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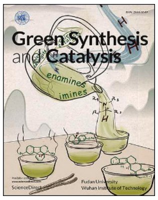

Review

# Recent advances in C–B bond formation by borylation with NHC–boranes

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ABSTRACT

Organoboron compounds play a pivotal role in synthetic, pharmaceutical, and material chemistry due to their distinctive properties. Developing efficient, regioselective methods for C–B bond construction *via* borylation remains a challenging yet highly desirable research goal. In this review, we provide an overview of recent advancements in borylation reactions of alkenes, alkynes, arenes, diazo compounds, imines, amides, and isocyanides using NHC–boranes as the borylation reagents, facilitated by transition-metal catalysis, organocatalysis, photoredox catalysis, biocatalysis, and cooperative catalysis. The reaction parameters, generality and limitations of substrate scope, and typical reaction mechanisms are mainly discussed.

## 1. Introduction

Organic boron-containing compounds have many important and widespread applications in chemistry-related fields, including synthetic [1–3] and pharmaceutical chemistry [4], as well as advanced organic functional materials [5]. Organoboronic acids and their derivatives are widely used as coupling partners in transition-metal-catalysed cross-coupling reactions—such as Suzuki–Miyaura [6], Liebeskind–Srogl [7], and Chan–Evans–Lam couplings [8] to form C–C and C–X (X = *N*, O, S) bonds. They also serve as chiral or achiral ligands, catalysts, or co-catalysts in various transformations [9–11]. Owing to their unique electronic, structural, and chemical properties, boron-derived organic skeletons offer significant application potential in material chemistry [12,13]. For example, boron-doped polycyclic aromatic hydrocarbons (B-PAHs) are widely studied and used in the aspect of organic electronics, optoelectronics, catalysis and so on [14–16]. Moreover, boron-containing compounds have emerged as an important source of new drug molecules, with several FDA-approved treatments for multiple myeloma, onychomycosis, and eczema (Fig. 1) [4]. These organoboron compounds share one common structural feature: the carbon–boron (C–B) bond. So, efficient methods for the construction of C–B bonds are foundational to accessing organoboron compounds. Significant efforts have been devoted to this frontier research area for many years.

$BH_3$, the simplest borane molecule, possesses the properties of a Lewis acid and can exist stably in the form of borane complexes (or adducts) with Lewis bases. Amine-borane, phosphine-borane, and pyridine-borane are among the most representative examples [17–19]. *N*-heterocyclic carbene borane complexes (often called NHC–boranes or NHC–$BH_3$) are a class of compounds where an *N*-heterocyclic carbene (NHC) is coordinated to borane ($BH_3$) derivatives [20]. Compared to typical amine- and phosphine-boranes [21], NHC–borane complexes present unique advantages: better thermal and chemical stability due to the strong $\sigma$-donating ability of NHCs which results in a robust boron-carbene bond, and tunable electronic and steric properties through *N*-substituent modification [22], and lower B–H bond dissociation energy (79–80 kcal.mol$^{-1}$)

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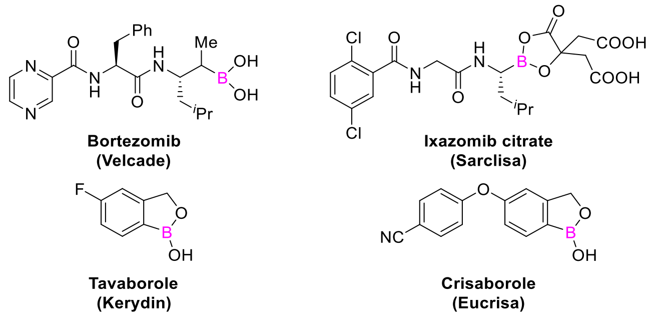


**Fig. 1.** Selected boron-containing drugs.

which leads to much richer reactivity by developing different activation modes of B–H bond [23].

Borylation reactions, known for their mild conditions, high selectivity, and excellent functional group compatibility, are valuable for synthesising complex and high-value-added organoboron compounds. A prominent example is the Brown hydroboration of alkenes and alkynes, first reported in 1956 by Herbert C. Brown, who received the 1979 Nobel Prize in Chemistry for this work [24]. Over recent decades, NHC–boranes have attracted considerable interest in synthetic chemistry owing to their unique properties and utility in synthesising diverse boron-based compounds with C–B bond, achieved *via* transition-metal or organocatalytic B–H activation. Many groups around the world, in particular, Curran and Taniguchi, Fensterbank, Lacôte, Malacria, Zhu, and Wang have made outstanding contributions in exploring the versatility and fruitful reactivity of NHC–boranes.

There have been some notable and comprehensive reviews [25–30] toward C–B bond formation including (i) hydroborylation of unsaturated compounds (alkenes and alkynes *etc.*) [31–34], (ii) C–H bond borylation [35–40], (iii) C–C bond borylation [41,42], (iv) C–X (X = N, O, S *etc.*) bond borylation [41,42], and C–F bond borylation [41,43]. Boranes (*e.g.*, HBpin and HBcat), diboron reagents (*e.g.*, $B_2pin_2$ and $B_2cat_2$), and haloboranes (*e.g.*, $BCl_3$ and $BBr_3$) are the most widely used boron sources [34]. Some examples using NHC–boranes are involved in these review reports as well [25–43]. From the perspective of synthetic chemistry, these various borane compounds each have their own distinct characteristics, which define the respective application fields. For example, the diboron reagents typically possess an electrophilic boron centre and are commonly activated by a transition-metal catalytic system. So, they have versatile applications in transition-metal-catalysed C–X bonds (*e.g.*, sp$^2$ C–C [44] and C–H bonds [45]) borylation reactions. NHC-boranes are particularly efficient reagents in radical borylation and chain-transfer reactions through nucleophilic or radical pathways, a role where traditional diboron reagents are generally ineffective. The stability of diboron reagents under radical conditions is a major advantage; by contrast, NHC-boranes exhibit excellent thermal and air/moisture stability. Thus, NHC-boranes serve as a valuable complement to diboron reagents, expanding the toolbox for boron incorporation. Back in 2011, the synthesis, characterisation, and reactions of NHC–borane complexes were systematically summarised by Curran, Fensterbank, and Lacôte [20]. Several reviews focus on recent developments in radical borylation reactions employing NHC-boryl radicals were presented [22,46–49]. For example, Taniguchi, in 2021, summarises the application of NHC–boryl radicals in main group chemistry, polymer chemistry, and synthetic chemistry [22]. Recently, Wang group presented their contributions to carbon–boron bond formation and carbon–heteroatom bond functionalization enabled by NHC–boryl radicals [48]. To our knowledge, no systematic review has summarised recent advances in C–B bond formation *via* borylation reactions involving B–H activation of NHC–boranes under various activation modes (Table 1). This review covers literature from 2012 to early 2025 and is organised by coupling partners: alkenes, alkynes, arenes, diazo compounds, and miscellaneous substrates (imines, amides, isocyanides). It excludes transformations involving NHC–borane complexes in catalysis, main-group, and polymer chemistry.

## 2. C–B bond formation *via* borylation of alkenes

Alkenes, as highly available and versatile feedstocks, have been extensively investigated in polyfunctionalization reactions as coupling receptors. The alkenes borylation is a straightforward and powerful route to forge a C–B bond by direct C–X (X = H or F) cleavage and B–H bond activation of NHC–boranes, but it remains a big challenge topic in synthetic chemistry. This section discusses C–B bond formation through alkene borylation using NHC–boranes as boron sources (Fig. 2). Based on reaction mechanism and substrate properties, they can be classified into five types: hydroborylation of alkenes (Fig. 2A), hydroborylation of

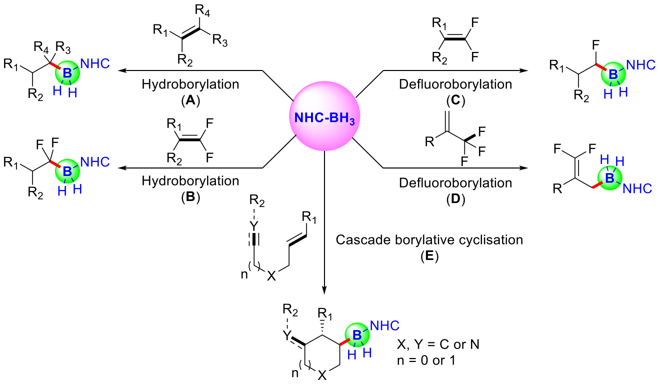


**Fig. 2.** General procedure for C–B bond formation *via* borylation of alkenes with *N*-heterocyclic carbene boranes.

**Table 1**
Various B–H bond activation modes of NHC-boranes.

| B–H Bond activation mode | Representative activation system | Main contributors | Substrate scope |
|---|---|---|---|
| Transition-metal catalysis | [Rh(nbd)$_2$]BF$_4$/(*S*)-BINAP, CuCl/*t*-BuOK, Rh$_2$(esp)$_2$ | J.L. Parrain, D.P. Curran | Allyl-substituted NHC-boranes, Alkynes, Diazo compounds |
| Organocatalysis | Tf$_2$NH, I$_2$, Thiols/Radical initiators, $^i$Pr$_2$NEt, B(C$_6$F$_5$)$_3$, Radical initiators, Et$_2$Zn | D.P. Curran, E. Vedejs, M.J. Ingleson, Y.F. Wang, H. Du, X. Liu, J.K. Jin, H. Wang, T. Taniguchi, H. Wang, W.P. Unsworth, R. Matsubara | Alkenes, Alkynes, Arenes, Diazo compounds, Isocyanides |
| Photoredox catalysis | Transition-metal photocatalysts,<br>Transition-metal photocatalysts/Thiols,<br>Organic photosensitizers,<br>Organic photosensitizer/Thiol, Disulfides,<br>Thiols, Heterogenerous photocatalysts | H. Yang, C. Zhu, D.P. Curran, W. Dai, Y. Wang, X. Chen, Y.F. Zeng, Y. Quan, Y.F. Wang, J. Wu, H. Cao, J. Xuan, T. Kawamoto X. Wang | Alkenes, Arenes, Alkynes, Diazo compounds, Imines, Amides |
| Biocatalysis | *Rma cyt c* | K. N. Houk, F. H. Arnold | Diazo compounds |

*gem*-difluoroalkenes (Fig. 2B), defluoroborylation of *gem*-difluoroalkenes (Fig. 2C), defluoroborylation of $\alpha$-trifluoromethylalkenes (Fig. 2D), and cascade borylative cyclisation of alkene derivatives (Fig. 2E).

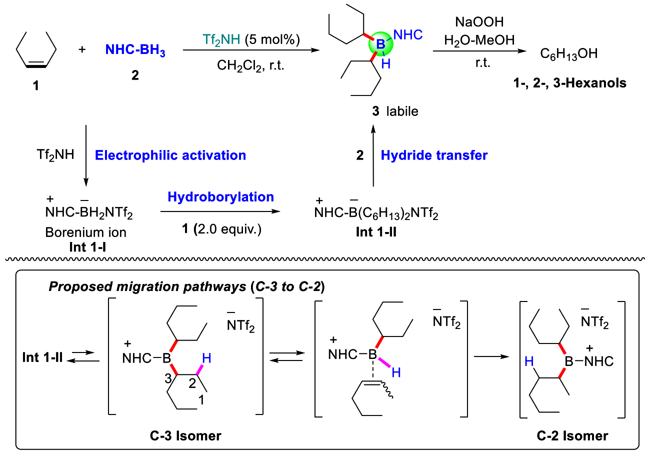
### 2.1. Organo- or transition-metal catalysed borylation of alkenes

In the initial stage of the development of hydroborylation of simple olefins, many efforts have been devoted to establishing an efficient activation method of B–H bond of NHC–boranes. Several elegant activation strategies using amine, rhodium complex catalyst, I$_2$, B(C$_6$F$_5$)$_3$, or radical initiator as activators were subsequently developed by Parrain, Chuzel, Vedejs, Malacria, Fensterbank, Lacôte, Curran, Wang, and Du *et al.* According to specific reaction conditions, the borylated reaction may follow radical or ionic pathways.

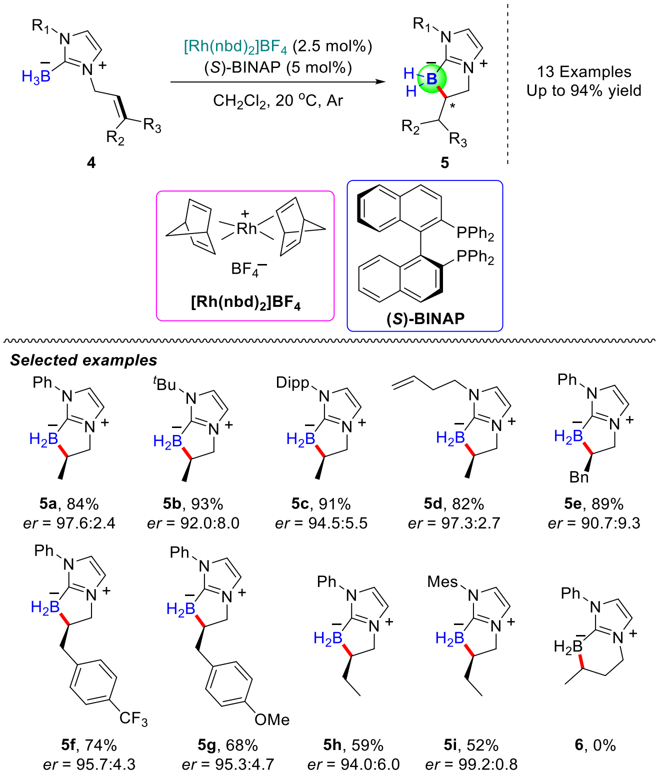
In 2012, Vedejs and Curran jointly reported the first hydroborylation reaction of unactivated aliphatic alkenes **1** with NHC–BH$_3$ **2** to the construction of C–B bond at room temperature (Scheme 1) [50]. Trifluoromethanesulfonimide (Tf$_2$NH: (CF$_3$SO$_2$)$_2$NH) was employed as the activator to activate the B–H bond. This hydroborylation procedure contains several key steps, including electrophilic activation, hydroborylation, and hydride transfer. NHC–borenium **Int 1–I** and its equivalents formed *in situ* from NHC–borane and electrophilic activator are viewed as the real catalysts [43,46,47,51]. The intramolecular migration of the borane substituent is observed, preferentially delivering the dihydroboration C-2 isomer as the main product (16 examples, up to 94% yield). Due to the labile nature of the desired borylation products, which could not be purified by column chromatography and had a narrow substrate scope, thus limiting the practicability of this methodology.

In the same period, Parrain and Chuzel reported the activation of B–H bond by cationic rhodium(I)/diphosphane complex-catalysed asymmetric intramolecular hydroboration of NHC–boranes **4**, attaching an allyl group on the nitrogen atom (Scheme 2) [52]. Various 5-membered cyclic boranes **5** were successfully assembled with *anti*-Markovnikov regioselectivity in moderate to excellent yields (13 examples, 40%–94% yields) and high enantioselectivity (*er* up to 99.2:0.8). However, 6-membered cyclic borylated product **6** from homoallyl substituted NHC–borane cannot be constructed.

Subsequently, Curran and co-workers improved the hydroborylation process of alkenes by employing cheaper and easily handled I$_2$ as the B–H bond activating agent (Scheme 3) [53]. Mechanistically, this method also follows consequent activation, hydroboration, and hydride transfer. The generation of NHC–BH$_2$I intermediate with one B–I covalent bond is the key step. Polysubstituted alkylethylenes and conjugated dienes **7** could be well involved to deliver the monohydroboration products **8** in moderate to good yields (up to 75%). In the case of substituted styrenes, the C–B bonds were preferentially formed at the $\alpha$-position of the aromatic ring in satisfactory yields (50%–80%). These borylated products are stable to air and water, and could be isolated by column chromatography. But this methodology is sterically sensitive to NHC–boranes with large *N*-substituents.



Scheme 1. Borenium ion-catalysed ionic hydroborylation of aliphatic alkenes.

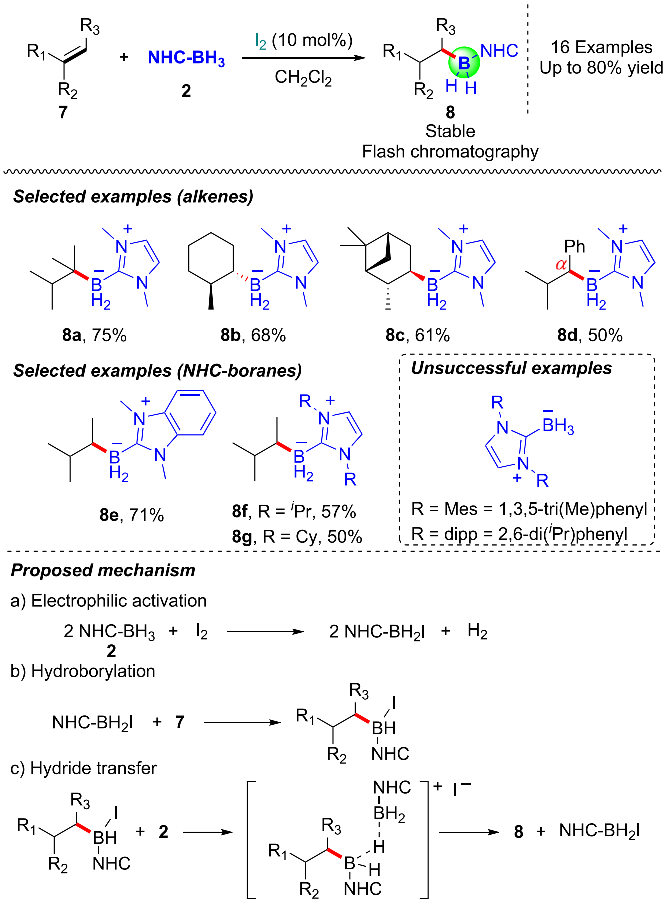


**Scheme 2.** Rh(I)-catalysed intramolecular hydroborylation of unactivated alkenes.

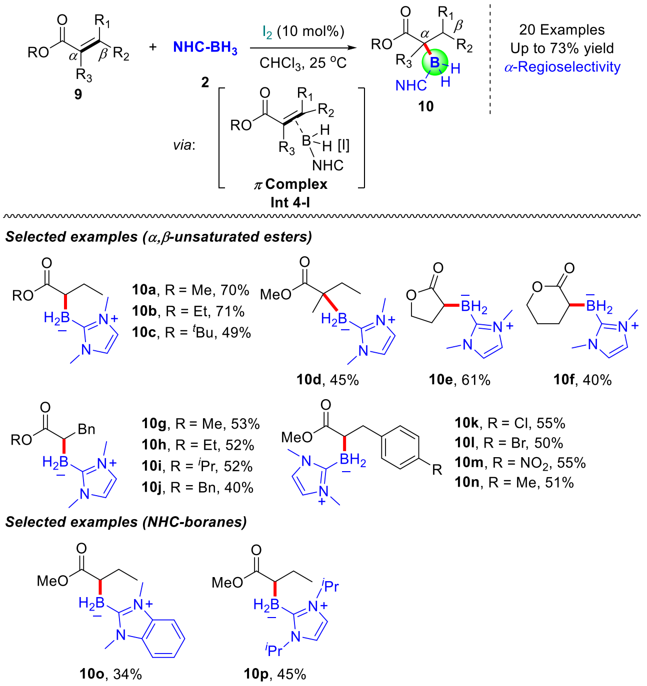
Inspired by the pioneering work of Curran [53], the $\alpha$-borylation of $\alpha,\beta$-unsaturated carbonyl compounds **9** was realised using iodine as the activator for the construction of the C–B bond at room temperature by Ingleson *et al.* in 2019 (Scheme 4) [54]. Under metal-free conditions, a series of commercially available alkyl $\alpha,\beta$-unsaturated esters were readily borylated with NHC–boranes at the $\alpha$-position, affording cyclic or acyclic $\alpha$-boryl esters **10** in moderate to good yields (20 examples, 34%–73%). Methyl cinnamates attached Me, Br, Cl, and even deactivated NO$_2$ group on the phenyl ring, also could be involved to realise the borylation procedure in medium reactivity (50%–55%).

