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Visible Light-Mediated Metal-Free Synthesis of Trifluoromethylselenolated Arenes: Scope and Mechanism

Clément Ghiazza,^[a] Vincent Debrauwer,^[a] Cyrille Monnereau,^[b] Lhoussain Khrouz,^[b] Maurice Médebielle,^[a] Thierry Billard*^[a, c] and Anis Tlili*^[a]

Abstract: The first visible light-mediated synthesis of trifluoromethylselenolated arenes under metal free conditions is reported herein. The use of an organic photocatalyst allows the trifluoromethylselenolation of arene diazonium salts, using the shelf-stable reagent trifluoromethyl tolueneselenosulfonate, at room temperature. The reaction does not require the presence of any additive and shows a large functional group tolerance covering a very broad scope of starting materials. Mechanistic investigations, including EPR, fluorescence and cyclic voltammetry allow the rationalisation of the reaction mechanism.

The combination of the trifluoromethyl group with chalcogens has gained widespread interest in modern organofluorine chemistry. The unique properties resulting from this conjunction are the key factor for the perpetual and growing interest in life sciences and materials,^[1] as they affect the physicochemical properties^[2], most significantly their lipophilicity.^[3]

Thus, even though efforts have been made for a long time to incorporate trifluoromethyl-chalcogen groups into organic molecules, a real renaissance has been seen in the last decade.^[4] Within that framework, reagents development and design as well as discrete catalyst synthesis were the key points for such achievements. Indeed, on the one hand, catalysis allowed encompassing very large panels of fluorinated moieties. On the other hand, the developed reagents constitute one of the major toolbox for synthetic organofluorine chemistry. Taking advantage of those new tools, several research groups investigated the synthesis of a plethora of different reagents for the introduction of trifluoromethyl-chalcogen moieties. During this span, trifluoromethylthiolation reactions have been well developed,^[4d-j] whereas trifluoromethylselenolation reactions are still underdeveloped although selenolated compounds are involved in a large panel of applications^[5] and could be considered as one of the most lipophilic group.^[6] In this regard,

our group has been active in the development and design of new reagents for the introduction SeCF₃ moiety into organic substrates.^[4e] More recently, we reported the synthesis as well as use of new shelf-stable reagents for electrophilic trifluoromethylselenolation, namely trifluoromethyl tolueneselenosulfonate.^[7]

With our continuous interest to discover and develop new synthetic methodologies, we turned our attention to study the formation of C(sp²)-SeCF₃ bonds using the above-mentioned compound. Regarding the state of the art, the use of nucleophilic ammonium trifluoromethylselenide is the most studied approach in conjunction with aryl halides under nickel^[8] or palladium^[9] catalysis. Also, arene diazonium salts^[10] and arylboronic acids^[7b, 11] have been used as starting materials. Finally, discrete σ -bonded copper-SeCF₃ complexes have been employed in stoichiometric fashion for the trifluoromethylselenolation of aryl iodides and activated bromides.^[12]

From a conceptual standpoint, we questioned whether organic photoredox catalysis^[13] might leverage the orthogonality of transition-metal-catalyzed C(sp²)-SeCF₃ bond formation under mild reaction conditions.^[14] We envisioned the use of arene diazonium salts that exhibit mild reduction potentials. This class of substrates can easily be prepared from readily available anilines. Next, we selected Eosin Y^[15] as an organic photocatalyst, known as a potential reducer for arene diazonium salts. The first test was performed by mixing the diazonium salt **1a** with our shelf-stable reagent **I** in the presence of 5 mol% of Eosin Y in DMSO at room temperature under irradiation of a white led lamp. This initial attempt led to the formation of the desired product in 77% yield (Table 1, Entry 1). The product was also formed in DMF as solvent although with a significantly lowered yield of 42% (Table 1, Entry 2). When THF or ACN were tested, only traces of the product were formed. Blank reactions were performed which did not lead to the formation of any traces of the desired product proving the necessity for both, Eosin Y and light irradiation in the reaction mechanism (Table 1, Entries 5-7).

