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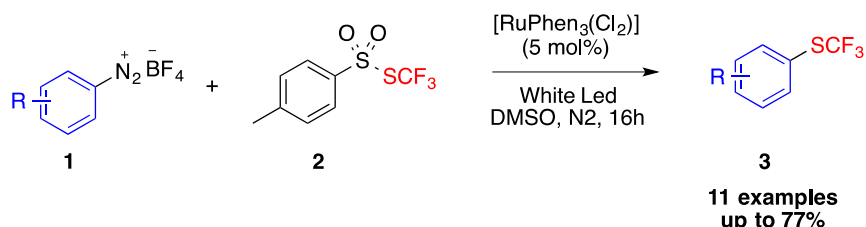
Visible-Light Mediated Synthesis of Trifluoromethylthiolated Arenes

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The visible light-mediated synthesis of trifluoromethylthiolated arenes in the presence of ruthenium based photocatalyst under mild reaction conditions is reported herein. The trifluoromethylthiolated arenes are obtained using the shelf-stable reagent trifluoromethyl tolueneselenosulfonate, at room temperature. The reaction proceeds selectively and does not require the presence of any additive. According to mechanistic investigations, a mechanism was proposed based on the obtained results of EPR as well as luminescence

Key words Visible light • Trifluoromethylthiolation • Arene diazonium • Radical • Reaction mechanism

Direct formation of C-SCF₃ chemical bond has recently been the object of many research endeavours.¹ Indeed, the Hansch parameter of SCF₃ ($\pi_R = 1.44$)² confers to trifluoromethylthiolated molecules a high lipophilicity, thus contributing to a better transmembrane permeation of CF₃S-substituted molecules allowing improved bioavailability, thus making it a much sought-after feature.³ Among the most studied reactions, we can find the direct trifluoromethylthiolation of arenes or heteroarenes.

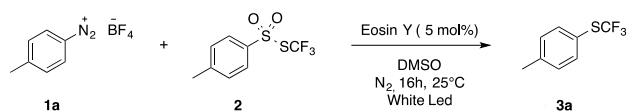
Analysis of state of the art literature on the topic put forwards two distinct families of reactions that differ by the nature of the trifluoromethylthiolating reagent. On the one hand, nucleophilic reagents (R₄N⁺SCF₃ or σ -bonded metal-SCF₃) can be associated with electrophilic arene sources under transition metal catalysis (including Pd, Ni and Cu).^{1f-h, 4} On the other hand, shelf-stable electrophilic trifluoromethylthiolating reagents have been also successfully employed in the presence of nucleophilic arene sources (e.g. aryl boronic acid derivatives and aryl Grignard reagents).^{1e, 1f, 1h, 5} Besides, transition metal free procedures using ammonium trifluoromethylthiolate salts with arene diazonium salts have also been disclosed.⁶

We recently demonstrated that the formation of C(sp₂)-SeCF₃ could be performed selectively under visible light catalysis involving radical intermediates starting from the shelf stable reagent trifluoromethyl tolueneselenosulfonate.⁷ We questioned whether such a procedure could be extrapolated to the formation of C(sp₂)-SCF₃. Consequently, a similar trifluoromethylthiolating reagent (TsSCF₃, **2**) has been synthesized in almost quantitative yield starting from our 2nd generation of trifluoromethanesulfenamide reagent.⁸

With our continuous interest to discover and develop new synthetic methodologies, we turned our attention to study the formation of C(sp₂)-SCF₃ bonds from arenes diazonium salts using this shelf stable reagent. During this work, similar results have been described.⁹

