Photocatalysis

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Visible-Light-Induced Selective Defluoroborylation of Polyfluoroarenes, *gem*-Difluoroalkenes, and Trifluoromethylalkenes

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Abstract: *Fluorinated organoboranes serve as versatile synthetic precursors for the preparation of value-added fluorinated organic compounds. Recent progress has been mainly focused on the transition-metal catalyzed defluoroborylation. Herein, we report a photocatalytic defluoroborylation platform through direct B−H activation of N-heterocyclic carbene boranes, through the synergistic merger of a photoredox catalyst and a hydrogen atom transfer catalyst. This atom-economic and operationally simple protocol has enabled defluoroborylation of an extremely broad scope of multi-fluorinated substrates including polyfluoroarenes, gem-difluoroalkenes, and trifluoromethylalkenes in a highly selective fashion. Intriguingly, the defluoroborylation protocol can be transition-metal free, and the regioselectivity obtained is complementary to the reported transition-metal-catalysis in many cases.*

Introduction

Approximately 20% of all pharmaceuticals and 30% of all agrochemicals contain carbon–fluorine bonds.[1] There is currently an increasing demand for introduction of fluorinated building blocks into organic frameworks, and compounds of this sort have found a wide range of applications in the development of novel pharmaceutical agents,[2] insecticides,[3] catalysts,[4] and materials.[5] However, fluoroaromatic and vinyl fluoride compounds do not exist naturally and must be synthesized.[6] Despite spectacular advances in single-site catalytic fluorination, synthetic access to polyfluorinated compounds in a selective fashion is still challenging.[7] In this context, fluorinated organic boranes can serve as versatile synthetic precursors to obtain distinct organic fluorides through a wide spectrum of established and reliable derivatization reactions.[8] The most straightforward way to access fluorinated organic borane building blocks is selective C−F bond borylation of polyfluorinated organic compounds. However, this is inherently challenging for several reasons: 1) The C−F bond is among the most unreactive functional groups. 2) The high bond energy of metal-fluorine intermediates can lead to sluggish catalytic turnover in transition-metal-catalyzed C−F activation. 3) Boron reagents are fluorophilic and serve as fluorine scavengers in C−F derivatization.

Most success in catalytic defluoroborylation so far has relied on catalysis by transition-metal, including Rh,[9] Ni,[10] Cu,[11] Co,[12] and Fe-based[13] catalysis (Scheme 1 a). However, higher temperatures are generally required in these reactions, and stoichiometric metallic additives are often employed to scavenge the fluoride ions generated in situ. Photocatalysis has witnessed dramatic developments over the past decade which have enabled previously inaccessible synthetic transformations.[14] In particular, photolytically-induced borylation of C−F bonds in electron-rich monofluoroarenes has been realized by Li[15] and by Larionov[16] though the formation of triplet aryl cations by the heterolysis of C(sp^2)−F bonds using strong ultraviolet (UV) light. Very recently, the group of Guo, Radius, Steffen, and Marder demonstrated a visible-light-promoted C−F borylation protocol that employs a Rh photosensitizer to accelerate the difficult transmetalation step in the nickel-catalyzed C−F activation.[17]

Polyfluorinated arenes and alkenes have been applied to C−C bond formation by photocatalytic C−F bond functionalization. Weaver et al. have achieved a variety of C−C couplings of perfluoroarenes with alkenes, alkynes, arenes, and prenyl reagents by photoredox catalysis.[18] This coupling was initiated by polyfluoroaryl radicals generated through light-promoted single electron reduction of polyfluoroarenes followed by extrusion of fluoride (Scheme 1 b). Remarkably, Xie, Hashmi and co-workers recently demonstrated a photo-mediated mono-defluoroalkylation of *gem*-difluoroalkenes using *N*-aryl amines by a radical–radical coupling pathway.[19a] They subsequently expanded the scope to polyfluoroarenes for controllable defluoroalkylation (Scheme 1 b).[19b] The Molander group achieved a fascinating synthesis of *gem*-difluoroalkene moieties by photoredox-induced carbon radical addition to α-trifluoromethylalkenes.[20]

On the other hand, the development of boron-centered radical chemistry has recently gained increasing momentum,

