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Metal-Free Direct Deoxygenative Borylation of Aldehydes and Ketones

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ABSTRACT: Direct conversion of aldehydes and ketones into alkylboronic esters via deoxygenative borylation represents an unknown yet highly desirable transformation. Herein, we present a one-step and metal-free method for carbonyl deoxyborylation under mild conditions. A wide range of aromatic aldehydes and ketones are tolerated and successfully converted into the corresponding benzylboronates. By the same deoxygenation manifold with aliphatic aldehydes and ketones, we also enable a concise synthesis of 1,1,2-tris(boronates), a family of compounds that currently lack efficient synthetic methods. Given its simplicity and versatility, we expect that this novel borylation approach could show great promise in organoboron synthesis and inspire more carbonyl deoxygenative transformations in both academic and industrial settings.

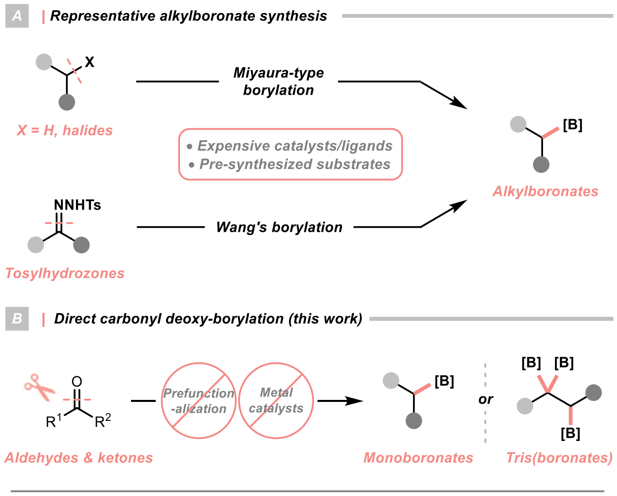
1. INTRODUCTION

Alkylboronic acids and their derivatives are valuable reagents in organic synthesis,[1] as they play indispensable roles in numerous downstream transformations. Of equal importance, they are also prevalent in medicinal chemistry, acting as potent isosteres of bioactive carboxylic acids.[2] However, due to their rarity in nature, access to boron compounds mainly relies on chemical synthesis (Scheme 1A).

Traditional approaches to prepare aliphatic organoboron compounds involve the reactions between stoichiometric organometallic nucleophiles and boron electrophiles or hydroboration of olefins.[1c, 3] In modern chemistry, the synthesis of alkylboronates is considerably advanced by transition-metal-catalyzed C-X (X = H[4] or (pseudo)halide[5]) borylation. With the contribution by the research groups of Aggarwal,[6] Jiao,[7] Paolo,[8] Studer[9], and many others,[10] the borylation toolkit is further enriched by various metal-free strategies with different radical precursors. Within the area of metal-free borylation, Wang and his co-workers described an alternative approach by coupling the bis(pinacolato)diboron (B_2pin_2) or pinacolborane (HBpin) with tosylhydrazones, achieving an indirect deoxygenative hydroboration on the carbonyl carbon.[11] Despite these achievements, a simple and reliable synthetic route for alkylboronic esters that features the direct usage of abundant and renewable starting materials in the absence of metal catalysts remains underexplored.

Aldehydes and ketones are privileged chemical entities in the synthetic community by virtue of their ubiquity and chemical versatility.[12] These attractive features continuously encourage chemists' exploration of their novel reactivities and applications. Among these efforts, the deoxygenative functionalization is an area of increasing interest.[13] In this context, our group disclosed a series of transition-metal-catalyzed "interrupted Wolff-Kishner reactions" of hydrazones, which furnished numerous C-C bond-forming products.[14] Our ongoing interest in carbonyl deoxygenation chemistry led us to consider the possibility of converting carbonyls into organoboron compounds. Ideally, we planned to replace the oxygenous moiety of the carbonyl with the boryl group simply by using readily available boron reagents. Moreover, it would be preferable to avoid any pre-functionalization and the usage of precious transition metal catalysts during this transformation.

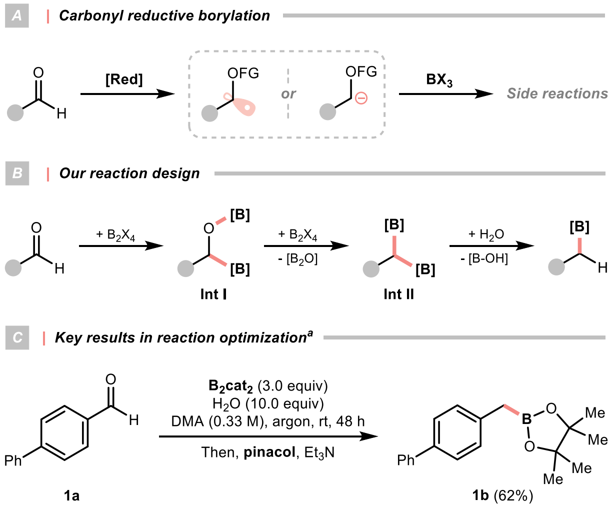
Scheme 1. Aliphatic organoboron compound synthesis



[B], boryl group; Ts, tosyl group.

