ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/d5cc03741g

Received 2nd July 2025,
Accepted 10th July 2025

DOI: 10.1039/d5cc03741g

rsc.li/chemcomm

Electrochemical seleno-/tellurocyclization of propargyl carboxylic acids†

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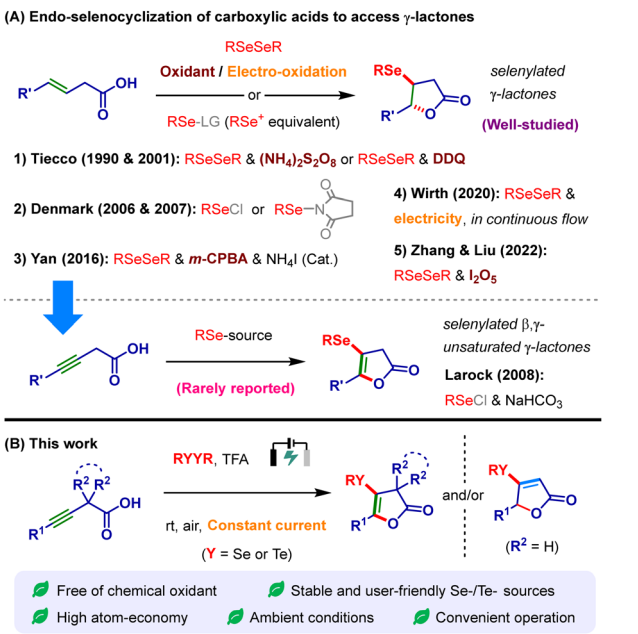
Reported herein is a novel and sustainable electrochemical seleno-/tellurocyclization of propargyl carboxylic acids, affording a diverse range of valuable Se-/Te-incorporated unsaturated γ-lactones under ambient conditions. Preliminary mechanistic studies suggest that this transformation predominantly proceeds *via* a cationic pathway.

Unsaturated γ-lactones, also known as γ-butenolides or furanones, are commonly found as enantioenriched scaffolds within natural product architectures, serving as attractive synthetic targets as well as versatile building blocks.[1] In recent years, both selenium- and tellurium-containing organic compounds have garnered increasing attention due to their promising applications in the pharmaceutical industry, materials chemistry, and organic catalysis/synthesis, among others.[2] As a consequence, the development of efficient methods for incorporating Se-/Te-containing substituents into molecular frameworks, particularly cyclic structures such as γ-lactones, has emerged as a highly sought-after research objective.[3]

Carboxylic acids serve as bench-stable, cost-effective, and readily accessible starting materials for the synthesis of esters and lactones.[4] Specifically, for the construction of Se-containing γ-lactones, the *endo*-lactonization of β,γ-unsaturated carboxylic acids with simultaneous Se-incorporation represents an attractive strategy. Accordingly, a variety of methodologies have been established for the alkene-tethered carboxylic acids, utilizing either diselenides (RSeSeR) under oxidative conditions or preformed selenylating reagents (RSe-LG, LG = leaving group) to afford saturated lactones.[5] Although this may seem like a straightforward analogy, the corresponding seleocyclization of alkyne-tethered substrates (*i.e.*, propargyl carboxylic acids), which leads to valuable unsaturated γ-lactone products,[6] remains largely unexplored (Scheme 1A).

Recent years have witnessed the remarkable resurgence of organic electrosynthesis as a sustainable synthetic platform, exploiting controllable electrons as an ideal alternative to chemical oxidants/reductants for selective redox processes.[7] Given the successful applications of mild electrochemical methods in diverse heterocycle construction,[8] we questioned whether such a selenocyclization of propargyl carboxylic acids could be enabled electrochemically. In line with our ongoing interest towards sustainable synthetic methodologies,[9] we hereby report a straightforward electrochemical seleno-/tellurocyclization of propargyl acids, yielding a diverse range of Se-/Te-incorporated unsaturated γ-lactones under ambient conditions (Scheme 1B). The current strategy eliminates the need for



Scheme 1 5-*endo*-Cyclization of unsaturated carboxylic acids for the synthesis of Se-/Te-incorporated γ-lactones. (A) Prior arts. (B) This work.

