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Visible Light-Mediated Trifluoromethylation of Fluorinated Alkenes via C–F Bond Cleavage

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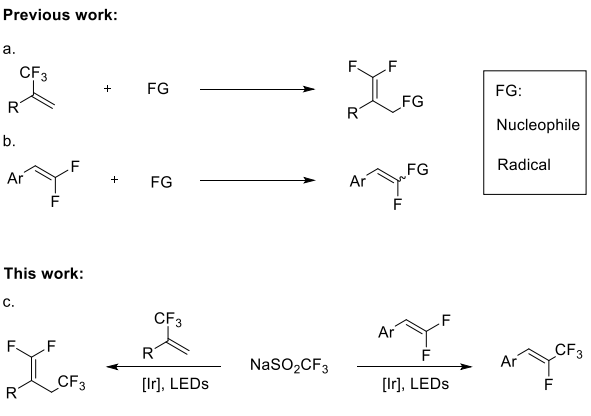
Abstract: A convenient photoredox-catalyzed defluorinative trifluoromethylation of *α*-trifluoromethyl alkenes and *gem*-difluoroalkenes is developed. The reactions proceeded efficiently via trifluoromethyl radical addition followed by *β*-fluorine elimination process, providing a new entry to multifluorinated alkenes in moderate to good yields with excellent stereoselectivity.

Keywords: Photocatalysis; C-F bond cleavage; Trifluoromethylation; Iridium; Sodium triflinate

Organofluorine compounds play a very important role in pharmaceutical chemistry and agriculture chemistry, mainly owing to their unique chemical and biological properties.[1] Therefore, the construction of fluorinated compounds has gained considerable momentum in recent years. Transformation of multifluorinated compounds via C–F bond functionalization provides a novel approach for the preparation of functional and bioactive fluorine-containing molecules. Despite the C–F bond's high dissociation energy, numerous strategies have been developed to achieve the cleavage of C–F bonds.[2] Compared to traditional methods, which normally need harsh reaction conditions or stoichiometric organometallic reagents, visible light-mediated C–F bond cleavage by using photoredox catalysis has emerged as a promising option for the functionalization of multifluorinated compounds under mild reaction condition.[3]

Among the various multifluorinated compounds, *α*-trifluoromethyl alkenes are considered to be versatile building blocks which generally undergo S_N2'-type reactions with nucleophiles to achieve C–F bond cleavage of the CF_3 group (Scheme 1a).[4] Recently, radical processes to access *gem*-difluoroalkenes from *α*-trifluoromethyl alkenes by employing photoredox catalysis have been achieved.[5] Meanwhile, the functionalization of *gem*-difluoroalkenes by using nucleophiles via C–F bond cleavage in the presence of transition metal has also been explored.[6] Particularly, an efficient visible light photoredox-catalyzed monofluoroalkenylation of *gem*-difluoroalkenes has been reported by the Hashmi and Fu groups (Scheme 1b).[7]

In the last few years, photocatalytic trifluoromethylation has received considerable attention from synthetic chemists and has been widely investigated.[8] Meanwhile, our group has reported a series of work on trifluoromethylation of alkenes and C–F bond functionalization.[9] However, we realized that the synthesis of multifluorinated molecules by means of trifluoromethylation via *β*-fluorine elimination is still underdeveloped. Moreover, due to the involvement of radical process in photocatalysis, the stereoselectivity is poorly controlled when unsymmetrical *gem*-difluoroalkenes are employed as substrates. Herein, we reported an efficient and practical photoredox-catalyzed trifluoromethylation of fluorinated alkenes through C–F bond cleavage by using CF_3SO_2Na as trifluoromethyl source,[10] providing CF_3-containing multifluorinated molecules with excellent stereoselectivity (Scheme 1c).



Scheme 1. Strategies to functionalize multifluorinated compounds via C–F bond cleavage.

