

Electrochemical Synthesis of Organoselenium Compounds: A Graphical Review

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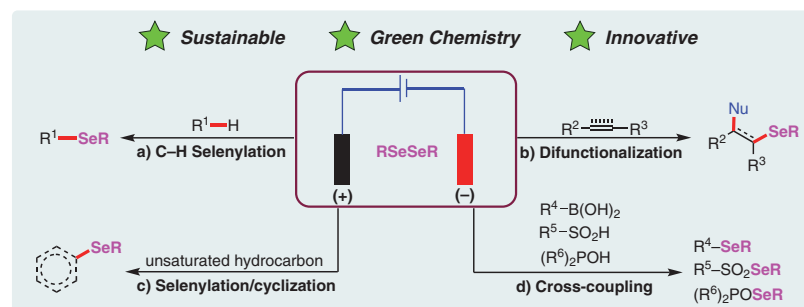
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Abstract Electrochemical synthesis, due to its environmentally benign, sustainable, and practical nature, has become an appealing and powerful substitute for traditional methods for oxidizing and reducing organic compounds. Thus, numerous valuable changes have been established in the field of organic synthesis through the utilization of electrochemistry. Among these electrochemical transformations, the formation of C–Se bonds stands out as an exceptionally noteworthy reaction type. In this graphical review, we present a succinct summary of the progress in utilizing electrochemical strategies for synthesizing organoselenium compounds.

Key words electrochemistry, organoselenium compounds, selenylation, difunctionalization, cyclization, cross-coupling

Organoselenium chemistry has remained a field of persistent exploration ever since selenium was recognized as an essential trace element within the human body. The significance of organoselenium compounds has experienced a substantial surge, particularly since the 1970s,

marked by the discovery of numerous intriguing compounds boasting diverse applications in synthesis and biology. Notably, among these compounds, diselenides have emerged as immensely valuable organic entities. The presence of Se–Se bonds confers their distinctive chemical attributes, enabling their involvement in a range of reactions as electrophilic (RSe^+), nucleophilic (RSe^-), or free-radical (RSe^\cdot) agents.

Over the past decades, advancements have propelled the synthesis of organoselenium molecules, a field often characterized by the routine utilization of costly catalysts and a variety of transition metals. This has spurred an ongoing quest to unearth more economical and environmentally friendly methodologies for generating selenium-containing compounds. Notably, recent breakthroughs in this pursuit have culminated in the development of an efficient and ecologically sound electrochemical selenylation process.

Electrochemistry has become an important strategy in organic synthesis, leading to the development of a multitude of beneficial transformations. One of its strengths lies in its capacity to induce carbon–carbon and carbon–heteroatom bond formation through anodic oxidation, all within an environment free from external oxidants. Notably, the domain of electrochemical synthesis has witnessed a surge in its utilization within the context of the formation of organoselenium compounds. Within the scope of this graphical review, our aim is to provide readers with an extended collection of instances exemplifying the utilization of electrochemical techniques in the synthesis of organoselenium compounds.

Biographical Sketches



Balati Hasimujiang was born in Xinjiang Province, P. R. of China. He earned his B.S. in 2011 and his M.S. in 2018, both from Xinjiang Normal University in 2011. In 2020, he joined the group of Prof. Ruan at the School of Pharmaceu-

tical Sciences, Guangzhou Medical University, where he performed his graduate studies and obtained his Ph.D. in June 2023. He is currently undertaking postdoctoral research in the laboratory of Prof. Ruan. His research inter-

ests focus on new methodologies in electrochemical synthesis, selenium chemistry, and the synthesis of biologically active compounds.



Zhixiong Ruan was born in Guangdong, P. R. of China. After obtaining his B.Eng. in pharmaceutical engineering at Guangdong University of Technology and his M.Sc. in medicinal chemistry at Jinan University, he joined the re-

search group of Prof. Dr Lutz Ackermann at Georg-August-Universität Göttingen, and obtained his Ph.D. in chemistry in 2017. He was subsequently employed as a professor at the School of Pharmaceutical Sciences, Guangzhou Medi-

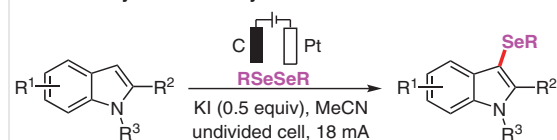
cal University. His current research interests are focused on organic electrochemistry, peptide modification and synthetic medicinal chemistry.

Notable features

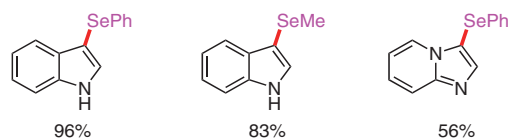
- Iodide salts employed as both electrolyte and catalyst.
- Electrochemical regioselective C(sp²)-H selenylation.

Seminal studies:

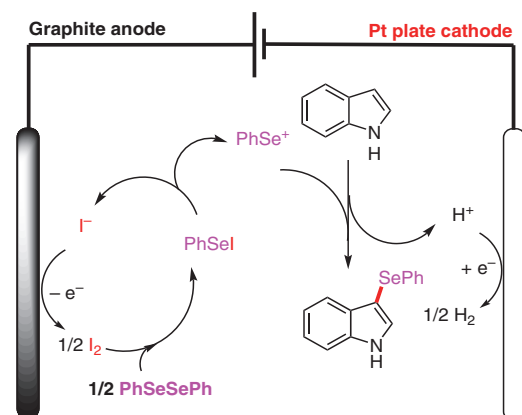
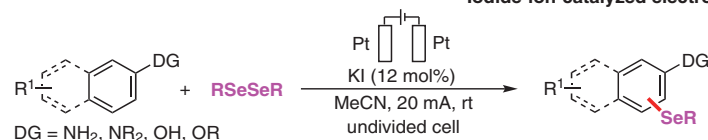
Electrocatalytic C-H selenylation of indoles



