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Visible-Light-Induced Radical Defluoroborylation of Trifluoromethyl Alkenes: An Access to *gem*-Difluoroallylboranes

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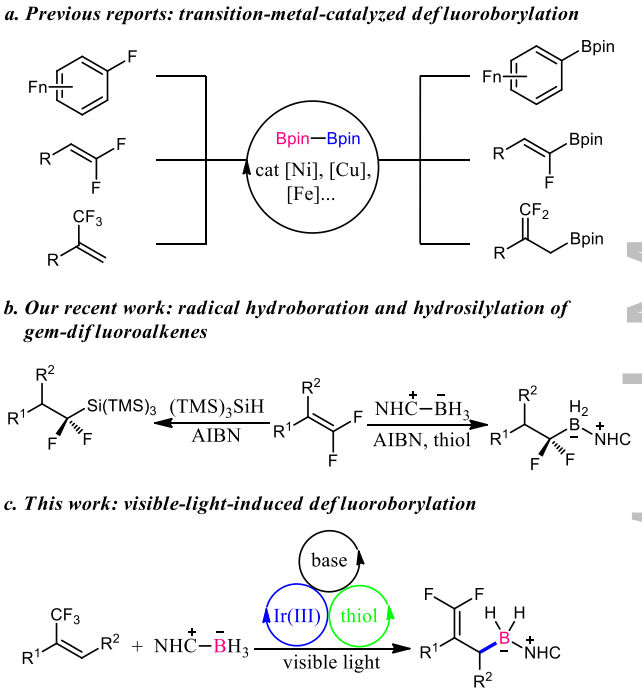
Abstract. A photoredox-catalyzed defluoroborylation of trifluoromethyl alkenes with *N*-heterocyclic carbene boranes is described for the synthesis of *gem*-difluoroallylboranes. This protocol exhibits a broad substrate scope and good functional group compatibility, which enables the late-stage functionalization of structurally complex compounds. Further transformations of the defluoroborylation products to valuable CF_2-containing molecules are also demonstrated.

Keywords: photocatalysis; iridium; defluoroborylation; *N*-heterocyclic carbene boranes; trifluoromethyl alkenes

Organofluorine compounds play a vital role in modern medicine. Approximately 20% of all pharmaceuticals in the market nowadays contain fluorine.[1] Among all the organic functional groups related to fluorine, the *gem*-difluoroalkene is an intriguing structural motif that is commonly found in molecules of pharmaceutical interests.[2] In terms of the electrosteric properties, *gem*-difluoroalkene resembles carbonyl groups but has less liability to the *in vivo* metabolism, serving as a potentially valuable carbonyl bioisostere with improved pharmaceutical properties.[3] Moreover, *gem*-difluoroalkenes are also versatile building blocks for the construction of more complicated organofluorine molecules.[4] These features have triggered substantial research efforts directed towards the development of more efficient synthetic strategies for their syntheses, including direct difluoroolefination of carbonyl or diazo groups,[5] the incorporation of *gem*-difluorovinyl-containing precursors into the target molecules,[6] and defluorinative functionalization of trifluoromethyl alkenes.[7,8] However, for the sake of modular synthesis, the construction of *gem*-difluoroalkenes bearing easily transformable functional groups is highly desirable but attracts far less attention.



Scheme 1. Methods for the synthesis of fluorinated organoboron compounds.

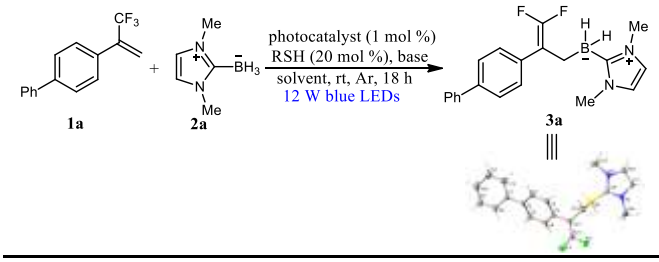
On the other hand, organoboron compounds are one of the most popular intermediates in organic synthesis due to the high versatility of the C−B bonds in the formation of other C−X (X = C, N, O, etc.) bonds.[9] Substantial efforts have been devoted to the development of efficient strategies to access these synthetically valuable fluorine-substituted organoboron compounds in this aspect.[10] Among the protocols reported, the catalytic defluoroborylation of fluorine-containing compounds has emerged as one of the most straightforward pathways to achieve this goal (Scheme 1a).[8e-h,11] The current transformations

largely depend on the assistance of transition metals (Ni, Cu, Fe, etc.) in the C−B bond formation. Therefore, a new pathway to achieve the defluorinative borylation is highly desired.