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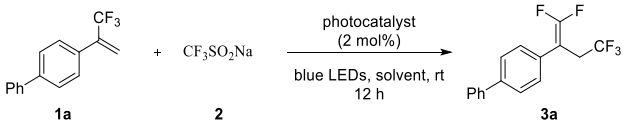
Initially, 4-(3,3,3-trifluoroprop-1-en-2-yl)biphenyl (**1a**) and CF_3SO_2Na (**2**) were chosen as the model substrates to explore the optimum reaction conditions under the irradiation of blue LEDs (Table 1). Among different solvents screened in the presence of $[Ir(ppy)_2dtbpy]PF_6$ (**PC1**), the use of CH_3CN, DMSO, or acetone led to poor product yields (entries 1-3), while the use of DMF provided a moderate product yield (entry 4). Subsequent optimization showed that $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (**PC2**) was more efficient, improving the yield of **3a** to 71% (entry 5), which might be rationalized by **PC2**'s higher oxidizing excited state ($E_{1/2}^{III*/II}$ = +1.21 V *vs* SCE), as compared with **PC1** ($E_{1/2}^{III*/II}$ = +0.66 V *vs* SCE).[11] Based on the results, it seemed that polar solvents were preferred in this transformation. A further survey of other polar solvents showed that DMA was the solvent of choice, producing **3a** in 90% yield (entry 6).[12] Notably, halving the catalyst would reduce the product yield (entry 7), and control experiments demonstrated that both light and photocatalyst are essential in this reaction (entries 8 and 9).

Table 1. Optimization of visible light-mediated defluorinative trifluoromethylation of **1a**.[a]



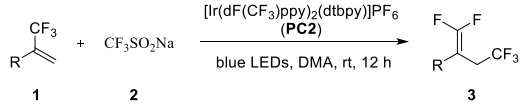
1a 2 3a

Entry	Catalyst	Solvent	Yield [%][b]
1	**PC1**	CH_3CN	21
2	**PC1**	DMSO	22
3	**PC1**	acetone	15
4	**PC1**	DMF	48
5	**PC2**	DMF	71
6	**PC2**	DMA	90
7	**PC2**	DMA	83[c]
8	**PC2**	DMA	0[d]
9	--	DMA	0

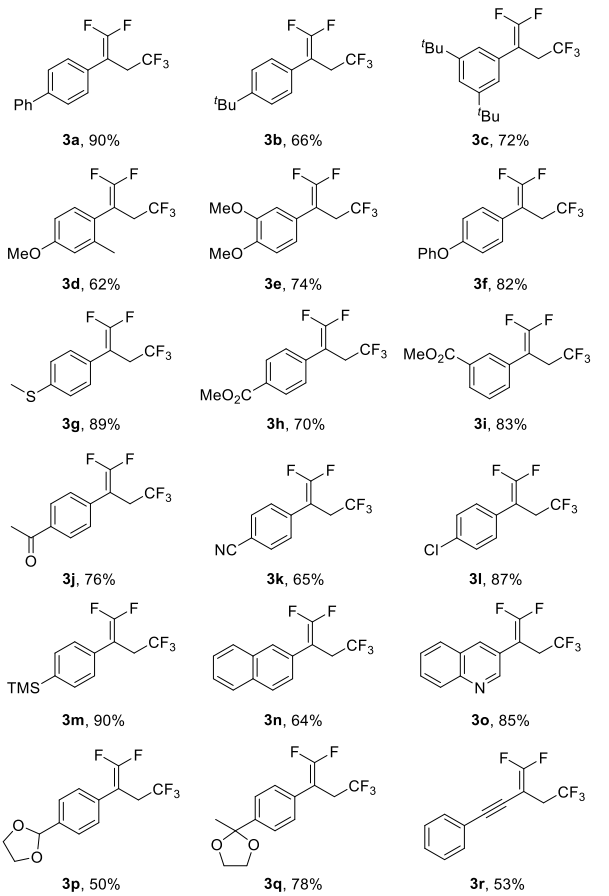
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), photocatalyst (0.004 mmol), blue LEDs, solvent (1 mL), rt, 12 h.
[b] Isolated yield.
[c] Photocatalyst (0.002 mmol).
[d] Without light.

