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Photocatalytic three-component 1,2-boroarylation and carbopyridylation of alkene†

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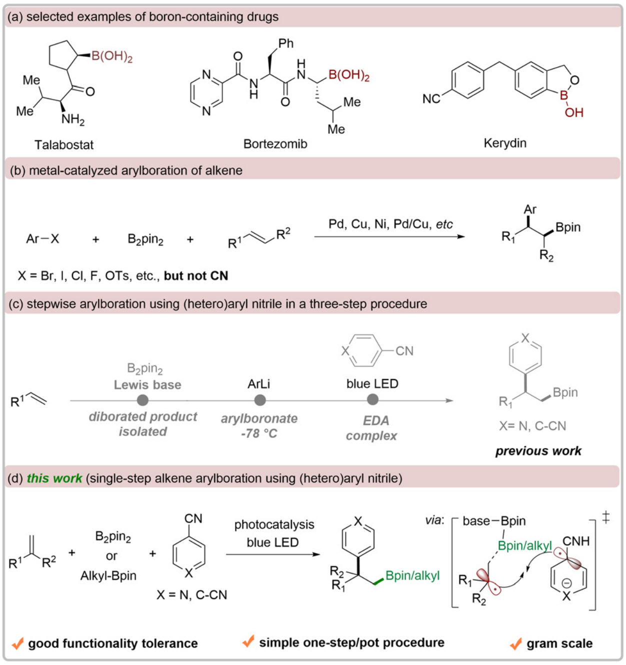
In the present work, we developed a photocatalytic three-component 1,2-boroarylation of alkenes using readily available alkenes, bis(pinacolato)diboron, and (hetero)aryl nitriles in the presence of base and photocatalyst—to afford a diverse array of boryl-enriched 1,1-diarylalkane compounds. Alkylboronic pinacol esters were also found to be suitable substrates for the reaction, giving the corresponding carbopyridylation products. Control experiments and DFT calculations supported our proposed photoinduced generation of a boryl unit and aryl nitrile radical anion, which sequentially coupled to alkene. This protocol exhibited mild reaction conditions, good functional group tolerance and a one-pot procedure, serving as a complementary approach to transition-metal-catalyzed coupling reaction.

Introduction

Boronic functional groups are frequently found in drugs (Scheme 1a).[1] Alkene carboboration serves as an efficient strategy for the facile synthesis of elaborated organoborons from simple feedstocks.[2] Of particular utility are arylborations of aromatic alkenes affording diverse boryl-enriched 1,1-diarylalkane derivatives,[3] which are key structural motifs in bioactive compounds and medicines (Scheme 1b).[4] In this regard, transition-metal catalysis has played a privileged role in alkene arylboration,[5] proceeding through two reaction pathways: one combining *in situ*-generated Cu-Bpin complexes with dual-metal-catalyzed (*e.g.*, Pd/Cu, Ni/Cu) oxidative addition of aryl halides[6] and the other involving single-metal-catalyzed cross-coupling (*e.g.*, Ni, Cu).[7] Nevertheless, aryl precursors are limited to aryl halides and tosylates in these reactions. Additionally, undesirable pathways, involving both Heck-type and hydroarylation reactions, were shown to be involved in the reaction of α-methyl styrene with $B_2(pin)_2$ and arylbromide.[7d] Thus, it is still very important to pursue a new alkene borylation methodology with suitable aryl sources for the selective arylboration of alkenes.

Radical-based chemistry provides an appealing alternative strategy to accomplish this goal, due to its high functional group compatibility and mild reaction conditions.[8] Visible light can catalyze the formation of highly reactive pyridyl radicals from aryl nitriles.[9] Importantly, this method of generating pyridyl radicals is recognized as a valuable approach for making versatile building blocks suitable for diverse synthetic transformations.[10] Unfortunately, there are few examples of photocatalytic incorporation of a boryl moiety and aryl nitriles across an alkene. Aggarwal pioneered a photoinduced formal



Scheme 1 (a) Representative examples of bioactive organoboron compounds, and (b and c) alkene arylboration, (d) this work.