From the pioneering works by MacMillan and Yoon,[12] visible-light-induced catalysis, highlighted by the environment-friendliness, the mild conditions, and the low-energy irradiation, has attracted significant interests in organic synthesis. This has led to a growing demand for developing environmentally benign and sustainable synthetic protocols.[13] On the other hand, the chemistry of boron-centred radicals, particularly the *N*-heterocyclic carbene (NHC)–boryl radicals, has gained increasing popularity.[14] Progress has been made recently towards the inverse hydroboration of imines with NHC–boranes by synergistic organocatalysis and photocatalysis.[15] Inspired by this result as well as our more recent work on radical hydroboration and hydrosilylation of *gem*-difluoroalkenes (Scheme 1b),[10m] we envisioned that the NHC–boryl radical could be generated through a photoinduced hydrogen atom abstraction process (HAAP) under mild conditions, which would circumvent the use of potentially toxic radical initiators and high temperature. Herein, we would like to present a concise and efficient assembly of *gem*-difluoroallylboranes from trifluoromethyl alkenes and NHC–boranes under photoredox conditions (Scheme 1c).

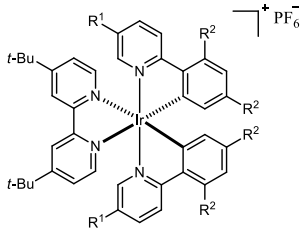
We started with the treatment of 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl **1a** (1.0 equiv.) and NHC–borane **2a** (1.2 equiv.) with photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ (**PC1**, 1 mol %), cocatalyst *tert*-dodecanethiol (**S1**, 20 mol %), and K_2CO_3 (1.0 equiv.) in DMSO under irradiation with a 12 W blue LEDs at room temperature for 18 h, which provided the desired defluoroborylation product **3a** in 33% isolated yield (Table 1, entry 1). The structure of **3a** was unambiguously confirmed by spectroscopic data and X-ray diffraction analysis of the single crystal.[16] Encouraged by the promising result, further screening of the reaction conditions was performed. Among the solvents examined, acetone gave the best result (entries 2–5). Replacing K_2CO_3 with LiOH, Li_2CO_3, or Na_2CO_3 proved to be detrimental to the yield (entries 6–8). Other photocatalysts including $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**PC2**), $Ir(ppy)_3$ (**PC3**), $[Ru(bpz)_3][PF_6]_2$ (**PC4**), and Mes-Acr$^+$ (**PC5**) did not catalyse the anticipated reaction (entries 9–12). Further experiments revealed that other thiols, including 2-methylpropane-2-thiol (**S2**), triisopropylsilanethiol (**S3**), and 2,4,6-triisopropylthiophenol (TRIP thiol, **S4**), were inferior to **S1** (entries 13–15). Further adjustment of the thiol loading to 10 mol % and photocatalyst loading to 2 mol %, the yield was improved to 67% (entry 18). The yield decreased dramatically in the absence of thiol or base, and no reaction occurred in the dark or in the absence of photocatalyst, suggesting that light, photocatalyst, thiol, and base were all essential for efficient defluoroborylation (entries 19–22).

Table 1. Optimization of the reaction conditions.[a]

