



## Editorial Organosulfur and Organoselenium Chemistry

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Organosulfur- and organoselenium-containing compounds play a crucial role in organic synthesis. These sulfur-containing molecules are widely applied in pharmaceuticals [1,2], materials [3–5], natural products [6], and food [7,8]. They are also useful building blocks in organic synthesis. Additionally, sulfur and selenium show divergent functions and potencies in different oxidative states, leading to the rich chemistry of their transformations. This *Molecules* Special Issue introduces organosulfur and organoselenium chemistry in fields such as organic synthesis, material, chemical biology, and computational chemistry, and contains eleven articles and four reviews. We collected excellent contributions from scientists across these different research areas, demonstrating the global reach of organosulfur and organoselenium chemistry; the authors contributing to this Special Issue hail from China, Canada, France, Germany, America, Poland, Japan, the Czech Republic, and Croatia. Six articles and three reviews reported on organosulfur chemistry, while five articles and one review reported on organoselenium chemistry.

The contributions related to organosulfur chemistry are summarized briefly below. Madec's article (contribution 1) explored tetrahydro-4H-thiopyran-4-one 1-oxide and sulfinyl-di-tert-butylpropionate as sulfenate sources for the preparation of symmetrical biarylsulfoxides via pallado-catalyzed cross-coupling. Moreover, they discovered a thermally activated delayed fluorescence phenomenon on biarylsulfoxide products via their photophysical studies. Bi et al. (contribution 2) developed a reaction of acetone and thiols promoted by methanesulfonic anhydride/sulfuric acid for the synthesis of thioacetals/thioketals and  $\beta$ -sulfanyl ketones in excellent yields. Their strategy can furnish thioacetals/thioketals and thia-Michael addition products in a controllable manner. Smith's group (contribution 3) explored five durable composites via a simple one-pot reaction of lignin oil and  $S_8$ . These sulfur-containing composites were remelted and reshaped several times without losing mechanical strength, and displayed compressive strengths and flexural strengths exceeding that of ordinary Portland cement. Żurawiński et al. (contribution 4) reported the effect of sulfur oxidation on the structures and photophysical properties of [1]benzothieno[3,2-b][1]benzothiophene (BTBT) derivatives. Their studies found that the process of sulfur oxidation can change the crystal packing, thermal stability, and photophysical properties of BTBT derivatives. Wang et al. (contribution 5) developed a BF<sub>3</sub>·OEt<sub>2</sub>-mediated reaction of alkynes and sodium sulfonates for the preparation of  $\beta$ -keto sulfones in good yields. Their reaction was metal-free, performed under mild conditions and showed good functional group compatibility. Bi et al. (contribution 6) reported the FeCl<sub>3</sub>-catalyzed sulfonylmethylation of imidazo[1,2-α]pyridines, N,Ndimethylacetamide (DMA) and sodium sulfonates in  $H_2O$  conditions (DMA: $H_2O = 2:1$ ). Diverse 3-(sulfonylmethyl)imidazo[1,2- $\alpha$ ]pyridines were furnished in good yields and showed excellent functional group compatibility. Their mechanism studies found that the current reaction may undergo an oxidation addition step, with DMA as the carbon source. The review by Zhao et al. (contribution 7) summarized the representative examples of desulfonylative reactions of inactive  $C(sp^2)$ -SO<sub>2</sub> bonds in (hetero)arylsulfones and their mechanistic insights into these accomplishments. Their review includes two parts: transition metal-catalyzed desulfonylative reactions and photo-/electrocatalytic radical



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**Copyright:** © 2024 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). desulfonylative reactions. The review of Krupka et al. (contribution 8) discussed the synthesis of thionated perylenediimides (PDIs) by using Curphey's reagent (the association of phosphorus pentasulfide with hexamethyldisiloxane) to replace Lawesson's reagent. This review demonstrated that Curphey's reagent displays higher reactivity compared with Lawesson's reagent for the synthesis of multi-thionated PDIs. Queneau's review (contribution 9) summarized the strategies used for synthesizing thioamides using different sulfur sources over the past decade. Elemental sulfur, as one of the most practical and clean reagents used for the synthesis of thioamides, was highlighted in this review.

The contributions related to organoselenium chemistry are summarized below. Back et al. (contribution 10) performed a computational study on a variety of hetero-selenoxide syn elimination reactions, with the heteroatoms including O, N, and S. They found that selenoxides usually have lower activation energies, while the corresponding selenones exhibit higher activation energies. Hilt et al. (contribution 11) developed an electrochemical cross-electrophile coupling reaction by using aryl iodides and diselanes as electrophiles under the conditions of a Ni(acac)<sub>2</sub> catalyst for the synthesis of unsymmetrical diorganyl selanes. Heteroaryl iodides, including thiophene and pyridine derivatives, were very tolerant in their reactions. Yasuike et al. (contribution 12) explored the regioselective C-H selenation of indoles with diaryl diselenides for the general synthesis of 3-selanylindoles by using Bil<sub>3</sub> as a catalyst. Their reaction displayed excellent atomic economy through the utilization of both selanyl groups of the diselenides. Lhoták et al. (contribution 13) reported the Sonogashira coupling of metaiodocalix[4]arene with terminal acetylenes to obtain the corresponding alkynylcalixarenes, which were subsequently subjected to FeCl3- and diorganyl diselenide-mediated electrophilic closure. They found that the calix[4] arenes provided totally different bridging products than the non-macrocyclic starting materials. Blažević et al. (contribution 14) described using morphological changes and changes in glucosinolate content in broccoli and rocket to track the stress caused by selenate. Lukesh et al. (contribution 15) highlighted new  $H_2$ Se-releasing chemical tools and methods for selenide detection and quantification. In their review, they also discussed perspectives and unsolved problems related to H<sub>2</sub>Se donation and detection.