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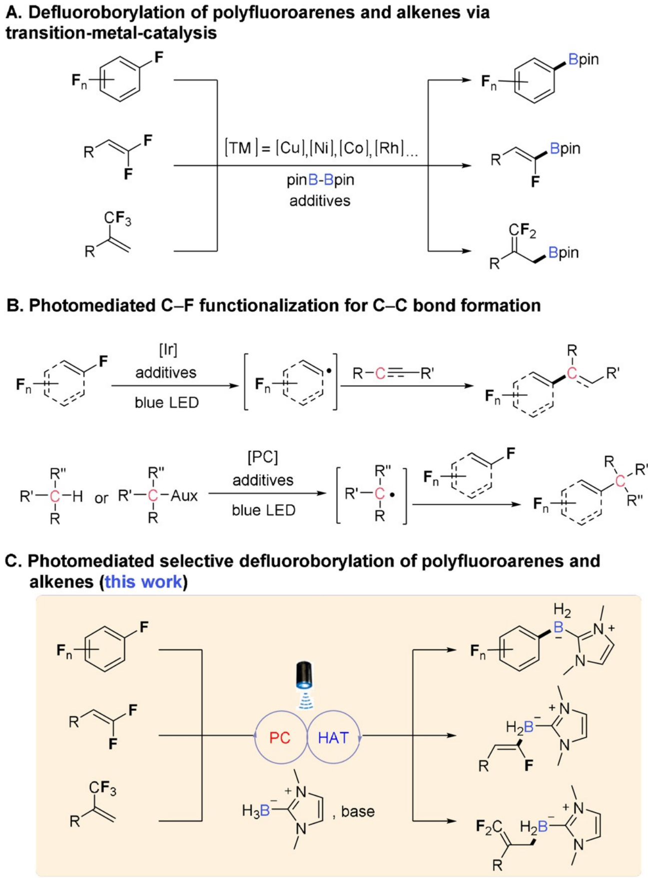


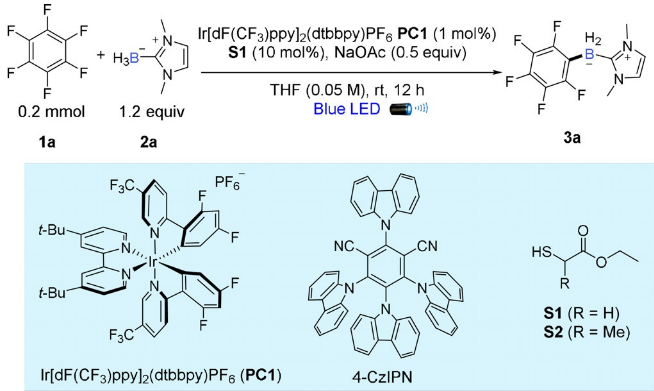
Scheme 1. C–F bond activation of fluoroarenes and alkenes. TM = transition-metal catalyst; pinB-Bpin = bis(pinacolato)diboron; PC = photocatalyst; HAT = hydrogen atom transfer; LED = light-emitting diode.

and is conceptually appealing because it may offer regio- or stereoselectivities different from those of transition-metal-catalysis.[21] Elegant work from Fensterbank, Lacôte, Malacria, and Curran has shown that N-heterocyclic carbene (NHC)–boryl radicals can be generated by hydrogen atom abstraction from NHC–BH_3 complexes,[21a,22] which are powerful intermediates useful in building a wide range of value-added boron compounds. For instance, Wang has developed radical borylation/cyclization cascade of 1,6-enynes with NHC–BH_3,[21c] and Curran and Taniguchi reported the Sato–Myers cyclization triggered by NHC–boryl radicals.[22d] Consistent with our continuing interest in development of atom-economic and redox-neutral transformations through hydrogen atom transfer (HAT)-based photocatalysis,[23] we envisioned that a photo-mediated catalytic HAT process with NHC–BH_3 might deliver the boryl radical in a mild pathway, which could react with polyfluoroarenes and alkenes to introduce synthetically valuable fluorinated organic boranes (Scheme 1c). Notably, Lacôte and Lalevée developed visible-light induced NHC–boryl radical formation through a HAT process with thiyl radicals.[22c] During the course of our investigation, the group of Xie and Zhu has reported an elegant study on photocatalytic version of this reaction to realize the inverse hydroboration of imines.[24]