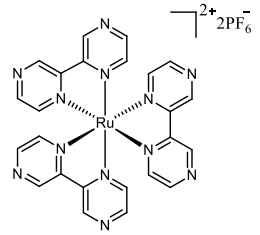


Entry	Photocatalyst	RSH	Base	Solvent	Yield[b]
1	**PC1**	**S1**	K_2CO_3	DMSO	33
2	**PC1**	**S1**	K_2CO_3	MeCN	42
3	**PC1**	**S1**	K_2CO_3	DMF	10
4	**PC1**	**S1**	K_2CO_3	acetone	61
5	**PC1**	**S1**	K_2CO_3	DCE	29
6	**PC1**	**S1**	LiOH	acetone	32
7	**PC1**	**S1**	Li_2CO_3	acetone	55
8	**PC1**	**S1**	Na_2CO_3	acetone	36
9	**PC2**	**S1**	K_2CO_3	acetone	trace
10	**PC3**	**S1**	K_2CO_3	acetone	0
11	**PC4**	**S1**	K_2CO_3	acetone	0
12	**PC5**	**S1**	K_2CO_3	acetone	0
13	**PC1**	**S2**	K_2CO_3	acetone	23
14	**PC1**	**S3**	K_2CO_3	acetone	35
15	**PC1**	**S4**	K_2CO_3	acetone	50
16[c]	**PC1**	**S1**	K_2CO_3	acetone	54
17[d]	**PC1**	**S1**	K_2CO_3	acetone	62
18[d,e]	**PC1**	**S1**	**K_2CO_3**	**acetone**	**67**
19[e]	**PC1**	–	K_2CO_3	acetone	37
20[d,e]	**PC1**	**S1**	–	acetone	43
21[d]	–	**S1**	K_2CO_3	acetone	0
22[d,e,f]	**PC1**	**S1**	K_2CO_3	acetone	0

Photocatalysts used

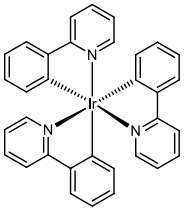


$R^1 = R^2 = H$, $Ir(ppy)_2(dtbbpy)PF_6$ (**PC1**)

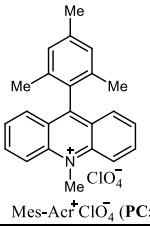


$[Ru(bpz)_3][PF_6]_2$ (**PC3**)

$R^1 = CF_3$; $R^2 = F$, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**PC2**)

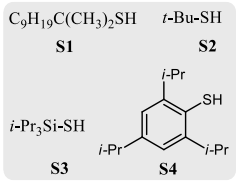


$Ir(ppy)_3$ (**PC4**)



Mes-Acr$^+$$ClO_4^-$ (**PC5**)

Cocatalysts used



[a] Reaction conditions: **1a** (0.3 mmol, 1.0 equiv.), **2a** (0.36 mmol, 1.2 equiv.), photocatalyst (1 mol %), thiol (20 mol %), base (0.3 mmol, 1.0 equiv.), solvent (3 mL), 12 W blue LEDs, argon atmosphere, room temperature, 18 h.

[b] Isolated yield.

[c] **S1** (30 mol %) was used.

[d] **S1** (10 mol %) was used.

[e] **PC1** (2 mol %) was used.

[f] Without LEDs.

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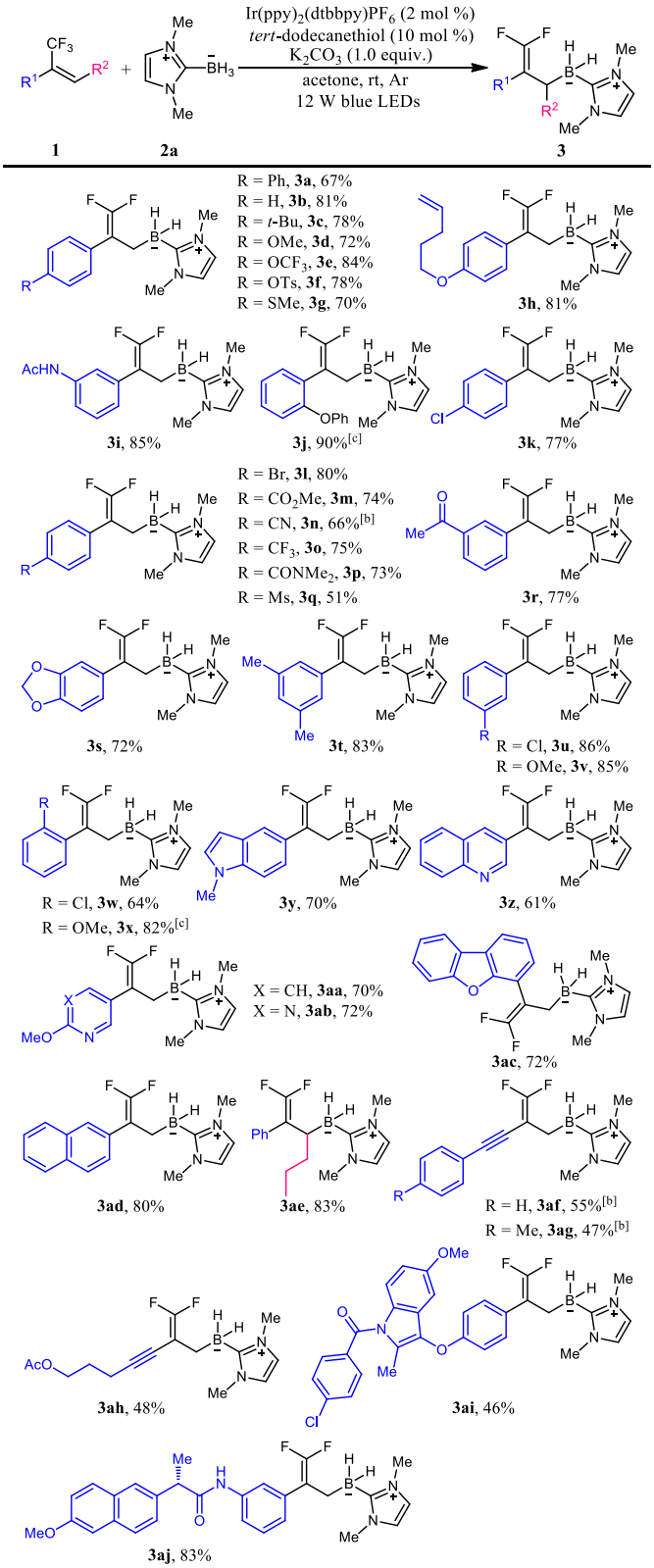
Table 2. Substrate scope with respect to trifluoromethyl alkenes.[a]