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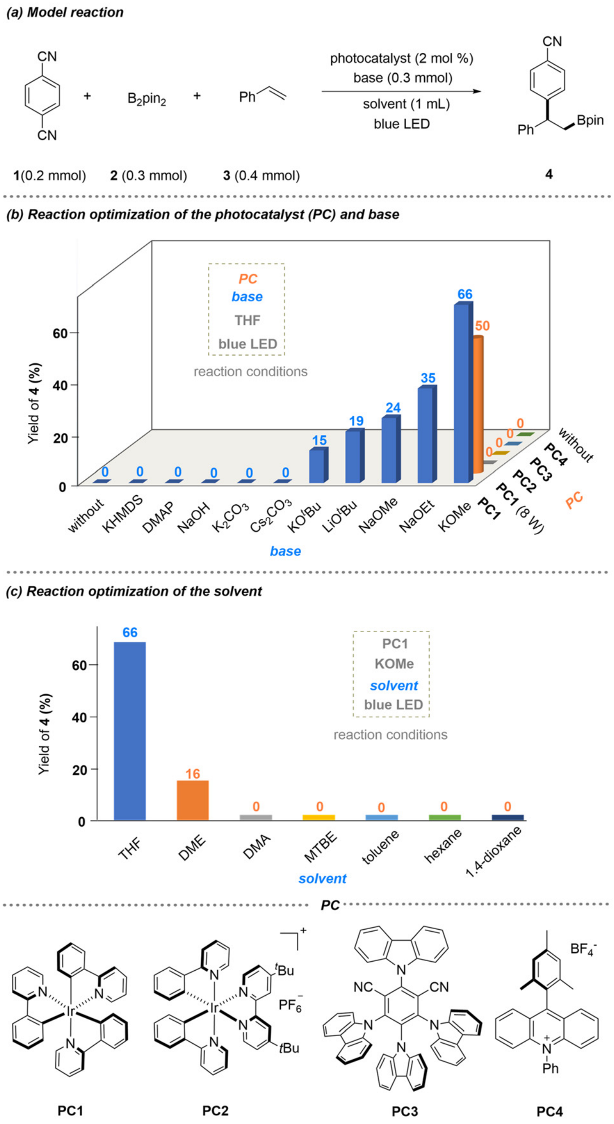
1,2-arylboration *via* the reaction of 1,2-bis-boronic esters with (hetero)aryl nitriles in the presence of aryllithium (Scheme 1c).[11] However, this protocol requires a three-step procedure and the use of a dangerous organolithium reagent. Moreover, radical arylboration of alkenes was developed with cyanoarenes as arylating components and N-heterocyclic carbene (NHC)-BH_3 complexes as boryl radical precursors from Zhang's group. This procedure suffered from a narrow substrate scope and from having to pre-synthesize the (NHC)-BH_3 partner.[12]

Diboron(4) compounds have been widely used as boron precursors in organic synthesis, because they are stable and easy to handle.[13] Given that base-ligated diboron(4) compounds have emerged as boryl precursors that can then undergo a nucleophilic process[14] or single-electron transfer (SET) pathway,[15] we envisioned that a three-component coupling would be possible if photo-mediated SET between base-ligated diborane and aryl nitriles takes place in one reaction system, sequentially coupling the boryl fragment and aryl radical anion to an alkene to produce selectively a 1,2-boroarylated product (Scheme 1d). To manipulate this transformation, two key factors need to be considered: first the use of a single photocatalyst to trigger single-electron transfer between base-ligated diborane adduct and aryl nitriles; and second, avoiding the undesirable borofunctionalizations of alkene, such as hydroboration and diboration side reaction. To the best of our knowledge, a one-pot three-component arylboration involving alkene, diborane, and aryl nitriles has not been reported. We present a three-component arylboration of alkenes, specifically from readily available alkenes, $B_2(pin)_2$, and (hetero)aryl nitriles. This protocol features a simple operation, mild reaction conditions, and excellent functional group tolerance, and thus serves as a complement to the traditional approach.

