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Visible-Light Photoredox Decarboxylation of Perfluoroarene Iodine(III) Trifluoroacetates for C–H Trifluoromethylation of (Hetero)arenes

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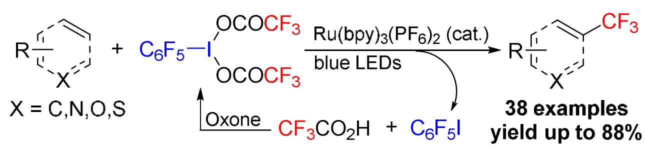
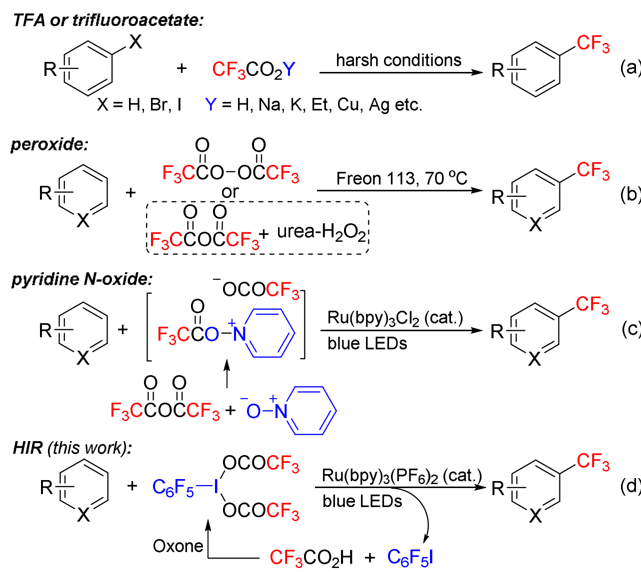


ABSTRACT: A scalable and operationally simple decarboxylative trifluromethylation of (hetero)arenes with easily accessible $C_6F_5I(OCOCF_3)_2$ under photoredox catalysis has been developed. This method is tolerant of various (hetero)arenes and functional groups. Notably, C_6F_5I is recycled from the decarboxylation reaction and further used for the preparation of $C_6F_5I(OCOCF_3)_2$. The combination of photoredox catalysis and hypervalent iodine reagent provides a practical approach for the application of trifluoroacetic acid in trifluoromethylation reactions.

KEYWORDS: *trifluoromethylation, photocatalysis, decarboxylation, trifluoroacetic acid, iodine(III) reagent*

The trifluoromethylated compounds have found wide applications in materials, pharmaceuticals, and agrochemicals.[1] Over the last decade, tremendous methods have been developed for the incorporation of trifluoromethyl group into organic molecules,[2] using electrophilic,[3] nucleophilic,[4] and radical[5] trifluoromethylating reagents. Nonetheless, some of the trifluoromethylating reagents employed in these reactions[2-5] are cost-prohibitive or gaseous, which limits their application on a large scale. Consequently, the development of new trifluoromethylation reactions with inexpensive and easily handled CF_3 sources is highly desirable.

Because of low cost and the ease of handling,[6] trifluoroacetic acid (TFA) and its derivatives represent as attractive trifluoromethylating reagents. The decarboxylative trifluoromethylation of TFA and trifluoroacetates has been extensively studied.[7-10] However, the decarboxylative reactions normally require the electrochemical methods,[7] stoichiometric transition-metals and high temperature,[8] or strong oxidants[9] (Scheme 1a). Recently, new advancements have been reported to make the decarboxylative trifluoromethylation more generally applicable. For example, Buchwald demonstrated that the application of continuous flow technology could enable the rapid and scalable trifluoromethylation of aryl halides with CF_3CO_2K.[10a] Zhang and co-workers reported a radical

