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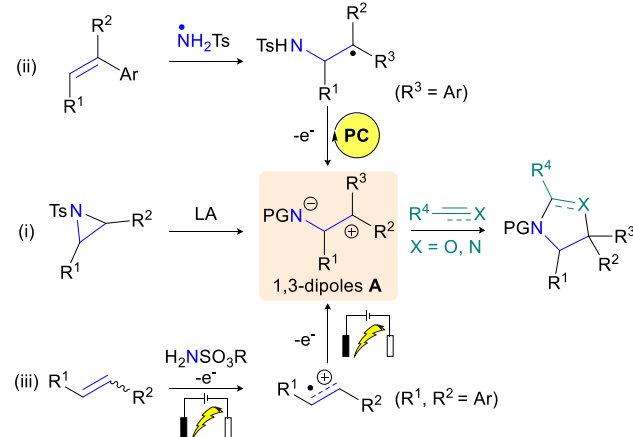
Electrochemical tandem trifluoromethylation of allylamines /formal (3+2)-cycloaddition for the rapid access to CF₃-containing imidazolines and oxazolidines

Aur lie Claraz,*^a Aur lie Djian,^a G raldine Masson*^a

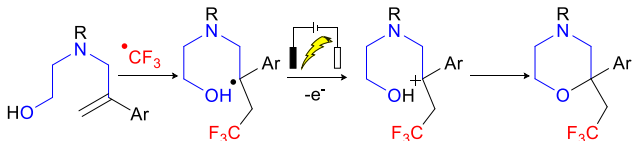
An electrochemical tandem radical trifluoromethylation of allylamines/formal (3+2)-cycloaddition with nitrile and carbonyl compounds has been developed under mild and environmentally benign reaction conditions. Such multicomponent reaction allowed the construction of CF₃-containing imidazolines and oxazolidines by creating three new bonds from simple and easily available starting materials.

Imidazolines and oxazolidines are important five-membered azacycles existing in a number of natural products and bioactive molecules.^{1,2} They also serve as versatile intermediates in organic synthesis and effective ligand in asymmetric catalysis.³ A considerable effort has been dedicated to the efficient construction of these heterocycles.^{4,5} Privileged methods for their syntheses are based on the formal (3+2)-cycloaddition of *N*-tosylaziridines as masked-1,3-dipoles **A** with nitrile or carbonyl compounds (Scheme 1a, eq. (i)).^{6,7} Recently, Xu *et al.* have reported a complementary method which involves a photochemical generation of 1,3-dipoles **A** by the addition of *N*-centered radicals to aromatic alkenes followed by single electron transfer oxidation of the resulting β -amino radical intermediate (eq. (ii)).⁸ Alternatively, Cheng *et al.* have disclosed an electrochemical formation of 1,3-dipoles **A** through an anodic oxidation of stilbenes, nucleophilic addition of sulfamates and second anodic oxidation step (eq. (iii)).⁹ However, little attention has been paid to the synthesis of trifluoromethylated imidazolines and oxazolidines¹⁰ whereas the incorporation of a trifluoromethyl (CF₃) group¹¹ may produce heterocycles of high interests for medicinal, agrochemical and synthetic applications. Moreover, most of protocols used for that purpose are limited to the synthesis of 2-imidazolines and 1,3-oxazolidines bearing a CF₃ group at the 2-position. Alternatively, Hanamoto *et al.* have developed elegant methods giving rise to those heterocycles with a CF₃ group at the 5-position but requiring nevertheless the prior preparation of trifluoromethylated aziridines.^{12,13} Therefore, the development of novel synthetic methods that allow efficient and rapid access to trifluoromethylated imidazolines and oxazolidines is still highly desirable. Herein, we report an electrochemical three-components tandem process for the preparation of 4-(2,2,2-trifluoroethyl)-2-imidazolines and 4-(2,2,2-trifluoroethyl)-1,3-oxazolidines.

