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Photoredox Catalysis Mediated Application of Methyl Fluorosulfonyldifluoroacetate as the CF_2CO_2R Radical Source

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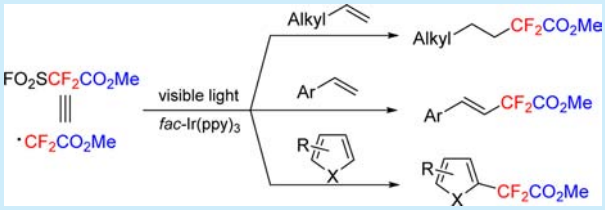
Supporting Information

ABSTRACT: A new application of trifluoromethylating reagent, methyl fluorosulfonyldifluoroacetate ($FO_2SCF_2CO_2Me$, Chen's reagent), as the carbomethoxydifluoromethylating reagent under visible light photoredox conditions is reported. The visible-light-induced reaction of $FO_2SCF_2CO_2Me$ with unactivated alkenes, styrenes, or heteroarenes affords a variety of carbomethoxydifluoromethylated products.



Difluoromethylene-containing compounds have attracted considerable attention in pharmaceuticals, agrochemicals, and materials[1] because of the unique properties of the difluoromethylene group (CF_2).[2] In particular, the difluoromethylene group has been used as an isopolar and isosteric substitute for oxygen atoms in drug discovery and development. However, in contrast to the significant advances of trifluoromethylation[3] and difluoromethylation,[4] the analogous difluoromethylenation has been less explored, probably due to the shortage of the difluoromethylenating agents.

Molecules containing a CF_2CO_2R moiety can not only alter the properties of the molecules but also provide valuable CF_2-containing building blocks for the synthesis of other difluoromethylenated compounds.[5] Traditionally, the CF_2CO_2R-containing compounds were prepared by fluorination of a carbonyl moiety.[6] The direct introduction of the CF_2CO_2R moiety to organic molecules has provided an alternative strategy for the preparation of these compounds. In this context, significant advances have been achieved recently using $BrCF_2CO_2Et$ (**A**, Figure 1) as the CF_2CO_2R source through a radical pathway[7] or transition-metal-catalyzed coupling.[8] The difluoromethylenation with $ClCF_2CO_2Et$ (**B**) or ICF_2CO_2Et (**C**) has also been reported to adopt similar strategies.[9] As a typical nucleophilic difluoromethylenating agent, $TMSCF_2CO_2Et$ (**D**) has found wide applications in the preparation of various difluoromethylenated compounds.[10] Furthermore, Fuchigami and co-workers initially developed the photolysis of ethyl α,α-difluoro-α-(phenylthio)acetate (**E**) or ethyl α,α-difluoro-α-(phenylseleno)acetate (**F**) to generate the CF_2CO_2Et radical, which can be trapped by a series of unsaturated compounds.[11] Recently, Dolbier and co-workers reported the carbomethoxydifluoromethylation of double bonds with methyl chlorosulfonyldifluoroacetate (**G**).[12] Despite the advances of the aforementioned direct difluoromethylenation protocols, the development of new, readily accessible CF_2CO_2R sources remains to be explored.

Methyl fluorosulfonyldifluoroacetate (**H**, $FO_2SCF_2CO_2Me$) is a commercially available and easy to handle liquid. In 1989, Chen and Wu first reported that $FO_2SCF_2CO_2Me$ was used as a suitable reagent for trifluoromethylation in the presence of CuI.[13] Nowadays, $FO_2SCF_2CO_2Me$ (Chen's reagent) is widely applied for the preparation of various trifluoromethylated compounds (Scheme 1a).[14] The mechanistic studies of this trifluoromethylation showed that the copper salt ($FO_2SCF_2CO_2Cu$) was initially formed and the salt then easily decomposed to release $:CF_2$ and F^-,[13] which were in

