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Kevin Grollier,[a] Clément Ghiazza,[a] Anis Tlili,[a] Thierry Billard, [a],[b] Maurice Médebielle[a]* and Julien C. Vantourout[a]*

[a] K. Grollier, C. Ghiazza, Dr. A. Tlili, Dr. T. Billard, Dr. M. Médebille, Dr. J. C. Vantourout
Univ Lyon, Université Lyon 1, CNRS, INSA, CPE-Lyon, ICBMS, UMR 5246
1 rue Victor Grignard, 69622 Villeurbanne Cedex, France.
E-mail: maurice.medebielle@univ-lyon1.fr (Dr. M. Médebielle) and julien.vantourout@univ-lyon1.fr (Dr. J. C. Vantourout)
Homepage URL: https://mmedebielle.wordpress.com/
[b] Dr. T. Billard
CERMEP In Vivo Imaging Groupement Hospitalier Est
59 Bd Pinel, F-69003 Lyon, France.

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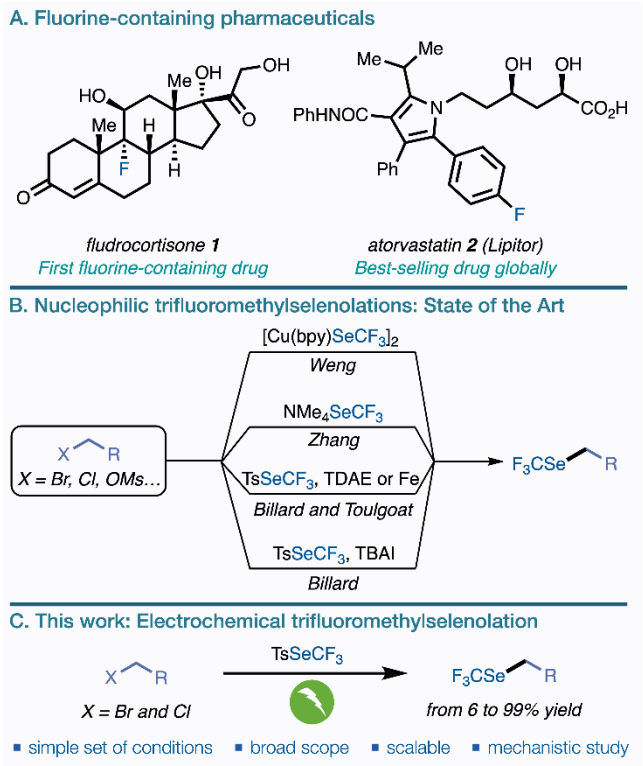
Abstract: A practical electrochemical method for the generation of CF_3Se^- anion from a shelf-stable reagent ($TsSeCF_3$) is reported allowing the metal-free trifluoromethylselenolation of activated alkyl halides. Trifluoromethylselenolated compounds have been obtained in modest to excellent yields under the optimized reaction conditions. Finally, cyclic voltammetric and ^{19}F NMR studies are presented and allowed to gain insight into the reaction mechanism.

Introduction

Since 1954 and the discovery of fludrocortisone **1** (Scheme 1A), fluorine-containing molecules keep flourishing and have found applications in the fields of medicinal and agrochemical chemistry as well as material science.[1-16] Strikingly, about three out of the five top-selling drugs bear at least one fluorine atom with atorvastatin **2** (Lipitor) being the best-selling pharmaceutical (Scheme 1A).[3,17] This trend relies on the various effects that fluorine and fluorine-containing substituents can convey on properties of organic compounds such as basicity, acidity, lipophilicity, stability, conformation, and electrostatic interactions.[18,19] Therefore, being able to modulate those properties is highly important and desirable.[3,8]

In this context, new fluorine-containing motifs have been developed and their incorporation into structures has been widely investigated.[20] If to date, the trifluoromethyl (CF_3) is the most used fluoroalkyl group, trifluoromethyl chalcogens (OCF_3, SCF_3 and $SeCF_3$) are of significant interest since their increased lipophilicity and steric hindrance can considerably alter the properties of organic molecules.[20,21] Out of the three trifluoromethyl chalcogens, $SeCF_3$ has received less attention[21,22] as some Se-containing substrates are sensitive to air and present high toxicity.[23] However, selenium is a crucial trace element of the human machinery,[24-26] and selenolated compounds have found plethora of applications in multiple areas including life sciences and materials.[27-33] Therefore, several research groups recognized the potential



