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# Intermolecular oxidative radical fluoroalkylfluorosulfonylation of unactivated alkenes with (fluoroalkyl)trimethylsilane, silver fluoride, sulfur dioxide and *N*-fluorobenzenesulfonimide†

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An intermolecular oxidative radical fluoroalkylfluorosulfonylation reaction of unactivated alkenes with convenient and commercially available (fluoroalkyl)trimethylsilane, silver fluoride, sulfur dioxide and *N*-fluorobenzenesulfonimide (NFSI) is described. This transformation efficiently affords various fluoroalkyl-containing alkyl sulfonyl fluorides with good functional group tolerance under mild conditions. Silver fluoroalkyl complexes as the fluoroalkyl radical source generated from (fluoroalkyl)trimethylsilane and silver fluoride may be the key intermediate.

The fluoroalkyl group is one of the most important fluorine-containing groups with unique physical and chemical properties. Its selective introduction into diverse classes of organic molecules commonly has beneficial and profound effects on the properties of parent organic molecules.<sup>1</sup> Although impressive progress has been made in direct fluoroalkylation reactions in recent years,<sup>2</sup> there is still a high demand for rapid and efficient installation of a range of fluoroalkyl groups to target molecules using convenient and commercial available fluoroalkylation reagents. Additionally, due to the unusual stability of the S<sup>VI</sup>–F bond, fluorosulfonyl (FSO<sub>2</sub>) groups have unique reactivity–stability patterns and have broad applications in the field of chemical biology, organic synthesis and materials.<sup>3</sup> Notably, although most sulfonyl fluorides studied or utilized in the literature are aromatic sulfonyl fluorides,<sup>4</sup> the corresponding aliphatic derivatives have also shown promising results as tool compounds in chemical biology<sup>3a,5</sup> and as better alternatives to sulfonyl

chlorides in sulfonylation reactions, especially for parallel synthesis.<sup>6</sup> The underestimation of aliphatic sulfonyl fluorides in the literature is probably due to the lack of direct and efficient synthetic approaches to them. To address these issues, an efficient and promising method is to concomitantly introduce a fluoroalkyl group and a fluorosulfonyl group into valuable synthetic targets in one step, and the fluoroalkylfluorosulfonylation of alkenes *via* a radical pathway should be a desirable entry to fulfil the task since the intermolecular radical 1,2-difunctionalization type fluoroalkylation of alkenes has emerged as a powerful tool for the introduction of versatile fluoroalkyl groups into target molecules.<sup>7</sup>

Recently, we developed a novel intermolecular oxidative radical trifluoromethylfluorosulfonylation reaction of unactivated alkenes with readily available Ag(O<sub>2</sub>CCF<sub>2</sub>SO<sub>2</sub>F) and *N*-fluorobenzenesulfonimide (NFSI) (Scheme 1a).<sup>8</sup> Although the reaction efficiently resulted in CF<sub>3</sub>-containing alkyl sulfonyl fluorides, only the CF<sub>3</sub> group can be incorporated. Preliminary mechanistic experiments showed that AgCF<sub>3</sub>

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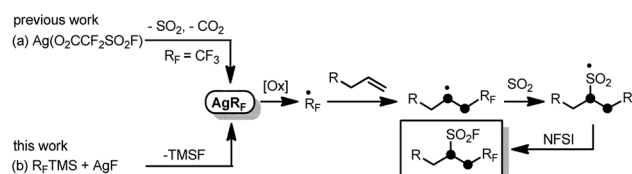
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**Scheme 1** Intermolecular oxidative radical fluoroalkylfluorosulfonylation of unactivated alkenes.

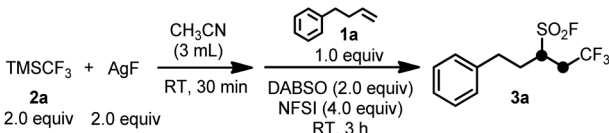
species may be involved in the reaction mechanism as the key intermediate. Also inspired by the recent advance in radical insertion reactions of sulfur dioxide,<sup>9</sup> we then envision that if the key silver fluoroalkyl complexes ( $\text{AgR}_\text{F}$ )<sup>10</sup> generated from convenient and commercially available reagents  $\text{TMSR}_\text{F}$  and  $\text{AgF}$  can be utilized in similar reactions in combination with sulfur dioxide, introduction of various fluoroalkyl groups and fluorosulfonyl groups into unactivated alkenes may be expected (Scheme 1b). As a continuation of our research interest in radical fluoroalkylation and sulfur dioxide utilization,<sup>8,11</sup> we herein present the results.

