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Photocatalytic [3 + 2]-annulation *via* sodium tetraarylborate: a fundamental approach for synthesizing 1,4,2-diazaborole analogs†

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Substantial advancements have been achieved in the field of photocatalytic borylation utilizing 4c-7e Lewis base-boryl radicals. However, the utilization of 3c-5e neutral boryl radicals for C–B bond formation remains relatively underexplored due to their inherent instability. In this study, we successfully demonstrated the direct construction of C–B bonds using sodium tetraarylborate as a key reagent. This was accomplished by effectively stabilizing diaryl boryl radicals with nitrile compounds, thereby facilitating the synthesis of valuable boron-containing compounds. Overall, our research elucidates the significant role played by sodium tetraarylborate in enabling an efficient and versatile approach for synthesizing of 1,4,2-diazaborole analogs through a photocatalyzed [3 + 2]-annulation reaction. This mild and adaptable methodology expands synthetic strategies for obtaining diverse derivatives of 1,4,2-diazaboroles, with the RCN–BAR₂ complex serving as an effective boron–nitrogen synthon that opens up pathways to multiple boron–nitrogen heterocycles. Furthermore, this breakthrough significantly enhances the applicability of sodium tetraarylborate in photoredox catalysis.

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Introduction

Boron-containing compounds have become focal points in both scientific research and industrial development due to their unique chemical properties and diverse applications.^{1–5} Since the late 1990s, small boron-based molecules have garnered significant interest in the fields of chemistry and biomedicine.^{6–18} Among these, boron–nitrogen heterocycles stand out for their distinctive properties, finding utility in manufacturing, optoelectronics, and cosmetics.^{19–37} Representative cases are illustrated in Scheme 1A. One notable instance is 1,4,2-diazaborole, a five-membered boron–nitrogen heterocycle with the boron and nitrogen atoms occupying positions 1, 4, and 2 respectively. Structurally resembling 2-imidazoline,^{38–40} the inclusion of boron imparts unique electronic properties and reactivity to this compound. These attributes enhance its appeal for applications in organic chemistry and materials science while attracting growing interest from researchers.^{28–37}

Ongoing research on the analogs of 1,4,2-diazaborole has been primarily focused on its exploration and synthesis optimization, with various boron reagents developed to date (Scheme 1B). As early as 1984, the Sadhu group devised a strategy utilizing α -iodoboronic ester in combination with amidine and *n*-BuLi to synthesize a single compound 1,4,2-diazaborole, achieving moderate yields.²⁹ Subsequently, the Pawelke group synthesized the key boron reagents known as azoniaboratacyclopropanes which underwent ring-opening and expansion reactions to yield several derivatives of 1,4,2-diazaborole.³⁰ Later on, the Erker group established a mild three-component sequential protocol using their described FmesBH₂ along with isocyanides and nitriles. This showcased an efficient synthetic strategy.³⁶ Recently, the Miyata group has developed a mild synthetic strategy using potassium α -amino-borate and azirine, thereby providing opportunities for further exploration.³⁷ Despite recent advancements, there is still a strong demand for a more concise, efficient, and step-economical synthesis of 1,4,2-diazaborole analogs from readily available starting materials. We propose investigating the utilization of an economical and commercially available boron reagent for their direct synthesis.

In the field of photocatalytic borylation, significant advancements have been made in the realm of boryl radical chemistry in recent years.^{41–68} While Lewis base-boryl radicals, such as N-heterocyclic carbene (NHC) boryl radicals^{46–54} and amine boryl radicals,^{55–62} have been extensively studied, our group has also conducted relevant studies in this field.^{57,59}