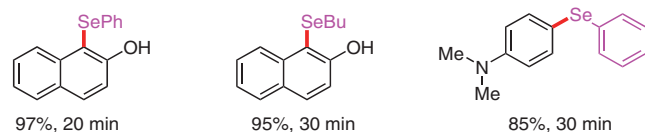
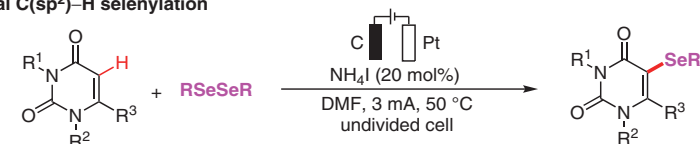
Selected scope



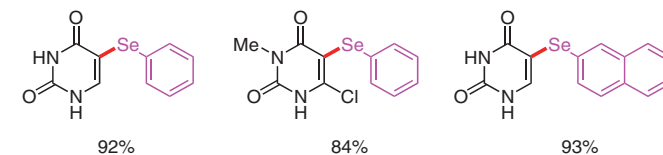
Reaction mechanism:

(1a) Sun, *Chem. Commun.* **2018**, 54, 8781.Iodide-ion-catalyzed electrochemical C(sp²)-H selenylation

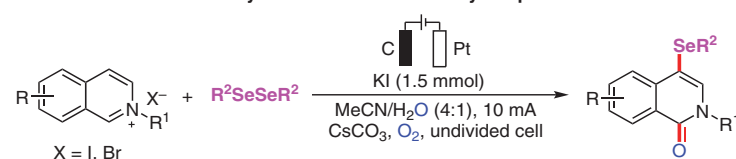
Selected scope

(1b) Mendes, *Eur. J. Org. Chem.* **2019**, 6465.See also: (1c) Mendes, *Eur. J. Org. Chem.* **2021**, 4411.

Selected scope

(1d) Xu, *Eur. J. Org. Chem.* **2020**, 4384.

Electrochemical selenylation/oxidation of N-alkylisoquinolinium salts

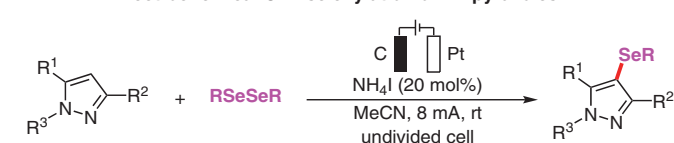


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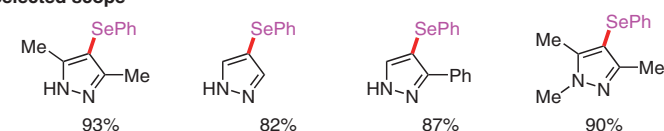
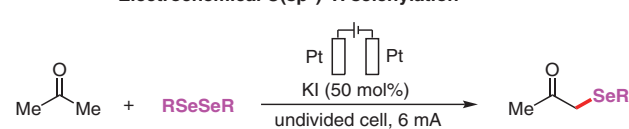
(1e) Cao, *Chem. Commun.* **2020**, 56, 15325.

exhibited excellent antiviral activity against tobacco mosaic virus

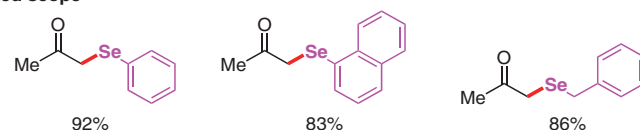
Electrochemical C-H selenylation of 1H-pyrazoles



Selected scope

(1f) He, *Tetrahedron Lett.* **2021**, 77, 153257.See also: (1g) Feng, *Asian J. Org. Chem.* **2023**, 12, e202200719.Electrochemical C(sp³)-H selenylation

Selected scope

(1h) Wang, *Chin. J. Org. Chem.* **2021**, 41, 3726.

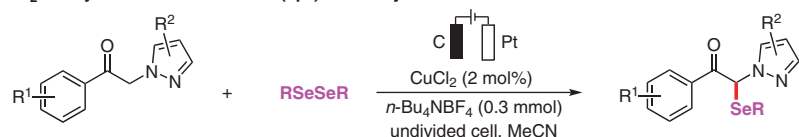
Further reading

- Other contributions of KI-mediated electrochemical selenylation:
- (1i) He, *Chin. J. Catal.* **2021**, 42, 1445.
 - (1j) Brahmachari, *J. Org. Chem.* **2023**, 88, 1049.
 - (1k) Badsara, *Chem. Commun.* **2023**, 59, 5415.
 - (1l) Chen, *ChemistrySelect* **2023**, 8, 1049.

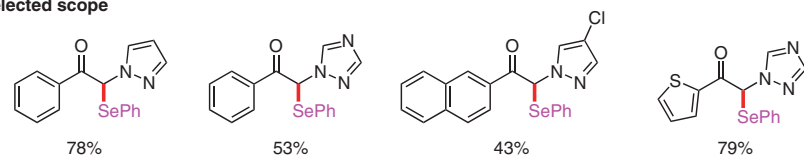
Figure 1 Electrochemical C-H selenylation (part 1)^{1a-l}

Notable features

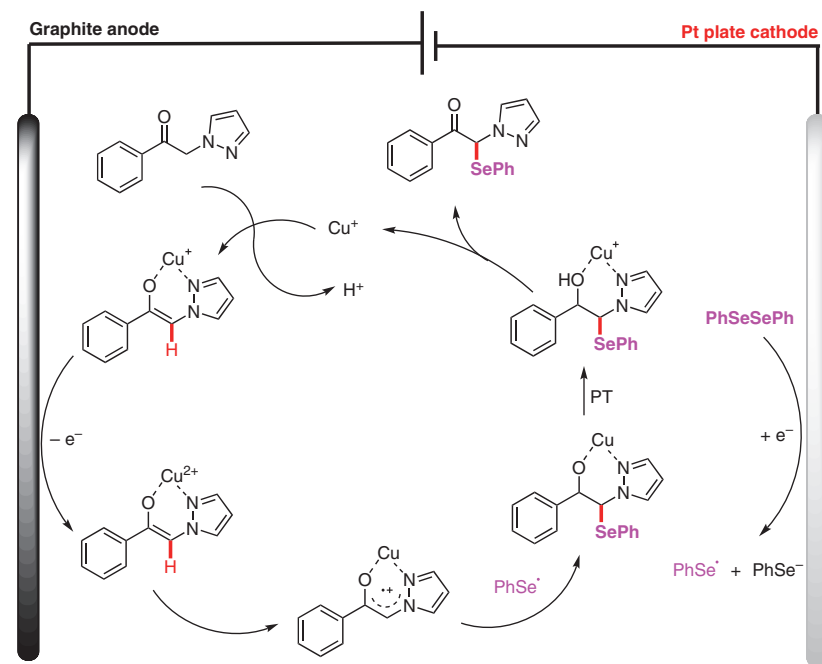
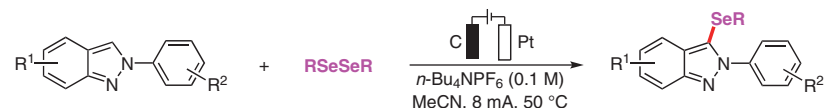
- Copper-catalyzed electrochemical C(sp³)-H selenylation.
- Direct electrochemical C(sp²)-H selenylation.

