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# Photoredox borocarbonylation through 1,2-boron migration

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Organoboron compounds are fundamental building blocks in organic synthesis, and recent advances in boron-migration reactions have attracted significant attention. However, carbonylative transformations featuring a 1,2-boron shift remain largely unexplored, with limited strategies available for the incorporation of exogenous carbonyl groups. We report an unprecedented 1,2-boron migratory carbonylation enabled by visible-light photoredox catalysis, in which carbon monoxide (CO) serves as an abundant and convenient C1 source to trap translocated alkyl radicals generated after 1,2-boron migration. The methodology provides an efficient and streamlined approach to synthesize structurally complex and diversely functionalized  $\beta$ -boryl thioesters under mild conditions. Notably, this reaction enables a functional-group translocation within a single molecule, allowing for the positional exchange between a carbonyl and a boryl group *via* sequential CO<sub>2</sub> extrusion, 1,2-boron migration, and CO insertion.

## Introduction

Organoboron compounds are of paramount importance in organic synthesis, finding broad applications in pharmaceuticals,<sup>1</sup> functional materials,<sup>2</sup> bioactive molecules,<sup>3</sup> and synthetic methodologies.<sup>4–8</sup> They serve as key reagents for constructing diverse carbon–carbon and carbon–heteroatom bonds through reactions such as the Suzuki–Miyaura coupling,<sup>9–11</sup> hydroboration,<sup>12</sup> and Chan–Lam coupling.<sup>13,14</sup> The capacity of these building blocks to undergo diverse, high-value transformations has motivated the development of a series of elegant strategies to achieve the efficient synthesis of organoboronates. While those methods have indeed broadened the scope of boron chemistry, they primarily focus on diversifying the boron moiety, thereby constraining the functionalization of organoboron compounds to boron-discarded transformations.<sup>15–19</sup> In contrast, the boron-retaining reactions have recently garnered substantial interest, because the resulting boron-containing products are not only valuable compounds in their own right but can also undergo additional C–B bond transformations, thus facilitating the creation of multifunctionalized products.<sup>20–25</sup>

Migration reactions have long been recognized as a powerful strategy for constructing boron-containing compounds, ever

since 1960s.<sup>26–34</sup> While extensive efforts have been devoted to 1,2-migrations of tetracoordinated borate species, radical-driven 1,2-boron migrations remain comparatively less explored. The earliest study dates back to 1999, when Batey and Smil disclosed that boron-tethered radical cyclizations could undergo a 1,2-boryl radical shift.<sup>35</sup> After nearly two decades of inactivity, Studer and co-workers realized a notable intermolecular radical 1,3-difunctionalization by employing simple allylboron compounds as boryl-migrating substrates.<sup>36–38</sup> Independently, Aggarwal and co-workers developed a photocatalytic single-electron oxidation of 1,2-diborates to efficiently generate  $\beta$ -boryl radicals.<sup>39–41</sup> Very recently, Song's work advanced radical 1,2-boron migration by designing specialized boronic ester precursors to overcome limitations in  $\beta$ -boron radical generation.<sup>42</sup> Subsequently, Li group developed a photocatalysis/NHC co-catalysis strategy to achieve 1,2-boron migratory acylation reaction for the efficient synthesis of  $\beta$ -boryl ketones.<sup>43</sup> However, despite boron's versatile reactivity profile, current borylation-mediated carbonylation transformation face inherent regiochemical limitations in incorporating exogenous carbonyl groups (Fig. 1).

Carbon monoxide (CO) serves as an inexpensive and readily available C1 source, making it a cornerstone reagent in classical carbonylation chemistry.<sup>44–46</sup> Nevertheless, traditional metal-catalyzed carbonylations frequently rely on elevated temperatures and toxic noble-metal catalysts (Pd, Rh, Ir), which inevitably narrows the substrate scope and raises both capital and environmental costs.<sup>47–57</sup> Radical-mediated carbonylation has attracted increasing interest owing to its broad radical-generation strategies and relatively

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**Fig. 1** a, Traditional 1,2-boron migration via tetracoordinate borons. b, Radical induced 1,2-boron migration. c, This work: metal-free 1,2-boron migrative carbonylation.