Scheme 1. Introduction. (A) Fluorine-containing pharmaceuticals, (B) Nucleophilic trifluoromethylselenolations: State of the Art, and (C) This work: Electrochemical trifluoromethylselenolation.

of merging the CF_3 group with selenium, especially in the context of drug design,[34,35] to incorporate $SeCF_3$ moieties into organic structures.[21-22] The direct formation of C(sp^2)-$SeCF_3$ bond formation has been extensively studied and elegant trifluoromethylselenolation methods for the functionalization of aryl compounds have been reported.[21,22,36] Conversely, access to alkyl trifluoromethylselenylated entities has proven more challenging, and to date, only a few strategies have been described in the literature.[21-23,37] The most expedient way to afford such compounds remains the direct nucleophilic substitution of activated alkyl species with the CF_3Se^- anion to forge the desired C(sp^3)-$SeCF_3$ bond (Scheme 1B).[21-23,37] Due to the synthetic challenge associated to the generation of the CF_3Se^- anion, several copper-based methodologies

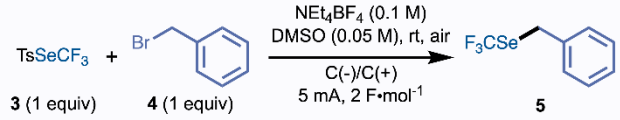
have been reported (Scheme 1B, a).[38-40] In 2003, Tyrra and co-workers reported the convenient synthesis of the air-stable $(Me_4N)SeCF_3$ reagent[41] which was subsequently used as a trifluoromethyselenylating reagent with various electrophiles by the Zhang group (Scheme 1B, b).[42] Recently, Billard, Tlili and co-workers described efficient electrophilic and radical trifluoromethylselenolation reactions using bench-stable trifluoromethylselenotoluenesulfonate reagent **3** ($TsSeCF_3$).[43-47] In 2019, the same group demonstrated that this reagent could be reduced by tetrakis(dimethylamino)ethylene (TDAE) to perform nucleophilic trifluoromethylselenolation reactions via *in situ* generation of the CF_3Se^- anion (Scheme 1B, c).[48] Despite the excellent yields obtained, sensitivity of TDAE encouraged the authors to develop a complementary way to achieve a similar umpolung approach. Replacing TDAE with tetrabutylammonium iodide (TBAI) allowed the *in-situ* formation of CF_3SeI under non-reductive conditions (Scheme 1B, d).[49] The milder set of conditions afforded good to excellent yields with reactive electrophiles (benzylic, allylic or propargylic) but provided lower conversions with non-activated substrates. More recently, they also reported a metal-based reductive approach that employs iron powder to reduce the $TsSeCF_3$ reagent.[50]

The reductive approaches rely on the low reduction potential of $TsSeCF_3$ in polar solvents such as DMSO (- 0.51 V/SCE) and DMF (- 0.65 V/SCE). Therefore, we envisioned to use electrochemistry to replace the stoichiometric quantities of reducing or activating agents. Indeed, when it comes to manipulation of electrons, electrochemistry is certainly the easiest and most economical method to use.[51-57] The direct cathodic reduction of $TsSeCF_3$ would *in situ* mildly generate the CF_3Se^- anion affording a set of conditions for the metal-free trifluoromethylselenolation of activated alkyl halides.