CuCl₂-catalyzed electrochemical C(sp³)-H selenylation

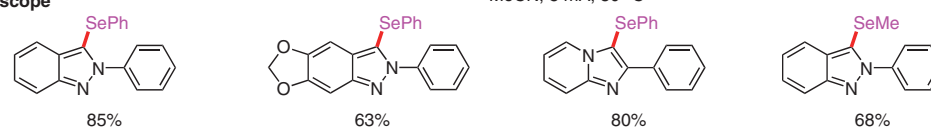
Selected scope



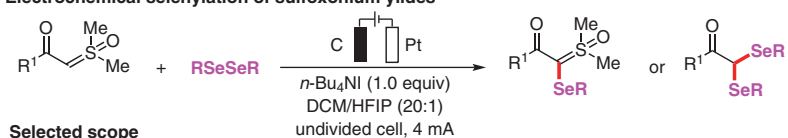
Reaction mechanism:

(1m) Wu, *Mol. Catal.* **2023**, *540*, 113038.Direct electrochemical C-H selenylation of 2*H*-indazoles

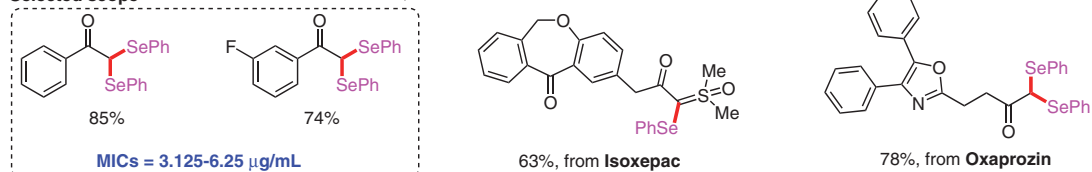
Selected scope

(1n) Ruan, *Org. Biomol. Chem.* **2021**, *20*, 117. Further reading: (1o) He, *Chin. Chem. Lett.* **2021**, *33*, 1501.

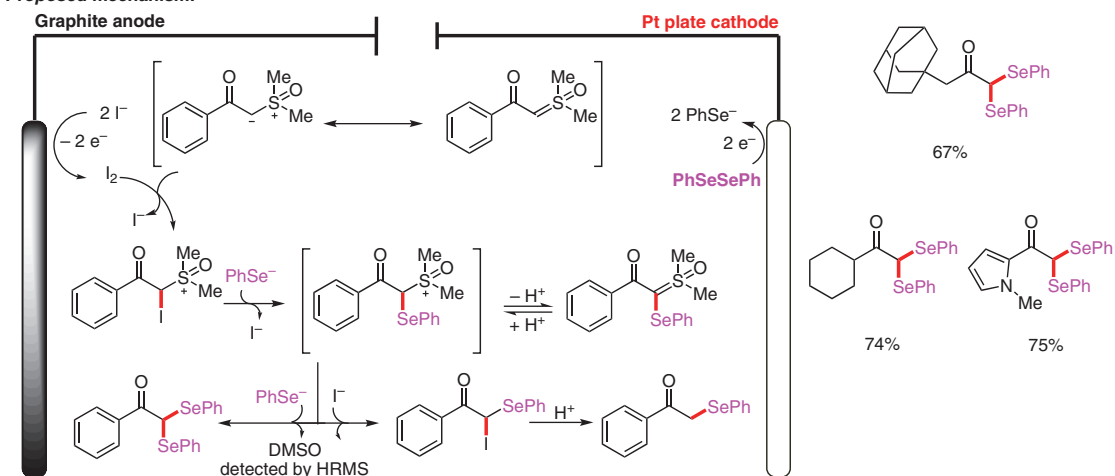
Electrochemical selenylation of sulfoxonium ylides