mild reaction conditions. In these processes, a transient carbon-centered radical is intercepted by CO to give an acyl radical, which can subsequently be transformed into esters,<sup>58–66</sup> amides<sup>67–77</sup> or ketones.<sup>78–81</sup> The key advantage is that the radical generation step can be decoupled from the metal-mediated bond-forming events; light, peroxides or SET reagents can be used to trigger the radical chain, after which the acyl radical is quenched by a nucleophile or engaged in cross-coupling.<sup>82–86</sup> Inspired by the powerful ability of visible-light photocatalysis to generate radical species amenable to carbonylative transformations, as demonstrated in our previous work on radical carbonylations, we envisioned carbon monoxide (CO) as a key radical trapping agent. This strategy would leverage the generated alkyl radicals not only

for migration but crucially for coupling with CO, thereby installing a carbonyl group concurrently with the 1,2-boron shift, unlocking new synthetic pathways for structurally complex boronic esters. In addition, achieving functional-group translocation within a single molecule to enable positional exchange remains highly challenging, as it demands exceptional regioselectivity and chemoselectivity. Such transformations often require precise bond activation without perturbing other functionalities and are frequently complicated by the inherent stability of the original groups and potential side reactions. Therefore, efficient and selective intramolecular functional group translocation remains a formidable synthetic challenge. Moreover, this strategy also enables a functional-group translocation within a single



molecule, allowing for the positional exchange between a carbonyl and a boryl group *via* sequential CO<sub>2</sub> extrusion, 1,2-boron migration, and CO insertion.

## Results and discussion

To test the feasibility of the above hypothesis, we initiated an optimization study of a model reaction between 1,3-dioxoisindolin-2-yl 3-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**1a**) and *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (**2a**) in the presence of a photocatalyst and a base under a blue LED lamp (Table 1). The desired product **3a** was obtained in 46% isolated yield when using Ir(ppy)<sub>3</sub> as a photocatalyst, diisopropylethylamine (DIPEA) as base, Hantzsch ester (HE) as reductant in DCE under the irradiation of two 40 W blue LED lamp (entry 1, Table 1). Recognizing the potential influence of solvent polarity on reaction, we surveyed ethereal, halogenated and ester solvents. Solvent examinations showed that EA was the optimal one to deliver the target product **3a** in 54% yield (entries 1–3, Table 1). A screening of photocatalysts, such as eosin Y, Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, Acid red 94, and so on, demonstrated that Acid red 94 was the most effective catalyst, yielding **3a** in 59% yield (entries 4–9, Table 1. Also see SI for details). Further assessment on the amount of reductants indicated that 1.5 equiv. HE and 1 equiv. DIPEA were the best combination (entries 10–13, Table 1). Finally, we explored the molar ratio of **1a** and **2a**. Gratifyingly, running the reaction with an exactly equimolar **1a/2a** mixture (0.1 mmol

each) in EA (0.2 M) for 18 h reproducibly afforded **3a** in 69% isolated yield (entries 15–17, Table 1).

With the optimized conditions established, we set out to investigate the generality and limitation of the photocatalyzed 1,2-boron migrative carbonylation accelerated (Table 2). For  $\beta$ -boryl NHPI esters, when acyclic alkyl groups were used to replace the cyclohexyl group in the substrate, the carbonylated products were obtained in good yields with little variation in yields (**3b–3f**). To understand the impact of the stability of radicals on the reactivity and selectivity, substrates containing methylene tethers with different lengths were exposed to the reaction as well, it was found that the length of the chain does not affect the formation of the desired products (**3g–3i**). The generality with respect to the thiosulfonate coupling partner proved equally broad. A series of thiosulfonates with electron-donating groups such as –Me and –OMe could generate the desired products (**4a–4d**) in good yields. Furthermore, different functional groups, such as naphthalene ring, primary alkyl chains and trimethylsilyl group (**4e–4i**) could be tolerated. Meanwhile, thiosulfonates with trimethylsilyl group could also generate the products **4g** in 63% yield. Remarkably, Alkenyl sulfones participated *via* radical addition yielding vinyl-functionalized ketone **4j** in 64% yield, which provides a unique modification pathway for functional molecules containing olefinic fragments and also supports the radical nature of this transformation. The universality of thiosulfonates bearing substituents is further demonstrated in the synergistic reaction with  $\beta$ -boryl NHPI esters. When the thiosulfonate