Results and Discussion

We started our investigation by using one equivalent of both $TsSeCF_3$ **3** and benzyl bromide **4** in dry DMSO under air at room temperature using NEt_4BF_4 as electrolyte. The electrochemical undivided cell was equipped with a graphite anode and a graphite cathode. A current of 5 mA was applied for 2 $F.mol^{-1}$ affording 58% of the desired trifluoromethylselenolated product **5** (Scheme 2A, entry 1). Running the reaction under inert atmosphere did not improve the yield (Scheme 2A, entry 2). As expected (see cyclic voltammetry data, see SI for details), solvents dramatically impact the reaction outcome of the reaction with DMF delivering desired product **5** with an efficiency comparable to DMSO (Scheme 2A, entries 3−5). Changing the electrolyte to $TBAPF_6$, $TBABF_4$, KPF_6 or $LiClO_4$ slightly lowered the yield of the reaction (Scheme 2A, entries 6−9). Cathodic materials were also investigated but none of them improved the

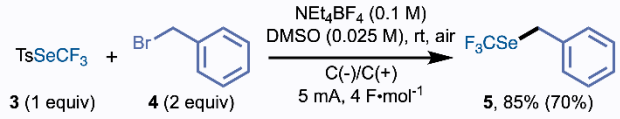
A. Influence of parameters



3 (1 equiv) **4** (1 equiv) **5**

Entry	Deviation from standard conditions	Yield of 5[a]
1	None	58%
	Atmosphere	
2	Argon	57%
	Solvent	
3[b]	DMF	55%
4[b]	DMA	31%
5[b]	MeCN	11%
	Electrolyte	
6	$TBAPF_6$	41%
7	$TBABF_4$	51%
8	KPF_6	49%
9	$LiClO_4$	48%
	Cathode	
10	Nickel plate	55%
11	Platinum	50%
12	RVC	27%
13	Ni foam	48%
	Anode	
14[c]	Zinc	74%
15[c]	Magnesium	67%
	Concentration	
16	0.1 M	20%
17	0.025 M	63%
	*Equivalents of $TsSeCF_3$ (**3**)*	
18	2	47%
	*Equivalents of BnBr (**4**)*	
19	2	63%
	$F•mol^{-1}$	
20	4	64%
	Current	
21	0 mA	n.r.

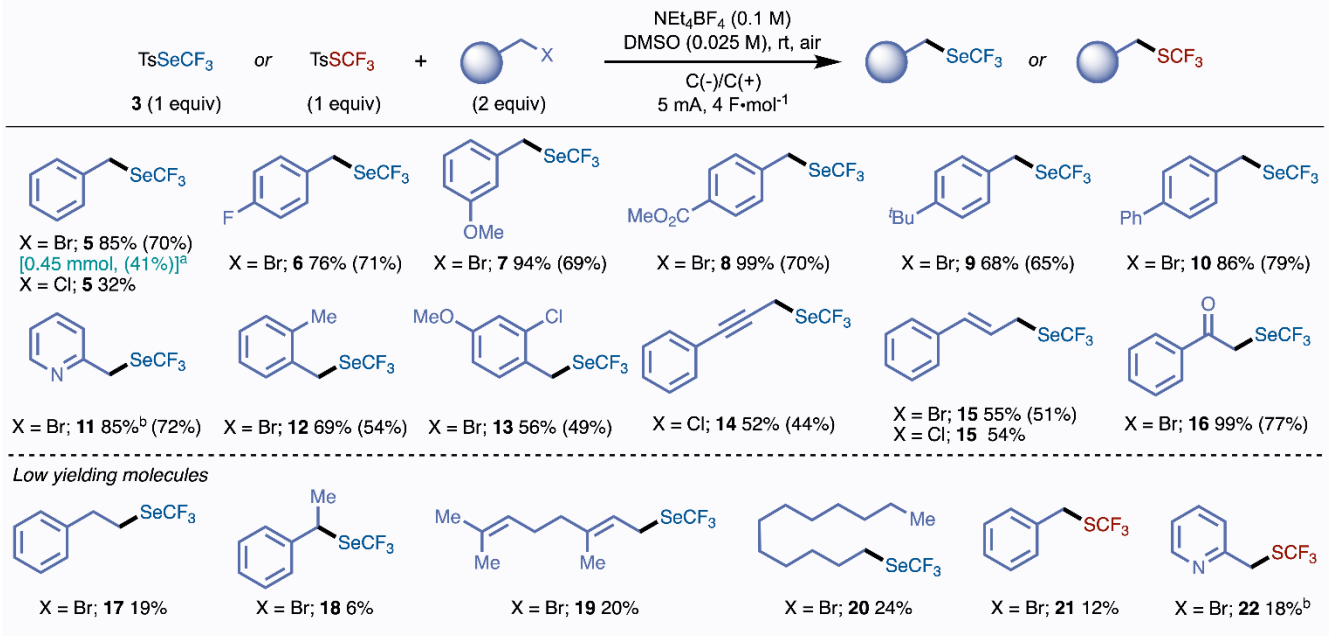
B. Optimized set of conditions



3 (1 equiv) **4** (2 equiv) **5**, 85% (70%)