Initial attempt was devoted to study the influence of the solvents on the reaction outcome. Indeed, our previous studies on related selenide reagents had evidenced a crucial influence of this parameter.⁷ Indeed, while reaction using Eosin Y (5 mol%) as photocatalyst allowed reaching 59 % of product formation using DMSO as solvent at room temperature (entry 1), the use of other solvents showed the formation of desired products in lower yields (entries 2-5). Next, we tested the influence of the photocatalyst on the reaction outcome. Only marginal amount of the product was formed when Rhodamine 6G was used as photocatalyst. The use of transition metal based photocatalyst showed good reactivity when Ir(ppy)₃ was used (entry 7) but the best yield was obtained with Ru(II) as photocatalyst as the targeted product was formed in 67% yield (entry 8). We also verified that the presence of the photocatalyst is primordial for the formation of the product since only traces were observed in the blank experiment (entry 9). **Table 1. Reaction optimisation^a**

Entry	Deviation from standard conditions	Yields ^b (%)
1	none	59
2	DMF instead of DMSO	31

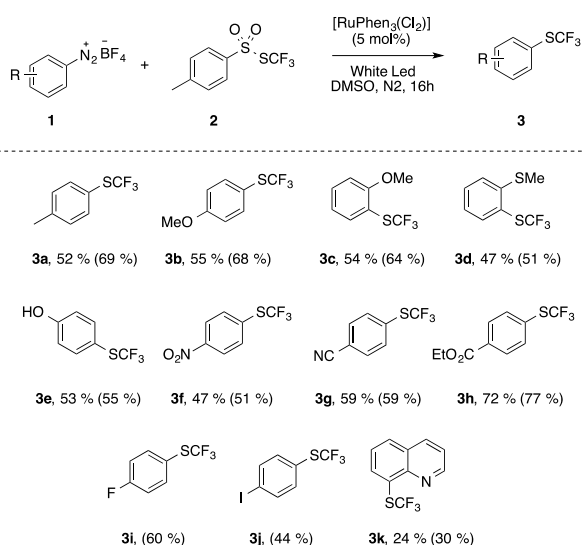


3	EtOH instead of DMSO	47
4	THF instead of DMSO	27
5	ACN instead of DMSO	45
6	Rhodamine 6G instead of Eosin Y	19
7	Ir(ppy) ₃ instead of Eosin Y	59
8	[Ru(phen) ₃ Cl ₂].xH ₂ O instead of Eosin Y	67
9	No photocatalyst	< 5

[a] Reactions were performed with TsSCF₃ (0.3 mmol, 3 equiv.), arene diazonium (0.1 mmol, 1 equiv.), Photocatalyst (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.

With the best conditions in hand we turned our focus to study the reaction scope. Initial attempts demonstrated that electron donating groups could be transformed to the desired product in moderate to very good yields (up to 69%) and no significant change was observed when the starting aryl diazonium salts **1c** and **1d** were substituted in the *ortho* position. Interestingly, taking in advantage the base free conditions, free hydroxyl aryl diazonium salt was also tolerated, furnishing the desired product **3e** in 55% yield. Similarly, aryl diazonium salts substituted with electron withdrawing groups were also successfully evaluated under our reaction conditions. Obviously, very strong electron withdrawing substituted arenes (including NO₂, CN and EtO₂C) could be converted to their trifluoromethylthiolated analogues in acceptable to very good yields (up to 77%). Halogenated products were also tolerated since **3i** and **3j** could be formed in moderate to good yields. Finally, we could demonstrate through the example of product **3k** that a heterocyclic starting material could be also converted to its desired product although in low reaction outcome.

