A Platinum Open Access Journal for Organic Chemistry

Paper

Free to Authors and Readers | DOAJ Seal | *Arkivoc* **2026** (2) 202612576

Electrochemical functionalization of allylic amines: a straightforward route to relevant aza-compounds

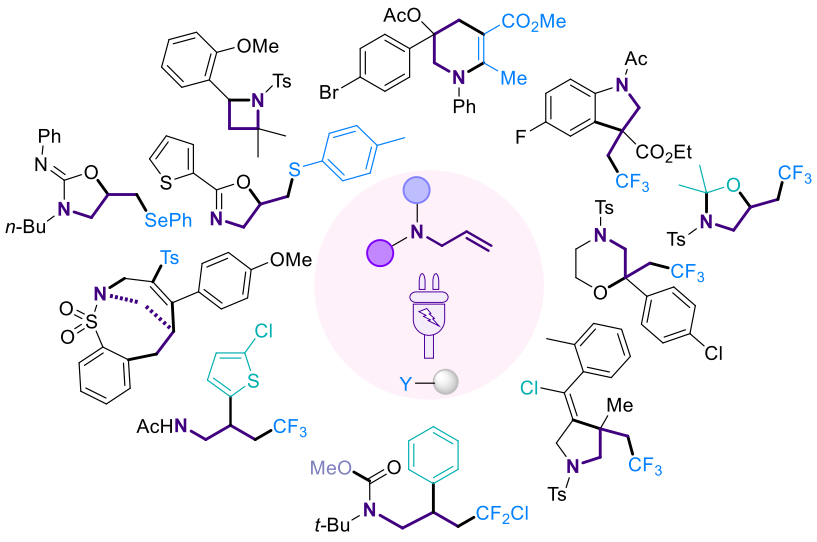
Aurélie Claraz

Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Univ. Paris-Saclay, 91198 Gif-sur-Yvette, France
Email: aurelie.claraz@cnrs.fr

Received 03-11-2026 **Accepted** 06-02-2026 **Published on line** 06-15-2026

Abstract

Allylic amines are versatile building blocks in organic synthesis that can be readily transformed into relevant azacompounds through functionalization of the carbon–carbon double bond. Practical electrochemical approaches offer the advantage of operating under mild, safe, eco-friendly, and cost-effective conditions. This short review summarizes advances in the electricity-enabled functionalization of allylic amines, with particular emphasis on mechanistic insights. It highlights the synthesis of valuable azacycles and β-arylethylamines. Finally, future directions are discussed to inspire synthetic chemists to pursue increasingly complex nitrogen-containing architectures via electrochemical functionalization of allylic amines.



Keywords: Electrosynthesis, radical, olefin, functionalization, azacycle, β-arylethylamine.

Table of Contents

1. Introduction

Allylic amines and amides are versatile motifs in organic synthesis. Their C–C double bond can be reduced or oxidized to access a variety of useful compounds. More importantly, due to the nearby sp^3-hybridized nitrogen atom bearing different substituents, functionalization of the double bond can trigger direct cyclization, cascade reactions, or rearrangements, providing multiple opportunities to access valuable functionalized aza-compounds. In line with the goals of sustainability and green chemistry, these transformations must be mild, safe, and cost-effective.

Organic electrosynthesis, which directly employs safe, inexpensive, and readily available electrons as traceless reagents, constitutes an attractive alternative to conventional methods that rely on stoichiometric oxidants and reductants to run redox transformations. This atom-economical approach can advantageously limit side reactions through precise control of the applied current and potential.[1] Long regarded as daunting by organic chemists, it has recently experienced a renewed surge of interest, driven by technological advances in instrumentation, simplified implementation, and improved reproducibility.[2]

This article highlights advances in the electrochemical functionalization of allylic amines. The adoption of electrochemical strategies has significantly enhanced conventional methodologies, making them safer, more sustainable, and more cost-effective. Notably, it has also unlocked new reactivity patterns, enabling access to unprecedented compounds. The synthesis of aza-cycles is discussed first, followed by an examination of the electrochemical preparation of β-aryl ethylamines via Truce–Smiles rearrangements.

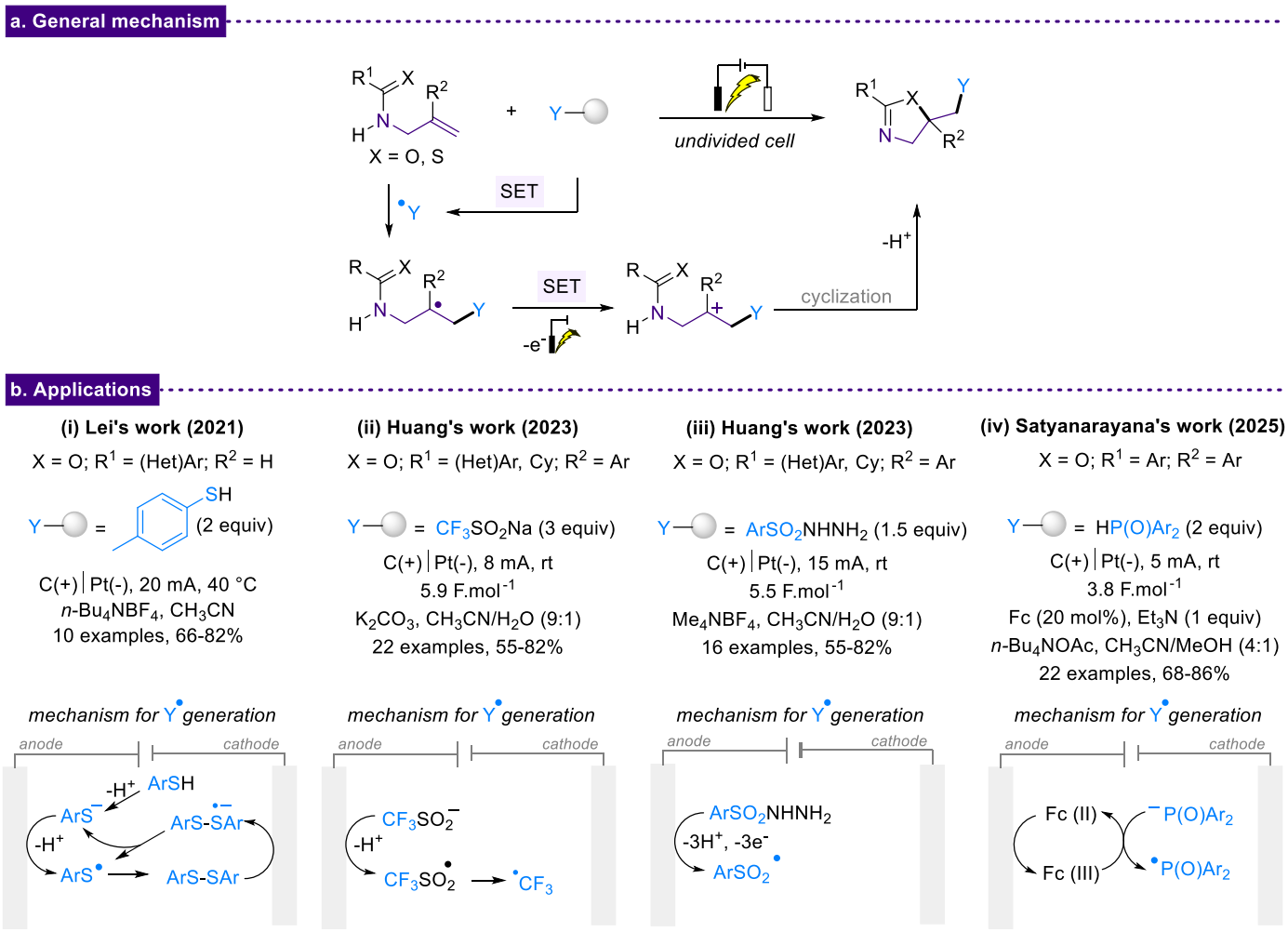
2. Synthesis of Azacycles

2.1 Cyclization of *N*-allyl (thio)amides

Oxazolines and thiazolines are prominent five-membered heterocycles widely found in natural products, pharmaceuticals, and bioactive molecules,[3] and are frequently employed as ligands in asymmetric catalysis.[4,5] Electrophilic oxidative cyclization of *N*-allyl (thio)amides constitutes a powerful method for the synthesis of

diversely functionalized oxazolines and thiazolines from readily available starting materials. Adoption of an electrochemical approach obviates the need for harsh reaction conditions, stoichiometric amounts of oxidants, transition-metal catalysts, and prolonged reaction times. This strategy relies on activation of the carbon–carbon double bond by an anodically generated radical or electrophilic species, proceeding via radical or ionic mechanisms, respectively.

2.1.1 Radical pathway. During an electricity-induced radical cyclization of *N*-allyl (thio)amides, an electrochemically generated electrophilic radical regioselectively adds to the carbon–carbon double bond. The resulting nascent alkyl radical subsequently undergoes anodic oxidation to the corresponding carbocation, which triggers oxa- or thia-cyclization through a radical-polar crossover process. Cathodic reduction of the released proton via the hydrogen evolution reaction (HER) or deprotonation with an additional base further prevents any back reaction, thereby delivering the desired five-membered *N*,*O*- or *N*,*S*-heterocycle (Scheme 1a).



Scheme 1. Radical functionalization of *N*-allyl(thio)amides for the synthesis of oxazolines and thiazolines.

In 2021, the group of Lei[6] reported the electrosynthesis of sulfurated oxazolines in an undivided cell composed of a carbon graphite anode and a platinium cathode under constant current. The reaction was exemplified with 4-methylbenzenethiol as a source of thiyl radical delivering the desired heterocycles in good

yields. Cyclic voltammetry analyses hinted that the aryl sulfonyl radical was generated either upon anodic oxidation of the thiophenol (E = 1.51 V *vs* aq. Ag/AgCl) or cathodic reduction of the *in situ* generated *p*-tolyl disulfide (E = -1.14 V *vs* aq. Ag/AgCl) (Scheme 1b(i)).

The trifluoromethyl group possesses unique electronic and steric properties that can dramatically affect various physiochemical and biological characteristics of the parent molecule. With the aim of accessing CF_3-containg oxazolidines under mild electrochemical conditions, the group of Huang employed the Langlois reagent (sodium trifluoromethyl sulfinate)[7,8] as an attractive source of trifluoromethyl radical upon anodic oxidation (E = 1.16 V *vs* SCE in CH_3CN) and subsequent spontaneous release of sulphur dioxide. The electrolysis was conducted under galvanostatic conditions in an undivided cell equipped with a carbon graphite anode and a platinium cathode with potassium carbonate as an additional base in a CH_3CN/H_2O (9:1) solvent mixture. Using *N*-(2-arylallyl)benzamides as starting materials, this process offered a direct access to CF_3-containing diaryl oxazolidines in good yields (Scheme 1b(ii)).[9] Importantly, only styrenic alkenes were reactive, likely because they facilitated the addition of the electrophilic trifluoromethyl radical and/or the subsequent oxidation of the tertiary radical.