Results and Discussion

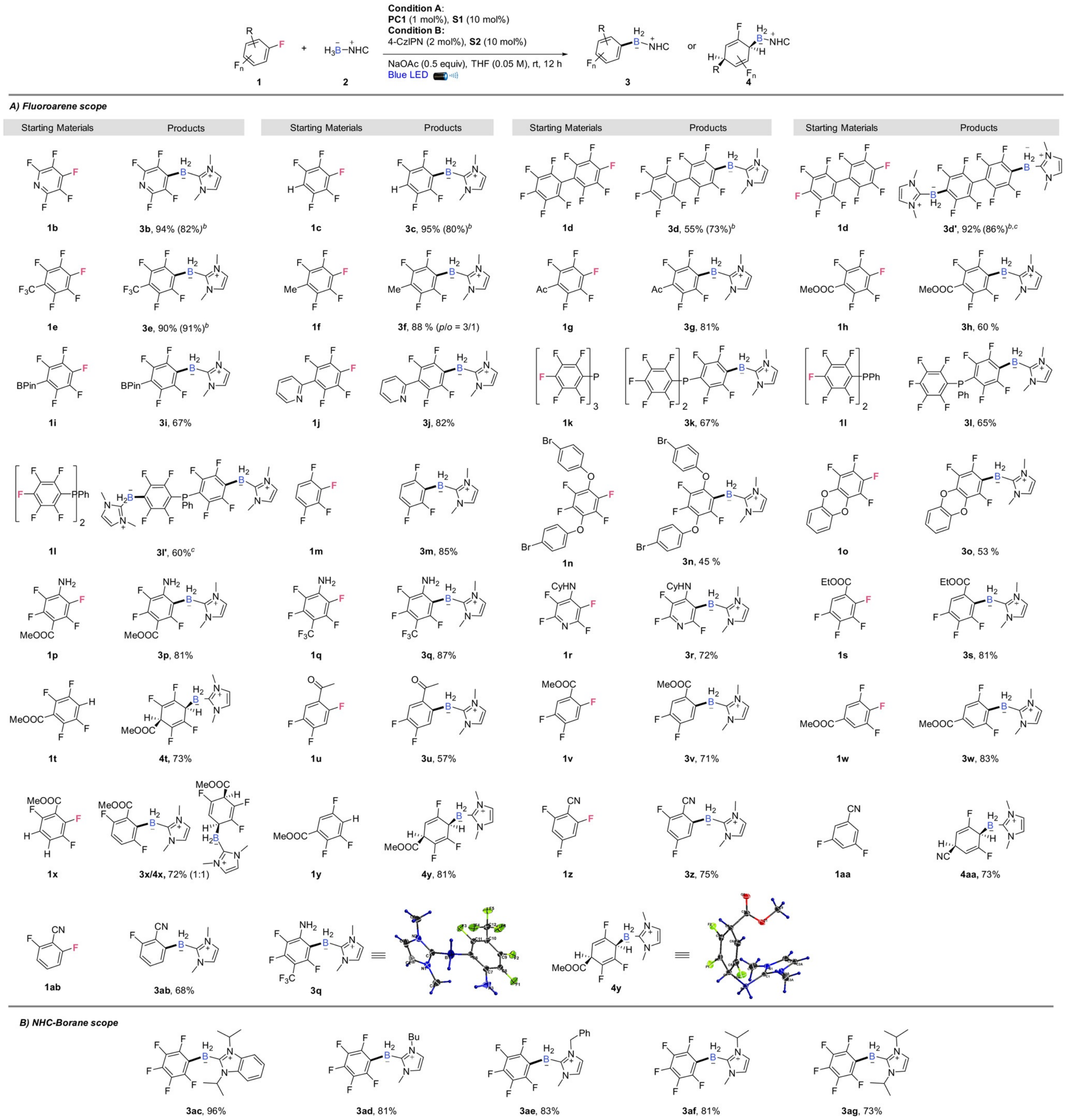
Our investigation was initiated with examination of the defluoroborylation of hexafluorobenzene (**1a**) with NHC–borane **2a** as the model substrates in the presence of a photoredox catalyst and a HAT catalyst under blue LED irradiation. After extensive evaluation (Table 1 and Table S1 in the Supporting Information), we established that a combination of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (**PC1**) (1 mol%), thiol (**S1**) (10 mol%), and NaOAc (0.5 equiv) in THF (0.05 M) at ambient temperature was optimal and produced the desired defluoroborylation product (**3a**) in 94% isolated yield (Table 1, entry 1). Increasing the catalyst loading to 2 mol% gave a similar yield (entry 2). Ir(ppy)$_3$, which was previously employed in Weaver's photocatalytic hydrodefluorination,[25] showed no catalytic activity in the defluoroborylation (entry 3). Other Ir photocatalysts, such as Ir(ppy)$_2$(dtbbpy)PF_6 and Ir(dFppy)$_2$(dtbbpy)PF_6 exhibited much lower efficiency (entries 4 and 5). Moderate yield could be obtained by using the organic dye, 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) as the photocatalyst, which possesses redox properties similar to those of **PC1** (entry 6).[26] The yield can be improved to 90% by replacing the thiol HAT catalyst **S1** with **S2**, enabling an effective transition-metal-free photo-

Table 1: Condition optimization for photo-mediated defluoroborylation of polyfluoroarenes.