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However, compared to the well-studied 4c-7e boryl radicals, the inherently unstable 3c-5e neutral boryl radicals have received considerably less attention. Amongst the precursors for neutral boryl radical, sodium tetraarylborate has garnered attention since the 1960s due to its affordability and stability.^{63,64} Nevertheless, its role in photochemistry has primarily focused on biaryl compound synthesis while leaving unexplored potential for generating neutral boryl radicals.⁶⁵ In 2022, the Xia group achieved a significant breakthrough by employing neutral diaryl boryl radicals for the activation of the C–O bond in benzyl alcohol.⁶⁶ The Wang group further employed diaryl boryl radicals as precursors for aryl radicals in reactions.⁶⁷ Subsequently, the Sharma group demonstrated a core strategy by using diphenyl boryl radicals for C–Br bond activation.⁶⁸ The aforementioned research studies successfully employed neutral boryl radicals derived from sodium tetraarylborate in photoredox catalysis to generate key carbon radicals; however, their application in C–B bond formation for boron-containing compounds remains unexplored (Scheme 1C).

A: Certain functional boron–nitrogen heterocycles



B: Previous Work in the Synthesis of 1,4,2-Diazaborole Analogs



C: The application of natural diaryl boryl radical in photoredox catalysis.



D: Our design: Photocatalyzed [3+2] annulation of boron radical with imine.

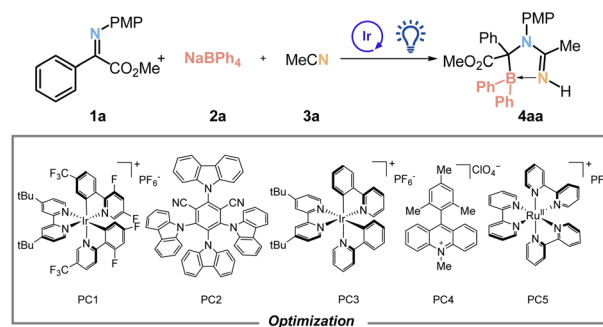


Scheme 1 Research background.

Inspired by groundbreaking previous research, our focus is on the development of a catalytic strategy for synthesizing 1,4,2-diazaborole analogs, a distinct class of five-membered boron–nitrogen heterocycles. The [3 + 2]-annulation reaction serves as an efficient method for rapidly constructing five-membered carbon (hetero) cycles. Therefore, we propose to investigate whether neutral diphenyl boryl radicals can facilitate this reaction with suitable substrates, thereby enabling the rapid synthesis of 1,4,2-diazaborole analogs.

Building on the aforementioned literature, we propose that nitrile compounds, possessing a lone pair of electrons on the nitrogen atom, can function as Lewis bases by coordinating with electron-deficient diphenyl boryl radicals to yield intermediate **II**, specifically the MeCN–BPh₂ complex.^{34,69} Intermediate **II** features two reactive sites: an electrophilic cyanide carbon and a nucleophilic boryl radical. This imparts significant potential for it to serve as a [3 atoms]-synthon in [3 + 2]-annulation reactions. Furthermore, we hypothesize that this synthon could interact with imines to construct the C–B bond and facilitate the synthesis of 1,4,2-diazaborole analogs through a [3 + 2]-annulation pathway.

Table 1 The optimization of reaction conditions



Entry	PC	1a : 2a	Solvent	Additive	Yield ^{a,b}
1	PC1	1 : 2	MeCN	—	47
2	PC2	1 : 2	MeCN	—	33
3	PC3	1 : 2	MeCN	—	22
4	PC4	1 : 2	MeCN	—	0
5	PC5	1 : 2	MeCN	—	0
6	PC1	1 : 1	MeCN	—	34
7	PC1	1 : 3	MeCN	—	49
8	PC1	1 : 4	MeCN	—	44
9	PC1	1 : 3	MeCN	—	51 ^c
10	PC1	1 : 3	MeCN	4 Å MS (20 mg)	55 ^c
11	PC1	1 : 3	MeCN + DCM	4 Å MS (20 mg)	60 ^c
12	PC1	1 : 3	MeCN + DCM	4 Å MS (20 mg)	73 ^{c,d}
13	PC1	1 : 3	MeCN + DCM	4 Å MS (20 mg)	58 ^{c,e}
14	PC1	1 : 3	MeCN + DCM	4 Å MS (20 mg)	78 ^{c,f}
15	PC1	3.5 : 1	MeCN + DCM	4 Å MS (20 mg)	91 ^{c,f}
16			Without PC		Trace
17			Without light		N.R.