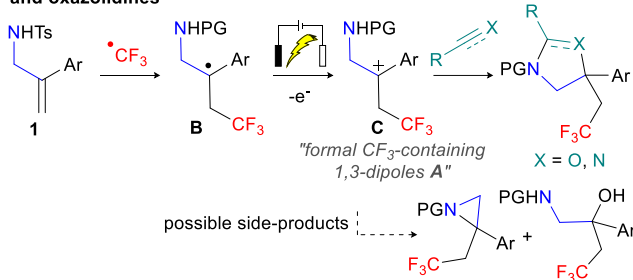
a) Synthone A for the synthesis of imidazolines and oxazolidines



b) Our previous work : electrochemical oxytrifluoromethylation



c) This work: electrochemical access to CF₃-containing imidazolines and oxazolidines



Scheme 1 Synthesis of imidazolines and oxazolidines.

Recently, we have described an efficient electrochemical¹⁴ oxytrifluoromethylation of *N*-tethered alkenyl alcohols using the Langlois reagent¹⁵ as a trifluoromethyl precursor (Scheme 1b).^{16–18} On the basis of our previous work, we wished to develop a one-pot electrochemical procedure for the construction of CF₃-containing 2-imidazolines and 1,3-oxazolidines from easily available allylic amines and Langlois reagent. We envisaged a scenario in which the CF₃ radical generated by electrooxidation could selectively react with *N*-tosyl allylamines **1** and the resulting 1,3-dipole **C**, formed after an additional oxidation step of the radical **B**, could be subsequently engaged in a formal (3+2)-cycloaddition with

^aInstitut de Chimie des Substances Naturelles, Universit  Paris Saclay, CNRS, UPR2301, 1 Avenue de la Terrasse, 91198 Gif-sur-Yvette cedex, France. E-mail : geraldine.masson@cns.fr, aurelie.claraz@cns.fr.

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nitriles or carbonyls to furnish the desired CF₃-containing 5-membered heterocycles. However, the development of such approach is not exempt of risk since the highly reactive carbocation **C** could be either intramolecularly trapped by nitrogen to form a trifluoromethylated aziridine¹⁹ or react with traces of water to give an amino-alcohol (Scheme 1c).

To evaluate our proposed approach, we began by examining the reaction of *N*-tosyl allylamine **1a** with the Langlois reagent (**2a**) in a mixture of acetonitrile and dichloromethane using LiClO₄ as supporting electrolyte (Table 1). The mixture was electrolyzed at constant current at room temperature. To our delight, we did form the three-component imidazoline adduct **3a** in 40% yield, together with the aziridine **4** and α -amino-alcohol **5**.

Table 1 Optimization of reaction conditions for the synthesis of imidazoline **3a**^a

Entry	Additive (equiv.)	Yield ^b (%)		
		3a	4	5
1 ^c	-	40	33	13
2	-	54	20	24
3	K ₂ CO ₃ (1)	49	21	7
4 ^d	-	36	34	17
5	CH ₃ COOH (1)	22	22	8
6	CF ₃ COOH (1)	45	27	19
7	Bi(OTf) ₃ (0.2)	45	19	20
8	Bi(OTf) ₃ (1)	48	0	22
9	BF ₃ .OEt ₂ (0.5)	40	31	17
10	BF₃.OEt₂ (1)	64 (62)	0	16
11 ^e	BF ₃ .OEt ₂ (1)	63	0	8
12 ^f	BF ₃ .OEt ₂ (1)	0	0	0

^a Reaction conditions: undivided cell, C(+)|Ni(-), **1a** (0.25 mmol), **2a** (0.5 mmol), additive, CH₃CN (2.5 mL), LiClO₄ (0.2 M), CCE (15 mA), 3.2 F (1 h 25), rt. ^b NMR yield; isolated yield is written between parentheses. ^c CH₂Cl₂/CH₃CN (1:1) instead of CH₃CN. ^d 2.2 F (1 h) instead of 3.2 F. ^e C(+)|C(-) instead of C(+)|Ni(-). ^f No electricity.