Entry	Deviation	Yield of 3a[a]
1	none	94[b]
2	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.0 mol%)	93
3	Ir(ppy)$_3$ instead of **PC1**	0
4	Ir(ppy)$_2$(dtbbpy)PF_6 instead of **PC1**	88
5	Ir(dFppy)$_2$(dtbbpy)PF_6 instead of **PC1**	87
6	4CzIPN (2 mol%) instead of **PC1**	76
7[c]	4CzIPN (2 mol%) instead of **PC1**	90
8	without light or **PC1**	0
9	without **S1**	16
10	without base	68

Reaction conditions: hexafluorobenzene (**1a**, 0.20 mmol), NHC–borane (**2a**, 0.24 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (**PC1**, 1 mol%), **S1** (10 mol%), NaOAc (0.10 mmol), THF (4 mL), 18W blue LED irradiation, room temperature, 12 h. [a] Yields were determined by analysis of the crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. [b] Yields of isolated products. [c] **S2** was used instead of **S1**. THF = tetrahydrofuran.



Scheme 2. Scope of photo-mediated selective defluoroborylation of polyfluoroarenes.[a] [a] Yields of isolated products. Product was produced as a single regioisomer unless otherwise noted. Condition A was employed unless otherwise noted. [b] Condition B was employed. [c] **2a** (2.4 equiv) was used.

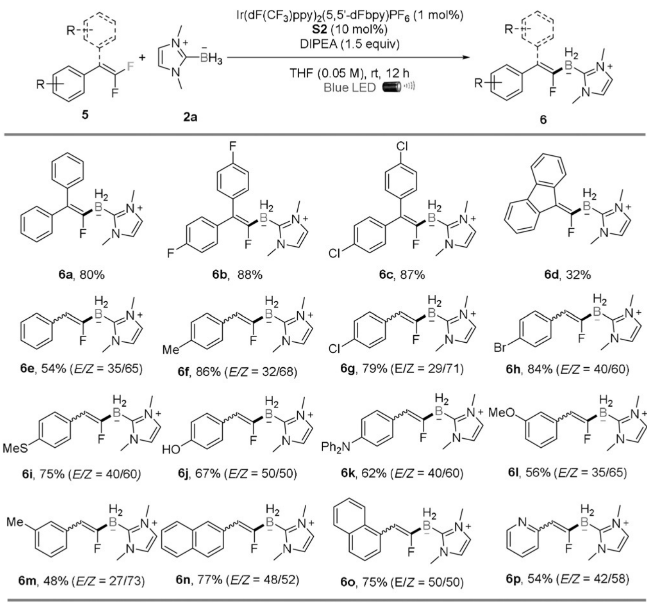
catalytic defluoroborylation protocol (entry 7). Control experiments demonstrated that light, photocatalyst, thiol, and base were all essential for efficient defluoroborylation (entries 8–10).

With the optimal photo-induced defluoroborylation conditions in hand, we explored the substrate scope using the Ir photocatalyst-based protocol (Condition A) or the transition-metal-free protocol (Condition B) (Scheme 2). A series of pentafluoroarene derivatives underwent regioselective defluoroborylation efficiently (**1b**–**1l**). Notably, the transition-metal-free protocol (Condition B) afforded products (**3b**–**3e**) in yields comparable to those obtained with the Ir protocol (Condition A), demonstrating a practical strategy to prepare fluorinated organic boranes in a transition-metal-free manner. Functionalities such as a trifluoromethyl group (**3e**), ketone (**3g**), ester (**3h**), boronic ester (**3i**), pyridine (**3j**), and phosphine (**3k**, **3l**) were well-tolerated. Diborylation could be selectively achieved in good yields using 2.4 equivalents of