Herein, we present a practical method for the synthesis of alkylboronic acid derivatives from the corresponding aldehydes and ketones by using commercially available diboron reagents (Scheme 1B). This efficient strategy allows the direct deoxygenative monoboration of aromatic aldehyde and ketones without pre-functionalization and metal catalysts at mild temperatures. The same borylation manifold could also enable an unprecedented deoxygenative triboration reaction, thereby providing a general route for preparing various synthetically appealing 1,1,2-tris(boronates) from the corresponding aliphatic aldehydes and ketones.

Scheme 2. Reaction design and optimization.



entry	variation from the conditions above	NMR yield (1b)
1	B_2pin_2 or $B_2(OH)_4$	Trace
2	$B_2(OH)_4$ + catechol (1 : 2)	27%
3	DMF (0.33 M)	56%
4	CH_3CN (0.33 M)	25%
5	20.0 equiv H_2O	22%
6	4-Ph-C_5H_4N (20 mol%), NaOMe (1.3 equiv)	28%
7	CH_3CO_2H (1.5 equiv)	61%
8	50 °C, 8 h	62%
9	**80 °C, 8 h**	**77% (72% iso.)**
10	80 °C, 8 h, under air	53%

[a]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard unless otherwise specified. FG, functional group; B_2X_4, diboron compound; rt, room temperature; [Red], reduction; [B], boryl group; Iso., isolated yield.

2. RESULTS AND DISCUSSION

Reaction design and optimization. Reactions of carbon-centered radicals and anions with boron electrophiles are typical for forming C-B bonds.[10a-c] However, these reaction modes might not be suitable for the reductive borylation of aldehyde for two reasons (Scheme 2A). Firstly, as a consequence of single electron transfer (SET), the ketyl radicals generated from the aldehydes could undergo undesirable pinacol couplings or addition to alkenes and alkynes.[15] Secondly, α-oxy anions that are formed under harsher reducing conditions would be highly reactive towards some off-target electrophiles (e.g., H^+ and carbonyls).[13i, 16] These two species would lower the functional group tolerance and induce side reactions. Clearly, other reactivity paradigms are needed to strategize the C-B formation with aldehydes.

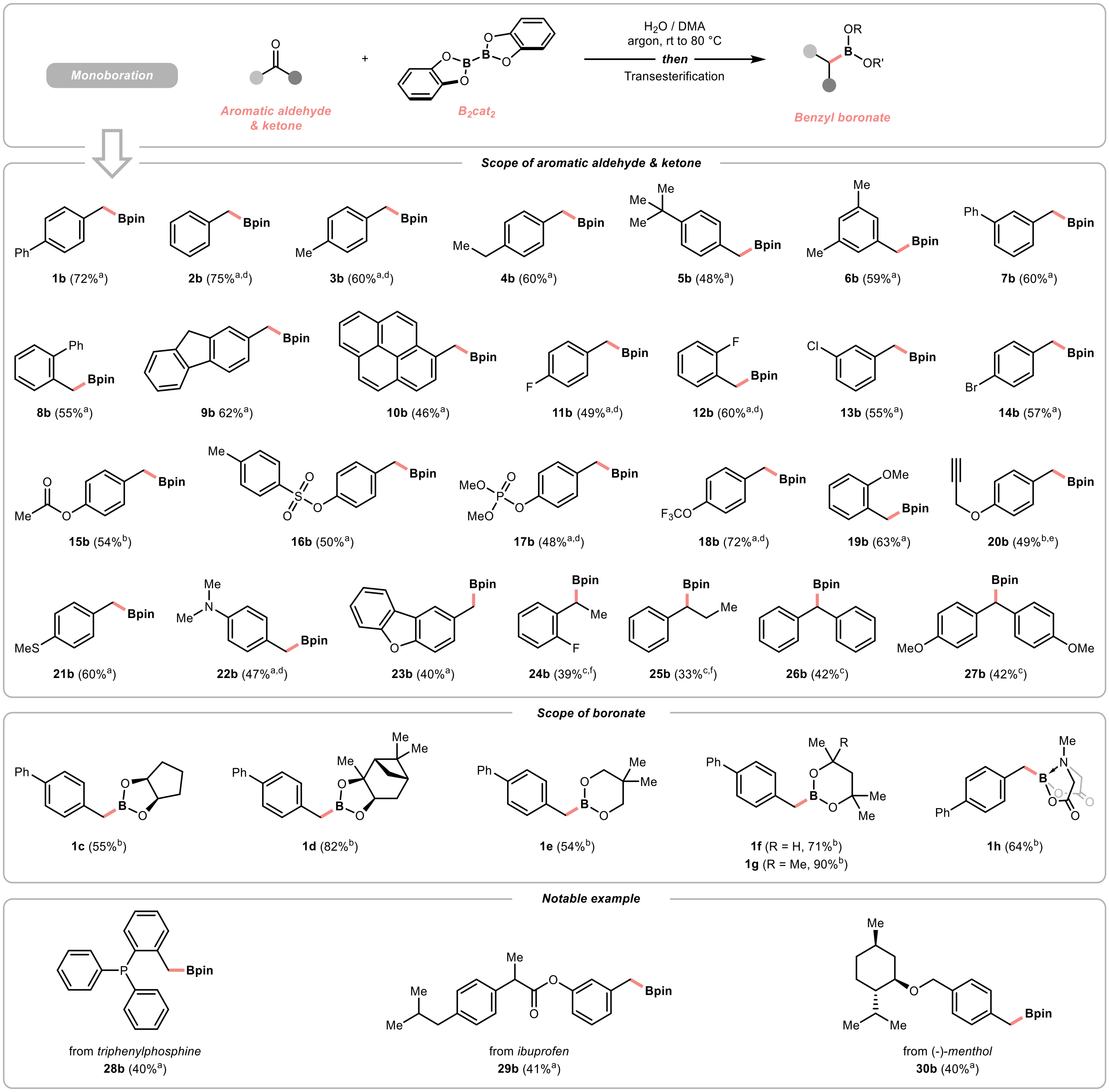
Brief reaction analysis revealed that this reductive borylation requires two key components: a moderate electron donor and a suitable borylating reagent. As such, we postulated that diboron reagents could be appropriate candidates as they could play both roles as the reductant and boron source.[17] Moreover, these compounds possess dual philicities, which could activate carbonyls as Lewis acids and implement borylative nucleophilic attack upon the coordination with Lewis bases.[18] Lastly, the formation of robust B-O bonds could facilitate the C-O bond cleavage.[19]