^a Isolated yield. ^b Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), NaBPh₄ (x mmol), PC (3 mol%), MeCN (0.5 mL), 30 W blue LEDs, 0 °C, 12 h, under an argon atmosphere. ^c [Ir(dF(CF₃)ppy)₂dtbbpy]PF₆ (4 mol%). ^d Reaction time extended to 24 h. ^e Reaction time extended to 30 h. ^f Reaction time extended to 27 h.



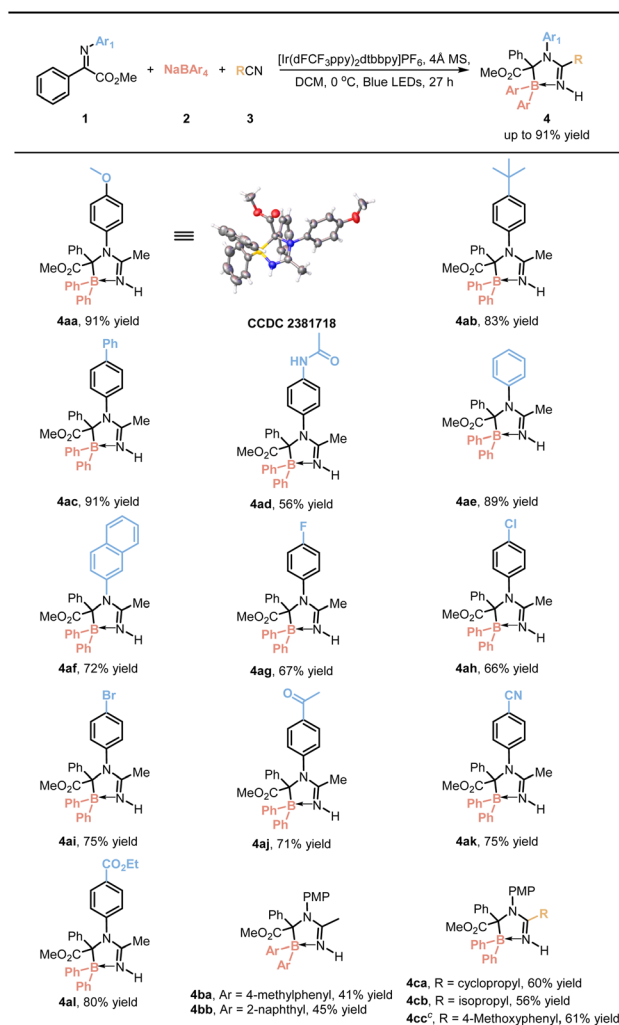
Results and discussion

To validate the feasibility of our hypothesis, imine **1a** and sodium tetraphenylborate **2a** were selected as model substrates and $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{dtbbpy}]\text{PF}_6$ was utilized as the photocatalyst under blue light irradiation in acetonitrile, resulting in the successful synthesis of target compound **4aa** with a yield of 47%. After extensive optimization, it was discovered that $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2\text{dtbbpy}]\text{PF}_6$ exhibited the highest efficacy (Table 1: entries 1–5), and using 3.0 equivalents of **2a** led to a significantly improved yield (entries 6–8). The optimization process involved fine-tuning the quantities of the photocatalyst, a 4 Å molecular sieve, solvent and reaction time, resulting in an enhanced yield of 78% (entries 9–14) (ESI Tables S2–S4†). Considering the susceptibility of imine **1a** to hydrogenation and dimerization, we systematically varied its amount alongside boron source **2a** as a reference point (ESI Table S5†). The highest yield of 91% was achieved with an equivalent ratio of 3.5 for compound **1a** (entry 15). Subsequently, the conditions outlined in entry 15 were identified as the optimal reaction parameters. Control experiments unequivocally demonstrate that both the photocatalyst and light play indispensable roles in this [3 + 2]-annulation reaction (entries 16–17).

