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Electrochemical radical borylation of N-heterocycles with NHC-boranes: efficient access to the B–N bond

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N-Heterocyclic carbene-stabilized boranes (NHC-boranes) have emerged as promising boryl radical precursors for constructing organoboron compounds. While traditional thermal and photocatalytic methods for generating NHC boryl radicals have been explored, electrochemical generation of NHC boryl radicals for B–N bond coupling has not been reported. Herein, we present the first electrochemical borylation of N-heterocycles using NHC-boranes, eliminating the need for radical initiators or mediators. This sustainable method employs electrons as clean redox agents and ionic liquids as green electrolytes. Mechanism studies support an anodic oxidation pathway to generate key boryl radical intermediates. The protocol exhibits broad substrate compatibility and is scalable *via* continuous-flow electrosynthesis, demonstrating significant potential for practical applications.

Green foundation

1. We firstly develop the green and sustainable electrochemical strategy for generating stable NHC boryl radicals. This approach eliminates the need for high temperature, radical initiators, photoredox catalysts or mediators (hydrogen atom transfer reagent or single-electron transfer reagent).
2. In this study, electrons and ionic liquids are employed as clean redox agents and electrolytes, respectively, with hydrogen as the sole byproduct. This protocol exhibits broad substrate compatibility and can be readily scaled up *via* continuous-flow electrosynthesis, highlighting its significant potential for practical applications. Overall, this strategy is simple, efficient, and scalable, and aligns with green chemistry principles.
3. Future research should target electrolyte recycling and electrode sustainability, and expand the substrate range, particularly for the promising ^{10}B-labeled compounds for Boron Neutron Capture Therapy.

Introduction

The unique properties of organoboron compounds have made them the focus of extensive research in multiple areas of chemistry, where they serve as synthetic reagents, materials, and medicines.[1–5] Over the past 20 years, radical chemistry has advanced significantly, with new reagents and methods enabling the discovery of diverse radical species and reactions. However, research on neutral boron-centered radicals (boryl radicals) remains limited compared to other radicals, likely due to several factors.[6] Stabilizing boryl radicals has been challenging because of synthetic constraints in boron chemistry. Additionally, few practical boryl radical precursors exist for general synthetic applications.[7,8]

Since Kuhn reported the first borane complex ligated by an N-heterocyclic carbene (NHC-borane) in 1993,[9] these compounds have demonstrated diverse and unique chemical properties that enable access to unconventional boron species and reactive intermediates.[10] Thereby they exert a significant impact beyond traditional main-group boron chemistry in organic synthesis.[11] These NHC-stabilized boron compounds offer the following advantages: (1) they exhibit high thermal stability and remain stable in air, moisture or weak acids; (2) the corresponding NHC boryl radicals can be stabilized by the NHC group through electronic and/or steric effects; and (3) NHC-borane molecules feature lower B–H bond dissociation energies (79–80 kcal mol^{-1}), leading to enhanced chemical reactivity achieved through various B–H bond activation

