Electrochemical Regioselective C(sp²)-H Selenylation of Pyrazolo[1,5-*a*]pyrimidines with Diorganyldiselenides at Room Temperature

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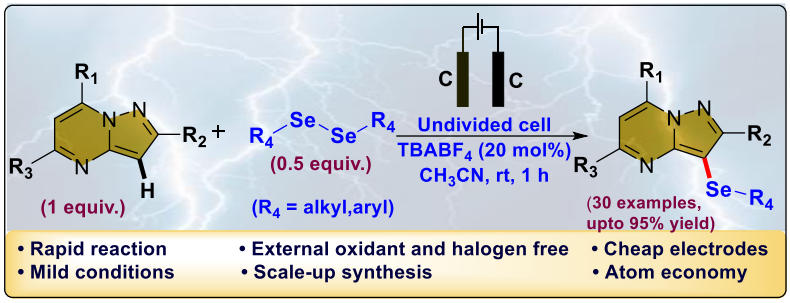
Graphical abstract:



Abstract

In this report, we disclose an electrochemical approach for the C(sp²)-H selenylation of pyrazolo[1,5-*a*]pyrimidines at room temperature. The reaction takes place within an undivided cell employing graphite electrodes, with $TBABF_4$ acting as the supporting electrolyte. This technique offers a rapid, oxidant as well as halogen free, and environmentally conscious protocol for achieving regioselective selenylation specifically at the C3 position of pyrazolo[1,5-*a*]pyrimidines. Key attributes of this methodology include its atom economy, mild reaction conditions, short reaction time, utilization of cost-effective electrode materials, reliable achievement of yields ranging from good to excellent, and an environmentally friendly reaction condition.

Introduction

Organoselenides are prevalent in pharmaceutically and therapeutically significant molecules, showcasing their widespread presence and importance in medicinal chemistry.[1] In addition to their roles in medicinal and synthetic chemistry, organoselenium compounds also find applications in diverse fields such as material sciences, agrochemicals, and catalysis.[2] The construction of C-Se bond formation stands as a critical juncture in synthetic chemistry, underscored by the profound significance of selenium-containing compounds. For the formation of C-Se bonds, organic chemists have adopted various strategies such as metal

catalysis, the utilization of iodine-based reagents, oxidant facilitated transformations, and photocatalysis.[3]

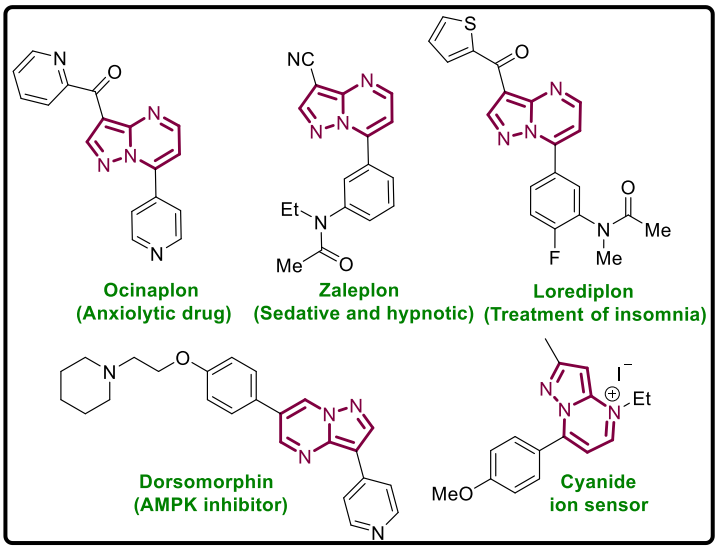
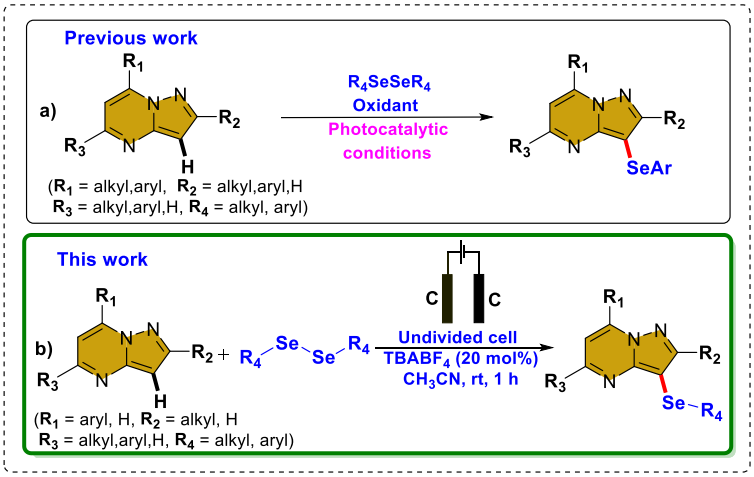