Results and discussion

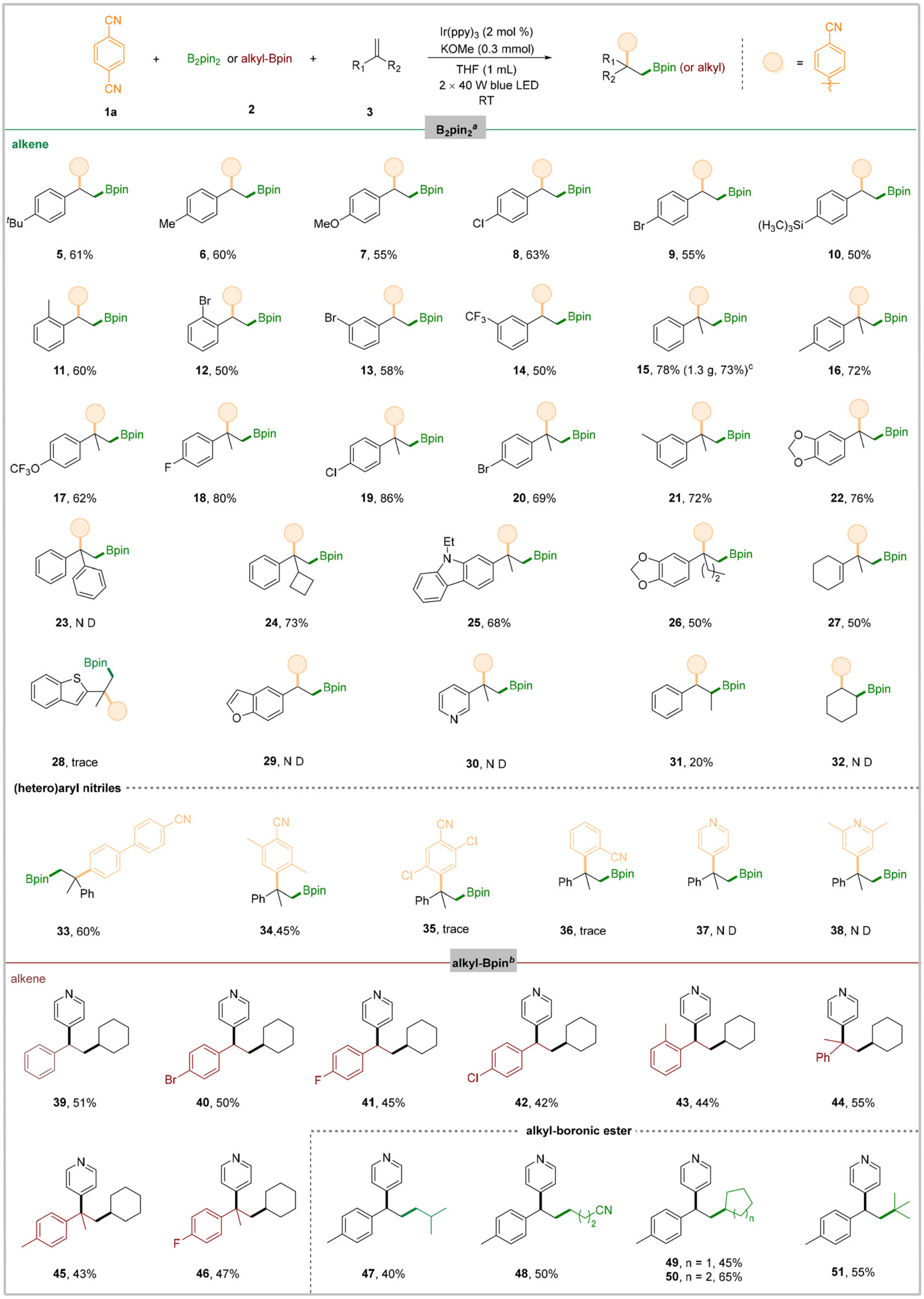
We began our experimental studies using 1,4-dicyanobenzene, B_2pin_2 and styrene as model substrates (Scheme 2a). The reaction mixture was irradiated under 40 W blue LED in the presence of photocatalyst (**PC1**) and KOMe in THF, affording the desired product **4** in 66% yield. We found that the product **4** was also obtained with 8 W blue LED, albeit in 50% yield. Using KOMe as base, different photocatalysts were screened (Scheme 2b). Other photocatalysts including **PC2–PC4** were not effective. Screening of bases showed that some bases (NaOEt, NaOMe, LiO^{t}Bu, NaO^{t}Bu) resulted in low yields, and other bases including Cs_2CO_3, K_2CO_3, NaOH, DMAP, KHMDS did not work at all. Further assessment of solvents found that THF was the best solvent (Scheme 2c). Control experiments demonstrated the necessity of photocatalyst, base, and light.