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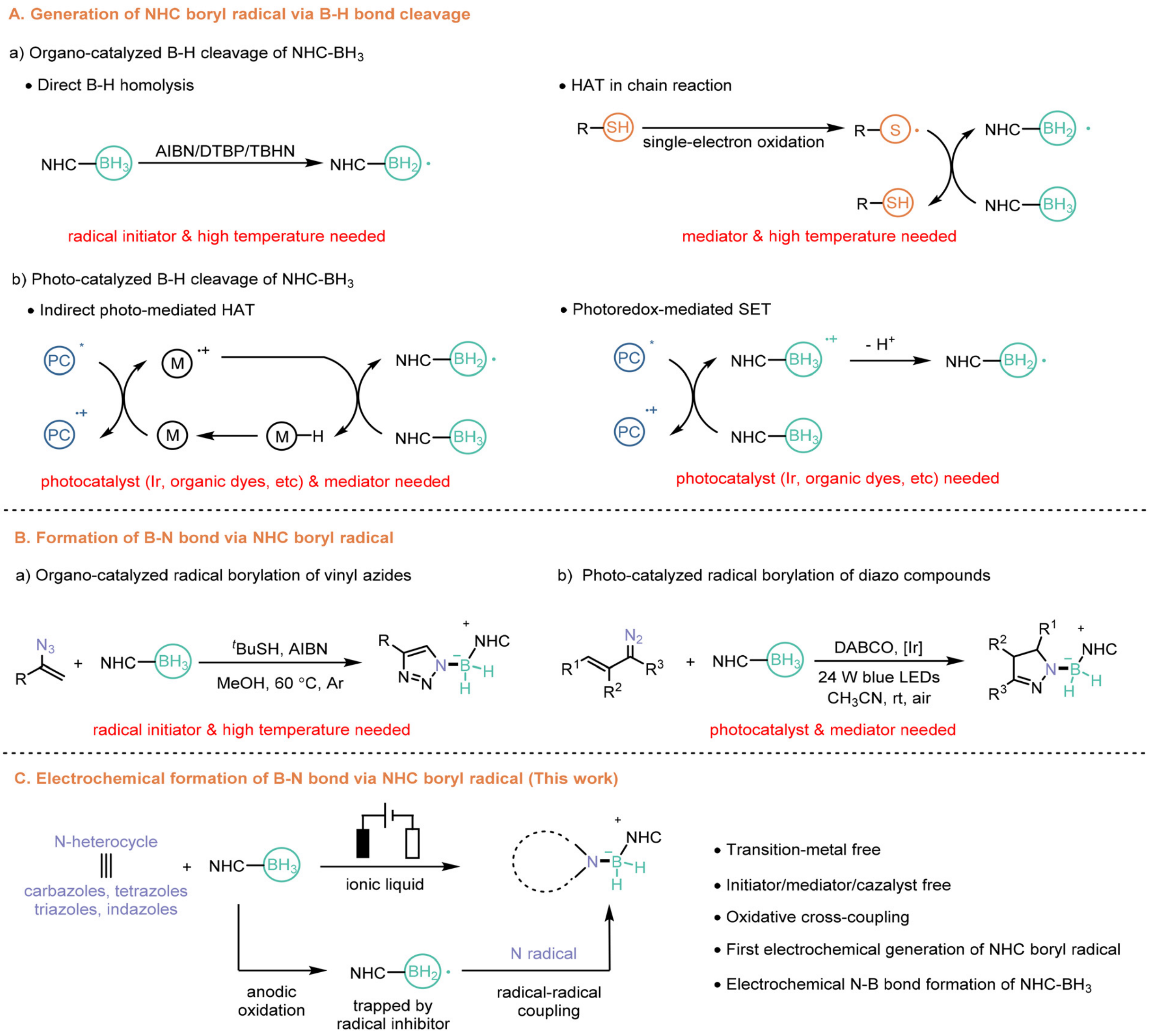
approaches.[12,13] Thus, such compounds are widely used as novel precursors of boryl radicals in organic synthesis.[14–17] The methods for generating such NHC boryl radicals can be categorized into two types. Traditional organo-catalytic methods typically require the introduction of radical initiators to generate radical intermediates *via* homolysis of B–H bonds.[18–21]

Subsequently, thiols are added as polarity-reversal catalysts to enhance hydrogen atom transfer (HAT) efficiency (Scheme 1Aa).[22–28] Alternatively, photocatalytic approaches can be utilized, where indirect HAT occurs in the presence of a mediator,[29–33] or direct single-electron transfer (SET) with the photocatalyst, followed by proton loss to afford the corresponding radicals (Scheme 1Ab).[34–38] Reactive NHC boryl radicals can be captured by a range of unsaturated systems or heteroatoms to form new C–B/B–X bonds.[39–42] However, the utilization of NHC boryl radicals for B–N bond formation remains significantly underexplored. The recent sporadic literature predominantly relies on thermal strategies (Scheme 1Ba).[43–45] In 2024, the Xuan group first reported utilizing photochemical methods to employ NHC boranes for B–N bond formation (Scheme 1Bb).[46] To the best of our knowledge, the electrochemical generation of NHC boryl radicals and their subsequent application in B–N bond formation remains unreported to date. In view of our long-term interest in electrochemical systems and heteroatom–heteroatom coupling reactions,[47–55] herein, we report the first electrochemical borylation of N-heterocycles with NHC-boranes (Scheme 1C). This method eliminates the need for transition metals, radical initiators, mediators, or catalysts, featuring mild reaction conditions and operational simplicity. It employs electrons as mass-free reagents and redox agents, with ionic liquids serving as green electrolytes, proceeding *via* oxidative cross-coupling to generate hydrogen gas as the sole byproduct, demonstrating both environmental friendliness and atom economy. Control experiments reveal that NHC-boranes undergo anodic oxi-



Scheme 1 Different types of reactions of the NHC-boryl radical.

dation to form boryl radical intermediates. The protocol is compatible with biologically active nitrogen-containing heterocyclic pharmaceuticals. Moreover, it is amenable to large-scale synthesis and single-path continuous-flow electrosynthesis, highlighting its significant potential for practical applications. Antiproliferation assays and live/dead cell staining experiments demonstrate that such boron-containing compounds exhibit significant application potential in the early stages of drug screening.