Mechanistic details were further investigated using luminescence spectroscopy. We first aimed at establishing the occurrence of an energy transfer process between the ruthenium catalyst and the tolyldiazonium reagent **1a** by following extinction of the former luminescence upon incremental additions of the latter (see SI for further experimental details). Quite surprisingly, unlike previously observed in earlier works dealing with Ru complexes, plot of the resulting data using a Stern Volmer model did not lead to a straight line. Instead, we noticed a distinct upward curvature of the plotted data. Such behavior suggests that, while a photoinduced reaction is clearly seen between the Ru catalyst and the diazonium quencher, it cannot be fully rationalized based on a diffusion-controlled charge transfer mechanism as postulated in the Stern Volmer Theory. Indeed, such positive curvature deviations from Stern Volmer model have been largely documented in the past, on a variety of donor/acceptor (D/A) pairs. Among the most currently admitted causes for this phenomenon, the occurrence of increased static quenching at high quencher concentration ([Q]) is often mentioned.¹⁰ The latter adds to the dynamic, diffusion controlled process encountered at low [Q], thus increasing the extent of quenching at high [Q]. Accordingly, those effects can find two distinct origins either 1/ the occurrence of a non-emissive ground state luminophore-quencher complex which is highly favoured at high [Q]¹¹ or 2/ the so-called "sphere of action" model,¹² in which concentration-dependent spatial proximity of the excited luminophore and the quencher molecule ensures that diffusion is not a limiting factor of the quenching process. The latter is also obviously favoured at high [Q] and is more prone to occur when slow charge transfer processes are involved within the D/A pair. Indeed, the latter model seems to account for the observed trend in our case, as plotting ln(I₀/I_t) vs [Q] affords a quasi linear evolution as predicted by the aforementioned model (See SI for details).



Scheme 2. [a] Reactions were performed with TsSCF_3 (0.6 mmol, 3 equiv.), arene diazonium salt **1** (0.2 mmol, 1 equiv.), $[\text{Ru}]$ (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 ^{19}F NMR spectroscopy with PhOCF_3 as internal standard are shown in parentheses.

Next, we determined the reaction quantum yield (QY), in order to establish whether a step or chain mechanism was more likely involved in the reaction. Using the Xenon lamp of the fluorimeter as an irradiation source, we performed controlled irradiation of a degassed 3 mL sample of the reaction medium set in a 1 cm quartz cuvette, and followed reactant-to-product conversion using ^{19}F NMR on aliquots of the reaction mixture taken up at various reaction time. As for our previously reported example using eosin as a catalyst, catalytic conversion was seen to proceed in two stages: first a buildup of a dimeric $\text{CF}_3\text{S}-\text{SCF}_3$ species, which was then consumed upon addition to the diazonium reagent. Linearization of the data collected in the initial stage of the reaction (first 30 minutes) allowed establishing a quantum yield *ca* 1.5, following the general methodology detailed in SI. This value, which clearly exceeds unity, is in line with a chain propagation mechanism, consistent with what had been previously shown with the selenium counterpart of the current sulfur reagent in the presence of eosin (with a QY slightly exceeding 1 in the latter case).

By analogy with our previous works on related trifluoromethylselenosulfonate reagents, radicals formed upon irradiation of the ruthenium catalyst-free sample are attributed to the outcome of a light induced homolytic cleavage of the trifluoromethyl toluenethiosulfonate reagent **2**. In this case, a hallmark of the reaction is the production of a $\text{CF}_3\text{S}^\bullet$ radical species that forms the most prominent adduct (65%) with PBN radical trap, which features ($a_{\text{N}}=14.4\text{G}$, $a_{\text{H}}=1.9\text{G}$) are in good agreement with what we previously reported for its $\text{CF}_3\text{Se}^\bullet$ counterpart. Formation of two other readily attributable species can be observed in the EPR spectrum: the first one (7% $a_{\text{N}}=14.4\text{G}$, $a_{\text{H}}=1.2\text{G}$) corresponds to the second member of the homolytic cleavage, the Ts^\bullet radical; the other by-product (8%, $a_{\text{N}}=14.4\text{G}$, $a_{\text{H}}=2.7\text{G}$) most likely corresponds to an adduct of an Ar^\bullet radical (tolyl) that evolves from this first Ts^\bullet radical intermediate, by elimination of SO_2 . Two other species of significant intensity are observed, but their chemical nature is less straightforward. The 5% species ($a_{\text{N}}= 8.1\text{G}$) and 15% species ($a_{\text{N}}= 12.4\text{G}$) can both be attributed to oxidation products of the aforementioned BPN-radical adduct as no hyperfine interaction with the adjacent proton (H_β) is observed (Figure 1).