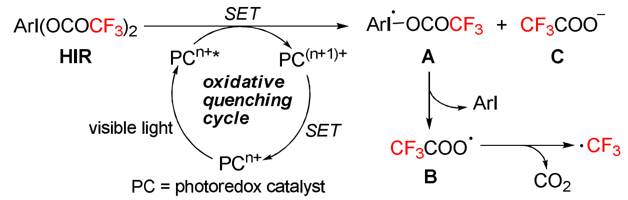


Scheme 1. Trifluromethylation Reactions Using TFA and Its Derivatives

trifluoromethylation of arenes with TFA under the conditions of $Ag_2CO_3/K_2S_2O_8$ at 120 °C.[10b] Very recently, Su and Li realized a novel photocatalytic C–H trifluoromethylation of (hetero)arenes with TFA using a Rh-modified TiO_2 nanoparticles as a photocatalyst.[10c] However, these modifications could not fundamentally solve the problems, such as high temperature[10a,b] or strong oxidants.[10b,c] In 1990, Yoshida and co-workers disclosed an alternative decarboxylative trifluoromethylation of aromatic compounds with bis(trifluoroacetyl) peroxide under mild conditions (Scheme 1b).[11a] This decarboxylative strategy has recently been adopted by Bräse[11b] and Sodeoka[11c] for radical trifluoromethylation of arenes and alkenes using the reagent combination of trifluoroacetic anhydride (TFAA)/urea–hydrogen peroxide (UHP). A significant breakthrough of decarboxylative trifluoromethylation of trifluoroacetic acid (TFA) and its derivatives was made by Stephenson and co-workers.[12] They demonstrated that the pyridine *N*-oxide/TFAA adduct was used to promote a high-yield and scalable trifluoromethylation reaction under photoredox catalysis (Scheme 1c). Despite the above achievements, the development of new trifluoromethylation reactions with TFA derivatives is still highly desirable.

Hypervalent iodine(III) reagents (HIRs) are widely used in organic synthesis because of their low toxicity, strong electrophilicity, and valuable oxidizing properties.[13] Recently, hypervalent iodine(III) carboxylates have evolved as powerful reagents to participate in the decarboxylative alkylation, alkenylation, and acylation under transition-metal catalysis[14] or visible-light photoredox catalysis.[15] However, the decarboxylative trifluoromethylation with hypervalent iodine(III) trifluoroacetates (HITFAs) is largely ignored and remains to be a challenge. In 1991, Togo and Yokoyama reported a decarboxylative alkylation of heteroaromatic bases with carboxylic acids in the presence of HITFAs.[16a] This work clearly demonstrated that the decarboxylation of HITFAs for the formation of a CF_3 racial was much harder than that of the nonfluorinated HIRs. Very recently, Maruoka described a photolytically induced C–H difluoromethylation of heteroarenes with hypervalent iodine(III) difluoroacetates, but the decarboxylative trifluoromethylation with 3,5-(*t*-Bu)$_2C_6H_3I(OCOCF_3)_2$ was relatively inefficient.[16b] In continuation of our research interest in visible-light-induced fluoroalkylation reactions,[17] we herein disclose a scalable and operationally simple decarboxylative trifluromethylation of (hetero)arenes with the commercially available $C_6F_5I(OCOCF_3)_2$ under photoredox catalysis (Scheme 1d). This HIR is easily accessible from C_6F_5I and TFA in the presence of Oxone,[18] and C_6F_5I could be recycled from the decarboxylation reaction.

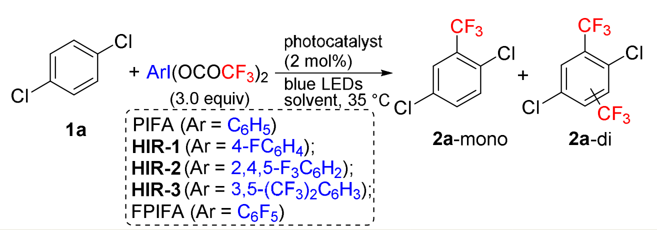
On the basis of visible-light-induced decarboxylation reactions[15] and our experience in decarboxylative hydroaryldifluoromethylation,[17d] we proposed a photoredox catalytic cycle for decarboxylative trifluoromethylation. As shown in Scheme 2, we assumed that photoredox catalyst (PC) involved single electron transfer (SET) appro aches could provide the CF_3 radial (via radical intermediates **A** and **B**), which could be used for trifluoromethylation reactions. Importantly, the reactivity and selectivity might be controlled by judicious choice of proper HIRs and PCs.