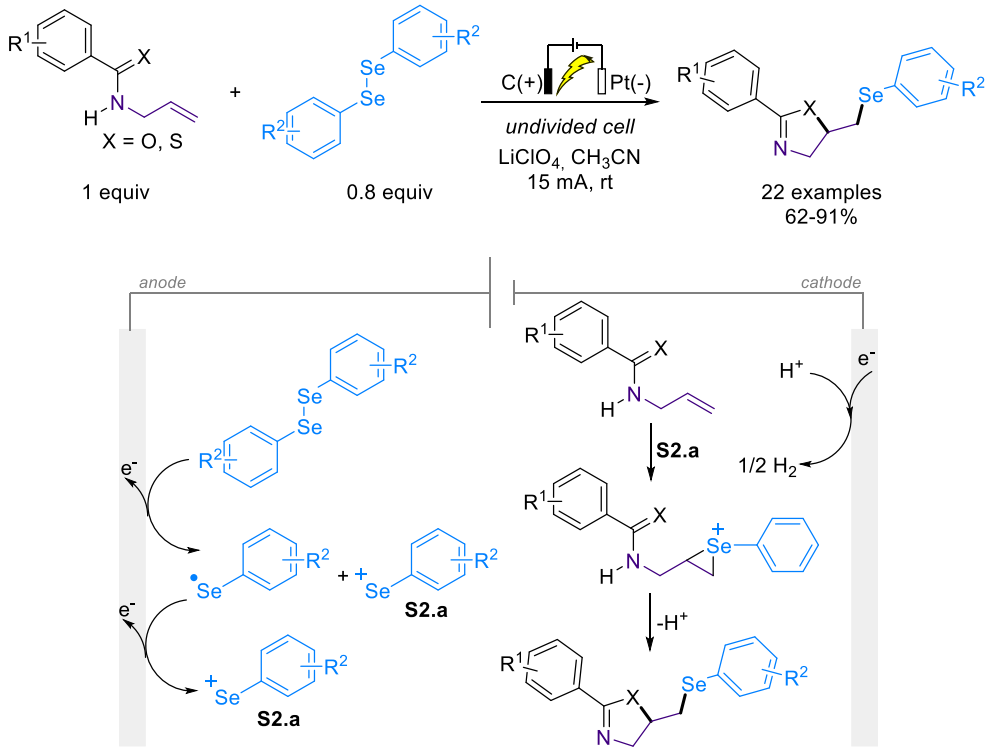
The same authors extended this procedure to a sulfonylation reaction with arylsulfonyl hydrazides[10] as source of arylsulfonyl radicals upon anodic oxidation,[11] deprotonation and extrusion of nitrogen (Scheme 1b(iii).[9]

Organophosphorus compounds have found widespread applications in pharmaceuticals, flame retardants, agrochemicals and materials chemistry. Recently, the group of Satyanarayana and Sharada have reported the synthesis of a range of phosphorylated oxazolines from *N*-(2-arylallyl)benzamides and diarylphosphine oxides. The success of this transformation relied on the use of ferrocene as an electrocatalyst. Cyclic voltammetry analyses indicated that ferrocene undergoes first anodic oxidation to ferrocenium (E = 0.07 V *vs* $Ag/AgNO_3$), which subsequently oxidizes the diarylphosphine oxide with the assistance of triethylamine to form the required P-centered radical. The reaction tolerated a broad range of substituents on the aromatic rings, affording the desired heterocycles in good yields (Scheme 1b (iv)).[12]

2.1.2 Ionic pathway. The activation of the carbon–carbon double by an electrochemically generated electrophilic reagent provides a complementary approach for introducing novel functional groups through a three-membered cyclic onium intermediate and 5-*exo*-cyclization.

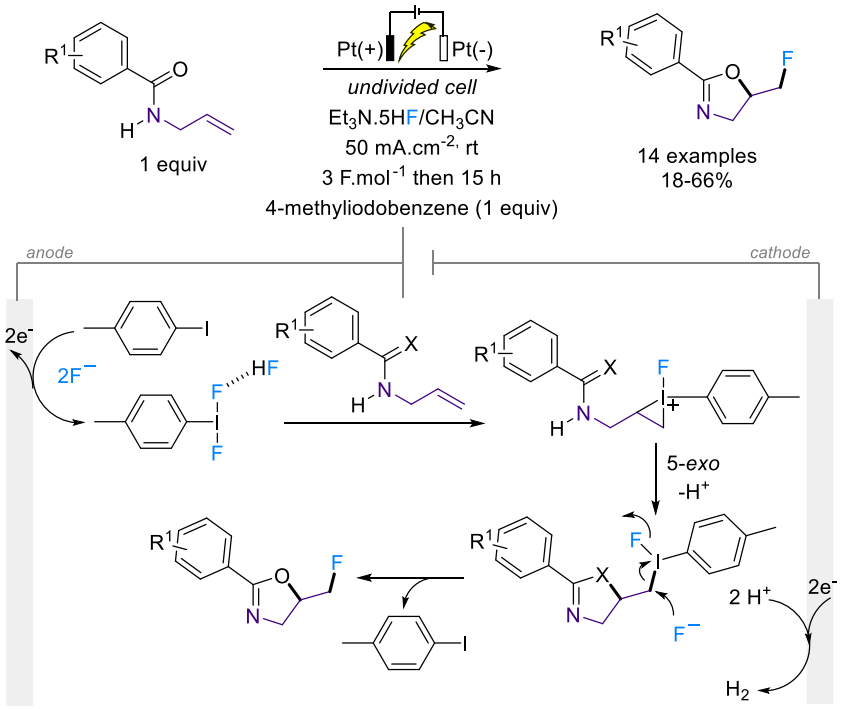
Organoselenated compounds have recently raised the interest of the synthetic community due to their wide applications. In 2020, the group of De Sarkar reported the electrosynthesis of selenofunctionalized oxazolines from *N*-allylbenzamides and diarylselenides in an undivided cell under galvanostatic conditions. Only a sub-stoichiometric amount of chalcogen source was employed under mild conditions enabling the compatibility with a wide range of functional groups (Scheme 2).[13] Interestingly, the standard procedure could be applied to *N*-allyl thiobenzamide furnishing the desired selenated thiazoline in good yield.[13,14] Additionally, the authors employed diaryl disulfides as source of thiyl radicals to form the corresponding sulfurated oxazolines providing an alternative method to the use of thiophenols, as proposed by Lei *et al.* (section 2.1.1).[6] Worthy of note, the group of Wirth developed a continuous flow electrochemical approach that could be easily scaled up and proceeded at a very low concentration of electrolyte.[15] From a mechanistic point of view, anodic oxidation of the diarylselenide (E = 1.66 V *vs* aq. Ag/AgCl in CH_3CN) furnished arylselenide cation and aryl selenide radical. The latter underwent further anodic oxidation to form another arylselenide cationic species. Subsequent activation of the double bond via the three-membered cyclic phenylselenonium ion triggered nucleophilic cyclization by the amide oxygen (Scheme 2).[13,15] Alternatively, a second mechanism involving cathodic reduction of the diphenyl selenide (E = -1.44 V *vs* aq. Ag/AgCl in CH_3CN)[13,15,16] to the

corresponding phenylselenide radical with concomitant anodic oxidation/deprotonation of the *N*-allylbenzamide (E = 1.32 V *vs* aq. Ag/AgCl in CH_3CN) and further cyclizative radical-radical cross-coupling was not ruled out (not shown).[13]



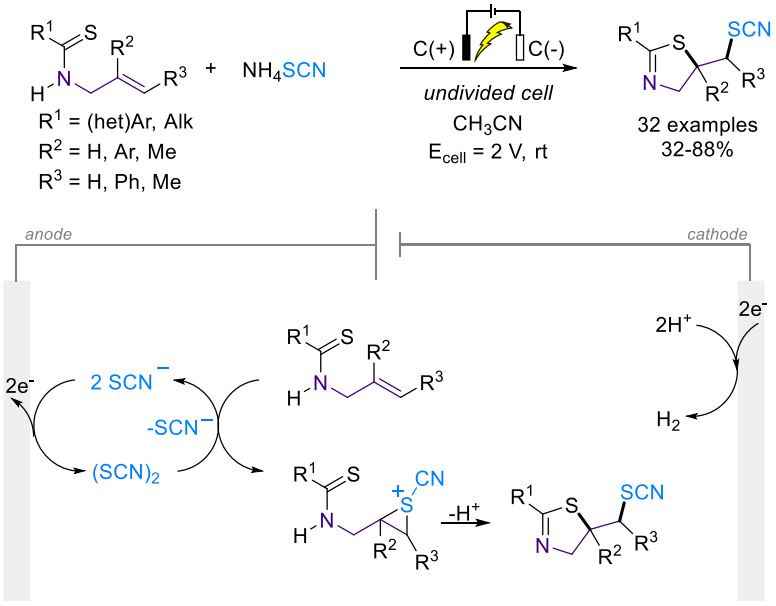
Scheme 2. Synthesis of selenofunctionalized oxazolines and thiazolines.

Fluorination reaction is a popular transformation in medicinal chemistry because the incorporation of fluorine in pharmaceutical can improve lipophilicity, metabolic stability, and overall biological activity. In 2019, the group of Waldvogel reported a concise route to 5-fluoromethyl-2-oxazolines by electrochemical fluorocyclization of *N*-allylcarboxamides using 4-methyliodobenzene as a mediator and triethylamine pentahydrofluoride as a fluoride source. The electrolysis was conducted in an undivided cell arranged with two platinium electrodes under constant current. Worthy of note, no additional electrolyte was required. After 3 $F.mol^{-1}$ of charge, the reaction was further stirred overnight. Mechanistically, a two electron anodic oxidation of the iodoarene in the presence of fluoride anion allowed the *in situ* generation of hypervalent (difluoro)iodoarene, which activated the carbon−carbon double bond through a three-membered cyclic iodonium salt. Intramolecular ring opening by the carbonyl group and nucleophilic substitution of the resulting 5-(λ3-iodanyl)methyl oxazoline by fluoride anion delivered the fluorinated oxazoline.[17] This electrochemical approach constitutes an alternative to the previous catalytic procedure employing Selectfluor® as a terminal oxidant.[18]



Scheme 3. Synthesis of fluorinated oxazolines and thiazolines.