When ruthenium catalyst is added to the mixture, EPR signal obtained upon photoirradiation is enhanced by almost one order of magnitude. Moreover, species distribution pattern is largely different from that obtained in the absence of catalyst. As a consequence of the electron transfer taking place between $\text{Ru}(\text{II})$ catalyst and the diazonium reactant **1a**, decomposition of the latter by elimination of nitrogen provides a Ar^\bullet tolyl radical (40% $a_{\text{N}}=14.6\text{G}$, $a_{\text{H}}=2.8\text{G}$) that is within error margin identical to the abovementioned evolution product of the Ts^\bullet radical, thereby retrospectively confirming the attribution of the latter. Surprisingly, the two others adducts (40%, $a_{\text{N}}=12.3\text{G}$, 20%, $a_{\text{N}}=8.2\text{G}$) does not seem to correspond to the $\text{CF}_3\text{S}^\bullet$ radical as observed in the absence of ruthenium, but to similar PBN oxidation products as monitored in the absence of the ruthenium catalyst.

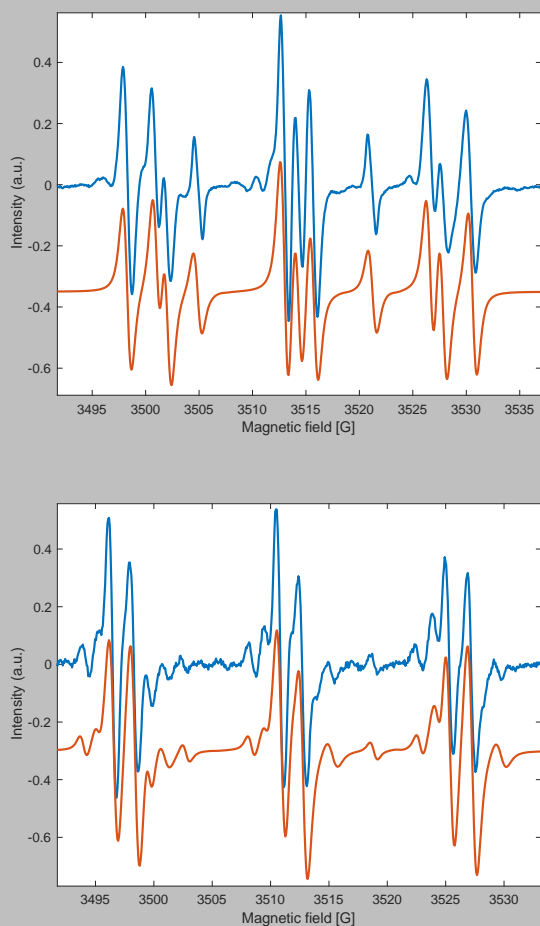
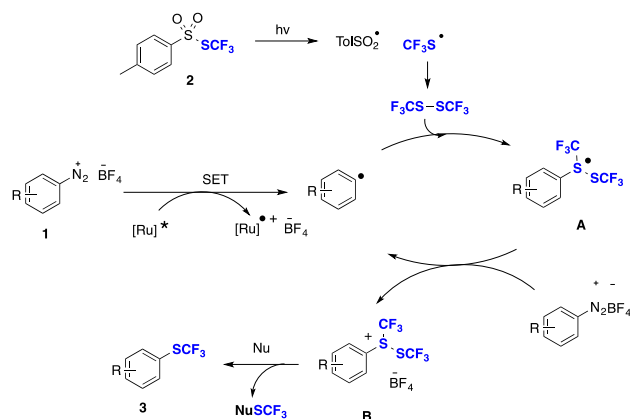


Figure 1: EPR spin-trapping spectra on visible irradiation in the presence of PBN in DMSO at room temperature. Blue: experimental, red simulated after 4 minutes with Ru (top) and 7 minutes without Ru (bottom) of irradiation