Scheme 2. Optimization. [a]Yields were determined by ^{19}F NMR using trifluoromethoxybenzene as internal standard. Isolated yields are shown in brackets. [b]Reaction was run under argon atmosphere instead of air. [c]1 $F.mol^{-1}$ instead of 2 $F.mol^{-1}$.

conversion to the desired product (Scheme 2A, entries 10−13 and see SI for more details). To avoid any unnecessary oxidation processes, zinc or magnesium sacrificial anodes were tested (Scheme 2A, entries 14−15). Yields obtained were good but significant product formation was observed in the absence of electricity due to direct reduction of $TsSeCF_3$ **3** by the metal.[50] To suppress this competitive pathway and to limit the generation of undesired metal salts, graphite was selected as the anode material. Interestingly, concentration had a significant impact on the reaction outcome. While concentrating the reaction was detrimental (Scheme 2A, entry 16), higher dilution proved beneficial and afforded compound **5** in 63% yield (Scheme 2A, entry 17). Using an excess of reagent **3** lowered the yield from 58% to 47% (Scheme 2A, entry 18). Increasing both the equivalent of benzyl bromide **4** and the number of electrons delivered to the system positively impact the yield of the reaction (Scheme 2A, entries 19 and 20). Finally, in the



Scheme 3. Scope of the reaction. Yields were determined by ^{19}F NMR using trifluoromethoxybenzene as internal standard. Isolated yields are shown in brackets. [a]0.45 mmol scale using a 20 mL vial, 10 mA and 8 F.mol^{-1}. [b]Starting from the hydrobromide salt.

absence of current, no desired product **5** was observed when running the reaction with a graphite anode (Scheme 2A, entry 21).

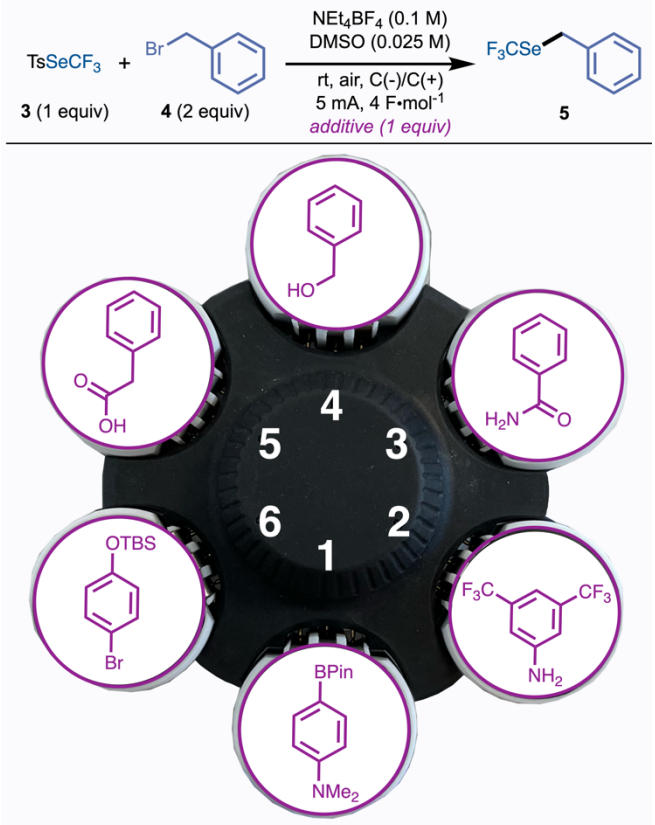
All the aforementioned observations led to the optimized set of reaction conditions (Scheme 2B). Three modifications have been made compared to the original attempt: (a) two equivalents of benzyl bromide **4** instead of one; (b) concentration of 0.025 M instead of 0.05 M and (c) 4 F.mol^{-1} instead of 2 F.mol^{-1} affording the desired trifluoromethyselenolated product **5** in 85% (70% isolated). A 6-time scale-up of the reaction was conducted (0.45 mmol instead of 0.08 mmol) and desired product **5** was obtained in 41% yield (see SI for details).