Mechanistically, an I$_2$ involved concerted catalytic procedure is proposed. The formation of the $\pi$-complex intermediate **Int 4–I** between ester and NHC–BH$_2$I is the key to ensuring the high stereoselectivity of borylated products. However, the substrate scope mainly restricts to $\alpha,\beta$-unsaturated esters; similar structural $\alpha,\beta$-unsaturated amides are not suitable feedstocks, only leading to a complex mixture, albeit with high conversion of starting materials. $\alpha,\beta$-Unsaturated ketones cannot be tolerated either; no $\alpha$-borylated products were detected.

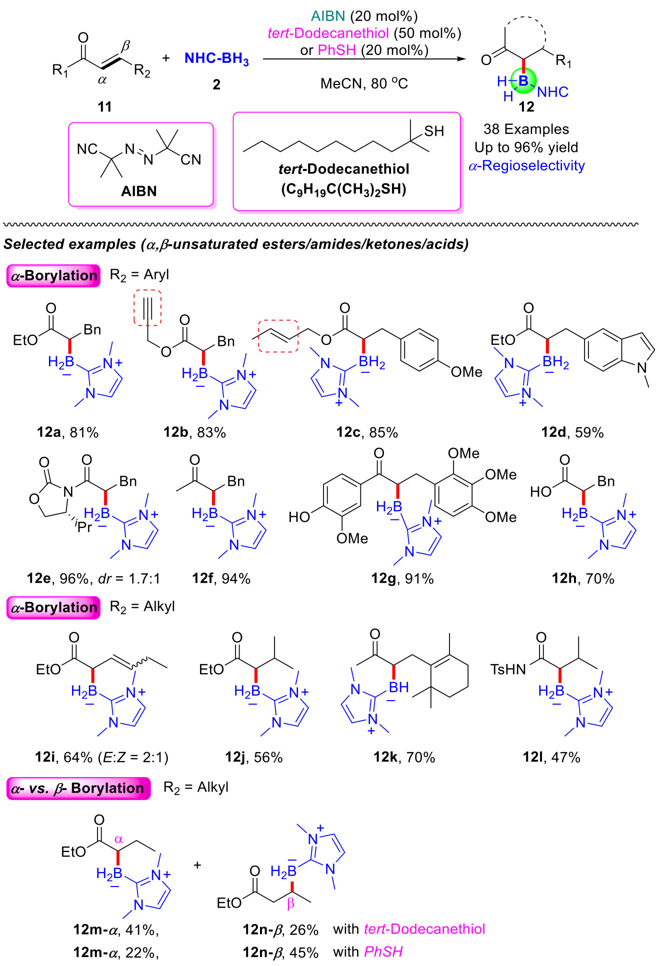
In the same year, employing polarity reversal catalysis [55,56], a more practical and versatile B–H activation method was presented by Wang and collaborators with NHC–BH$_3$ as the borylation reagent (Scheme 5) [57]. Thiols (*tert*-dodecanethiol or benzenethiol) and AIBN (2,2-azobis(isobutyronitrile)) were optimized as the best polarity reversal catalyst and radical initiator, respectively, and both of them are indispensable. This protocol features good regioselectivity and a wide spectrum of substrates (38 examples). Varied $\alpha,\beta$-unsaturated carbonyl compounds **11**, including esters, amides, ketones, and acids could be well tolerated, affording the corresponding $\alpha$-borylated products **12** with up to 96% yield.



**Scheme 3.** Iodine-catalysed ionic hydroborylation of alkenes.



**Scheme 4.** Iodine-catalysed ionic $\alpha$-hydroborylation of $\alpha,\beta$-unsaturated esters.

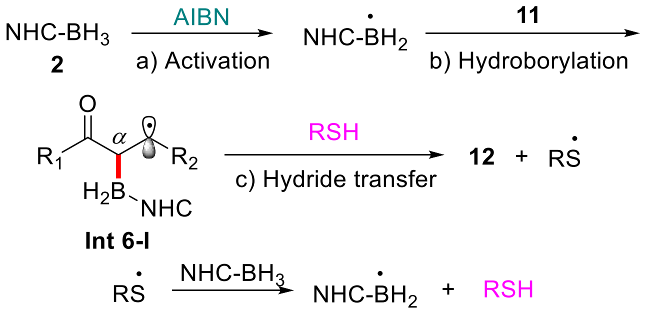


**Scheme 5.** Radical $\alpha$-borylation of $\alpha,\beta$-unsaturated carbonyl compounds enabled by AIBN and thiol.

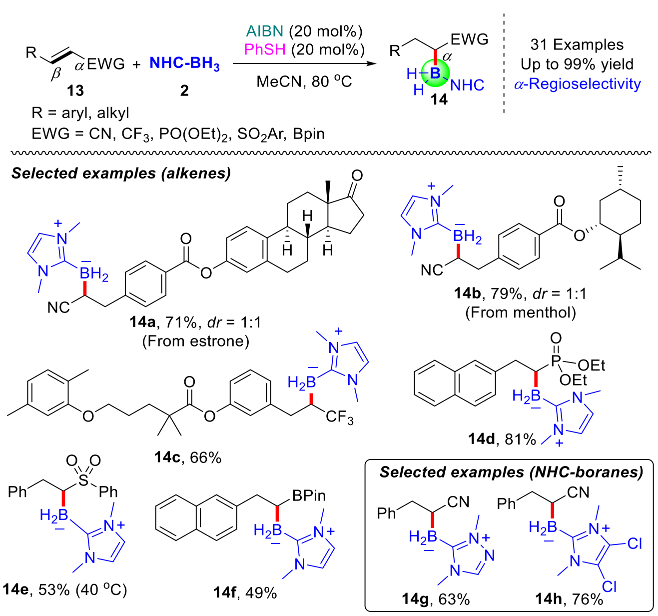
Due to the stabilisation effect of the aromatic ring on the carbon radical, the preferential addition of boron radical at the $\alpha$-position (intermediate **Int 6-I**) of $\beta$-aryl $\alpha,\beta$-unsaturated carbonyl compound **11** assembled the thermodynamically favored product **12**, which is consistent with the results of DFT calculations and kinetic experiments (Scheme 6). For $\beta$-alkyl $\alpha,\beta$-unsaturated carbonyl compounds, the C–B bonds are also mainly formed at the $\alpha$-position due to the energetically favored hydrogen atom transfer step, but arylthiol is facilitated to give the $\beta$-borylation product (**12n-$\beta$**).

Notably, this B–H activation tactic could be further expanded to other electron-deficient aryl-/alkylalkene derivatives **13** terminally substituted with electron-withdrawing groups such as CN, $CF_3$, PO$(OEt)_2$, $ArSO_2$, and Bpin (Scheme 7) [58]. A series of structurally diverse $\alpha$-borylated products **14** were assembled in moderate to excellent yields (31 examples, 39%–99%), which provides the possibility to transform them to synthetically useful synthons.

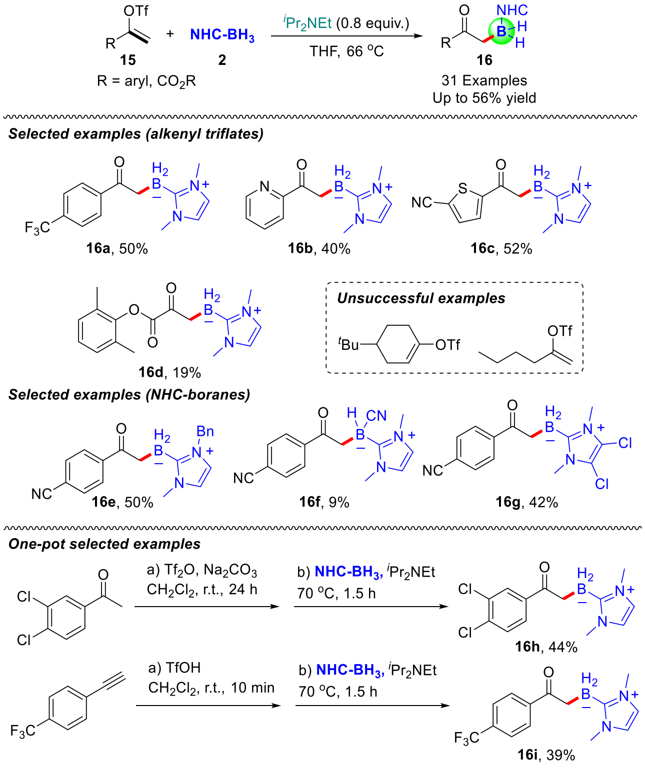
In view of the literatures reported that vinyl triflates can be transformed to $\alpha$-trifluoromethyl ketones through radical rearrangement [59]. Curran group, in 2019, performed the synthesis of $\alpha$-borylated ketones containing C–B bonds through the radical borylation of vinyl triflates **15** with NHC-boranes (Scheme 8) [60]. Importantly, the desired $\alpha$-borylated ketone compounds **16** could be readily obtained from readily available acetophenones and phenylacetylenes in one-pot with moderate yields, further enhancing the possible practicality of this



**Scheme 6.** Proposed mechanism for radical $\alpha$-borylation of $\alpha,\beta$-unsaturated carbonyl compounds enabled by AIBN and thiol.



**Scheme 7.** Radical $\alpha$-hydroborylation of electron-deficient alkenes enabled by AIBN and Thiol.



**Scheme 8.** Radical borylation of alkenyl triflates enabled by $^{i}Pr_2NEt$.

method. Various aryl(heteroaryl) vinyl triflates and NHC–boranes decorated with various substituents on *N* or B atoms could be tolerated, albeit with moderate or relatively lower isolated yields (31 examples, up to 56% yield), but alkyl vinyl triflates are not suitable coupling partners.

The radical pathway was supported by a radical trapping experiment with the addition of 2 equivalents of TEMPO (2,2,6,6-tetramethylpiperidoxyl). Under traditional radical initiator (such as azo and peroxide derivatives) free conditions, alkylamine ($^{i}Pr_2NEt$) was required as activator to generate the $CF_3$ radical, which abstracts a proton of NHC–borane to form the key NHC boryl radical. KIE experiment showed that the activation of B–H bond is involved in the rate-determining step.

In 2021, Du and co-workers exploited the activation of NHC–boranes in the manner of frustrated Lewis pairs (FLPs) generated *in situ* from $B(C_6F_5)_3$ and NHC–$BH_3$ (Scheme 9) [61]. In the presence of 5 mol% $B(C_6F_5)_3$ as the Lewis acid catalyst, whatever the activated arylalkenes (stilbenes and $\beta$-methylstyrenes) or unactivated alkylalkenes **17**, the monohydroborylation reactions proceeded smoothly to assemble the target organoboranes **18** in moderate to excellent yields (24 examples, 64%–98%). When it comes to terminal styrenes, the dihydroborylation products were exclusively formed in good yields (5 examples, 73%–77%). KIE experiments suggested that B–H bond cleavage is involved in the rate-determining step.

Initially, $B(C_6F_5)_3$ and NHC–$BH_3$ react to form the zwitterionic frustrated Lewis pair **Int 9–I**. Electrophilic addition of **Int 9–I** to olefin **17** then generates a new zwitterion **Int 9–II**, establishing the C–B bond regioselectively. The hydroborylation product **18** forms *via* hydride transfer from HB-$(C_6F_5)_3$ to the carbocation, though direct hydride transfer from NHC–$BH_3$ cannot be ruled out.

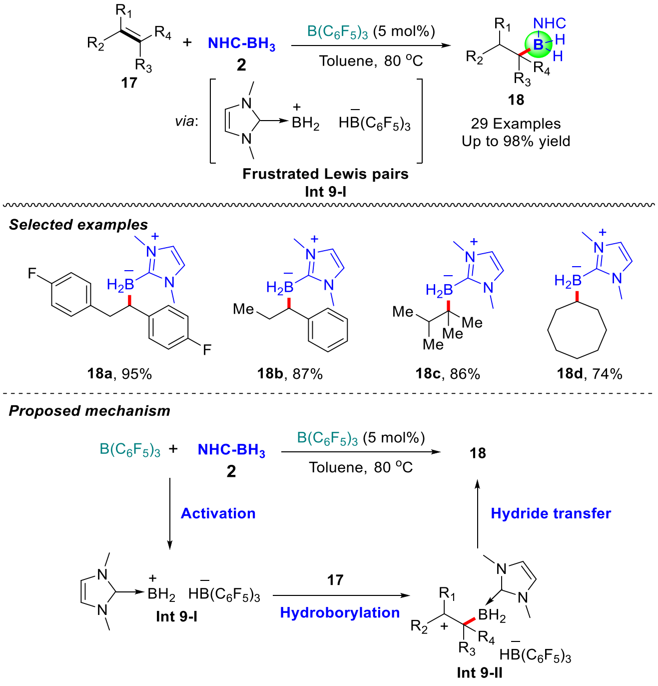
In 2022, Liu and co-workers developed the synthesis of $\alpha$-boryl ketones **20** by radical borylation through the reaction of vinyl azides **19** with NHC–boranes **2** (Scheme 10) [62]. As expected, various aryl- and heteroaryl-substituted vinyl azides were converted into their target $\alpha$-boryl ketone products **20** in medium yields (27 examples, 41%–67%) in the presence of 1.5 eq. of *tert*-butylthiol and 0.5 eq. of $CS_2CO_3$. Alkyl vinyl azides and *ortho*-substituted aryl vinyl azides could not be tolerated. Notably, replacement of base with 1.2 equiv. of radical initiator AIBN, the borylated triazoles **21** were tuned as the major products by the radical borylation cyclisation pathway in acceptable yields (27 examples, 34%–63%).

Mechanistically, thiol or AIBN could generate the boryl radical. For $\alpha$-boryl ketones formation, boryl radical addition to vinyl azide **19** forms the imine intermediate **Int 10–I**, which obtains a hydrogen and then is hydrolysed to give product **20**. For borylated triazoles formation, boryl radical addition to vinyl azide furnishes the key intermediate **Int 10–III**, which is transformed to carbon radical intermediate **Int 10–V** through consecutive tautomerization and cyclisation. Subsequently, the reaction of **Int 10–V** with RSSR yields the triazole **21** by elimination of a molecule of RSH.

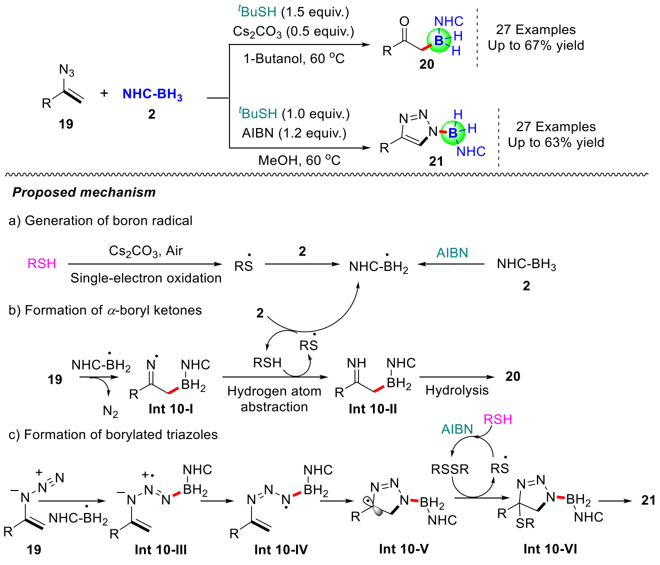
Very recently, Jin and Wang group described the hydroborylation of enamine carboxylates **22** with NHC-borane **23** to access $\beta$-borylated amino acid ester derivatives **24** (Scheme 11) [63]. Various *anti*-amino boron compounds were efficiently constructed in moderate to good yields (27 examples, 53%–94%) with high regio- and diastereoselectivity (*dr* > 95:5). An ACCN (1,1′-azobis(cyclohexanecarbonitrile)) initiated radical mechanism is proposed to rationalise the distinct selectivity of this procedure.

### 2.2. Homogeneous photocatalysed hydroborylation of alkenes

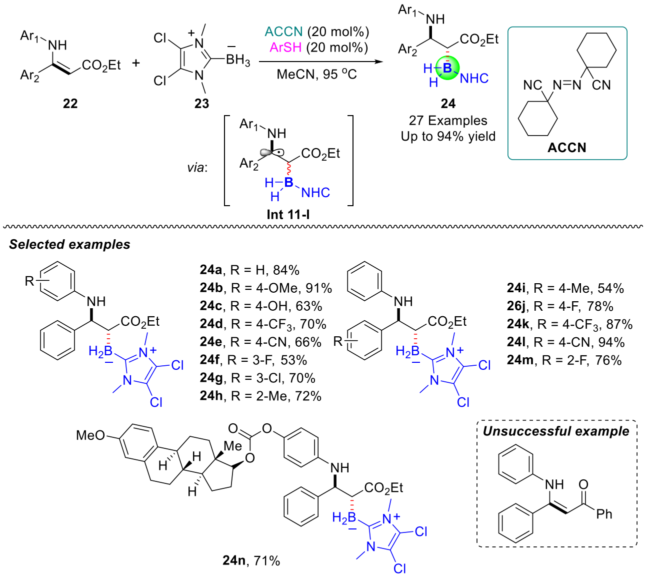
In recent years, visible-light-mediated photoredox catalysis has experienced a rapid renaissance, which provides a new avenue for



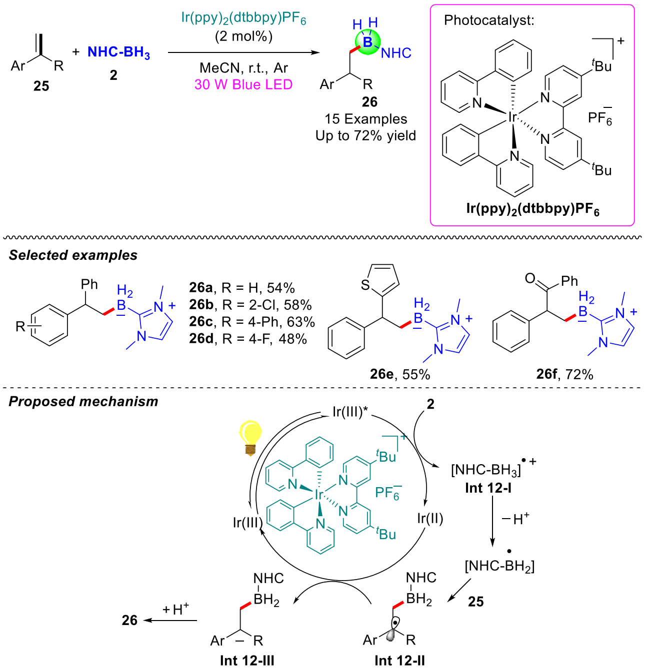
**Scheme 9.** $B(C_6F_5)_3$-catalysed hydroborylation of alkenes.