Table 1 Optimization of the reaction conditions<sup>a</sup>



Entry	PC (x mol%)	HE (y equiv.)	DIPEA (z equiv.)	Solvent	Yield <sup>b</sup>
1	Ir(ppy) <sub>3</sub> (2 mol%)	1.5	2	DCE	46%
2	Ir(ppy) <sub>3</sub> (2 mol%)	1.5	2	EA	54%
3	Ir(ppy) <sub>3</sub> (2 mol%)	1.5	2	1,4-Dioxane	49%
4	Eosin Y (2 mol%)	1.5	2	EA	57%
5	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (2 mol%)	1.5	2	EA	54%
6	Ir(ppy) <sub>3</sub> (2 mol%)	1.5	2	EA	57%
7	Acid red 94 (2 mol%)	1.5	2	EA	58%
8	Acid red 94 (3 mol%)	1.5	2	EA	59%
9	Acid red 94 (5 mol%)	1.5	1	EA	55%
10	Acid red 94 (3 mol%)	1.5	1.5	EA	57%
11	Acid red 94 (3 mol%)	1.5	0	EA	Trace
12	Acid red 94 (3 mol%)	2	1	EA	34%
13	Acid red 94 (3 mol%)	1	1	EA	62%
14 <sup>c</sup>	Acid red 94 (3 mol%)	1.5	1	EA	62%
15 <sup>d</sup>	Acid red 94 (3 mol%)	1.5	1	EA	69%
16 <sup>e</sup>	Acid red 94 (3 mol%)	1.5	1	EA	69%
17 <sup>f</sup>	Acid red 94 (3 mol%)	1.5	1	EA	69%

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv., 0.15 mmol), photocatalyst (2 mol%, 0.002 mmol), HE (1.5 equiv., 0.3 mmol), DIPEA (2 equiv., 0.2 mmol), solvent (1 mL) and CO (60 bar), 40 W blue LEDs, rt, 18 h. <sup>b</sup> Isolated yield. <sup>c</sup> EA (2 ml). <sup>d</sup> **1a** (0.2 mmol), **2a** (0.1 mmol). <sup>e</sup> **1a** (0.15 mmol), **2a** (0.1 mmol). <sup>f</sup> **1a** (0.1 mmol), **2a** (0.1 mmol). HE (diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate), DIPEA (*N,N*-diisopropylethylamine), EA (ethyl acetate), DCE (1,2-dichloroethane). Eosin Y (CAS: 17372-87-1). Acid red 94 (CAS: 632-69-9).



Table 2 Scope of the reaction with respect to the  $\beta$ -boryl NHPI esters and thiosulfonates substrates<sup>a</sup>

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), acid red (5 mol%), HE (1.5 equiv., 0.3 mmol), DIPEA (1 equiv., 0.1 mmol), solvent (2 mL) and CO (60 bar), 40 W blue LEDs, rt, 18 h. All yields were isolated yields.

containing different substituents (*e.g.*, electron-withdrawing group and electron-donating group) was combined with the acyclic alkyl-containing  $\beta$ -boronyl NHPI ester, the reaction system still maintained its high efficiency, and structurally diversified bifunctionalized products (**5a–5g**, 68–82%) were successfully constructed. For example, thiosulfonates containing *p*-fluorophenyl (**5b**), *o*-methoxyphenyl (**5d**), and *tert*-butyl (**5f**) were compatible with boronic acid ester precursors containing primary/secondary carbons at the

$\alpha$ -position, demonstrating that the free radical migration and thiosulfonation processes are insensitive to both electronic and site-resistance effects.

To gain deeper mechanistic insights into the origin of the observed reactivity and to delineate the elementary steps responsible for product formation, we carried out a comprehensive suite of control experiments that systematically probed each putative mechanism. The complete suppression of the reaction in the presence of radical scavengers such as



TEMPO, coupled with the detection of corresponding radical trapping adducts by HRMS, revealed the involvement of radical intermediates. High-resolution mass-spectrometric (HRMS) analysis of the crude reaction mixture revealed a prominent peak at  $m/z = 422.3436$ , corresponding to the TEMPO-trapped carbon-centered radical adduct  $[M + H]^+$  (calcd for  $C_{30}H_{49}BO_4$ , 422.3436). Having confirmed radical involvement, we next evaluated the individual contributions of each component to the overall catalytic cycle. In a stepwise fashion, we omitted the photocatalyst, base, HE and visible-light irradiation ( $\lambda = 456$  nm, 40 W blue LEDs). In every case, the reaction was completely arrested, with no detectable product formation ( $\leq 1\%$  by  $^1H$  NMR). Notably, extending the reaction time did not significantly increase the reaction yield. The strict requirement for every component (photocatalyst, base, Hantzsch ester, and light) demonstrates that synergistic coordination of multiple catalytic cycles is essential to achieve this transformation.