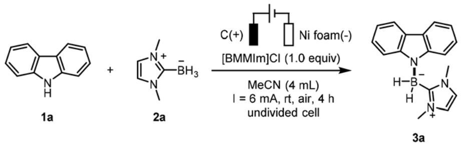
Results and discussion

Our initial attempt at electrochemical borylation began with the reaction of 9*H*-carbazole **1a** with N-heterocyclic carbene-borane ($NHC-BH_3$) **2a** as the starting materials. The desired product **3a** was successfully obtained in 52% yield when employing [BMMIm]Cl as the electrolyte and MeCN as the solvent, with a graphite rod serving as the anode and Ni foam as the cathode in an undivided cell under constant current electrolysis (6 mA) (Table 1, entry 1). Utilizing other electrolytes, for example, Et_4NCl or $[C_{12}MIm]Cl$, failed to improve the productivity of **3a** (entries 2 and 3). Variation of the cathode material to Pt or the anode material to copper did not significantly promote the reaction (entries 4 and 5). Increasing or decreasing the current intensity both led to a decrease in the yield (entries 6 and 7). Notably, the transformation was highly dependent on electricity, since no desired product formed without it (entry 8). Employing 3.0 equiv. of **2a** profitably affected the formation of **3a**, increasing the yield to 68% (entry 9). Besides, this reaction demonstrated pronounced moisture sensitivity. Consequently, the use of rigorously dried MeCN as a solvent combined with 1.0 equiv. of anhydrous Na_2SO_4 as the additive afforded the product in optimal yield (entry 10). For details, see the SI, Tables S1–S5.

With the optimized conditions established, the scope of carbazoles was then evaluated (Scheme 2). Carbazoles bearing halogen (**3b–3g**) at either *ortho*/*para*/*meta* position, as well as di-halogens (**3h–3k**) demonstrated excellent reactivity, delivering the desired products in moderate to high yields. Electron-deficient substrates, such as *para*-nitro or cyano substituted carbazoles (**3l** and **3m**) were also compatible, albeit with reduced efficiency. Moreover, carbazoles bearing electron-donating groups such as alkyl, alkyl ether or phenyl participated effectively, affording NHC-borane derivatives (**3n–3t**) in 46–85% yields. Additionally, heteroaryl carbazole derivatives (**3u**) proved viable. Sterically demanding systems such as dibenzofuranyl, naphthyl and fluorenyl carbazoles (**3v–3z**) were well tolerated, enabling access to sterically hindered boranes that are challenging to prepare *via* conventional methods. Reactions between other aromatic amines/N-heterocycles and NHC-BH3 were also employed. However, no desired product was observed under the standard conditions. The structure of **3a** was determined by X-ray crystallography (see the SI).

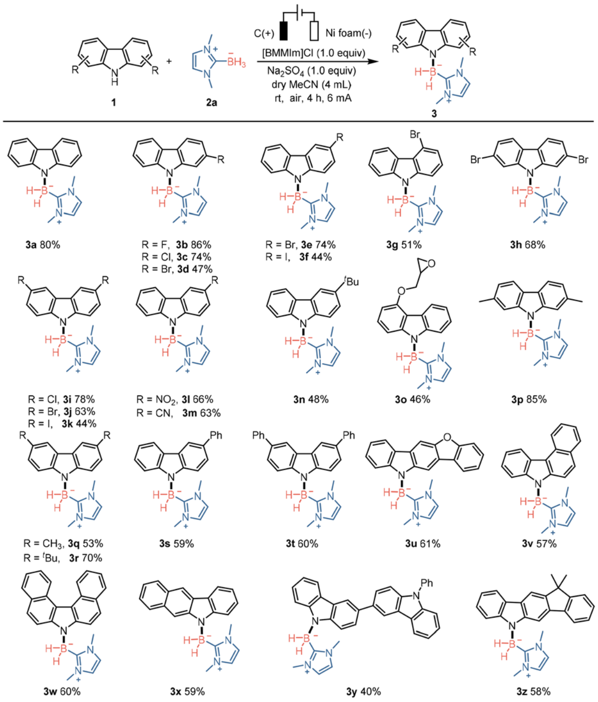
Notably, various nitrogen-containing heterocycles were capable of reacting with NHC-boranes to form B–N bonds *via* cross-coupling (Scheme 3). Optimization of reaction conditions revealed that the reaction proceeded efficiently in the