With these results in hand, we are able to propose a plausible mechanism. The diazonium salt is firstly reduced through a single electron transfer (SET) by the triplet state ruthenium photocatalyst. The resulting aryl radical could then react with the transient dimer CF_3SSCF_3 , obtained from the reagent **2** under light irradiation. The obtained trivalent sulfur radical **A** is then oxidized by the diazonium salt furnishing the cationic species **B** and a new aryl radical. Finally, the cationic intermediate could react with a nucleophile from the reaction media (DMSO can also play this role), yielding the desired product **1**.



Scheme 3. Proposed mechanism

To conclude, the direct synthesis of trifluoromethylthiolated arenes could occur under visible light catalysis starting with arene diazonium salts and a shelf-stable reagent under mild reaction conditions. Furthermore, mechanistic investigations were also

performed to shed some light on the reaction pathway. It turns out that trifluoromethylsulfur radical is a key intermediate in the reaction mechanism. Further developments are under way in our laboratory.

Procedures

Synthesis of 1a-1d and 1f-1k: In a 25 mL round bottom-flask are added aniline (10 mmol) and aqueous HBF₄ 48% (20 mmol, 2.6 mL) in absolute EtOH (3 mL). The mixture is stirred until total homogeneity and cooled at 0°C. *t*-BuONO 90% (20 mmol, 2.7 mL) is added dropwise to the solution. The reaction is stirred at room temperature for 30 minutes. Et₂O (10 mL) is then added to precipitate the salt. The solid is then filtered and washed 3 times with Et₂O and dried under reduced pressure to afford the desired product.

Synthesis of 1e: In a 25 mL round bottom-flask are added aniline (10 mmol) and aqueous HBF₄ 48% (20 mmol, 2.6 mL). The mixture is stirred until total homogeneity and cooled at 0°C. NaONO (20 mmol, 1.38 mg) dissolved in water (2 mL) is added dropwise to the solution. The reaction is stirred at room temperature for 30 minutes. Et₂O (10 mL) is then added to precipitate the salt. The solid is then filtered and washed 3 times with Et₂O and dried under reduced pressure to afford the desired product.

Synthesis of 2: To a flame-dried flask under nitrogen atmosphere equipped with a magnetic stir bar are added 4-Methyl-N-[(trifluoromethyl)sulfanyl]-benzene-1-sulfonamide (37.2 mmol, 1 equiv.), sodium sulfonate (44.6 mmol, 1.2 equiv.) and acetic acid (70 mL). The reaction is stirred at 25°C for 16 hours. The reaction mixture is partitioned between EtOAc and brine. The aqueous layer is extracted with EtOAc 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** obtained as colorless liquid (9.2 g, 35.9 mmol, 97 %).

Eluent for the flash chromatography: Cyclohexane/EtOAc : 100/0 to 95/5

¹H NMR (300 MHz, CDCl₃) δ = 7.88 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 2.49 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ = -38.48 (s, 3F).

Characterization data matched that reported in the literature.¹³

General procedure: To a flame-dried flask under nitrogen atmosphere equipped with a magnetic stir bar are added **2** (0.6 mmol, 3 equiv.), aryldiazonium salt **1** (0.2 mmol, 1.0 equiv.), dichlorotris(1,10-phenanthroline) ruthenium (II) hydrate [Ru(phen)₃Cl₂] (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 **3**.

Synthesis of 1-methyl-4-[(trifluoromethyl)sulfanyl]benzene (3a)

Slightly yellow liquid (20 mg, 0.104 mmol, 52 %)

Eluent for the flash chromatography: *n*-Pentane 100%

¹H NMR (300 MHz, CDCl₃) δ = 7.54 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ = -43.20 (s, 3F).