Figure 1. Important compounds containing pyrazolo[1,5-*a*]pyrimidine scaffold

Pyrazolo[1,5-*a*]pyrimidines constitute a significant class of N-fused heterocyclic scaffolds with versatile biological activities, encompassing antiviral,[4] anticancer,[5] anti-malarial,[6] and anxiolytic properties.[7] This structural motif serves as the core foundation for pharmaceutical agents such as zaleplon, lorediplon, ocinaplon, and dorsomorphin. These compounds play pivotal roles in the treatment of insomnia and anxiety disorders, exemplifying the diverse therapeutic applications of pyrazolo[1,5-*a*]pyrimidines in modern medicine.[8] Pyrazolo[1,5-*a*]pyrimidine derivatives are crucial in material sciences, offering intriguing optical properties and applications in chemo-sensing[9]. Their unique structure makes them valuable for developing materials with distinct optical attributes, showcasing versatility beyond medicinal uses. Thus, the synthesis of functionalized pyrazolo[1,5-a]pyrimidines holds great significance.

In past few years, electrochemical synthesis of organic molecules has emerged as a powerful and environmentally friendly approach for the synthesis of organic compounds.[10] The advantages of electrochemical synthesis, such as oxidant free and gentle reaction conditions, short reaction durations, and the utilization of electrons as reagents, distinguish it from conventional synthesis methods. This approach not only proves to be environmentally friendly by minimizing waste through the avoidance of stoichiometric amounts of oxidants but also embraces an eco-conscious strategy by directly harnessing electrical energy for organic synthesis.[11] Furthermore, electrochemical synthesis demonstrates scalability for industrial applications, as it can be seamlessly conducted in continuous flow, facilitating the efficient scaling up of organic synthesis processes.[12]
Previously, visible light-promoted, KI-catalyzed chalcogenation of pyrazolo[1,5-*a*]pyrimidines in the presence of potassium peroxodisulfate ($K_2S_2O_8$) as an oxidant is known (**Scheme 1a**).[13]



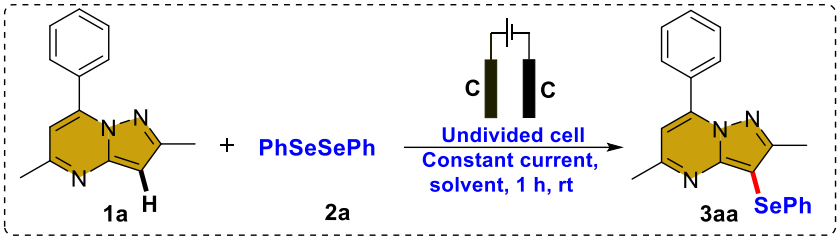
Scheme 1. Previous work on selenyation of pyrazolo[1,5-*a*]pyrimidines

Continuing our exploration of environmentally friendly approaches for the direct C-H selenylation of heterocycles,[14] here we report external oxidant as well as halogen free direct C3 selenylation of pyrazolo[1,5-*a*]pyrimidines under ambient conditions (**Scheme 1b**). This technique utilizes tetrabutylammonium tetrafluoroborate ($TBABF_4$) as an efficient and economical electrolyte (20 mol%), 0.5 equivalent of diphenyl diselenide as a selenium source with graphite serving as a cost-effective and readily available electrode material.

