Photoredox Catalysis

International Edition: DOI: 10.1002/anie.201510533
German Edition: DOI: 10.1002/ange.201510533

Radical Fluoroalkylation of Isocyanides with Fluorinated Sulfones by Visible-Light Photoredox Catalysis

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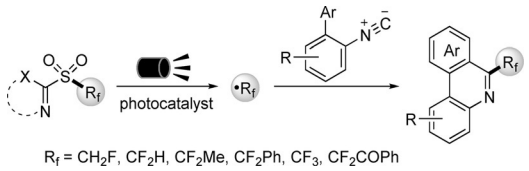
Abstract: *The radical fluoroalkylation of isocyanides with fluorinated sulfones is enabled by visible-light photoredox catalysis. A wide range of readily available mono-, di-, and trifluoromethyl heteroaryl sulfones can thus be used as efficient radical fluoroalkylation reagents under mild conditions. This method not only describes a new synthetic application of fluorinated sulfones, but also provides a new route to fluoroalkyl radicals.*

The incorporation of fluorinated moieties into organic molecules can often lead to significant changes of their physical, chemical, or biological properties.[1–3] Consequently, great efforts have been made to develop efficient strategies, methods, reagents, and catalysts for the incorporation of fluorine atoms or fluorinated moieties into organic molecules by nucleophilic, electrophilic, and radical pathways.[4] In recent years, radical fluoroalkylation reactions by visible-light photoredox catalysis have attracted much attention because of their mild reaction conditions and broad functional-group tolerance,[5,6] and many radical fluoroalkylation reagents, including fluoroalkyl halides (such as CF_3I,[7] $PhSO_2CF_2I$,[8] $BrCF_2COOEt$,[9] and $BrCHFCOOEt$[9b]), fluoroalkanesulfonyl halides (such as CF_3SO_2Cl,[10] HCF_2SO_2Cl,[11] and CH_2FSO_2Cl),[11a] the Umemoto reagents,[12] the Togni reagents,[4c,13] and the Langlois reagent,[14] have been used for this purpose. Although great progress has been made in photoredox fluoroalkylation,[6] especially trifluoromethylation, the known reagents suffer from limitations, such as the operational complexity introduced by removal of the activation group and the difficulty associated with handling some of the gaseous starting materials required to prepare these reagents. Therefore, it is still of great significance to develop operationally simple, easy-to-handle, and practical fluoroalkylation reagents that are suitable for efficient fluoroalkyl group transfer under photoredox catalysis.

As the "chemical chameleon" in organic synthesis, the sulfone functional group is ideal for various types of reactions, and its electron-withdrawing ability can be easily tuned.[15] In the past decade, fluorinated sulfones have been developed as versatile fluoroalkylation reagents and widely used for the incorporation of diverse fluoroalkyl groups into organic molecules by us and others.[4e] However, the use of fluoroalkyl sulfones and their derivatives for radical fluoroalkylation by R_f–SO_2 (R_f = fluoroalkyl) bond cleavage to form $R_f^{\bullet}$ radicals is challenging owing to the limitations of conventional radical initiators or single-electron-transfer (SET) reductants.[16] In recent years, visible-light photoredox catalysis has emerged as a powerful synthetic method for bond activation and construction processes that are usually difficult to achieve with conventional methods.[5] We envisioned that photoredox catalysts that can generate highly reactive SET reductants under mild conditions could be used to activate the R_f–SO_2 bonds of fluoroalkyl sulfones for radical fluoroalkylation. Herein, we report the use of mono-, di-, and trifluorinated heteroaryl sulfones as a new class of readily available, bench-stable, and reactivity-tunable radical fluoroalkylation reagents under visible-light photoredox catalysis (Scheme 1). The high efficiency of this method is demonstrated by the radical fluoroalkylation of various isocyanides as excellent radical acceptors[17] to afford fluoroalkylated phenanthridine derivatives.



Scheme 1. Radical fluoroalkylation with fluorinated sulfones.