**Scheme 10.** Radical borylation of vinyl azides.



**Scheme 11.** Radical hydroborylation of enamine carboxylates enabled by ACCN and thiol.

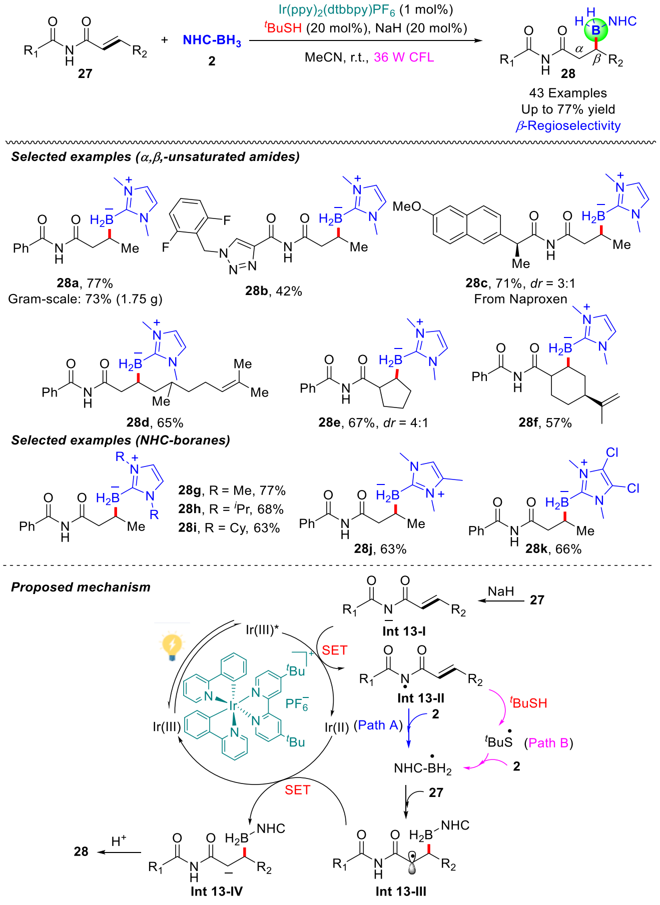


**Scheme 12.** Homogeneous photocatalytic radical hydroborylation of arylalkenes with Ir(III) complex.

catalytic C–B bond formation with NHC–boranes [64,65]. The B–H bond of NHC–boranes is activated by photoinduced single-electron transfer (SET) or hydrogen-atom transfer (HAT) process.

In 2020, a visible light-induced photoredox-catalysed radical hydroborylation of arylalkenes was described by Yang, Chen, Xiang, and co-workers (Scheme 12) [66]. Under an Ar atmosphere, with the irradiation of 30 W blue LED, the C–B bond was smoothly constructed at room temperature through the C–H bond cleavage of arylalkenes **25** in the presence of Ir(III) complex ($Ir(ppy)_2(dtbpy)PF_6$) as the photocatalyst. A possible SET reaction mechanism involving a boryl radical is proposed based on control experiments. The deprotonation of radical cation $[NHC–BH_3]^{\bullet+}$ **Int 12–I** generated by B–H bond activation with excited Ir(III)* catalyst through SET is conducted to yield the NHC boryl radical $[NHC–BH_2]^{\bullet}$. Addition of the boryl radical to arylalkene **25** yields the carbon radical intermediate **Int 12–II**, which is reduced by Ir (II) to carbanion intermediate **Int 12–III**, along with the rebirth of Ir(III) catalyst. Finally, the protonation of the carbanion intermediate leads to the desired hydroborylated product **26**.

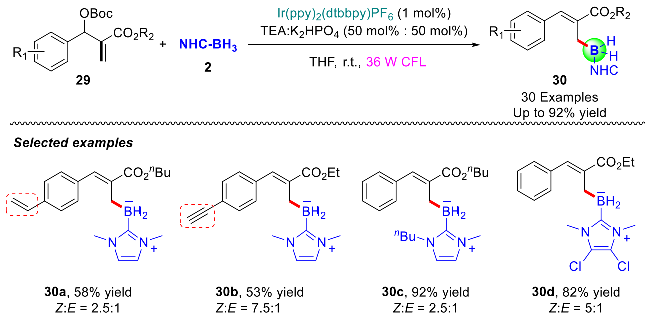
In the same year, Zhu, Li, Xie, and cooperators realised an elegant hydroboration reaction of electron-deficient internal alkenes attached amide groups **27** with $NHC–BH_3$ under visible light-mediated photoredox catalysis (Scheme 13) [67]. A series of borylated products **28** with β-C–B bonds were furnished by the combination of Ir(III) complex as the potocatalyst and alkyl thiol as the hydrogen atom transfer catalyst employing a compact fluorescent light (CFL) as the light source. This



**Scheme 13.** Homogeneous photocatalytic radical hydroborylation of $\alpha,\beta$-unsaturated amides with Ir(III) complex and thiol catalyst.

protocol features wide substrate scopes both for alkenes and boranes, high functional group compatibility, good regioselectivity, and gram scale synthesis (43 examples). Based on DFT calculations, the exclusive $\beta$-position selectivity of desired addition products ascribed to the photoredox catalysis, which lowered the reaction activation energy. This methodology is a competent complement and expansion to Wang's work [57], which mainly leads to the $\alpha$-borylated products through thermal radical hydroborylation of $\alpha,\beta$-unsaturated compounds.

To rationalise the inverse borylation procedure, a radical hydroboration mechanism is proposed. The photooxidation of Ir(III) catalyst under CFL irradiation delivers the excited Ir(III)*, which oxidises the nitrogen anion intermediate **Int 13–I** generated by the deprotonation of alkenes **27** to the nitrogen radical **Int 13–II**. Under the synergistic action of **Int 13–II** (path A) and the thiol radical (path B), the boryl radical is obtained *via* B–H bond activation. The regioselective radical addition of boron radical to carbon–carbon double bond of alkenes at the $\beta$-position to assemble the carbon radical intermediate **Int 13–III**. The final coupling products were formed through the continuous oxidation/protonation sequence.



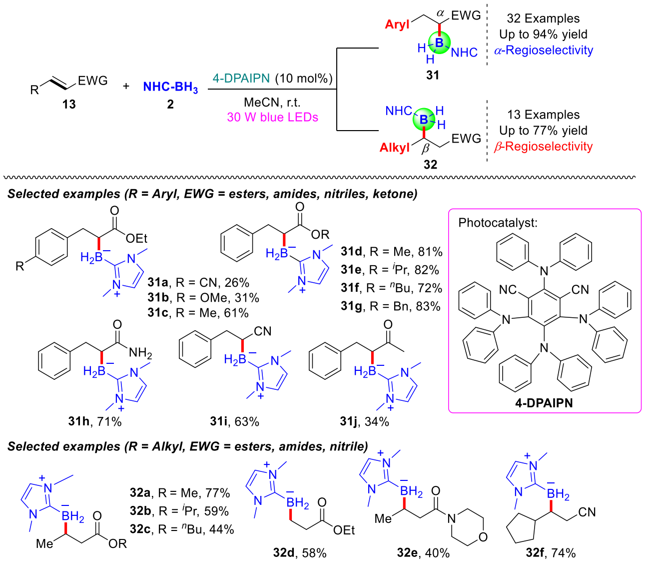
**Scheme 14.** Homogeneous photocatalytic radical hydroborylation of acrylates.

Lately, the construction of allylboranes **30** through the radical hydroboration of allyl carbonates **29** as the electron-deficient alkenes was also established in the absence of thiol catalyst by the same group under similar photocatalytic tactics (Scheme 14) [68]. This methodology showed good chemoselectivity, keeping terminal carbon–carbon double and triple bonds untouched, albeit with moderate *Z/E* stereoselectivity (30 examples, 48%–92%).

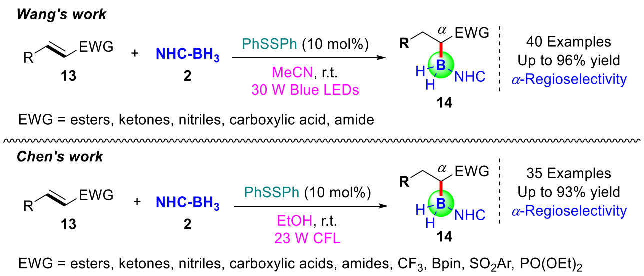
Subsequently, various B–H bond activation strategies by organic photosensitizers enabled SET mechanism to be successively developed. In 2021, Dai and Curran firstly demonstrated the radical hydroboration of electron-deficient alkenes **13** with 4-DPAIPN (2,4,5,6-tetrakis (diphenylamino)isophthalonitrile) as the organic photocatalyst (Scheme 15) [69]. The regioselectivity of desired borylated products was controlled by the structure of starting materials. From $\beta$-aryl or $\beta$-alkyl substituted $\alpha,\beta$-unsaturated carbonyls and their analogues, the corresponding $\alpha$- or $\beta$-borylated products **31** and **32** were respectively formed in good yields and selectivity.

In 2022, Wang [70] and Chen [71,72] groups presented their independent work on regioselective C–B bond formation through radical hydroboration of unsaturated internal alkenes (Scheme 16). Compared to Dai and Curran's method [69], one of the biggest differences lies in the use of disulfide or thiol as the organic photocatalysts, which need additional $N_2$ protection during the borylation pathway. Under the irradiation of visible light, the thiyl radical was formed to deliver the key NHC boryl radical intermediate through the hydrogen abstraction of B–H bond, thereby triggering the whole catalytic reaction system. Subsequently, Zeng and Wang *et al.* developed the visible light mediated hydroborylation of terminal alkenes with NHC-boranes utilising PhSSPh as the photocatalyst [73].

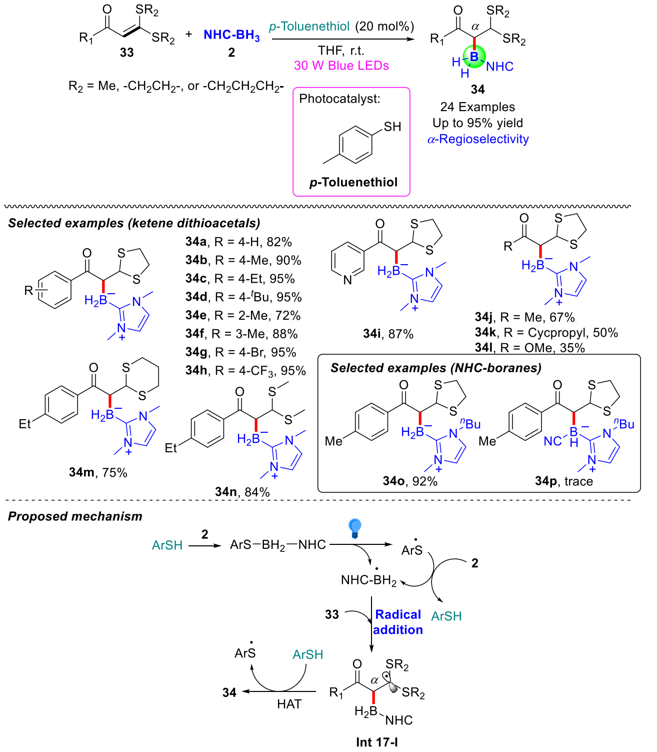
Ketene dithioacetals as versatile synthons have attracted much attention from organic synthetic community in recent years due to their push-pull electronic properties [74]. In 2023, Wang and co-workers expanded their catalytic radical hydroboration reaction system to $\alpha$-oxo ketene dithioacetal compounds **33** (Scheme 17) [75]. $\beta$-Borylated dithiane derivatives **34** were afforded smoothly in moderate to excellent yields (24 examples). Similarly with Chen's reports [71,72], employing 4-methylbenzenethiol as the HAT catalyst and proton source, the boryl radical is generated through the reaction of ArSH and NHC–$BH_3$ under



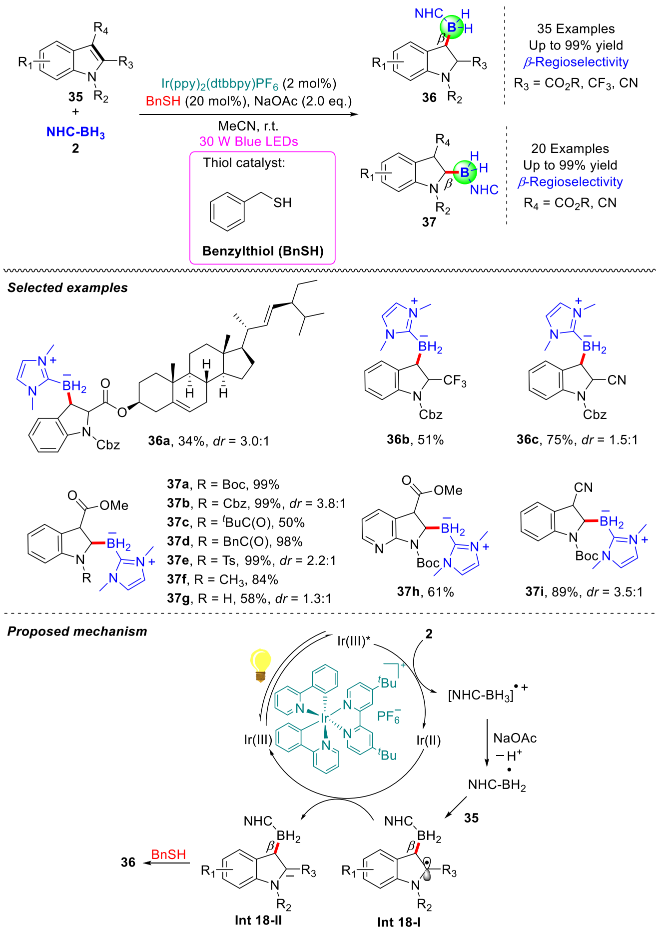
**Scheme 15.** Homogeneous photocatalytic radical hydroborylation of alkenes with 4-DPAIPN.



**Scheme 16.** Homogeneous photocatalytic radical hydroborylation of alkenes with disulfide or thiol.



**Scheme 17.** Homogeneous photocatalytic radical hydroborylation of ketene dithioacetals.



**Scheme 18.** Homogeneous photocatalytic radical hydroborylation of indoles.

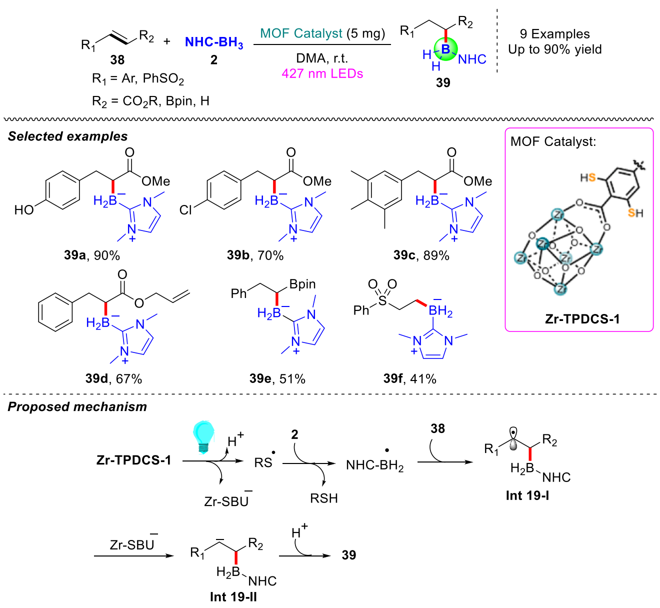
visible-light irradiation and base-free conditions. Then, boryl radical addition to ketene dithioacetal **33** produces carbon radical intermediate **Int 17–I**, which abstracts a proton from ArSH to deliver product **34**. Notably, a photocatalyst-free strategy for C–B bond formation *via* radical hydroborylation of alkenyl triflates was also developed by Yang and Xiang *et al.*, yielding one NHC–BH$_3$-derived product in 87% yield [76].

Very recently, utilising B–H bond activation enabled by Ir(III) complex/thiol combined catalytic system, Wang and An group reported a radical hydroborylation of indoles **35** (Scheme 18) [77]. This protocol provides a reliable method for the construction of C–B bond with indoles and NHC-boranes, various borylated indoline derivatives at C-2 **36** and C-3 **37** positions were efficiently assembled with up to quantitative yield (55 examples). Gram-scale experiments and late-stage modification experiments strengthen the practicality of this methodology. Oxygen and sulfur containing heterocycles such as benzofuran and benzothiophene are well compatible with the reaction, delivering the corresponding products in 47% and 93% yields, respectively. It is worth mentioning that the protection group at nitrogen atom is crucial to ensuring the good reaction efficiency, nitrogen free starting material only furnished the target product in a medium yield (46%). Moreover, the high regioselectivity of the borylation of indoles heavily depends on the pre-functionalization of feed stocks, which leaves room for further developing more general protocol in the future.

## 2.3. *Heterogeneous photocatalysed hydroborylation of alkenes*

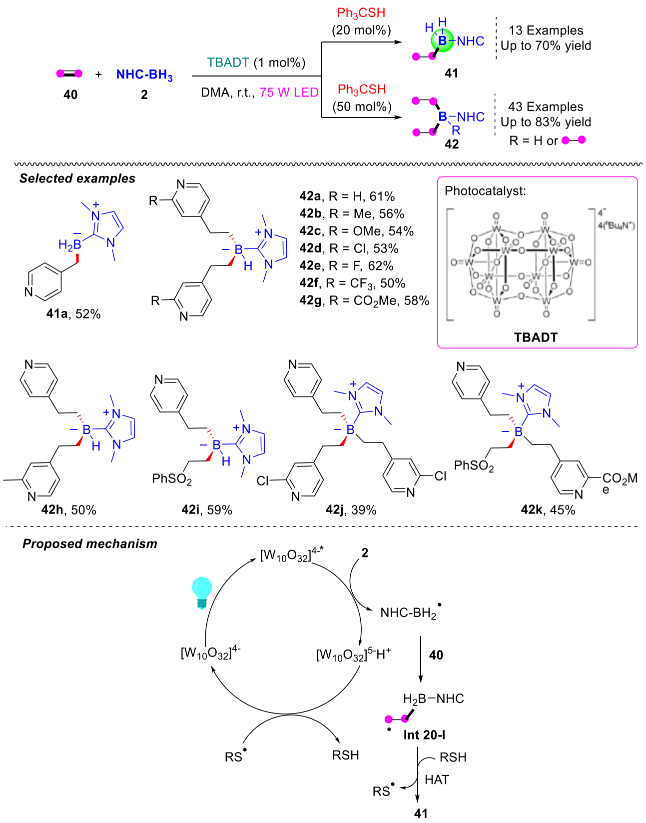
Heterogeneous photocatalysis bearing both merits of heterogeneous catalysis and photochemistry has emerged as a powerful and promising tool for organic transformations [78–80]. Recently, the intermolecular radical hydroborylation of alkenes with NHC–boranes has been developed by heterogeneous photocatalysis, which serves as an alternative to homogeneous photocatalysis.

In 2023, Quan and Xu *et al.* designed and synthesised a novel Zr-based metal-organic frameworks (MOFs) involving TPDCSH arylthio ligands (TPDCS: 3,3″,5,5″-tetramercaptol[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylate) and Zr$_6$ cluster as heterogeneous photocatalysts by solvothermal synthesis (Scheme 19) [81]. In view of the thiyl radical, which could be generated through the electron transfer from ligands to the metal centre under visible light irradiation, the radical hydroborylation of alkenes **38** was utilised to test the photocatalytic activity of the Zr-based MOFs photosensitizers. Under standard conditions with Zr-TPDCS-1 as the photocatalyst and 427 nm blue LED as the light source, substituted cinnamates, vinyl boronic pinacol ester, and phenyl vinyl sulfone are viable substrates, various *α*-borylation products **39** were obtained in yields ranging from 41% to 90% at room temperature.