With the optimized reaction conditions in hand (Table 1, entry 6), we then investigated the substrate scope of the present transformation (Table 2). Substrates containing electron-donating, electron-withdrawing, or halide substituents in *ortho*, *meta* or *para* position were amenable to the reaction conditions to give products **3b**-**l** in 62-89% yields. It was noteworthy that a substrate bearing a silyl group underwent the reaction smoothly, even in the presence of F^-, leading to the product **3m** in an excellent yield, which is a versatile building block suitable for further modification. Moreover, the reaction was compatible to both naphthalene-substituted and heteroaryl-substituted substrates, giving rise to **3n** and **3o** in moderate to good yields. Especially noteworthy is that protected aldehyde and ketone (**3p** and **3q**) also proved to be suitable candidates for this organic transformation. Furthermore, enynyl substrate, 2-trifluoromethyl-1,3-enyne, was also capable of undergoing the present trifluoromethylation smoothly to produce the corresponding 1,1-difluoro-1,3-enyne **3r** in 53% yield.

Table 2. Defluorinative trifluoromethylation of α-trifluoromethyl alkenes.[a]



1 2 3

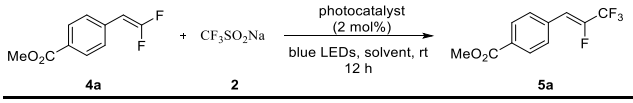


[a] Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), **PC2** (0.004 mmol), blue LEDs, DMA (1 mL), rt, 12 h. Yields of isolated products are given.

Encouraged by the results of trifluoromethylation via C–F bond cleavage of α-trifluoromethyl alkenes, we further explored the defluorinative trifluoromethylation of *gem*-difluoroalkenes in this transformation (Table 3). Unfortunately, under the afore-mentioned reaction conditions, the reaction involving *gem*-difluorostyrene **4a** only provided the desired product **5a** in a low yield with extremely poor stereoselectivity (entries 1-3). Compared to **PC2**, the use of $[Ir(dF(CF_3)ppy)_2(5,5'$-

d(CF_3)bpy)]PF_6 (**PC3**), whose reduced Ir^{II} state has higher reduction potential ($E_{1/2}^{III/II}$ = -1.07 V *vs* Fc^+/Fc), as compared to the reduced state of **PC1** and **PC2**,[13] led to good stereoselectivity (*Z*/*E* = 94:6) with slightly higher yield (entry 4). Among the various solvents and additives surveyed in this reaction (entries 5-9), **PC3** in combination with $LiClO_4$[14] as additive in acetone was identified as the best choice to afford the product **5a** in 52% yield with excellent stereoselectivity (*Z*/*E* = 99:1, entry 9), indicating that less polar solvent is more appropriate for this transformation.[15]

Table 3. Optimization of the visible light-mediated defluorinative trifluoromethylation of **4a**.[a]

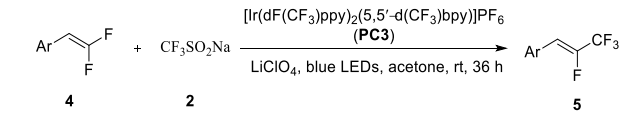


4a **2** **5a**

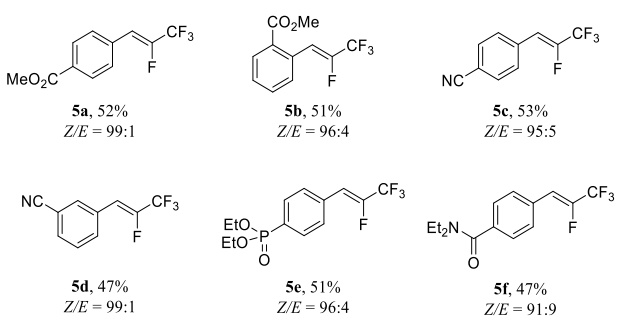
Entry	Catalyst	Additive	Solvent	Yield [%][b]	*Z*/*E*[c]
1	**PC2**	--	DMA	15	50:50
2	**PC2**	--	DMSO	22	50:50
3	**PC1**	--	DMSO	15	55:45
4	**PC3**	--	DMSO	28	94:6
5	**PC3**	--	CH_3CN	33	99:1
6	**PC3**	--	acetone	37	99:1
7	**PC3**	--	acetone	43[d]	99:1
8	**PC3**	Li_2CO_3	acetone	45[d]	99:1
9	**PC3**	$LiClO_4$	acetone	52[e]	99:1