With the optimized reactions in hand, we investigated the substrate scope of this three-component coupling reaction. As shown in Table 1, with 1,4-dicyanobenzene and $B_2(pin)_2$ as the reaction partners, a series of *para*-substituted styrenes on the benzene ring (Me, Br, Cl, MeO, $Si(Me)_3$, CF_3) efficiently reacted using this protocol, yielding the corresponding boroarylated products **5–10** in 50%–63% yields. *ortho*- and *meta*-substituted (Me, Br, CF_3) styrene derivatives were well transformed into the products **11–14** in moderate yields. Additionally, α-methyl-substituted styrenes were suitable substrates, affording the corresponding products **15–22** in moderate to good yields. Utilizing the more sterically hindered 1,1-diphenylethylene did not yield the desired product **23**. Notably, sterically congested alpha cyclobutyl-substituted styrene was converted to the desired product (**24**) in 73% yield. Other alpha-methyl arylethenes containing carbazole and benzodioxole could be converted into the corresponding products (**25**, **26**) in moderate yields. This



Scheme 2 Reaction conditions: 1,4-dicyanobenzene (0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (0.3 mmol, 1.5 equiv.), photocatalyst (2 mol%), base (0.3 mmol), styrene (0.4 mmol), 2 × 40 W blue LED, solvent (1.0 mL), isolated yield. THF = tetrahydrofuran. DMAP = 4-dimethylaminopyridine. KHMDS = potassium bis(trimethylsilyl)amide. DMA = *N*,*N*-dimethylacetamide. DME = 1,2-dimethoxyethane. MTBE = methyl *tert*-butyl ether. PC = photocatalyst, N D = not detected.

Table 1 Substrate scope[a]