NHC-borane (**3d′**, **3l′**). 1,2,3,4-Tetrafluorobenzene was defluoroborylated in excellent regioselectivity to deliver product **3m** in 85 % yield. Tetrafluorobenzenes bearing functional groups such as aryl bromides and benzyl ethers also participated in the defluoroborylation to afford **3n** and **3o** in 45 % and 53 % yield, respectively. Tetrafluorobenzenes containing an amine substituent underwent defluoroborylation selectively at the *ortho*-position to the amino group (**3p**–**3r**). The regioselectivity was confirmed by crystallographic analysis of the product **3q**.[27] Defluoroborylation of ester-substituted tetrafluoroarenes occurred exclusively at the position *ortho* to the ester group (**3s**). Importantly, the substrate scope could be successfully expanded to trifluoroarenes and even difluoroarenes substituted with electron-deficient functionalities such as ketone (**3u**), ester (**3v**–**3x**), and nitrile (**3z** and **3ab**) in a highly selective fashion. Surprisingly, hydroborylation occurred to produce dearomatization products (**4t**, **4x**, **4y**, and **4aa**) in good yields as a single diastereomer if the *para*-position of an electron-withdrawing functional group (ester and nitrile) was unsubstituted in the polyfluoroarenes. The stereo-configuration of **4y** was identified by X-ray crystallographic analysis, illustrating a *trans* hydroborylation,[28] and the structures of other dearomatization products were assigned by analogy. The scope for NHC-boranes was subsequently evaluated. Various NHC–boranes more sterically hindered than **2a** were good candidates, giving products **3ac**–**3ag** with 73 % to 96 % yields.

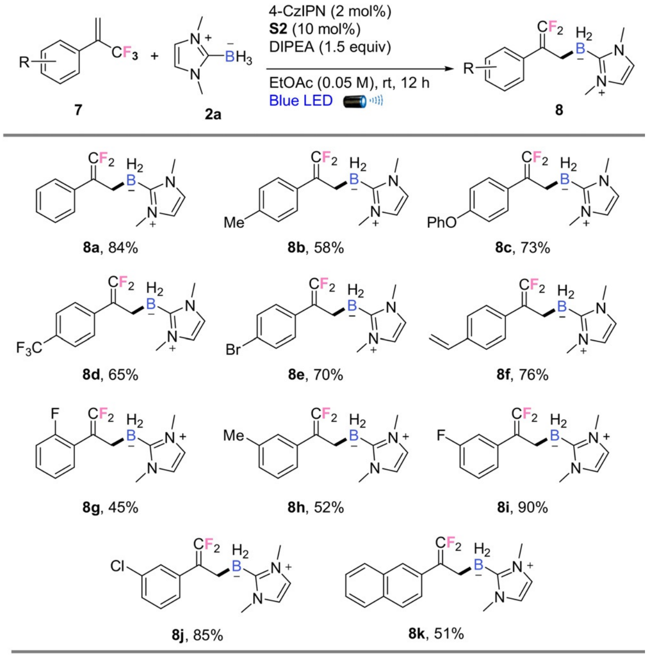
The most intriguing part of this method is probably the excellent regioselectivity for C−F bond activation achieved with polyfluoroarene substrates. Even though a general prediction mode cannot be established at the current stage, and may require sophisticated kinetic studies and computational calculations, the following trends can be observed and may be instructional with respect to the other radical-based C−F functionalization of polyfluoroarenes. 1) Polyfluoroarenes with electron-deficient substituents are generally more reactive and selective than those with electron-rich substituents (**1e** vs. **1f**). 2) For pentafluoroarenes, the fluoride substitution took place at the most electronegative site of the radical anion intermediates derived from pentafluoroarenes (**1b**–**1l**).[29] 3) For tetrafluoroarene (**1s**) and trifluoroarene (**1u**–**1x**, **1z**) with an electron-withdrawing substituent (such as, ester, ketone, nitrile), the C−F activation reactivity trend was *ortho* > *para* > *meta.* 4) In the case of fluoroarenes containing an amine substituent (**1p**–**1r**), the reaction was directed by intramolecular hydrogen bonding and occurred at the *ortho* position of the amine substituent. The hydrogen bond might facilitate the fragmentation step and direct the regioselectivity to overcome the innate electronics of the fluorinated arene substrates.[30] 5) Hydroborylation may occur to produce dearomatization products if a proton was located at the *para*-position of an electron-withdrawing group (**1t**, **1x**, **1y**, and **1aa**). Notably, in some cases, such as **3c** and **3j**, the regioselectivity is different from that obtained with the transition-metal-catalyzed processes where *ortho* defluoroborylation was observed,[9c,10b,17] providing an orthogonal strategy for regioselective defluoroborylation of polyfluoroarenes.