Table 1 Optimization of the reaction conditions[a]

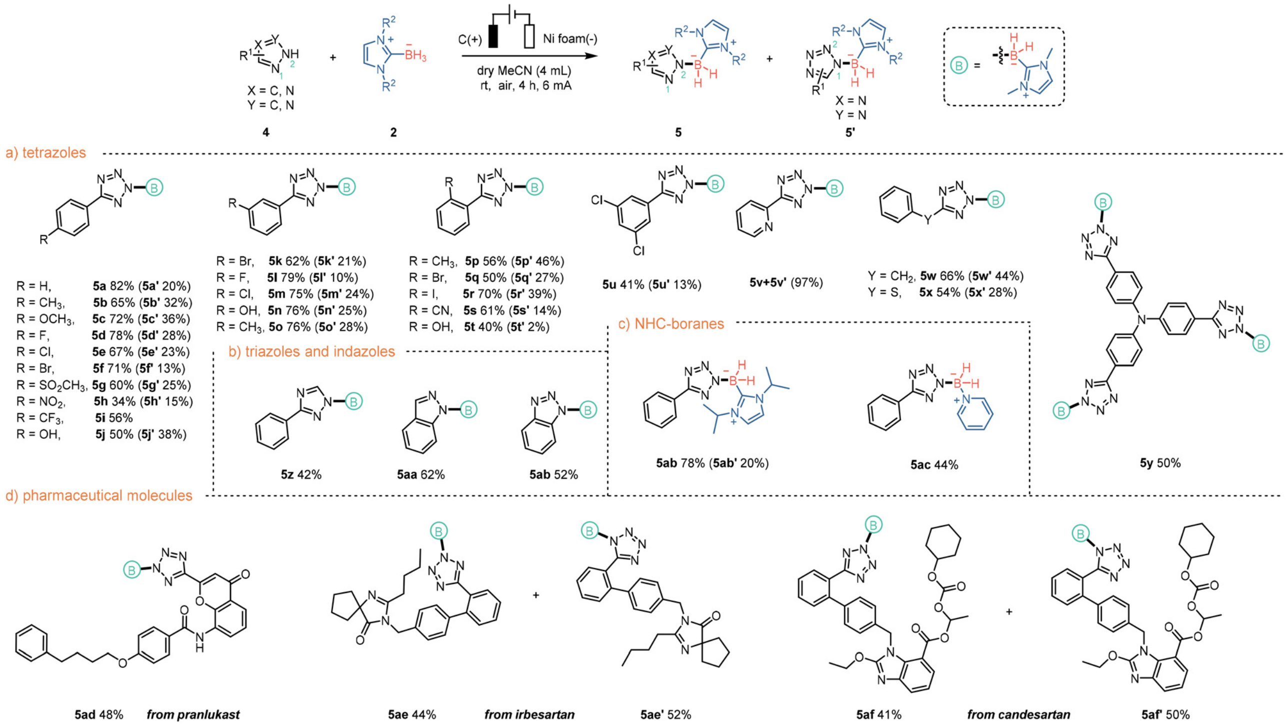


Entry	Deviation from above	Yield[b] (%)
1	None	52
2	Et_4NCl instead of [BMMIm]Cl	49
3	$[C_{12}MIm]Cl$ instead of [BMMIm]Cl	36
4	Pt cathode	46
5	Cu anode	53
6	3 mA	25
7	8 mA	27
8	Without current	n.r.
9	**2a** (3 equiv.)	68
10[c]	**2a** (3 equiv.), Na_2SO_4 (1 equiv.) as the additive	80