**Scheme 19.** Heterogeneous photocatalytic radical hydroborylation of alkenes by MOF-based thiol catalyst.

The control experiment employing TPDC-SH as the thiol catalyst only gave a trace product, highlighting the necessity of introducing MOF fragment. And, the generation of sulfur-centred radical was demonstrated by the treatment of MOF catalyst with $NH_4SCN$. Mechanistically, the thiyl radical is yielded through LMCT (ligand-to-metal charge transfer) under photoinduced conditions. Then, deprotonation of NHC–$BH_3$ with thiyl radical to form the boryl radical, which underwent radical addition, reduction, and protonation to furnish the final borylated product **39**.



**Scheme 20.** Heterogeneous photocatalytic radical hydroborylation of electron-deficient alkenes by TBADT catalyst.

In the same year, the selective hydroborylation of electron-deficient alkenes **40** by cooperative catalysis with decatungstate and thiol was also developed by Quan group (Scheme 20) [82]. Tetrabutylammonium decatungstate (TBADT) and alkylthiol were optimized as the photocatalyst and polarity reversal catalyst, respectively. With 390 nm LED as light source and 20 mol% $Ph_3CSH$ as thiol catalyst, various substituted vinylpyridines, phenyl vinyl sulfone, and cinnamate derivatives **40** were selectively mono-borylated, furnishing the corresponding C–B bond coupling products **41** in 13%–70% yields (13 examples). Increasing the loading of $Ph_3CSH$ to 50 mol%, the disubstituted borane products were predominantly formed with a broad substrate scope, good functional group compatibility, and satisfied reaction yields (34 examples, 34%–83%). Furthermore, utilising the stepwise synthetic strategy, the unsymmetrical di- and triborylation products were smoothly constructed, which supports the possibility for subsequent diversified transformations.

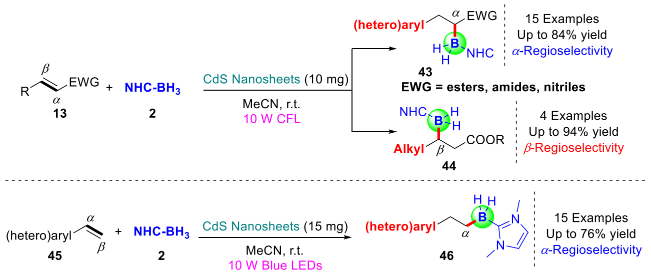
With regard to the reaction mechanism, the boryl radical is yielded through B–H bond activation by excited TBADT. Then, the radical addition of boryl radical to alkene substrate **40** delivers a carbon radical intermediate **Int 20–I**, which is converted to the final product **41** with the assistance of thiol through HAT procedure.

Very recently, Dai and Curran collaboratively established a universal pathway for C–B bond formation by borylation with NHC–$BH_3$ as the boron source with heterogeneous photocatalysis (Scheme 21) [83]. After systematic studies on the catalytic activity of CdS in various morphologies (nanorods, nanowires, nanospheres, and nanosheets), ultrathin CdS nanosheets were optimized as the best heterogeneous semiconductor photocatalysts. Under the irradiation of 10 W compact fluorescent light (CFL) or blue LED, a wide array of alkenes **13** and **45** including $\alpha,\beta$-unsaturated esters/nitriles/amides and functionalized arylethylenes were smoothly borylated to give borane derivatives **43**, **44**, and **46** with good functional group compatibility, high regioselectivity, and medium to excellent conversions, albeit with moderate isolated yields for most products (totally 35 examples). Blank experiments verified the indispensability of the CdS catalyst and light irradiation. The NHC–boryl radical produced by the oxidation of NHC–borane with photogenerated hole is involved in this procedure based on control experiments.

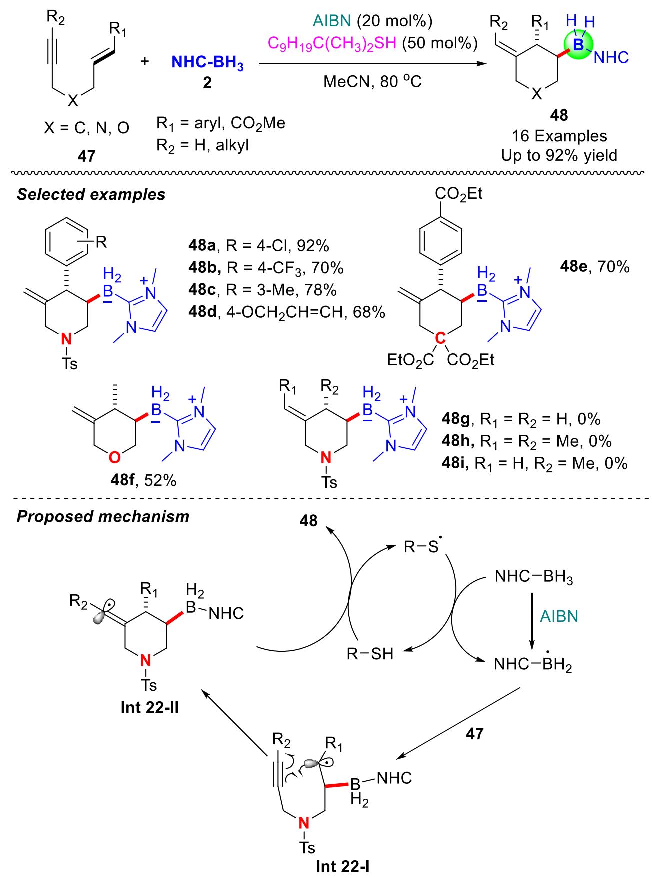
### 2.4. Cascade borylative cyclisation of alkenes

Cascade cyclisation reactions of unsaturated hydrocarbons have gained great progress in the synthesis of complicated carbo- and heterocycles *via* the construction of multiple C–C and/or C–X bonds in one-pot [84]. With the emergence of radical chemistry, radical cascade cyclisation reactions of unsaturated hydrocarbons have become a research hotspot in synthetic chemistry [85].

Wang and co-authors reported their continuous efforts for building boron-substituted carbo- and heterocycles through the radical initiated



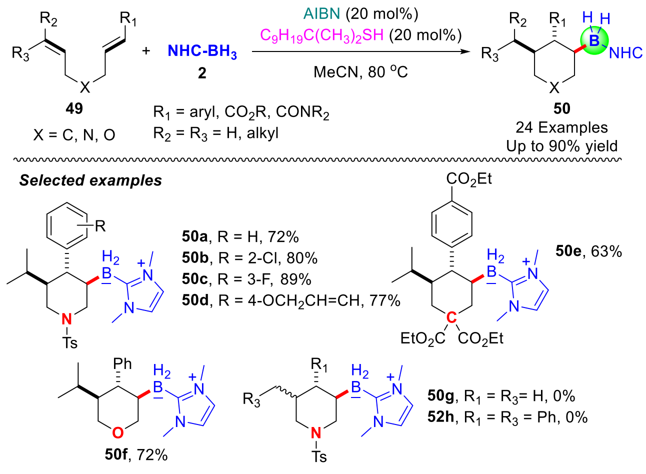
**Scheme 21.** Heterogeneous photocatalytic radical hydroborylation of alkenes by CdS nanosheet catalyst.



Scheme 22. Cascade radical borylative cyclisation of 1,6-enynes.

cascade borylative cyclisation of unsaturated hydrocarbons with NHC–boranes [86–88]. Firstly, in 2017, they developed a radical cascade cyclisation reaction for the preparation of boron-substituted six-membered hetero- and carbocycles **48** from 1,6-enynes **47** and NHC–boranes (Scheme 22) [86]. This reaction employs AIBN as the radical initiator and *tert*-dodecanethiol as the polarity reversal catalyst to activate the B–H bond. Various 1,6-enynes containing an intramolecular C–B bond are compatible with delivering the borylated products in high chemo- and regioselectivity (16 examples, up to 92% yield).

Mechanistically, radical clock experiment favors a radical pathway. When alkene moiety **47** is attached to the phenyl ring as the starting material, boryl radical preferentially adds to the carbon–carbon double bond of enynes and initiates the radical cyclisation procedure. The formed stable alkyl radical **Int 22–I** undergoes the *6-exo-dig* cyclisation to form vinyl radical intermediate **Int 22–II**, which grabs a hydrogen from thiol under polarity reversal catalysis to form the final product **48**.



Scheme 23. Cascade radical borylative cyclisation of 1,6-dienes.

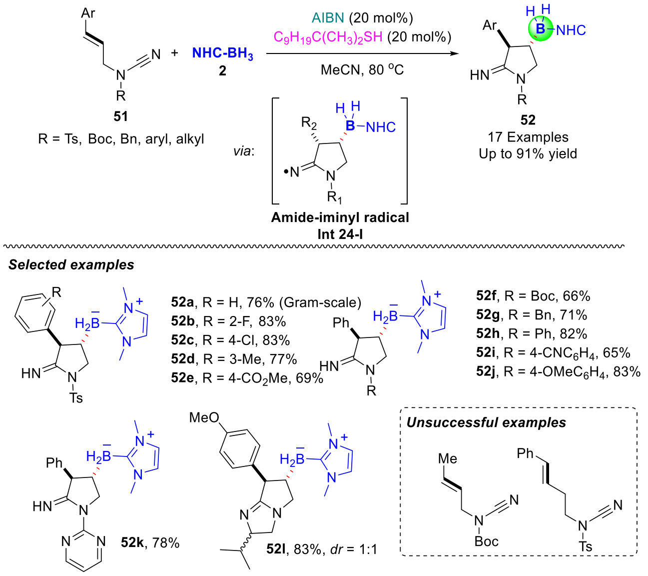
Subsequently, in 2018, the same group further presented their serial research on radical tandem cyclisation reactions of 1,6-dienes or *N*-allylcyanamides **49** with NHC–boranes to the construction of borylated cyclic compounds **50** (Scheme 23) [87]. Under similar cyclisation conditions of 1,6-enynes, the radical borylative cyclisation of 1,6-dienes was conducted to assemble boron derived six-membered piperidine, pyran, and cyclohexane products (24 examples, up to 90% yield). Notably, this protocol could be utilised to synthesise boron-substituted polycyclic scaffolds and antidepressant drug analogues, but substrates with two terminal double bonds or cinnamyl groups failed to undergo the cyclisation reaction.

This cyclisation strategy could also be expanded to *N*-allylcyanamides **51** (Scheme 24) [88], which were transformed into five-membered amidine heterocycles **52** in good yields and *trans* stereoselectivity (18 examples, up to 91% yield). With respect to the mechanism, a key iminyl radical **Int 24-I** produced by the radical addition of benzyl radical to cyano group is involved.

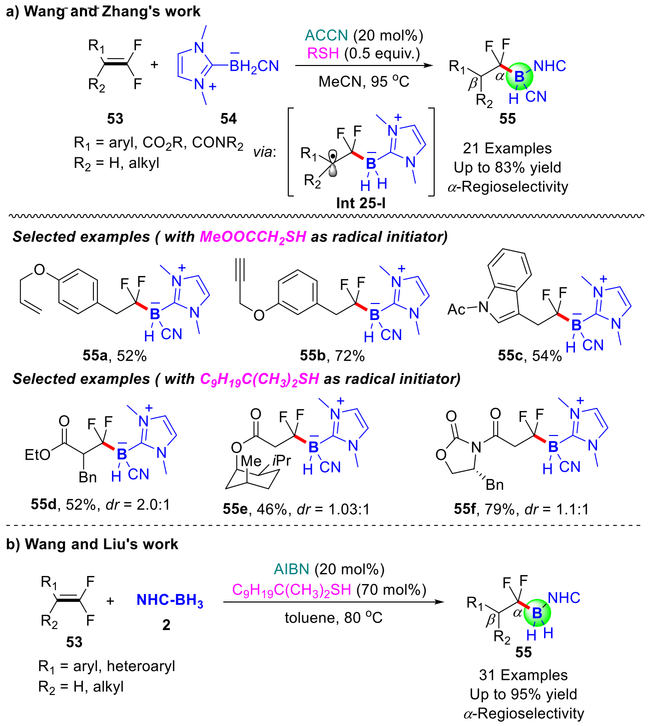
## 2.5. Hydroborylation/defluoroborylation of gem-difluoroalkenes or defluoroborylation of a-trifluoromethylalkenes

As one kind of important fluoro-containing organic compounds, $CF_2$- and alkenylfluoro-containing compounds have been widely used in the field of medicine and material science due to their unique biological activity and electronic properties [89].

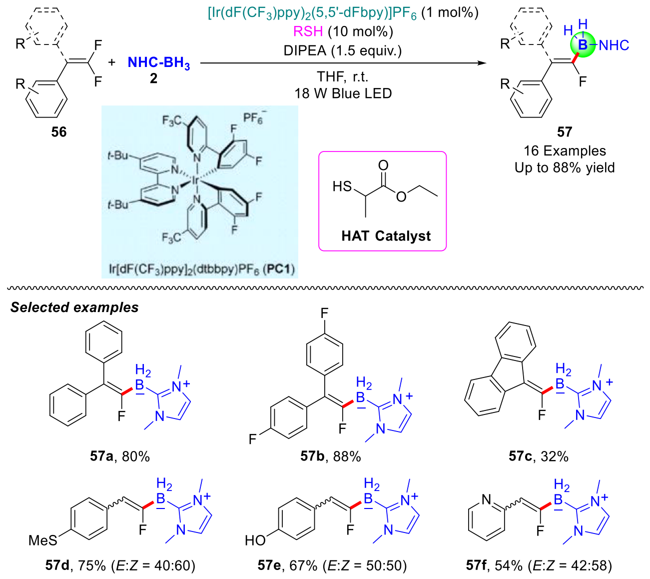
In 2019, Wang and Zhang *et al.* presented the synthesis of difluoromethyl functioned alkylboron scaffolds **55** through the hydroboration of *gem*-difluoroalkenes **53** under thermal catalysis in the absence of a transition-metal catalyst [90]. The B–H bond activation was realised by utilising ACCN and alphatic thiols ($MeOOCCH_2SH$ and $C_9H_{19}C(CH_3)_2SH$) as the radical initiator and the polarity reversal catalyst, respectively. However, the borylation reagent of this method is only restricted to NHC–$BH_2CN$ **54** which has lower reduction activity and can furnish the stable addition products with C–B bond in moderate to good yields (21 examples, 46%–83%). Almost at the same time, a similar organic catalytic strategy combining AIBN and $C_9H_{19}C(CH_3)_2SH$ was independently reported by Wang, Liu, and co-workers to the formation of C–B bond through difunctionalization of *gem*-difluoroalkenes using



Scheme 24. Cascade radical borylative cyclisation of *N*-allylcyanamides.



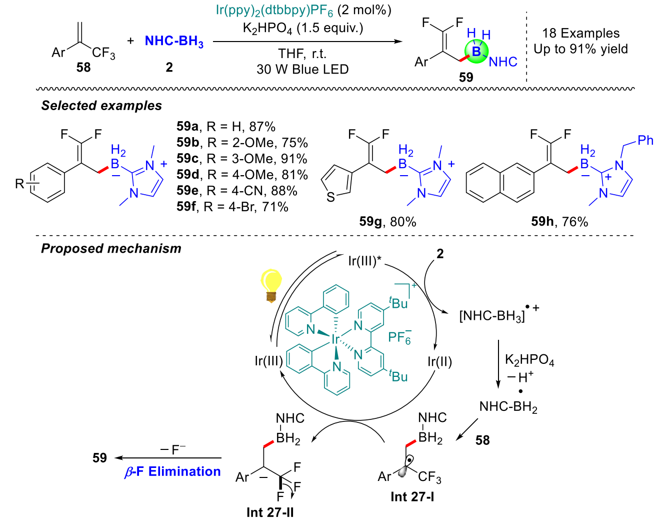
**Scheme 25.** Radical hydroborylation of *gem*-difluoroalkenes under thermal catalysis.



**Scheme 26.** Photocatalytic radical defluoroborylation of *gem*-difluoroalkenes.

NHC–$BH_3$. Regrettably, these two protocols could not be applied to the hydroboration of alkyl-substituted *gem*-difluoroalkenes (Scheme 25) [91].

Subsequently, a transition-metal Ir(III)-catalysed visible-light driven C–B bond formation approach in virtue of the defluoroborylation of *gem*-difluoroalkenes **56** with NHC–$BH_3$ was developed by Wu group (Scheme 26) [92]. With 1 mol% Iridium(III) complex (Ir[dF($CF_3$)ppy]$_2$(dtbbpy) $PF_6$) as the photosensitizer and thiol as the HAT catalyst, the tetrasubstituted monofluoroborylated products **57** were produced in moderate to good yields from symmetrical or unsymmetrical *gem*-difluoroalkene feedstocks by B–H bond and alkenyl $sp^2$ C–F bond activation (16 examples, 32%–88% yields).



**Scheme 27.** Photocatalytic radical defluoroborylation of *α*-trifluoromethylalkenes.

In contrast to the well-established defluorinative functionalization of trifluoromethyl substituted alkenes to the construction of C–C bond, the formation of C–B bond by radical defluoroborylation has not yet been fully studied [93]. The visible-light induced Ir(III)-catalysed radical hydroborylation of terminal arylalkenes developed by Yang *et al.* could be successfully extended to the defluoroborylation of *α*-trifluoromethylstyrenes **58** under slightly modified photocatalysis conditions (Scheme 27) [66]. With the same Ir(ppy)$_2$(dtbpy)$PF_6$ as the Ir(III) photocatalyst and 30 W blue LED as the light source, a series of $CF_2$-containing allylborane derivatives **59** were obtained at room temperature in 61%–91% yields through the C–F bond cleavage employing $K_2HPO_4$ as the additional base. This reaction followed the similar SET process, including boryl radical generation and radical addition. The difference lies in that the desired defluoroborylation product was generated by the cleavage of one C–F bond through E1cB-type fluoride elimination.

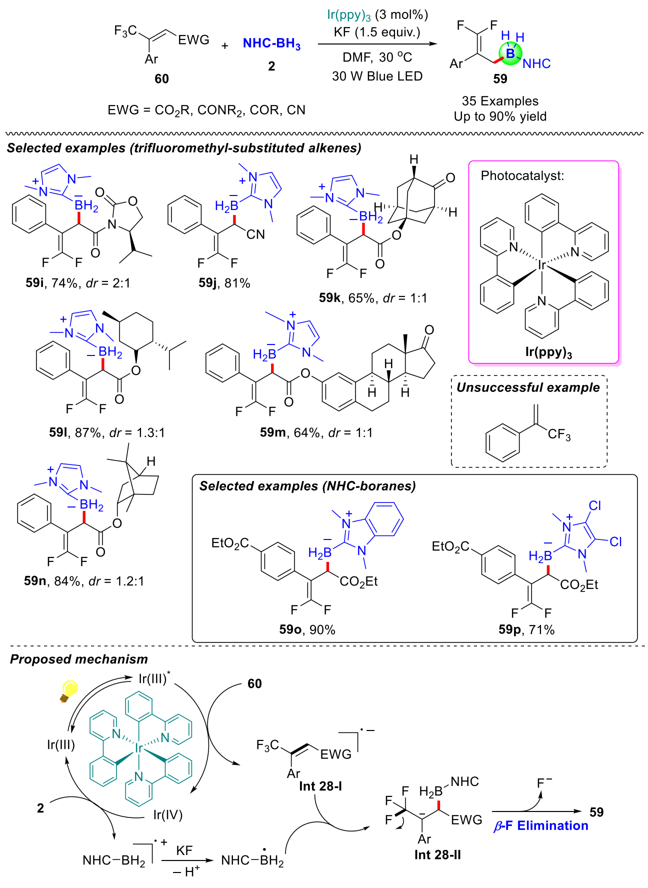
In the same year, Wu and Liu groups also separately realised the similar transformations from *α*-trifluoromethylstyrenes and NHC–$BH_3$ complexes employing organic photosensitizer (4-CzIPN) [92] and (Ir(ppy)$_2$(dtbbpy)$PF_6$) [94], respectively, except that their catalytic systems both need the assistance of alkylthiol as the HAT catalyst to cleave the B–H bond of NHC–boranes.