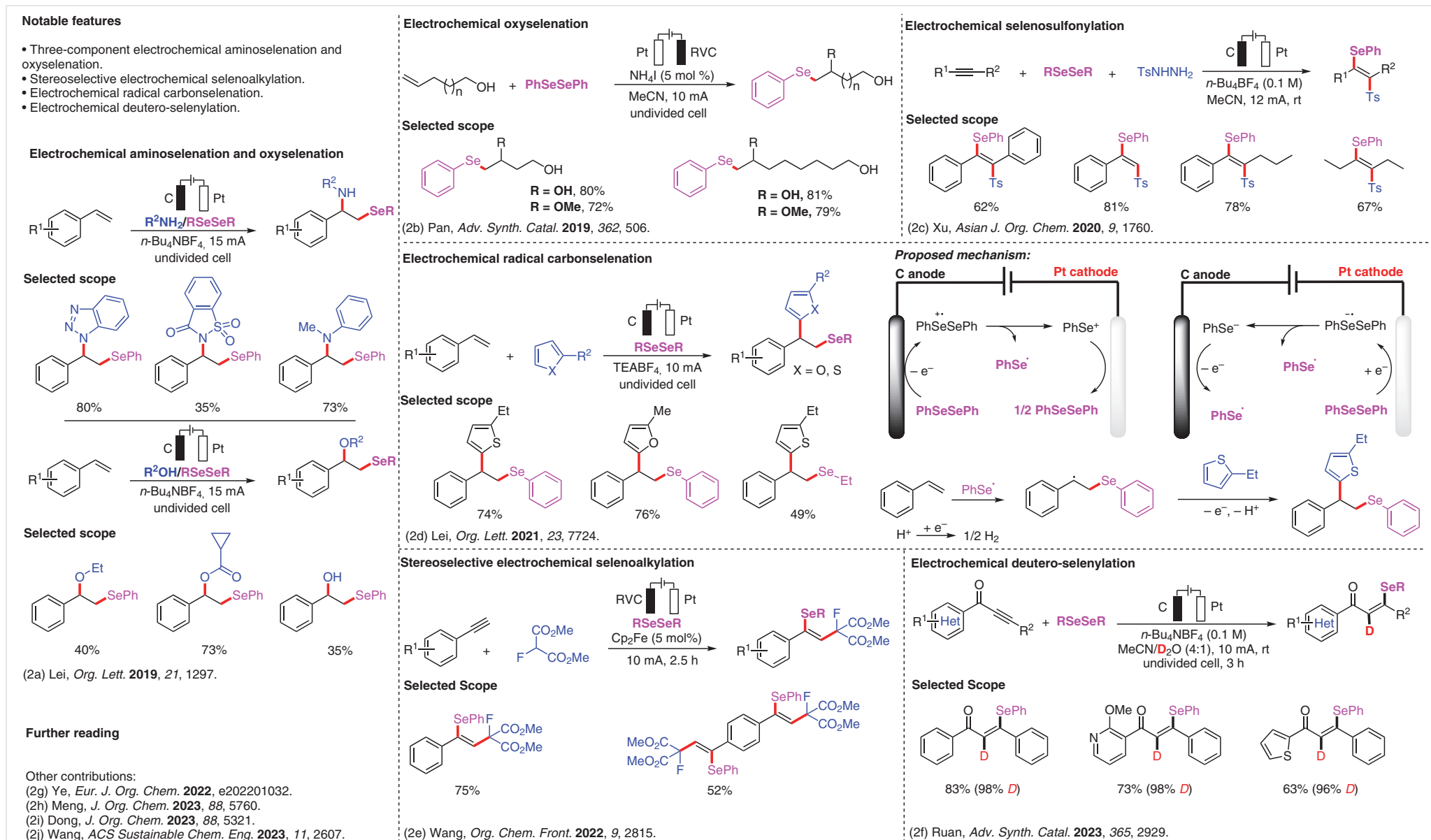


Selected scope



Proposed mechanism:

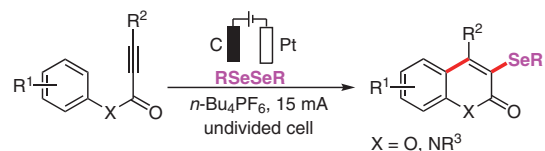
(1p) Ruan, *J. Org. Chem.* **2023**, *88*, 5572.Figure 2 Electrochemical C-H selenylation (part 2)^{1m-p}

Figure 3 Electrochemical difunctionalization^{2a-j}

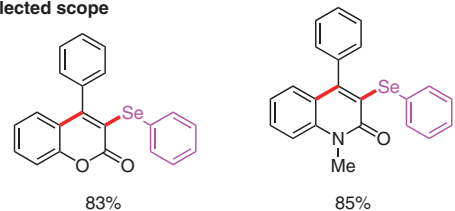
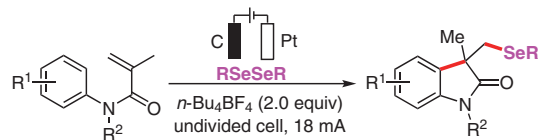
Notable features

- Electrochemical cyclization of *N*-arylacrylamides.
- Electrochemical radical selenylation.
- Electrochemical synthesis of selenylbenzo[*b*]furan.

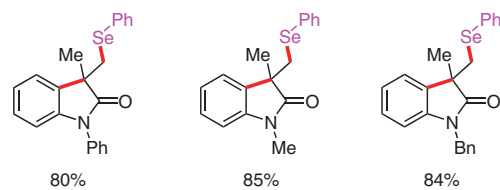
Electrochemical oxidative cyclization of activated alkynes



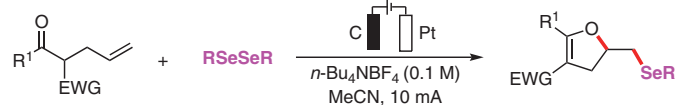
Selected scope

(3a) Guo, *Green Chem.* **2019**, *21*, 4706.Electrochemical cyclization of *N*-arylacrylamides

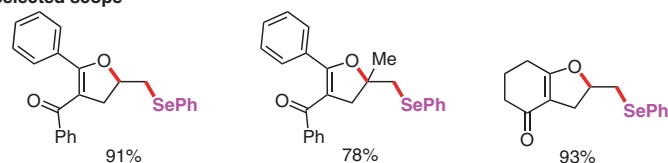
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(3b) Pan, *Adv. Synth. Catal.* **2021**, *363*, 208.

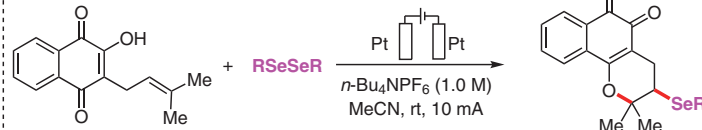
Electrochemical oxidative cyclization of olefinic carbonyls



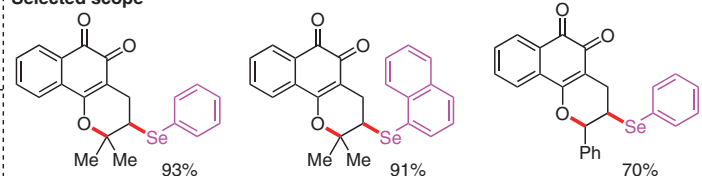
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(3c) Lei, *Green Chem.* **2019**, *21*, 4976.