With these concerns in mind, we proposed our reaction design in Scheme 2B. Initially, the reaction of an aldehyde with a diboron compound simultaneously forms the C-B and O-B bonds of **Int I**. As a pivotal step, the carbonyl bisborylation not only gives the desired C-B bond but also reduces the C=O bond order.[20] Considering its similarity to alkene vicinal diboration,[3c] a highly electrophilic diboron reagent with a compatible basic activator would be beneficial.[21] Because of the Lewis acidity of the trivalent boron,[1h] both neighboring boron atoms could contribute to the C-O bond activation in **Int I**,[20g, 20h] and consequently, the C-O bond becomes cleavable. With another incoming diboron, an α,α-bisborylated intermediate **Int II** is formed. At this stage, selective hydrolysis will give the desirable boronic ester as the final product.[1k, 11a, 22]

In the preliminary study, we envisioned that bis(catecholato)diboron (B_2cat_2) and *N*,*N*-dimethylacetamide (DMA) could be a feasible combination.[6, 9, 10d] Delightfully, when 4-biphenylcarboxaldehyde (**1a**) was selected as the model substrate, we obtained the targeted product in the presence of 3.0 equiv B_2cat_2 and 10.0 equiv H_2O in 0.33 M at room temperature under argon for 48 hours. For convenient characterization, a simple transesterification was performed to give the 4-phenylbenzylboronic acid pinacol ester (**1b**) in 62% yield (Scheme 2C). Consistent with our surmise, less electrophilic B_2pin_2 and $B_2(OH)_4$ showed dramatically poor performance (entry 1). Interestingly, *in situ* formation of B_2cat_2 by adding $B_2(OH)_4$ with catechol (see Supporting information for details) could also promote the desired transformation, although in only 27% yield (entry 2). We found that changing the solvents did not improve the yield. Switching the solvent to the analogous *N*,*N*-dimethylformamide (DMF) slightly lowered the reaction efficiency (entry 3); however, acetonitrile (CH_3CN), which was commonly employed in dehalo-borylation,[23] dramatically depressed the yield (entry 4). It was found that a higher proportion of water (20.0 equiv) resulted in a lower yield, possibly due to the pronounced hydrolysis of B_2cat_2 (entry 5). The effect of some other additives was also examined. By applying 4-phenylpyridine (4-Ph-C_5H_4N) with sodium methoxide (NaOMe), which was used in Jiao's borylation work,[7, 23d] only 28% yield of the pinacol ester was afforded; yet, the borylation was barely affected by acetic acid (entries 6-7). To our delight, at 50 °C, the reaction time could be significantly shortened with the same productivity (entry 8). Encouraged by this result, by raising the temperature to 80 °C, the reaction yield was further improved to 77%. Under these optimal conditions, the desired **1b** was isolated in 72% yield (entry 9). The control experiment showed that the reaction still proceeded smoothly under air (entry 10).

Substrate scope of monoboration. With the optimal conditions in hand, we investigated the substrate scope of this deoxygenative borylation. Aromatic aldehydes bearing different electronic and steric properties were first evaluated (Scheme 3A). While benzaldehyde (**2a**) furnished a similar 75% yield to that of **1a**, other derivatives with various substituents like methyl, ethyl, *tert*-butyl, and phenyl groups, irrespective of their positions, were all effective substrates (**2b** to **9b**). Notably, a moderate degree of the steric hindrance could be tolerated in this reaction, as shown

