction conditions: **1a** (0.2 mmol), NaI (0.1mmol), B_2cat_2 (**2**) (0.4 mmol), DMF (0.5 mL), blue LEDs, Ar, rt, 36 h; then, pinacol (4 equiv), rt, overnight.

With the optimized reaction conditions in hand, we examined the generality of this radical borylation (Table 2). Previous methods worked well with alkyl iodides and bromides, so this radical borylation of alkyl chlorides was firstly investigated. Since benzyl pinacol esters are unstable on silica gel, leading to varying yield loss during the purification process,[17] and methyliminodiacetyl (MIDA) boronate showed some advantages in terms of stability and ease of purification, so we preferentially used MIDA as chelating agents for boron. Benzyl chlorides (**1c**, **1d**, **1e**) were also tolerated, and the substituent position on benzene ring has no obvious influence on the efficiency of this transformation. Meanwhile, the substrates with an electron-rich group (**1f**, **1g**, **1h**, **1i**) also provided moderate yields. Gratifyingly, our system displayed outstanding selectivity: aryl fluoride (**1j**), aryl bromide (**1k**), and aryl iodide (**1l**, **1m**) were all tolerated and only the desired benzylboron products were obtained. High conversions and excellent yields were obtained for the substrates with electron-withdrawing group, such as -CF_3 (**1n**) and -OCF_3 (**1o**). Naphthyl-chlorides were borylated under the standard conditions with excellent yields (**1p-1q**). Olefin was compatible in our system and only product **1r** was obtained in 73% yield while leaving C-C double bond intact. Moreover, we were very pleased to find that when the amount of NaI was increased, the non-benzylic primary alkyl bromides (**1s-1u**) can also smoothly undergo this radical borylation to deliver the corresponding products **3s-3u** in moderate to good yields (56-80%).

N-Heterocyclic moieties are ubiquitous motifs in natural products and active pharmaceutical ingredients.[18] However, for common synthetic methods, the borylation of substrates containing *N*-heterocycles was a big challenge owing to the compatibility.

Table 2 Scope of the dehalogenative borylation reaction[a,b]

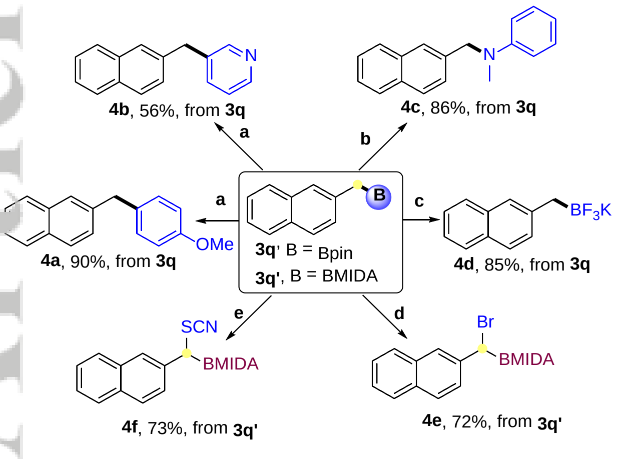


[a] Reaction conditions: **1a**-**1ak** (0.2 mmol), NaI (0.1mml), B_2cat_2 (**2**) (0.4 mmol), DMF (0.5 mL), blue LEDs, Ar, rt, 36 h; then, pinacol (4 equiv), rt, overnight, or MIDA (4 equiv), 90 °C, 4 h. [b] Isolated yields. [c] 1 equiv NaI was used, and the reaction time was extended to 48 h. [d] Reaction was performed at 40 °C

Gratifyingly, our approach displayed a high level of tolerance towards *N*-heterocycles, such as oxazole (**1aa**), *N*-(chloromethyl) phthalimide (**1ab**), benzotriazole (**1ac**) and pyridine (**1ad**). In addition, borylation of other heterocyclic compounds, for instance, furan (**1ae**), vinylene carbonate (**1af**) and benzothiophene (**1ag**) were also successfully proceeded, and the desired products were procured in moderate to good yields. The utility of this method was further demonstrated by applying it to the borylation of pharmaceutical derivatives, such as naproxen (**1ah**), probenecid (**1ai**), lithocholic acid (**1aj**) and indomethacin (**1ak**), and the corresponding target molecules were obtained in satisfactory to excellent yields.