[a] Reaction conditions: **1** (0.5 mmol, 1.0 equiv.), **2a** (0.6 mmol, 1.2 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol %), *tert*-dodecanethiol (10 mol %), K_2CO_3 (0.5 mmol, 1.0 equiv.), acetone (5 mL), 12 W blue LEDs, argon atmosphere, rt, 12–36 h. Yields of isolated products are given.

[b] MeCN (5 mL) was employed instead of acetone (5 mL).

[c] **2a** (0.75 mmol, 1.5 equiv.).

After the establishment of the optimal reaction conditions, we then examined the generality of this defluoroborylation reaction by evaluating the substrate scope of trifluoromethyl alkenes (Table 2). A series of aryl substituted trifluoromethyl alkenes bearing electron-donating or electron-withdrawing substituents on the aromatic ring were subjected to the reaction with NHC–BH_3 **2a**. The reactions all proceeded smoothly to deliver the desired corresponding products in moderate to excellent yields (**3a**-**3t**) regardless of electronic nature of the substituents. Interestingly, substrate **1h** underwent this reaction selectively without any side reaction at the terminal alkene group. Substrate **1g** with an active thioether moiety was also compatible to the reaction conditions, delivering the desired product **3g** in 70% yield. α-CF_3 styrenes bearing chloro- and methoxy-substitution all proved to be applicable substrates regardless of their substitution position, leading to the desired products in moderate to good yields (**3d**, **3k**, **3u**-**3x**). It is worth noting that this protocol was also efficient for heteroaryl-, naphthyl-, and alkynyl-substituted trifluoromethyl alkenes, and the corresponding products were obtained in moderate to good yields. Furthermore, the reaction of internal alkene **1ae** with **2a** furnished the desired product **3ae** in 83% yield, further demonstrating good applicability of the method. Unfortunately, in the case of aliphatic trifluoromethyl alkenes as substrates, the reactions failed to afford the desired products (see the Supporting Information for details).

Based on the results above, we decided to pursue the application of our method in the late-stage modification of drug molecules. Two trifluoromethyl alkenes derived from indomethacin and naproxen were then examined under the present reaction conditions. Gratifyingly, the defluoroborylation products (**3ai**, **3aj**) were successfully obtained from this transformation in 46% and 83% yields, respectively.

Next, the scope of the reaction was explored with respect to different NHC–boranes (Table 3). Several NHC–boranes that were derived from 1,3-dialkylimidazolium iodides were reactive towards this reaction, affording the corresponding products in 64% to 74% yields (**4ab**-**4ae**). Notably, CN-substituted borane **2f** could smoothly participate in the process to provide the desired product **4af** in 67% yield.

