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► **To cite this version:**

Anis Tlili, Dan Louvel, Aida Chelagha, Jean Rouillon, Pierre-adrien Payard, et al.. Metal-Free Visible-Light Synthesis of Arylsulfonyl Fluorides: Scope and Mechanism. *Chemistry - A European Journal*, 2021, 27 (34), pp.8704-8708. 10.1002/chem.202101056 . hal-03394548

HAL Id: hal-03394548

<https://hal.science/hal-03394548>

Submitted on 22 Oct 2021

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Metal-Free Visible-Light Synthesis of Arylsulfonyl Fluorides: Scope and Mechanism

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Abstract: The first metal-free procedure for the synthesis of arylsulfonyl fluorides is reported. Under organophotoredox conditions, aryl diazonium salts reacts with readily available SO₂ source (DABSO) to afford the desired product via simple nucleophilic fluorination. The reaction scope tolerates the presence of both electron-rich and -poor aryls and demonstrated a broad functional group tolerance. To shed the light on the reaction mechanism, several experimental techniques have been combined including fluorescence, NMR, EPR spectroscopy as well as DFT calculations.

Arylsulfonyl fluorides (ArSO₂F) are ubiquitous building blocks that find a plethora of applications in life science technologies.^[1] In particular, ArSO₂F are routinely used as covalent protein inhibitors and biological probes.^[2] In comparison to other arylsulfonyl halides, ArSO₂F present numerous advantages such as their high resistance toward reduction and high thermodynamic stability toward nucleophilic substitutions including hydrolysis. In addition, arylsulfonyl fluorides are substrate of choice for fluoride exchange (SuFEx) for click chemistry leading to a variety of aryl sulfones derivatives.^[3] In spite of the general interest of ArSO₂F, their direct synthesis is scarcely reported in the literature. Regarding the state of the art, the most often used methods rely on halogen exchange starting from the unstable arenesulfonyl chloride. Other indirect methods have been also disclosed in the literature (figure 4)^[4], yet the direct construction of carbon-SO₂F constitute a highly attractive option. Within this framework, the group of Bagley, Willis and their co-workers reported a one-pot two-steps procedure for the synthesis of ArSO₂F starting from (heteroaryl)aryl iodides or bromides in conjunction with, commercially available and easy to handle 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO)^[5] for the *in situ* generation of sulfinate under palladium catalysis, followed by an addition of N-fluorobenzenesulfonimide (NFSI) as an electrophilic fluorine source.^[6] The same approach was also extended to alkenyl triflates.^[7] A similar strategy was disclosed by the group of Ball where Selectfluor was used as an electrophilic fluorine source.^[8] Finally, the group of Liu and Chen recently reported a copper catalyzed approach to forge *in situ* aryl sulfonyl chloride starting with arene diazonium salt and DABSO followed by the use an external fluoride source to obtain the desired product.^[9] It should be mentioned that a copper free

procedure has been also developed using Na₂S₂O₅ in the presence of electrophilic fluorine source (Selectfluor) at 70°C (figure 4).^[4c] In spite of those recent successes, the development of metal free, mild and straightforward procedure towards C-SO₂F bond formation remains highly desirable especially from a late-stage functionalization perspective. In this context, Organophotoredox catalysis constitute an attractive option as it will leverage the orthogonality of transition metal catalysis through SET processes.^[10]

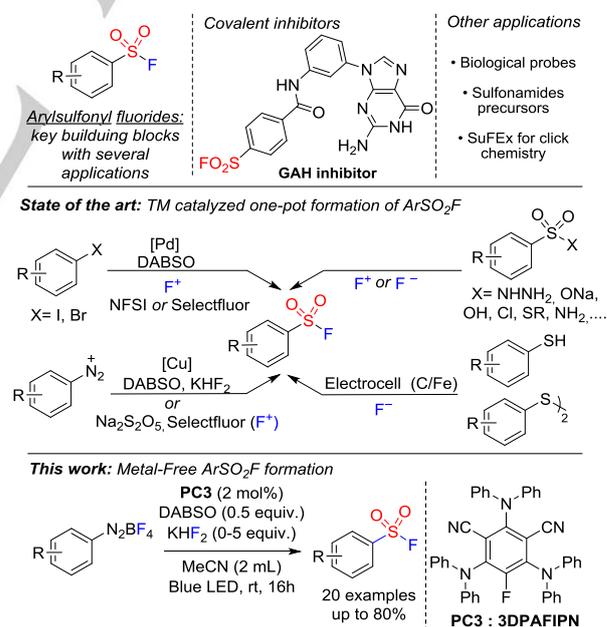


Figure 1. Introduction to arylsulfonyl fluorides.