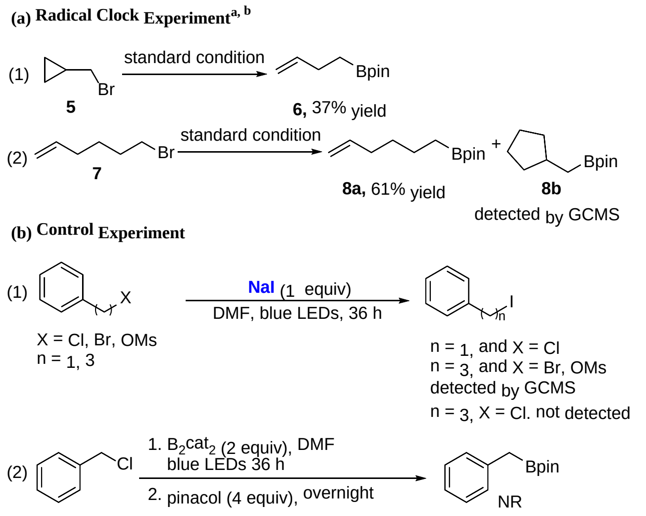
Meanwhile, we also explored the synthetic utility of our borylationtion method, through the further diversification of naphthylmethylboronate products **3q** and **3q'**. Firstly, the boronates were subjected to Suzuki-Miyaura coupling, giving the corresponding products **4a** and **4b** respectively. Secondly, amination of **3q** under reaction conditions developed by Kuninobu et al[19] delivered the corresponding aminated product **4c** in 86% yield. Product **3q'** could be readily transformed to a series of α-functionalized alkyl boronates **4d** and **4e** with Wang's photochemical radical C-H halogenations.[20] Finally, potassium trifluoroborate salt **4f** could be prepared in excellent yield by treating **3q** with KHF_2 in MeOH.

Scheme 2 Functionalization of boronate products



Reaction conditions: (a) Aryl bromide (0.3 mmol), **3q** (0.2 mmol), $Pd(P(tBu)_3)_2$ (5 mmol%), Cs_2CO_3 (0.6 mmol), dioxane (1 mL), H_2O (0.25 mL), 100 °C, overnight. (b) N-methylaniline (0.138mmol), **3q** (0.125 mmol), $(tBu)_2O$ (0.25 mmol), $Cu(OAc)_2$ (5 mmol%), toluene (0.5 mL), 50 °C, overnight. (c) KHF_2 (0.9 mmol), MeOH (2mL). (d) NBS (0.11 mmol), **3q'** (0.1 mmol), BPO (3 mol%), DCE (1.0 mL), 100 °C, 3 h. (e) NBS (0.11 mmol), **3q'** (0.1 mmol), BPO (3 mol%), DCE (1.0 mL), 100 °C, 3 h; then change the solvent to DMF (1.0 mL), add KSCN (0.12 mmol), 60 °C, 6 h.

Scheme 3 Mechanistic experiments

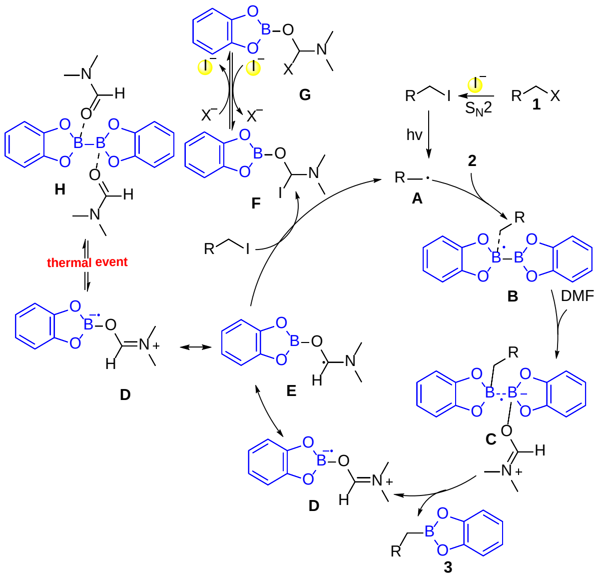


[a] Reaction conditions: alkyl halides (0.2 mmol), NaI (0.2 mmol), B_2cat_2 (**2**) (0.4 mmol), DMF (0.5 mL), blue LEDs, Ar, rt, 48 h; then, pinacol (4 equiv), rt, overnight. [b] Isolated yields.