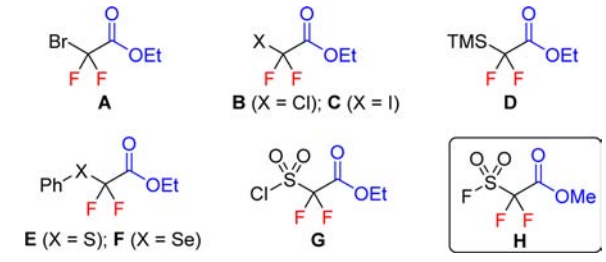
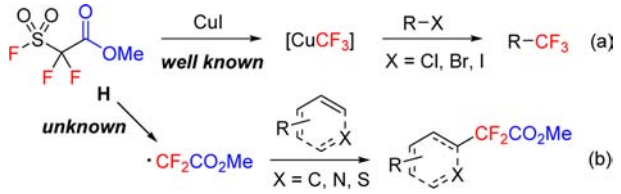


Figure 1. Various CF_2CO_2R sources.

Scheme 1. Synthetic Application of $FO_2SCF_2CO_2Me$



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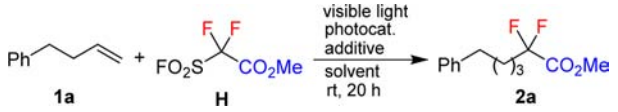
equilibrium with the trifluoromethyl anion. To extend its application further, we envisaged that $FO_2SCF_2CO_2Me$ might be used as a CF_2CO_2R radical source under visible light catalysis on the basis of photopromoted fluoroalkylation with fluoroalkylsulfonyl chlorides.[12,15] However, the S−F bond is stronger than the S−Cl bond,[16] which makes it more difficult to generate the CF_2CO_2Me radical from $FO_2SCF_2CO_2Me$ than that from $ClO_2SCF_2CO_2Me$. In our continuing effort to develop photocatalytic fluoroalkylation reactions,[17] we disclose here a new application of $FO_2SCF_2CO_2Me$ as a CF_2CO_2R source for the preparation of carbomethoxydifluoromethylated alkanes, alkenes, and heteroaromatics under visible light catalysis (Scheme 1b).

Initially, we focused on the hydrocarbomethoxydifluoromethylation of but-3-en-1-ylbenzene (**1a**) with $FO_2SCF_2CO_2Me$ in DMF by irradiation with blue LEDs at room temperature (Table 1). Among the common photocatalysts, such as

Table 1. Optimization of Reaction Conditions[a]



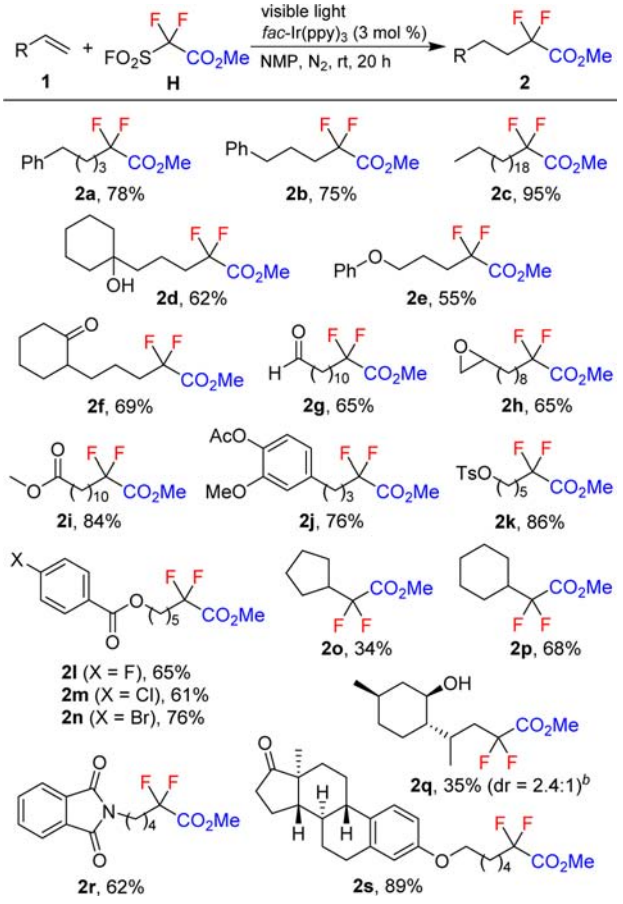
entry	photocat.	solvent	additive	yield[b] (%)
1	$Ru(bpy)_2Cl_2$	DMF		0
2	*fac*-Ir(ppy)$_3$	DMF		22
3	methylene blue	DMF		0
4	eosin Y	DMF		0
5	*fac*-Ir(ppy)$_3$	NMP		43
6	*fac*-Ir(ppy)$_3$	DMI		37
7	*fac*-Ir(ppy)$_3$	NMP	1,4-CHD	38
8	*fac*-Ir(ppy)$_3$	NMP	Hantzsch ester	28
9	*fac*-Ir(ppy)$_3$	NMP	Ph_3SiH	25
10[c]	*fac*-Ir(ppy)$_3$	NMP		70
11[d]	*fac*-Ir(ppy)$_3$	NMP		81
12[d,e]	*fac*-Ir(ppy)$_3$	NMP		86