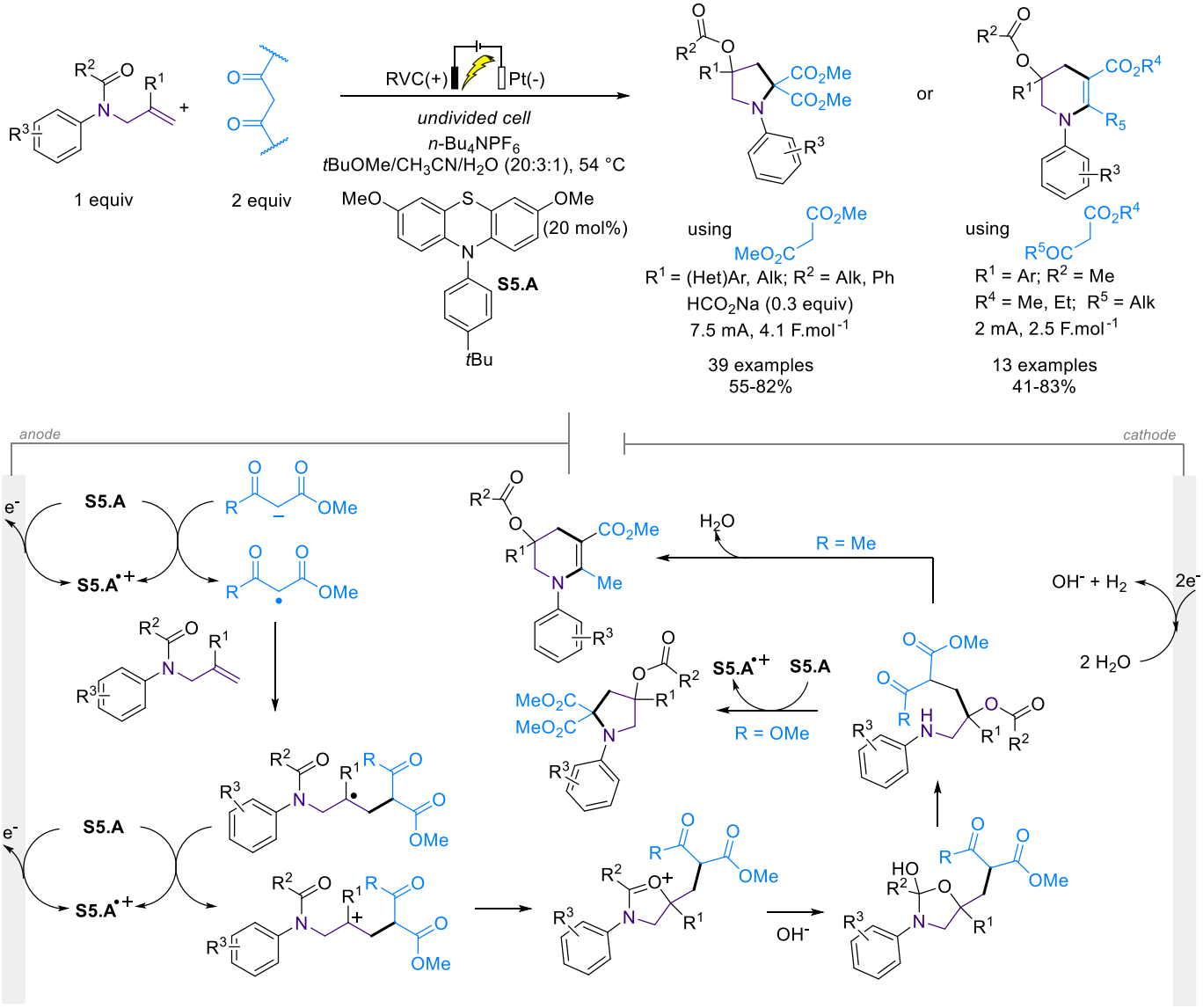
In 2020, Guo *et al.* disclosed the electrochemical access to SCN-containing via thiocyanothiocyclization of *N*-allylthioamides under constant potential. Key features of this procedure include the use of inexpensive carbon graphite electrodes and ammonium thiocyanate as a readily available thiocyanating reagent. Control experiments in the presence of radical scavenger ruled out a radical mechanism. As such, the authors proposed initial anodic oxidation of the thiocyanate salt to *in situ* generate thiocyanogen. Subsequent activation of the N-allylthioamide through a three-membered cyclic sulfonium salt and 5-*exo*-cyclization furnished the desired thiazoline (Scheme 4).[19]



Scheme 4. Synthesis of thiocyanato-substituted thiazolines.

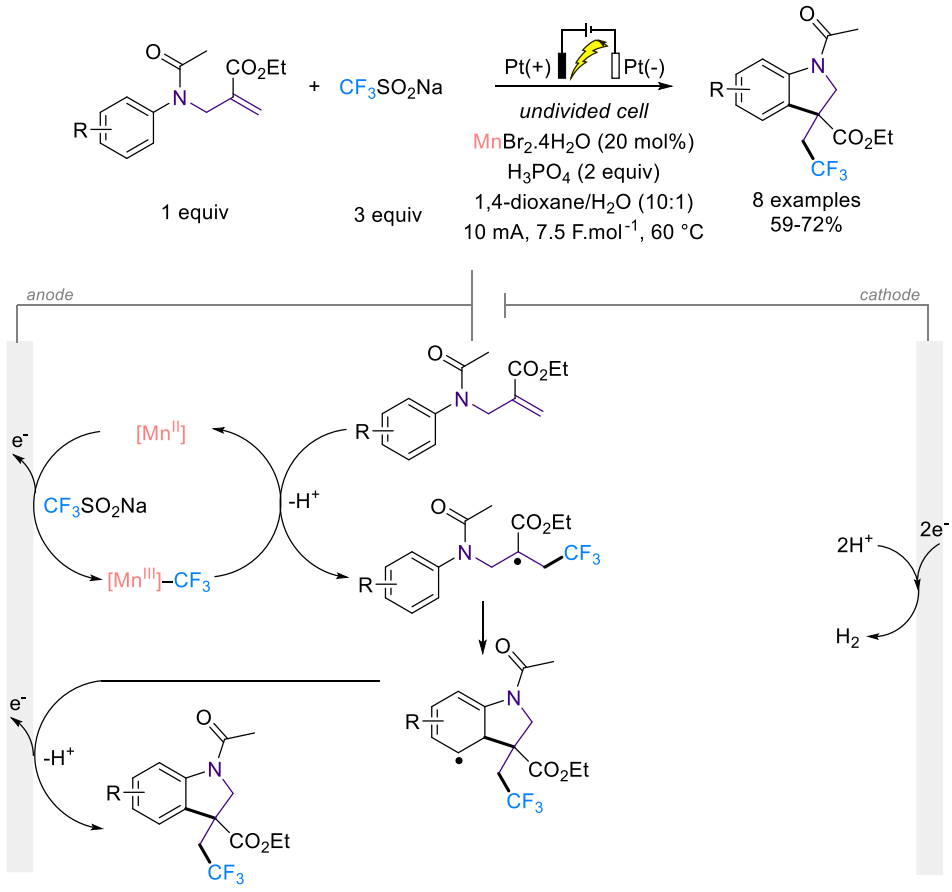
2.2 Cyclization of *N*-aryl-*N*-allyl amides

In 2018, the group of Xu developed an electrocatalytic dehydrogenative annulation of *N*-allyl amides with 1,3-dicarbonyl compounds. The electrolysis was carried out under constant current in an undivided cell using a reticulated vitreous carbon (RVC) anode and a platinum cathode. Using a well-designed phenothiazine-based organic electrocatalyst, this transformation enabled the construction of pyrrolidines and tetrahydropyridines from dimethyl malonate and β-ketoesters, respectively. Based on cyclic voltammetry studies and control experiments, the authors proposed a mechanism involving the initial anodic oxidation of the electrocatalyst ($E_{p/2}$ = 0.52 V *vs* SCE) to the corresponding radical cation. The latter subsequently oxidized *in situ* deprotonated 1,3-dicarbonyl compound to generate the corresponding electrophilic secondary alkyl radical, which then added to the olefin. Further oxidation of the resulting tertiary benzylic radical triggered oxyclization from the amide carbonyl group. Addition of hydroxide anion induced ring opening of the 5-membered ring via an unusual C–N bond cleavage. The resulting secondary amine underwent intramolecular dehydrogenative C(sp^3)–H/N–H coupling with the malonyl group (R = OMe) or intramolecular dehydration (R = Me), ultimately providing the desired functionalized pyrrolidines or tetrahydropyridine, respectively (Scheme 5).[20]



Scheme 5. Synthesis of pyrrolidines and tetrahydropyridines via electrocatalytic dehydrogenative annulation of *N*-aryl-*N*-allyl amides.

In 2019, the group of Mo described an electrocatalytic radical trifluoromethylation of *N*-aryl-*N*-allyl acetamides for the construction of CF_3-containing indolines using the Langlois reagent as the trifluoromethyl radical source. The transformation was carried out in an undivided cell employing 2 platinium electrodes and manganese dibromide as the electrocatalyst under constant current conditions. Interestingly, no additional electrolyte was required. In sharp contrast to Huang's (Scheme 1)[9] and Xu's (Scheme 5)[20] above-mentioned works, the amide moiety does not participate in the cascade process; instead, the aromatic ring is involved. Indeed, the transformation entailed the regioselective radical trifluoromethylation of the alkene, followed by C(sp^2–H) aromatic functionalization via a 5-*exo*-trig cyclization and anodic oxidation/deprotonation to yield the desired trifluoromethylated indolines. Cathodic reduction of the phosphoric acid counterbalanced the overall process. Only acrylate derivatives were exemplified, probably to prevent oxidation of the intermediate tertiary alkyl radical (*vide supra*). Control experiments unveiled the critical role of the electrocatalyst, which would enable the anodic oxidation generation of persistent [Mn^{III}]–CF_3, thereby facilitating the reaction with the electron poor alkene and overcoming any side reaction[21,22] such as the generation of trifluoromethane through C–H abstraction (Scheme 6).[23]

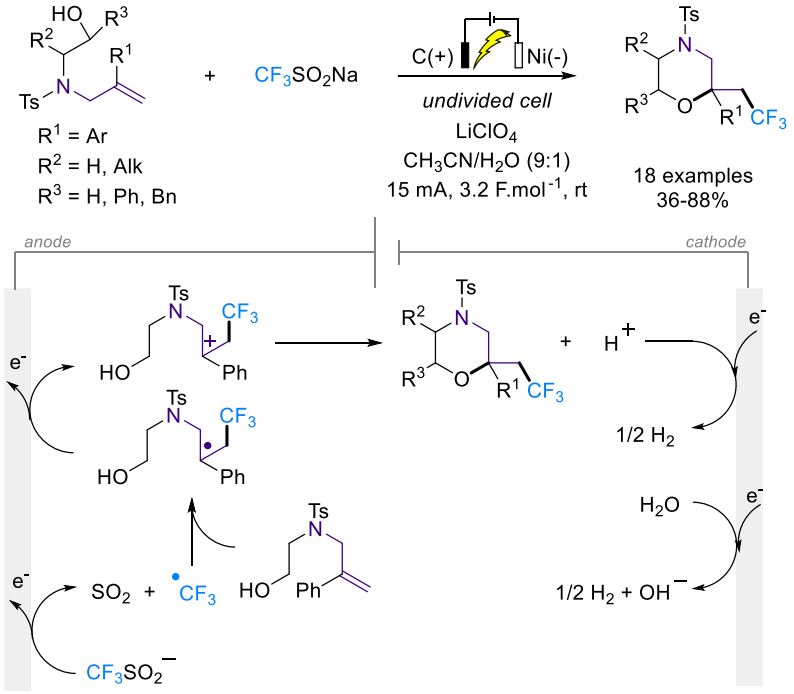


Scheme 6. Synthesis of CF_3-containing indolines via electrocatalytic trifluoromethylation/C (sp^2–H) functionalization of *N*-aryl-*N*-allyl amides.