Lately, Wang group presented their independent research about the radical defluoroborylation of internal trifluomethyl arylalkenes **60** bearing electron-withdrawing groups, including ester, amide, ketone, and cyano substituents with NHC–borane complexes *via* photocatalysis (Scheme 28) [95]. Blue light and Ir(III) photocatalyst were also used in this methodology, but differing from Yang's work [66], a photoredox cycle involving the Ir(III)/Ir(IV) transformation and the olefin radical anion intermediate **Int 28–I** is put forward to rationalise the reaction pathway. And the final borylated product **59** is achieved by the cross-coupling of the NHC–boryl radical and intermediate **Int 28–I**. Remarkably, this methodology can be smoothly expanded to the difunctionalization of *trans*-alkenes with NHC–$BH_3$ and cyanoarene precursors, delivering the carbonborylation products with *trans*--stereoselectivity. However, *α*-trifluoromethylstyrene cannot produce the desired borylated product.

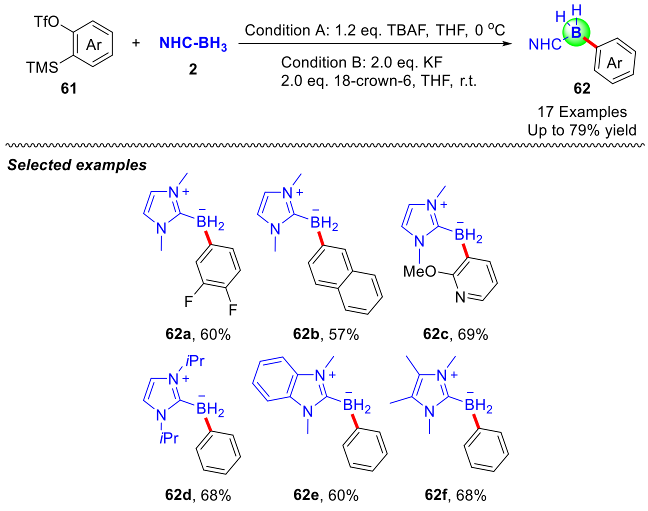
## 3. C–B bond formation *via* borylation of alkynes

### 3.1. *Hydroborylation of arynes*

Aryne (benzyne) chemistry is an "old" and occupies significant position in organic synthesis [96]. Curran and Taniguchi



**Scheme 28.** Photocatalytic radical defluoroborylation of $CF_3$-substituted alkenes.



**Scheme 29.** Hydroboration of *o*-benzynes generated *in situ*.

realised the first example on C–B bond formation through spontaneous hydroboration of arynes (*o*-benzyne) **61** with NHC–$BH_3$ in 2014 (Scheme 29) [97]. Under optimal conditions, activating *o*-silyl aryl triflates with fluoride anion as aryne precursors, a mixture of monoaryl and diaryl boranes (ratio > 90:10) was assembled with monoaryl boranes **62** as the main product in medium to good yields (38%–79%). This protocol features benign compatibilities for both varied structural arynes (functionalized aryl- and pyridine-based precursors) and various NHC–boranes. The unsymmetrical disubstituted boranes could be constructed in acceptable yields by the second hydroborylation of monoaryl boranes. Amine-borane could produce the sole phenylborane product in 32%–38% yields, while other borane complexes, including pyridine-, phosphine-, sulfide-, and furan-borane adducts, all failed to furnish the corresponding boronated products.

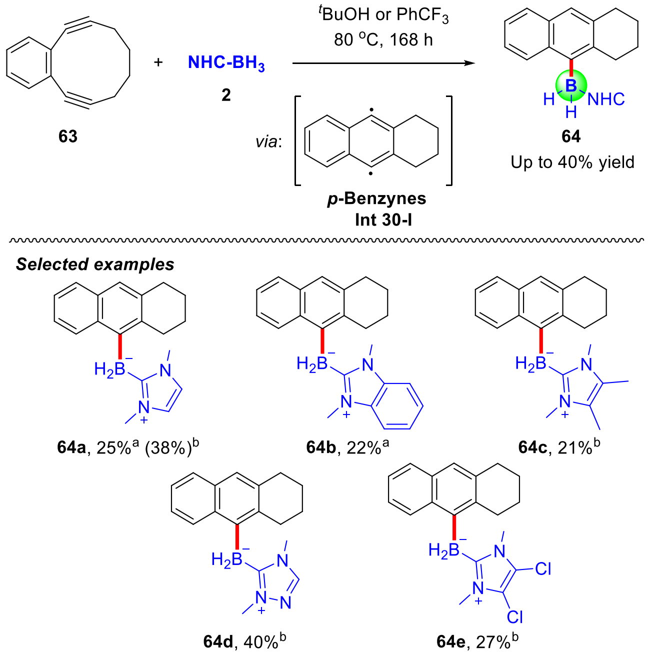
A hexadehydro-Diels-Alder cycloaddition of triynes and hydroboration of *o*-benzyne intermediates formed *in situ*, a cascade reaction system was immediately reported by the same group for the synthesis of borylated arenes [98].

In 2017, they found that Masamune-Bergman type cyclic products, including borylated 1,2,3,4-tetrahydroanthracenes **64** and 1,2,3,4-tetrahydroanthracenes were obtained from 10-membered cyclic 1,5-diynes **63** under thermal conditions (80 °C) in *tert*-butanol or $PhCF_3$ (Scheme 30) [99]. However, the chemoselectivity of this method is low; the two target products were generated in varied yields. *p*-Benzyne (1,4-biradical) intermediate **Int 30-I** is viewed as the key biradical intermediate, and NHC–$BH_3$ functions as both the borylation reagent and H-donor.

## 3.2. Hydroborylation of alkynes

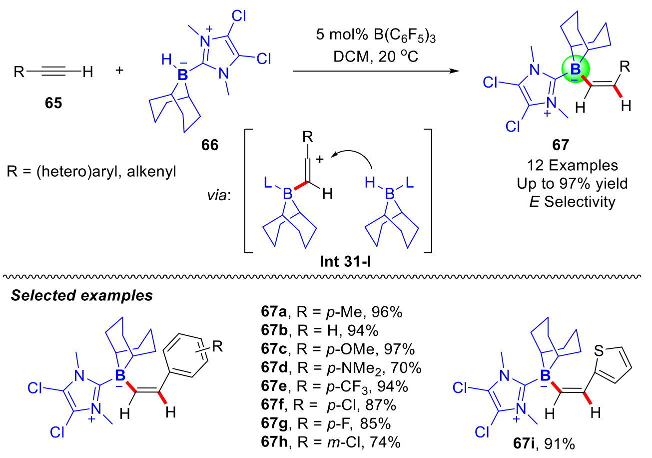
The hydroboration of easily available unsaturated hydrocarbons with carbon–carbon triple bonds is one of the most reliable ways to the construction of alkenylboranes in a regio- and stereoselectively controllable manner. The traditional hydroboration reaction usually depends on the use of transition metal catalysts or directing groups and preferentially forms the *syn* addition products through a concerted process, which limits the wide application of this methodology [100]. In contrast, the *trans*-hydroboration of linear alkynes is just at the very beginning and has received increasing attention in recent years.

In 2016, Ingleson *et al.* demonstrated the installation of C–B bond by way of the $B(C_6F_5)_3$ enabled *trans*-hydroboration of terminal alkynes **65** using (NHC)9-BBN(H) (9-BBN: 9-borabicyclo(3.3.1)nonane) **66** as the borane reagent (Scheme 31) [101]. *Z*-Vinylborane derivatives **67** were exclusively formed in good to excellent yields (12 examples, 56%–97%) from variable substituted (hetero)arylacetylenes and conjugated enynes bearing terminal triple bonds. The *Z* stereoselectivity of borated



[a] ${}^tBuOH$ as solvent. [b] $PhCF_3$ as solvent.

**Scheme 30.** Hydroboration of *p*-benzynes generated *in situ*.



**Scheme 31.** $B(C_6F_5)_3$ enabled ionic *trans*-hydroborylation of terminal alkynes with *Z*-selectivity.

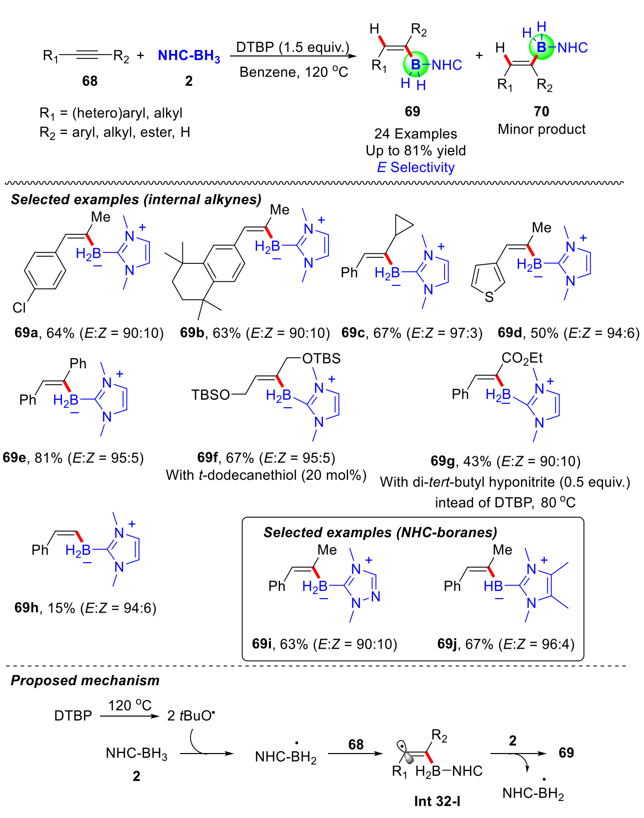
products originated from the successive electrophilic addition of borenium cations to the triple bond and back-hydride transfer.

Following these pioneering works on the formation of alkenyl C–B bond, the *trans*-hydroboration of several kinds of alkynes, including internal alkyne [102], ynamides [103,104], and 1,3-diynes [105] was probed with *N*-heterocyclic carbene boanes involving organocatalysis, transition metal catalysis, and photoredox catalysis. These works expand the application range of hydroboration reaction to more diverse feedstocks.

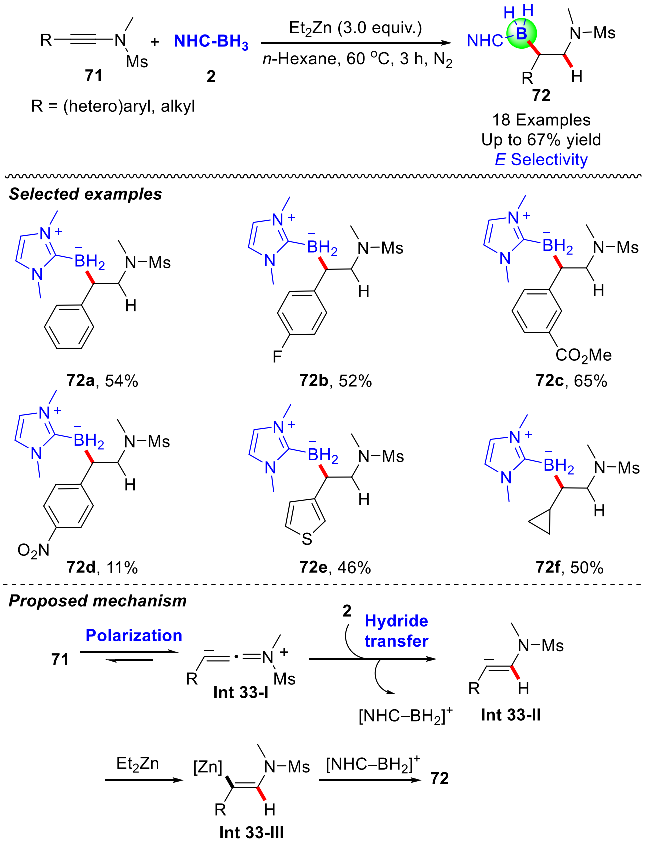
In 2018, Taniguchi and Curran group realised the radical initiated *trans*-hydroboration of internal alkynes **68** to the synthesis of *E*-alkenylboranes **69** (Scheme 32) [102]. 1-Phenyl-1-propyne and its analogues were selected for hydroboration with DTBP (di-*tert*-butyl peroxide) as the radical initiator and the target vinyl NHC–boranes were generated with particular *E* stereoselectivity (*E*:*Z* > 90:10) and beta-regioselectivity under additional catalyst and directing group free conditions. Further transformations of these obtained borylated alkenes to synthetically useful *Z*-trisubstituted alkenes showcased their potential practicality. However, this methodology is limited to internal alkynes; phenylacetylene only led to the *Z* selectivity product in low yield (15%) due to the Cahn-Ingold-Prelog (CIP) rule, albeit with a good ratio of *E*/*Z* isomers (94:6). Actually, this methodology and Ingleson's work [101] are complementary to each other, albeit with different reaction pathways.

Mechanistically, a radical-chain process is proposed to rationalise the reaction results. The boron-centred radical is initially generated by the B–H bond activation of NHC–borane with $^t$BuO radical. Then, the boron radical adds to the carbon atom adjacent to phenyl ring of carbon–carbon triple bond to yield a stable alkenyl radical intermediate **Int 32–I**, which determines the *β*-regioselectivity. The desired product **69** is finally assembled by the reaction of the alkenyl radical with NHC–boryl radical through the hydrogen-transfer procedure, which indicates the *E* stereoselectivity.

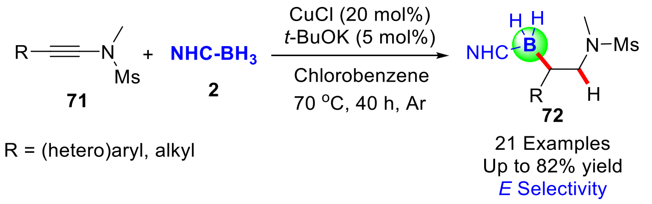
A transition-metal mediated *trans*-hydroboration reaction of ynamides **71** was realised in 2020 by Wang and co-workers (Scheme 33) [103]. In this study, the model product was delivered in 54% in the presence of three equivalents of $Et_2Zn$ at 60 °C for 3 h. Due to the susceptibility of $Et_2Zn$, the reaction needed to be conducted under $N_2$. The structure and *E* configuration of the desired product were definitely determined by X-ray crystallographic analysis. Various electron-donating groups (Me, Et, *t*-Bu) and electron-withdrawing groups (F, Cl, Br, $CF_3$, COOMe, Ph) substituted aryl ynamides, heteroaryl ynamides, as well as alkyl ynamides could take part in this reaction to produce the borylation products **72** (18 examples, up to 67% yield), albeit with medium isolated yields (about 50%, except



**Scheme 32.** Radical initiated *trans*-hydroborylation of internal alkynes with *E*-selectivity.



**Scheme 33.** $Et_2Zn$-mediated *trans*-hydroborylation of ynamides by ionic pathway.



**Scheme 34.** Copper(I)-catalysed radical *trans*-hydroborylation of ynamides.

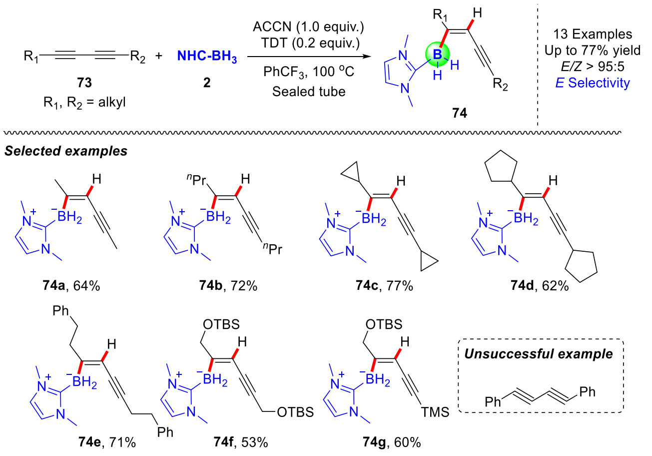
$NO_2$ with 11% yield). Notably, replacing the Ms group on the nitrogen atom with TS or Ns failed to yield any products.

An ionic pathway is mainly proposed to rationalise the *trans*-hydroboration procedure. Initially, the ynamide **71** is transformed to the keteniminium intermediate **Int 33–I**, which obtains a hydrogen through hydride transfer to form the carbanion intermediate **Int 33–II** and generates a borenium ion. Then, the alkenylzinc species **Int 33–III** is formed by the reaction of $Et_2Zn$ with **Int 33–II**. Finally, **Int 33–III** is borylated by borenium ion to deliver the corresponding C–B bond coupling product **72**.

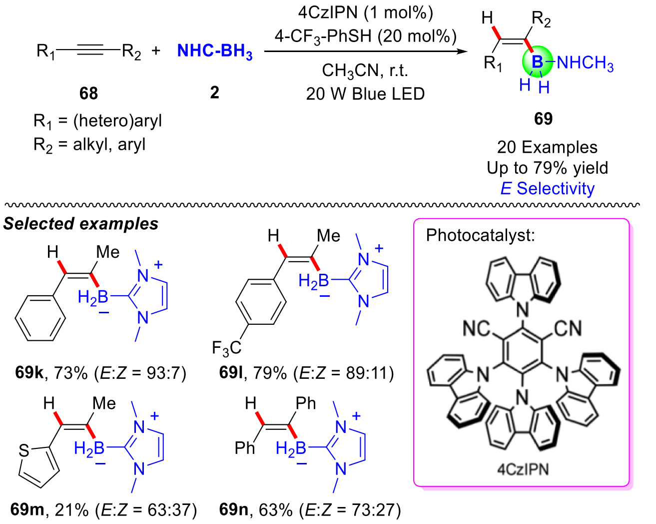
Another very related Cu(I) catalytic system with a strong base ($^t$BuOK) in chlorobenzene at 70 °C was developed recently as an improved version of Wang's work mentioned above (Scheme 34) [104]. By contrast, this radical protocol has a similar substrate scope and functional group compatibility of ynamides in relatively higher isolated yields (55%–82%), but requires significantly increasing the reaction time (40 h *versus* 3 h).

In 2021, as the extension of their continuous work on radical *trans*-hydroborylation of internal alkynes [102], employing ACCN as the radical initiator and TDT (*tert*-dodecanethiol) as the polarity-reversal catalyst, Taniguchi and Curran group established the *trans*-hydroboration of 1,3-diynes **73** with NHC–$BH_3$ at 100 °C in benzotrifluoride (Scheme 35) [105]. Only one triple bond was hydroborylated with high *trans*- and regioselectivity, affording many monoborylated conjugated enyne compounds **74** of *E*-isomer in good yields. Such a method makes it possible to construct conjugated molecular systems by way of *trans*-hydroborylation reaction. Both symmetrical and unsymmetrical alkyl-substituted 1,3-diynes were viable feed stocks, but aryl-substituted 1,3-diyne failed to give the borylated product.

The visible-light photoredox catalysis can also be employed in the research of *trans*-hydroboration of internal olefins **68** with NHC–boranes (Scheme 36) [106]. With the aid of 4CzIPN (1 mol%) as the organic photocatalyst and arylthiol (4-$CF_3$-PhSH, 20 mol%) as the hydrogen-atom transfer catalyst, a variety of alkenylboranes **69** were smoothly constructed in moderate to good yields and *E*-selectivity from arylalkylalkynes and diphenylacetylene under the irradiation of blue LED for 48 h (20 examples, up to 79% yield). In regard to the reaction process, a photoredox catalysis mediated radical mechanism is proposed. The similar alkenyl radical proposed by Curran's propose [97] is viewed as the key intermediate, which is formed through the addition of boryl radical to *β* position of the triple bond. Very recently, Zeng and co-workers successfully realised the visible-light promoted *trans*-hydroboration of internal olefins with Eosin Y as the organic photosensitizer [107]. This protocol also produced the alkenyl radical intermediate and showed good tolerance to terminal and internal olefins, but it needs an excessively large amount of NHC-boranes (15 equiv.) as the coupling reagents.