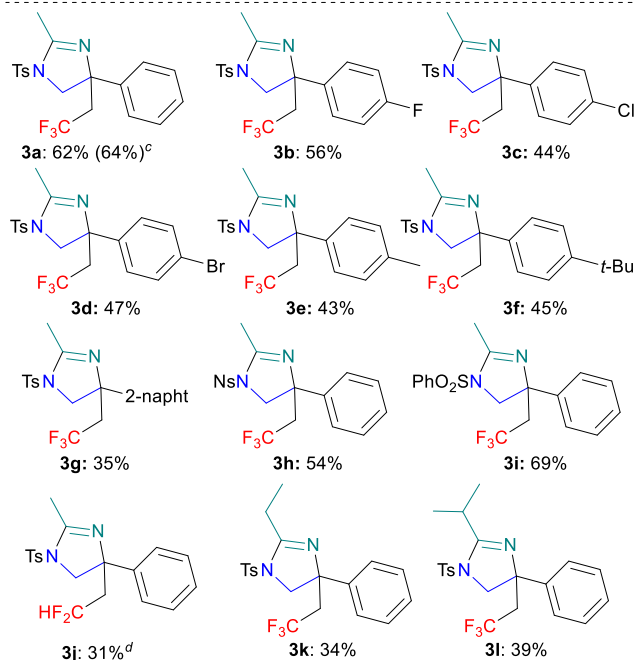
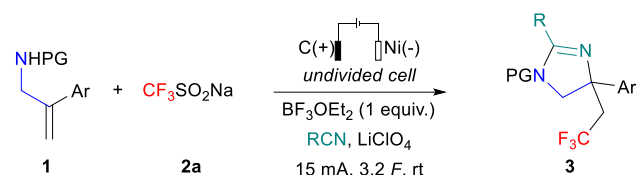
The addition of a base afforded no benefits, while the use of acetonitrile as the sole solvent made a small improvement to the conversion but had little effect on selectivity (entries 2-3). Lower yields were obtained with organic supporting electrolytes.²⁰ Interestingly, shortening the reaction time afforded a higher amount of aziridine **4** (entries 4 vs 2). This result led us to assume that the formation of imidazoline **3a** might proceed through an aziridine intermediate **4** which then could react with acetonitrile in a formal (3+2)-cycloaddition. Therefore, different acidic additives, which are known to mediate the ring opening of aziridines, were evaluated (entries 5-10).⁶ Gratefully, upon adding one equivalent of BF₃.OEt₂, the formation of aziridine **4** was totally suppressed and the desired

imidazoline **3a** could be isolated in 62% yield (entry 10).²¹ It is also worth mentioning that similar yield was obtained with the cheap graphite electrode as cathode instead of nickel (entry 11).

With the best reaction conditions in hand, the scope of this three-component reaction was examined. As shown in scheme 2, allylamines **1a-f** bearing both electron donating as well as electron withdrawing groups on the aromatic ring reacted smoothly affording the corresponding imidazolines **3a-f** in moderate to good yields. The synthesis of imidazoline **3g** with a 2-naphthyl ring has been also achieved albeit with slightly lower yield. Other sulfonamides such as 2-nosyl and phenyl sulfonyl acted as good reaction partners to form the corresponding imidazolines **3h** and **3i** in 54% and 69% yields, respectively. However, no product was obtained with *N*-benzyl allylic amines, probably due to the direct oxidation of amine at the electrode. Remarkably, this multicomponent reaction could be performed with easily prepared sodium difluoromethylsulfinate **2b**²² furnishing the desired CF₂H-containing imidazoline **3j** in 31% yield. Pleasingly, the propionitrile and the sterically hindered *iso*-butyronitrile were found to react with **1a** and Langlois reagent to yield 2-ethyl and 2-isopropyl imidazoline **3k-l**, albeit with slightly lower yields probably due to the lower dielectric constants of these solvents.²³ To demonstrate the synthetic potential of this 3-components tandem protocol, a 1 mmol scale experiment with substrate **1a** was carried out affording the corresponding CF₃-containing imidazoline **3a** in 64% yield.