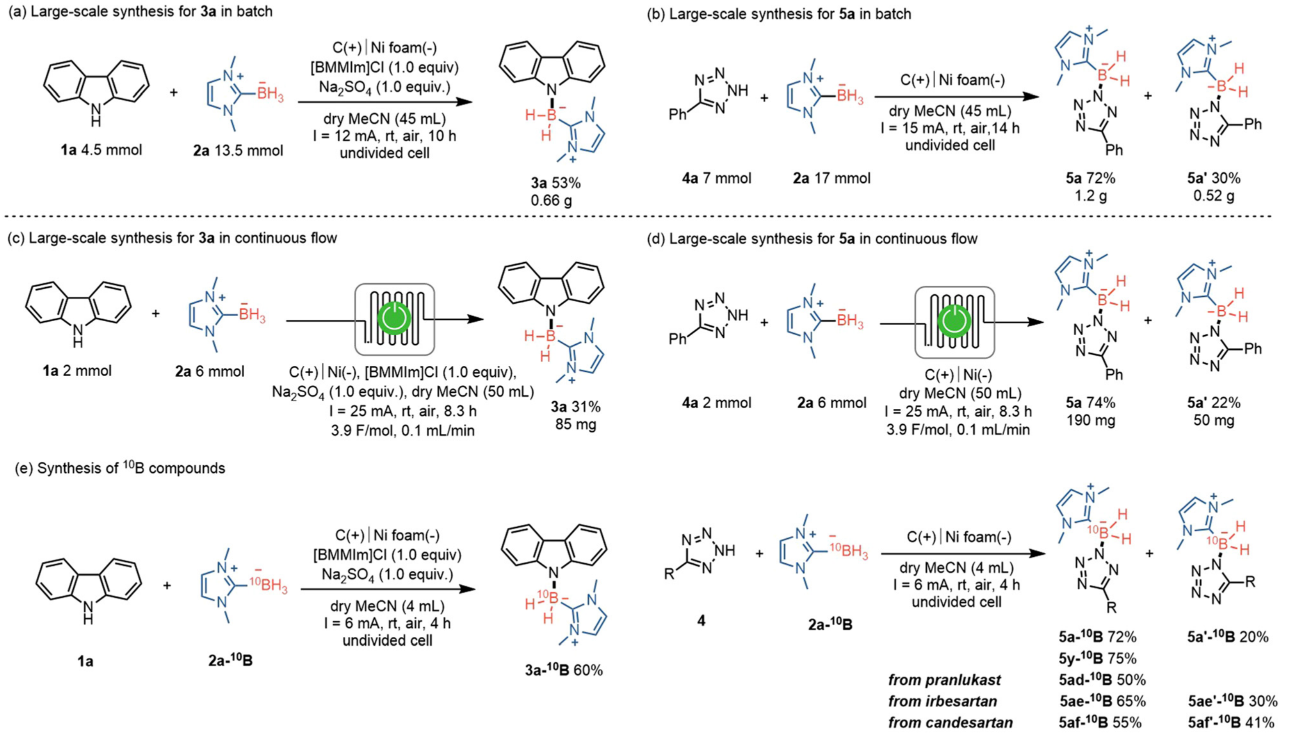
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), [BMMIm]Cl (0.2 mmol), MeCN (4.0 mL), C anode (15 mm × 10 mm × 1 mm), Ni foam cathode (15 mm × 10 mm × 1 mm), the distance between the electrodes (10 mm), constant current = 6 mA, 4 h, 4.5 F mol^{-1}, room temperature, under air, undivided cell. [b] Isolated yields. [c] MeCN replaced with dry MeCN. n.r. = no reaction.



Scheme 2 Substrate scope of **1**. Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), [BMMIm]Cl (0.2 mmol), Na_2SO_4 (0.2 mmol), dry MeCN (4.0 mL), C anode (15 mm × 10 mm × 1 mm), Ni foam cathode (15 mm × 10 mm × 1 mm), the distance between the electrodes (10 mm), constant current = 6 mA, 4 h, 4.5 F mol^{-1}, room temperature, under air, undivided cell. Isolated yields.