We subsequently attempted to extend this methodology to *gem*-difluoroalkenes, which are readily available building blocks.[31] The optimal conditions for defluoroborylation of *gem*-difluoroalkenes were defined using a combination of $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}dFbpy)]PF_6$,[32] thiol (**S2**) and DIPEA in THF at room temperature under blue LED irradiation for 12 h. As illustrated in Scheme 3, symmetrical *gem*-difluoroalkenes participated well to afford mono-fluoroalkenylboranes in moderate to good yields (**6a**–**6d**). In the case of unsymmetrical *gem*-difluoroalkenes, mixtures of *E*/*Z* isomers (**6e**–**6p**) were obtained. Electron-withdrawing substituents such as chloride (**6g**) and bromide (**6h**), as well as electron-rich substituents including methyl sulfide (**6i**), phenol (**6j**), amine (**6k**), and methyl ether (**6l**) were well-tolerated. *meta*-Substituted aryl (**6l**, **6m**) and 1- or 2-naphthyl (**6n**, **6o**) *gem*-difluoroalkenes delivered the defluoroborylation products smoothly. A fluoroalkene containing a pyridyl substituent was also a good candidate for this transformation (**6p**).



Scheme 3. Photo-mediated defluoroborylation of *gem*-difluoroalkenes.[a] [a] Yields of isolated products. *E*/*Z* ratios were determined by the analysis of ^1H NMR spectra. DIPEA = *N*,*N*-diisopropylethylamine.

gem-Difluoroallylboranes are important synthons for preparation of bioactive fluorinated compounds.[13] We speculated that the HAT-induced nucleophilic NHC–boryl radical [33] could add to an α-trifluoromethyl alkene, and a subsequent single electron reduction [20] would promote an E1cB-type fluoride elimination [34] to access such boranes. Indeed, after slight modifications of the photo-induced defluoroborylation protocol, this transformation was achieved efficiently under the transition-metal free conditions, with 4-CzIPN as the photocatalyst. The scope of trifluoromethylalkenes is illustrated in Scheme 4. The reactions proceeded smoothly with *para*-, *ortho*-, and *meta*-substituted α-trifluoromethylstyrenes to deliver *gem*-difluoroallylboranes in moderate to good yields (**8a**–**8j**). Styryl systems bearing a phenyl ether (**8c**),

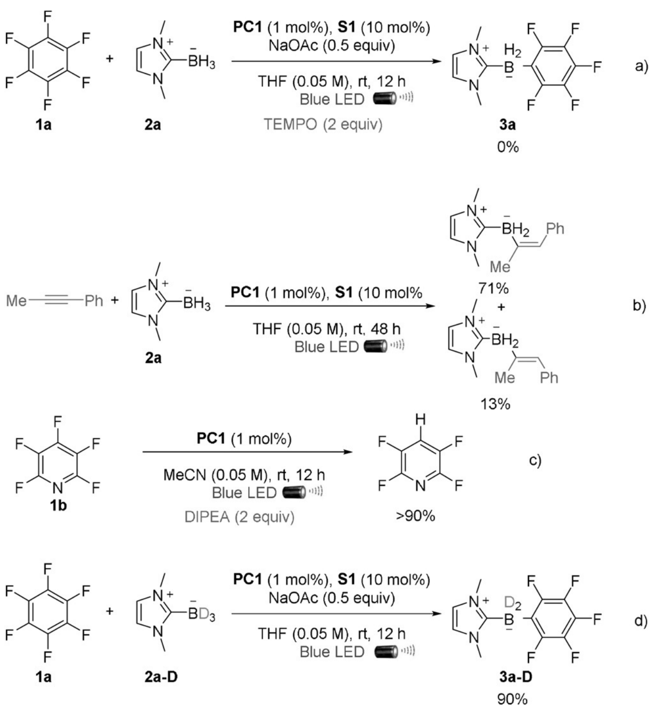


Scheme 4. Photo-mediated defluoroborylation of trifluoromethylalkenes.[a] [a] Yields of isolated products.