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d5cc03741g

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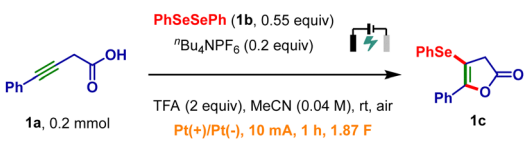
hazardous chemical oxidants and unstable selenium-/tellurium-based reagents, demonstrates excellent atom economy, and operates under mild reaction conditions.

Initially, the electrochemical selenocyclization of 4-phenylbut-3-ynoic acid (**1a**) with diphenyl diselenide (**1b**) was chosen as the model reaction (Table 1). The desired selenylated β,γ-unsaturated lactone **1c** was obtained in 70% isolated yield from a mixture of **1a** (0.2 mmol), **1b** (0.55 equiv.), trifluoroacetic acid (2 equiv.) and $^{n}Bu_4NPF_6$ (0.2 equiv.) in acetonitrile (5 mL) after 10 mA constant current electrolysis (CCE) with Pt electrodes for 1 h (entry 1). Application of less **1b** (0.50 equiv.) led to a noticeable drop in the yield of **1c**, while addition of more **1b** (0.75 equiv.) did not further improve the yield (entry 2). Within the same passed charges (1.87 F), employing a lower current at 5 mA provided a diminished yield of 65% (entry 3). Different electrolytes and solvents were also examined, providing no better result than the $^{n}Bu_4NPF_6$/MeCN combination (entries 4–6). Acid additives were proven beneficial to this transformation, likely serving as proton donors to facilitate hydrogen evolution at the cathode; whereas a base such as 2,6-lutidine completely inhibited the reaction (entries 7–9). Compared with graphite electrodes, Pt electrodes showed better performance in accelerating the conversion (entry 10). Finally, the control experiment without electric current indicated that this reaction is powered by electricity (entry 11).

With the optimized conditions established, we first examined the scope of propargyl carboxylic acids (**a**), using commercially available diselenide **1b** as the selenyl source (Scheme 2). It should be noted that selenylated β,γ-unsaturated lactones (**c**) were always produced as the predominant isomers, with the corresponding α,β-unsaturated lactones (**c′**) as separatable minor isomers. However, in certain cases, products **c** underwent olefin migration to form **c′** during the isolation process, affording isomer mixtures as the products. For aryl-substituted but-3-ynoic acids (**1a–12a**) bearing groups with different electronic effects, the desired selenocyclization proceeded smoothly, affording unsaturated γ-lactone products in moderate to good yields (40–76%). Among these examples, selenylated β,γ-unsaturated lactones **3c**, **4c**, and **7c** were obtained with minor α,β-unsaturated isomers; while in contrast, **8c′–11c′** were obtained as the major isomers from the corresponding systems. Moreover, the reaction of **12a** bearing a –NO_2 group yielded α,β-unsaturated lactone **12c′** as the only product. Based on these results, it appears that lactones **c** with electron-deficient aryl groups as R^1 are more susceptible to isomerization, which may possibly be attributed to the effect of the R^1 substituent on the acidity of the lactone proton.[10] Further attempts with an alkyl-substituted but-3-ynoic acid (**13a**) worked out, providing β,γ-unsaturated lactone **13c** in 65% yield. With two extra substituents (R^2) to inhibit isomerization, terminal (**14a**) and trimethylsilyl-substituted (**15a**) alkynyl acids were next subjected to the standard conditions with **1b**. As expected, lactones **14c** and **15c** were isolated in 90% and 62% yields, respectively.