To shed light on the mechanism of the borylation reaction, we conducted two radical cascade experiments. Cyclopropylmethyl bromide (**5**) gave exclusively the ring opening product **6** when it was subjected to the standard conditions (Scheme 3a-1). In terms of 6-bromo-1-hexene (**7**), the uncyclized boronate **8a** was mainly obtained under the standard conditions with small amount of the cyclized product **8b** detected by GCMS (Scheme 3a-2). These results all support the involvement of an aliphatic radical and its further reaction with the boron species. In the control experiments, phenylpropyl bromide or mesylate, and benzyl chloride could convert into corresponding iodide in the presence of NaI (Scheme 3b-1). Phenylpropyl chloride cannot be converted, which was consistent with the fact that the non-benzylic primary alkyl chlorides cannot participate in this borylation reaction. In addition, benzyl chloride did not produce any products in the absence of NaI (Scheme 3b-2). These results indicated that iodide might be the key reaction intermediate and a part of iodide ions in the reaction were reused.

Based on these experiments and previous reports,[2a, 13] we proposed that the reaction involves a radical mechanism that is initiated by both a photoinduced event and a less efficient thermal event, and the proposed mechanism is shown in Scheme 4. For the photoinduced process, alkyl electrophile reacts with NaI through an S_N2 pathway to generate alkyl iodide. Then, under excitation by visible light, the C–I bond homolyzes to generate the radical **A** which could react with B_2cat_2 to obtain a radical **B**. The ensuing boron-centered radical **B** is then intercepted by dimenthylformamide (DMF) to afford intermediate **C**. Subsequently, the radical **C** collapses to form the desired product alkyl boronic ester **3** and DMF-stabilized boryl radical **D** which can be tautomerized to carbon radical **E**. Finally, the cycle is closed by an I-atom transfer reaction of the alkyl iodide via **E** to eventually give **G** and radical **A**. And for the thermal process, the 2:1 DMF/B_2cat_2 complex **H** undergoes thermal homolytic fragmentation to give two DMF-stabilized boryl radical **D**, which can be tautomerized into carbon radical **E** to propagate the cycle as described above. In addition, benzyl bromide is a highly reactive alkyl halide that could occur a Br-atom transfer reaction via **E** to give **G** and radical **A** in the absence of NaI, and then allow the reaction to proceed.

Scheme 4 Proposed mechanism



Conclusions

In summary, we have developed a visible-light-induced NaI-promoted radical borylation of alkyl halides and pseudohalides. This approach proceeds under mild conditions and features a broad substrate scope. This method can be a privileged alternative to current known catalytic methods for the construction of alkylboron derivatives from less reaction alkyl halides and pseudohalides.

Experimental

General procedure for the borylation reaction

A 25 mL Schlenk tube was charged with a mixture of B_2cat_2 (**2**) (95 mg, 0.4 mmol, 2 equiv), NaI (15 mg, 0.1 mmol, 0.5 equiv, or 30 mg, 0.2 mmol, 1 equiv), alkyl halides **1** (0.2 mmol, 1 equiv). The tube was evacuated and backfilled with Argon for three times. Dimethylformamide (DMF) 0.50 mL was added, then the tube was quickly evacuated and backfilled with Argon for four times (*IMPORTANT!*) (If the alkyl halides are a liquid, add it after degassing). The reaction mixture was stirred under blue LEDs irradiation for 36 or 48 h. Then, methyliminodiacetic acid (118 mg, 0.8 mmol, 4 equiv) was added and the reaction mixture heated to 90 °C for 4 hours, after which the solvent was removed in vacuo. The reaction mixture was diluted with ethyl acetate (20 mL) and saturated $NaHCO_3$ solution (10 mL), then organic phase was separated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. Alternatively, pinacol (95 mg, 0.8 mmol, 4 equiv) was added to the reaction vessel and the mixture was stirred overnight at ambient temperature, after which water was added, and the aqueous layer was extracted with ethyl acetate (20 mL). Then organic phase was separated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography to give the corresponding product **3**.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

Acknowledgement

Financial support from the National Natural Science Foundation of China (21772046, 2193103, 22001038) are gratefully acknowledged.

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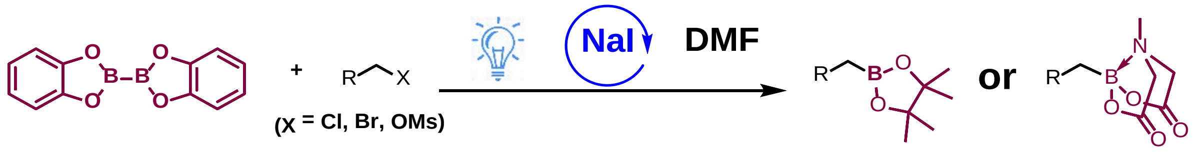

A method for photoinduced NaI-promoted radical borylation of aliphatic halides and pseudohalides has been developed that enables synthesis of a series of alkylboronates.