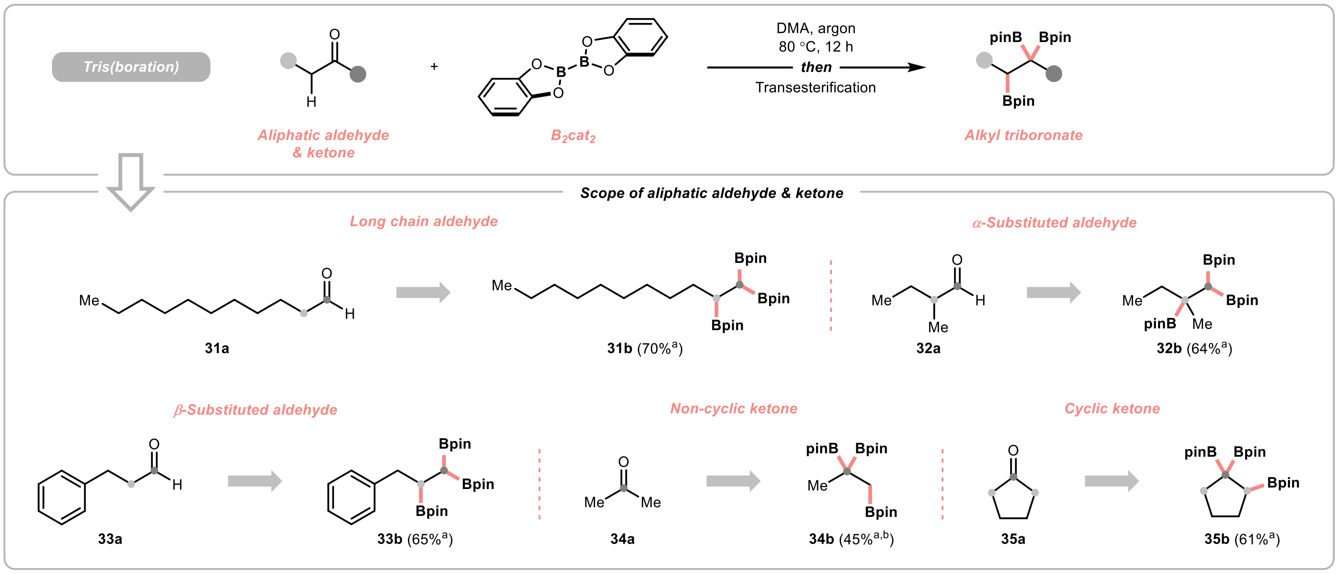
Scheme 3A. Substrate scope of deoxygenative monoboration



See Supporting Information for details. Yields are for isolated products after purification unless otherwise specified. ^{a}Condition A: reactions were performed with aromatic aldehyde (0.20 mmol, 1.0 equiv), B_2cat_2 (0.60 mmol, 3.0 equiv), H_2O (2.0 mmol, 10.0 equiv) in DMA (0.60 mL) under argon at 80 °C for 12 hours; then transesterification. ^{b}Condition B: same as condition A but performed at room temperature for 72 hours. ^{c}Condition C: reactions were performed with aromatic ketone (0.20 mmol, 1.0 equiv), B_2cat_2 (0.60 mmol, 3.0 equiv) in DMA (0.60 mL) under argon at 80 °C for 72 hours; then transesterification. ^{d}Reaction yields were determined by NMR due to the volatility or instability of targeted compounds. ^{e}Based on the recovered starting material. ^{f}1,2-bis(boronate) were detected in the GC-MS analysis.

in the case of 2-biphenylcarboxaldehyde (**8b**). Aldehydes with large conjugated chromophores such as pyrene were compatible with our standard conditions and successfully converted to the desired product (**10b**), although an exhaustive reduction product, 1-methylpyrene, was also identified in the reaction mixture (see Supporting Information for details). When our optimal conditions were applied to the benzaldehydes with weakly withdrawing or donating groups, such as fluoro, chloro, bromo, acetoxy, tosyloxy as well as phosphoryloxy groups, moderate yields were given (**11b** to **17b**). As these disubstituted products contain functional handles with complementary reactivities, they could serve as useful synthons for cross-couplings in polymer chemistry. Noticeably, -OCF_3 group, a long-sought-after functionality in medicinal chemistry as it was often linked to the potency enhancement of drug leads, survived the reductive borylation (**18b**).[24] Regarding substrates with

Scheme 3B. Substrate scope of deoxygenative triboration



See Supporting Information for details. Yields are for isolated products after purification unless otherwise specified. [a]Condition A: reactions were performed with aliphatic aldehyde and ketone (0.20 mmol, 1.0 equiv), B_2cat_2 (0.60 mmol, 3.0 equiv) in DMA (0.60 mL) under argon at 80 °C for 12 hours; then transesterification. [b]Low yield was obtained in the case of acetone probably due to its volatility.

strong electron-donating groups including methoxy, propargyloxy, methylthio and dimethylamino groups, unaltered reaction efficiencies were generally observed, affording the boronic esters in yields ranging from 47% to 63% (**19b** to **22b**). Although unsaturated functional groups (e.g., triple bond) were susceptible to borylation in the presence of diboron,[3c] we were pleased to see that borylation occurred chemoselectively at the aldehyde site with the alkyne remaining intact (**20b**). Encouragingly, the reaction of carboxaldehyde with heteroaromatic core such as dibenzofuran was also successful (**23b**). However, aromatic aldehydes with strongly withdrawing groups were ineffective under our conditions (see Supporting Information for details).[13i] Although the reasons behind these failed examples remain unclear, we thought that the diminished basicity of carbonyl oxygens of these reactants might cause their inefficient coordination towards B_2cat_2, therefore, the poor reactivities. Pleasingly, aromatic ketones were also applicable with our deoxy-monoboration method, providing a series of α-substituted benzylboronates. As lower conversion was not uncommon for ketones under previous conditions, prolonged reaction time was necessary. For alkyl aryl ketones, their deoxy-hydroboration could give the expected products successfully with similar performance (**24b** and **25b**). Despite the bulky geminal groups of diarylketones, their borylation could also proceed smoothly (**26b** and **27b**).