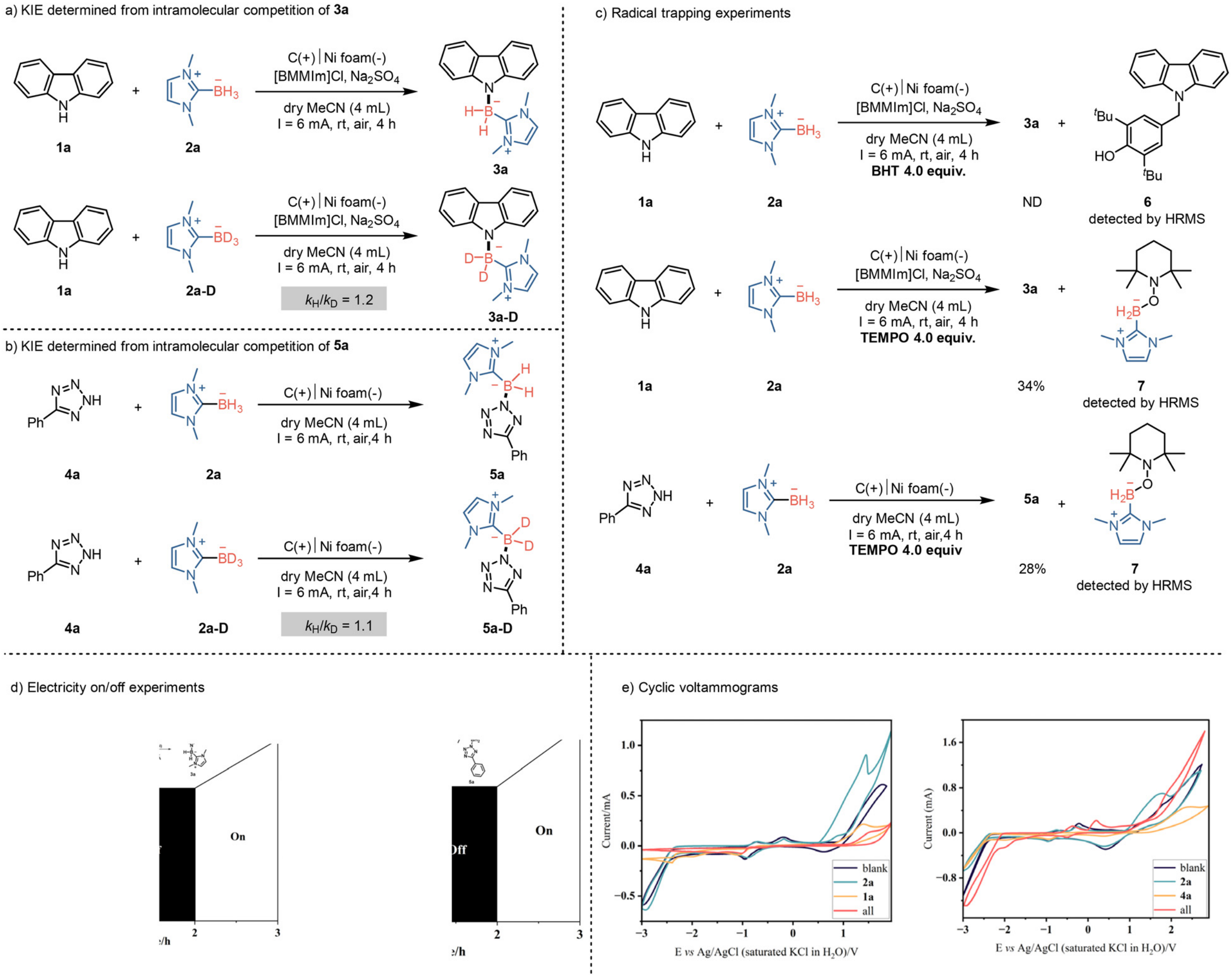
Scheme 3 Substrate scope of **4**. Reaction conditions: **4** (0.3 mmol), **2** (0.9 mmol), dry MeCN (4.0 mL), C anode (15 mm × 10 mm × 1 mm), Ni foam cathode (15 mm × 10 mm × 1 mm), the distance between the electrodes (10 mm), constant current = 6 mA, 4 h, 4.5 F mol^{-1}, room temperature, under air, undivided cell. Isolated yields.



Scheme 4 Large-scale synthesis and synthesis of ^{10}B compounds.

absence of an electrolyte or additive, making it more environmentally friendly (for details, see the SI, Table S6). 5-Aryl-2*H*-tetrazoles featuring electron-donating groups (**5a–5c**) or halogens (**5d–5f**) at the *para* positions exhibited excellent reactivity, delivering the target adducts in 65–80% yields. Electron-deficient variants (**5g–5i**) exhibited lower reactivity, yielding products modestly. It is noteworthy that substrates bearing active hydroxyl substituents (**5j**) were also compatible with this transformation. Alternatively, substrates bearing *ortho*-, *meta*- or di-substituents (**5k–5u**) could also readily undergo the corresponding transformation. Heteroaromatic tetrazoles, including 5-pyridyl, proved competent coupling partners (**5v**). 5-Benzyl-1*H*-tetrazole (**5w**) or 5-(phenylsulfanyl)-1*H*-tetrazole (**5x**) showed good reactivity and gave the corresponding product in moderate yields. Sterically hindered substrates containing multiple tetrazole rings (**5y**) could also react smoothly. The reaction system also successfully incorporates other N-heterocycles, exemplified by triazoles and indazole (**5z–5ab**). A series of structurally diverse NHC-borane complexes demonstrated excellent compatibility in the N–H borylation of tetrazoles (**5ab** and **5ac**), with variations in the wingtip group and NHC heterocycles all being well tolerated. The reaction displayed exceptional tolerance toward structurally complex substrates. Pharmaceutical derivatives, including pranlukast, irbesartan and candesartan (**5ad–5af**), could undergo borylation without compromising efficiency. We also attempted reactions between borane trimethylamine complexes and triphenylphosphine borane with 5-phenyl-tetrazole, respectively. But regrettably, we failed to obtain the desired product. The structures of **5a** and **5a′** were determined by X-ray crystallography (see the SI).