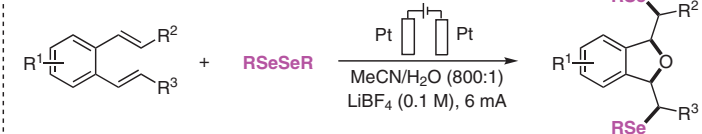
Electrochemical selenation/cyclization of quinones



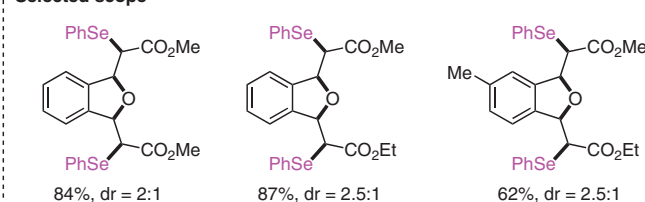
Selected scope

(3e) Ackermann, *Eur. J. Org. Chem.* **2020**, 4474.

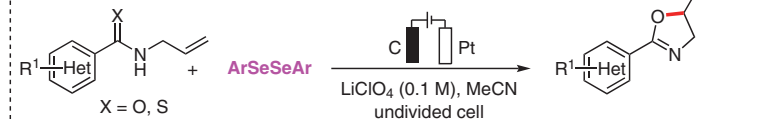
Electrochemical radical selenylation



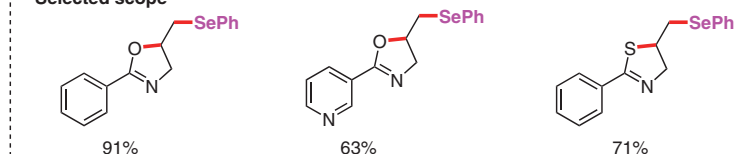
Selected scope

(3g) Liu, *Org. Biomol. Chem.* **2022**, *20*, 2813.

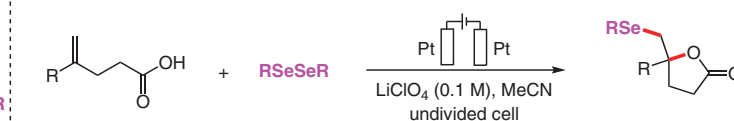
Electrochemical selenylation of unsaturated amides



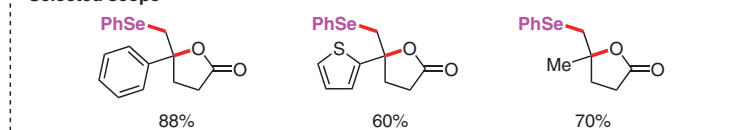
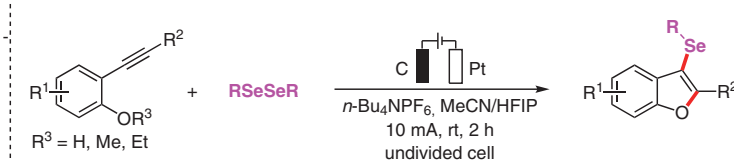
Selected scope

(3d) De Sarkar, *Adv. Synth. Catal.* **2020**, *362*, 1046.

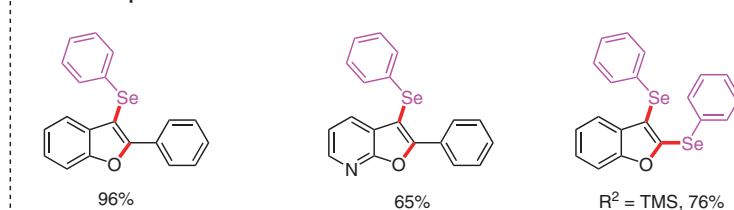
Electrochemical oxidative selenolactonization of alkenoic acids



Selected scope

(3f) Kim, *Asian J. Org. Chem.* **2021**, *10*, 3271.Electrochemical synthesis of selenylbenzo[*b*]furans

Selected scope

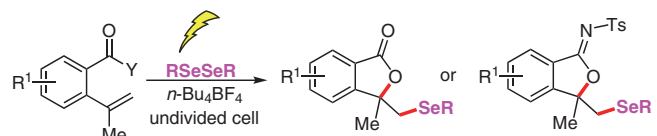
(3h) Ruan, *Molecules* **2022**, *27*, 6314.

See also:

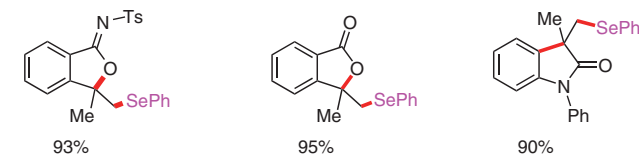
(3i) Braga, *Front. Chem.* **2022**, *10*, 880099.Figure 4 Electrochemical selenylation/cyclization (part 1)^{3a-i}

Notable features

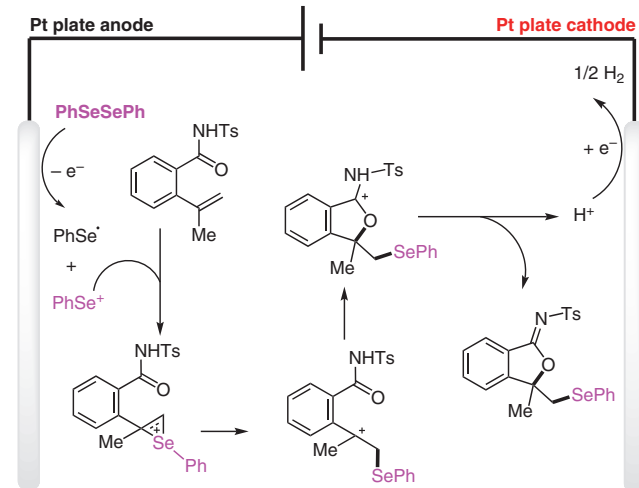
- Electrochemical selenylation/cyclization.
- Electrochemical selenocyclization of alcohols.
- Electrochemical tandem cyclization of unsaturates.



Selected scope Y = OH, NHTs



Reaction mechanism:

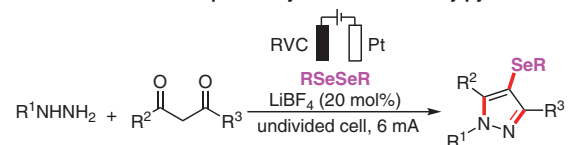


(3j) Ruan, *J. Org. Chem.* **2021**, *86*, 16045.