In addition to the pinacol esters, other boronates could be conveniently accessed simply through the transesterification of catechol ester intermediate. As such, various five- and six-membered ring boronic acid derivatives were prepared in 54% to 90% yields (**1c** to **1g**), including the (+)-pinanediol ester, whose congeners were frequently encountered in the stereoselective synthesis.[25] Other than the above-mentioned boronates, by reacting with *N*-methyliminodiacetic acid (MIDA), the tetravalent MIDA boronate could also be assembled successfully (**1h**).

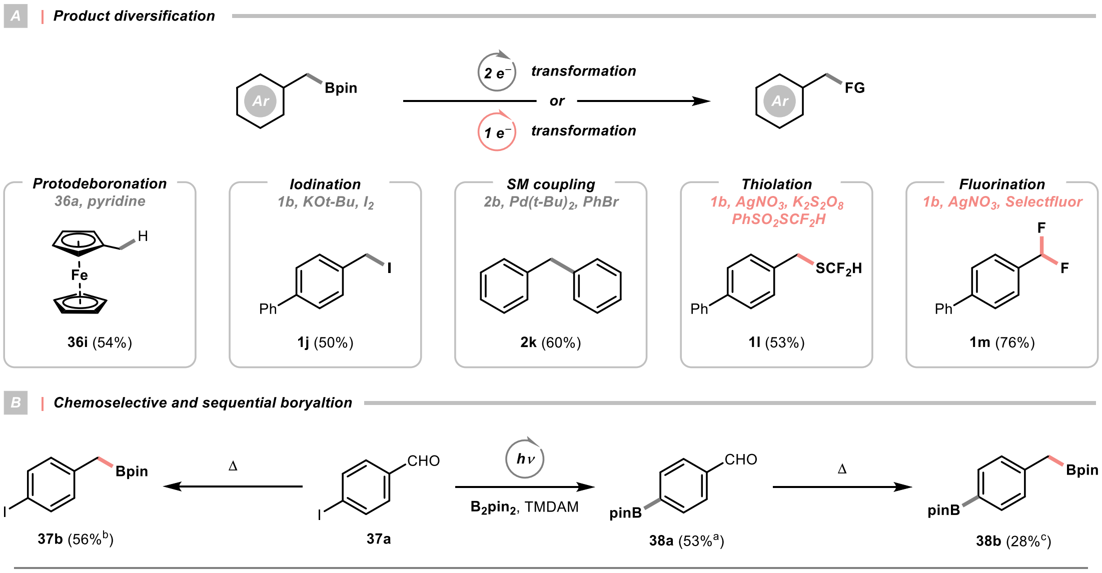
For convenient diversifications, installing the boryl group on compounds with high molecular complexity would be advantageous for their post-synthetic modification. With this consideration, aldehydes bearing triphenylphosphine, ibuprofen and (-)-menthol moieties were subjected to our deoxygenative borylation conditions. Delightfully, all of them could furnish the corresponding boronate products (**28b** to **30b**). Substrates with phosphino groups are often problematic in the metal-catalyst-involved process. By leveraging our metal-free conditions, the phosphine group remained untouched, which allowed the easy diversification of phosphine-based ligands and catalysts.

Substrate scope of triboration. In the synthetic community, multi-borylated alkanes are valuable targets due to their essential roles as conjunctive reagents and bioactive agents.[1h, 26] Among them, 1,1,2-tris(boronate) is a unique subset as it allows multiple deborylative transformations on two neighboring carbons selectively and sequentially.[26c, 26f, 26g] Surprisingly, an in-depth investigation of its reactivity and application remains rare, which was possibly attributed to the limited methods for its preparation.

During our investigation in deoxy-borylation of aliphatic aldehydes and ketones, an exclusive α,α,β-triboration occurred instead of the regular monoboration (Scheme 3B). A brief survey of the substrate scope indicated that linear and branched (α- or β-substituted) aldehydes underwent the deoxygenative triboration smoothly (**31b** to **33b**), so did the cyclic and non-cyclic ketones (**34** and **35b**). Due to its simplicity and efficiency, we believe that such a deoxygenation method could become a practical route to access this class of valuable organoboron compounds.