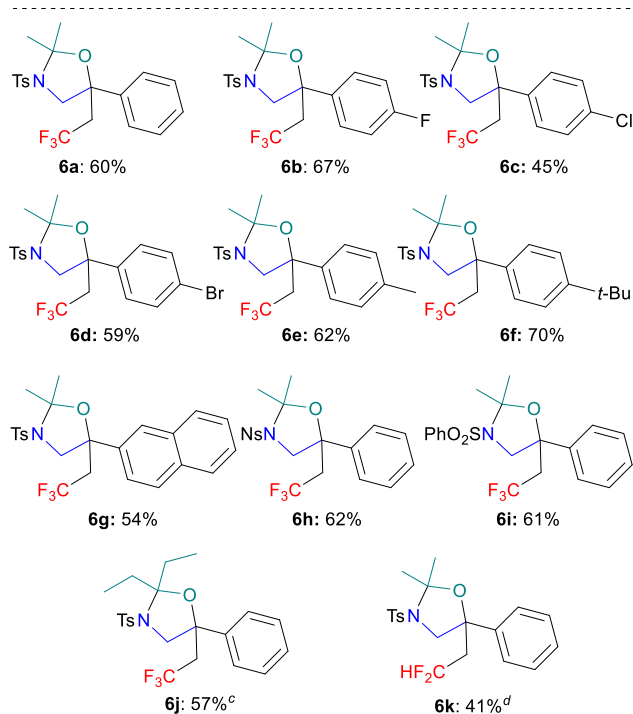
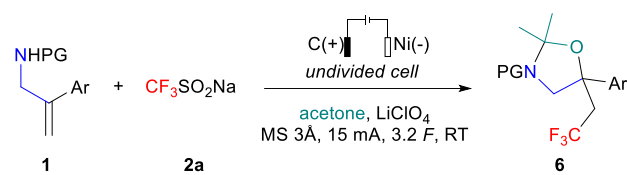
Encouraged by this result, we next sought to extend this electrochemical multicomponent process to carbonyls as dipolarophiles (Table 2). Pleasingly, the reaction proceeded smoothly in acetone as solvent to afford the corresponding oxazolidine **6a** in 49% yield (entry 1) along with amino-alcohol product **5** (29%). Interestingly, no formation of aziridine **4** was detected at the end of the reaction even in the absence of BF₃.OEt₂ (entry 2). Finally, we were pleased to find that the yield of **6a** increased when molecular sieves were added to trap traces of water present in the reaction media.

A variety of allylamines **1a-i** bearing various aryl rings and aza-protecting groups were subjected to these conditions, furnishing the corresponding CF₃-containing oxazolidines **6** in up to 70% yields (Scheme 3). Generally, the yields were slightly higher than for the construction of imidazolines. Pleasingly, slight modifications on the reaction conditions permitted the use of pentan-3-one as solvent instead of acetone delivering the corresponding oxazolidine **6j** in good yield (57%). More specifically, with this sterically hindered carbonyl compound, one equivalent of BF₃.OEt₂ was added at the end of the electrolysis to fully transform the remaining aziridine **4** into the desired 5-membered ring **6j**. CF₂H-containing oxazolidine **6k** could also be prepared in a decent yield by using sodium difluoromethylsulfinate **2b**.