With the optimized electrochemical conditions in hands, we evaluated the scope and limitations of the reaction (Scheme 3). Good to excellent yields were obtained with benzylic starting materials bearing both electron withdrawing and donating groups on the aromatic component (**5**−**10, 12** and **13**). Noteworthy, heterocyclic moieties such as pyridine were tolerated under the reaction conditions (**11**). Ortho-substituted aromatic, allylic and propargylic halide compounds also proved competent and afforded good yields (**12**-**15** and **19**). Disappointingly, the reaction seems to be very sensitive to steric hindrance as illustrated by the low yield obtained for compound **18**. In addition, aliphatic substrates only delivered low yields (**17** and **20**) except for activated α-bromo acetophenone which afforded quantitative amount of desired product **16**. Chloride starting materials gave modest to moderate yields (**5**, **14** and **15**). This observation matches with previous studies, where the Cl^- anion proved better nucleophile than the CF_3Se^- anion. To further assess the scope of our electrochemical method, we undertaken a robustness test where our model reaction was doped with additives bearing different functional groups (Scheme 4).[58] At the end of the experiment, we measured the yield of the desired product **5** by ^{19}F NMR and the amount of additive recovered by GCMS. Pleasingly, functional groups such as trifluoromethyl, silyl ether, and boronic esters as well as primary amide, unprotected aniline, free alcohol, and free carboxylic acid were tolerated affording moderate to good yields of **3** and high recovery of the corresponding additives. Noteworthy, the electrochemical protocol affords similar yields than the previously reported approaches that require stoichiometric quantities of reducing or activating agents.[43-50] Comparable limitations are also observed with non-activated alkyl halides delivering low yields of the desired products.

Through the course of our study, cyclic voltammetric measurements revealed that $TsSCF_3$ owns a similar reduction potential (- 0.58 V/SCE, see SI for details) to $TsSeCF_3$ in DMSO (- 0.51 V/SCE, see SI for details). Therefore, we attempted to use $TsSCF_3$ as a trifluoromethylthiolation reagent under our electrochemical procedure. Unfortunately, compounds **21** and **22** were only obtained in low yields of 12% and 18%, respectively. The instability of the *in-situ* generated CF_3S^- anion could certainly explain the lower efficiency of the trifluoromethylthiolation process.[59,60]

To gain insight into the reaction mechanism, several experiments were conducted (Scheme 4). All mechanistic events are described in a stepwise fashion (Scheme 4A and B):

1. $TsSeCF_3$ reagent **3** is initially reduced leading to the formation of Ts^- anion **II** (+ 0.36 V/SCE in DMSO) along with $CF_3Se^•$ radical **III** (Scheme 4C, panel 1).



Carousel position	Yield of **5**[a]	Additive recovery[b]
1	51%	87%
2	37%	83%
3	58%	>95%
4	65%	>95%
5	44%	89%
6	62%	93%

Scheme 4. Robustness test of the reaction. Yields for compound **5** were determined by ^{19}F NMR using trifluoromethoxybenzene as internal standard. Yields for the additives were determined by GCMS using 1,3,5-trimethoxybenzene as internal standard.