Synthetic application. To demonstrate the utility of our new borylation method, we submitted the benzylboronate products for further diversification (Scheme 4A). Firstly, the boronates were subjected to protodeboronation, deborylative iodination as well as Suzuki-Miyaura coupling, giving the corresponding C-H, C-I and C-C bond-forming

Scheme 4. Applications



See Supporting Information for details. Yields are of isolated products after purification unless otherwise specified. [a]Condition A: reactions were performed with 4-iodobenzaldehyde (0.10 mmol, 1.0 equiv), B_2pin_2 (0.20 mmol, 2.0 equiv), TMDAM (0.10 mmol, 1.0 equiv) in CH_3CN (1.0 mL) under argon at room temperature and irradiated by >250 nm light. [b]Condition B: reactions were performed with aldehyde (0.20 mmol, 1.0 equiv), B_2cat_2 (0.60 mmol, 3.0 equiv), H_2O (2.0 mmol, 10.0 equiv) in DMA (0.60 mL) under argon at 80 °C for 12 hours; then transesterification. [c]Condition C: same as condition C but performed at room temperature for 72 hours. FG, functional group; TMDAM, *N*,*N*,*N'*,*N'*-tetramethyldiaminomethane; *t*-Bu, *tert*-butyl; *hv*, photon; Δ, heating.

products, respectively. Later, the benzylboronic ester was shown to be amenable in the radical processes meditated by silver (I). Using the protocol developed by Shen's group,[27] we realized the catalytic radical difluoromethylthiolation with **1b**, successfully converting the -Bpin into -SCF_2H group (**1l**). Interestingly, the oxidative mono-fluorination conditions that were reported by Li and his colleagues[28] gave us an unexpected benzylic difluorination product (**1m**). This finding not only showcased the uniqueness of benzylboronic esters but also opened up a new approach to prepare the difluorotoluenes. Secondly, given the appreciable chemoselectivity of our method, the sequential borylation of the bifunctional 4-iodobenzaldehyde (**37a**) becomes conceivable (Scheme 4B). Although iodide has been validated as an excellent leaving group in both metal-catalyzed and metal-free borylations,[10a-c] our carbonyl-selected borylation protocol could still afford the 4-iodobenzylboronic ester as the major product (**37b**). On the contrary, based on our previous work[23b] and others',[18b, 29] photo-induced deiodo-borylation of **37a** was also realized, leaving the -CHO functionality in 4-formylphenylboronic ester (**38a**) for subsequent deoxy-borylation (**38b**).

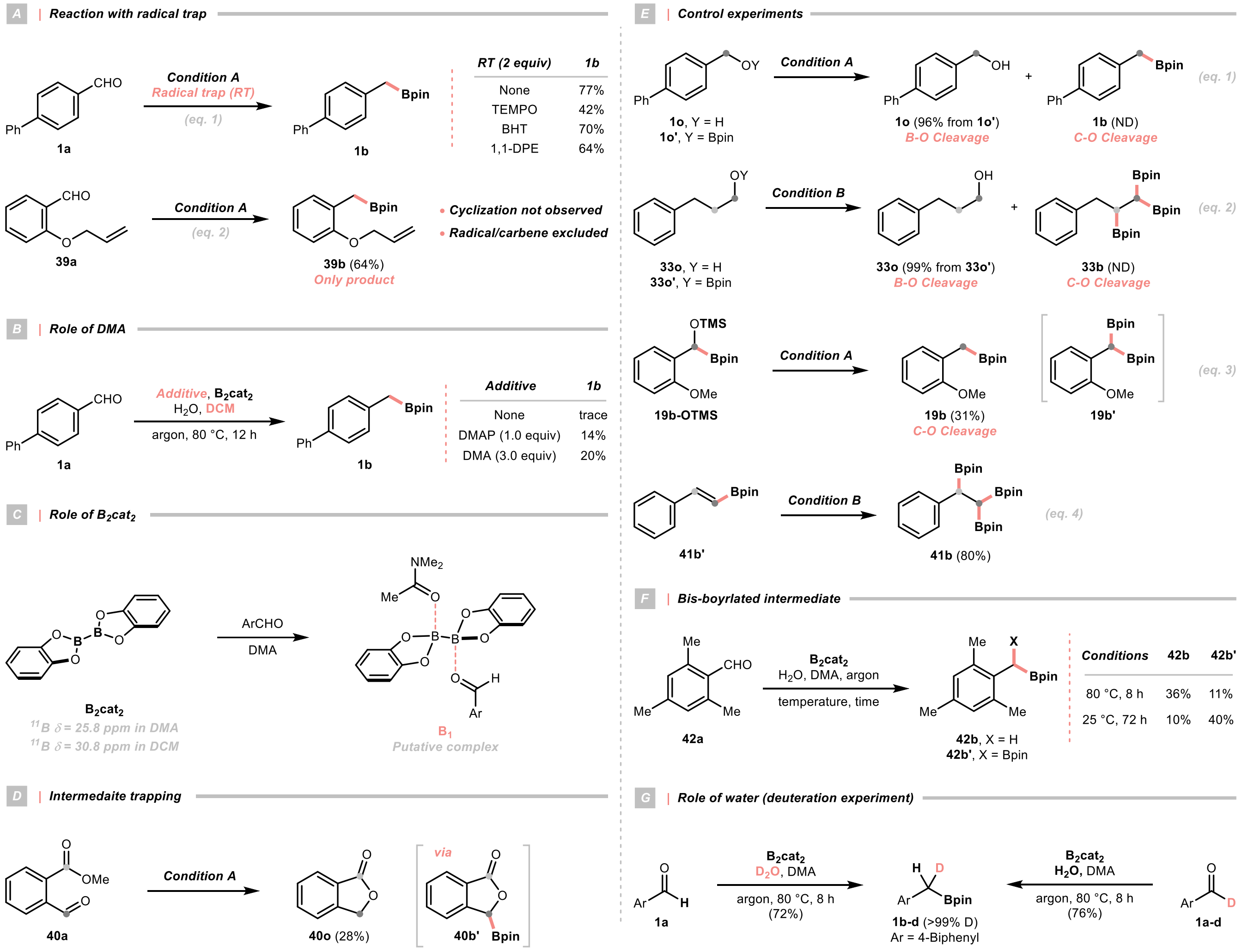
Mechanistic study. To better understand this process, a series of experiments were performed. Firstly, the possibility of involving open-shell intermediates was evaluated with radical quenchers 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), butylated hydroxytoluene (BHT) and 1,1-diphenylethylene (1,1-DPE). Yields of targeted boronic ester **1b** mostly remained unaffected except in the case of TEMPO (Scheme 5A). Further experiments explained that the decreased yield was mainly caused by the direct reaction between TEMPO and B_2cat_2 (see Supporting Information for details). Additionally, the deoxy-borylation of 2-allyloxybenzaldehyde (**39a**) was found to generate the acyclic boronic ester as the only product in 64% yield (**39b**). Combining the results from inter- and intramolecular trapping experiments, the involvement of radical or carbene intermediates seems unlikely in this transformation.