Scheme 2. Decarboxylative Trifluoromethylation with Hypervalent Iodine Trifluoroacetates

To test our hypothesis, 1,4-dichlorobenzene (**1a**) was chosen as the model substrate to react with $C_6H_5I(OCOCF_3)_2$ (PIFA) in the presence of $Ru(bpz)_3(PF_6)_2$ in CH_3CN under blue light-emitting diodes (LEDs). To our disappointment, no trifluoromethylated product was detected (Table 1, entry 1). Considering the fact that introduction of fluorine atom(s) or trifluoromethyl group into the aromatic ring of HIRs can distinctly increase their oxidizability and solubility,[19] we then examined a series of fluorinated $ArI(OCOCF_3)_2$ (entries 2-5). To our delight, the desired reaction occurred using fluorinated HIRs, and $C_6F_5I(OCOCF_3)_2$ (FPIFA) was optimal to give the desired product **2a** in 42% yield (entry 5). Switching $Ru(bpz)_3(PF_6)_2$ to other PCs showed that $Ru(bpy)_3(PF_6)_2$ gave the highest yield (entries 6-9). When this reaction was performed in DMF or DCM, no desired product was formed (entries 10 and 11). Furthermore, the addition of base, such as CF_3COONa or KF, had no or little effect on the yield (entries 12 and 13). Finally, decreasing the amount of FPIFA to 2.5 equivalents resulted in a comparable yield (entry 14). The control experiments showed that the blue LEDs irradiation was required for this reaction (entry 15). **2a** was formed in low yield in the absence of a PC (entry 16), which is consistent with Marouka's work.[16b,20]

Table 1. Optimization of Reaction Conditions[a]

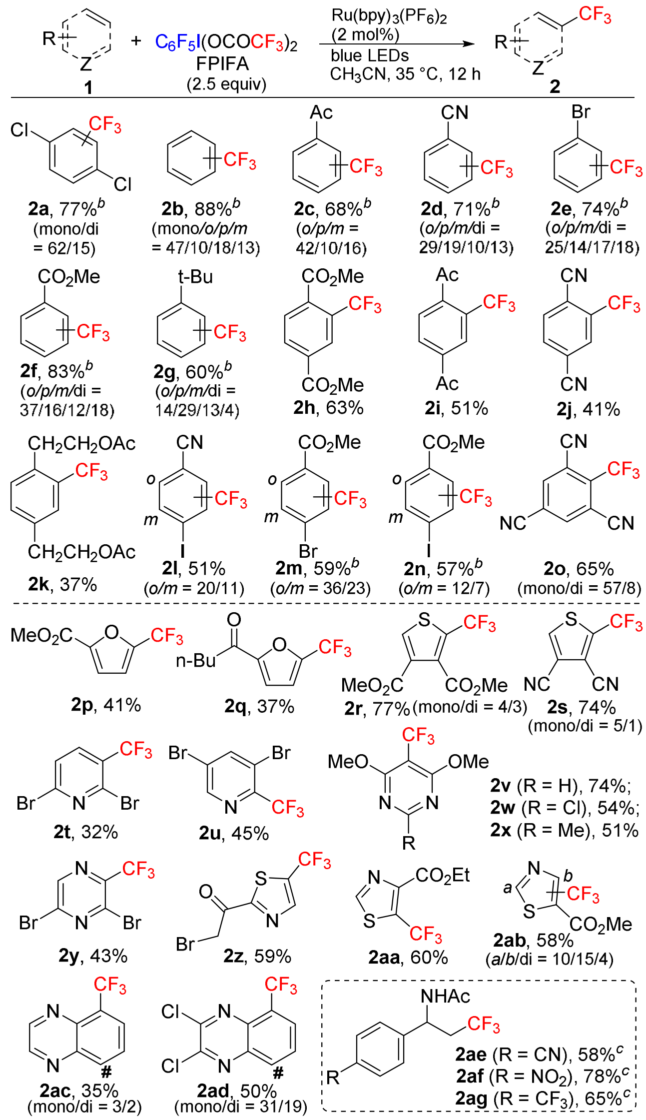


entry	photocatalyst	$ArI(OCOCF_3)_2$	slovent	yield (%)[b] **2a**-mono/**2a**-di
1	$Ru(bpz)_3(PF_6)_2$	PIFA	CH_3CN	0/0
2	$Ru(bpz)_3(PF_6)_2$	**HIR-1**	CH_3CN	11/0
3	$Ru(bpz)_3(PF_6)_2$	**HIR-2**	CH_3CN	23/0
4	$Ru(bpz)_3(PF_6)_2$	**HIR-3**	CH_3CN	16/0
5	$Ru(bpz)_3(PF_6)_2$	FPIFA	CH_3CN	42/trace
6	$Ru(bpm)_3Cl_2$	FPIFA	CH_3CN	51/3
7	$Ru(bpy)_3(PF_6)_2$	FPIFA	CH_3CN	60/12