Result and discussion

The electrochemical selenylation of 2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine (**1a**) was carried out in an undivided cell for the duration of 1 hour under a constant current of 10 mA, utilizing 0.5 equivalents of diphenyl diselenide (**2a**), 20 mol% of $TBABF_4$ as an electrolyte, DMSO as the solvent, and graphite electrodes as cathode and anode. This reaction yielded the desired selenylated product **3aa** in a 41% yield (**Table 1**, Entry 1). Maintaining all other parameters constant, we opted to investigate the influence of different solvents on the reaction conditions. When ethanol was employed as the solvent (entry 2), product **3aa** was obtained with a yield of 31%. Shifting to methanol as the solvent (entry 3) resulted in a substantial enhancement, yielding a noteworthy 62% of **3aa**. The use of dimethyl carbonate (DMC) as a solvent proved ineffective in generating product **3aa** (entry 4). Interestingly, when acetonitrile was utilized as the solvent, the yield of product **3aa** significantly increased to 89% (entry 5), indicating that acetonitrile is the optimal solvent for the selenylation process. Further, we evaluated the influence of different electrolytes such as potassium iodide and tetrabutylammonium bromide (TBAB) on the reaction outcome. When potassium iodide was employed, the desired selenylated product **3aa** was not formed (entry 6). However, in contrast, when TBAB was utilized, product **3aa** was obtained in 56% yield (entry 7), this suggested that $TBABF_4$ was the optimal electrolyte for the reaction. Subsequently, we opted to conduct the reaction under reduced currents of 8 mA and 6 mA. However, as the current decreased, so did the yield of the reaction (entries 8 and 9). In the absence of electric current, no product formation was observed, underscoring the essential role of electricity in driving the reaction forward (entry 10).

Table 1. Optimisation of reaction conditions[a]

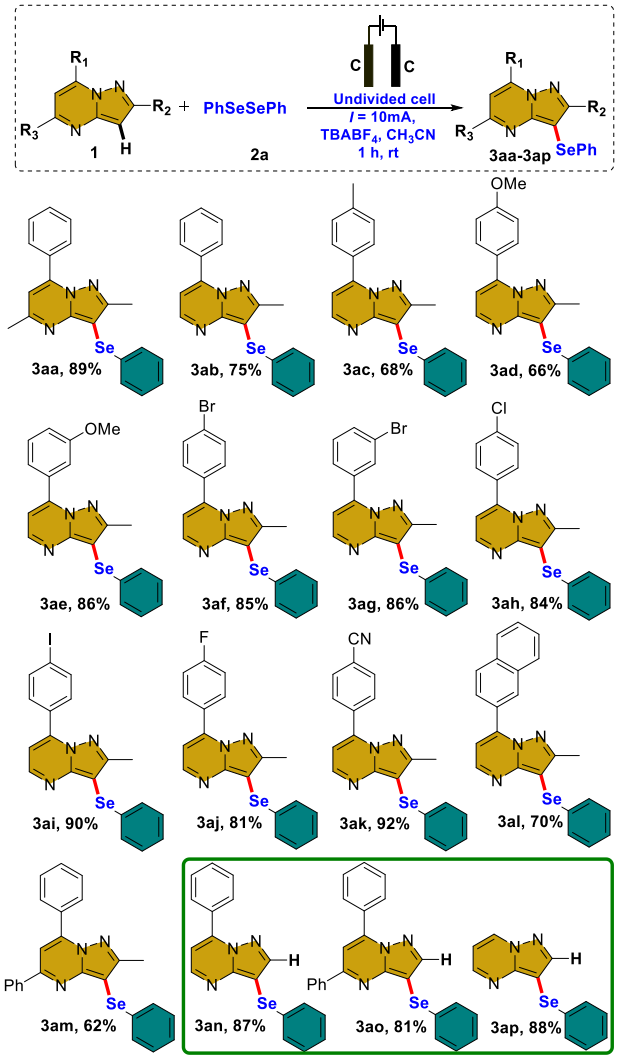


Entry	Electrolyte (20 mol%)	Solvent	Current	Yield[b]
1.	$TBABF_4$	DMSO	10 mA	41%
2.	$TBABF_4$	EtOH	10 mA	31%
3.	$TBABF_4$	MeOH	10 mA	62%
4.	$TBABF_4$	DMC	10 mA	NR
5.	**$TBABF_4$**	**CH_3CN**	**10 mA**	**89%**
6.	KI	CH_3CN	10 mA	NR
7.	TBAB	CH_3CN	10 mA	56%
8.	$TBABF_4$	CH_3CN	8 mA	70%
9.	$TBABF_4$	CH_3CN	6 mA	58%
10.[c]	$TBABF_4$	CH_3CN	0 mA	NR
11.[d]	$TBABF_4$	CH_3CN	10 mA	78%
12.[e]	$TBABF_4$	CH_3CN	10 mA	67%
13. [f]	$TBABF_4$	CH_3CN	10 mA	57%
14. [g]	$TBABF_4$	CH_3CN	10 mA	87%

[a]**Reaction conditions**: **1** (0.2 mmol), **2** (0.1 mmol), electrolyte (20 mol%), solvent 4.0 mL, constant current, rt, reaction mixture was electrolysed in Electrasyn 2.0 instrument for 1 h. [b]Isolated yields, [c]no electric current, [d] C(+)|Pt(-), [e] Pt(+)|C(-),[f] 10 mol% $TBABF_4$,[g] 30 mol% $TBABF_4$.