With our continuous interest for the development of new organophotoredox processes we report herein an unprecedented strategy for the direct access to arylsulfonyl fluorides under metal-free visible-light conditions.^[11]

The optimisation started with 4-methylphenyldiazonium salts **1a** as a model substrate in the presence of 1 equivalent of DABSO, 4CzIPN (**PC1**) as an organophotocatalyst in MeCN under blue LED irradiation at room temperature for 16h. Conversion of reagent **1a** to the desired product **2a** was

observed albeit in a low yield of 10% (table 1, entry 1). Encouraged by this first result we decided to investigate the impact of the solvent and photocatalyst on the reaction outcome. Using **PC1**, only traces of the desired product were observed in butyl acetate (5%, table 1 entry 2). Screening other solvents including DMSO, toluene, MeOH as well as Et₂O were deleterious to the reaction outcome (table 1, entries 3-6).

Table 1. Reaction optimisation ^a

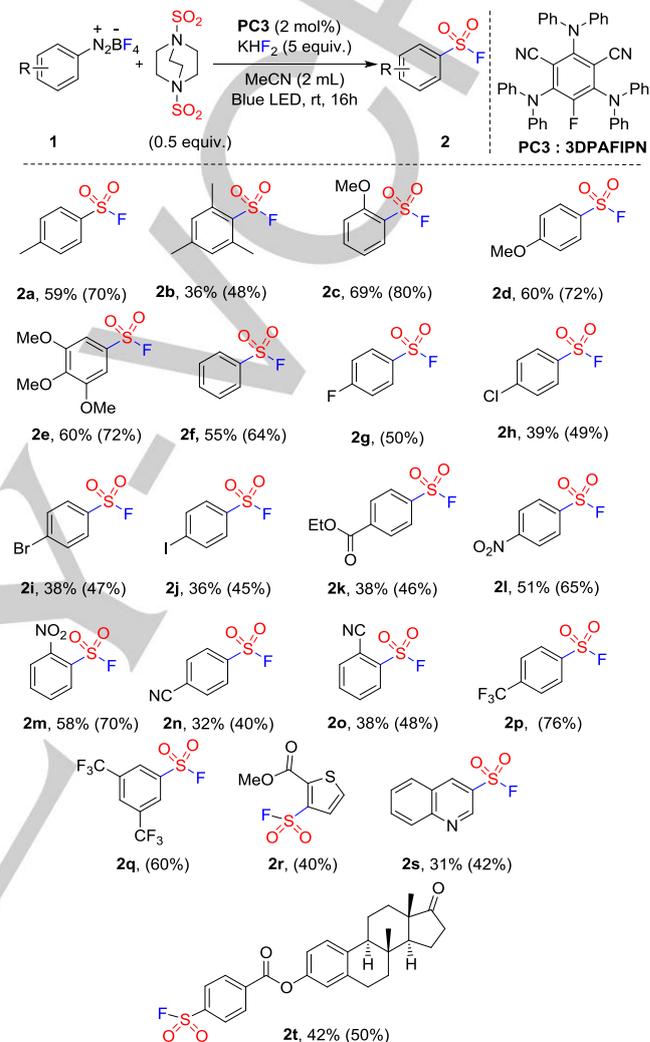


Entry	PC	Solvent	Additive	Yield (%) ^[b]
1	PC1	MeCN	-	10
2	PC1	Butyl Acetate	-	5
3	PC1	DMSO	-	0
4	PC1	PhMe	-	0
5	PC1	MeOH	-	0
6	PC1	Et ₂ O	-	0
7	PC3	MeCN	-	60
8	PC4	MeCN	-	60
9 ^[c]	PC5	MeCN	-	5
10	PC6	MeCN	-	10
11	PC3	MeCN	KHF₂	70
12	PC3	MeCN	LiBF ₄	10
13	PC3	MeCN	NaPF ₆	<5
14 ^[d]	PC3	MeCN	KHF ₂	0
15 ^[d]	-	MeCN	KHF ₂	0
16	-	MeCN	KHF ₂	0