8	$Ir(ppy)_3$	FPIFA	CH_3CN	31/0
9	$Ir(Fppy)_3$	FPIFA	CH_3CN	29/0
10	$Ru(bpy)_3(PF_6)_2$	FPIFA	DMF	0/0
11	$Ru(bpy)_3(PF_6)_2$	FPIFA	DCM	0/0
12[c]	$Ru(bpy)_3(PF_6)_2$	FPIFA	CH_3CN	60/12
13[d]	$Ru(bpy)_3(PF_6)_2$	FPIFA	CH_3CN	62/13
14[e]	$Ru(bpy)_3(PF_6)_2$	FPIFA	CH_3CN	62/15
15[f]	$Ru(bpy)_3(PF_6)_2$	FPIFA	CH_3CN	0/0
16	—	FPIFA	CH_3CN	8/0

[a]Reaction conditions: **1a** (0.1 mmol), $ArI(OCOCF_3)_2$ (0.3 mmol), photocatalyst (0.002 mmol), solvent (1.5 mL), blue LEDs, under N_2, 35 °C, 12 h. [b]Yields determined by ^{19}F NMR using trifluoromethoxybenzene as an internal standard. [c]CF_3COONa (0.1 mmol). [d]KF (0.1 mmol). [e]FPIFA (0.25 mmol). [f]No light.

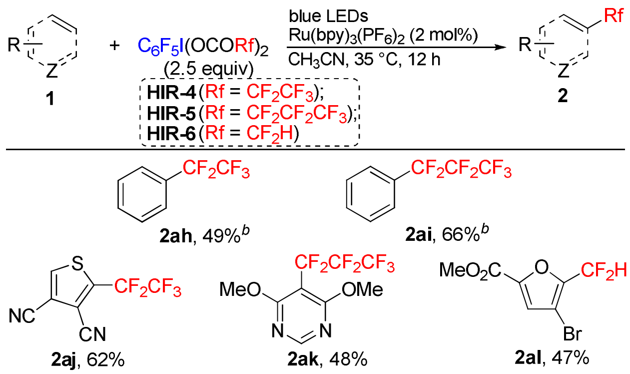
With the optimized reaction conditions in hand (Table 1, entry 14), the scope of this photoredox-catalyzed decarboxylative trifluoromethylation was investigated (Scheme 3). Various monosubstituted or disubstituted arenes bearing different functional groups such as halogen, acetyl, ester, *tert*-butyl, and nitrile underwent this reaction to afford the corresponding products in moderate to good yields (**2a-2n**). In some cases the trifluoromethylated products were obtained as mixture of isomers, which is consistent with the general radical trifluoromethylation of arenes.[5a,10b,10c] Moreover, 1,3,5-tricyanobenzene **1o** was smoothly converted to the corresponding trifluoromethylated products (**2o**). The extension of this decarboxylative trifluoromethylation to heteroarenes was delightfully successful. Electro-rich heteroarenes including furans and thiophenes (**1p-1s**) were compatible with the reaction conditions. Meanwhile, electron-deficient heteroarenes (pyridines, pyrimidines, pyrazines, and thizaoles, **1t-1ab**) were also amenable to the reaction. Notably, the trifluoromethylation of these heteroarenes exhibited excellent site-selectivity at the electro-richer position (**2t-2ab**). Unfortunately, pyrroles and benzopyrroles were not visible for this protocol. In the case of quinoxalines (**1ac** and **1ad**), the trifluoromethylation took place at the C-5 position or both C-5 and C-8 positions (**2ac** and **2ad**), whereas the trifluoromethylation occurred at the C-5 or C-6 position in Baran's CF_3SO_2Na/t-BuOOH system.[5b] The structure of compounds **2aa**, **2ab**-b, and **2ac**-di were confirmed by X-ray analysis (see the supporting information).[21] Finally, we extended the substrate scope to styrenes. Treatment of styrenes (**1ae-1ag**) with FPIFA (1.1 equiv) under the standard reaction conditions afforded the aminotrifluoromethylated products (**2ae-2ag**) in moderate to good yields.[22]



Scheme 3. Substrate Scope of Decarboxylative Trifluoromethylation with FPIFA[a]

[a]Reaction conditions: **1** (0.5 mmol), FPIFA (1.25 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol), CH_3CN (7.5 mL), blue LEDs, 35 °C, under N_2, 12 h, isolated yields. The isomer ratio was determined by ^{19}F NMR using trifluoromethoxybenzene as an internal standard. [b]Yields determined by ^{19}F NMR using trifluoromethoxybenzene as an internal standard. [c]FPIFA (0.55 mmol).