Based on the control experiments, a possible reaction mechanism is proposed as outlined in Fig. 2. One possible reaction pathway is that the photocatalyst was excited upon irradiation of visible light. Then, single-electron transfer (SET) from visible light-excited photocatalyst  $PC^*$  to  $\beta$ -boryl NHPI esters **1a** generates a radical anion **A** and  $PC^{*+}$ , the latter is then reduced by Hantzsch ester to PC. Next, radical anion **A** undergoes a decarboxylation reaction, releasing  $CO_2$ , phthaloyl anion ( $Phth^-$ ) and generating an alkyl radical **B**, which transform into a more stable radical **C** through a facile 1,2-boron migration.  $^{42,43}$  Trapping of this alkyl radical by CO forms an acyl radical **D**, which subsequently engages in PhS-group transfer with **2a**. This critical step delivers the observed product **3a** while generating thiyl radical **E**. With the proton transfer from the Hantzsch ester radical cation, culminating in the formation of pyridine **F** and *p*-toluene sulfinic acid.<sup>87,88</sup>

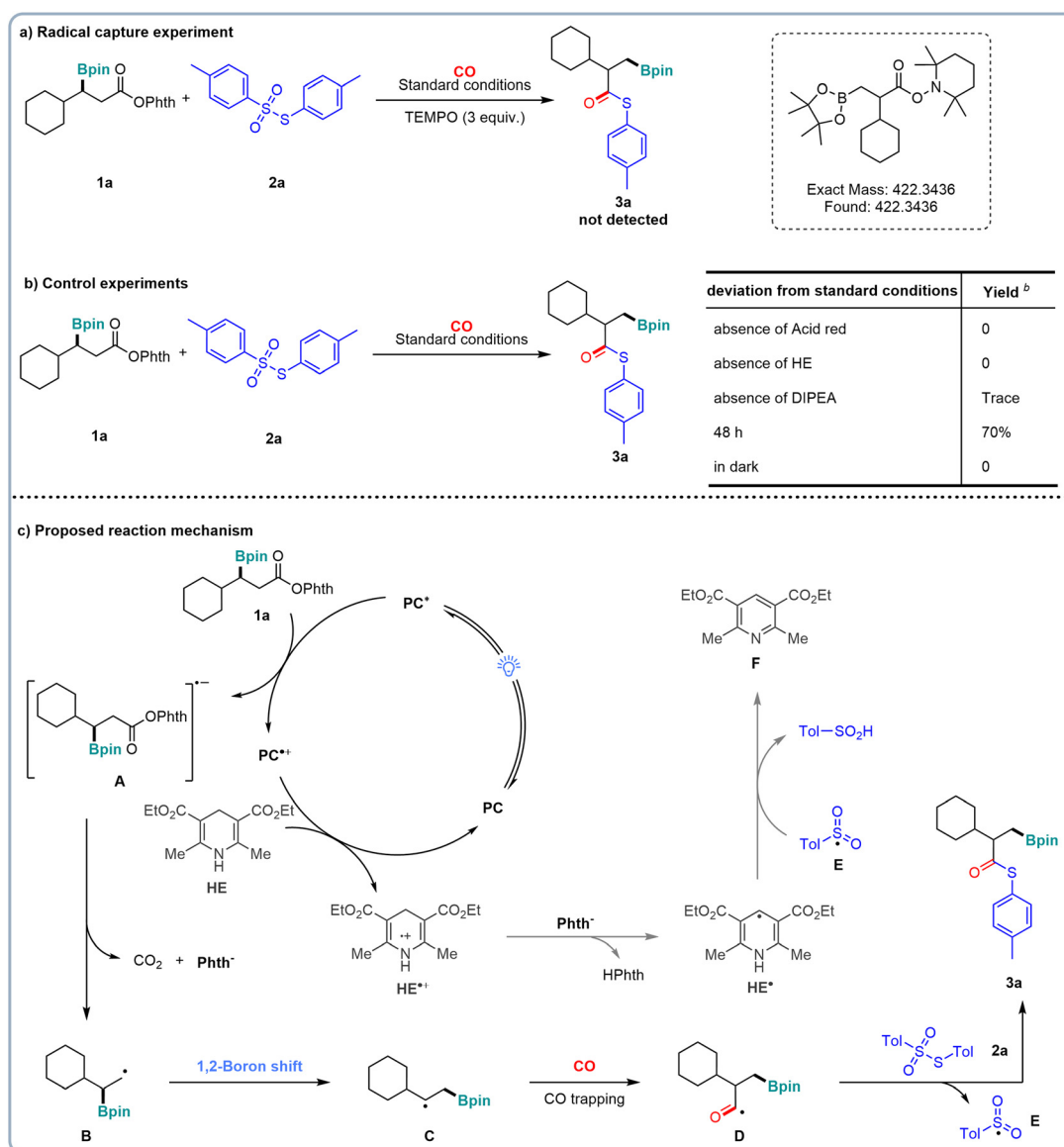


Fig. 2 a, Radical capture experiment. b, Control experiments. c, Proposed reaction mechanism.



To further underscore the preparative utility and broad synthetic reach of the newly developed 1,2-boron-migrative acylation protocol, we carried out an extensive set of scale-up experiment and synthetic transformations. First, the reaction was first translated from the standard 0.1 mmol scale to a 1.0 mmol scale under standard conditions. Gratifyingly, the 1,2-boron shift proceeded smoothly, delivering **3a** in 60% isolated yield, only a

modest erosion compared to the 69% obtained on 0.1 mmol scale. Then, to examine the range of various *S*-phenyl sources, a range of control experiments were performed. Neither simple thiophenol (PhSH) nor diphenyl disulfide (PhSSPh) furnished detectable product **4b** under the standard photoredox conditions (<5% by LC-MS), consistent with their inability to generate the requisite sulfur radical or sulfonyl radical. In contrast, methyl