[a] Reactions were performed with diazonium salt **1** (0.3 mmol, 1 equiv.), DABSO (0.15 mmol, 1 equiv.), (1.5 mmol, 5 equiv.), PC (2 mol%) and MeCN (2 mL) unless otherwise noted. The reaction mixture was stirred at room temperature for 16 hours under blue LED irradiation and inert conditions; [b] yields determined by ¹⁹F NMR spectroscopy with PhCF₃ as internal standard; [c] Under green LED irradiation; [d] Without light irradiation.

Changing the organophotocatalyst to other cyanoarenes organophotocatalyst (**PC3** and **PC4**, table 1, entries 7-8) was beneficial in improving the yield up to 60%. Eosin Y (**PC5**, table 1, entry 9) as well as Fukuzumi catalyst (**PC6**, table 1, entry 9) were not effective under our conditions providing yields that did not

exceed 10%. To further enhance the reaction outcome, the impact of additives was studied. When using KHF₂ (5 equiv.) the desired product was obtained in 70% yield (table 1, entry 11). Other fluoride sources such as LiBF₄ and NaPF₆ were tested but only provided marginal yields (table 1, entries 12 and 13). It is important to note that no product formation was observed either without blue LED irradiation or in the absence of the photocatalyst (table 1, entries 14-16).



With the optimized conditions in hand, we turned our focus to study the scope of the reaction (Scheme 1). Initial investigations were carried out with arene substituted with electron donating groups. Herein, good to excellent yields were obtained in the presence of methyl or methoxy groups (**2a-e**). Interestingly steric hindrance was not deleterious to the reaction outcome, since up to 80% yield were reached for ortho substituted methoxyphenyl (**2c**). Furthermore, we investigated the presence of halogen on the arene ring. Taking advantage of metal-free catalytic procedure we demonstrated that, fluoro, chloro bromo as well as iodo-arenes could be converted to the

desired sulfonyl fluoride derivatives with synthetically useful yields (**2g-j**). Afterwards, we decided to investigate electron poor substituted arenes starting material. In particular, we demonstrated that our reaction conditions tolerate the presence of several electron withdrawing groups including, ester, trifluoromethyl, cyano as well as nitro motifs. Herein also, ortho, meta or para position were smoothly converted to the corresponding products (**2k-q**). Interestingly, heterocyclic compounds could also be converted to their corresponding sulfonyl fluorides in moderate yields (**2r-s**). Finally, we demonstrated that our protocol could be extended to complex molecular architecture and compound **2t** was obtained in a good yield of 50% demonstrating the potential application for late-stage transformation.

Having illustrated the broad scope and the high functional group tolerance of the developed metal-free procedure we started investigating the reaction mechanism. Fluorescence studies, EPR spectroscopy as well as DFT calculations were combined to understand the role of the photocatalyst, and its efficiency was assessed by measuring of the photoconversion quantum efficiency. Assuming a photoinduced single electron transfer (P-SET) as the initial stage of the reaction sequence, the hypothetical catalytic cycle may either start by oxidation of DABSO (or *in situ* generated DABCO) or by reduction of the diazonium. In order to evaluate the occurrence of (potentially concurrent) electron transfers between the photocatalyst and the different species, and to quantify the associated kinetics, **PC3** was involved in successive Stern-Volmer experiments with the diazonium salt **1a**, DABSO and DABCO (Figure 2, I). In agreement with the facile reduction of diazonium salt, it turns out that the luminescence of the excited photocatalyst is efficiently quenched in his presence, with a Stern-Volmer constant $K_{SV} = 256 \text{ M}^{-1}$. We also confirmed efficient quenching of the luminescence of the excited photocatalyst in the presence of DABCO ($K_{SV} = 229 \text{ M}^{-1}$), but also to a slightly lesser extent with DABSO ($K_{SV} = 164 \text{ M}^{-1}$). With a measured luminescence lifetime $\tau_f = 4.2 \text{ ns}$ for **PC3**, it was possible to derive for the later a quenching rate coefficient k_q of $6.1 \cdot 10^{10}$, $5.45 \cdot 10^{10}$ and $3.9 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ with **1a**, DABCO and DABSO, respectively. These three values appear in quantitative agreement with the hypothesis of a dynamic, diffusion limited quenching process, and suggest that multiple SET pathways may occur in solution.