2.3 Cyclization of *N*-alkyl-*N*-allyl sulfonamides

Morpholine derivatives rank among the 25 most frequently occurring *N*-heterocycles in US FDA-approved drugs, underscoring the persistent need for efficient and versatile synthetic methods to access this heterocycle with diverse substitution patterns. In 2018, we established an electrochemical intramolecular

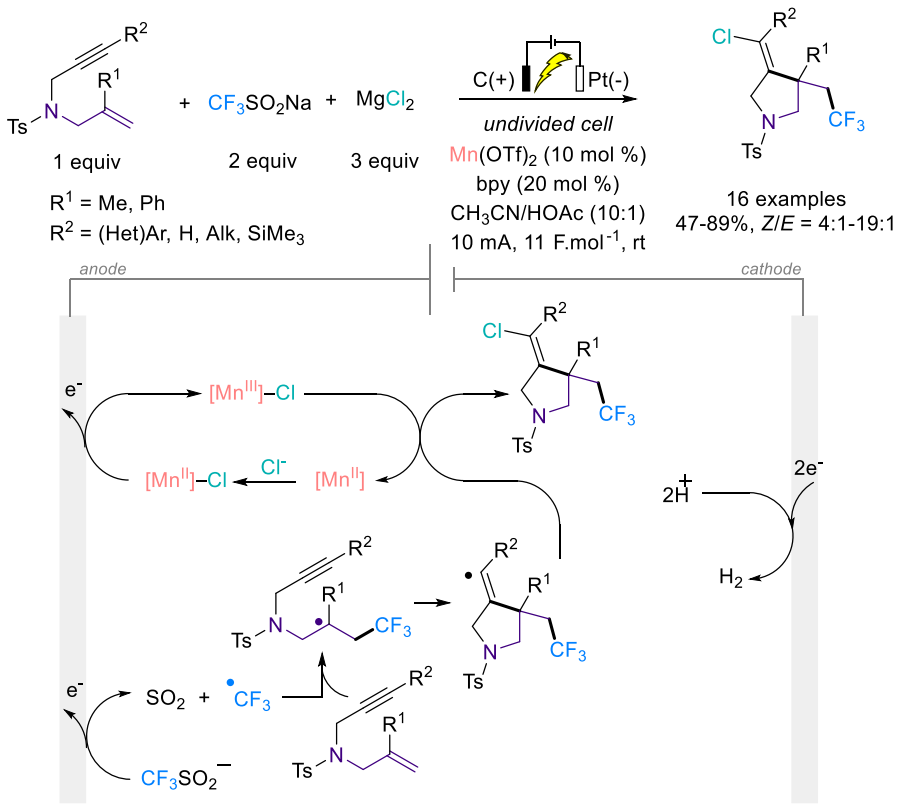
oxytrifluoromethylation of *N*-tethered alkenols, furnishing a novel family of CF_3-containing morpholines using the Langlois reagent as a trifluoromethyl radical source. Electrolysis was conducted under constant current in an undivided cell equipped with an inexpensive graphite carbon anode and a nickel cathode. The transformation tolerated a wide range of substituents on the aromatic ring. Additionally, 2,5- and 2,6-disubstituted morpholines were readily obtained, albeit with moderate diastereoselectivities. Interestingly, the use of sodium difluoromethylsulfinate in place of the Langlois reagent was also feasible, affording the corresponding CF_2-containing morpholines. From a mechanistic standpoint, initial anodic oxidation of the Langlois reagent (1.48 V *vs* Ag/AgCl in CH_3CN/H_2O 9:1) followed by spontaneous extrusion of sulfur dioxide generated the key trifluoromethyl radical, which subsequently underwent regioselective addition to the alkene. Subsequent anodic oxidation of the resulting tertiary radical triggered oxycyclization to form the desired morpholine ring with concomitant proton loss (Scheme 7).[24]



Scheme 7. Synthesis of CF_3-containing morpholines via oxytrifluromethylation of *N*-tethered alkenols.

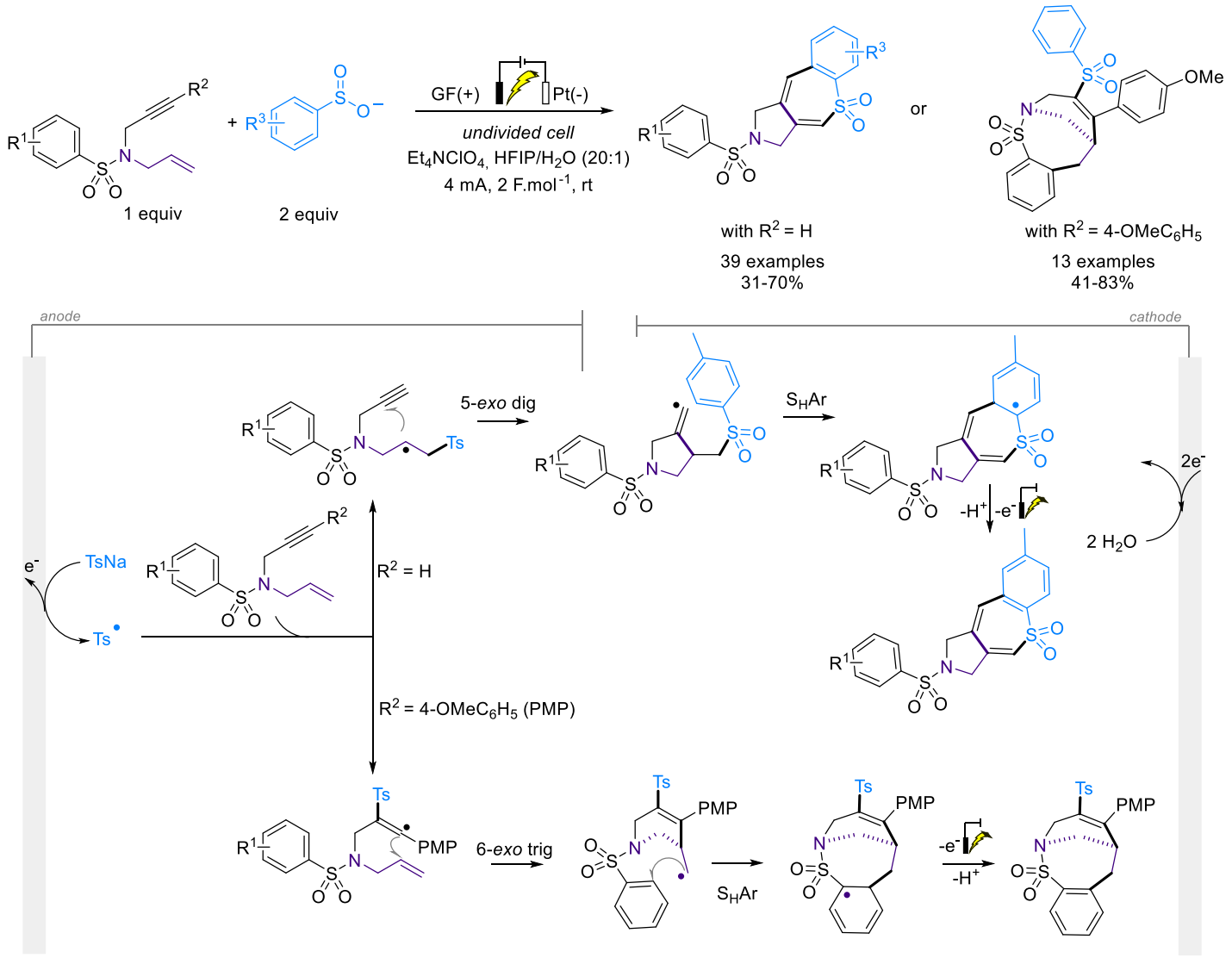
In 2018, the group of Song Lin achieved an electrocatalytic stereoselective chlorotrifluoromethylated pyrrolidines by radical cyclization of *N*-tethered 1,6-enynes giving rise to highly functionalized pyrrolidines. Readily available Langlois reagent and magnesium chloride were utilized as source of trifluoromethyl and chlorine radicals, respectively. A manganese salt was employed as electrocatalyst to control this anodically coupled electrolysis, while the introduction of a 2,2'-bipyridine (bpy) as chelating ligand allowed high stereoselectivity of the *exo* double bond in the obtained pyrrolidine products. The transformation was mostly extended with aromatic alkynes. Nevertheless, alkyl- and silyl-substituted or terminal alkynes were also compatible delivering the corresponding pyrroline in good yield, albeit with lower diastereoselectivities. Noteworthy, N-Boc tethered alkenols were suitable offering the corresponding N-Boc pyrrolidines that could be easily deprotected. From cyclic voltammetry studies, the simultaneous anodic oxidation of the Langlois reagent and the *in situ* generated [Mn^{II}]–Cl species was inferred. Subsequent addition of the transient CF_3 radical to the alkene, followed by 5-*exo*-dig cyclization, led to an alkenyl radical, which then underwent radical

coupling with the persistent chelated [Mn^{III}]–Cl to afford the chlorotrifluoromethylated heterocycle in good yield, albeit with low Faradic efficiency (Scheme 8).[25]



Scheme 8. Stereoselective synthesis of alkenyl pyrrolidines via anodically coupled electrolysis.