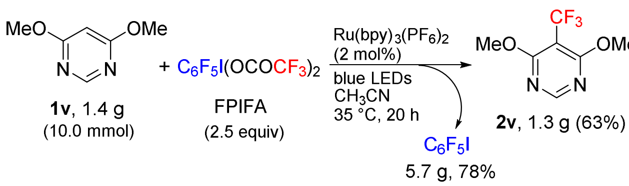
To extend the application of this reaction, we then examined the analogous fluoroalkylation reactions with HIRs. Several $C_6F_5I(OCORf)_2$ (**HIR-4/5/6**) were synthesized[23] and subjected to the C–H fluoroalkylation of (hetero)arenes. To our delight, these reactions proceeded smoothly under the standard conditions, resulting in the pentafluoroethylated, heptafluoropropylated, and difluoromethylated products (**2ah-2al**) in moderate yields (Scheme 4). Unlike the trifluoromethylation reactions, perfluoroalkylation reactions only afforded monosubstituted products, probably owing to the higher electronegativity of perfluoroalkyl group.[24]



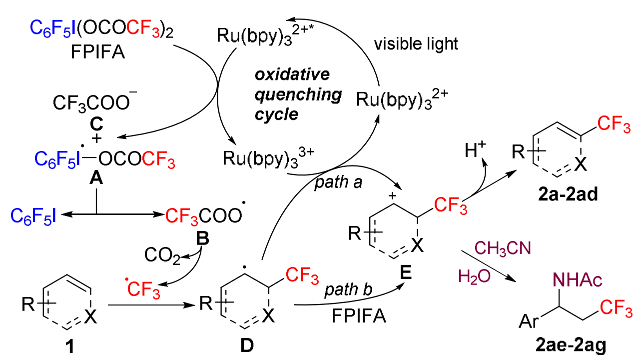
Scheme 4. Substrate Scope of Decarboxylative Perfluoroalkylation Reaction[a]

[a]Reaction conditions: **1** (0.5 mmol), $C_6F_5I(OCORf)_2$ (1.25 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol), CH_3CN (7.5 mL), blue LEDs, 35 °C, under N_2, 12 h, isolated yields. [b]Yields determined by ^{19}F NMR using trifluoromethoxybenzene as an internal standard.

To demonstrate the scalability of the present photocatalytic reaction, the decarboxylative trifluoromethylation of **1v** with FPIFA was carried out on a 10.0 mmol scale (Scheme 5). The desired product **2v** was isolated in 63% yield (1.3 g), which was slightly inferior to the corresponding reaction presented in Scheme 3. Simultaneously, pentafluoroiodobenzene was recycled in 78% yield (5.7 g) and could be used for the preparation of FPIFA (see the supporting information).