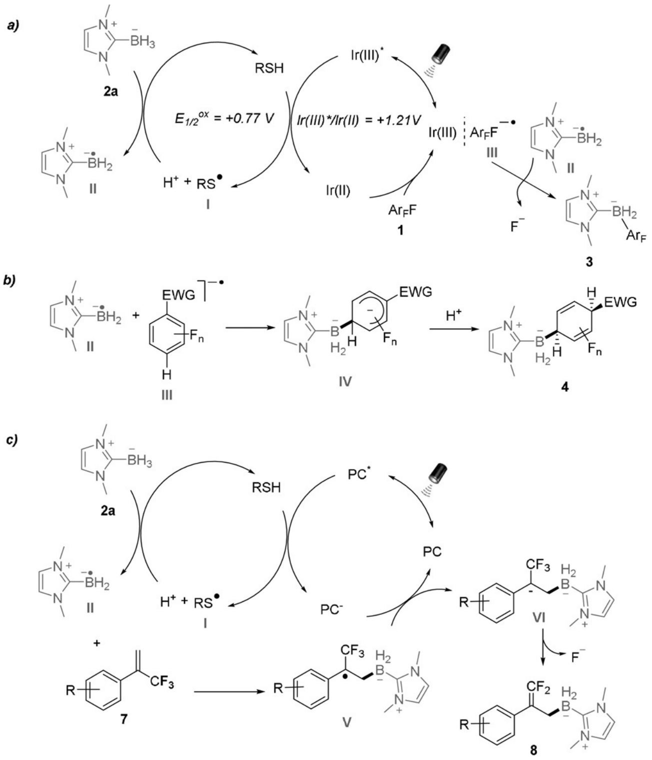
a trifluoromethyl substituent (**8d**), a bromide (**8e**), an alkene (**8f**), a fluoride (**8g** and **8i**), and a chloride (**8j**) were all effectively transformed into their corresponding *gem*-difluoroallylboranes. Naphthyl-substituted trifluoromethyl alkene also underwent successful defluoroborylation (**8k**).

A series of control experiments were conducted to further elucidate the reaction mechanism (Scheme 5). No product was observed in the presence of 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO), indicating a radical-based pathway (Scheme 5a). Stern–Volmer quenching studies illustrated that the thiol can quench the excited photocatalyst, whereas the polyfluoroarene, *gem*-difluoroalkene, and trifluoromethylalkene cannot (see the Supporting Information). Under similar conditions, the hydroboration of alkynes proceeded in high efficiency (Scheme 5b), which suggested the presence of boryl radical intermediates.[21e] Hydrodefluorination could be achieved with the same photocatalyst (Scheme 5c), indicating that a single electron reduction of the fluoroarene to fluoroaryl radical anion might occur.[25] The reaction of hexafluorobenzene with deuterated borane (**2a-D**) proceeded efficiently under the standard conditions to give deuterated product (**3a-D**) in 90% yield (Scheme 5d). The kinetic isotope effect (KIE) was determined to be 1.1 by measuring the initial rates of parallel reactions of **2a** and **2a-D** with hexafluorobenzene (see the Supporting Information), which suggested that the HAT of NHC–borane may not be involved in the rate-determining step. A radical chain-based mechanism was unlikely as the measured quantum yield was 0.43.[35]

Plausible mechanistic pathways for the defluoroborylation were proposed in light of all the experimental data. As illustrated in Scheme 6a, after photoexcitation of Ir^{III} catalyst, the $Ir^{III}*$ ($E_{1/2}^{*III/II} = +1.21$ V vs. saturated calomel electrode (SCE)) undergoes a single electron transfer with a thiol ($E_{1/2}^{ox} = +0.77$ V vs. SCE) through a proton-coupled electron transfer to produce an Ir^{II} species and thiyl radical **I** in the presence of base. A kinetically favored polarity-matched HAT[22] between electrophilic thiyl radical **I** and NHC−BH_3 (BDE of B−H = 72.8 kcal mol^{-1} based on DFT calculations,



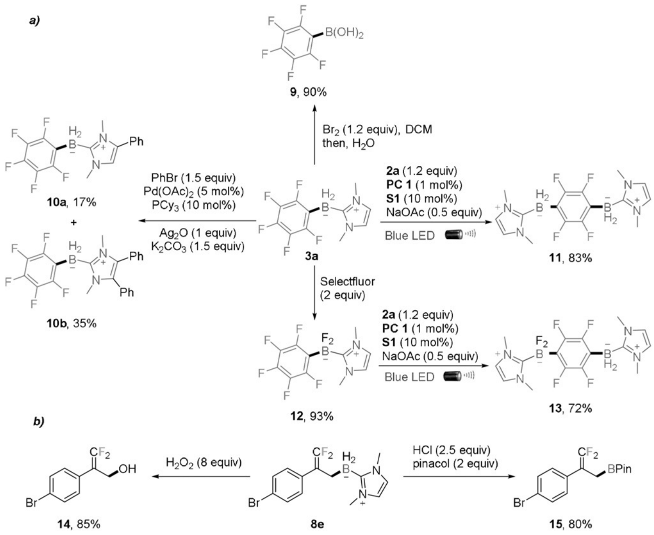
Scheme 5. Control experiments to elucidate reaction mechanisms.