With these optimized conditions in hand, we turned our focus to the scope of the reaction (Scheme 1). The system is tolerant to electron donating groups and shows that **1a** and **1b** are converted to their corresponding trifluoromethylselenolated product in good to excellent yields (up to 83%). In addition, steric hindrance is tolerated to a significant extent. Indeed, the presence of one or two substituents in the *ortho* position, including methoxy (**1c**), methyl (**2d**) and even SME substituents (**2e**) were tolerated under these conditions. Taking advantage of the metal free conditions, halogenated derivatives such as iodine (**1f**) and fluorine (**1g**) containing arenes were selectively converted into their corresponding products in very good to excellent yields (up to 78%). Electron-deficient arene diazonium

[a] C. Ghiazza, V. Debrauwer, Dr. M. Médebielle, Dr. T. Billard, Dr. A. Tlili
Institute of Chemistry and Biochemistry (ICBMS-UMR CNRS 5246)
Univ Lyon, Université Lyon 1, CNRS, CPE-Lyon, INSA
43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France
E-mail: thierry.billard@univ-lyon1.fr
anis.tlili@univ-lyon1.fr
www.FMI-Lyon.fr

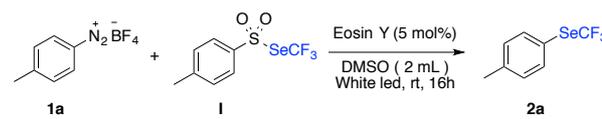
[b] Dr. C. Monnereau, L. Khrouz
Univ Lyon, Ens de Lyon, CNRS UMR 5182, Université Lyon 1,
Laboratoire de Chimie, F-69342, Lyon, France

[c] Dr. T. Billard
CERMEP – in vivo imaging
Groupement Hospitalier Est
59 Bd Pinel, 69003 Lyon, France

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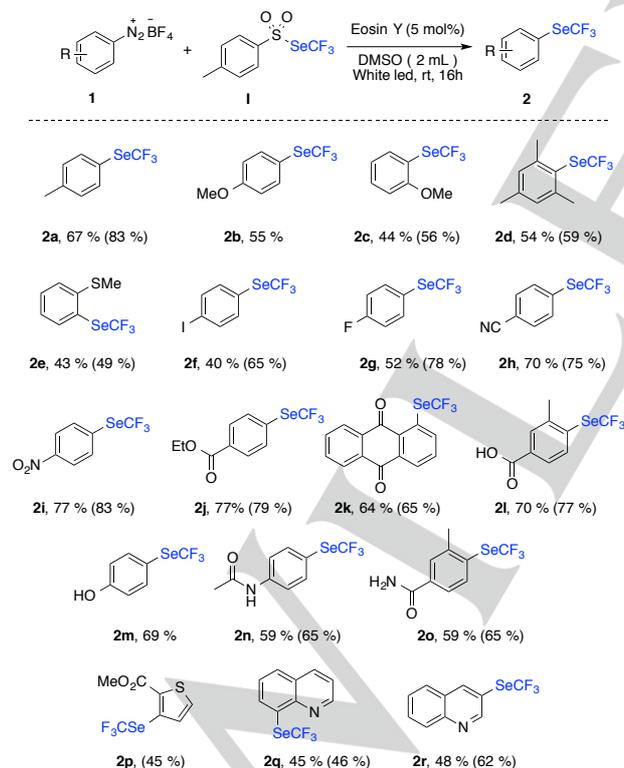
salts were also tolerated and their corresponding trifluoromethylselenolated arenes analogues were formed in very good to excellent yields (up to 83%) including nitro (**1i**) and electrophilic functional groups, such as nitrile, ester and ketone moieties (**1h**, **1j**, **1k**). More interestingly, the presence of acid (**1l**), free hydroxy (**2m**) as well as amide derivatives (**2n** and **2o**) underwent a selective trifluoromethylselenolation. Finally, heterocyclic compounds including thiophene derivative (**2p**) as well as quinoline derivatives (**2q**, **2r**) were successfully transformed.