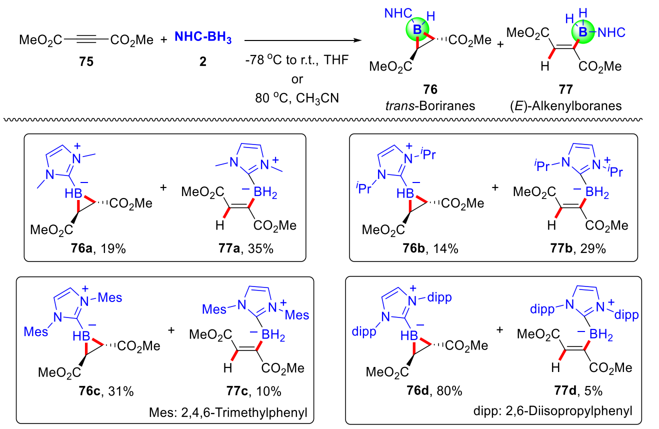
**Scheme 35.** Radical *trans*-hydroborylation of 1,3-diynes under thermocatalysis.



**Scheme 36.** Radical *trans*-hydroborylation of internal alkynes under photocatalysis.

Boriranes (also called boracyclopropanes) are one kind of three-membered cyclic organoboranes structurally similar to cyclopropanes, which may have rich chemistry [108]. However, the lack of effective synthetic methods to access boriranes has impeded their latent application.

In 2017, without additional catalyst or initiator, the reaction of dimethyl acetylenedicarboxylate (DMAD) **75** and NHC-borane in THF was initially conducted at −78 °C to room temperature to furnish the expectable (*E*)-alkenylborane **77** in 35% yield, concomitantly yielding the minor borirane product **76** (19%) (Scheme 37) [109]. Heating the NHC–borane with large steric hindrance group such as 2,6-diisopropylphenyl on nitrogen atom in MeCN, the borirane was predominantly achieved as the major product **76d** (80% yield). The alkenylborane comes from the typical



**Scheme 37.** Radical *trans*-hydroborylation of acetylenedicarboxylates to access borirane and alkenylborane.

*trans*-hydroboration of internal alkynes, while the borirane with *trans* ester groups is accidently obtained for the first time through the formal double hydroboration of alkynes with the formation of two C–B bonds. Due to the stabilisation of the NHC, the NHC–borirane is bench-stable even in solution under heating and could be isolated by column chromatography. Theoretical calculations and experimental studies support that both alkenylborane and borirane generated through the same reaction intermediate involving *trans* hydride transfer and they could not be interconverted each other. Subsequently, employing the strategy of hydrogen abstraction to activate the B–H bond of NHC–boranes with DTBP as radical initiator, boriranyl radicals from boracyclopropanes were firmly observed by EPR spectroscopy [110].

Under similar conditions, instead of the generation of the desired boraallyl radicals, the above obtained (*E*)-alkenylboranes unprecedentedly result in one kind of novel structure of five-membered cyclic boralactones involving 1,2-oxborole radicals through the 5-*endo* cyclisation reactions [111,112].

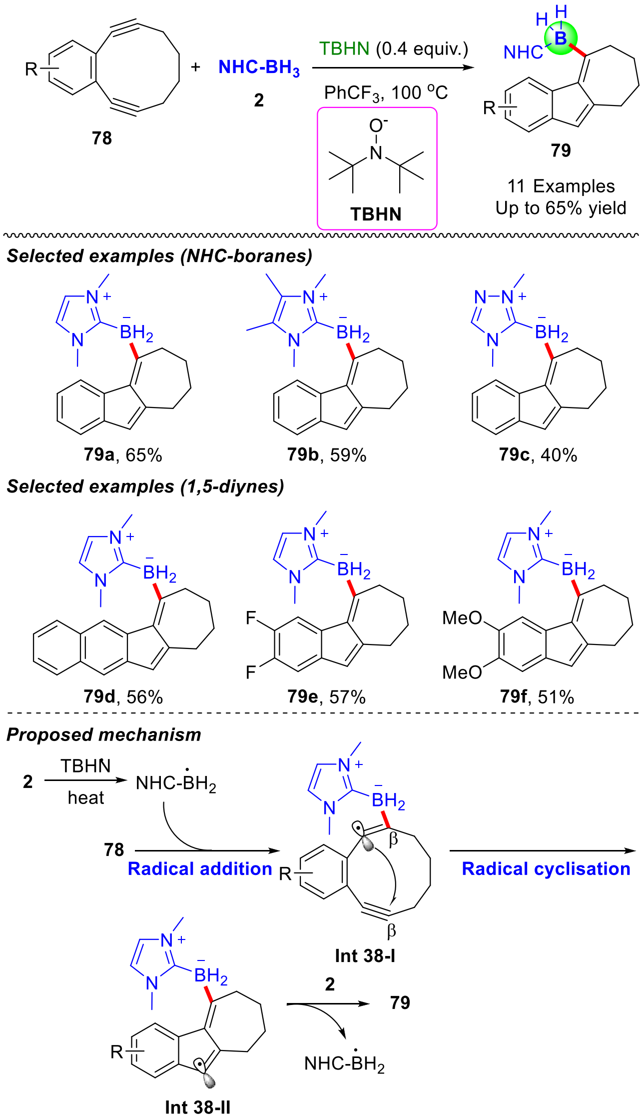
### 3.3. Cascade borylative cyclisation of alkynes

Radical cascade cyclisation strategy is also expanded to the construction of C–B bond by borylative cyclisation of alkynes. Generally, the B–H bond is activated by hydrogen abstraction of NHC–boranes with the action of a radical initiator under thermal catalysis.

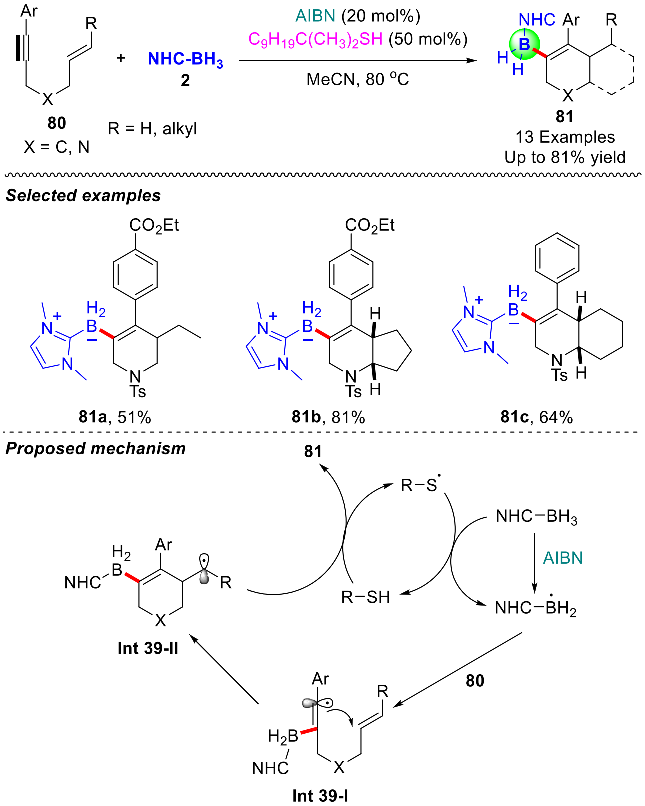
In 2017, Taniguci and Curran presented the radical cyclisation reactions of 10-membered cyclic 1,5-diynes **78** with NHC–$BH_3$ (Scheme 38) [113]. With di-*tert*-butyl hyponitrite (TBHN) as the $^tBuO$ radical precursor, a sequence of benzo[*α*]azulene derivatives **79** was obtained by heating diynes and boranes in $PhCF_3$ at 100 °C for half an hour (11 examples, up to 65% yield). With regard to the reaction mechanism, the boryl radical is firstly generated with the assistance of TBHN. Then, the radical addition of boryl radical to *β*-carbon of carbon–carbon triple bond leads to a stable alkenyl radical intermediate **Int 38–I**, which further addition-cyclisation to another *β*–position of triple bond delivers a second alkenyl radical **Int 38–II**. The product **79** is finally formed through the acquisition of hydrogen atom from NHC–borane and regenerates the boryl radical. With DTBP as the radical initiator, a bridged borepin was obtained by the double *trans*-hydroboration of 11-membered cyclic 1,5-diynes with NHC–borane [114].

In the same year, the Lewis base–boryl radical triggered borylation/cyclisatin cascade reactions of 1,6-enyne derivatives **80** were developed by Wang group (Scheme 39) [86]. Compared to the cyclisation of 1,6-enynes in Scheme 23 employing AIBN as the radical initiator, the bory radical preferentially and exclusively adds to the carbon–carbon triple bond to form an alkenyl radical **Int 39–I** due to the stabilizing effect of aryl groups (13 examples, up to 81% yield). Under polarity reversal catalysis, the borylated six-membered nitro- and carbocyclic products **81** were generated in chemo- and regioselective fashion from feed stocks with aryl-substituted alkynes.

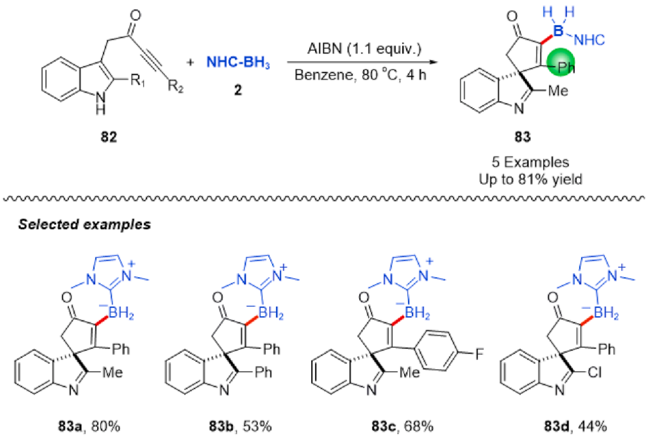
Recently, indole-ynones **82** were exploited as one kind of general skeleton towards functionalized spirocyclic compounds along with the formation of C–CN, C–$SO_2$R, C–$CF_3$, C–Sn, and C–B bonds by Unsworth and James *et al.* (Scheme 40) [115]. Under optimal conditions, the desired borylated spirocycles **83** were manufactured with yields ranging from 44% to 81% through the radical dearomatizing spirocyclisation



**Scheme 38.** Cascade radical borylative cyclisation of 1,5-diynes.



**Scheme 39.** Cascade radical borylative cyclisation of 1,6-enynes.

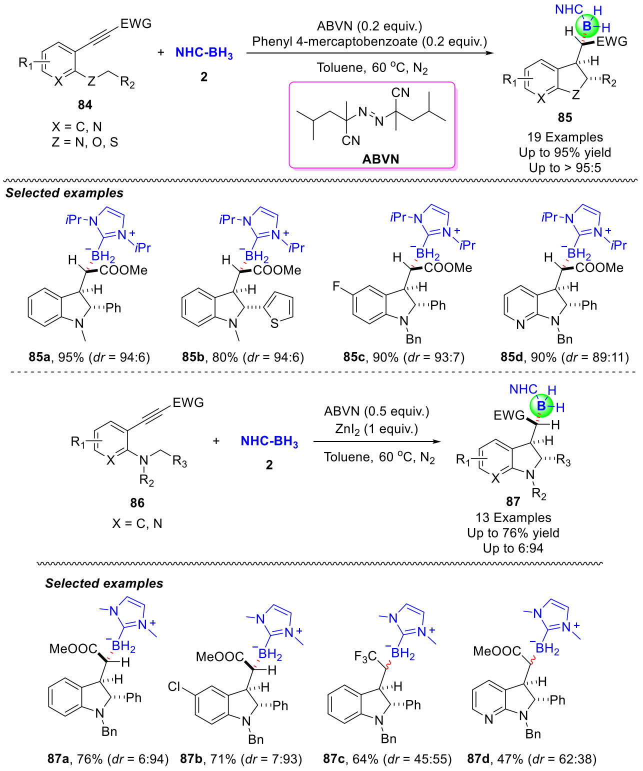


**Scheme 40.** Cascade radical borylative cyclisation of indole-ynones.

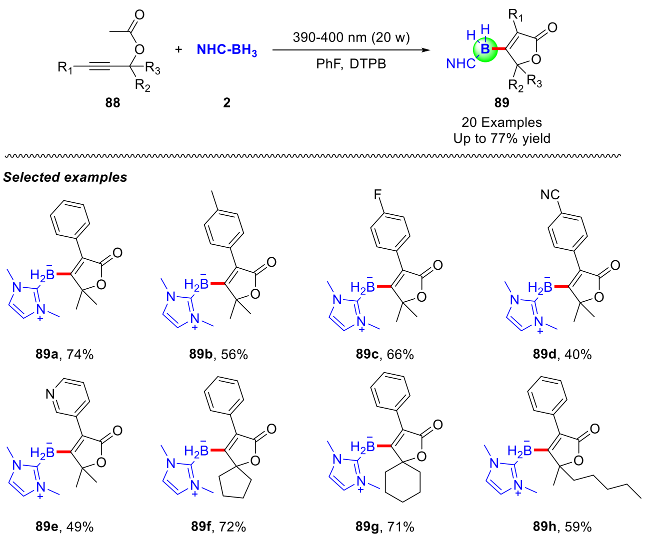
cascade reactions. Using NHC-borane as the coupling partner, NHC–boryl radical was generated in benzene at 80 °C with the assistance of stoichiometric AIBN. Mechanistically, the borylated alkenyl radical produced by the radical addition of NHC–boryl radical to carbon–carbon of ynones is proposed as the key reaction intermediate.

In the meantime, utilising the synergistic control tactics, Wang, Yu and co-authors realised the diastereodivergent synthesis of indoline skeletons **85** and **87** involving a boron-substituted stereocenter in good yields and diastereomeric ratio through the successive boryl radical addition, 1,5-H shift, and intramolecular 5-*exo* cyclisation sequences (Scheme 41) [116]. The HAT step is the key to controlling the stereochemistry of the target products. Experimental studies and DFT calculations revealed the origin of stereoselectivity of these two complementary ways, which was switched by the combination of NHC–BH$_3$/thiol catalyst or NHC–BH$_3$/Lewis acid.

In 2025, Liu and Ni realised the light-promoted radical borylation/lactonization cascade reactions of propargyl acetates **88** in the absence of a photocatalyst (Scheme 42) [117]. Under the irradiation of 20 W LEDs, various borylated furanone derivatives **89** were obtained in moderate to good yields (32%–77%).



**Scheme 41.** Cascade radical borylative cyclisation of arylpropiolates.



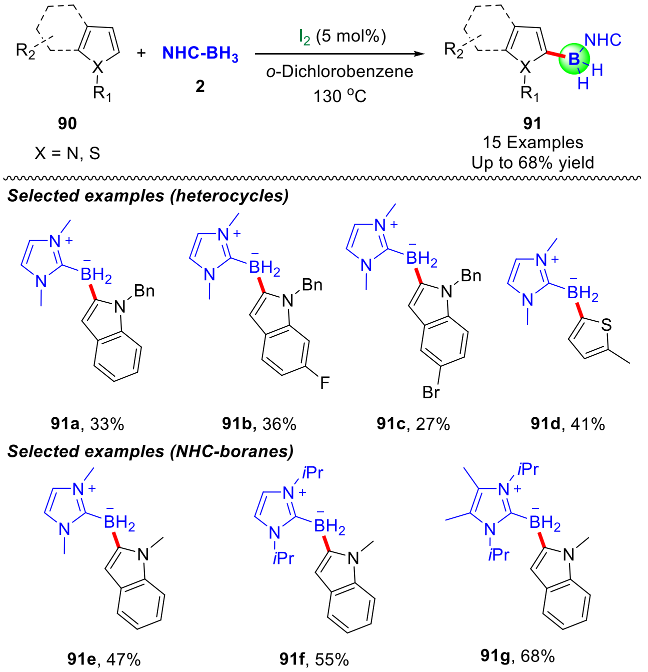
**Scheme 42.** Cascade radical borylative/lactonization of propargyl acetates.

## 4. C–B bond formation *via* borylation of arenes

### 4.1. Arylborylation via aromatic C–H bond cleavage

Catalytic regioselective functionalization of simple arenes and heteroarenes *via* direct C–H bond activation is one of the long-term research interests in the field of organic synthesis [118].

Inspired by Curran's work on C–B bond formation by direct C(alkenyl)–H bond borylation using catalytic amount of I$_2$ to activate the B–H bond of NHC–boranes [53], in 2017, Ingleson and co-authors described the direct electrophilic borylation of indole heterocycles **90** with total C-2 selectivity using NHC–BH$_3$ as the boron source through



**Scheme 43.** I$_2$-Catalysed C-2 selective borylation of indoles.

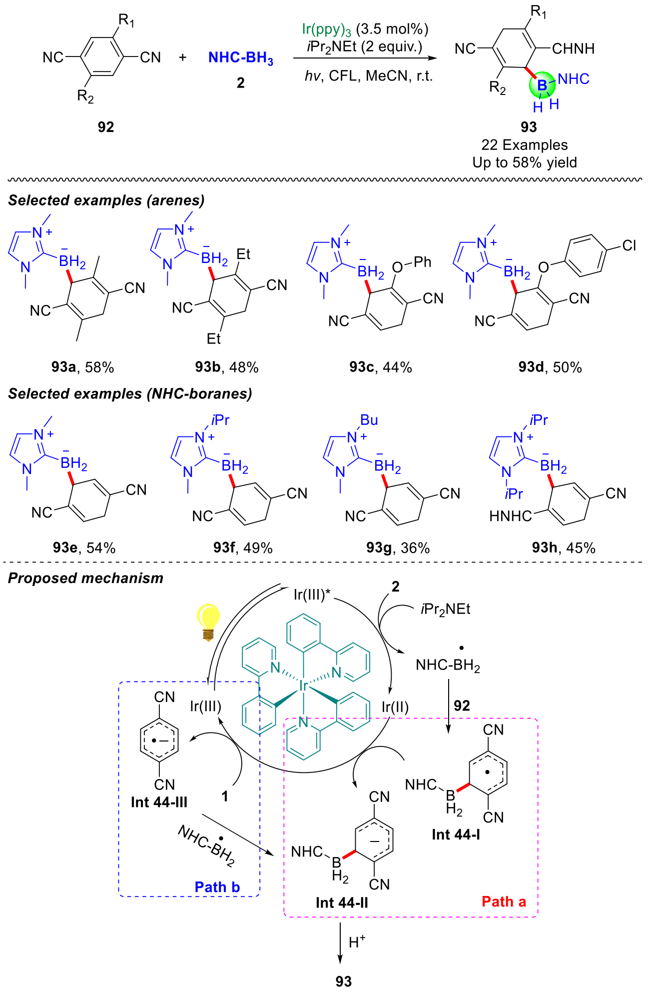
aromatic C–H cleavage under metal- and base-free conditions (Scheme 43) [119]. Using catalytic amount of $I_2$ (5 mol%) as the catalyst and activator is the key to ensuring the smooth formation of C2 isomeric borylated products **91**. In contrast, Brønsted acids such as HOTs, HCl, $CF_3COOH$, $HNTf_2$, and $B(C_6F_5)_3$ are inferior to $I_2$. Regrettably, this methodology only shows moderate reactivity (27%–41%), though NHC–boranes with moderate steric hindrance on nitrogen atom can slightly improve the isolated yields of target products up to 54%. Mechanistically, control experiments favored the catalytic cycle of $S_EAr$ involving C3 position electrophilic addition and C3 to C2 boron migration assisted with HI generated *in situ* as the Brønsted acid.