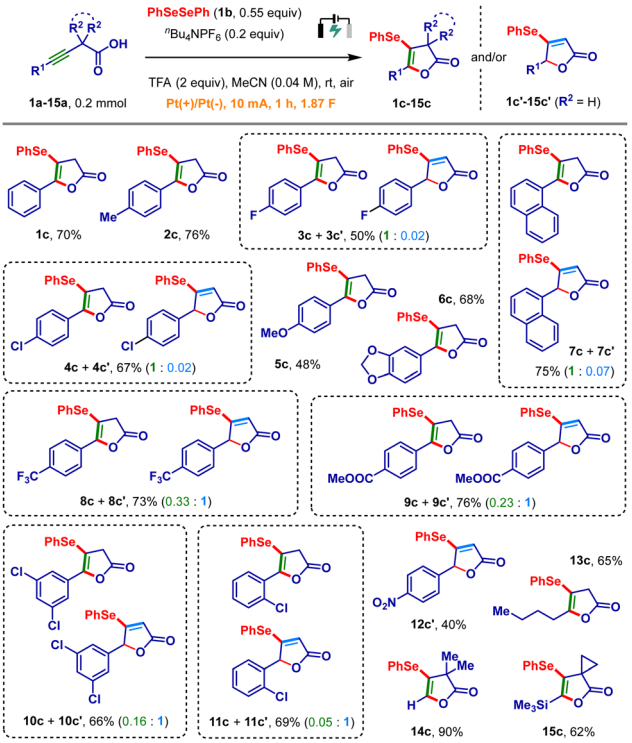
The scope of dichalcogenides was next evaluated (Scheme 3). Employing **2a** as the precursor for cyclization, aromatic diselenides with Me, F, or OMe groups (**1b–3b**), and aliphatic ones such as dibenzyl (**4b**) and dimethyl diselenide (**5b**) were proven as competent reaction partners, affording the desired unsaturated lactones **1d–5d** in 36–80% yields either with or without minor isomers **d′**. Interestingly, in an additional reaction between fluorine-containing propargyl carboxylic acid **3a** and BnSeSeBn (**4b**), the α,β-unsaturated isomer **6d′** was obtained as

Table 1 Optimization of the reaction conditions

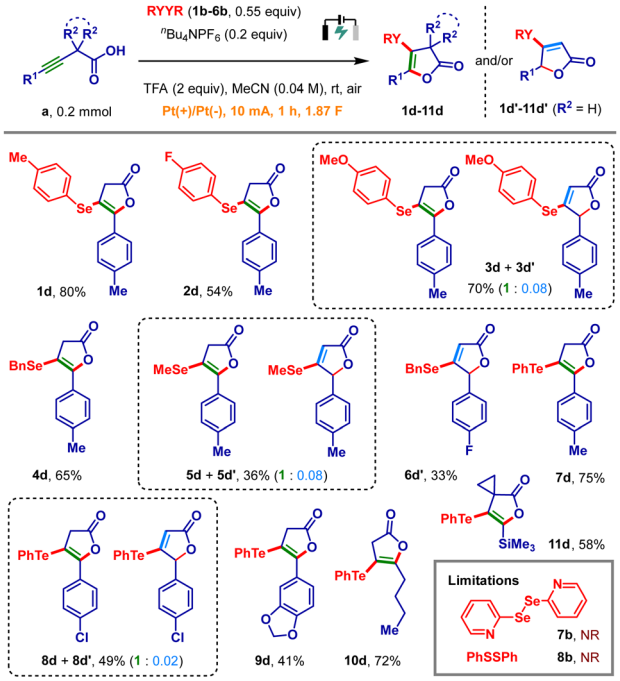


Entry	Variation from the standard conditions[a]	Yield[b] of **1c** (%)
1	None	70
2	0.50 or 0.75 equiv. of **1b**	62, 71
3	5 mA CCE for 2 h	65
4	$^{n}Bu_4NClO_4$, $^{n}Bu_4NBF_4$, or $^{n}Bu_4NI$ instead of $^{n}Bu_4NPF_6$	69, 64, trace
5	HFIP or 1,2-DCE as solvent	56, 29
6	DMF, DMSO, or MeCN : H_2O = 9 : 1 as solvent	Trace
7	Without TFA	45
8	1 or 4 equiv. of TFA	60, 69
9	AcOH or 2,6-lutidine instead of TFA	54, trace
10	C(+)/Pt(−), Pt(+)/C(−), or C(+)/C(−)	62, 44, 34
11	Without electric current	NR

[a] Standard conditions: **1a** (0.2 mmol), **1b** (0.11 mmol), $^{n}Bu_4NPF_6$ (0.04 mmol), TFA (0.4 mmol), MeCN (5 mL), Pt plate electrodes (10 × 10 × 0.2 mm), undivided cell, 10 mA CCE for 1 h (1.87 F), air, room temperature. [b] Isolated yield of **1c**. NR: no reaction.