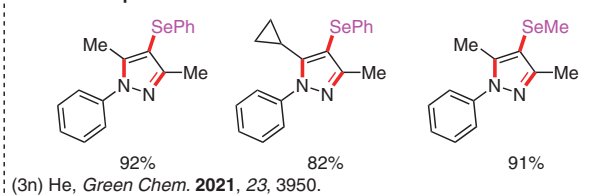
Further reading

- Other contributions:
 (3k) Guo, *Org. Biomol. Chem.* **2021**, *19*, 3207.
 (3l) Lei, *Green Chem.* **2021**, *23*, 7982.
 (3m) Lei, *Org. Chem. Front.* **2022**, *9*, 2786.

Electrochemical multicomponent synthesis of 4-selanylpyrazoles

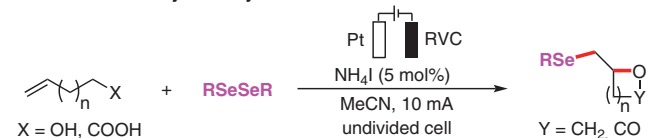


Selected scope

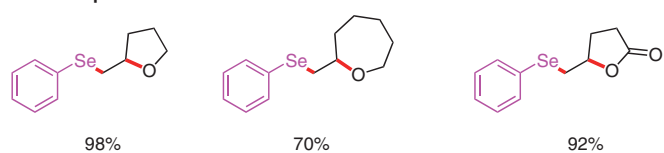


(3n) He, *Green Chem.* **2021**, *23*, 3950.

Electrochemical selenylation/cyclization

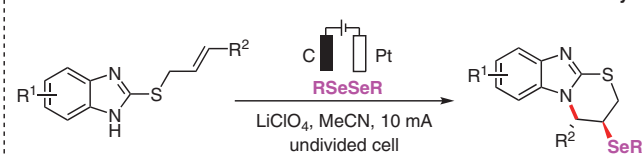


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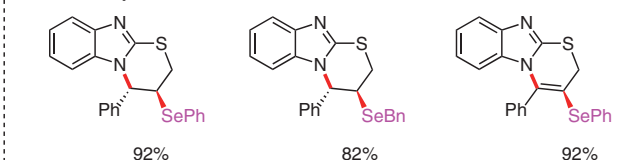


(2b) Pan, *Adv. Synth. Catal.* **2019**, *362*, 506.

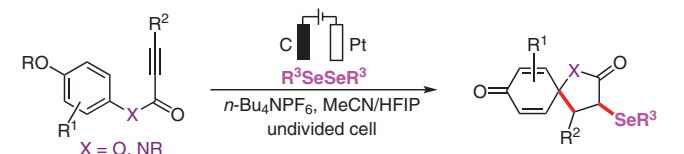
Electrochemical tandem cyclization of unsaturates



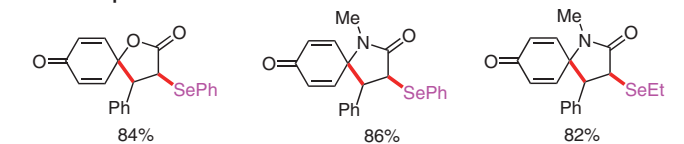
Selected scope



(3o) De Sarkar, *Chem. Asian J.* **2021**, *16*, 3895.

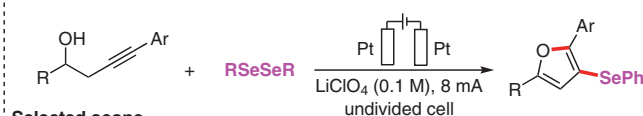


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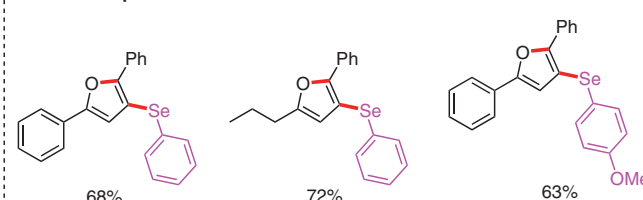


(3p) Guo, *ChemSusChem* **2020**, *13*, 2053.

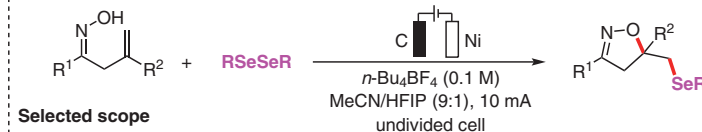
See also: (3q) Chen, *J. Org. Chem.* **2021**, *86*, 917.



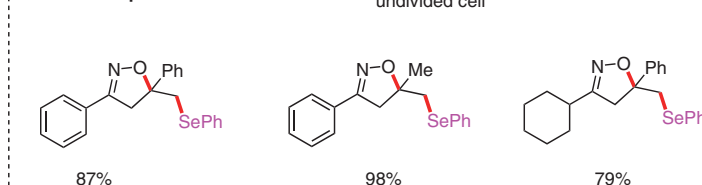
Selected scope



(3r) De Sarkar, *J. Org. Chem.* **2021**, *86*, 16084.



Selected scope



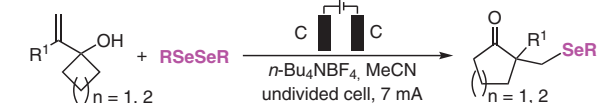
(3s) Xu, *Eur. J. Org. Chem.* **2021**, 2431.

Figure 5 Electrochemical selenylation/cyclization (part 2)^{2b,3j-s}

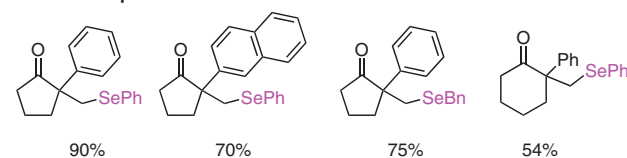
Notable features

- Electrochemical synthesis of significant selenoheterocycles.
- Electrochemical selenylation involving RSe^* or RSe^+ intermediates.