[a]Reaction conditions: **1a** (0.2 mmol), $FO_2SCF_2CO_2Me$ (0.3 mmol), photocatalyst (0.01 mmol), additive (0.2 mmol), solvent (1.0 mL), visible light, rt, under N_2, 20 h. [b]Yields determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c]NMP (2.0 mL). [d]NMP (4.0 mL). [e]*fac*-Ir(ppy)$_3$ (0.006 mmol).

$Ru(bpy)_2Cl_2$, *fac*-Ir(ppy)$_3$, methylene blue (3,7-bis-(dimethylamino)phenothiazin-5-ium chloride), and Eosin Y, only *fac*-Ir(ppy)$_3$ could promote this reaction to give the desired product **2a** in 22% yield (entry 2). Switching the solvent to NMP or DMI resulted in slightly higher yields (entries 5 and 6). To improve the reaction yield, different hydrogen sources including 1,4-CHD (1,4-cyclohexadiene), Hantzsch ester (diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate), and Ph_3SiH were added to the reaction (entries 7−9). However, no higher yield of **2a** was observed. In contrast, more HCF_2CO_2Me was generated. The yield of **2a** was significantly increased when the reaction was performed in lower concentration (entries 10 and 11). Interestingly, the optimal yield (86%) of product **2a** was obtained when the amount of *fac*-Ir(ppy)$_3$ was decreased to 3 mol % (entry 12). It is noteworthy that no atom-transfer radical addition (ATRA) product was formed in the reaction system. This is a unique property of $FO_2SCF_2CO_2Me$ that is substantially different from other CF_2CO_2R sources.[9a,11,12c,15d,18]

The substrate scope of hydrocarbomethoxydifluoromethylation of alkenes is summarized in Scheme 2. Various unactivated

Scheme 2. Substrate Scope of Hydrocarbomethoxydifluoromethylation of Alkenes[a]



[a]Reaction conditions: **1** (0.4 mmol), $FO_2SCF_2CO_2Me$ (0.6 mmol), *fac*-Ir(ppy)$_3$ (0.012 mmol), NMP (8.0 mL), visible light, rt, under N_2, 20 h, isolated yields. [b]Diastereomeric ratio determined by ^{19}F NMR analysis of the crude reaction mixture.

alkenes were transformed into the corresponding products in moderate to excellent yields. The present reaction tolerates a variety of functional groups, such as alcohol (**1d**), ether (**1e**), ketone (**1f**), aldehyde (**1g**), epoxide (**1h**), ester (**1i,j**), amide (**1r**), sulfonic ester (**1k**), and halides (**1l−n**). The hydrocarbomethoxydifluoromethylation of internal alkenes (**1o,p**) and disubstituted alkene (**1q**) also proceeded to give the desired products **2o−q** in moderate yields. Furthermore, the estrone-derived terminal olefin (**1s**) was quite viable for this protocol. It was found that the reaction of styrenes (**3a,b**) with $FO_2SCF_2CO_2Me$ yielded alkenyl-CF_2CO_2Me products **4**, not the hydrocarbomethoxydifluoromethylated compounds (Scheme 3).

Next, we turned our attention to carbomethoxydifluoromethylation of heteroaromatics with $FO_2SCF_2CO_2Me$. As shown in Scheme 4, indoles (**5a,b**), pyrrole (**5c**), benzothiophene (**5d**), and thiophene (**5e**) were subjected to the visible-light photoredox conditions to give products **6a−e** in moderate yields. In the cases of benzofuran and furan, the yields were relatively low.