Remarkably, this electrosynthetic system demonstrated excellent scalability, as evidenced by successful large-scale transformations of **2a** under optimized B–N bond formation conditions using a Ni plate as the cathode (Scheme 4). Both batch and continuous-flow modes afforded products in moderate yields, underscoring the method's practical utility (Scheme 4a–d). Boron Neutron Capture Therapy (BNCT) serves as a precision cancer therapy by selectively delivering boron-10 to tumor cells and utilizing neutron irradiation to trigger nuclear reactions that generate high-energy alpha particles and lithium nuclei, enabling highly localized tumor cell destruction while sparing the surrounding healthy tissues.[56]

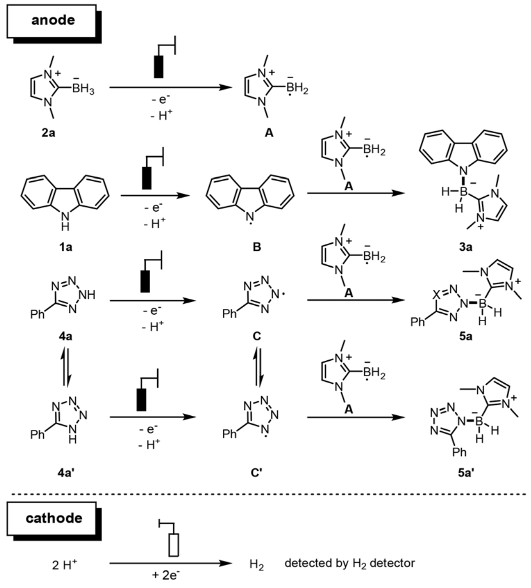


Scheme 5 Control experiment.

The development of boron-10 carriers is therefore critically important, as it aims to achieve sufficient tumor-specific boron accumulation, which is fundamental to realizing the full therapeutic potential and precision targeting of BNCT.[57,58] Based on this, starting from boron-10-labeled NHC-borane compounds, we successfully synthesized a series of ^{10}B compounds under electrochemical conditions. Notably, inherently bioactive drug molecules all afforded their corresponding boron-10-labeled derivatives in moderate to excellent yields (Scheme 4e).

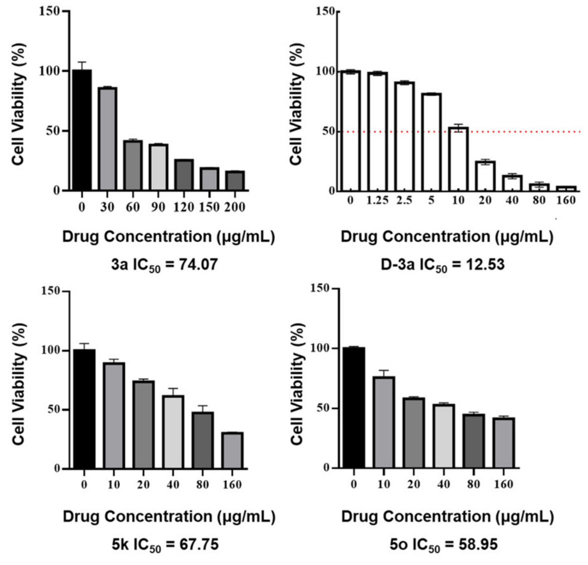
Several control studies were employed to elucidate the reaction pathway (Scheme 5). Kinetic isotope effect (KIE) experiments were conducted to probe the rate-determining step of the B–H activation process. Two separate, parallel reactions of carbazole with NHC-borane **2a** and **D-2a** were performed to determine the KIE value, and the result revealed that the B–H bond cleavage was not involved in the rate-determining step (Scheme 5a). Likewise, in the reaction of tetrazole with NHC-borane, B–H bond activation did not serve as the rate-determining step (Scheme 5b). Subsequently, a series of radical trapping experiments were conducted (Scheme 5c). Upon addition of 4 equivalents of radical inhibitors (BHT or TEMPO), the reaction yield significantly decreased or was completely suppressed. Furthermore, compounds **6** and **7** were detected by HRMS analysis, corresponding to the trapped carbazole radical or borane radical adducts, respectively. These results suggested that this transformation likely proceeded *via* a radical pathway. Electrochemical control experiments revealed that N–B bond coupling was strictly electricity-dependent, with no reaction observed under open-circuit conditions (Scheme 5d). According to cyclic voltammetry (CV) experiments (Scheme 5e), upon the addition of **1a** and **2a**, the oxidation-side current density decreased, which ultimately indicated the occurrence of the reaction. This result indicated that the combination of **1a** and **2a** was easier to be oxidized. For the tetrazole system, the oxidation peak of **4a** decreased upon the addition of **2a**. Further detailed analysis of the EPR signals, including precise radical identification, remains an ongoing challenge and is subject to future investigation.