2. Radical **III** then reacts with $TsSeCF_3$ reagent **3** to afford $(SeCF_3)_2$ **I** (Scheme 4C, kinetic profile and panel 2a). Indeed, we demonstrated that under the reaction conditions, after 0.5 $F.mol^{-1}$, $TsSeCF_3$ **3** was fully consumed, and dimer $(SeCF_3)_2$ **I** was formed in 44% along with 12% of desired product **5**. In addition, running the electrolysis in a divided setup and in the absence of benzyl bromide **4**, $TsSeCF_3$ **3** was quantitatively reduced to dimer **I** after only applying 0.5 $F.mol^{-1}$.
3. Dimer **I** can then be reduced to form the CF_3Se^- anion **IV** and $CF_3Se^\bullet$ radical **III** as highlighted by the cyclic voltammetry experiment described in panel 1. Reduction of dimer **I** occurs at − 0.45 V/SCE in DMSO whereas oxidation of the CF_3Se^- anion **IV** is observed at + 0.04V/SCE in DMSO (Scheme 4C, panel 1). Formation of anion **IV** was further established by ^{19}F NMR when reducing dimer **III** in a divided setup in the absence of benzyl bromide (Scheme 4C, panel 2b).
4. Radical **III** certainly reacts with $TsSeCF_3$ reagent **3** to afford $(SeCF_3)_2$ **I**. However, direct dimerization of $CF_3Se^\bullet$ radical **III** cannot be ruled out.
5. Electrochemically generated CF_3Se^- anion **IV** can react with starting material activated alkyl bromide **4** to afford desired product **5** (Scheme 4C, panel 2c).
6. Based on cyclic voltammetric data, both Ts^- anion **II** (+ 0.36 V/SCE in DMSO) and CF_3Se^- anion **IV** (+ 0.04V/SCE in DMSO) can potentially be oxidized at the anode affording $Ts^\bullet$ radical **V** and $CF_3Se^\bullet$ radical **III** respectively (Scheme 4C, panel 1). $Ts^\bullet$ radical **V** is easily reduced and therefore competes with the productive reduction of dimer **I**, explaining why more electrons need to be passed through the system to achieve higher conversions. $Ts^\bullet$ radical **V** was also trapped in a control experiment where the reaction was conducted in the presence styrene instead of benzyl bromide **4** affording both isomers of 1-methyl-4-(styrylsulfonyl)benzene (Scheme 4C, panel 3).

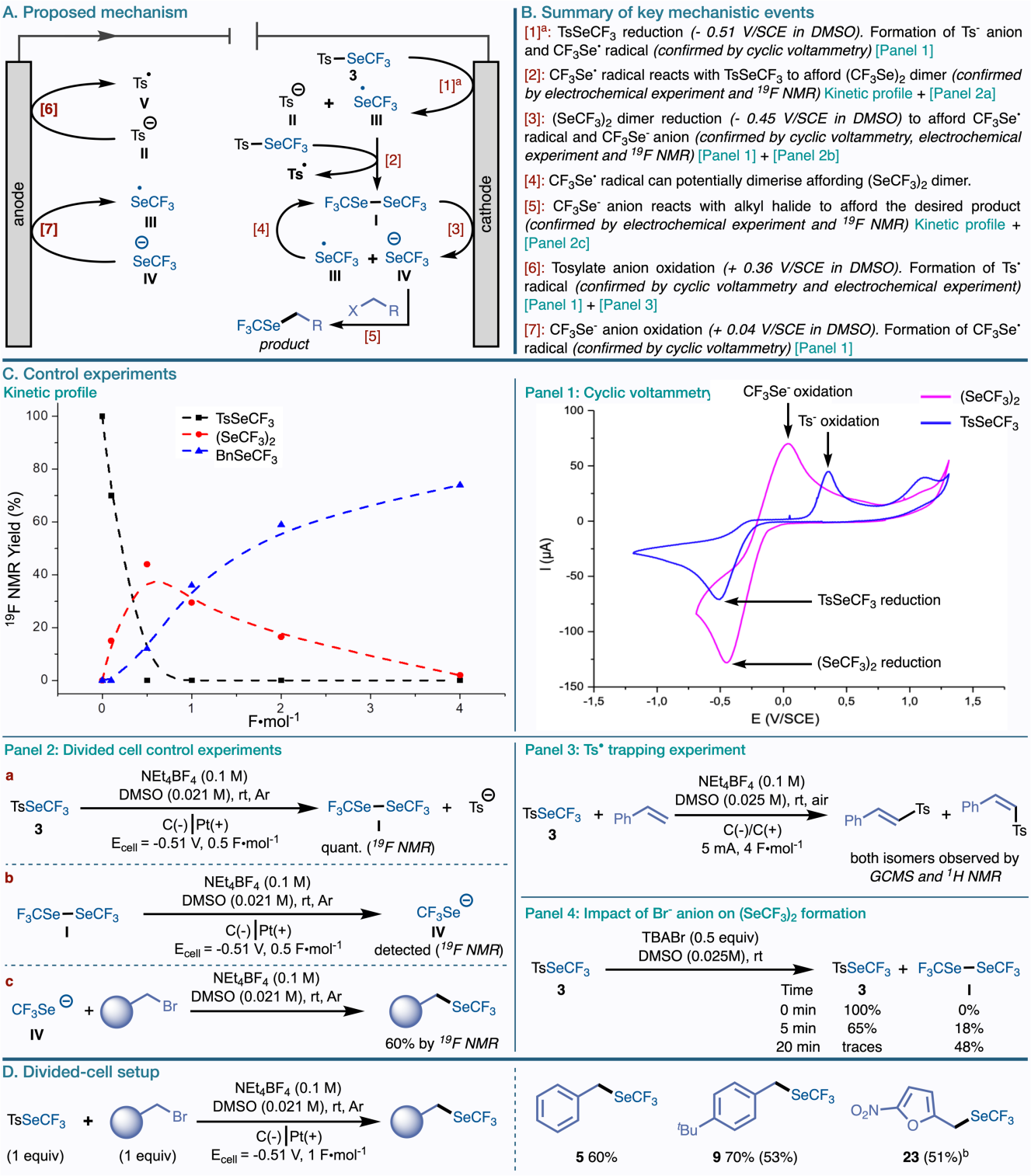
Based on these observations, it was envisioned to suppress the competing reduction of $Ts^\bullet$ radical **V** by using a divided cell setup at a constant potential of − 0.51 V/SCE corresponding to the reduction potential of $TsSeCF_3$ (Scheme 4D and see SI for details). Under these conditions, compounds **5**, **9**, and **23** were obtained in 60%, 70% and 51% yield with only 1 $F.mol^{-1}$ validating the aforesaid hypothesis. Noteworthy, based on the mechanistic pathway, a maximum yield of 50% should have been obtained under these conditions. However, Br^- anion formed through the course of the reaction can react with $TsSeCF_3$ reagent **3** to form dimer **I**. Therefore, as soon as product **5** is formed, the only required electrochemical event is the reduction of dimer **I** (Scheme 4C, Panel 4).