Table 1. Reaction optimisation



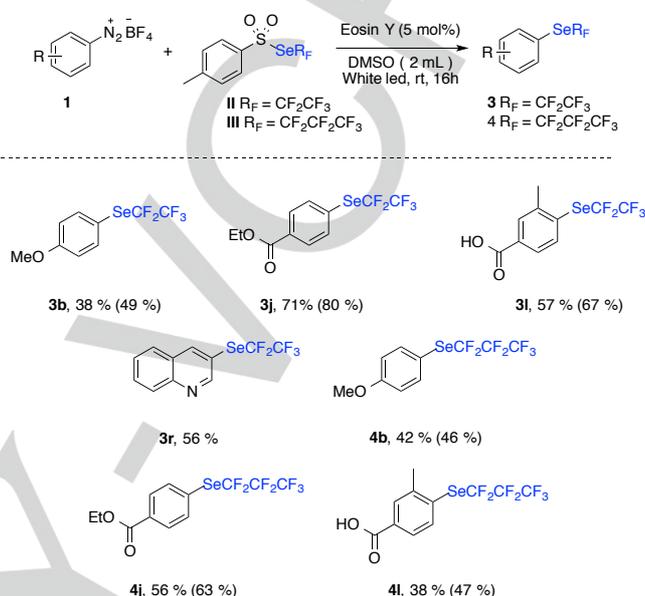
Entry ^[a]	Deviation from standard conditions	Yield [%] ^[b]
1	None	77
2	DMF instead of DMSO	42
3	THF instead of DMSO	<1
4	ACN instead of DMSO	<1
5	No Eosin Y	0
6	No light	0
7	No light and no Eosin Y	0

[a] Reactions were performed with TsSeCF₃ (0.3 mmol, 3 equiv.), arene diazonium (0.1 mmol, 1 equiv.), Eosin Y (5 mol%), and solvent (1 mL). The reaction mixture was stirred at rt for 16 hours under inert conditions. [b] Determined by ¹⁹F NMR spectroscopy with PhOCF₃ as an internal standard.



Scheme 1. [a] Reactions were performed with TsSeCF₃ (0.6 mmol, 3 equiv.), arene diazonium (0.2 mmol, 1 equiv.), Eosin Y (5 mol%), and DMSO (2 mL). The reaction mixture was stirred at room temperature for 16 hours under inert conditions. Yields shown are those of isolated products; yields determined by ¹⁹F NMR spectroscopy with PhOCF₃ as internal standard are shown in parentheses.

Having successfully demonstrated the versatility of our approach with respect to trifluoromethylselenolation and its tolerance towards a variety of functional group, we next focused on extending the methodology to higher homologs. In general, moderate to excellent yields were isolated starting from reagents **II** or **III**. Substitution reactions follow a similar trend as with trifluoromethylselenolation (Scheme 2).



Scheme 2. [a] Reactions were performed with TsSeR_f (0.6 mmol, 3 equiv.), arene diazonium salt (0.3 mmol, 1 equiv.), Eosin Y (5 mol%), and DMSO (2 mL). The reaction mixture was stirred at room temperature for 16 hours under inert conditions. Yields shown are those of isolated products; yields determined by ¹⁹F NMR spectroscopy with PhOCF₃ as internal standard are shown in parentheses.

We then turned our attention to characterize the reaction mechanism. Occurrence of a possible electron or energy transfer process using Stern-Volmer (SV) quenching experiments between eosin Y and the aryldiazonium species was first investigated. Although thermodynamically, excited state of Eosin Y is able to reduce the trifluoromethylselenolating agent in DMSO (see SI for cyclic voltammetry studies), no changes were observed regarding the emission at 530 nm.

In contrast, we demonstrated that diazonium salts quenched the luminescence of Eosin Y under the reaction conditions, as proposed by König^[15d] and von Wangelin.^[15e] Indeed, a decrease of the emission was observed at higher concentrations of **1a** (see SI) which at first sight could be fitted with acceptable correlation with SV fitting model. However, it was found that quenching was irreversible as it translated into a progressive decay of eosin absorbance (see SI), thus ascertaining the occurrence of a photobleaching process under the SV experiments conditions. Interestingly, only a marginal photobleaching of eosin Y occurred when irradiation was performed in the absence of de diazonium quencher, in otherwise similar experimental conditions (see SI). This led us to the following conclusions that: i) electron transfer occurs from eosin Y to aryldiazonium, and can be fitted to a dynamic SV model; ii) this transfer occurs irreversibly and translates into degradation of the "photocatalyst".