Initial studies were carried out using (trifluoromethyl)trimethylsilane ( $\text{Me}_3\text{SiCF}_3$  or  $\text{TMSCF}_3$ , commonly known as the Ruppert–Prakash reagent, widely-used and a commercially available nucleophilic trifluoromethylating agent)<sup>12</sup> and silver fluoride to generate the key  $\text{AgCF}_3$  species,<sup>10</sup> 4-phenyl-1-butene (**1a**) as the model alkene substrate, 1,4-diazabicyclo[2.2.2]octane-bis(sulfur dioxide) adduct (DABSO)<sup>13</sup> as a convenient and commercially available solid source of  $\text{SO}_2$ , and NFSI as an electrophilic fluorination reagent. In our optimization studies of the reaction conditions, it was found that 2.0 equiv. of  $\text{TMSCF}_3$ , 2.0 equiv. of  $\text{AgF}$ , 1.0 equiv. of **1a**, 2.0 equiv. of DABSO, and 4.0 equiv. of NFSI in 3 mL of  $\text{CH}_3\text{CN}$  at room temperature were the suitable conditions to afford the desired product **3a** in excellent yield (86%, Table 1, entry 1). Replacement of  $\text{CH}_3\text{CN}$  with other common reaction solvents,

such as DMF, DMSO NMP or THF resulted in lower yields of **3a** (Table 1, entries 2–4). Notably, water was found to be harmful for the desired reaction since using small amounts of water as the co-solvent resulted in no formation of **3a** (Table 1, entry 5). An attempt at increasing the yield of the desired product by utilizing some additives met with failure (Table 1, entries 6–13). While increased reaction temperatures had a deleterious effect on the desired reaction, room temperature or 0 °C led to an excellent yield of the target product **3a** (Table 1, entries 1, 14 and 15). Finally, the increased concentration of  $\text{TMSCF}_3$  and  $\text{AgF}$  did not have a significant effect on the reaction (Table 1, entry 16).

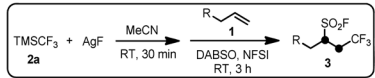
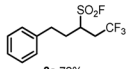
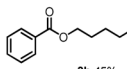
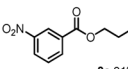
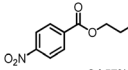
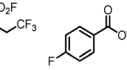
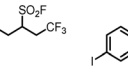
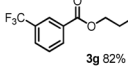
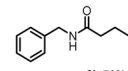
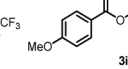
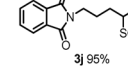
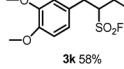
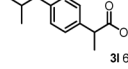
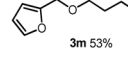
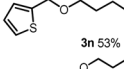
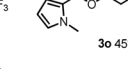
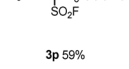
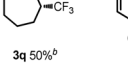
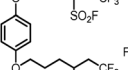
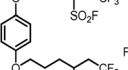
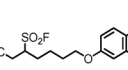
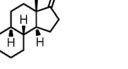
With the optimal reaction conditions established, the substrate scope of the intermolecular oxidative radical fluoroalkyl-fluorosulfonylation reactions with respect to unactivated alkenes was explored. As shown in Table 2, a range of unactivated alkenes participated in our protocol, providing good yields of the desired products **3**. Various functional groups including nitro (**3c**, **3d**), halogen (**3e**, **3f**), amide (**3h**), phthalimide (**3j**), ether (**3i**, **3k**, **3r**, **3s**), ester (**3b–i**, **3l–p**), and heterocyclic (**3m–o**) were well tolerated under the reaction conditions providing the corresponding target products in good yields. In particular, the iodo group in substrate **1f** can survive the standard reaction conditions, affording the desired product **3f** in good yield. Substrate **1r** with two terminal alkenyl groups was