Scheme 2 Three-component synthesis of CF₃-containing imidazolines.^{a,b}

^a Reaction conditions: undivided cell, C(+)|Ni(-), **1a** (0.25 mmol), **2a** (0.5 mmol), BF₃·OEt₂ (0.25 mmol), RCN (2.5 mL), LiClO₄ (0.2 M), CCE (15 mA), 3.2 F, rt. ^b Isolated yield. ^c Reaction conducted on 1 mmol scale. ^d **2b** instead of **2a**.



Scheme 3 Three-component synthesis of CF₃-containing oxazolidines.^{a,b}

^a Reaction conditions: undivided cell, C(+)|Ni(-), **1a** (0.25 mmol), **2a** (0.5 mmol), MS 3A (300 mg), acetone (2.5 mL), LiClO₄ (0.2 M), CCE (15 mA), 3.2 F, rt. ^b Isolated yield. ^c With pentan-3-one instead of acetone, **2a** (0.625 mmol), LiClO₄ (0.4 M), 35 °C, CCE (15 mA), 2.8 F, 35 °C; then BF₃·OEt₂ (0.25 mmol), overnight, rt. ^d **2b** instead of **2a**.

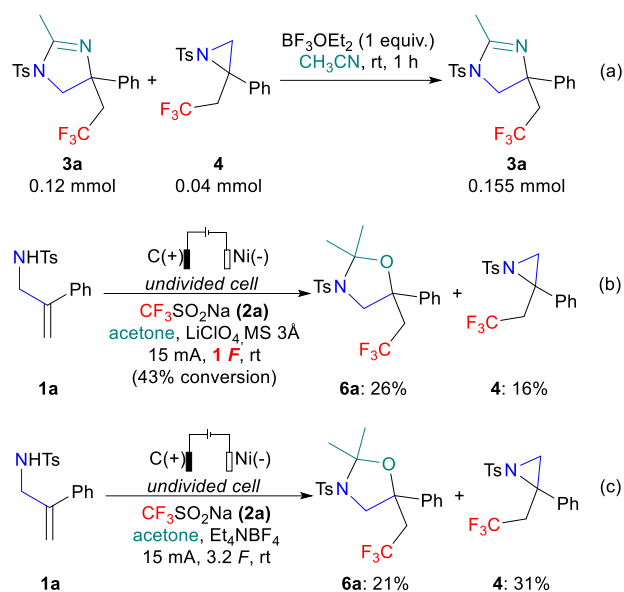
Table 2 Optimization of reaction conditions for the synthesis of oxazolidines **6a**^a

Entry	Additive (equiv.)	Yield ^b (%)		
		6a	4	5
1 ^c	BF ₃ ·OEt ₂ (1)	49	0	29
2	-	52	0	40
3	MS 3A (300 mg)	69 (60)	0	0

^a Reaction conditions: undivided cell, C(+)|Ni(-), **1a** (0.25 mmol), **2a** (0.5 mmol), additive, acetone (2.5 mL), LiClO₄ (0.4 M), CCE (15 mA), 3.2 F (1 h 25), rt. ^b NMR yield; isolated yield is written between parentheses.

A set of control experiments were conducted to shed light on the reaction mechanism. No reaction occurred in the absence of current (Table 1, entry 12). Measuring the redox behavior of the reagents by cyclic voltammetry analysis revealed that the Langlois reagent **2a** exhibited lower oxidation potentials (1.45 V vs Ag/AgCl) than that of *N*-tosyl allylamine **1a** (2.11 V vs Ag/AgCl).²⁰ To clarify the role of BF₃·OEt₂, the following additional experiment was performed: one equivalent of BF₃·OEt₂ was added to a mixture of imidazoline **3a** and aziridine **4**. After 1 h, an almost complete conversion of **4** into **3a** was observed (Scheme 4, eq. (a)), thus supporting that BF₃·OEt₂ works as a Lewis-acid to promote the formal (3+2)-cycloaddition between aziridine **4** and acetonitrile.^{6d-h} As mentioned above, no aziridine was observed at the end of the electrolysis when acetone was used as formal dipolarophile. However, when the reaction was stopped at 43% conversion of **1a** (1 F) under optimized conditions, the aziridine **4** was formed in 16% yield (Scheme 4, eq. (b)). This result inferred that aziridine **4** is also a key intermediate in this transformation. Based on this result, we reasoned that the lithium perchlorate electrolyte certainly served²⁴ to mediate the formal (3+2)-cycloaddition between aziridines and acetone. Indeed, when LiClO₄ was replaced by Et₄NBF₄ as electrolyte, the aziridine **4**