After establishing the optimal reaction conditions, we proceeded to expand our investigation in order to assess the substrate scope and generality of the reaction. Initially, a variety of imines derived from aromatic amines were subjected to testing. As indicated in Table 2, the incorporation of electron-donating groups such as methoxy (**4aa**), *tert*-butyl (**4ab**) and phenyl (**4ac**) onto the aniline aromatic ring consistently resulted in favorable results, thereby demonstrating compatibility within the reaction system. However, it should be noted that introducing an amido group (**4ad**) led to a modest reduction in yield. Furthermore, both unsubstituted aniline-derived imine (**4ae**) and 2-naphthylamine-derived imine (**4af**) exhibited commendable yields. In contrast, halogen-substituted anilines (**4ag–4ai**) showed a slight decrease in yields. Notably, electron-withdrawing groups such as acetyl (**4aj**), cyano (**4ak**), and ester groups (**4al**) were well tolerated, resulting in a slight reduction in yields. Next, different boron sources were investigated. Substituting the phenyl group in sodium tetraphenylborate with 4-methylphenyl (**4ba**) and 2-naphthyl (**4bb**) still afforded the target product, albeit with reduced yield. Subsequently, nitriles were tested. In addition to acetonitrile, cyclopropyl nitrile (**4ca**), isobutyronitrile (**4cb**) and 4-methoxybenzenecarbonitrile (**4cc**) also underwent successful transformation, demonstrating the method's broad applicability. The configuration of compound **4aa** was determined by X-ray crystal structure analysis (CCDC 2381718).

The reaction's scope and versatility were evaluated by testing various imines derived from α -ketoesters. As indicated in Table 3, the reaction provided moderate to good yields for imines derived from α -ketoesters, with increased steric hindrance resulting in lower yields (**4am–4ar**). Subsequently, the influence of electron-donating substituents on the aromatic ring of α -ketoesters, such as methyl (**4as**), ethyl (**4at**), *tert*-butyl (**4au**),

Table 2 Reaction scope with respect to the boron sources, nitriles and imines derived from various aromatic amines^{a,b}



phenyl (**4av**), and methoxy groups (**4aw**), was investigated, yielding slightly lower results compared to the model substrate.

Remarkably, when an iodine substituent was introduced at the para position (**4ax**), a yield of 89% was achieved, demonstrating the robustness of the reaction pathway against this substitution.

To further broaden the applicability of our methods, sodium tetraphenylborate can also undergo photocatalytic [3 + 2]-annulation reactions with alkenes, leading to the generation of additional classes of boron–nitrogen heterocycles. This shows that introducing both electron-withdrawing group-substituted styrenes (**6a–6c**) and electron-rich 1,1-diphenylethylene (**6d**) into the template reaction yields the desired azaborole in moderate to good efficiency (Table 4). To demonstrate



Table 3 Reaction scope with respect to the imines derived from various α -ketoesters^{a,b}

^a Reaction conditions are as follows: imine (0.05 mmol), NaBPh₄ (0.175 mmol), PC1 (4 mol%), 4 Å molecular sieves (20 mg), MeCN (0.5 mL), DCM (0.5 mL), 30 W blue LEDs, 0 °C, 27 h, under an argon atmosphere. ^b Isolated yield.

Table 4 Photocatalyzed [3 + 2]-annulation of the boryl radical with styrenes



the practicality of our method, we conducted a scale-up experiment, successfully synthesizing 1.1 grams of the target product with a yield of 77% (Table 5a). These results highlight the advantages of our strategy for synthesizing diverse boron-nitrogen heterocycles, including mild reaction conditions and broad functional group compatibility.