Based on the earlier work of MacMillan on photoredox aromatic substitution reaction [120], Curran *et al.* planned to probe the borylation reaction of electron-deficient arenes **92** through the cleavage of C–CN bond under a similar photochemical strategy. An unexpected 1,4-hydroborylated cyclohexadiene product was mainly obtained in 54% by the reaction of $IMe_2{\cdot}BH_3$ and 1,4-dicyanobenzene with $Ir(ppy)_3$ as the photocatalyst (Scheme 44) [121]. A variety of dearomatized 3-NHC–boryl-1,4-cyclohexadienes **93** with an alkyl C–B bond were obtained in moderate yields (up to 58% yield) from variable boranes and arenes. Notably, NHC–boranes are the only suitable boron sources, and the substitution reaction preferentially occurs at carbon atoms with high steric resistance for multisubstituted asymmetrical arenes.

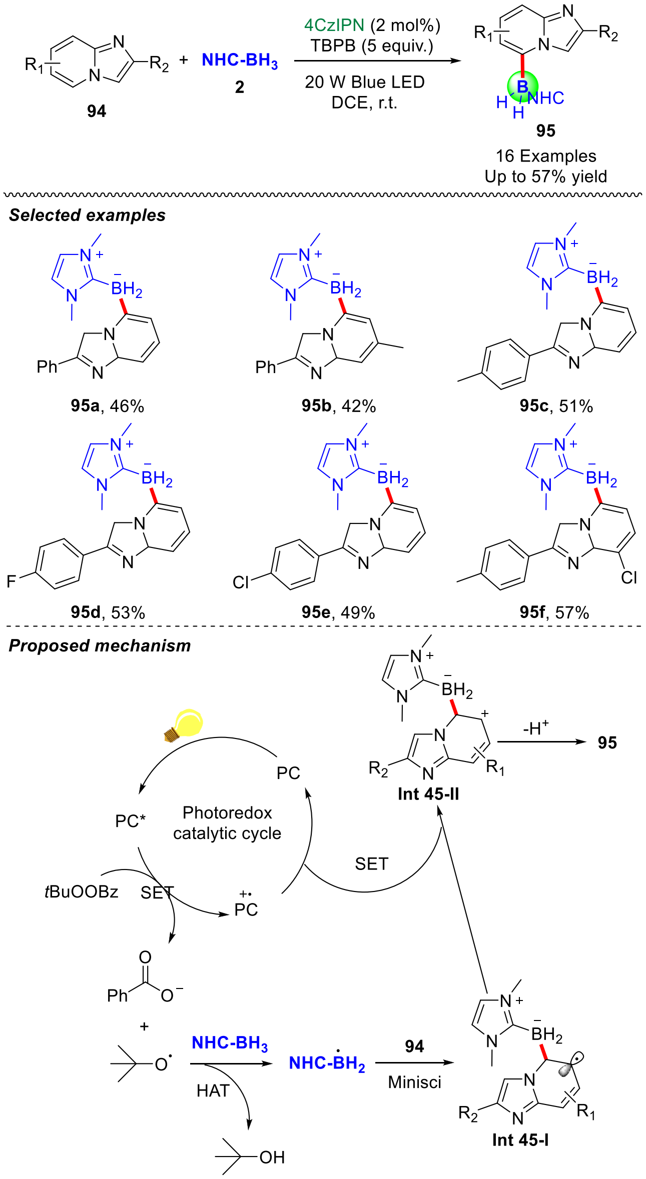
With regard to the reaction mechanism, the B–H bond is initially activated by the oxidation of NHC–$BH_3$ with excited-state Ir(III)* intermediate to deliver NHC–boryl radical, and the hydrogen atom of the last protonation step comes from water based on isotope labelling experiments. In view of the novel results including the unique regioselectivities of desired products, the exact mechanism is still unclear at present. Two possible pathways for the generation of the cyclohexadienyl anion **Int 44–II** are postulated including radical addition (path a) and radical/radical anion coupling (path b).

Recently, Cao and Liu group reported the completely C-5 selective borylation of imidazo[1,2-*a*]pyridine compounds **94** promoted by visible-light catalysis with 4CzIPN as the organic photosensitizer (Scheme 45) [122]. A variety of borylated pyridine derivatives **95** with good functional group compatibility were smoothly assembled in acceptable yields (28%–57%) utilising NHC–$BH_3$ as the coupling partner. Under standard conditions, N–B bond instead of C–B bond was formed when azines were employed as the starting materials.

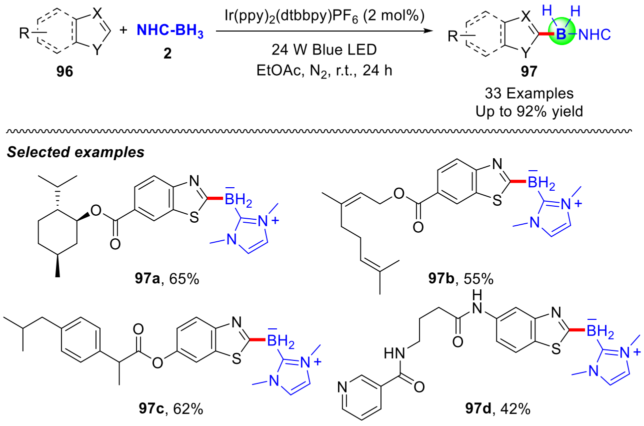
Radical trapping experiments favored the free radical procedure. The NHC–boryl radical is initially formed by the hydrogen atom transfer with the help of $^t$BuO. Then, the C-5 position of imidazo[1,2-*a*]pyridine **94** is attached by the boron radical following the Minisci-type mechanism to deliver the alkyl radical intermediate **Int 45–I**. The final coupling product **95** is constructed by successive oxidation and deprotonation.



**Scheme 44.** Photocatalytic 1,4-hydroborylation of electron-deficient (hetero)arenes.



**Scheme 45.** C-5 Selective borylation of imidazo[1,2-*a*]pyridines.



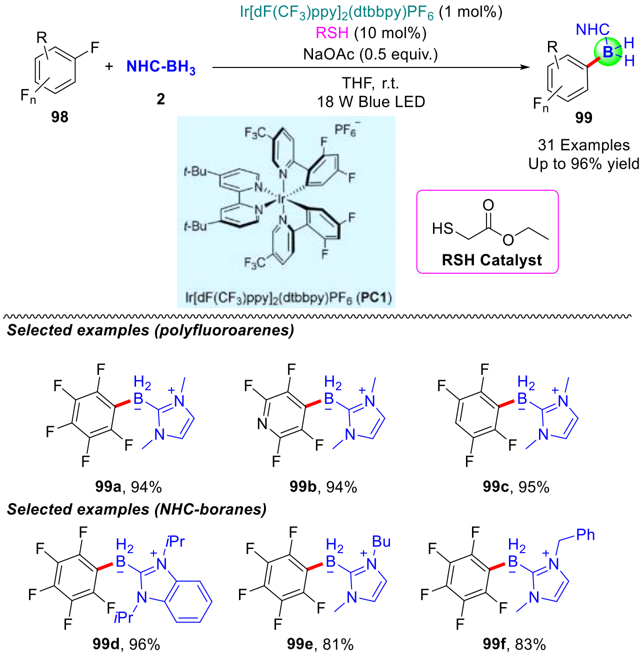
Scheme 46. Photocatalytic direct C–H borylation of azole heterocycles.

Very recently, Xuan and Koenigs realised the photocatalytic direct C–H borylation of 5-membered azole heterocycles **96** with NHC–boranes (Scheme 46) [123]. Under the irradiation of 24 W blue LED, azoles and boranes were activated in the assistance of Ir[III] complex as a photocatalyst. A series of C2-borylated heterocyclic compounds **97** were obtained in moderate to good yields. In addition, late-stage modification of bioactive benzothiazole derivatives and the transformation of borylated products show the broad application potential of this methodology.

### *4.2. Arylborylation via aromatic C–F/C–S bond cleavage*

Polyfluoroarenes are widely used in the areas of material science, biochemistry, and pharmaceutical chemistry. The transformation of polyfluoroarenes through C–F bond cleavage for example, defluoroborylation is an important route to prepare other value-added fluoro-containing aromatic compounds [124].

In 2020, Wu group described a photochemical approach for the synthesis of borylated polyfluoro aromatic and heteroaromatic hydrocarbon compounds from *N*-heterocyclic carbene borane adducts (Scheme 47) [92]. This defluoroborylation reaction was realised by the highly regioselective C–F bond activation enabled by visible light induced photoredox catalysis. Two cooperative photocatalytic systems were established independently by the combination of photoredox catalyst (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ or 4CzIPN) and hydrogen atom transfer catalyst (ethyl 2-mercaptoacetate or ethyl 2-mercaptopropanoate). Compared to the C–B bond formation by aromatic C–H activation mentioned above, the isolated yields of borylated products produced by the split of C–F bond improved significantly. A wide spectrum of boron-containing organofluorine compounds **99** (31 examples, up to 96% yield) were installed smoothly from variable penta-, tetra-, tri-, and difluoroarene starting materials.

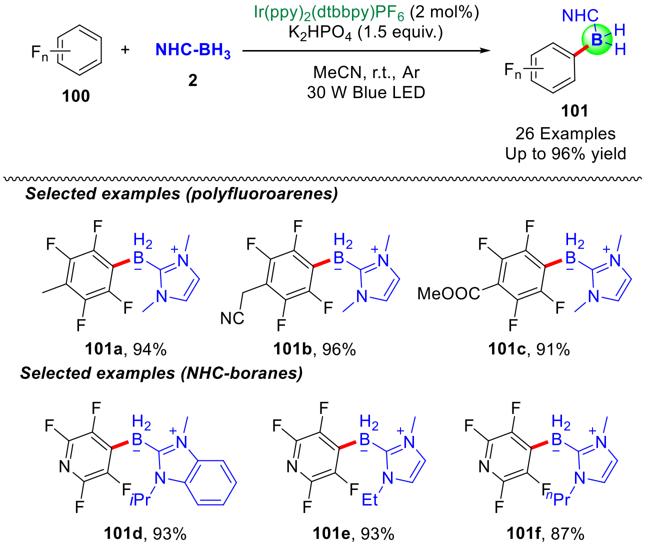


Scheme 47. Visible-light promoted defluoroborylation of polyfluoroarenes with Ir(III) and HAT catalyst.

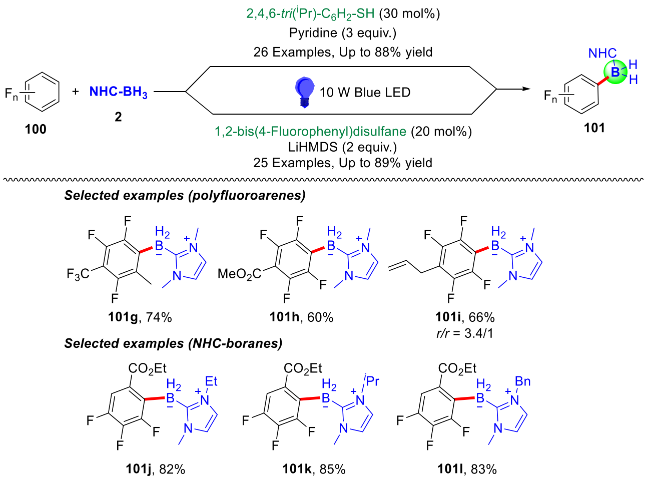
Later, following the photocatalytic C–F bond activation tactics, Yang and co-workers presented a similar work on C–B bond formation through the reaction of NHC–BH$_3$ and multifluoro substituted arene and pyridine derivatives **100** (Scheme 48) [125]. Compared to Wu's work [92], this protocol proceeded well with Ir(III) complex as the optimal photoredox catalyst under the irradiation of blue LED without the need of additional thiol as the hydrogen atom transfer catalyst, but with a much longer reaction time (48 h *versus* 12 h). Except NHC–BH$_3$, borane-pyridine complex could also be used as the coupling partner. After extensive control experimental research and DFT calculation, a feasible radical addition of NHC–boryl radical generated by single-electron-transfer to polyfluoroarenes is proposed as the reaction mechanism. The B–H bond break is the rate-determining step of the reaction in view of the KIE value of 3.3.

In the same period, a thermal initiated radical C–F bond activation was developed by Taniguchi and Curran [126]. With DTBP as the precursor of *t*-BuO radical, a sequence of borylated polyfluoroarenes were prepared in (trifluoromethyl)benzene at 120 °C in a sealed tube.

Very recently, the visible-light promoted defluoroborylation of polyfluoroarenes **100** under transition-metal photocatalyst free conditions was established by Chen and Liu et al. (Scheme 49) [127,128]. Sulfur-containing compounds such as aryl thiol and diaryl disulfide were selected as the catalysts to activate the B–H bond of NHC–boranes, and 2,4,6-triisopropyl-thiophenol and 1,2-bis(4-fluorophenyl)disulfane were optimized as the best choice. Under irradiation of blue LED in the presence of pyridine or LiHMDS (lithium bis(trimethylsilyl)amide) as the bases, various substituted polyfluoroarenes **101** attaching CF$_3$, esters, Cl, ketone, CN, Me, MeO, allyl and so on, are well compatible with moderate to good yields (32%–89% yields). EPR and radical trapping experiments indicated that the radical pathway was involved in the reaction mechanism, and the radical-adduct product of boryl radical and TEMPO was firmly demonstrated by HRMS analysis.

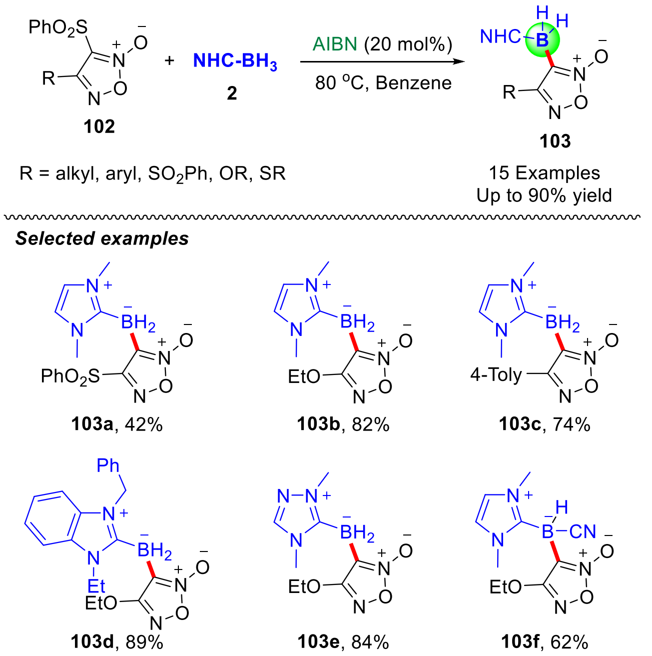


Scheme 48. Visible-light promoted defluoroborylation of polyfluoroarenes with Ir(III) photocatalyst under HAT catalyst free conditions.

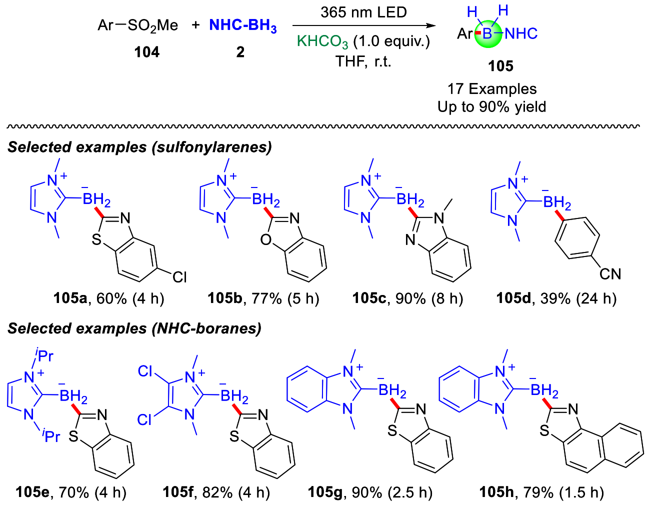


**Scheme 49.** Visible-light promoted defluoroborylation of polyfluoroarenes with aryl thiol or diaryldisulfane.

Catalytic C–C and C–X bond formation through selective C–S bond activation and cleavage is among the most powerful and reliable tools in organic synthesis [129]. In 2021, Matsubara and collaborators developed the desulfurative borylation example of C–B bond formation through the reaction of phenylsulfonyl modified furoxans **102** with NHC–$BH_3$ complexes (Scheme 50) [130]. This protocol takes advantage of AIBN as the radical initiator to yield the NHC–boryl radical by way of the hydrogen atom abstraction. All kinds of imidazole-, benzimidazole-, and triazole-based NHC–$BH_3$, as well as pyridine-$BH_3$, are suitable boron radical sources. The unique regioselectivity for boron radical addition at the 3-position was observed, which is consistent with their previous study on C–C bond formation by carbon radical addition to furoxan heterocycle catalysed by $AgNO_3/K_2S_2O_8$ system [131]. However, the introduction of phenylsulfonyl to C3 position of furoxan cycles by multistep preparation limits the scope of borylated products, only $PhSO_2$-, EtO-, EtS-, 4-$MeC_6H_4$-, and $PhCH_2CH_2CH_2$- substituents at C4 position could be tolerated. The desired borylfuroxan products **103** could be conveniently converted into various 1,2-dioxime analogues, which have extensive application prospects in the fields of organic synthesis, coordination chemistry, pharmaceutical molecular design and so on.



**Scheme 50.** C–B Bond formation by thermal initiated radical desulfurization borylation.

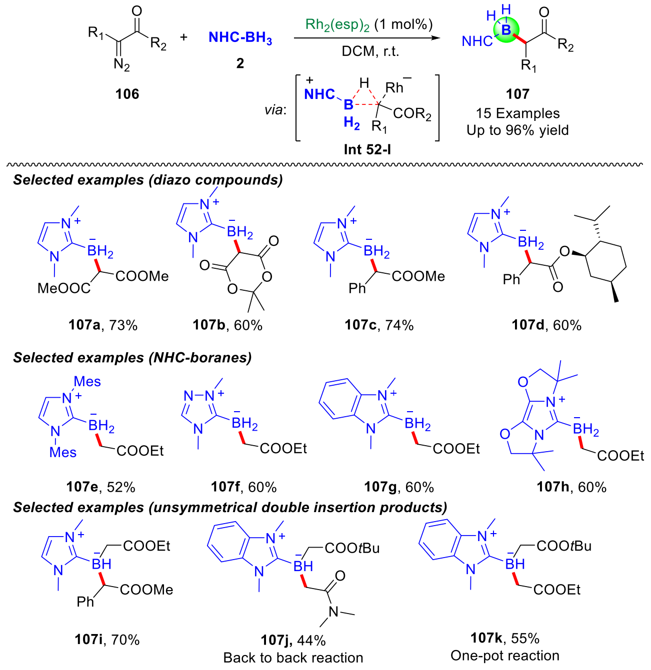


**Scheme 51.** C–B Bond formation by photoinduced radical desulfurization borylation.

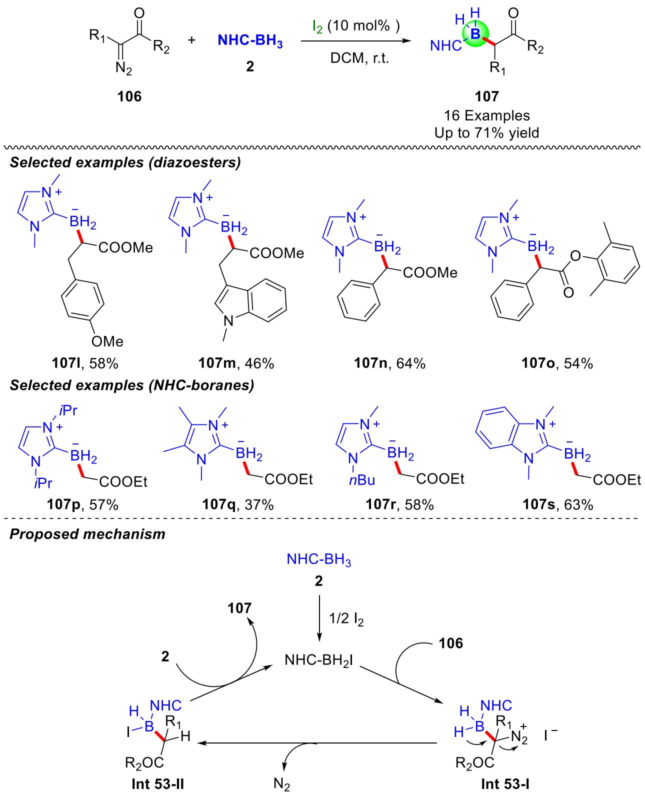
Very recently, Taniguchi and Shirakawa group reported the photoinduced B–H arylation of NHC–boranes with sulfonyl(hetero)arenes **104** without additional photocatalyst (Scheme 51) [132]. Under the irradiation of 365 nm LED, the B–H and C–S bonds were cleaved to form the new C–B bond in 32%–90% yields (17 examples). $KHCO_3$ was used as the base to neutralize the acidity byproduct.