We first investigated the radical reactivity of a series of difluoromethyl sulfones **2** by using isocyanide **1a** as a model substrate (Table 1). According to the first reduction potentials of several difluoromethyl sulfones (**2a**: −1.80 V; **2b**: −1.50 V; **2c**: −1.35 V; **2d**: −1.17 V versus the saturated calomel electrode, SCE) that we measured by cyclic voltammetry (see the Supporting Information), we initially used sulfone **2d**, which has the highest reduction potential, for the radical difluoromethylation of **1a** under photoredox conditions with $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ as the catalyst (2 mol%), Na_2CO_3 (2 equiv) as the base, and CH_3CN as the solvent (entry 1). We were pleased to find that the desired product **3a** was formed in 22% yield. Solvent screening showed that polar solvents were beneficial to this reaction (entries 1–7). In

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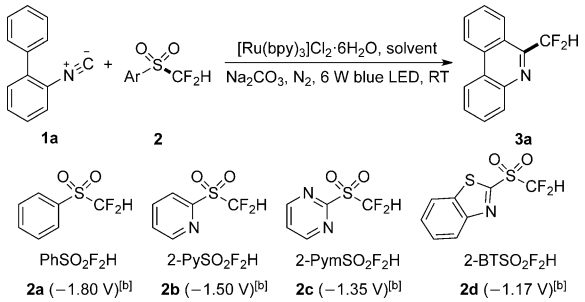
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510533.

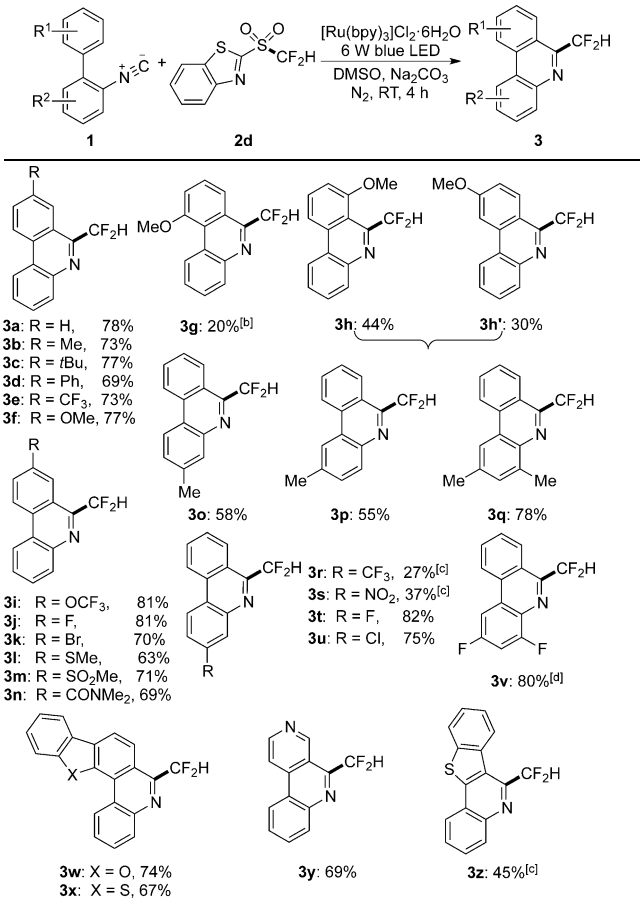
Table 1: Optimization of the reaction conditions.[a]



Entry	**2** (equiv)	Solvent	*t* [h]	Yield[c] [%]
1	**2d** (1.2)	CH_3CN	12	22
2	**2d** (1.2)	DMF	12	58
3	**2d** (1.2)	NMP	12	68
4	**2d** (1.2)	DMSO	12	78
5	**2d** (1.2)	THF	12	4
6	**2d** (1.2)	CH_2Cl_2	12	NR
7	**2d** (1.2)	toluene	12	NR
8	**2a** (1.2)	DMSO	12	NR
9	**2b** (1.2)	DMSO	12	15
10	**2c** (1.2)	DMSO	12	31
11[d]	**2d** (1.2)	DMSO	12	73
12[e]	**2d** (1.2)	DMSO	12	75
13	**2d** (1.0)	DMSO	12	68
14	**2d** (1.5)	DMSO	12	81
15	**2d** (2.0)	DMSO	12	64
16[f]	**2d** (1.5)	DMSO	12	64
17[g]	**2d** (1.5)	DMSO	12	78
18	**2d** (1.5)	DMSO	2	68
19	**2d** (1.5)	DMSO	4	81
20	**2d** (1.5)	DMSO	8	78

[a] Reaction conditions: **1a** (0.25 mmol), **2**, $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (2 mol%), and Na_2CO_3 (0.5 mmol) in DMSO (5 mL) were irradiated with a 6 W blue LED for 4 h at room temperature under N_2 atmosphere. [b] All potentials vs. SCE. [c] Determined by ^{19}F NMR spectroscopy with $PhCF_3$ as the internal standard. [d] 2 mL DMSO. [e] 10 mL DMSO. [f] 1 mol% [Ru]. [g] 5 mol% [Ru]. NR = no reaction.