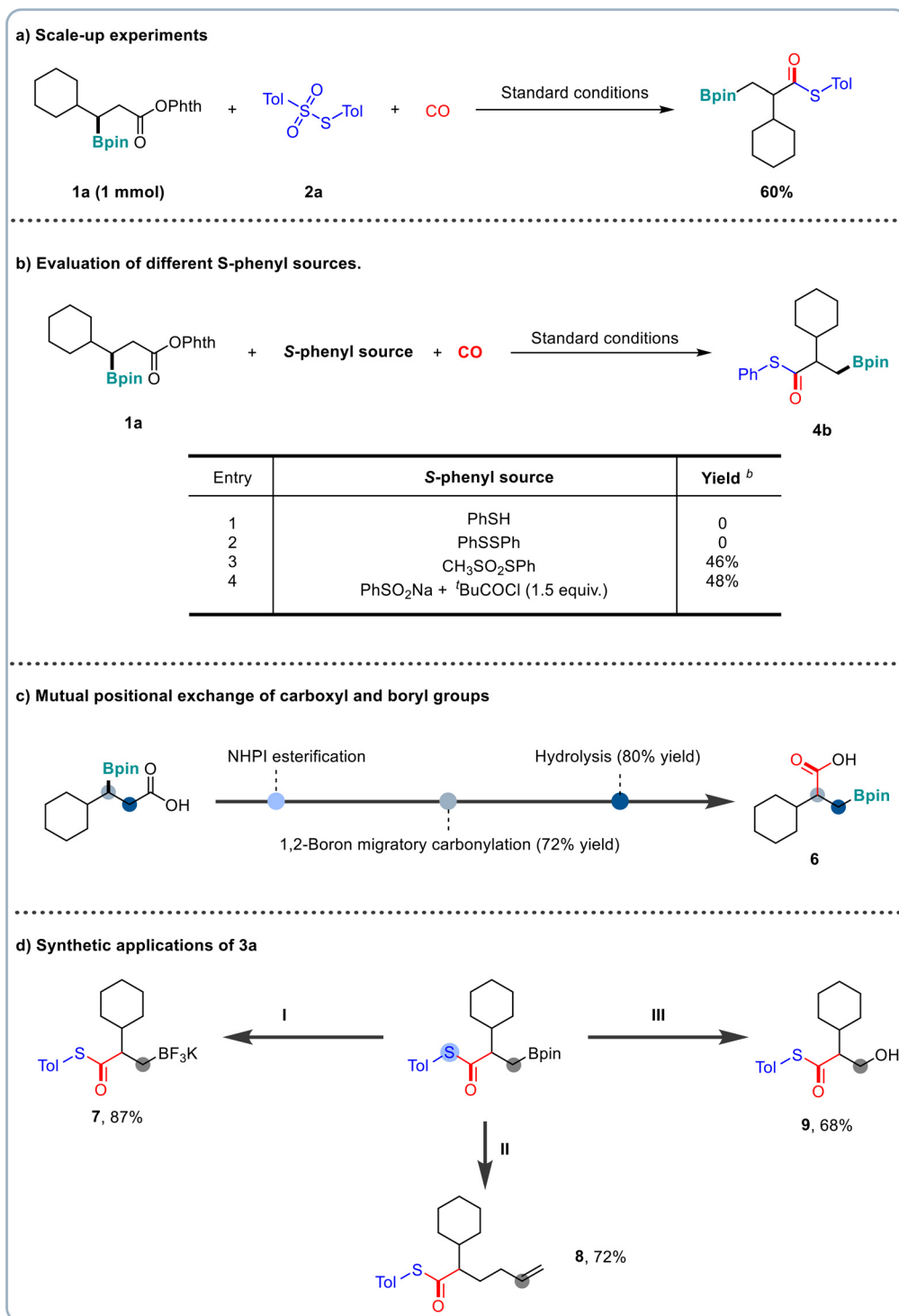


Fig. 3 a, Scale-up experiments. b, Evaluation of different *S*-phenyl sources. c, Mutual positional exchange of carboxyl and boryl groups. d, Synthetic transformations.



benzenesulfonate ( $\text{CH}_3\text{SO}_2\text{Ph}$ ) and sodium benzenesulfonate ( $\text{PhSO}_2\text{Na}$ ) both participated productively, providing **4b** in 46% and 48% isolated yield, respectively. To showcase the versatility of the boryl-carbonyl motif as a synthetic linchpin, we subjected representative adduct **3a** to a concise sequence of chemoselective manipulations.

The positional exchange of two functional groups within a single molecule presents significant challenges, primarily due to the need for high regioselectivity and chemoselectivity. Such transformations require the precise cleavage and formation of specific bonds without affecting other functionalities, often necessitating finely tuned reaction conditions and catalysts. Moreover, the inherent stability of the original functional groups and the potential for undesired side reactions further complicate the process. Achieving an efficient and selective intramolecular functional group transposition remains a formidable synthetic challenge in organic chemistry. We successfully achieved the functional group exchange between the carboxyl and boryl groups within a single molecule through a sequence involving NHPI esterification, 1,2-boron migratory carbonylation, and subsequent hydrolysis. As shown in Fig. 3c, LiOH-mediated hydrolysis of compound **3a** proceeded rapidly and afforded the corresponding acid **6** in excellent yield.