In 2023, the group of Ackermann presented an elegant electrooxidative, radical sulfonylation-induced cascade cyclization of *N*-tethered 1,6-enynes, leading to seven- and nine-membered sulfonamide-containing rings depending on the alkyne substitution pattern. The electrolysis was carried out in a mixed solvent system of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/H_2O (20:1), using a graphite felt anode and a platinum cathode under constant-current conditions. Control experiments confirmed the involvement of a sulfonyl radical. Accordingly, it was proposed that the cascade reaction was initiated by anodic oxidation of the sodium arylsulfinate. With an unsubstituted alkyne, the resulting electrophilic sulfonyl radical chemoselectively and regioselectively reacted with the more electron-rich C–C double bond. Subsequent 5-*exo*-dig cyclization, followed by homolytic aromatic substitution on the aryl ring of the sulfone, a second anodic oxidation, and deprotonation delivered a tricyclic compound containing a seven-membered ring. In contrast, when aromatic alkynes, particularly a *para*-methoxyphenyl-substituted alkyne, were employed, the electrophilic sulfonyl radical chemoselectively and regioselectively added to the C–C triple bond. The resulting stabilized vinyl radical underwent 6-*exo*-trig cyclization, followed by homolytic aromatic substitution on the aromatic ring of the sulfonamide, a second anodic oxidation, and deprotonation to afford a bridged-ring product containing a nine-membered ring (Scheme 9).[26]

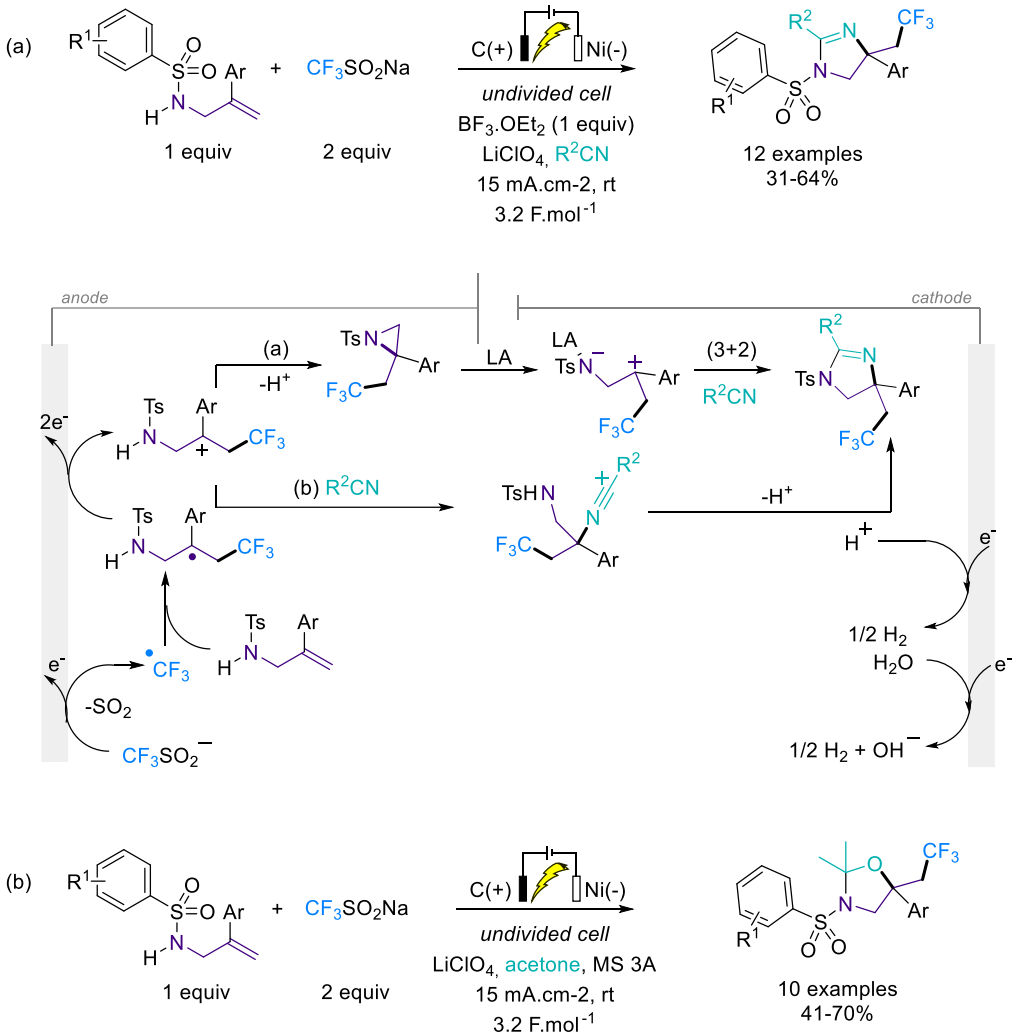


Scheme 9. Radical sulfonylation of *N*-tehered 1,6-enynes induced-divergent cascade cyclization.

2.4 Cyclization of secondary-*N*-allyl sulfonamides

In 2020, our group disclosed an electricity-driven three-component reaction involving secondary *N*-allyl sulfonamides, the Langlois reagent, and a nitrile solvent, leading to CF_3-containing imidazolines. The electrolysis was performed in an undivided cell equipped with a graphite carbon anode and a nickel cathode. A crucial factor for the success of this transformation was the addition of boron trifluoride etherate as a Lewis acid. On the basis of cyclic voltammetry studies and control experiments, a plausible mechanism was proposed. Anodic oxidation of the Langlois reagent generated a trifluoromethyl radical, which underwent regioselective addition to the C–C double bond. The resulting benzylic radical was further oxidized to a carbocation, which undergoes azacyclization from the sulfonamide nitrogen and deprotonation to afford a CF_3-substituted aziridine intermediate. Lewis acid–promoted ring opening then gave a 1,3-dipolar species that engaged in a (3+2) cycloaddition with the nitrile solvent, ultimately delivering the desired imidazoline. Alternatively, a second minor pathway could involve direct addition of the solvent to the benzylic carbocation, followed by azacyclization from the sulfonamide (Scheme 10a). This transformation was further extended to the construction of CF_3-containing oxazolidines using acetone as the solvent. In this case, the addition of boron

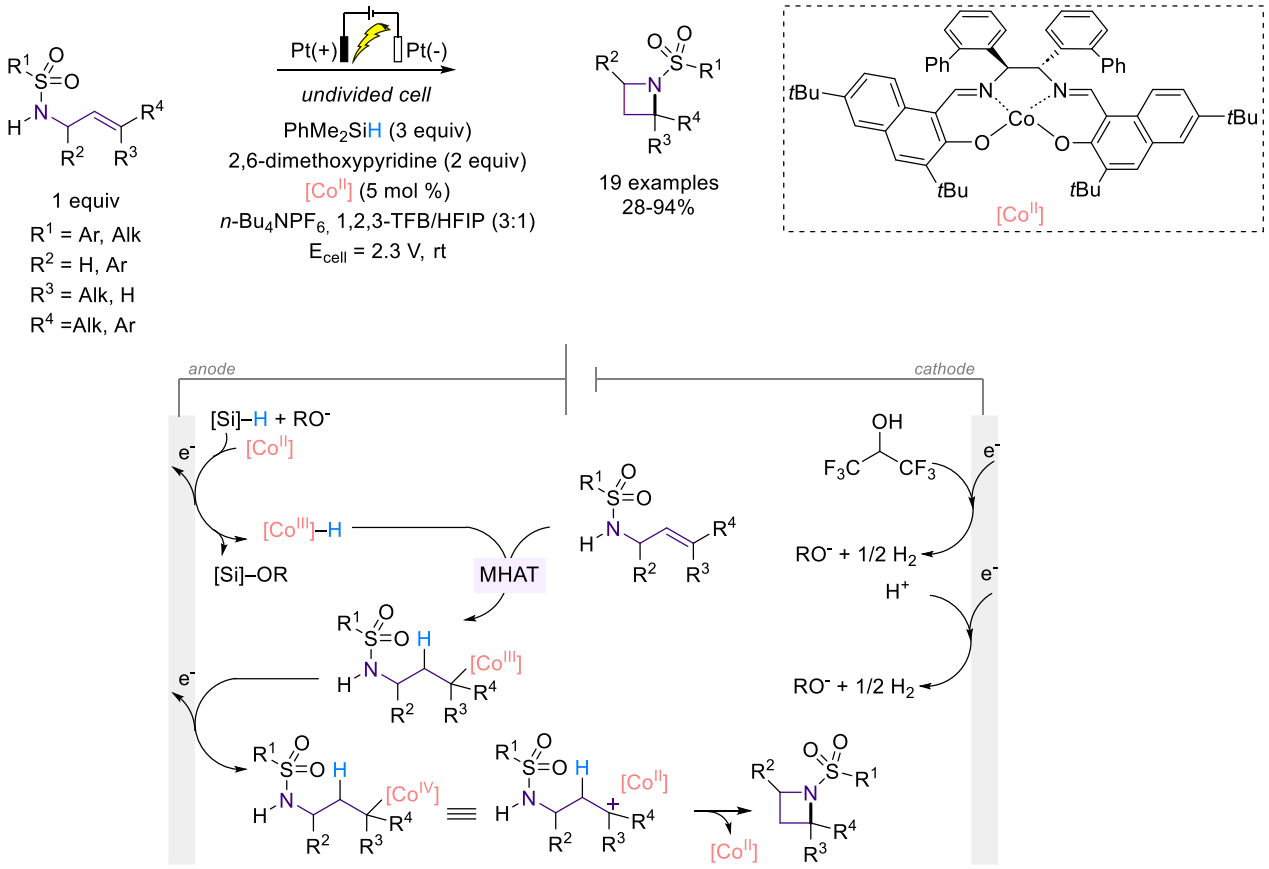
trifluoride etherate was not required, as the lithium salt electrolyte probably played the role of a Lewis acid in promoting ring opening of the aziridine intermediate (Scheme 10b).[27]



Scheme 10. Synthesis of CF_3-containing imiazolines and oxazolidines via a 3-component reaction.