Table 2: Difluoromethylation of isocyanides with sulfone **2d**.[a]



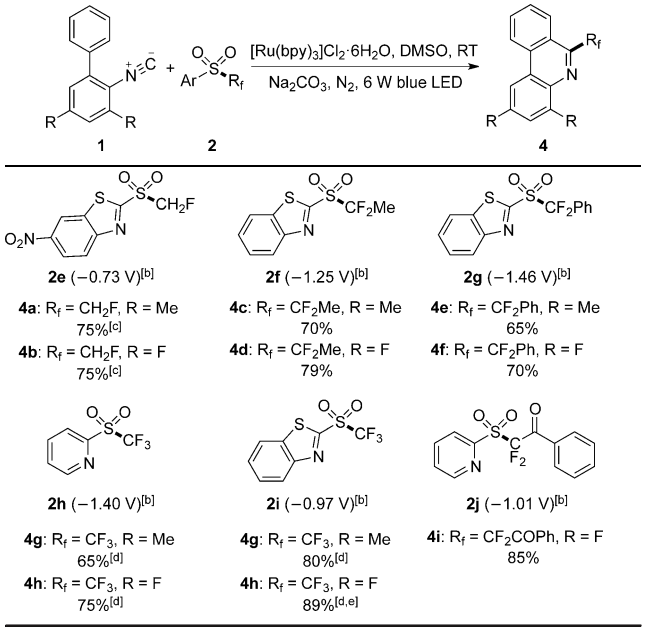
[a] Reaction conditions: **1** (0.25 mmol), **2d** (0.375 mmol), $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (2 mol%), and Na_2CO_3 (0.5 mmol) in DMSO (5 mL) were irradiated with a 6 W blue LED for 4 h at room temperature under N_2 atmosphere. Yields of isolated products are given. [b] **2d** (0.75 mmol); irradiation time: 12 h. [c] **2d** (0.75 mmol); irradiation time: 24 h. [d] Irradiation time: 2 h.

DMSO as the optimal solvent, a comparison of the reactions of sulfones **2a**–**2d** with isocyanide **1a** showed that their reactivity was in line with their reduction potentials, and sulfone **2d**, with the highest reduction potential, gave the best result (entries 4 and 8–10).[18] Finally, an optimization of several reaction parameters, including the concentration of the reactant, the catalyst and sulfone loadings, as well as the reaction time (entries 11–20), revealed that product **3a** could be obtained in the highest yield when the reaction of isocyanide **1a** was conducted with 1.5 equiv of sulfone **2d** and 2 mol% of $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ in DMSO at room temperature for four hours (entry 19).

With the optimized reaction conditions in hand (Table 1, entry 19), we further examined the scope of this radical difluoromethylation by using structurally diverse isocyanides **1**. As shown in Table 2, various substituents on the aryl ring, both electron-donating (**1b**–**1d**, **1f**, **1i**, and **1l**) and electron-withdrawing (**1e**, **1j**, **1k**, **1m**, and **1n**), are compatible with the reaction conditions, and the products were obtained in good yields. The 2-methoxy-substituted isocyanide **1g** was converted in poor yield (20%), presumably because only one *ortho* hydrogen atom was available on the aryl ring. The 3-methoxy-substituted isocyanide **1h** produced two products, **3h** and **3h′**, in yields of 44% and 30%, respectively. Isocyanides with various substituents on the aryl ring carrying the isocyanide group were also tested. Those with strongly electron-withdrawing groups, such as trifluoromethyl (**1r**) or nitro (**1s**) groups, gave poor yields. Others with weaker electron-withdrawing groups (**1t**, **1v**, and **1u**) or electron-donating groups (**1o**, **1p**, and **1q**), as well as those fused to other aryl (**1w** and **1x**) or heteroaryl (**1y** and **1z**) moieties, are all suitable substrates for this transformation, and the corresponding products **3** were obtained in moderate to good yields.