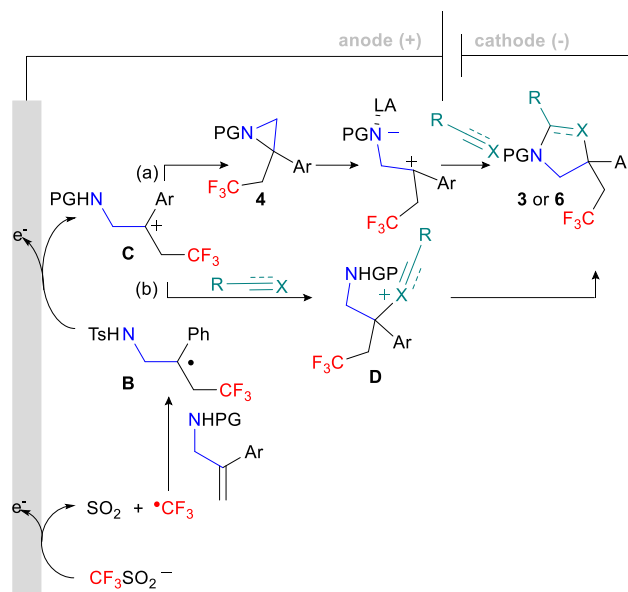
was obtained in 31% yield supporting the crucial role of the lithium cation (Scheme 4, eq. (c)).



Scheme 4 Control experiments.^a

^a Chemical amounts, yields and conversions were determined by ¹H NMR analysis of the crude material using 1,3,5-trimethoxybenzene as an internal standard.

On the basis of the control experiments and the literature,¹⁶⁻¹⁸ a plausible reaction mechanism is outlined in Scheme 5. Initially, the anodic oxidation of Langlois reagent via a single-electron-transfer (SET) can deliver trifluoromethyl radical after fast extrusion of gaseous SO₂. The regioselective addition of this radical onto the double bond could afford benzylic radical **B**, which can be further oxidized to carbocation **C**. An intramolecular attack of nitrogen atom on **C** could produce aziridine **4**, which subsequently could undergo a formal (3+2)-cycloaddition with nitriles or carbonyls in the presence of a Lewis acid to afford the corresponding imidazolines **3** or oxazolidines **6** (pathway a). The reductions of the proton H⁺ and SO₂ would be the counter reactions taking place at the cathode to balance the overall transformation. Nevertheless, at the present stage of the development, we cannot totally exclude an alternative pathway involving a direct addition of nitriles or the acetone on the carbocation **C** followed by attack of sulfonamide on the resulting nitrilium and oxocarbenium ions **D** to form heterocyclic products **3** or **6** (pathway b). Both mechanisms may operate, although the dominant process certainly occurs *via* pathway a.



Scheme 5 Proposed mechanism.

Conclusions

In summary, we have developed an electrochemical three-component reaction for the rapid access to new CF₃-containing imidazolines and oxazolidines from easily prepared allylic amines and cheap Langlois reagent as CF₃ source. This original transformation proceeds through the tandem radical trifluoromethylation of allylic secondary amines/formal (3+2)-cycloaddition with nitrile or carbonyl compounds allowing the creation of three new bonds under mild reaction conditions. This electrochemical process was also applicable to the construction of CF₂H-containing imidazoline and oxazolidine. Further investigations of new electrochemical multicomponent tandem processes for the construction of heterocycles are currently under way in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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