Secondly, the requirement of amide solvents suggested the importance of a basic and coordinating environment for B_2cat_2 to promote the desired transformation.[6, 9, 10d] Therefore, ^{11}B nuclear magnetic resonance (NMR) spectra of B_2cat_2 were recorded in DMA and the control solvent dichloromethane (DCM), respectively. In line with the literature reports,[6a, 10d] broadened and upfield ^{11}B NMR signal was observed in DMA (25.8 ppm) relative to DCM (30.8 ppm), suggesting the loose complexation of B_2cat_2 with the former solvent. This interaction seemed crucial to enable the deoxy-borylation reaction, as no targeted product was detected in the non-coordinating DCM. Interestingly, the addition of 4-dimethylaminopyridine (DMAP) or DMA could retrieve some desired reactivities (Scheme 5B).

Being aware of the electrophilic character of B_2cat_2 and the high chemoselectivity of this reaction, we surmised that B_2cat_2 could ligate with the carbonyl oxygen of aldehyde in a similar way to DMA. Accordingly, we proposed that a ternary species **B1** was formed reversibly,[6a, 30] activating both the carbonyl and diboron, and bringing them in close proximity (Scheme 5C). To get more insight, NMR and ultraviolet-visible (UV-Vis) spectra were used to characterize the aldehyde, B_2cat_2 as well as their mixture in DMA. Indeed, changes in the spectroscopic behavior of their mixture compared to the individual component were observed,[6a] which substantiated the formation of **B1** in low concentration.

Similar to copper-catalyzed vicinal diboration of carbonyls,[20a-i] an intramolecular boryl group migration to the formyl carbon of **B1** might occur, resulting in an alcoholate.

Scheme 5. Mechanistic study.



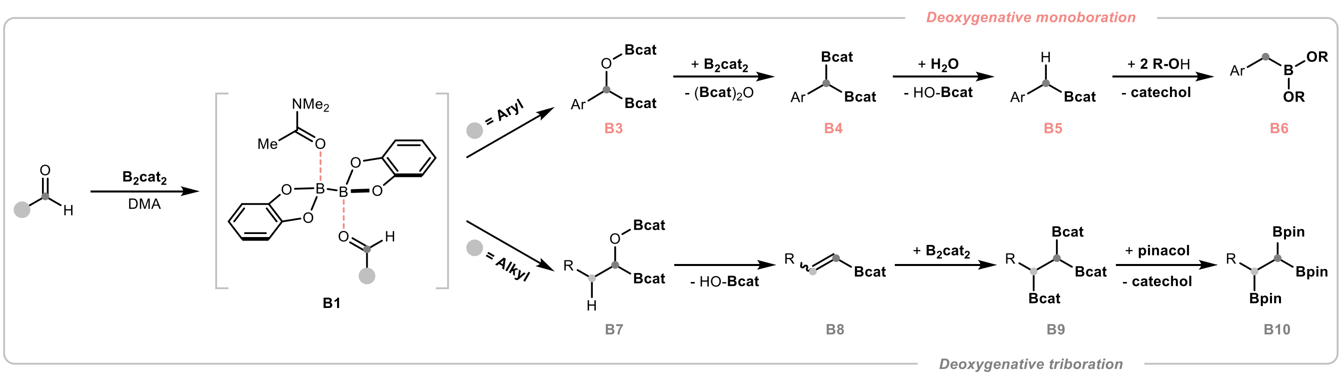
See Supporting Information for details. Catecholatoboronates are converted into pinacol esters and their yields are determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard unless otherwise specified. Condition A: reactions were performed with aldehyde or its equivalence (0.20 mmol, 1.0 equiv), B_2cat_2 (0.60 mmol, 3.0 equiv), H_2O (2.0 mmol, 10.0 equiv) in DMA (0.60 mL) under argon at 80 °C for 12 hours. Condition B: same as the Condition A but without H_2O. ND, not detected; Ar, aryl group; TMS, trimethylsilyl group.