Scheme 5. A Gram-Scale Decarboxylative Trifluoromethylation Reaction



Scheme 6. Proposed Reaction Mechanism

On the basis of the results in Table 1 as well as previous reports,[15,17d] a plausible reaction mechanism is proposed in Scheme 6. First, irradiation of $Ru(bpy)_3^{2+}$ with visible light gives the excited-state $*Ru(bpy)_3^{2+}$. Then, SET oxidation of $*Ru(bpy)_3^{2+}$ [$E_{1/2}(Ru^{II}*/Ru^{III})$ = -0.81 V vs SCE in CH_3CN][25] by FPIFA (E_{pc} = -0.08 V vs SCE in CH_3CN, see the supporting information) affords $Ru(bpy)_3^{3+}$ and the iodanyl radical **A**. The Stern-Volmer fluorescence quenching studies confirmed that FPIFA could quench $*Ru(bpy)_3^{2+}$ effectively (Figure 1). Subsequently, intermediate **A** undergoes a homolytic scission of the I-O bond to generate pentafluoroiodobenzene and a trifluoroacetoxy radical **B**. In this step, the difference of the calculated I-O bond homolytic dissociation enthalpy between intermediates **A** and **A'** (Scheme 7) reveals that the radical intermediate **A'** from PIFA is harder to proceed a homolytic scission, which partly interprets why PIFA could not undergo the decarboxylative trifluoromethylation reaction (Table 1, entry 1). The resulting radical **B** extrudes CO_2 to generate the CF_3 radical, which is then added to arenes **1** for the formation of intermediate **D**. Radical **D** might be oxidized by $Ru(bpy)_3^{3+}$ (path a) and/or FPIFA (path b) to afford the corresponding cation **E**. Finally, intermediate **E** undergoes deprotonation or nucleophilic attack to give the desired products **2**.

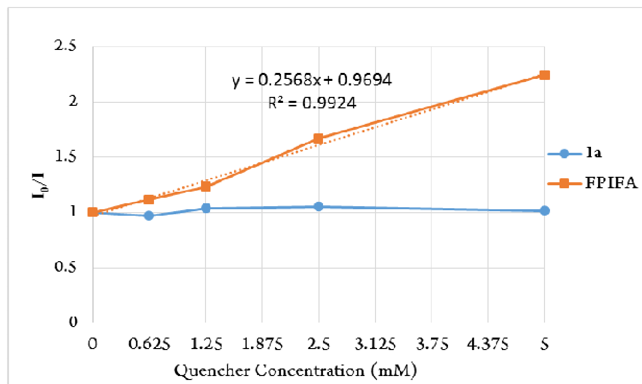
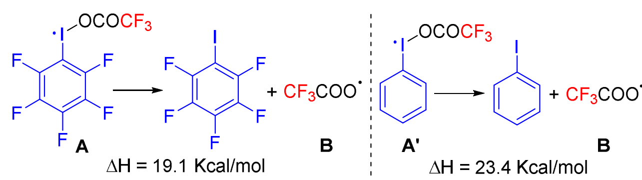
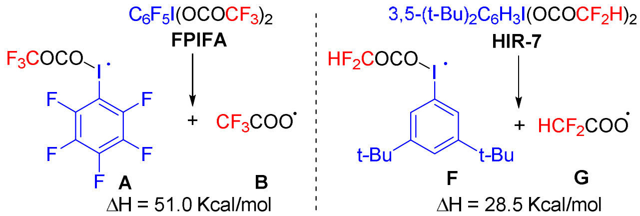


Figure 1. $Ru(bpy)_3(PF_6)_2$ Emission Quenching with FPIFA and 1a.



Scheme 7. DFT-Calculated I-O Bond Dissociation Enthalpy for Intermediates A and A' in CH_3CN (M062X/6-311++G)**

To compare the current photoredox catalysis decarboxylation trifluoromethylation protocol with Maruoka's photolysis difluoromethylation without photocatalyst,[16b] the DFT calculations of the I-O bond dissociation enthalpy of PFIPA and 3,5-(t-Bu)$_2C_6H_3I(OCOCF_2H)_2$ (**HIR-7**)[16b] were conducted. As shown in Scheme 8, the calculated I-O bond homolytic dissociation enthalpy of FPIFA (ΔH = 51.0 Kcal/mol) is much higher than that of CF_2H-containing **HIR-7** (ΔH = 28.5 Kcal/mol). These results explain why a photocatalyst was required for the formation of intermediate **A** from FPIFA (Scheme 6).



Scheme 8. DFT-Calculated I-O Bond Dissociation Enthalpy for FPIFA and HIR-7 in CH_3CN (M062X/6-311++G)**

In conclusion, we have developed a practical visible-light-induced decarboxylative trifluoromethylation of (hetero)arenes using the easily accessible FPIFA as the trifluoromethylating reagent. This method is tolerant of various (hetero)arenes and functional groups. The combination of photoredox catalysis and HIRs provides a practical approach for the application of TFA as a trifluoromethyl source.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

Detailed experimental procedures, characterization data, mechanistic study data, copies of ^{1}H, ^{19}F and ^{13}C NMR spectra, and X-ray crystal structure of **2aa, 2ab**-b, **2ab**-di.

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SYNOPSIS TOC.