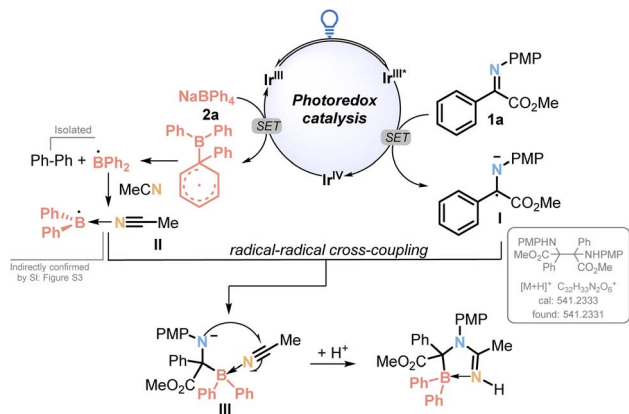
Table 5 The scale-up reaction and mechanistic investigations



We then conducted a series of experiments to elucidate the reaction mechanism. Under standard conditions, the reaction was inhibited by radical scavengers, and the corresponding product formed through radical trapping was identified using high-resolution mass spectrometry (HR-MS) (Table 5b). Control experiments demonstrated that both light irradiation and the presence of a photocatalyst are indispensable for the reaction to occur (Table 1: entries 16–17). A radical clock experiment employing 1-phenylvinylcyclopropane and sodium tetraphenylborate yielded the formation of a cyclopropane ring-opened product, which was identified by HR-MS (Table 5c). These experimental findings provide support for a photoredox radical process. Fluorescence quenching experiments revealed that both imine and sodium tetraphenylborate can quench the excited state of the photocatalyst; however, imine **1a** exhibited a more pronounced effect (Table 5d, left). Further light on/off experiments reveal that any chain propagation process was transient and that light played a crucial role in the formation of the product (Table 5d, right). The existence of the radical intermediate **II** is indirectly confirmed by the hydrogen abstraction reaction (ESI Fig. S3[†]). Additionally, the dimeric product of the reduced imine, confirmed by HR-MS, provides evidence for the radical coupling pathway leading to the target product (Scheme 2). However, it cannot be completely ruled out that direct attack by the boryl radical on the imine *via* a single-electron transfer mechanism may occur (ESI Fig. S8[†]).

Based on the mechanistic studies, a plausible reaction mechanism is proposed in Scheme 2. Upon irradiation, an excited Ir^{III} undergoes single-electron transfer (SET) on the imine to deliver the α -amino radical anion **I** and a resulting Ir^{IV}. Subsequently, this Ir^{IV} species is reduced back to its ground state by NaBPh₄, while simultaneously oxidizing NaBPh₄ to produce a diphenyl boryl radical. In the presence of acetonitrile,





Scheme 2 Proposed mechanism.

it is hypothesized that nitrogen initially coordinates with the diphenyl boryl radical, forming intermediate **II**—indirectly confirmed by HR-MS. Intermediate **I** and **II** then engage in a radical–radical cross-coupling reaction to form **III**. The nitrogen anion in **III** subsequently undergoes nucleophilic addition with the cyano group, ultimately resulting in the target 1,4,2-diazaborole product.

Conclusions

We present a mild and efficient method for the formation of C–B bonds using sodium tetraarylborate, which stabilizes neutral boryl radicals with nitriles. This methodology enables the synthesis of 1,4,2-diazaborole analogs *via* photoredox catalyzed [3 + 2]-annulation. This approach offers gentle reaction conditions, facile substrate preparation, broad applicability, and flexible compatibility with various functional groups. Beyond expanding synthetic routes for 1,4,2-diazaborole analogs, this study highlights the versatility of sodium tetraarylborate in photoredox catalysis and its potential in boron–nitrogen heterocycle synthesis. Our ongoing research aims to further explore innovative applications of this compound in boron chemistry.

Data availability

All experimental data associated with this work are available in the ESI.†

Author contributions

H.-N. Q. planned and conducted most of the experiments; H.-W. J. offered constructive suggestions and revised the manuscript; Y. Z. supervised and supported this project. Saira Qurban and K.-C. W. revised the manuscript; P.-F. X. conceptualised and supervised the project and provided critical feedback during the whole process.

Conflicts of interest

There are no conflicts to declare.

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