To trap this potential alkoxide intermediate, we performed a reaction with methyl 2-formylbenzoate (**40a**, Scheme 5D). Interestingly, a lactone product **40o**, which might result from the hydrolysis of **40b'**, was identified. Moreover, the competition experiment showed that the borylation preferentially occurred with less hindered benzaldehyde over acetophenone. Both results evidenced the nucleophilic addition of diboron towards the carbonyl.[31]

Next, the mechanism of breaking the key C-O bond in the alcohol-related intermediates was investigated. Control experiments showed that neither the free alcohols **1o** and **33o** nor their *O*-Bpin derivatives **1o'** and **33o'** were viable intermediates (Scheme 5E, eq. 1 and 2). Like our original design, we hypothesized that the *C*,*O*-bisborylated species was the key intermediate for this deoxy-borylative transformation. In this case, a catecholato α-boryl-α-(boryloxy)toluene-type compound would be well-suited; however, because of its synthetic difficulty,[32] the analogous benzyl silyl ethers, a type of compounds recently reported by Ito's and Glorius's groups, were considered instead.[20d, 20f, 33] As expected, the targeted mono-boronate **19b** was obtained under our optimal conditions, which possibly resulted from the boro-substitution of C-OTMS bond in **19b-OTMS** and the subsequent hydrolysis of **19b'** (Scheme 5E, eq. 3).[20g, 20h] In terms of the triboration, we envisioned that a similar *C*,*O*-bisborylated intermediate **B7** was also involved. Since **B7** was precedented to eliminate the hydroxyborate under either acidic or basic conditions,[34] the elimination product vinylboronate was rationalized as another key species. Unsurprisingly, when the independently synthesized **41b'** was subjected to the triboration conditions, we could obtain the desired tris(boronate) in 80% yield (Scheme 5E, eq. 4). Although **B7** has the propensity for C-O borylation as well,[20g] the reason for such divergent reactivities remained uncertain.

In the proposed monoboration mechanism, the final product derives from a protodeboronation step. In principle, lower temperatures and more congested substituents around the boron centers might decelerate the hydrolysis of the *gem*-bisborylated species. By subjecting mesitaldehyde

Scheme 6. Proposed mechanism.



(**42a**) to the deoxy-borylation at room temperature, the bisborylated **42b'** was obtained as the major product, while a reversed product distribution was observed at 80 °C (Scheme 5F). As further evidence for the intermediacy of the *gem*-diboronate,[11a, 22b] benzyldiboronate **2b'** was independently prepared and submitted to our optimal conditions. As anticipated, **2b'** was fully converted into the monoprotodeboronated product **2b** under our standard conditions (see Supporting Information for details). Finally, two deuteration experiments were conducted to probe the role of water, the results of which unambiguously determined that one of the benzylic hydrogens of **1b** came from water, and the other originated from the aldehyde.

Putting all the information together, we depicted a tentative mechanism in Scheme 6. Firstly, DMA, B_2cat_2 and aldehyde were engaged as a three-membered complex **B1**, which simultaneously activated the diboron and aldehyde. Then, through a DMA-mediated intramolecular boryl group transfer, a 1,2-bis(catecholato)boronate intermediates **B3** and **B7** were formed for aromatic and aliphatic substrates, respectively. For the monoboration, **B3** was subjected to the C-O cleavage with the assistance of another B_2cat_2. After this metathesis process, the resulted benzylic α,α-diboronate **B4** could undergo a protodeboronation/transesterification sequence to furnish the desired boronate **B6**. Concerning the triboration, removal of HO-Bcat in **B7** resulted in the vinylboronate intermediate **B8**, which was bisborylated and transesterified to give tris(boronate) **B10**.

3. CONCLUSIONS

We have established a step-economic and metal-free approach for direct conversion of carbonyls into organoboron compounds. A series of monoboronates and tris(boronates) could be prepared from the corresponding aldehydes and ketones in a single step with the commercially available B_2cat_2 in wet DMA. The deoxy-borylation was performed under mild conditions, featuring a broad substrate scope and high chemoselectivity. Compared to the earlier literature methods, this approach does not require pre-functionalization, and it is capable of cleaving the strong C=O bond in the absence of metal catalysts. Preliminary mechanistic studies revealed the role of each reaction component and elucidated the key intermediacy of *gem*-diboronate and vinylboronate. These important intermediates would lead to the desired monoboronates and tris(boronates), respectively. The exploration of more mechanistic details is ongoing in our laboratory, and current efforts are focusing on investigating the formation of **B3** and **B8** via computation. Considering the simplicity and versatility of this deoxygenation borylation strategy, we envisioned that this approach could enrich the current toolkit of alkylboronate synthesis and inspire more research endeavors on carbonyl deoxygenative transformation.

ASSOCIATED CONTENT

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Experimental procedures, spectroscopic data and computational methods

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Notes

The authors declare no competing financial interest.

Author Contributions

All the authors contributed to the discussion of experimental results. The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

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