Conclusion

An electrochemical method for the metal-free trifluoromethylselenolation of activated alkyl halides has been developed which exhibits a broad scope and a high functional group tolerance. This transformation relies on the reduction of shelf-stable reagent $TsSeCF_3$ to afford the reactive CF_3Se^- anion which can further react with alkyl halide substrates via a nucleophilic substitution type mechanism. The main limitation of this protocol is the need to use a divided cell setup to avoid the reduction of sensitive substrates. A combination of cyclic voltammetric and ^{19}F NMR studies allowed to gain insight into the reaction mechanism. This new protocol reinforces the high versatility of $TsSeCF_3$ reagent in accomplishing electrophilic, radical, or nucleophilic reactions, depending on the conditions. It also demonstrates that depending on the substrate classes, reductive electrochemical conditions can be complementary to methods that require stoichiometric quantities of reducing or activating agents.

Acknowledgements

This work was supported by a grant from the French National Research Agency (ANR 18-CE07-0039-01). The NMR



Scheme 5. Mechanistic study. (A) Proposed mechanism, (B) Summary of key mechanistic events, (C) Control experiments, and (D) Divided-cell setup. Yields were determined by ^{19}F NMR using trifluoromethoxybenzene as internal standard. Isolated yields are shown in brackets. [a]For this step, the formation of CF_3Se^- anion along with $Ts^\cdot$ radical cannot be ruled out and is discussed in the SI. [b]CF_3Se^- anion was first prepared in the divided cell then the halide was added to reaction mixture.

Centre of the Université Claude Bernard Lyon 1 is thanked for their contribution. The authors are grateful to the French National Research Agency, the CNRS, Université Claude Bernard Lyon 1 and the French Ministry of Research for financial support. The French Fluorine Network (GIS-FLUOR) is also acknowledged for its support.

Keywords: Electrochemistry • Mechanistic investigations • Method development • Nucleophilic substitutions • Trifluoromethylselenolation

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