It is however important to underline that, while quantitatively similar for DABCO and DABSO, the SET process results in a markedly different evolution of the system. Thus, while **PC3** remains relatively photostable for moderate irradiation times (*ca* 10 min) in the presence of DABCO and DABSO, fast photobleaching occurs in the presence of **1a** with a kinetic rate that correlates well with the amount of added diazonium salt (Figure 2, Id). This is indicative of the formation of a reactive radical intermediate which, in the condition used in our spectroscopic measurements, evolves by addition onto **PC3** and ultimately clearance of the later. Such a behaviour agrees well with the expected characteristics of a tolyl radical.

To further investigate the nature of the formed radical in the reaction media we decided to undertake EPR experiments under visible light irradiation (Figure 2, II). Attempts to perform such experiments with mixtures either devoid of **PC3** or $[\text{PhN}_2]$ led to complex signatures with overall low intensities, suggesting a dead-end mechanisms. For the sake of clarity, description of

these spectra will not be discussed in the manuscript but is nevertheless available in SI. Irradiation of a mixture of **PC3** with diazonium salt **1a** with blue LED ($\lambda = 455 \text{ nm}$) in the presence of α -phenyl-*N-tert*-butyl-nitrone (PBN) as radical trap results in the clean formation of a single spin adduct **A** with a signature typical of a C- centered tolyl radical ($g = 2.006$, $a_N = 14.8 \text{ G}$ and $a_H = 2.8 \text{ G}$, Figure 2, II, top),^[12] as already observed in some of our previous works.^[11]

When mixing **PC3**, DABSO and diazonium salt **1a**, in the presence of PBN, the obtained signature comprises, in addition to a signal obtained in the previous irradiation experiment with **PC3** and **1a** only and attributed to a tolyl adduct ($g = 2.006$, $a_N = 14.8 \text{ G}$ and $a_H = 2.5 \text{ G}$), a secondary signal radical which characteristic values ($g = 2.006$, $a_N = 13.6 \text{ G}$ and $a_H = 1.6 \text{ G}$) are compatible with a O-centred radical species¹³, presumably on a tosyl radical. Complementary experiments using DMPO as a radical trap reveal, besides the presence of the abovementioned tolyl ($g = 2.006$, $a_N = 14.5 \text{ G}$ and $a_H = 21.4 \text{ G}$) and O-centred tosyl **B** ($g = 2.006$, $a_N = 12.8 \text{ G}$ and $a_H = 13.8 \text{ G}$) radical adducts a third species compatible with a S-centred tosyl adduct ($g = 2.006$, $a_N = 13.9 \text{ G}$ and $a_H = 15.0 \text{ G}$).^[14] In the experiment with PBN, the latter may overlap with that of the tolyl adduct. Worth of note, the formation of the tolyl radical was also observed by mixing DABSO and $[\text{PhN}_2^+]$ in the absence of photocatalyst (see the supporting information for the complete description of these experiments and associated DFT calculations). This radical is formed due to SET between *in situ* generated DABCO and the diazonium. However, under these conditions no tosyl radical species could be detected and the formation of the tolyl radical do not lead to the product.

Afterwards, the photochemical quantum yield of the reaction was investigated (Figure S2). In this study, reactant **1g** was preferred to **1a**, in order to facilitate monitoring of the reaction through ¹⁹F NMR. In the optimized concentration conditions (entry 7 in Table 1), following our previously reported NMR actinometric protocol^[15] depicted in full in the Supporting Information and monitoring in-time disappearance of **1g** we were able to determine a photoconversion quantum yield of the diazonium reactant $\Phi = 0.43$, indicating a stepwise mechanism. Interestingly, while the disappearance of **1g** could be nicely fitted with a first order kinetic model, a typical sigmoidal curve, with an induction period of about 10 minutes was observed for the appearance of **2g**, characteristic of a mechanism operating by successive reactions. Note also that similar experiment performed in the absence of DABSO but otherwise identical concentration conditions resulted in rapid photodegradation of the catalyst and therefore premature stalling of photoinduced disappearance of **1g**, in line with spectrofluorimetric experiments.