To further illustrate the synthetic value of this methodology, we explored a series of diverse and practical derivatizations of the Bpin moiety. First, the Bpin group was smoothly converted into the more stable trifluoroborate salt **7** in 87% yield (path I), enabling improved stability and handling for subsequent transformations. In addition, treatment of compound **3a** with vinylmagnesium bromide and  $\text{I}_2$  efficiently delivered the vinylated product **8** in 72% yield (path II), thereby expanding the molecular complexity *via* a facile C–C bond-forming process. Furthermore, the  $\beta$ -boryl ketone intermediate underwent facile oxidation to furnish the corresponding alcohol **9** in 68% yield (path III), showcasing the compatibility of the boryl group with post-functionalization strategies. Collectively, these successful transformations highlight the broad applicability and robustness of our protocol for late-stage diversification of structurally complex molecules, underscoring its potential utility in synthetic and medicinal chemistry.

## Conclusions

In summary, we have developed an unprecedented catalytic strategy for promoting boron carbonylation by photocatalysis to efficiently synthesize a broad spectrum of  $\beta$ -boryl thioesters under mild conditions. This is achieved by taking advantage of carbon monoxide (CO) as a readily available C1 source to trap the alkyl radicals generated following 1,2-boron migration. By combining 1,2-boron migration with CO intercalation, this work establishes a new platform for synthesizing valuable borylated building blocks and advances the frontiers of radical-based boron chemistry. Importantly, this transformation enables the functional group exchange between the acyl group and the boronic ester *via* a sequential process involving  $\text{CO}_2$  extrusion, 1,2-boron migration, and CO incorporation.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI).

Supplementary information: general comments, general procedure, analytic data, and NMR spectra. See DOI: <https://doi.org/10.1039/d5cy01255d>.

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