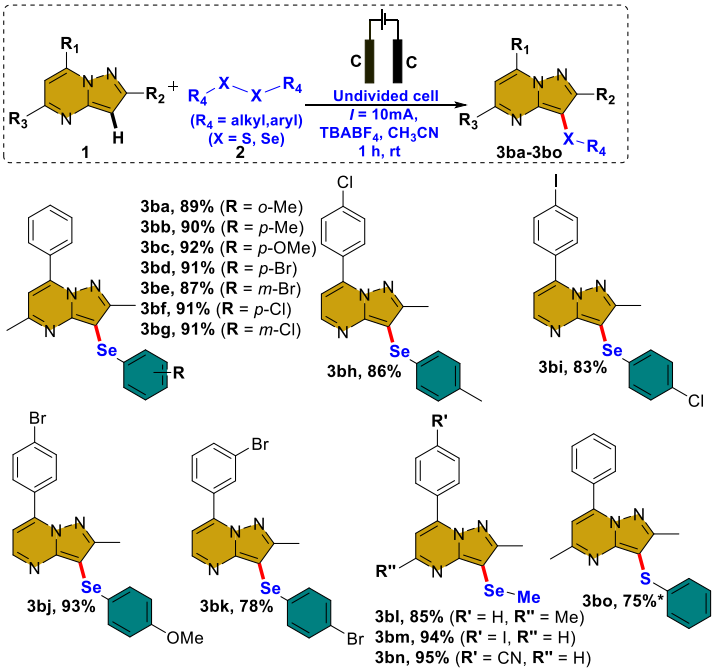
For further optimisation of the reaction conditions, we conducted test reactions in different undivided cells, specifically C || Pt and Pt || C, maintaining a constant current of 10 mA, acetonitrile served as the solvent, and $TBABF_4$ was utilized as the electrolyte, with reaction duration of 1 hour. Despite these adjustments, no enhancement in the reaction yield was observed in either case (entries 11 and 12). Reaction was also conducted using varying concentrations of the supporting electrolyte $TBABF_4$. At 10 mol% concentration of $TBABF_4$ reaction yield decreased to 57% (entry 13) while at 30 mol% concentration of $TBABF_4$ reaction yield was 87% (entry 14). As the concentration of the electrolyte was reduced, the reaction yield decreased. However, when the electrolyte concentration was increased, a yield nearly comparable to that achieved with a 20 mol% concentration was observed. Thus, we opted to maintain the electrolyte concentration at 20 mol%. The highest yield of product **3aa** was achieved by employing 1 equivalent of **1a**, 0.5 equivalent of diphenyl diselenide (**2a**), 20 mol% of $TBABF_4$, and conducting the reaction in an undivided cell with graphite anode and cathode under galvanostatic conditions (I = 10 mA), utilizing acetonitrile as the solvent for a duration of 1 hour. With this encouraging result we decided to check the substrate scope for the electrochemical selenylation of pyrazolo[1,5-*a*]pyrimidines using the optimised condition (**Scheme 2**). The selenylation of 2-methyl-7-phenylpyrazolo[1,5-*a*]pyrimidine was conducted under optimized conditions, resulting in the formation of the desired C-3 selenylated

compound **3ab** with a good yield of 75%. Subsequently, pyrazolo[1,5-*a*]pyrimidine derivatives containing electron-donating moieties (*p*-Me, *p*-OMe, *m*-OMe) on the phenyl ring exhibited good reactivity towards diorganyl diselenides, affording the selenylated products **3ac-3ae** in yields ranging from 66% to 86%, respectively. Pyrazolo[1,5-*a*]pyrimidine derivatives bearing halogen substituents (*p*-F, *p*-Cl, *p*-Br, *m*-Br, *p*-I) on the phenyl ring exhibited excellent reactivity in the electrochemical selenylation process, yielding products **3af-3aj** with outstanding yields ranging from 84% to 90% respectively. Under the optimized conditions, the pyrazolo[1,5-*a*]pyrimidine derivative featuring a strong electron-withdrawing cyano substituent demonstrated exceptional tolerance, affording the selenylated product **3ak** in an impressive yield of 92%. Additionally, both 2-methyl-7-(naphthalen-2-yl)pyrazolo[1,5-*a*]pyrimidine and 2-methyl-5,7-diphenylpyrazolo[1,5-*a*]pyrimidine exhibited robust reactivity with diphenyl diselenides under optimized conditions, giving the selenylated products **3al** and **3am** in yields of 70% and 62%, respectively. When subjected to electrochemical selenylation, pyrazolo[1,5-*a*]pyrimidine lacking substituents on the C2 position exclusively yielded the corresponding C3 selenylated products **3an-3ap** in good yields (81%-88%), emphasising the excellent regioselectivity inherent to the developed methodology.