Characterization data matched that reported in the literature.¹⁴

Synthesis of 1-methoxy-4-[(trifluoromethyl)sulfanyl]benzene (3b)

Colorless oil (23 mg, 0.110 mmol, 55 %)

Eluent for the flash chromatography: *n*-Pentane/Et₂O: 98/2

¹H NMR (300 MHz, CDCl₃) δ = 7.58 (m, 2H), 6.93 (m, 2H), 3.84 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ = -43.94 (s, 3F).

Characterization data matched that reported in the literature.¹⁴

Synthesis of 1-methoxy-2-[(trifluoromethyl)sulfanyl]benzene (3c)

Colorless oil (23 mg, 0.110 mmol, 54 %)

Eluent for the flash chromatography: *n*-Pentane/Et₂O: 98/2

¹H NMR (300 MHz, CDCl₃) δ = 7.62 (d, *J* = 7.3 Hz, 1H), 7.46 (td, *J* = 8.0, 1.7 Hz, 1H), 7.02-6.96 (m, 2H), 3.91 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ = -42.39 (s, 3F).

Characterization data matched that reported in the literature.¹⁵

Synthesis of 1-(methylsulfanyl)-2-[(trifluoromethyl)sulfanyl]benzene (3d)

Yellow oil (22 mg, 0.098 mmol, 47 %)

Eluent for the flash chromatography: *n*-Pentane 100%

¹H NMR (300 MHz, CDCl₃) δ = 7.64 (d, *J* = 7.7 Hz, 1H), 7.45 (td, *J* = 8.0, 1.5 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.17 (td, *J* = 7.6, 1.3 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ = 146.9, 138.3, 131.8, 129.6 (q, $^1J(\text{C},\text{F})$ = 310 Hz), 125.3, 125.2, 121.9 (q, $^3J(\text{C},\text{F})$ = 2 Hz), 15.8.

^{19}F NMR (282 MHz, CDCl_3) δ = -42.02 (s, 3F).

Synthesis of 4-[(trifluoromethyl)sulfanyl]phenol (3e)

Orange oil (21 mg, 0.108 mmol, 53 %)

Eluent for the flash chromatography: *n*-Pentane/Et₂O: 80/20

^1H NMR (300 MHz, CDCl_3) δ = 7.53 (d, J = 8.6 Hz, 2H), 6.87(m, 2H).

^{19}F NMR (282 MHz, CDCl_3) δ = -43.94 (s, 3F).

Characterization data matched that reported in the literature.¹⁴

Synthesis of 1-nitro-4-[(trifluoromethyl)sulfanyl]benzene (3f)

Yellow oil (21 mg, 0.094 mmol, 47 %)

Eluent for the flash chromatography: *n*-Pentane/Et₂O: 98/2

^1H NMR (300 MHz, CDCl_3) δ = 8.28 (m, 2H), 7.83 (d, J = 8.8 Hz, 2H).

^{19}F NMR (282 MHz, CDCl_3) δ = -41.32 (s, 3F).

Characterization data matched that reported in the literature.¹⁵

Synthesis of 4-[(trifluoromethyl)sulfanyl]benzotrile (3g)

Off white solid (24 mg, 0.118 mmol, 59 %)

Eluent for the flash chromatography: *n*-Pentane/Et₂O: 98/2

^1H NMR (300 MHz, CDCl_3) δ = 7.77 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H).

^{19}F NMR (282 MHz, CDCl_3) δ = -41.49 (s, 3F).

Characterization data matched that reported in the literature.¹⁵

Synthesis of ethyl 4-[(trifluoromethyl)sulfanyl]benzoate (3h)

Colorless liquid (36 mg, 0.144 mmol, 72 %)

Eluent for the flash chromatography: *n*-Pentane/Et₂O: 98/2

^1H NMR (300 MHz, CDCl_3) δ = 8.08 (m, 2H), 7.71 (d, J = 8.3 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H).

^{19}F NMR (282 MHz, CDCl_3) δ = -41.87 (s, 3F).

Characterization data matched that reported in the literature.¹⁶

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