Based on the control experiment and previous literature reports,[10,59] a feasible reaction mechanism for the electrochemical *N*-borylation of nitrogen-containing heterocycles was proposed, as illustrated in Scheme 6. Anodic oxidation of NHC-BH_3 **2a** gives NHC-boryl radical **A**. In parallel, anodic oxidation of carbazole **1a** generates a carbazole radical intermediate **B**, which then engages in radical–radical cross-coupling with the boron radical **A** to form the target product **3a**. For the tetrazole substrate **4a**, tautomerization occurs first, followed by anodic oxidation to generate two distinct nitrogen radical intermediates **C** or **C′**, which are subsequently captured by the boron radical **A** to afford the target compound **5a** and **5a′**. Protons are electrochemically reduced at the cathode surface, resulting in the evolution of hydrogen gas which is detected using a H_2 detector.

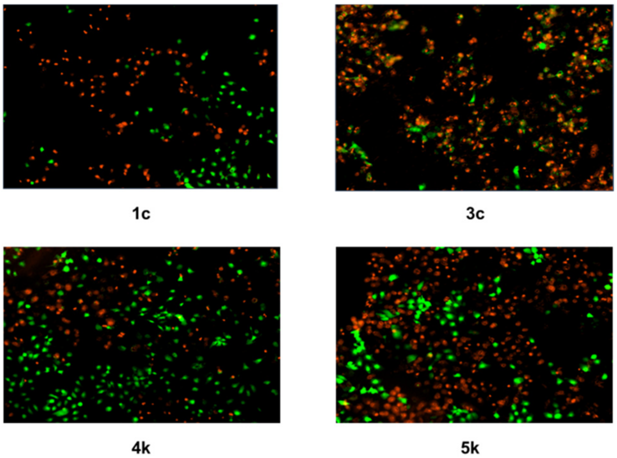


Scheme 6 Proposed mechanism.

In addition, we conducted anti-proliferation assays and live/dead cell staining experiments on relevant representative compounds (Schemes 7 and 8). The experimental results indicated that for carbazole-derived products, compound **3a** exhibited significant anti-proliferation effects, while its deuterated form **D-3a** demonstrated even better efficacy. For tetrazole-derived products, those with bromine or methyl substitutions at the *meta*-position (**5k** and **5o**) also showed excellent anti-proliferation activity. In the live/dead cell staining assay, compounds **3c** and **5k** demonstrated stronger cytotoxicity compared to the original substrates **1c** and **4k**. The results of this study indicated that the candidate compound exhibited potent *in vitro* cytotoxic activity, demonstrating significant potential in the early stages of drug screening (for details, see the SI).



Scheme 7 Anti-proliferation assay.



1c 3c

4k 5k

Scheme 8 Live/dead cell staining assay.

Conclusions

In summary, we have developed a novel electrochemical method for generating NHC-boryl radicals and applying them in N-heterocycle borylation. This metal- and catalyst-free approach uses electrons as clean redox agents and ionic liquids as green electrolytes, with H_2 as the sole byproduct. The reaction features mild conditions, excellent functional group tolerance, and compatibility with pharmaceutical scaffolds, while its scalability is demonstrated through batch and flow electrosynthesis. This work successfully develops a novel generation mode for NHC-boryl radicals and provides a new methodology for N–B bond formation. Further exploration of NHC-boryl radical chemistry is ongoing in our laboratory.

Author contributions

H. C. and J. W. conceived the project and designed the experiments. W. W. J. and C. J. L. directed the project. S. Y. Z. and H. C. performed the reaction and mechanistic studies. H. C. and J. W. performed the large-scale reaction and CV studies. M. M. D. performed the bioactivity experimental testing. S. Y. Z., W. W. J. and C. J. L. prepared the manuscript.

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: experimental procedures; mechanistic studies; the crystallographic data; spectroscopic data; copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{11}B NMR spectra; anti-proliferation assay; live/dead cell staining assay. See DOI: https://doi.org/10.1039/d5gc06005b.

CCDC 2451381, 2406846 and 2412782 contain the supplementary crystallographic data for this paper.[60a–c]

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