## 5. C–B bond formation *via* borylation of diazo compounds

Diazo compounds are significant and versatile building blocks, which can participate in various chemical transformations through catalytic X−H insertions and cyclopropanations involving carbene intermediates [133].

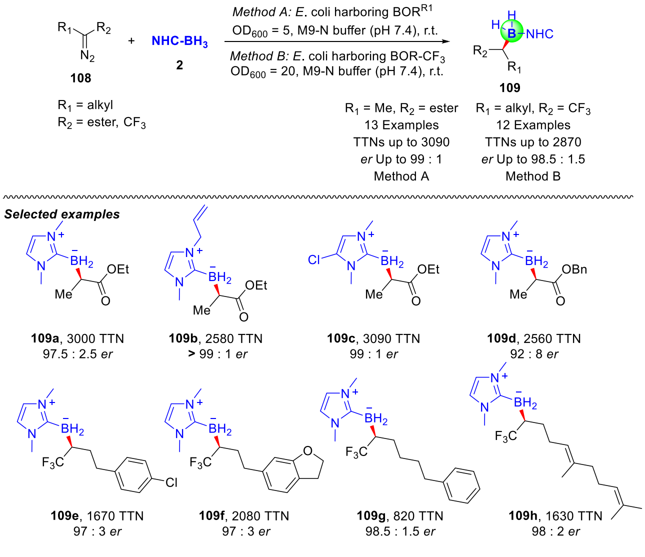


**Scheme 52.** Rh(II)-catalysed B−H insertion of NHC–$BH_3$ to diazocarbonyl compounds.

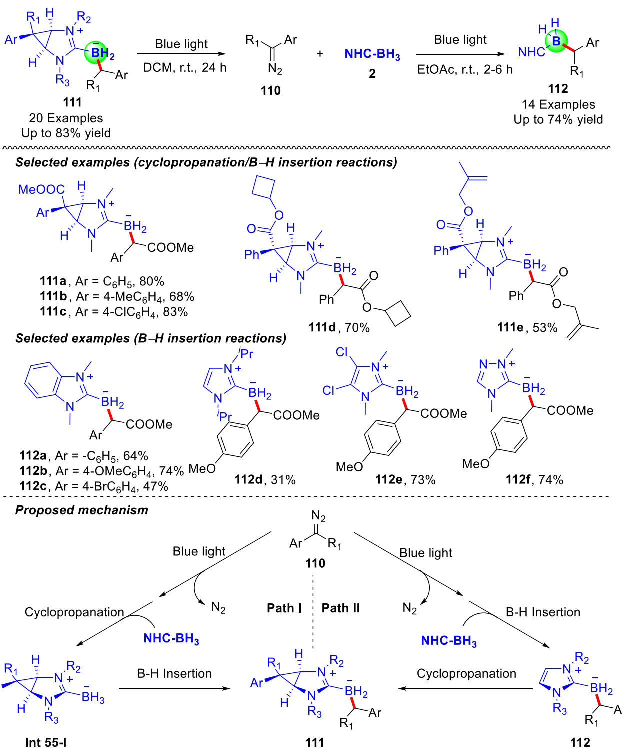


**Scheme 53.** $I_2$-Catalysed B−H insertion of NHC–$BH_3$ to diazoesters.

In 2013, Curran and co-workers reported the formation of C−B bonds through B−H insertion of *N*-heterocyclic carbene borane to rhodium carbenes derived from rhodium(II) catalyst and diazocarbonyl compounds **106** (Scheme 52) [134]. A concerted transition state containing the hydride abstraction (B−H activation) and C−B bond construction is proposed to rationalise the reaction pathway. This method has a broad substrate scope and good compatibility of functional groups. Various diazo compounds (diazoesters, diazoamides, and diazoketones) and NHC–boranes are well compatible (15 examples, 26%–96% yields). In addition, the unsymmetrical double insertion products can also be prepared smoothly.



**Scheme 54.** Enzyme-catalysed B−H insertion of NHC–$BH_3$.

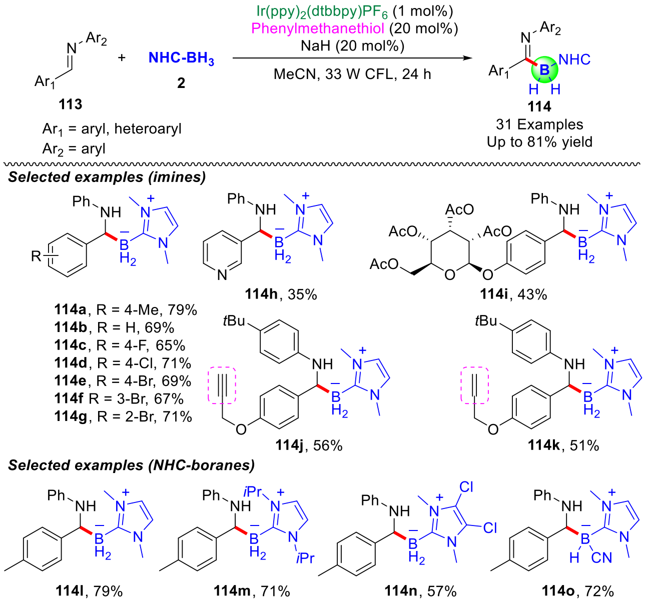


**Scheme 55.** Visible-light enabled B−H insertion of NHC–$BH_3$ to diazo compounds.

In 2017, the same research group realised the $I_2$-catalysed B−H insertion of NHC–$BH_3$ to diazo compounds (Scheme 53) [135]. This protocol avoids the transition-metal catalyst utilising diiodine as the activator and precatalyst, making the reaction much cheaper and more environmentally friendly. Initially, NHC–$BH_2I$ generated by the reaction of NHC–boranes and iodine is viewed as the real catalyst [54]. Then, the borylation of diazo compounds **106** generates the key *α*-NHC–boryl diazonium iodide intermediate **Int 53–I**, which undergoes hydride shift to give the boryl iodide **Int 53–II** with the release of $N_2$. Finally, the corresponding borylated product **107** is obtained after hydride exchange. This protocol also has good compatibility with diazo compounds and NHC–boranes, albeit diazo compounds are restrict to diazoester derivatives.

In 2017 and 2019, Arnold group reported the biocatalytic strategies for building chiral C−B bond through enzyme-catalysed B−H insertion of NHC–$BH_3$ to diazo compounds **108** (Scheme 54) [136,137]. Employing *Rhodothermus marinus cytochrome c* (*Rma cyt c*) as a highly versatile platform, the desired chiral organoborons **109** were obtained with high enantioselectivity.

Adopting visible-light irradiation as the activation tactic, in 2022, Xuan and Koenigs *et al.* developed a chemoselective photochemical carbene transfer reaction of diazoalkanes **110** with NHC–boranes under photocatalyst free conditions (Scheme 55) [138]. From simple imidazolium-based NHC–boranes, with the irradiation of blue light for 24 h, the difunctionalized products **111** were preferentially constructed by cascade cyclopropanation and B−H insertion reactions (20 examples, 36%–83% yields). From NHC–boranes blocked the imidazole ring, the B−H insertion products **112** were selectively formed within 2 h. This reaction exhibited a wide substrate scope and excellent functional group tolerance towards diazo compounds and NHC–boranes (14 examples, 17%–74% yields). Control experiments and DFT calculations favored that this methodology passed through cyclopropanation/B–H insertion sequence (**Path I**).

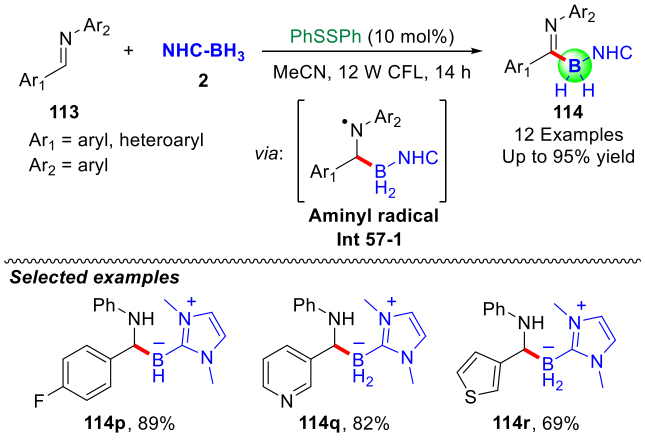


**Scheme 56.** Hydroborylation of imines by synergistic photoredox- and organocatalysis.

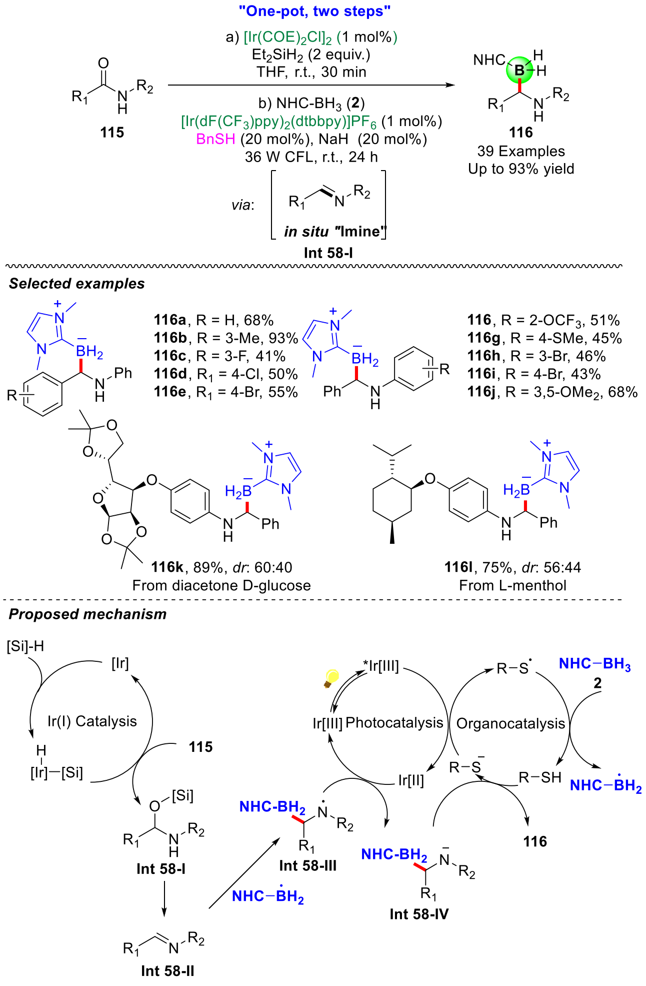
## 6. C–B bond formation *via* borylation of imines, amides, and isocyanides

In previous work, hydroboration was the main reaction for C=N bond reduction to amine. During this process, intermediates with N–B bonds are usually generated. However, there are few reports on inverse hydroboration with the formation of C–B bond.

In 2018, by a combination of photocatalysis and organocatalysis, the first synergistic catalytic system for C–B bond formation through inverse hydroboration of imines with NHC–boranes was reported by Zhu and Xie's group (Scheme 56) [139]. This protocol uses Ir(ppy)$_2$(dtbbpy)PF$_6$ as the photocatalyst and phenylmethanethiol as the organocatalyst. According to blank experiments, the Ir(III) complex, thiol catalyst, and light source are indispensable; no hydroborylation product was monitored. A series of aldimines **113** prepared from (hetero)aromatic aldehydes and arylamines were smoothly borylated at carbon atoms of C=N double bonds, delivering structurally diverse $\alpha$-aminoboron compounds **114** in 31%–81% yields. Remarkably, substrates concurrently containing C=N and C=C (or C$\equiv$C) bonds were regioselectively borylated at carbon–nitrogen double bond, leaving the carbon–carbon double and triple bonds intact.



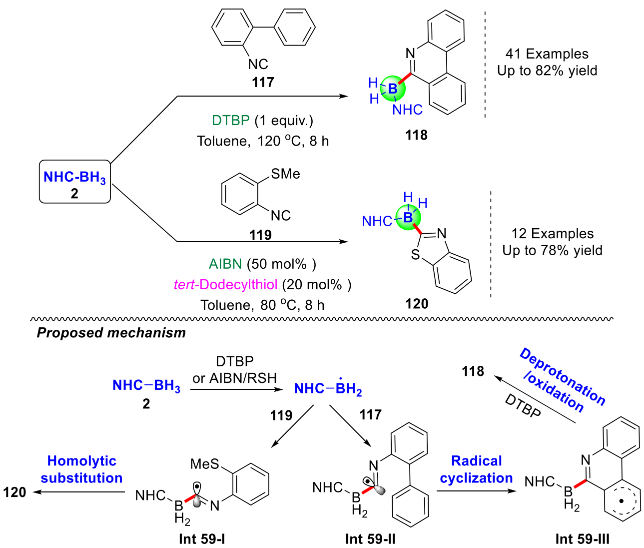
**Scheme 57.** Hydroborylation of imines promoted by organic photocatalysis.



**Scheme 58.** Deoxygenative radical borylation of inert amides.

Interestingly, in 2021, Kawamoto and co-workers realised a similar inverse radical hydroboration procedure of aromatic aldimines **113** with NHC-borane under visible light, enabling organic photocatalysis with the irradiation of 12 W CFL for 14 h (Scheme 57) [140]. Unlike Zhu and Xie's work [139], employing diphenyl disulfide as the screened organocatalyst, this protocol successfully achieved the building of C–B bond with better isolated yields (31%–81% *versus* 69%–99%) and higher reaction efficiency (14 h *versus* 24 h) in the absence of transition-metal photocatalyst.

Recently, Wang group reported the facile synthesis of $\alpha$-amino boron compounds **116** through borylation of carbon–nitrogen double bond of "imines" generated *in situ* from amides **115** (Scheme 58) [141]. This methodology includes two steps in fact: semi-reduction of amides and borylation of *in situ* "imines" enabled by photocatalysis. In the first step, Ir(I) complex ([Ir(COE)$_2$Cl]$_2$) was selected as the catalyst in the presence of Et$_2$SiH$_2$ as the reducing. In the second step, [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ and BnSH were used as the best cooperative catalytic system. Wide substrate scope, good functional group tolerance, and late-stage modification of complex amide architectures highlight the potential application prospects of this protocol. A possible reaction mechanism is proposed as follows: the *in situ* "imines" intermediate **Int 58–II** is primarily obtained by Ir-catalysed semi-reduction of intermediate **Int 58–I** with the silane. Then, the addition of NHC–boryl radical to "imines" intermediate to furnish the key amino radical species **Int 58–III,** which underwent further reduction and protonation to form the final C–B coupling product **116**.



**Scheme 59.** Cascade radical borylative cyclisation of isocyanides.

In 2021, Wang and co-workers reported an example of synthesis of borylated 5- or 6-membered heteroaromatic compounds by means of the radical borylative cyclisation of isocyanide precursors (Scheme 59) [142]. With DTBP as the initiator, 2-isocyano-1,1′-biphenyl analogues **117** and NHC–boranes were refluxed in toluene at 120 °C for 8 h to furnish borylated phenanthridines **118** with up to 82% yield. Switching the initiator to AIBN/thiol, 2-isocyanoaryl thioethers **119** were converted into borylated benzothiazole compounds **120** in 28%–78% yields. Mechanistically, the NHC–boryl radical is firstly formed under thermal conditions. Then, radical addition of boryl radical to the carbon atom of isocyano groups forms the borylimidoyl radical intermediate **Int 59–I** and **Int 59–II** with a new C–B bond, respectively. Six-membered heterocyclic phenanthridine **118** was obtained by a continuous radical borylative cyclisation/deprotonation/oxidation sequence. While homolytic substitution at the sulfur atom afforded the target five-membered benzothiazole **120**.

## 7. Conclusion and perspectives

Driven by the versatile reactivity, unique photophysical and photochemical properties, and rich biological activities of organoboron compounds, many efforts have been devoted to the synthesis of boron-containing compounds with C–B bonds. Various B–H activation strategies have been developed employing transition-metal complexes, organic amines, iodine, or radical initiators. Recently, by using bench-stable NHC–boranes as borylation reagents, diverse coupling partners—including alkenes, alkynes, arenes, diazo compounds, imines, amides, and isocyanides—have been efficiently borylated to access structurally novel organoboron derivatives that are challenging to prepare by traditional methods.

Although significant advances have been achieved in this field, research on the borylation of various precursors with NHC–boranes is still in its infancy. Firstly, future efforts should focus on expanding the range of coupling partners—such as electron-rich alkenes, *N*-heterocycles, and aliphatic hydrocarbons—to access novel bond formations and structural diversity. Secondly, it is highly desirable to conduct in-depth studies on the reaction mechanism, which will benefit the establishment of the general methodologies for the synthesis of complicated molecules. Thirdly, the asymmetric borylation using NHC–boranes for the synthesis of chiral organoboron compounds has not yet been studied. Moreover, the integration of electrochemical organic synthesis, flow chemistry, mechanochemistry, and artificial intelligence represents a future trend and deserves more attention from the scientific community. The recent discovery of visible-light-promoted alkene difunctionalization with NHC-boranes (*e.g.*, borylation/pyridylation and borylation/acylation) enables concurrent C–C and C–B bond formation, opening new research avenues [143,144]. Overall, NHC–borane chemistry is a rapidly evolving field, and this review aims to promote further development, uncover new applications, and deepen mechanistic understanding of these reactions.

## CRediT authorship contribution statement

**Weiwei Jin:** Writing – review & editing, Writing – original draft, Conceptualization. **Zhen Cheng:** Writing – review & editing, Writing – original draft. **Hong Chang:** Resources, Data curation. **Xiaoqin You:** Resources, Data curation. **Fangfei Zhou:** Resources, Data curation. **Shiyi Zhuang:** Resources, Data curation. **Huaxian Jin:** Resources, Project administration. **Chenjiang Liu:** Supervision, Project administration, Conceptualization. **Jun Xuan:** Writing – review & editing, Supervision, Project administration, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gresc.2025.09.002.

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