Azetidines have recently gained interest among medicinal chemists for drug discovery due to their unique physicochemical and pharmacokinetic profiles.[28] However, their inherent ring strain energy (RSE) imposes unfavorable conformational requirements for their formation, rendering the synthesis of this heterocycle highly challenging. In 2023, Kim, Choi, and Sin *et al.* reported the first intramolecular hydroamination of allylic amine derivatives via the electrochemical generation of carbocation equivalents, furnishing a broad array of azetidines bearing diverse functional groups in high yields and with high Faradaic efficiency. Key to the success of this transformation was the merger of cobalt catalysis and electricity. Methylphenylsilane and 2,6-dimethoxypyridine were employed as the hydride donor and base, respectively, in an undivided cell equipped with two electrodes under constant potential in 1,2,3-trifluorobenzene (TFB)/HFIP (3:1) solvent mixture. Cyclic voltammetry studies confirmed that the reaction was initiated by anodic formation of a cobalt hydride intermediate ([Co^{III}–H]) from [Co^{II}] ($E_{Co(II)/Co(III)}$ = 0.31 V *vs* Fc+/Fc) and phenylsilane. Subsequent metal–hydride hydrogen atom transfer (MHAT) to the alkene, followed by a second anodic oxidation of the resulting [Co^{III}–alkyl] intermediate, generated the key carbocationic species. This intermediate underwent azacyclization of

the sulfonamide to form the C–N bond upon proton loss, ultimately delivering the four-membered azacycle and regenerating the cobalt electrocatalyst. Electrochemical kinetic analysis suggested that either the second anodic oxidation event or the catalyst regeneration step by nucleophilic cyclization is the rate determining step (RDS) (Scheme 11).[29]

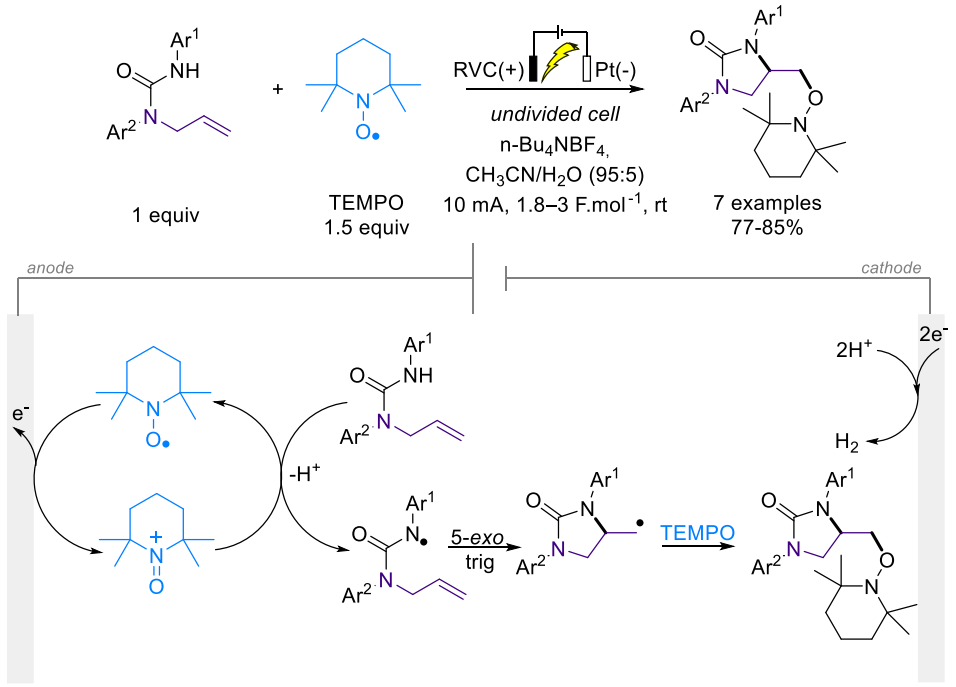


Scheme 11. Synthesis of azetines via intramolecular electrocatalytic allylic hydroamination.

2.5 Cyclization of *N*-allyl ureas

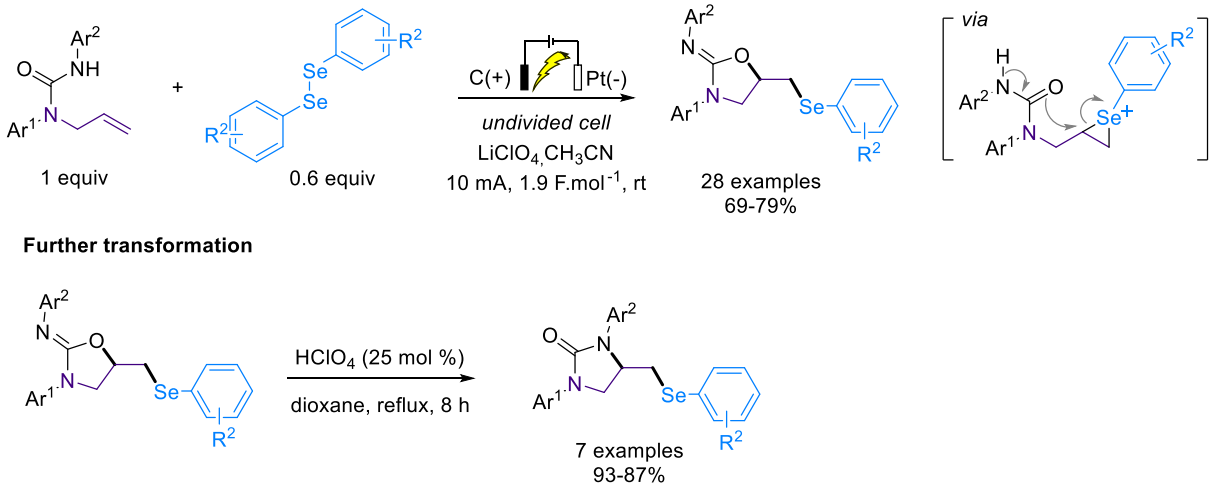
N-allyl ureas are readily prepared from the corresponding allylamines making them valuable precursors for the construction of functionalized cyclic (iso)ureas. Radical and ionic paths have been developed.

In 2018, Ahmed *et al.* achieved the electrochemical coupling between *N*-aryl-*N*-allyl ureas and 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO) to build functionalized imidazolidin-2-ones. The electrolysis was performed under constant current with RVC anode and platinum cathode. Mechanistically, TEMPO was proposed to play a dual role. First, it would act as a redox mediator, enabling the anodic generation of an N-centered radical. Then, following a 5-*exo*-trig cyclization, it trapped the resulting primary carbon-centered radical to form a C–O bond, in accordance with the persistent radical effect[30] (Scheme 12).[31] One year later, the authors adapted this oxyamination to a flow reactor, employing an inexpensive graphite anode instead of RVC and using Trion B as both the electrolyte and the base.[32]



Scheme 12. Synthesis of functionalized imidazolidinones via intramolecular radical amination of *N*-allyl ureas.

In 2024, De Sarkar *et al.* reported a procedure to access selenylated cyclic isoureas using electrochemical activation of diphenylselenide. The transformation exhibited good functional group tolerance under easy to implement constant current electrolysis. In accordance with their previous work,[13] it would involve activation of the double bond via a three-membered cyclic phenylselenonium ion, which triggered nucleophilic cyclization by the urea oxygen. Interestingly, the authors implemented an acid-catalyzed isomerization of the cyclic isoureas to form the corresponding selenated cyclic ureas (Scheme 13).[33]

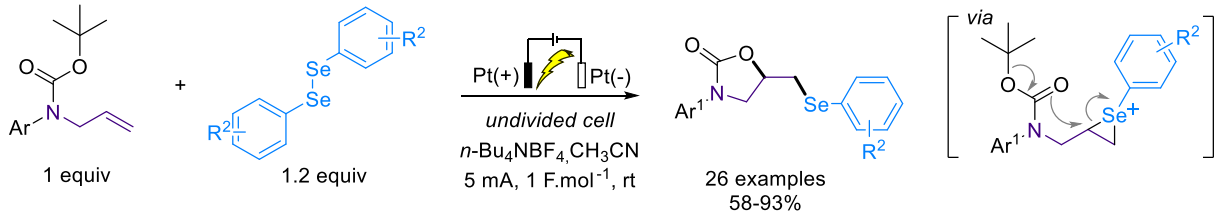


Scheme 13. Synthesis of selenated isoureas via electrophilic selenation.

2.6 Cyclization of *N*-aryl allyl carbamates

A similar electricity-enabled selenofunctionalization of C−C bond-triggered cyclization has been applied to *tert*-butyl *N*-aryl-*N*-allyl carbamates furnishing selenated oxazolidinones in good yields. The optimal reaction

conditions consist of a constant current of 5 mA with 2 platinum electrodes in acetonitrile. The proposed mechanism involves the *in situ* generation of a three-membered cyclic phenylselenonium ion. Ring opening by the carbamate carbonyl group leads to formation of the desired oxazolidinone, accompanied by loss of a *tert*-butyl cation that subsequently decomposes into isobutene upon deprotonation (Scheme 14).[34]



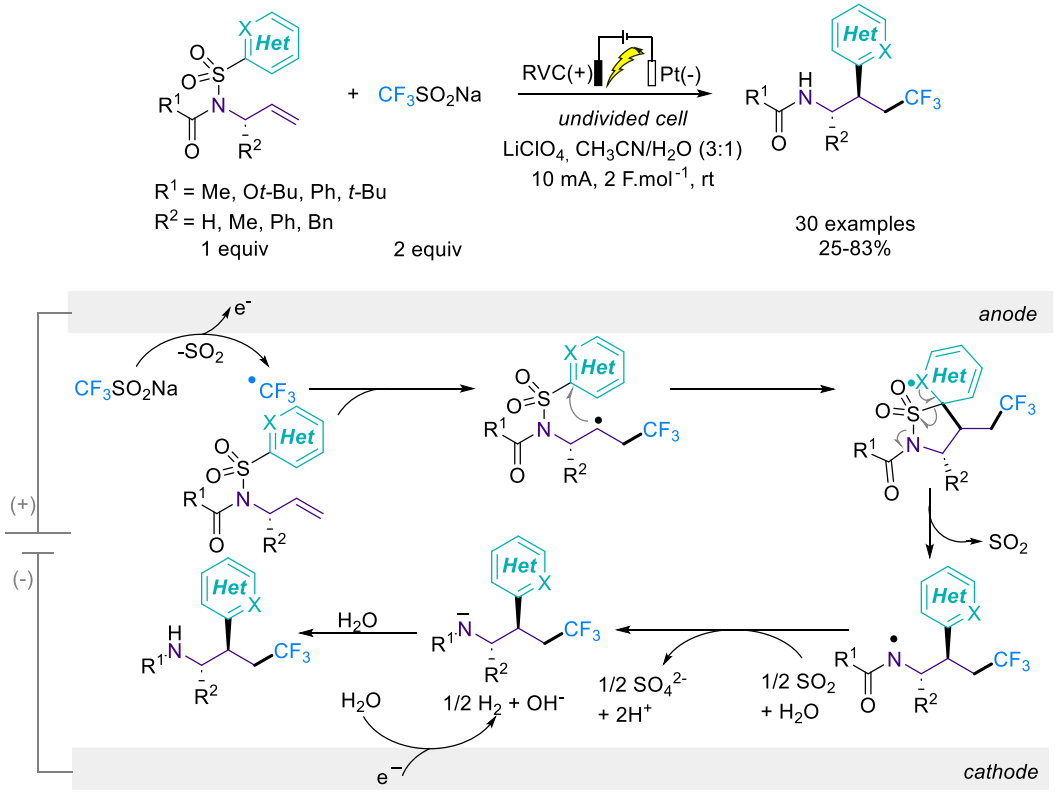
Scheme 14. Synthesis of selenated oxazolidinones via electrophilic selenation.

3. Synthesis of β-(Hetero)aryl Amines via a Truce-Smiles Rearrangement

Owing to the prevalence of the β-(hetero)arylamine motif in pharmaceutical drugs, particularly those used to treat central nervous system disorders, the development of efficient and sustainable methods to access this scaffold has attracted considerable attention. Among the various approaches, the radical Truce-Smiles rearrangement, which involves the migration of an (hetero)aromatic ring to a carbon-centered radical through a spirocyclic intermediate, is of particular interest. However, despite the power of this transformation, electrosynthetic variants have only recently been achieved.