To demonstrate the practicality and synthetic value of the protocol, the reaction between **1f** and **2a** was scaled up under the standard reaction conditions and the product **3f** was obtained in 66% yield (Scheme 2a). Subsequent treatment of **3f** with pinacol under acidic conditions provided *gem*-difluoroallylboronate **5** in 71% yield (Scheme 2b)[17], which is a useful synthon for further transformations. The addition reaction of **5** and 4-chlorobenzaldehyde **6** furnished the difluorinated homoallylic alcohol **7** in 73% yield.[8e] A three-component Petasis-type *gem*-difluoroallylation reaction of **5**, **6**, and 2-aminophenol **8** led to *gem*-difluorohomoallylamine **9** in 89% yield.

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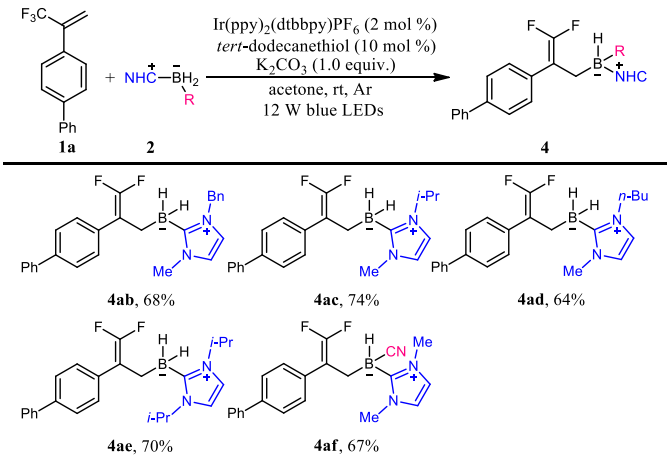
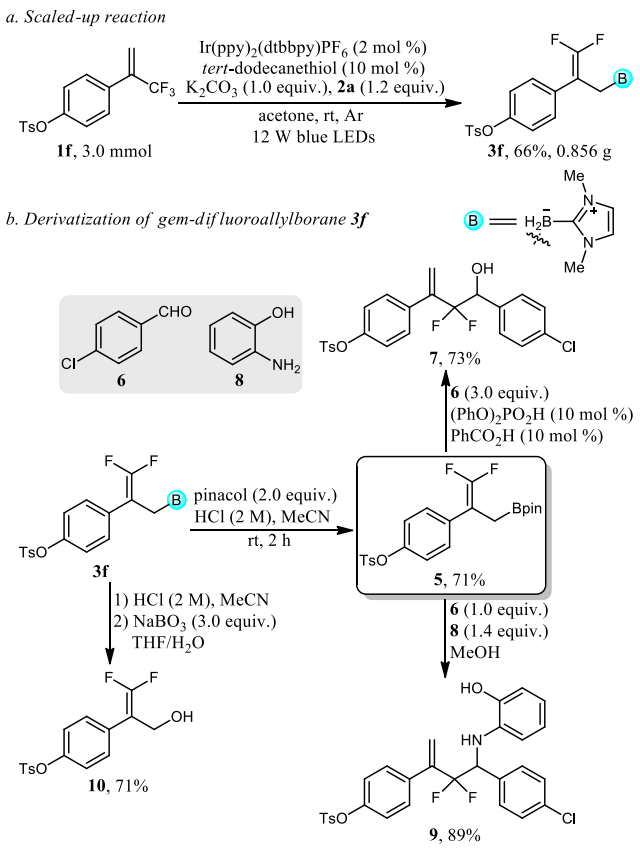
Table 3. Substrate scope with respect to NHC–boranes.[a]