In order to gain more insight on the reaction mechanism, DFT calculations were undertaken (Figure 2, III). Reaction of Ph^\cdot with DABSO to yield PhSO_2^\cdot and DABCO is favored ($-14.8 \text{ kcal mol}^{-1}$, Figure 2, III). Given the nature of the stepwise mechanism, the generated DABCO may reduce **PC3**⁺ formed upon reduction of the diazonium salt to regenerate the photocatalyst **PC3** and DABCO⁺. The latter may combine with PhSO_2^\cdot to generate the sulfonium salt intermediate **C** (Figure 2, III, $\Delta G = -10.4 \text{ kcal mol}^{-1}$).^[16] Subsequent nucleophilic substitution of DABCO by fluorine anion on the salt is easily accessible and yield the final product PhSO_2F .

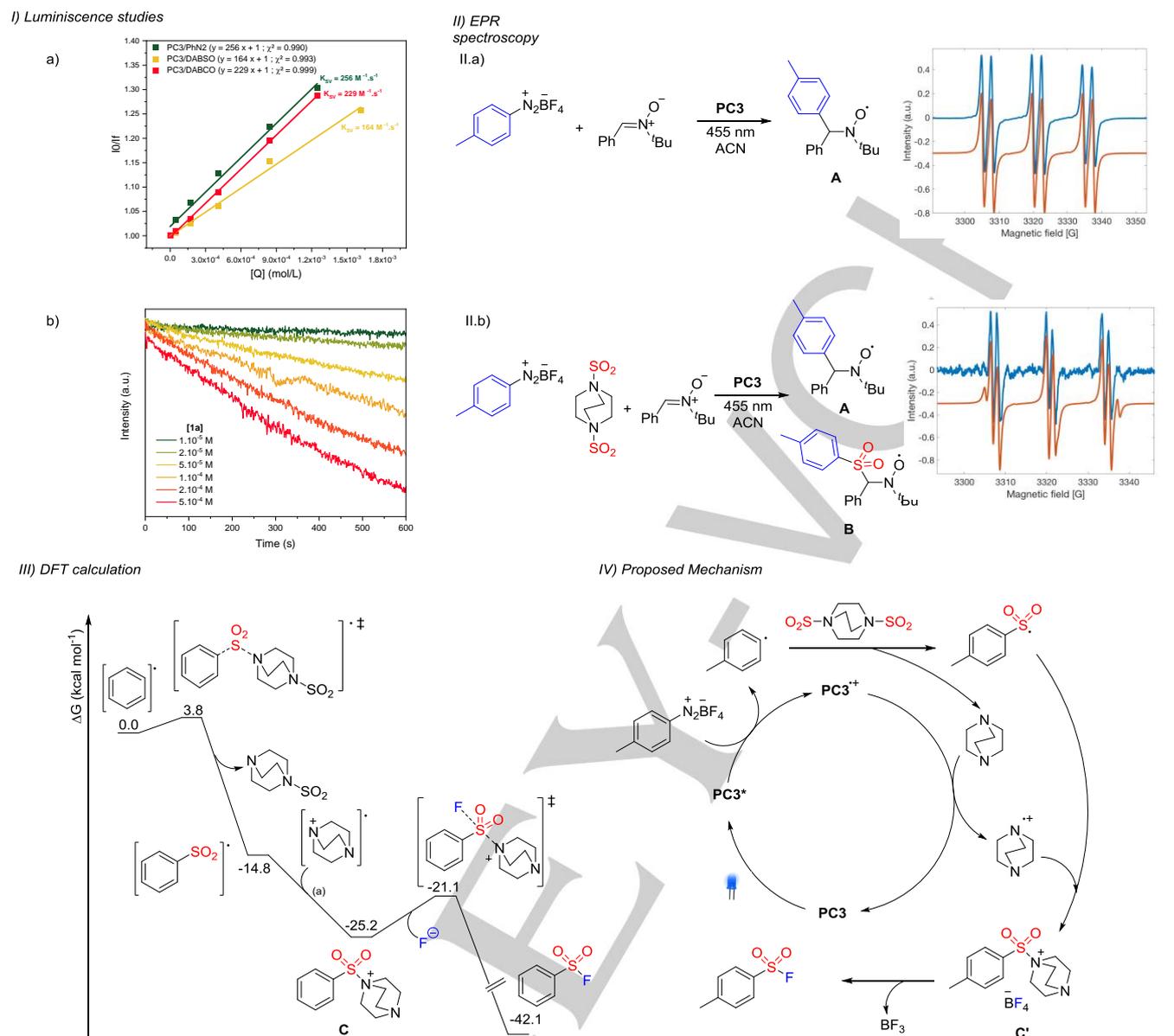


Figure 2. Mechanistic investigation: I, luminescence studies: (a) Stern Volmer plots of luminescence evolution of **PC3** upon incremental addition of **1a**(green), DABCO (red) and DABSO(orange);(b) in-time monitoring of **PC3** photobleaching in the presence of BPN in MeCN at room temperature. Blue = experimental, red =simulated. III. DFT calculation: Free energy (kcal mol $^{-1}$) pathway for reaction of photogenerated phenyl radical with DABSO calculated at the DFT level. (a) barrierless process in electronic energy see energy scan in SI IV. Proposed mechanism

In light of the obtained results, we propose the following mechanism. Photoinduced reduction of the diazonium salt occurs through SET from the excited **PC3**, yielding arene radical and radical cation photocatalyst (**PC3 $^+$**). Subsequently the aryl radical collapses with SO_2 to form a new radical tosyl species. The released DABCO is able to regenerate the photocatalyst **PC3** in its ground state and $\text{DABCO}^{\cdot+}$. This latter may combine with PhSO_2^{\cdot} to generate the sulfonium salt intermediate **C'**. Afterwards, a nucleophilic fluorine attack is taking place to form the desired arylsulfonyl fluoride and regenerate DABCO (Figure 2, IV).