Encouraged by the excellent radical reactivity of difluoromethyl sulfone **2d**, we further investigated the application of other sulfones as fluoroalkyl radical sources (Table 3). We chose relatively electron-rich isocyanide **1q** and relatively electron-poor isocyanide **1v** as model substrates to test the reactivity. Two reagents with a 2-benzo[*d*]thiazolyl sulfone scaffold, namely 1,1-difluoroethyl sulfone **2f** and (phenyl)-difluoromethyl sulfone **2g** reacted smoothly with isocyanides

Table 3: Fluoroalkylation of isocyanides with various fluoroalkyl sulfones.[a]

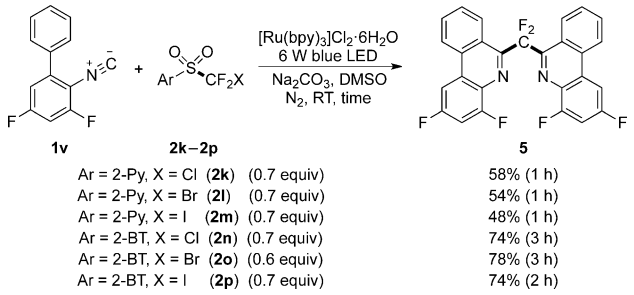


[a] Reaction conditions: **1** (0.25 mmol), **2** (0.375 mmol), $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (2 mol%), and Na_2CO_3 (0.5 mmol) in DMSO (5 mL) were irradiated with a 6 W blue LED for 4 h at room temperature under N_2 atmosphere. [b] All potentials are quoted vs. SCE. [c] **2** (0.75 mmol); irradiation time: 48 h. [d] **2** (0.30 mmol). [e] Irradiation time: 1 h.

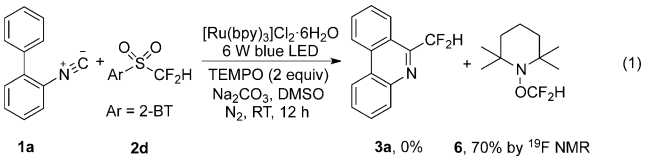
1v and **1q** to afford the corresponding difluoroalkylation products in good yields under the conditions optimized for difluoromethylation with sulfone **2d**. It is noteworthy that trifluoromethylation is not only achieved with 2-benzo[*d*]thiazolyl sulfone **2i**, but also by using sulfone **2h** with a less electron-deficient 2-pyridyl group owing to the stronger electron-withdrawing ability of the attached trifluoromethyl group. Similarly, radical (benzoyl)difluoromethylation could be carried out with 2-pyridyl sulfone **2j**. However, the generation of the monofluoromethyl radical from monofluoromethyl 2-benzo[*d*]thiazolyl sulfone was difficult under the same conditions owing to the poor electron-withdrawing ability of the monofluoromethyl group. However, we found that raising the reduction potential of the monofluoromethyl sulfone by introducing a nitro group on the 2-benzo[*d*]thiazolyl moiety significantly promoted the monofluoromethylation reaction (see **2e** in Table 3).

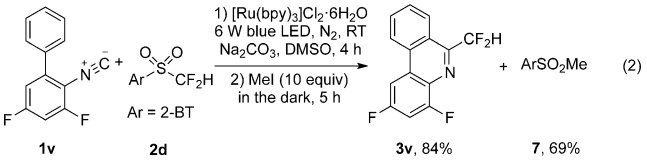
Furthermore, we also briefly investigated the reactivity of halodifluoromethyl sulfones (Scheme 2). When chloro-, bromo-, or iododifluoromethyl 2-pyridyl or 2-benzo[*d*]thiazolyl sulfone (**2k**–**2p**) was subjected to isocyanide **1v**, activation of both the R_f–X and R_f-SO_2 bonds afforded product **5** with a difluoromethylene group bridging two phenanthridine moieties (Scheme 2), suggesting that halodifluoromethyl sulfones can be used as equivalents of the difluoromethylene diradical.

To gain some insights into the reaction, we conducted a mechanistic study. First, control experiments showed that the reaction did not proceed in the absence of base, photocatalyst, or visible light (see the Supporting Information, Table S9). In the presence of the stable radical TEMPO, the reaction to form **3a** was fully inhibited, and product **6** was detected in 70% yield [Eq. (1)]. Second, the addition of methyl iodide after completion of the reaction could capture the sulfinate salt in 69% yield [Eq. (2)]. Third, a light on/off



Scheme 2. Fluoroalkylation with halodifluoromethyl sulfones. 2-BT = 2-benzo[*d*]thiazolyl.