3.1. Rearrangement of *N*-allyl arylsulfonamides

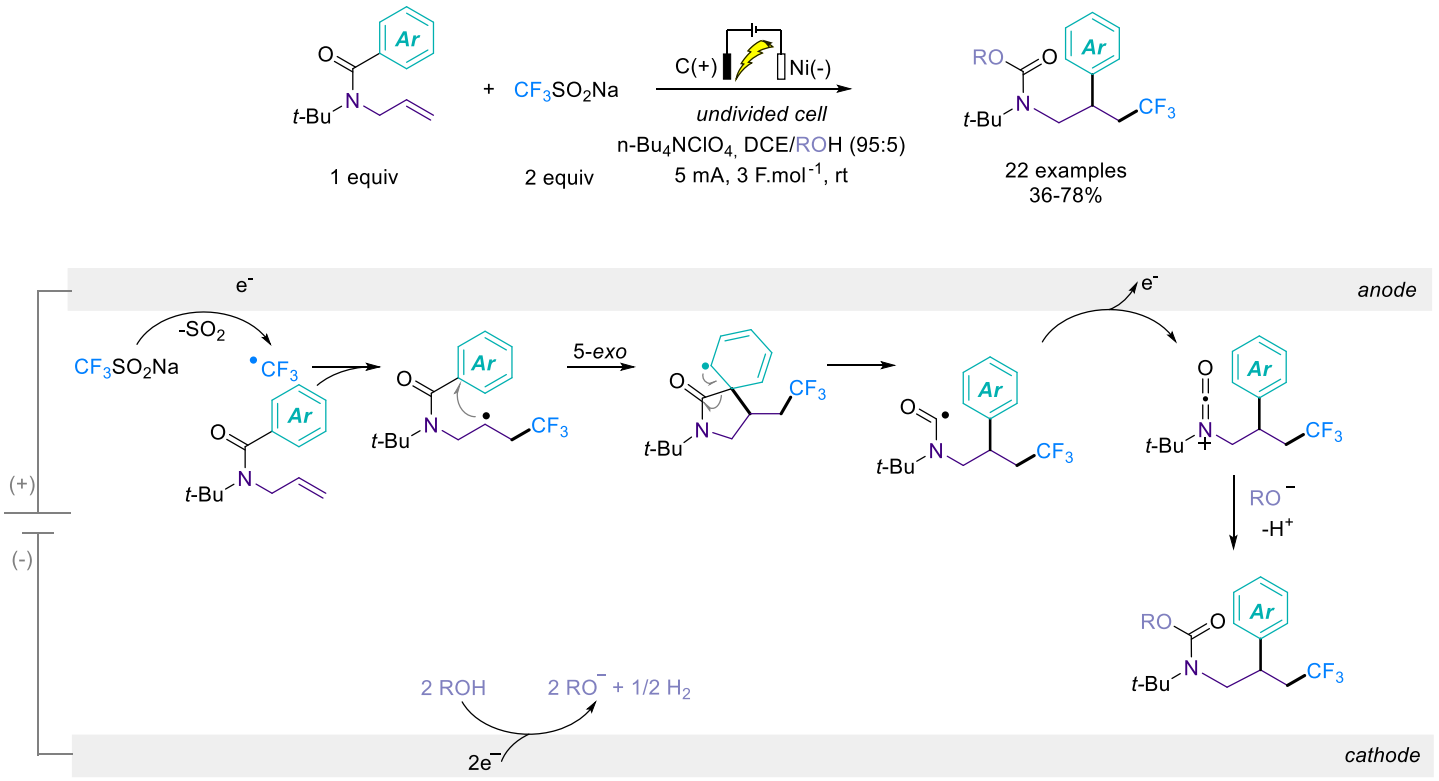
In 2022, the group of Zhu reported the electrochemical trifluoromethylation of *N*-allyl heteroarylsulfonamides leading to original CF_3-containing β-heteroaryl amines. The reaction was carried out in an undivided cell equipped with an RVC anode and a platinum cathode. Under a constant current, the electrolysis was initiated by the anodic oxidation of the Langlois reagent to generate the trifluoromethyl radical, which regioselectively add to the C–C bond to produce a β-amino alkyl radical. The latter triggered the radical Truce-Smiles rearrangement upon *ipso* addition/C–S bond breaking and SO_2 extrusion, ultimately leading to the migration of the heteroaromatic ring. The resulting amidyl radical was likely reduced by the dissolved SO_2 in the aqueous phase to deliver the desired trifluoromethylated β-heteroaryl amines. A variety of heteroaryl groups could efficiently migrate including (benzo)thiazoles, thiophenes, 1,3,4-thiadiazole, pyrimidine, pyridine, and quinoline. Noteworthy, starting from enantioenriched allylic amines, different optically active β-heteroaryl-γ-trifluoromethyl amines were obtained with good to excellent diastereoselectivities (Scheme 15).[35]



Scheme 15. Radical trifluoromethylation-triggered Truce-Smiles rearrangement of *N*-allyl arylsulfonamides.

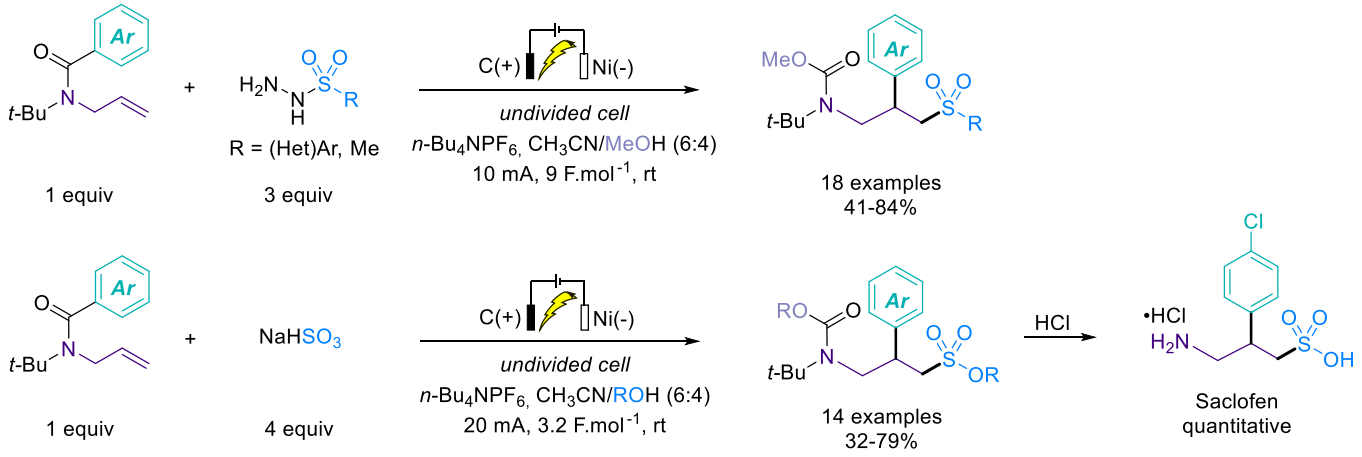
3.2. Rearrangement of *N*-allyl benzamides

Arylsulfonamides are the most commonly used substrates in radical Truce-Smiles rearrangements because extrusion of SO_2 renders irreversible the fragmentation of the spirocyclic intermediate. In 2024, we reported an original electrochemical radical trifluoromethylation-enabled Truce-Smiles rearrangement of *N*-allylbenzamides, which offer the advantage of being readily prepared from ubiquitous benzoic acids. Inexpensive graphite anode and nickel cathode were employed under constant-current electrolysis in an undivided cell in dichloroethane (DCE)/methanol solvent mixture. A wide range of aromatic rings were compatible as migratory groups, regardless of their electronic properties, enabling the synthesis of diverse trifluoromethylated β-arylethylamines. Notably, chlorodifluoromethylsulfinate salt could replace the Langlois reagent to smoothly afford the corresponding CF_2Cl-containing β-arylethylamines. The aryl migration was triggered by electrochemical trifluoromethylation of the olefin following anodic oxidation of the Langlois reagent. Subsequent 5-*exo* cyclization and C–C bond cleavage of the resulting spirocyclic intermediate generated a carbamoyl radical, which underwent further anodic oxidation. The carbamoyl cation thus formed was trapped by the alcoholic co-solvent to deliver functionalized, protected β-arylethylamines. Notably, selection of a *tert*-butyl group as the nitrogen protecting group was critical to achieving high selectivity for the 1,4-aryl migration, thereby suppressing the undesired 6-*endo* cyclization pathway. DFT calculations indicated that this sterically hindered group favours the *s-cis* conformation of the amide, which is more prone to spirocyclization than the *s-trans* conformer. Interestingly, the protecting group could be readily removed by acidic hydrolysis to afford the corresponding functionalized ammonium chloride salt (Scheme 16).[36]



Scheme 16. Radical trifluoromethylation-triggered Truce-Smiles rearrangement of *N*-allylbenzamides.

We subsequently extended this procedure to the preparation of sulfone- and sulfonate ester–containing β-arylethylamines. Arylsulfonyl hydrazines and sodium metabisulfite in methanol acted as precursors of sulfonyl radicals and methyl sulfonate ester radicals, respectively. The utility of this transformation was demonstrated through its application to the straightforward synthesis of Saclofen, a well-known $GABA_B$ receptor antagonist (Scheme 17).[37]



Scheme 17. Radical sulfonylation-triggered Truce-Smiles rearrangement of *N*-allylbenzamides.

Conclusions

With the resurgence of interest in organic electrosynthesis within the synthetic community, this approach has emerged as a powerful tool for the functionalization of various allylic amines. Depending on the reaction conditions and the nature of the nitrogen substitution, a range of valuable functionalized azacycles, including oxazolines, morpholines, pyrrolidines, pyrazolines, oxazolines, and β-aryl ethylamines are efficiently produced. These electrochemical strategies typically operate under mild, practical, and sustainable conditions, highlighting their potential as attractive alternatives to conventional redox methods. Despite significant progress, important challenges remain, and continued efforts are required to further advance the electrochemical functionalization of allylic amines. First, the use of flow electrochemistry has only been sporadically demonstrated, although it could enable a reduction in the amount of supporting electrolyte required and facilitate scalability, both key parameters for potential industrial applications.[38] Secondly, functionalization of the C–C bond in allylic amines remains restricted to a narrow range of groups, including fluoromethyl, phosphates, sulfinates, selenides, sulfides, and fluorine. Expanding the range of feasible functional groups would significantly broaden the diversity of accessible products. This could be achieved by developing indirect electrolysis with transition metal catalysts[39] or by combining electrochemistry with photocatalysis.[40] Furthermore, the development of electrochemical cascade processes and multicomponent reactions would enable the rapid construction of more complex molecular architectures.[41] Finally, controlling stereochemistry[42-44] would represent a major leap forward for the field, allowing electrochemical access to enantioenriched azacycles, β-aryl ethylamines, and maybe other valuable compounds.