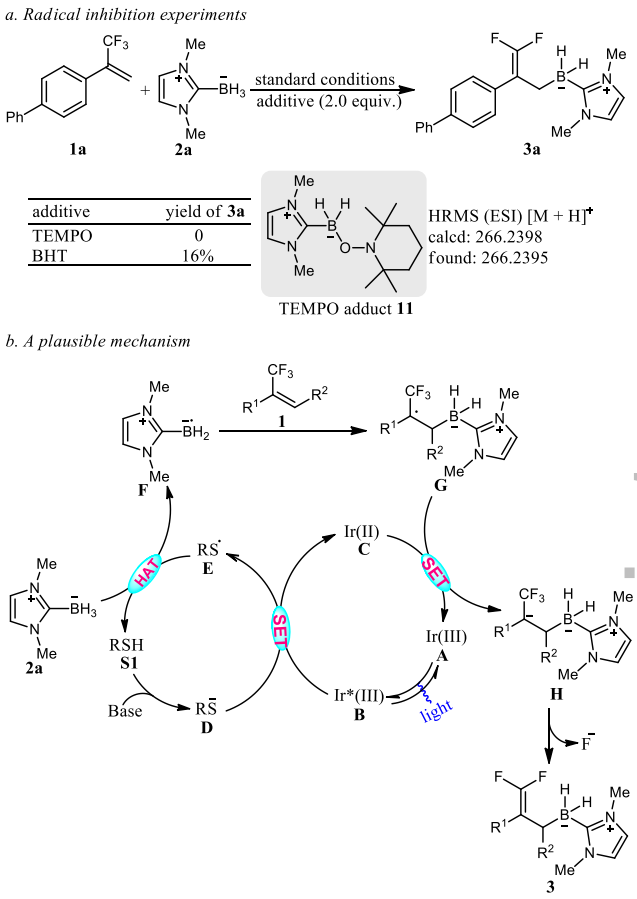
[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2** (0.6 mmol, 1.2 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol %), *tert*-dodecanethiol (10 mol %), K_2CO_3 (0.5 mmol, 1.0 equiv.), acetone (5 mL), 12 W blue LEDs, argon atmosphere, rt, 17–36 h. Yields of isolated products are given.



Scheme 2. Scaled-up reaction and further transformations of *gem*-difluoroallylborane **3f**.

[18] Finally, **3f** was oxidized to give *gem*-difluoroallyl alcohol **10** in 71% yield.[17]

To verify the radical reaction mechanism of this defluoroborylation, radical trapping experiments were performed. A significantly reduced yield of **3a** was



Scheme 3. Control experiments and proposed mechanism.

observed when stoichiometric amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added into the catalytic system. With the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), the reaction was completely suppressed under the standard reaction conditions. Notably, the radical adduct **11** was detected by HRMS analysis (Scheme 3a). Based on these observations and previous reports,[15,19] a plausible mechanism for the reaction is outlined in Scheme 3b. Initially, a photoexcitation of ground-state Ir(III) complex **A** by blue light generates excited-state Ir*(III) species **B**, which undergoes a single electron transfer (SET) with the thiol anion **D** to deliver an Ir(II) species **C** and thiol radical **E**. At this stage, the NHC−boryl radical **F** can be produced through a hydrogen atom transfer (HAT) process between the thiol radical **E** and **2a**, along with the regeneration of thiol **S1**. A regioselective radical addition of the radical **F** to trifluoromethyl alkene **1** followed by a SET reduction by Ir(II) **C** takes place to provide a carbanion **H** and reproduce the ground-state Ir(III) **A**. Finally, an E1cB-type *β*-fluoride elimination of **H** leads to the desired product **3**.

In summary, we have developed a visible-light-induced defluoroborylation of trifluoromethyl alkenes using NHC–boranes as the radical precursors under mild conditions,[20] which enabled a convenient access to a wide range of *gem*-difluoroallylboranes that exhibited remarkable potential for further

derivatization to valuable fluorinated molecules. Moreover, this method can also be applied to the late-stage functionalization of complicated bioactive substrates.

Experimental Section

General Procedure for the Synthesis of *gem*-Difluoroallylboranes

To an oven-dried reaction tube (25 mL) equipped with a magnetic stir bar, trifluoromethyl alkene **1** (0.5 mmol, 1.0 equiv.), NHC–borane **2** (0.6 mmol, 1.2 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (9.2 mg, 0.01 mmol, 2 mol %), K_2CO_3 (70.0 mg, 0.5 mmol, 1.0 equiv.), and acetone (5 mL, pre-degased) were added. The tube was sealed with a rubber septum and cooled to -10 °C. Then the tube was evacuated and backfilled with argon for 3 times. *tert*-Dodecanethiol (12.0 μL, 0.05 mmol, 10 mol %) was added via a syringe. The reaction mixture was stirred at room temperature under irradiation of 12 W blue LEDs (distance app. 3 cm) for the specified length of time (TLC tracking detection). After the reaction was finished, the reaction mixture was diluted with EtOAc (5 mL). The resulting mixture was filtered, and the filtrate was concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate/triethylamine) to give the desired product **3** or **4**.

Acknowledgements

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