Table 1 Optimization of the reaction conditions<sup>a</sup>

		
Entry	Deviation from the standard conditions	Yield of <b>3a</b> <sup>b</sup> (%)
1	None	86
2	DMF instead of $\text{CH}_3\text{CN}$	42
3	DMSO instead of $\text{CH}_3\text{CN}$	49
4	NMP or THF instead of $\text{CH}_3\text{CN}$	0
5	0.1 mL of $\text{H}_2\text{O}$ as a co-solvent	0
6	1.0 equiv. of pyridine as an additive	19
7	1.0 equiv. of 2,6-dimethylpyridine as an additive	63
8	1.0 equiv. of 2,2'-bipyridine as an additive	11
9	1.0 equiv. of o-phenanthroline as an additive	10
10	1.0 equiv. of 2,6-di- <i>tert</i> -butylpyridine as an additive	72
11	1.0 equiv. of $\text{PPh}_3$ as an additive	65
12	1.0 equiv. of $\text{Et}_3\text{N}$ as an additive	73
13	1.0 equiv. of 2,4,6-collidine as an additive	75
14	0 °C	86
15	50 °C	76
16	4.0 equiv. of $\text{TMSCF}_3$ and 4.0 equiv. of $\text{AgF}$	87

<sup>a</sup> General reaction conditions:  $\text{TMSCF}_3$  (0.4 mmol) and  $\text{AgF}$  (0.4 mmol) in  $\text{CH}_3\text{CN}$  (3 mL) were stirred at room temperature under an Ar atmosphere for 30 min, and then 4-phenyl-1-butene (**1a**, 0.2 mmol), DABSO (0.4 mmol) and NFSI (0.8 mmol) were added in turn and stirred for 3 h. <sup>b</sup> Yields were determined by  $^{19}\text{F}$  NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table 2 Substrate scope with respect to unactivated alkenes<sup>a</sup>

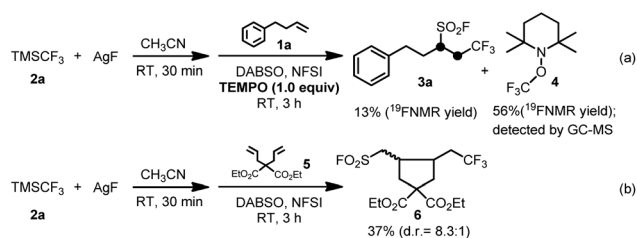
		
		
<b>3a</b> 72%	<b>3b</b> 45%	<b>3c</b> 81%
		
<b>3d</b> 57%	<b>3e</b> 85%	<b>3f</b> 71%
		
<b>3g</b> 82%	<b>3h</b> 79%	<b>3i</b> 85%
		
<b>3j</b> 95%	<b>3k</b> 58%	<b>3l</b> 69%
		
<b>3m</b> 53%	<b>3n</b> 53%	<b>3o</b> 45%
		
<b>3p</b> 59%	<b>3q</b> 50% <sup>b</sup>	<b>3r</b> 54%
		
<b>3s</b> 60%		

<sup>a</sup> Reaction conditions:  $\text{TMSCF}_3$  (0.6 mmol) and  $\text{AgF}$  (0.6 mmol) in  $\text{CH}_3\text{CN}$  (4.5 mL) were stirred at room temperature under an Ar atmosphere for 30 min, and then the alkene **1** (0.3 mmol), DABSO (0.6 mmol) and NFSI (1.2 mmol) were added in turn and stirred for 3 h. Yields refer to chromatographically pure material unless otherwise noted. <sup>b</sup> Yields were determined by  $^{19}\text{F}$  NMR spectroscopy with 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

smoothly applied to the fluoroalkylfluorosulfonylation reaction to result in the desired product **3r** in an acceptable yield. Moreover, an estrone derivative with an alkenyl group was also a suitable partner for this transformation to successfully produce the desired product **3s**.

To further explore the application of this protocol, various (fluoroalkyl)trimethylsilanes (TMSR<sub>F</sub>) were employed under the optimized reaction conditions (Table 3). As expected, replacement of CF<sub>3</sub> in TMSCF<sub>3</sub> with other perfluoroalkyl groups like the C<sub>2</sub>F<sub>5</sub> group resulted in the desired pentafluoroethylfluorosulfonylation products in good yields under similar reaction conditions (**3t–y**). However, the use of TMSCF<sub>2</sub>H instead of TMSCF<sub>3</sub> under the standard or modified reaction conditions resulted in no formation of the desired product **3z**, probably due to the relative unstability of the key intermediate AgCF<sub>2</sub>H and the decreased electrophilic ability of the CF<sub>2</sub>H radical compared with the perfluoroalkyl radical such as the CF<sub>3</sub> or C<sub>2</sub>F<sub>5</sub> radical. To our surprise, the use of TMSCF<sub>2</sub>COOEt as the reactant does not appear to be effective under the standard reaction conditions and led to lower yields of the target products **3aa** and **3bb**. Notably, good yields of the desired products **3aa** and **3bb** were achieved when the formation of the key intermediate AgCF<sub>2</sub>COOEt was performed at 0 °C in 15 min, which might be ascribed to the increased stability of AgCF<sub>2</sub>COOEt at lower reaction temperatures. All these experimental results showed that the intermolecular oxidative radical fluoroalkylfluorosulfonylation reaction of unactivated alkenes is sensitive to the stability of the key intermediate AgR<sub>F</sub> and the electronic properties of the corresponding fluoroalkyl radical generated from TMSR<sub>F</sub> and AgF.