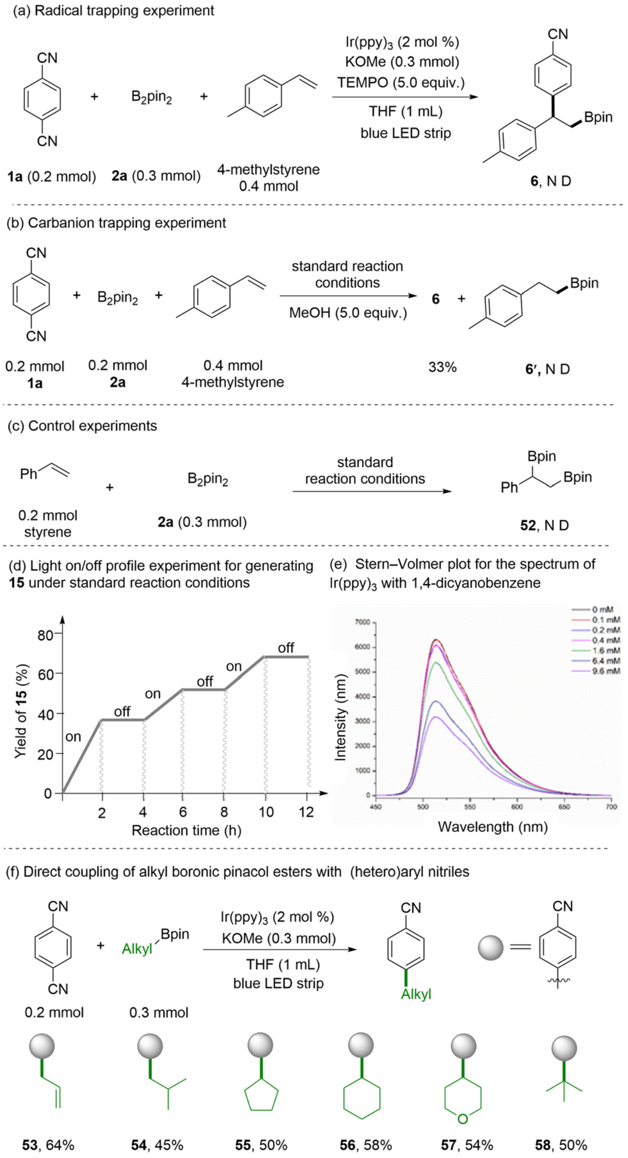
[a] Reaction conditions: (hetero)aryl nitriles **1** (0.2 mmol), $B_2(pin)_2$ (0.3 mmol), alkene **3** (0.4 mmol), KOMe (0.3 mmol), THF (1.0 mL), $Ir(ppy)_3$ (2 mol%), 24 h, 2 × 40 W blue LED, room temperature (RT). [b] Reaction conditions: 4-cyanopyridine (0.2 mmol), alkylboronic (alkyl-Bpin, 0.3 mmol), alkene (0.4 mmol), KOMe (0.3 mmol), THF (1.0 mL), $Ir(ppy)_3$ (2 mol%), 2 × 40 W blue LED, 24 h, RT. Isolated yield. [c] Reaction conducted on a scale of 5 mmol, see ESI† for details.

method was compatible with 1-(prop-1-en-2-yl)cyclohex-1-ene, providing the 1,2-boroarylated product **27** in 50% yield. Substituted aromatic alkenes containing benzothiophene, benzofuran, pyridine, an internal alkene like beta-methylstyrene, or an alkyl alkene such as cyclohexene were each found to be incompatible with this strategy (**28–32**). The substrate scope of (hetero)aryl nitriles was also investigated. 4-(4-Cyanophenyl) benzonitrile and 2,5-dimethylterephthalonitrile reacted, yielding the products **33** and **34** in 60% and 45% yields, respectively. Unfortunately, when more sterically hindered aryl nitriles including 2,5-dichloroterephthalonitrile and 1,2-dicyanobenzene, were subjected to standard conditions, they showed no reactivity (**35**, **36**). Heteronitriles, including 4-cyanopyridine and 2,6-dimethyl-4-cyanopyridine, did not work (**37**, **38**). The lack of suitability of 4-cyanopyridine derivatives as coupling partners of aryl units may have been due to: (1) the possible side reaction of alkene borations and (2) the potential interaction between 4-cyanopyridine and $\mathrm{B_2(pin)_2}$.[16]

To demonstrate the practical applicability of this protocol, we reacted 1,4-dicyanobenzene with $\mathrm{B_2pin_2}$ and styrene simultaneously on a 5 mmol scale, yielding the corresponding product **15** in 73% yield (1.3 g).