Scheme 6. Proposed plausible mechanisms.

slightly lower than the previous calculated value in the range of 74–80 $kcal\,mol^{-1}$[21a,36]) gives NHC–boryl radical **II** and recovers the thiol catalyst (BDE of S–H = 76.1 $kcal\,mol^{-1}$). The defluoroborylation of polyfluoroarenes and *gem*-difluoroalkenes can be achieved by three possible pathways involving the NHC–boryl radical **II** and the fluoro substrate. 1) The generated Ir^{II} species ($E_{1/2}^{III/II} = -1.37$ V vs. SCE) can be oxidized by fluoroarene ($E_{1/2}^{red} = -2.38$ V vs. SCE for **1a**) or *gem*-difluoroalkene ($E_{1/2}^{red} = -1.04$ V vs. SCE for **5a**)[19a] to reproduce the Ir^{III} catalyst and a radical anion **III**. This process is supported by the control experiment (Scheme 5c) and may be accelerated by the stabilization induced by the interaction between fluoroaryl radical anion **III** and the positively charged Ir^{III} catalyst.[19] Radical recombination occurs between the fluoroaryl radical anion **III** and NHC boryl radical **II** followed by the fluoride fragmentation to give the desired product **3** or **6**. 2) Fluoride extrusion from radical anion **III** may occur before the radical recombination. 3) Direct addition of NHC-boryl radical **II** to the fluoroarene or *gem*-difluoroalkene and subsequent single-electron reduction by the Ir^{II} species, followed by fluoride extrusion delivers the final product. When a proton is located at the *para*-position of an electron-withdrawing group in the polyfluoroarene, protonation of intermediate **IV** occurs to generate the dearomatized hydroborylation product **4** (Scheme 6b), which may exclude the second possible pathway. Detailed coupling mechanistic investigations to distinguish between these pathways and gain a better appreciation of the source of selectivity are currently under progress in our laboratory. With trifluoromethylalkene substrates, the in situ formed NHC–boryl radical **II** will undergo radical addition to the alkene followed by a SET reduction by the reduced state of 4-CzIPN to generate a carbanion **VI**.[20] The following E1cB-type fluoride elimination will provide the *gem*-difluoroallylborane product **8** (Scheme 6c).

The synthetic value of this method was further demonstrated by diversification of the defluoroborylation product **3a** and *gem*-difluoroallylborane **8e** (Scheme 7). (Perfluorophenyl)boronic acid **9** was produced in high yield by a simple bromination/hydrolysis cascade, which has been widely utilized in cross-coupling reactions to deliver valuable polyfluoroarene compounds.[8] Treatment of borane **3a** with phenyl bromide under palladium-catalyzed cross-coupling conditions led to mono- (**10a**) and di-arylation (**10b**) of the NHC part of **3a** in 17% and 35% yield, respectively. The mono-defluoroborylation product **3a** could undergo further defluoroborylation to achieve 1,4-diborane product **11** in good yield. The reaction between **3a** and Selectfluor afforded borane difluoride **12** in high yield, which could act as a boronic acid equivalent in further diversifications.[37] The borane difluoride **12** could also undergo further defluoroborylation, leading to the diborylated compound **13** with two distinguishable boron substituents. *gem*-Difluoroallylboranes **8e** can be directly transformed to *gem*-difluoroallyl alcohol **14** under oxidative conditions or *gem*-difluoroallylboronates **15** with pinacol under acidic conditions.



Scheme 7. Further transformations of fluoroarylborane (**3a**) and *gem*-difluoroallylborane (**8e**).

Conclusion

In summary, we have developed a practical and selective defluoroborylation of polyfluoroarenes, *gem*-difluoroalkenes, and trifluoromethylalkenes in an atom- and redox-economic manner through photoredox and HAT-induced B–H activation. The selectivity is generally high and can be orthogonal to transition-metal-catalyzed defluoroborylation. Fluorinated organoboranes with different degrees of fluorination and a wide range of functionalities were accessed by operationally simple and mild protocols, even in a transition-metal-free manner, and will likely find broad applications for the synthesis of value-added organofluorine compounds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boryl radical · defluoroborylation · hydrogen atom transfer · photocatalysis · polyfluoroarene

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