[a] Reaction conditions: **4a** (0.2 mmol), **2** (0.4 mmol), photocatalyst (0.004 mmol), additive (0.3 mmol), blue LEDs, solvent (1 mL), rt, 12 h.
[b] Isolated yield.
[c] The *Z*/*E* ratio was determined by crude ^{19}F NMR.
[d] Photocatalyst (0.006 mmol).
[e] Photocatalyst (0.006 mmol), 36 h.

Table 4. Defluorinative trifluoromethylation of *gem*-difluoroalkenes.[a]



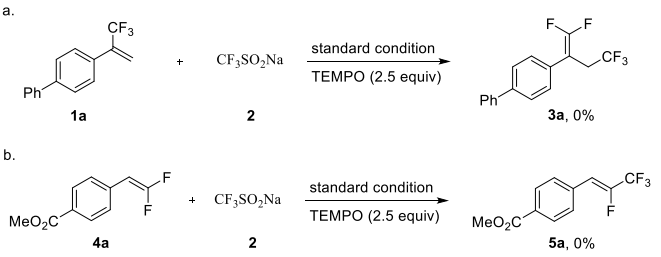
4 **2** **5**



[a] Reaction conditions: **4** (0.2 mmol), **2** (0.4 mmol), **PC3** (0.006 mmol), $LiClO_4$ (0.3 mmol), blue LEDs, acetone (1 mL), rt, 36 h. Yields of isolated products are given. *Z*/*E* ratio was determined by crude ^{19}F NMR.

Next, the substrate scope and limitations with *gem*-difluoroalkene derivatives were investigated (Table 4). In this transformation, substrates bearing electron-withdrawing groups reacted smoothly to deliver the corresponding products **5a-f** in moderate yields. However, substrates containing electron-donating groups were not suitable in this reaction, which was possibly ascribed to its low reactivity or the instability of the formed α-trifluoromethylcarbanion intermediate during the course of the transformation. Notably, *gem*-difluoroalkenes bearing important functional groups such as ester, cyanide, organophosphate, and amide were amenable to this reaction. The transformation proceeded with excellent stereoselectivity (up to 99:1 *Z*/*E*). This result is in agreement with the reported result based on calculation,[16a] where the *Z* isomer displays thermodynamically higher stability and kinetically lower energy barrier in the transition state. Also, compared to fluoride, the trifluoromethyl group is bulkier and thus it prefers to attack the C-C triple bond via an orientation trans to the sterically hindered aryl group, thereby giving a less hindered *Z* isomer.[16] In addition, it should be mentioned that when the optimized reaction conditions were applied to the trifluoromethylation of compound **3a** which also contains a *gem*-difluoroalkene moiety, only traces of the defluorinative product was obtained.

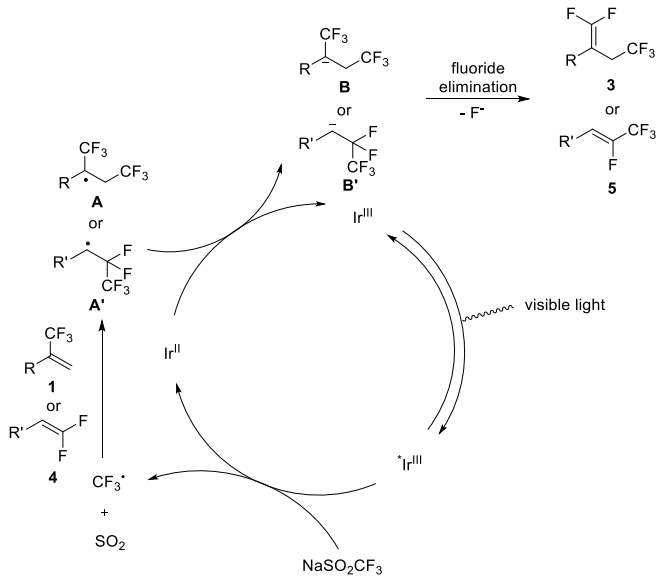
To gain mechanistic insight into this defluorinative trifluoromethylation, radical trapping experiments were performed. When the reaction mixture of **1a**/**4a** and **2** were treated with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) under the standard reaction conditions, the defluorinative trifluoromethylation was completely inhibited (Scheme 2a and 2b). The results implied that a radical process is likely involved in this reaction. In order to further explore possible isomerization mechanism of **5**, *E*/*Z*-**5a** was introduced into the reaction system under standard reaction conditions (Table 3, entry 9). However, the *E*/*Z* ratio remained the same after reaction, suggesting that isomerization was not likely induced through energy transfer process.[3d,17]