In parallel, we monitored the stability of trifluoromethyl tolueneselenosulfonate **I** in solution. We observed that reagent **I** in DMSO under light quantitatively furnishes the $(\text{CF}_3\text{Se})_2$ dimer within 1 hour. After adding the photocatalyst and the diazonium salt **1a**, we could observe the formation of the desired product in 80 % yield. In turn, the homolysis of S-Se bond under light could take place. The radical trifluoromethylselenyl dimerizes very quickly to furnish $(\text{CF}_3\text{Se})_2$, which could also be considered as an active reagent for the trifluoromethylselenolation.

In this context, in order to investigate the formation of the trifluoromethylselenyl radical, we decided to undertake EPR experiments. We irradiated with green light ($\lambda = 530 \text{ nm}$) a mixture of trifluoromethyl tolueneselenosulfonate **I**, Eosin Y and α -Phenyl-*N*-*tert*-Butylnitrone (BPN) as radical trap. The clean formation of a single spin adduct was obtained, supporting the formation of trifluoromethylselenyl radical ($g=2.003$, $a_N=15.1\text{G}$ and $a_H=2.7\text{G}$). Furthermore, when a mixture of trifluoromethyl tolueneselenosulfonate **I**, diazonium salt **1a**, Eosin Y, and BPN as radical trap was irradiated with green light, we observed the formation of two spin adducts. In addition to the trifluoromethylselenyl radical, $g=2.004$, $a_N=13.6\text{G}$ and $a_H=1.5\text{G}$, this values are slightly shifted due to the different physical environment of the radicals. A new species was observed consistent with a trivalent selenium radical species **A** (Figure 2). It should be mentioned that the presence of other radical traps including DMPO (5,5-Dimethyl-1-Pyrroline N-oxide) as well as MNP (2-Methyl-2-Nitrosopropane) confirms the same tendency in accordance with the two suggested species, the presence of trifluoromethylselenyl radical as well as the intermediate trivalent selenium radical species **A** (See SI).

Photochemical quantum yields of the reaction were next investigated, following the methodology depicted in SI. In the reaction conditions it was determined to be $\Phi = 1.07$. Although this yield remains close to unity, therefore precluding a strict discrimination between step-wise reaction and chain propagation, we however believe, given the observed rapid photobleaching of eosin Y in the reaction conditions, as aforementioned, that it most likely supports a radical chain process.

In light of the obtained results related to the reaction mechanism, we could propose the following (Scheme 3): the diazonium salt is reduced via a SET by the excited Eosin Y. The formed arene radical could react with the $\text{CF}_3\text{SeSeCF}_3$ dimer obtained after homolysis of reagent **I**, furnishing a trivalent selenium radical **B**. The intermediate **B** is then oxidized by the arene diazonium salt to furnish the electrophilic species **C**. The formed intermediate **C** reacts with DMSO to form the desired product and adduct **D**. Interestingly, a signal has been observed by ^{19}F NMR and could be assigned to the adduct **D**.

In conclusion, we demonstrated that the synthesis of trifluoromethylselenolated arenes could be mediated with visible light under metal free conditions. The reactions have been performed with arene diazonium salts and trifluoromethyl tolueneselenosulfonate, a shelf stable reagent, at room temperature. The reaction scope demonstrated an unprecedented reactivity. Moreover, mechanistic investigations

were performed including EPR, fluorescence and cyclic voltammetry. EPR spectroscopy allows us to identify two key intermediates, the formation of trifluoromethylselenyl radical as well as a trivalent selenium radical species **B**. Overall, based on the different experiments, a plausible mechanism has been proposed. New methodologies exploiting the formation of trifluoromethylselenyl radical are under investigations in our laboratory and will be reported in due course.