This protocol could be extended to the alkylboronic pinacol esters (Table 1). With 4-cyanopyridine and cyclohexylboronic acid pinacol ester as the coupling partner, various alkenes bearing F, Cl, Br, and Me functional groups on the benzene ring, respectively, were subjected to this alkene biofunctionalization, producing the corresponding 1,2-clohexylpyridylation products (**39–43**) in moderate yields. Relatively highly hindered alpha-methyl-substituted styrenes reacted, affording the corresponding products (**44–46**) in moderate yields. Primary boronic acids, including isobutylboronic acid pinacol ester and 3-cyano-1-propylboronic acid pinacol ester, were suitable substrates (**47**, **48**). Two secondary alkylboronic pinacol esters were converted into the corresponding products (**49**, **50**). Tertiary *tert*-butylboronic acid pinacol ester yielded the desired product **51** in 55% yield. During the preparation of this manuscript, Li *et al.* reported a photoredox-catalyzed three-component alkylarylation of vinyl arenes with alkylboronicpinacol esters and cyanoarenes, shown to proceed through amino-radical-transfer-mediated radical addition/cross-coupling pathways. Note the difference between an amino-radical-mediated phoredox process and our method, which instead involves a dual photocatalysis/base-mediated alkene carbopyridylation using alkylboronicpinacol esters and cyanoarenes.[10r]

To gain insight into the reaction mechanism, we conducted several control experiments. When 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO, 5.0 equiv.) added to the reaction of 1,4-dicyanobenzene, $\mathrm{B_2pin_2}$ and, styrene, the desired product **6** was not detected (Scheme 3a). When MeOH was added to the reaction mixture, the corresponding product **6** was obtained in 33% yield, and protoboration adduct **6′** was not detected (Scheme 3b). These results indicated a possible radical reaction mechanism. We also performed the reaction of $\mathrm{B_2pin_2}$ with styrene under standard conditions but detected neither boration product **52** nor other possible by-products, suggesting a possible lack of involvement of a diborated intermediate in this reaction (Scheme 3c). Light on–off experiments were performed, and the results implied the necessity of continuous visible light irradiation for this protocol (Scheme 3d). Stern–Volmer quenching studies were then conducted to investigate this mechanism, and the results indicated that the excited state of $\mathrm{Ir(ppy)_3}$ was quenched mainly by 1,4-dicyanobenzene (Scheme 3e, see ESI† for details). We also deployed cyclic voltammetry, to measure the electric potential of $\mathrm{B_2(pin)_2}$/KOMe and photocatalyst [$\mathrm{Ir(ppy)_3}$]. The results indicated that the combination of $\mathrm{B_2(pin)_2}$ and KOMe can be oxidized by $\mathrm{Ir(ppy)_3}$ in single-electron mannner (see ESI†). Additionally, cross-coupling of alkylboronic pinacol esters and (hetero)aryl nitriles yielded various aryl derivatives (**53–58**) in moderate yields (Scheme 3f). This result suggested the involvement of an alkyl radical during this process.



Scheme 3 Control experiments.