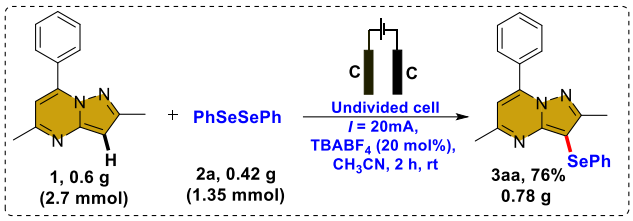
Scheme 2. Substrate scope for electrochemical selenylation of pyrazolo[1,5-*a*]pyrimidines. [a]Reaction conditions: **1** (0.2 mmol), **2a** (0.1 mmol), $TBABF_4$ (20 mol%), CH_3CN 4.0 mL, constant current (*I* = 10 mA), rt, reaction mixture was electrolysed in Electrasyn 2.0 instrument for 1 h. Yields are isolated yields.

Subsequently, the range of various aryl and alkyl diorganyl diselenides was explored for the electrochemical selenylation of pyrazolo[1,5-*a*]pyrimidine derivatives (**Scheme 3**). Diaryl diselenides possessing various electron donating (*o*-Me, *p*-Me, *p*-OMe) as well as electron withdrawing groups (*p*-Br, *m*-Br, *p*-Cl, *m*-Cl) reacted with 2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine exclusively giving respective C3 selenylated derivatives **3ba-3bg** with remarkable yields (87-92%). Upon subjecting diverse halogen-substituted pyrazolo[1,5-*a*]pyrimidine derivatives to reaction with an array of substituted diaryl diselenides, the resultant selenylated products **3bh-3bk** were obtained in good to excellent yields ranging from 78% to 93%. Furthermore, dimethyl diselenide underwent reactions with diverse substituted pyrazolo[1,5-*a*]pyrimidine derivatives under optimized reaction parameters, yielding products **3bl-3bn** with yields ranging from 85% to 95%, respectively. To our delight, diphenyl disulphide in acidic conditions also reacted with 2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine (**1a**) under optimised conditions to give corresponding C3 sulfenylated product **3bo** in 75% yield.



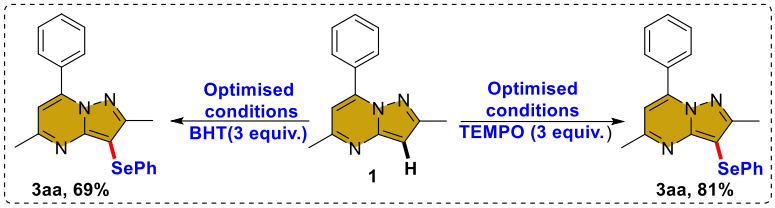
Scheme 3. Substrate scope of various diorganyl diselenides. [a]Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), $TBABF_4$ (20 mol%), CH_3CN 4.0 mL, constant current (*I* = 10 mA), rt, reaction mixture was electrolysed in Electrasyn 2.0 instrument for 1 h. Yields are isolated yields. *0.5 equiv. diphenyl disulfide was used in acidic conditions.

To demonstrate the practical applicability of the developed methodology, a scale-up reaction was conducted. Specifically, 0.6 g (2.7 mmol) of compound **1a** was reacted with 0.42 g (1.35 mmol) of diphenyl diselenide (**2a**), employing 20 mol% of $TBABF_4$ as a supporting electrolyte in the presence of 25 mL of acetonitrile under galvanostatic conditions (*I* = 20 mA) for a duration of 2 hours, as outlined in **Scheme 4**. The desired selenylated product **3aa** was obtained in a yield of 76%, thus affirming the scalability of the reaction.