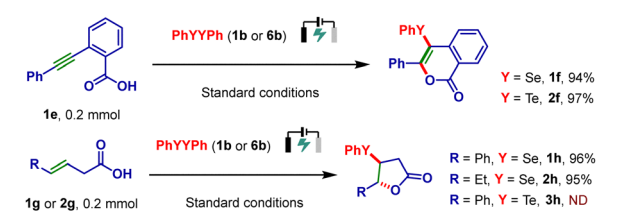
Scheme 2 Substrate scope with respect to propargyl carboxylic acids.



Scheme 3 Scope and limitations with respect to dichalcogenides.

the only product in 33% yield. Gratifyingly, diphenyl ditelluride (**6b**) also exhibited suited reactivity for the tellurocyclization of but-3-ynoic acids such as **2a**, **4a**, **6a**, **13a** and **15a**, providing the corresponding lactones **7d–11d** in 41% to 75% yields. Finally, it was found that diselenide **7b** with strong electron-withdrawing pyridyl substitutions and disulfide **8b** are inert substrates when subjected to the reaction with **2a** under the standard conditions.

The scalability of this electrochemical cyclization was demonstrated with two 10-fold scale-up reactions of **2a** with **1b** and **6b**, affording **2c** and **7d** in 65% and 60% yields, respectively (see the ESI† for details). Moreover, the standard conditions were also effectively applied to achieve the seleno- and tellurocyclization of three additional unsaturated carboxylic acids, delivering the corresponding lactone products in excellent yields (Scheme 4). For the construction of 4-selanyl- and 4-tellanyl-1*H*-isochromen-1-ones, the existing methods have primarily relied on the 6-*endo-dig* electrophilic cyclization of 2-alkynylaryl esters;[11] while the corresponding acid (**1e**) was proven as a viable substrate under our conditions to deliver **1f** and **2f** in 94% and 97% yields, respectively. Regarding the *5-endo-trig* cyclization of allyl-substituted carboxylic acids (**1g** and **2g**),[5] excellent yields were also obtained for the



Scheme 4 Applications to other carboxylic acids. ND: not detected.

selenium-containing lactones (**1h** and **2h**); however, the corresponding tellurium-incorporated product (**3h**) could not be obtained using the current methodology.

To shed light on the reaction mechanism, cyclic voltammetry (CV) studies were first carried out (Fig. 1A). As shown in the cyclic voltammograms: TFA showed no obvious oxidation peak; the distinct peak of **2a** appeared at +2.06 V; whereas **1b** and **6b** presented their first oxidation peaks at +1.19 V and +1.50 V, respectively (values *vs.* SCE). Such results indicated that additive TFA is inert under oxidative conditions, and dichalcogenides **1b**/**6b** are more susceptible to oxidation than carboxylic acid **2a**. Subsequently, a series of control experiments were conducted (Fig. 1B). Radical scavengers TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (2,6-di-*tert*-butyl-4-methylphenol) were parallelly added to two reactions of **2a** with **1b** under the standard conditions. It was observed that TEMPO nearly completely suppressed the desired reaction, whereas BHT showed minimal inhibitory effect. Considering that the oxidation potential of TEMPO is significantly lower than that of **1b**,[12] this outcome may not be conclusive evidence for the involvement of a radical mechanism.