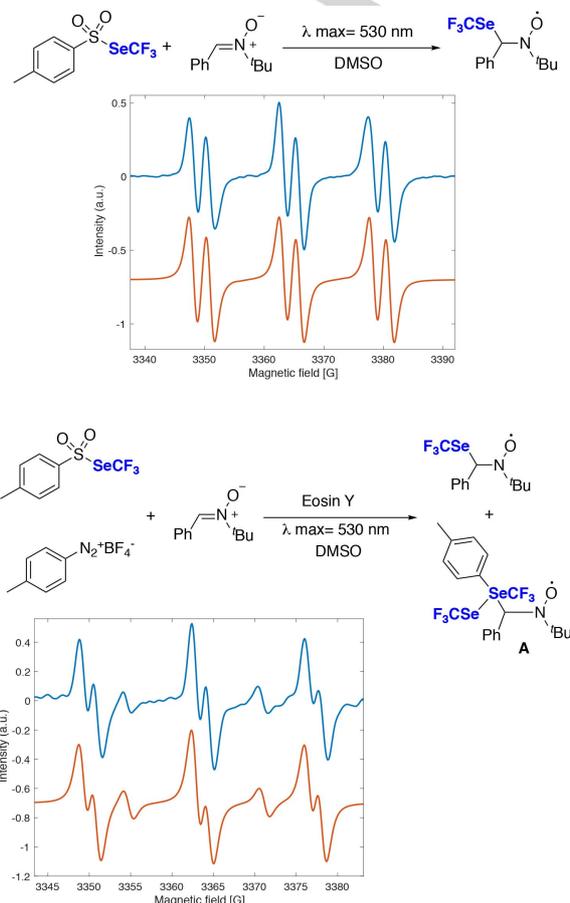
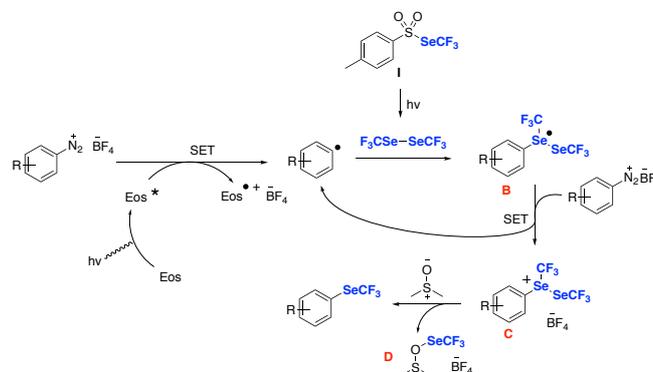


Figure 1. EPR spin-trapping spectra on irradiation ($\lambda = 530 \text{ nm}$) in the presence of BPN in DMSO at room temperature. Blue: experimental, red simulated



Scheme 3. Proposed mechanism

Experimental Section

To a flame-dried flask under nitrogen atmosphere equipped with a magnetic stir bar are added **I**, **II** or **III** (0.6 mmol, 3 equiv.), arene diazonium salt **1** (0.2 mmol, 1.0 equiv.), Eosin Y (0.01 mmol, 5mol%) and anhydrous dimethyl sulfoxide (2 mL). The reaction is stirred at 25°C under white led irradiation for 16 hours. Conversion is checked by ¹⁹F NMR with PhOCF₃ as internal standard. The reaction mixture is partitioned between Et₂O and water. The aqueous layer is extracted with Et₂O and the combined organic layers are dried over MgSO₄, filtered and concentrated to dryness. The crude residue is purified by chromatography to afford the desired product **2**, **3** or **4**.

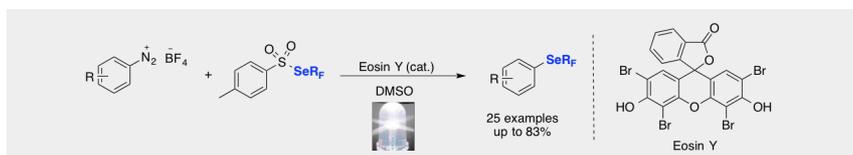
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Keywords: Visible light • Trifluoromethylselenolation • Metal-free • Radical • Trifluoromethyl tolueneselenosulfonate

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COMMUNICATION



Light can make it: Visible light-mediated synthesis of trifluoromethylselenolated arenes under metal-free conditions is reported herein. The reaction scope encompasses a large panel of functional groups. Moreover, mechanistic investigation has been undertaken pointing out the presence of trifluoromethylselenenyl radical.

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