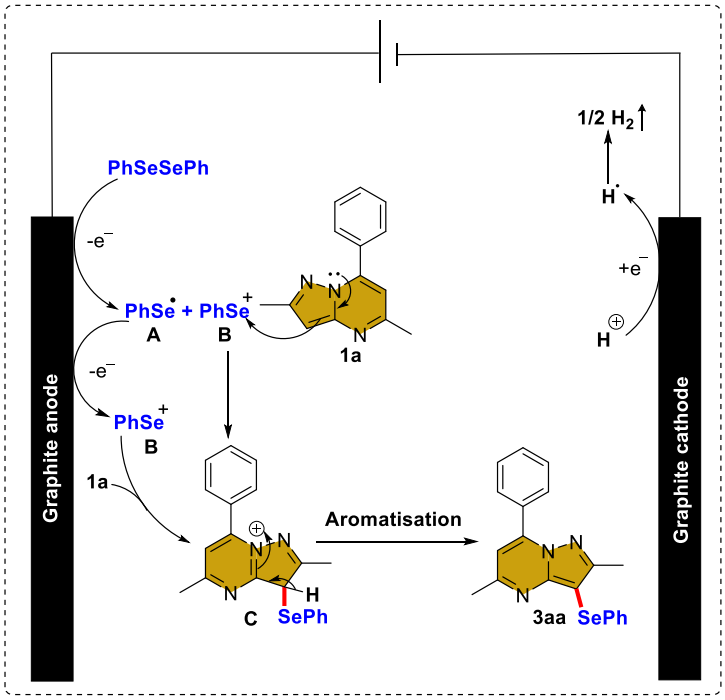
Scheme 4. Scale-up synthesis

Next to this a series of control experiments were carried out to gain insights into the reaction mechanism. The reactions were systematically carried out under optimized conditions, incorporating radical scavengers, namely 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT), to evaluate the potential engagement of radical intermediates (**Scheme 5)**. Despite the presence of the radical scavenging agents TEMPO and BHT, which were employed in an endeavour to hinder the formation of product **3aa**, only a modest reduction in the reaction yield was noted, resulting in the production of product **3aa** in 81% and 69% yields, respectively.



Scheme 5. Control experiments

To elucidate the potential mechanism underlying the selenylation reaction, cyclic voltammetry (CV) experiments were meticulously conducted, as detailed in the supporting information. As expected, the CV of $TBABF_4$ (0.1 M) revealed an absence of any oxidation peak. However, CV of compound **1a** (20 mM) in $TBABF_4$ (0.1 M) showed distinct oxidation peaks at +1.7 V and +2.5 V. Similarly, the CV analysis of diphenyl diselenide **2a** (20 mM) in 0.1 M $TBABF_4$ showed oxidation peaks at +1.6 V and +2.6 V. CV of the mixture of **1a** (20 mM), **2a** (20 mM) along with $TBABF_4$ (0.1 M) showed the oxidation peaks at +1.7 V, +1.9 V, +2.1 V, +2.6 V. The oxidation peaks at +1.9 V and +2.1 V were possibly due to the chemical interaction between the diphenyl diselenide and **1a**. The findings collectively suggested that the oxidation of diphenyl diselenide is indeed a pivotal step within the reaction mechanism. Based on the control experiments, cyclic voltammetry studies and previous literature reports[15] a plausible mechanism is depicted in **Scheme 6**.



Scheme 6. Plausible reaction mechanism

Initially, diphenyl diselenide (**2a**) is subjected to anodic oxidation, leading to the formation of radical species **A** and phenyl selenium cation **B**. Subsequently, intermediate **C** is formed through the nucleophilic attack of 2,5-dimethyl-7-phenylpyrazolo[1,5-*a*]pyrimidine **1a** on species **A**. Upon deprotonation, intermediate **C** transforms into the final product **3aa**. The phenyl selenium radical **A** formed in the first step again undergoes one electron oxidation to generate phenyl selenium cation **B** which further reacts with **1a**, this step facilitates the full utilization of the diorganyldiselenide reagent, enhancing the atom economy of the overall transformation by minimizing wastage. The overall electrochemical reaction cycle is completed by the cathodic reduction, which converts the released protons into hydrogen.

Conclusion

In summary, we have designed a protocol for direct, regioselective C-H selenylation of pyrazolo[1,5-*a*]pyrimidines using electro-catalysis via generation of electrophilic chalcogen species. The developed method uses mild reaction conditions, minimum amount of reagents as well as cheap electrode materials for the selenylation of pyrazolo[1,5-*a*]pyrimidine scaffold. Mechanistic studies (control experiments and CV experiments) were also carried out to understand the nature of reactive species and overall reaction mechanism. This method is rapid, high yielding, and scalable which proves its synthetic utility.

Acknowledgements

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