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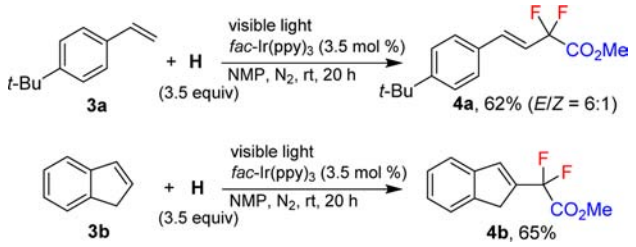
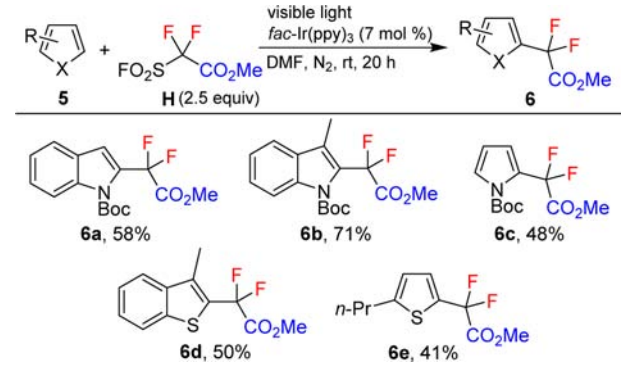
Scheme 3. Carbomethoxydifluoromethylation of Styrenes



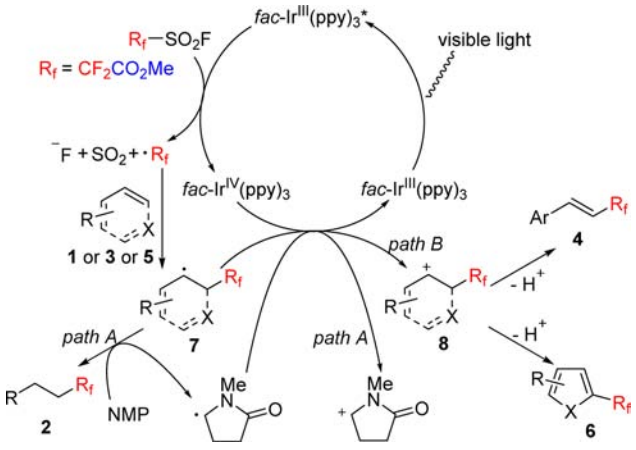
Scheme 4. Carbomethoxydifluoromethylation of Heteroarenes[a]



[a]Reaction conditions: **5** (0.4 mmol), $FO_2SCF_2CO_2Me$ (1.0 mmol), *fac*-Ir(ppy)$_3$ (0.028 mmol), DMF (8.0 mL), visible light, rt, under N_2, 20 h, isolated yields.

On the basis of the above results and related works,[12,15] a plausible reaction mechanism is depicted in Scheme 5. The

Scheme 5. Proposed Reaction Mechanism



irradiation of *fac*-Ir^{III}(ppy)$_3$ with visible light generates its excited state, *fac*-Ir^{III}(ppy)$_3$*. Then *fac*-Ir^{III}(ppy)$_3$* undergoes oxidative single-electron transfer (SET) with $FO_2SCF_2CO_2Me$ to form the CF_2CO_2Me radical, which subsequently adds to the substrates **1**, **3**, and **5** to afford radical intermediates **7**. The radical intermediates **7** might abstract hydrogen from NMP[10d,19] to give the hydrocarbomethoxydifluoromethylated product **2** (path A)[17b,c] or be oxidized to cation intermediates **8**, which further participate in deprotonation to produce **4** and **6** (path B).

In conclusion, we have disclosed a new application of Chen's reagent, $FO_2SCF_2CO_2Me$, as the carbomethoxydifluoromethylating reagent under visible-light photoredox conditions. Its reactivity was well demonstrated by carbomethoxydifluoromethylation of unactivated alkenes, styrenes, and heteroarenes. The commercial availability, ease of handling, and unique properties of $FO_2SCF_2CO_2Me$ in comparison to other CF_2CO_2R sources rendered it a highly attractive reagent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02580.

Experimental procedures, characterization data, and ^1H, ^{19}F, and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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