In summary, the first metal-free visible light induced protocol for the synthesis of arylsulfonyl fluorides was described. The key to success was the combination of aryl diazonium salts, DABSO and the cyanoarene **PC3** under blue LED irradiation. The mild

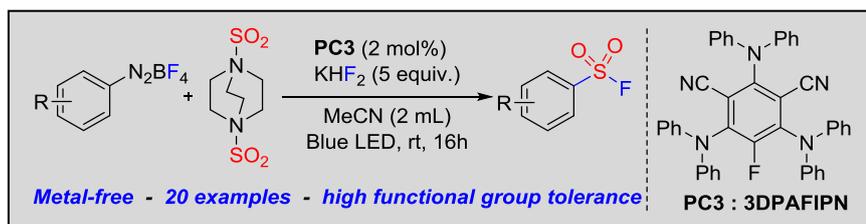
conditions afforded a broad scope and high functional group tolerance. Furthermore, mechanistic investigations were performed including luminescence, EPR spectroscopy, ^{19}F NMR spectroscopy as well as DFT calculation. Altogether, those studies allowed us to identify several key intermediates, based on which we proposed a plausible mechanism for the reaction. Further investigations exploiting the use of cyanoarenes as photocatalyst are under investigation in our laboratory for the selective formation of new radical as well as the synthesis of valuable building blocks.

Acknowledgements

D. L. thanks the French Ministry of Higher Education and Research for a doctoral fellowship. The authors are grateful to the CNRS, ICBMS (UMR 5246), ENS Lyon and the Agence Nationale de la Recherche for financial support (Grant to AT, ANR-JCJC-2020-CDI-DEOX). P.-A. P. thanks the CCIR of ICBMS for providing computational resources and technical support.

Keywords: Arylsulfonyl fluorides • Organophotoredox • Fluorine • Mechanistic investigations • Metal-free

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Metal-free Visible-light mediated synthesis of arylsulfonyl fluorides is reported herein, the key to success is the employment of the cyanoarenes PC3 as organophotocatalyst. A variety of arene diazonium salts were smoothly converted to the corresponding product. Moreover, mechanistic investigations including luminescence, EPR spectroscopy as well as DFT calculation allow us to identify several key intermediates and propose a plausible mechanism.

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