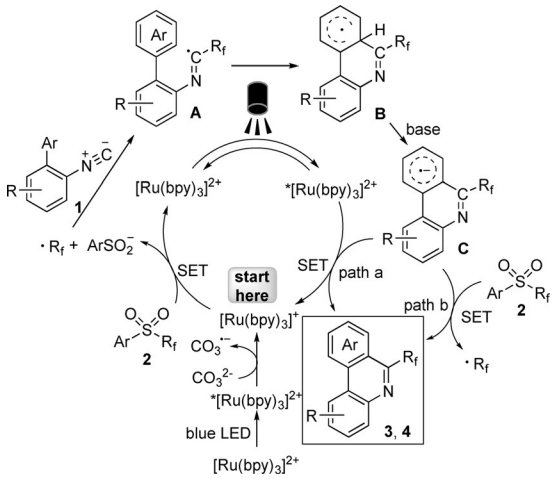




experiment showed that the yield of the desired product only increased when the light source was switched on (see the Supporting Information). These observations indicate that this fluoroalkylation reaction may proceed via a fluoroalkyl radical that is generated by one-electron reduction of the sulfone by the photocatalyst.

According to the measured reduction potentials of sulfones **2** (see Tables 1 and 3), we inferred that this fluoroalkylation reaction involves a reductive quenching cycle of the photocatalyst, $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ [$E_{1/2}(Ru^{2+}/Ru^{+}) = -1.33$ V vs. SCE].[19] In our reaction system, the carbonate ion (CO_3^{2-}) probably serves as the initial electron donor[20] to reduce $*[Ru]^{2+}$ to $[Ru]^{+}$ (for details, see the luminescence quenching experiments in the Supporting Information), and then $[Ru]^{+}$ reduces the fluoroalkyl sulfone to start the catalytic cycle.

On the basis of all of these results, a photoredox catalytic cycle is proposed in Scheme 3. First, the photocatalyst $[Ru]^{2+}$ is excited by irradiation with blue LEDs. The excited $*[Ru]^{2+}$ is reduced by CO_3^{2-} to $[Ru]^{+}$, which donates one electron to sulfone **2**, affording the sulfinate ion and a fluoroalkyl radical ($R_f^{\bullet}$). Then, $R_f^{\bullet}$ adds to isocyanide **1** to yield imidoyl radical **A**, which undergoes intramolecular radical cyclization to form intermediate **B**. Deprotonation of **B** by the base provides



Scheme 3. Proposed reaction mechanism.

radical anion **C**,[17b] which is oxidized by $*[Ru]^{2+}$ to generate product **3** or **4** and photocatalyst $[Ru]^{+}$ (path a). It is also possible that **C** reacts with fluoroalkyl sulfone **2** through a SET process to generate product **3** or **4** and $R_f^{\bullet}$ (path b).

In conclusion, the radical fluoroalkylation of isocyanides with fluorinated sulfones by R_f–SO_2 bond cleavage has been achieved by visible-light photoredox catalysis. A range of readily available, bench-stable, and reactivity-tunable fluoroalkyl sulfones have been shown to be monofluoromethyl, difluoromethyl, 1,1-difluoroethyl, (phenyl)difluoromethyl, (benzoyl)difluoromethyl, and trifluoromethyl radical precursors. This research opens a new door for the synthetic application of fluorinated sulfones as fluoroalkyl radical precursors. Further studies on radical fluoroalkylation reactions with sulfones are currently underway in our laboratory.

Acknowledgements

Support of our work by the National Basic Research Program of China (2015CB931900 and 2012CB821600), the National Natural Science Foundation of China (21372246, 21421002, and 21472221), the Chinese Academy of Sciences, Shanghai Science and Technology program (15XD1504400), and a Syngenta Ph.D. Studentship (to J.R.) is gratefully acknowledged. We thank Jianqing Sun at SIOC for cyclic voltammetry measurements. We also thank Dr. John Clough (Syngenta, Jealott's Hill International Research Centre) for critical reading of the manuscript.

Keywords: fluorine · isocyanides · photoredox catalysis · radical reactions · sulfones

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2743–2747
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[18] We also investigated the radical reactivity of sulfoximines **8a** and **8b** (see below) under the conditions given in Table 1, entry 4. Although N-silylated **8a** (TBS = *tert*-butyldimethylsilyl) was inert towards isocyanide **1a**, N-tosylated **8b** smoothly underwent the reaction to afford product **3a** in 18% yield, suggesting that fluorinated sulfoximines are potential fluoroalkyl radical sources; for a review, see: X. Shen, J. Hu, *Eur. J. Org. Chem.* **2014**, 4437.

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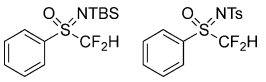

8a **8b**

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Received: November 13, 2015
Revised: December 12, 2015
Published online: January 19, 2016