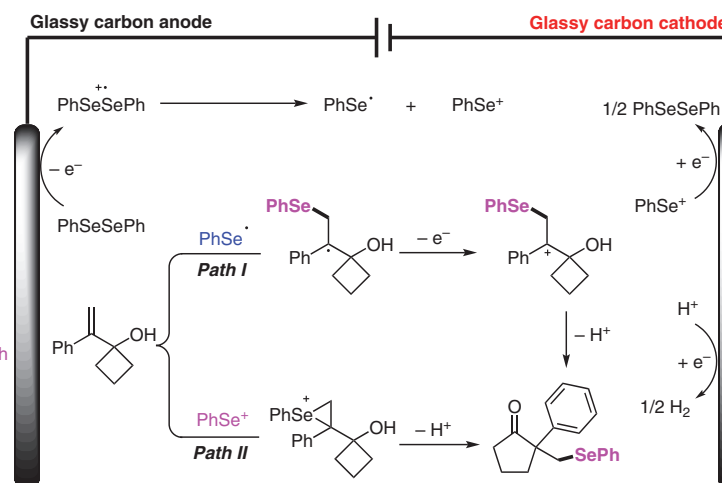
Electrochemical radical selenylation/1,2-carbon migration



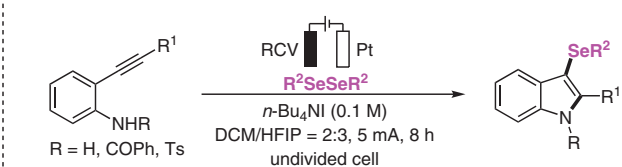
Selected scope

(3t) Kim, *Org. Lett.* **2019**, *21*, 1021.

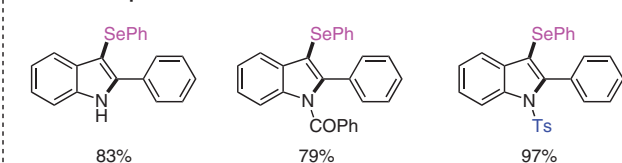
Proposed mechanism:



Electrooxidative selenylation of alkynes



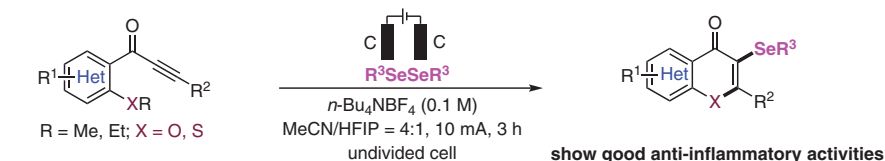
Selected scope

(3u) Ruan, *Isr. J. Chem.* **2023**, e202300088.

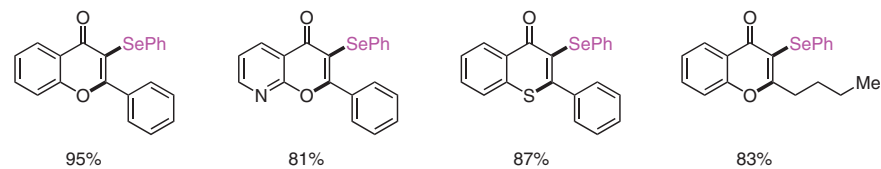
See also:

(3v) Lee, *Org. Biomol. Chem.* **2023**, *21*, 3002.(3w) Gedu, *Chem. Commun.* **2023**, *59*, 8719.

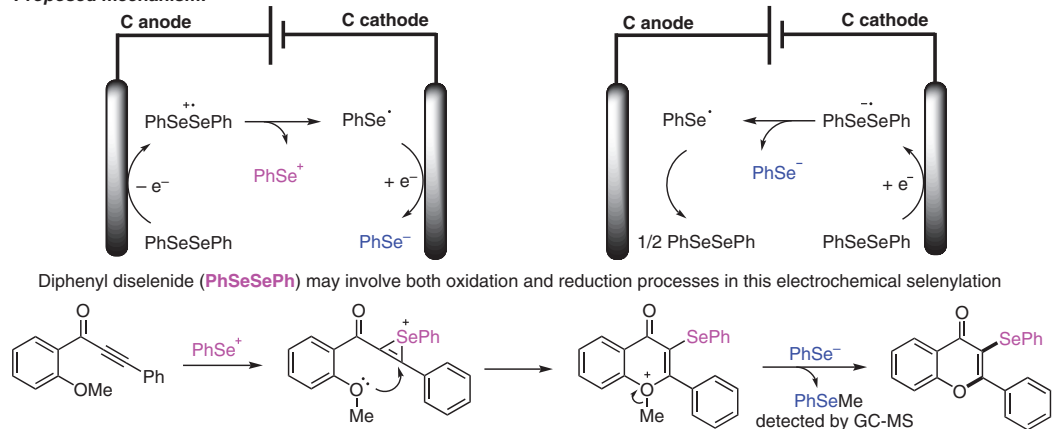
Electrochemical synthesis of selenylated chromones



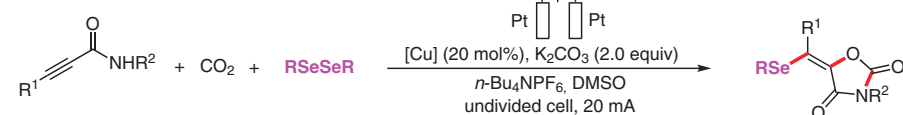
Selected scope

(2f) Ruan, *Adv. Synth. Catal.* **2023**, *365*, 2929.

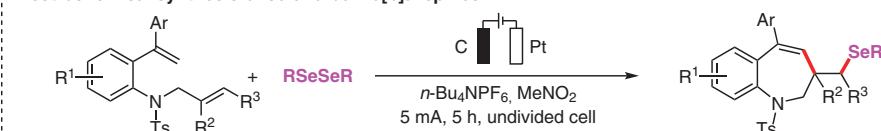
Proposed mechanism:



Electrochemical synthesis of selenylated oxazolidine-2,4-diones

(3x) Liang, *Adv. Synth. Catal.* **2023**, *365*, 2183.