Two sets of control experiments were carried out to shed light on the reaction mechanism. In the first experiment, 2,2,6,6-tetramethyl-1-piperidyl-oxyl (TEMPO) as a radical scavenger

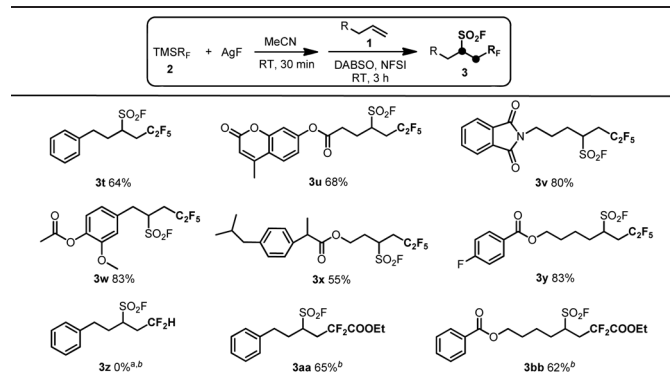


Scheme 2 Control experiments.

was used to trap the possible radical intermediates generated in the reaction system. The corresponding TEMPO-trapped complex **4** was obtained in 56% yield on the basis of <sup>19</sup>F NMR spectroscopic analysis along with only 13% yield of the desired product **3a** (Scheme 2a). In the second experiment, alkene **5** was subjected to the standard reaction conditions to generate the ring-closed product **6** in 37% isolated yield (Scheme 2b). We reasoned that the alkyl radical generated *in situ* from the addition of the CF<sub>3</sub> radical to alkene **5** undergoes an irreversible intramolecular cyclization at a much faster rate than that of the consequent radical insertion of sulfur dioxide and a rapid fluorination process. The above experiments strongly suggested that a radical reaction pathway may be involved in the fluoroalkylfluorosulfonylation reaction of unactivated alkenes, and the corresponding silver fluoroalkyl species as the key intermediate can produce a fluoroalkyl radical to initiate the desired reaction, and the resulting alkyl-sulfonyl radical derived from the radical insertion of sulfur dioxide is rapidly fluorinated by NFSI to give the final desired product (Scheme 1).

In conclusion, we have reported an intermolecular oxidative radical fluoroalkylfluorosulfonylation reaction of unactivated alkenes with convenient and commercially available (fluoroalkyl)trimethylsilane, silver fluoride, sulfur dioxide and *N*-fluorobenzenesulfonimide. This transformation efficiently affords various fluoroalkyl-containing alkyl sulfonyl fluorides with good functional group tolerance under mild conditions. Silver fluoroalkyl complexes generated from (fluoroalkyl)trimethylsilane and silver fluoride may be the key intermediate as the fluoroalkyl radical source, and the alkyl radical produced from the addition of a fluoroalkyl radical to an alkene undergoes radical insertion with sulfur dioxide and the consequent rapid fluorination with NFSI to afford the final product.

Table 3 Substrate scope with respect to (fluoroalkyl)trimethylsilane<sup>a</sup>



<sup>a</sup> Reaction conditions: TMSR<sub>F</sub> (0.6 mmol) and AgF (0.6 mmol) in CH<sub>3</sub>CN (4.5 mL) were stirred at room temperature under an Ar atmosphere for 30 min, and then the alkene **1** (0.3 mmol), DABSO (0.6 mmol) and NFSI (1.2 mmol) were added in turn and stirred for 3 h. Yields of isolated products were reported. <sup>b</sup> Reaction conditions: TMSR<sub>F</sub> (0.6 mmol) and AgF (0.6 mmol) in CH<sub>3</sub>CN (4.5 mL) were stirred at 0 °C under an Ar atmosphere for 15 min, and then the alkene **1** (0.3 mmol), DABSO (0.6 mmol) and NFSI (1.2 mmol) were added in turn and stirred for 3 h. Yields of isolated products were reported.

## Conflicts of interest

There are no conflicts to declare.

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