References

1. Yan, M.; Kawamata, Y.; Baran, P. S. *Chem. Rev.* **2017**, *117*, 13230–13319. https://doi.org/10.1021/acs.chemrev.7b00397.
2. Schotten, C.; Nicholls, T. P.; Bourne, R. A.; Kapur, N.; Nguyen, B. N.; Willans, C. E. *Green Chem.* **2020**, *22*, 3358–3375. https://doi.org/10.1039/D0GC01247E.
3. Zhang, H.-Z.; Zhao, Z.-L.; Zhou, C.-H. *Eur. J. Med. Chem.* **2018**, *144*, 444–492. https://doi.org/10.1016/j.ejmech.2017.12.044
4. Connon, R.; Roche, B.; Rokade, B. V.; Guiry, P. J. *Chem. Rev.* **2021**, *121*, 6373–6521. https://doi.org/10.1021/acs.chemrev.0c00844
5. Liang, Z.-Y.; Jiang, M.-X.; Chen, W.; Zhao, L.-H.; Xiong, S.-Y.; Yang, W.-D.; Chen, M.-H.; Xiao, X. *ChemistrySelect* **2025**, *10*, e02376. https://doi.org/10.1002/slct.202502376
6. Lu, F.; Xu, J.; Li, H.; Wang, K.; Ouyang, D.; Sun, L.; Huang, M.; Jiang, J.; Hu, J.; Alhumade, H.; Lu, L.; Lei, A. *Green Chem.* **2021**, *23*, 7982–7986. https://doi.org/10.1039/D1GC02914B
7. Tommasino, J. B.; Brondex, A.; Medebielle, M.; Thomalla, M.; Langlois, B. R.; Billard, T. Synlett 2002, 1697–1699. https://doi.org/10.1055/s-2002-34210
8. Bhaskaran, R. P.; Babu, B. P. *Adv. Synth. Catal.* **2020**, *362*, 5219–5237. https://doi.org/10.1002/adsc.202000996

9. Chen, S.-J.; Zhong, W;-Q.; Huang, J. *J. Org. Chem.* **2023**, *88*, 12630–12640. https://doi.org/10.1021/acs.joc.3c01310
10. Zhao, S.; Chen, K.; Zhang, L.; Yang, W.; Huang, D. *Adv. Synth. Catal.* **2020**, *362*, 3516–3541. https://doi.org/10.1002/adsc.202000466
11. Liu, W.; Hao, L.; Zhang, J.; Zhu, T. *ChemSusChem* **2022**, *15*, e202102557. https://doi.org/10.1002/cssc.202102557
12. Thondur, J. R.; Gowda, P. S.; Sharada, D. S.; Satyanarayana, G. *Chem. Commun.* **2025**, *61*, 14717–14720. https://doi.org/10.1039/D5CC03899E
13. Mallick, S.; Baidya, M.; Mahanty, K.; Maiti, D.; De Sarkar, S. *Adv. Synth. Catal.* **2020**, *362*, 1046–1052. https://doi.org/10.1002/adsc.201901262
14. Pan, C.; Liu, P.; Wu, A.; Li, M.; Wen, L.; Guo, W. *Chin. J. Org. Chem.* **2020**, *40*, 2855–2862. https://doi.org/10.6023/cjoc202004051
15. Alzaidi, O.; Wirth, T. *ACS Org. Inorg. Au* **2024**, *4*, 350–355. https://doi.org/10.1021/acsorginorgau.4c00008
16. Guan, Z.; Wang, Y.; Wang, H.; Huang, Y.; Wang, S.; Tang, H.; Zhang, H.; Lei, A. *Green Chem.* **2019**, *21*, 4976. https://doi.org/10.1039/C9GC02665G
17. Haupt, J. D.; Berger, M.; Waldvogel, S. R. *Org. Lett*. **2019**, *21*, 242–245. https://doi.org/10.1021/acs.orglett.8b03682
18. Scheidt, F.; Thiehoff, C.; Yilmaz, G.; Meyer, S.; Daniliuc, C. G.; Kehr, G.; Gilmour, R. *Beilstein J. Org. Chem.* **2018**, *14*, 1021–1027. https://doi.org/10.3762/bjoc.14.88
19. Zhang, Y.; Ding, Z.; Liu, P.; Guo, W.; Wen, L.; Li, M. *Org. Chem. Front.* **2020**, *7*, 1321–1326. https://doi.org/10.1039/D0QO00300J
20. Wu, Z.-J.; Li, S.-R.; Xu, H.-C. *Angew. Chem., Int. Ed.* **2018**, *57*, 14070–14074. https://doi.org/10.1002/anie.201807683
21. Fu, N.; Sauer, G. S.; Saha, A.; Loo, A.; Lin, S. *Science* **2017**, *357*, 575–579. https://doi.org/10.1126/science.aan6206.
22. Fu, N.; Sauer, G. S.; Lin, S. *J. Am. Chem. Soc.* **2017**, *139*, 15548–15553. https://doi.org/10.1021/jacs.7b09388
23. Zhang, Z.; Zhang, L.; Cao, Y.; Li, F.; Bai, G.; Liu, G.; Yang, Y.; Mo, F. *Org. Lett.* **2019**, *21*, 762–766. https://doi.org/10.1021/acs.orglett.8b04010
24. Claraz, A.; Courant, T.; Masson, G. *Org. Lett.* **2020**, *22*, 1580–1584. https://doi.org/10.1021/acs.orglett.0c00176
25. Ye, K.-Y.; Song, Z.; Sauer, G. S.; Harenberg, J. H.; Fu, N.; Lin, S. *Chem. Eur. J.* **2018**, *24*, 12274–12279. https://doi.org/10.1002/chem.201802167
26. Zhang, Y.; Cai, Z.; Zhao, C.; Zheng, H.; Ackermann, L. *Chem. Sci.* **2023**, *14*, 3541–3547. https://doi.org/10.1039/d2sc07045f
27. Claraz, A.; Djian, A.; Masson, G. *Org. Chem. Front.* **2021**, *8*, 288–296. https://doi.org/10.1039/D0QO01307B
28. Cheekatla, S. *Future Med. Chem*. **2026**, doi: 10.1080/17568919.2025.2610169. https://doi.org/10.1080/17568919.2025.2610169
29. Park, S. H.; Bae, G.; Choi, A.; Shin, S.; Shin, S.; Kwangmin, S.; Choi, C.; Hyunwoo, K. *J. Am. Chem. Soc.* **2023**, *145*, 15360–15369.

https://doi.org/10.1021/jacs.3c03172
30. Leifert, D.; Studer, A. *Angew. Chem., Int. Ed.* **2020**, *59*, 74–108. https://doi.org/10.1002/anie.201903726
31. Ahmed, N.; Khatoon, S. F *ChemistryOpen* **2018**, *7*, 576–582. https://doi.org/10.1002/open.201800064
32. Ahmed, N.; Vgenopoulou, A. *SynOpen* **2019**, *3*, 46–48. https://doi.org/10.1055/s-0037-1611772
33. Laxmikanta Sing, J.; Dutta, J.; Ghosh, S.; De Sarkar, S. *J. Org. Chem.* **2024**, *89*, 11323–11333. https://doi.org/10.1021/acs.joc.4c00991
34. Chen, Y.; Xu, Y.; Ma, Z.; Wang, H.; Chen, Q.; Zhang, S.; Feng, K.; Chen, X.; Kong, X. *Org. Biomol. Chem.* **2026**, DOI: 10.1039/D5OB01968K. https://doi.org/10.1039/D5OB01968K
35. Lan, J.; Lin, K.; Zhang, X.; Zhu, T. Stereoselective Migratory *Green Chem.* **2022**, *24*, 6138–6144. https://doi.org/10.1039/D2GC00960A.
36. Derat, E.; Masson, G.; Claraz, A. *Angew. Chem., Int. Ed.* **2024**, *63*, e202406017. https://doi.org/10.1002/anie.202406017.
37. Meyer, S.; Neuhut, A.; Claraz, A. *Org. Biomol. Chem.* **2024**, *22*, 8102–8108. https://doi.org/10.1039/D4OB01327A.
38. Regnier, M.; Vega, C.; Ioannou, D. I.; Noël, T. *Chem. Soc. Rev.* **2024**, *53*, 10741–10760. https://doi.org/10.1039/D4CS00539B
39. Ma, C.; Fang, P.; Liu, Z.-R.; Xu, S.-S.; Xu, K.; Cheng, X.; Lei, A.; Xu, H.-C.; Zeng, C.; Mei, T.-S. *Science Bull.* **2021**, *66*, 2412–2429. https://doi.org/10.1016/j.scib.2021.07.011
40. Deng, Y.; Mei, H.; Han, J.; Liu, D.; Wang, H. *Chem. Rev.* **2025**, *125*, 2431–2502. https://doi.org/10.1021/acs.chemrev.4c00464.
41. Yadav, M. K.; Chowdhury, S. *Green Chem.* **2023**, *25*, 10144–10181. https://doi.org/10.1039/D3GC01760E
42. Jiang, X.; Zou, C.; Zhuang, W.; Li, R.; Yang, Y.; Yang, C.; Xu, X.; Zhang, L.; He, X.; Yao, Y.; Sun, X.; Hu, W., *Green Chem.* **2025**, *27*, 915–945. https://doi.org/10.1039/D4GC05316H
43. Ma, C.; Guo, J.-F.; Xu, S.-S.; Mei, T.-S. *Acc. Chem. Res.* **2025***, 58,* 399–414. https://doi.org/10.1021/acs.accounts.4c00656
44. Liu, M.; Guo, C. *Acc. Chem. Res.* **2025***, 58,* 3427–3441. https://doi.org/10.1021/acs.accounts.5c00635

Author's Biographies

Aurélie Claraz completed her Ph.D. in 2012 at INSA Rouen (France) under the guidance of Dr. Vincent Levacher, investigating cooperative chiral ion pairs in asymmetric organocatalysis. She then joined the group of Prof. Petri Pihko to develop novel iminium-catalyzed transformations through the design of original enantiopure aminocatalysts (2013−2015, University of Jyväskylä, Finland). In 2015, she returned to France as a temporary assistant lecturer in the group of Dr. Sylvain Darses (2015–2016, Chimie ParisTech, Paris) and subsequently pursued postdoctoral research with Prof. Janine Cossy (2016−2017, ESPCI, Paris). At the end of 2017, she was first appointed as a CNRS researcher in the group of Dr. Géraldine Masson at the Institut de Chimie des Substances Naturelles (ICSN, Gif-sur-Yvette), before establishing her independent research group in 2023. Her research focusses on harnessing the potential of electricity to achieve original redox transformations, with particular emphasis on the synthesis of structurally relevant molecular architectures.