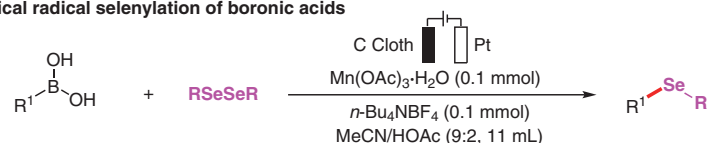
Electrochemical synthesis of seleno-benzo[b]azepines

(3y) Zhang, *J. Org. Chem.* **2023**, *88*, 7245. See also: (3z) Ruan, *Chem. Asian J.* **2022**, *17*, e202200762.Figure 6 Electrochemical selenylation/cyclization (part 3)^{2f,3t-z}

Notable features

- Electrochemical radical selenylation of boronic acids.
- Electrochemical oxidative cross-coupling.
- Electrochemical selenylation of phosphonates.

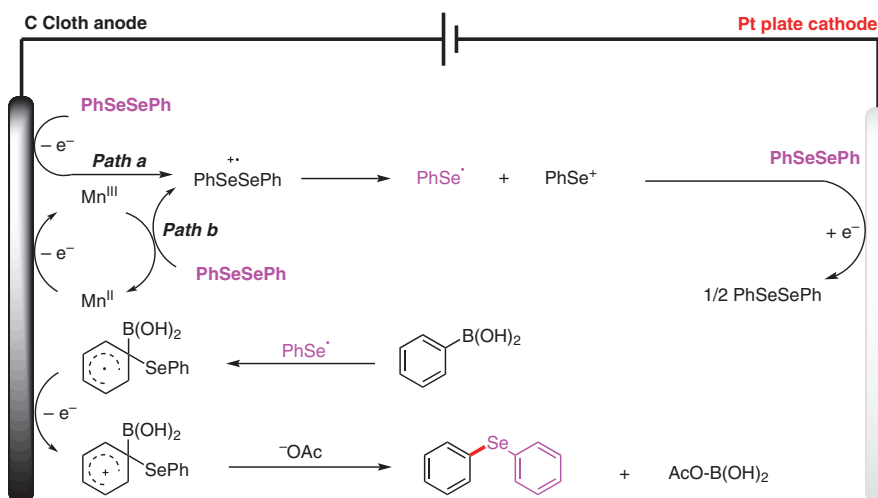
Electrochemical radical selenylation of boronic acids



Selected scope



Proposed mechanism:



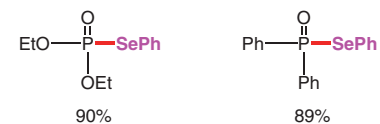
(4a) Lei, *Org. Lett.* **2022**, *24*, 3307. See also: (4b) Cai, *Green Chem.* **2022**, *24*, 130.

Electrochemical selenylation of phosphonates

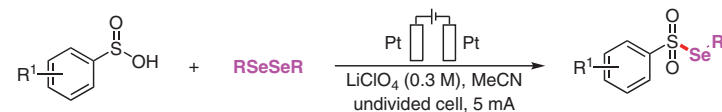


(4d) Guo, *Tetrahedron Lett.* **2020**, *61*, 151566.

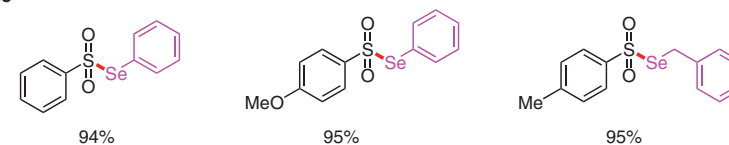
Selected scope



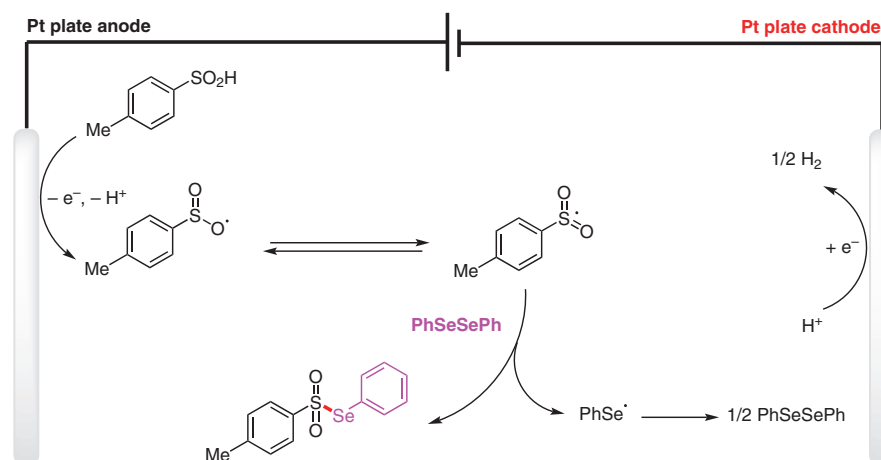
Electrochemical oxidative cross-coupling



Selected scope

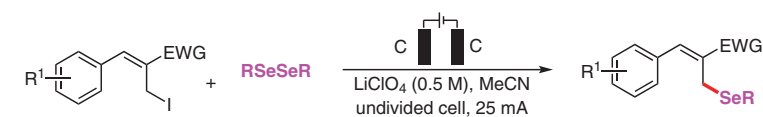


Proposed mechanism:

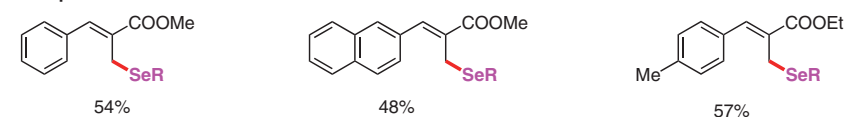


(4c) Sun, *Adv. Synth. Catal.* **2019**, *361*, 2014.

Electrochemical C–Se bond formation



Selected scope



(4e) Badsara, *J. Org. Chem.* **2023**, *88*, 6096.

Figure 7 Electrochemical cross-coupling reactions^{4a–e}

Conflict of Interest

The authors declare no conflict of interest.

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