Scheme 2. Control experiments.

On the basis of above experimental results, a plausible reaction mechanism was proposed (Scheme 3). Initially, $NaSO_2CF_3$ is oxidized by visible light-excited $^*Ir^{III}$ via a single electron transfer (SET) process to

generate trifluoromethyl radical ($CF_3^{\bullet}$), along with the generation of reduced Ir^{II}. Next, $CF_3^{\bullet}$ undergoes a radical addition to alkene **1** or **4** to deliver a transient *α*-trifluoromethyl radical **A** or **A´**, which subsequently undergoes a SET reduction by Ir^{II}, providing an *α*-trifluoromethyl anion **B** or **B´** with the concomitant regeneration of photocatalyst Ir^{III}. Finally, *β*-fluoride elimination readily occurs to furnish the desired product **3** or **5**.



Scheme 3. Proposed mechanism for photoredox-catalyzed trifluoromethylation of fluorinated alkenes through C(sp2 & sp3)–F bond cleavage.

In summary, an efficient defluorinative trifluoromethylation of *α*-trifluoromethyl alkenes and *gem*-difluoroalkenes via Ir photoredox catalyzed C–F bond cleavage has been developed. This reaction provides a convenient and efficient approach to construct substituted difluoroalkenes, which is compatible with various functional groups. Meanwhile, the reaction exhibits excellent stereoselectivity with *gem*-difluoroalkenes, which provides potential for further applications in pharmaceutical and agrochemical research.

Experimental Section

General procedures for the defluorinative trifluoromethylation of *α*-trifluoromethyl alkenes

To an 8 mL sample vial, charged with $[Ir(dF(CF_3)ppy)_2dtbpy]PF_6$ (**PC2**) (4.4 mg, 0.004 mmol, 2 mol%), and CF_3SO_2Na (46.8 mg, 0.3 mmol. 1.5 equiv) in dimethylacetamide (1 mL) was added *α*-trifluoromethyl alkene (0.2 mmol, 1 equiv) under nitrogen atmosphere at room temperature. The vial was sealed with screw cap and stirred at room temperature under blue LEDs for 12 h. The reaction mixture was diluted with EtOAc (10 mL), washed with water (2×20 mL), brine (20 mL), and concentrated under vacuum. Purification by silica gel column chromatograph using CH_2Cl_2 and hexane as eluent afforded the target product.

General procedures for the defluorinative trifluoromethylation of *gem*-difluoroalkenes

To an 8 mL sample vial, charged with $[Ir(dF(CF_3)ppy)_2(5,5'-d(CF_3)bpy)]PF_6$ (**PC3**) (7.0 mg, 0.006 mmol, 3 mol%), $LiClO_4$ (31.8 mg, 0.3 mmol, 1.5 equiv) and CF_3SO_2Na (62.4 mg, 0.4 mmol. 2.0 equiv) in acetone (1 mL) was added *gem*-difluoroalkene (0.2 mmol, 1 equiv) under nitrogen atmosphere at room temperature. The vial was sealed with screw cap and stirred at room temperature under blue LEDs for 36 h. The reaction mixture was diluted with EtOAc (10 mL), filtered through filter paper and concentrated under vacuum. Purification by silica gel column chromatograph using DCM and hexane as eluent afforded the target product.

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