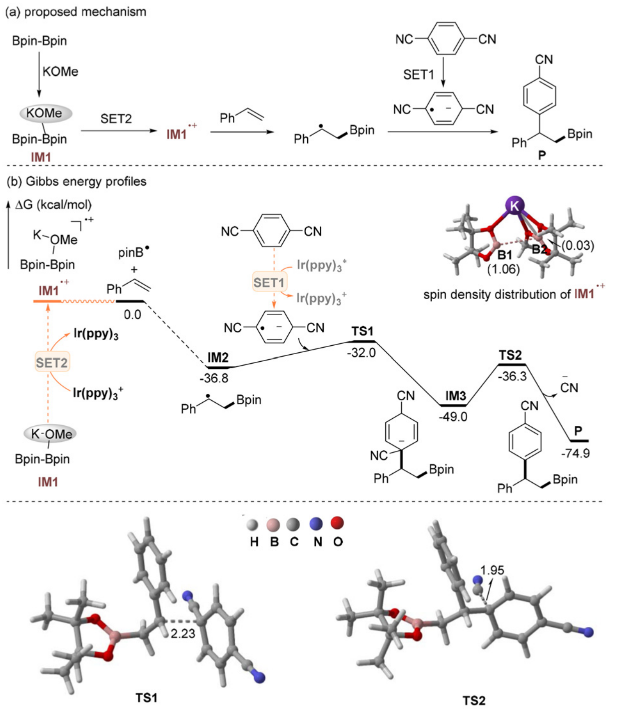


Fig. 1 (a) Proposed mechanism. (b) Calculated Gibbs energy profile for the arylboration of alkene with styrene, B_2pin_2 and 1,4-dicyanobenzene. Gibbs free energy (ΔG) values are in kcal mol^{-1}. Interatomic distances are in Å.

Based on control experiments, literature reports,[15] and density functional theory calculations (DFT, see ESI† for details), a plausible reaction mechanism was proposed, as exhibited in Fig. 1. Initially, under light irradiation, the excited state of $Ir(ppy)_3$ easily underwent single-electron transfer with 1,4-dicyanobenzene to generate a persistent 1,4-dicyanobenzene radical anion along with the oxidized photocatalyst $Ir(ppy)_3^+$ (SET1, barrier height, 0.7 kcal mol^{-1}), which was also confirmed by the previous experimental studies.[9a] Then, the ate complex between KOMe and B_2pin_2 (**IM1**) was oxidized by $Ir(ppy)_3^+$ generating the IM1 radical cation and regenerating $Ir(ppy)_3$ (SET2). Our DFT calculations showed the SET2 step to be exergonic by 20.2 kcal mol^{-1} with a barrier height of 3.4 kcal mol^{-1}, indicating both the kinetic and thermodynamic feasibility of this pathway. Additionally, the spin density of the **IM1** radical cation was calculated to be localized on the vacant boron center with a value of 1.0625 a.u, with a 3.52 Å length of the B–B bond in **IM1** (and 1.70 Å B–B bond length of $B_2(pin)_2$). The computational study supported the IM1 radical cation having included a B–B one-electron σ-bond. Fragmentation of **IM1** radical cation as a result of the B–B bond cleavage was proposed to release a boryl radical. Previous studies suggested base-ligated diborated compounds to be susceptible to interference by photocatalyst resulting in the formation of boryl radicals.[15] At this stage, the boryl radical was captured by styrene, leading to formation of the intermediate **IM2**, with this step exergonic by 36.8 kcal mol^{-1}. The **IM2** intermediate further coupled with 1,4-dicyanobenzene radical anion *via* transition state **TS1** with a barrier height of 4.8 kcal mol^{-1} (compared to the **IM2** intermediate and 1,4-dicyanobenzene radical anion), generating the intermediate **IM3**. Finally, a facile decyanation of **IM3** produced the product **P** with a barrier height of 12.7 kcal mol^{-1} (in relation to **IM3**). The whole reaction was calculated to be exergonic by 74.9 kcal mol^{-1}. These results can account for the observed selectivity.

Conclusions

In summary, we developed a new photocatalytic method for the synthesis of valuable boryl-containing 1,1-diarylalkane compounds *via* a one-pot reaction involving alkene, $B_2(pin)_2$, and a (hetero)aryl nitrile. This reaction is driven by a visible-light-induced single-electron transfer between base-ligated diborane and the aryl nitrile, generating both a boryl radical and aryl nitrile radical anion. Subsequent coupling of two radicals with the alkene affords the arylboration products. This reaction proceeds using a one-pot procedure under mild reaction conditions, serving to complement the transition-metal-catalyzed coupling reaction.

Author contributions

J. Cao conceptualized and designed the experiments, and carried out writing – review and editing and supervision of the project. B. B. Ji and Z. X. Wang designed the experiments. R. J. Wang and L. Z. Gao analysed the data and performed compound characterizations. All authors have given approval to the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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