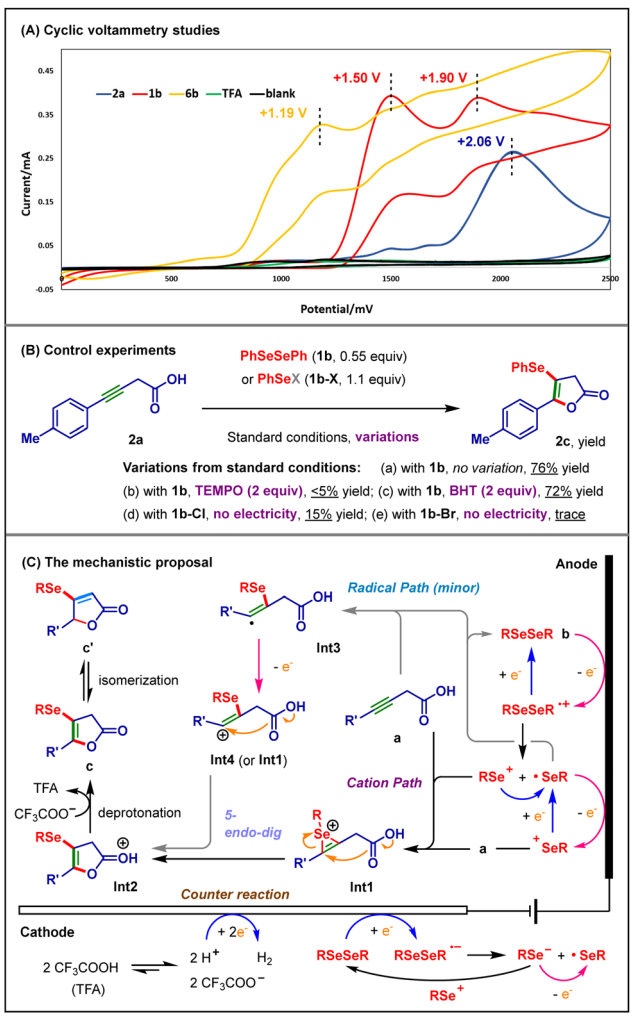


Fig. 1 Mechanistic aspects. (A) Cyclic voltammetry studies. (B) Control experiments. (C) The proposed mechanism.

In two follow-up experiments, electrophilic selenylating reagents **1b-Cl** and **1b-Br** were employed in place of **1b** under non-electrochemical conditions with **2a**. The corresponding product **1c** was obtained in low and negligible yields, respectively, suggesting the possible involvement of an ionic pathway; however, these $PhSe^+$ analogues appear to lack sufficient reactivity for efficient transformation under acidic conditions.

Based on the mechanistic studies and literature precedents,[6,12–14] a plausible mechanism is proposed in Fig. 1C, taking the selenocyclization for illustration. The anodic oxidation of diselenide **b** gives radical cation $RSeSeR^{\bullet+}$, which then collapsed into a cation RSe^+ and a radical $RSe^\bullet$. Further oxidation of $RSe^\bullet$ forms another molecule of RSe^+, which serves as the major reactive species to interact with propargyl carboxylic acid **a**, delivering selenonium **Int1**. The following *5-endo-dig* cyclization of **Int1** forms a five-membered cyclic intermediate **Int2**, which further undergoes deprotonation to afford the Se-incorporated β,γ-unsaturated lactone product **c**. In some cases, isomerization may occur to produce α,β-unsaturated lactone **c′**. Apart from this plausible cationic pathway, a radical mechanism involving the addition of $RSe^\bullet$ to the alkyne cannot be entirely excluded at this stage. However, the reaction of terminal alkyne **14a**, which afforded product **14c** in high yield (90%, see Scheme 2), significantly reduces the likelihood of such a radical pathway, since the terminal vinyl radical intermediate (**Int3**, R′ = H) would be highly unstable and therefore unlikely to form. On the other hand, the counter reaction at the cathode is hydrogen evolution through the reduction of protons provided by TFA and **Int2**. In addition, the cathodic reduction of other species (*e.g.*, $RSeSeR^{\bullet+}$, RSe^+, $RSe^\bullet$, RSeSeR, *etc.*), which may cause the reproduction of the starting materials or the quenching of reactive intermediates, is considered as an undesirable side reaction.

In summary, we have developed a facile electrochemical seleno-/tellurocyclization of propargyl acids with stable and user-friendly diselenides/ditellurides under ambient conditions. The current protocol represents a novel strategy for accessing Se-/Te-incorporated unsaturated γ-lactones, and aligns well with the principles of green chemistry. Preliminary mechanistic studies suggested that this transformation predominantly proceeds *via* a cationic pathway. Further exploration into novel and sustainable methodologies for heterocycle construction is currently ongoing in our laboratory.

The authors gratefully acknowledge the financial support from Beijing Normal University (No. 310432105).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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