I hope that this Special Issue will be useful to scientists, researchers, and graduate students in the fields of organic chemistry, material chemistry, chemical biology, and computational chemistry, and thank my many prominent colleagues for their contributions.

Conflicts of Interest: The author declares no conflicts of interest.

## List of Contributions

- Magné, V.; Cretoiu, I.; Mallet-Ladeira, S.; Maerten, E.; Madec, D. New Sulfenate Sources for Double Pallado-Catalyzed Cross-Coupling Reaction: Application in Symmetrical Biarylsulfoxide Synthesis, and Evidence of TADF Properties. *Molecules* 2024, 29, 4809. https://doi.org/10.3390/ molecules29204809.
- Ye, H.; Zhao, X.; Fu, Y.; Liu, H.; Li, J.; Bi, X. Controllable Synthesis of Thioacetals/Thioketals and β-Sulfanyl Ketones Mediated by Methanesulfonic Anhydride and Sulfuric Acid Sulfuric Acid from Aldehyde/Acetone and Thiols. *Molecules* 2024, 29, 4785. https://doi.org/10.3390/ molecules29204785.
- Tisdale, K.A.; Kapuge Dona, N.L.; Smith, R.C. The Influence of the Comonomer Ratio and Reaction Temperature on the Mechanical, Thermal, and Morphological Properties of Lignin Oil–Sulfur Composites. *Molecules* 2024, 29, 4209. https://doi.org/10.3390/molecules29174209.
- Rzewnicka, A.; Dolot, R.; Mikina, M.; Krysiak, J.; Żurawiński, R. Modulation of Properties in [1]Benzothieno[3,2-b][1]benzothiophene Derivatives through Sulfur Oxidation. *Molecules* 2024, 29, 3575. https://doi.org/10.3390/molecules29153575.
- Yu, S.-W.; Chen, Z.-J.; Li, H.-Q.; Li, W.-X.; Li, Y.; Li, Z.; Wang, Z.-Y. Oxysulfonylation of Alkynes with Sodium Sulfinates to Access β-Keto Sulfones Catalyzed by BF<sub>3</sub>·OEt<sub>2</sub>. *Molecules* 2024, 29, 3559. https://doi.org/10.3390/molecules29153559.
- Sun, S.; Ye, H.; Liu, H.; Li, J.; Bi, X. Iron-Catalyzed Sulfonylmethylation of Imidazo[1,2α]pyridines with N,N-Dimethylacetamide and Sodium Sulfinates. *Molecules* 2024, 29, 3196. https://doi.org/10.3390/molecules29133196.

- Huang, R.; Gu, B.; Wang, M.; Zhao, Y.; Jiang, X. Desulfonylative Functionalization of Organosulfones via Inert (Hetero)Aryl C(sp<sup>2</sup>)–SO<sub>2</sub> Bond Cleavage. *Molecules* 2024, 29, 4137. https://doi.org/ 10.3390/molecules29174137.
- Kharchenko, O.; Hryniuk, A.; Krupka, O.; Hudhomme, P. Synthesis of Thionated Perylenediimides: State of the Art and First Investigations of an Alternative to Lawesson's Reagent. *Molecules* 2024, 29, 2538. https://doi.org/10.3390/molecules29112538.
- Zhang, Q.; Soulère, L.; Queneau, Y. Towards More Practical Methods for the Chemical Synthesis of Thioamides Using Sulfuration Agents: A Decade Update. *Molecules* 2023, 28, 3527. https://doi.org/ 10.3390/molecules28083527.
- Doig, A.I.; Stadel, J.T.; Back, T.G. A Computational Study of Heteroatom Analogues of Selenoxide and Selenone *syn* Eliminations. *Molecules* 2024, 29, 4915. https://doi.org/10.3390/ molecules29204915.
- 11. Queder, J.; Hilt, G. Electrochemical Nickel-Catalyzed Synthesis of Unsymmetrical Diorganyl Selanes from Diaryl Diselanes and Aryl and Alkyl Iodides. *Molecules* **2024**, *29*, 4669. https://doi.org/10.3390/molecules29194669.
- Matsumura, M.; Umeda, A.; Sumi, Y.; Aiba, N.; Murata, Y.; Yasuike, S. Bismuth(III)-Catalyzed Regioselective Selenation of Indoles with Diaryl Diselenides: Synthesis of 3-Selanylindoles. *Molecules* 2024, 29, 3227. https://doi.org/10.3390/molecules29133227.
- Surina, A.; Salvadori, K.; Poupě, M.; Čejka, J.; Šimková, L.; Lhoták, P. Upper Rim-Bridged Calix[4]arenes via Cyclization of meta Alkynyl Intermediates with Diphenyl Diselenide. *Molecules* 2024, 29, 1237. https://doi.org/10.3390/molecules29061237.
- Đulović, A.; Usanović, K.; Kukoč Modun, L.; Blažević, I. Selenium Biofortification Effect on Glucosinolate Content of Brassica oleracea var. italic and Eruca vesicaria. *Molecules* 2023, 28, 7203. https://doi.org/10.3390/molecules28207203.
- Hankins, R.A.; Lukesh, J.C. An Examination of Chemical Tools for Hydrogen Selenide Donation and Detection. *Molecules* 2024, 29, 3863. https://doi.org/10.3390/molecules29163863.

## References

- 1. Ilardi, E.A.; Vitaku, E.; Njardarson, J.T. Data-Mining for Sulfur and Fluorine: An Evaluation of Pharmaceuticals to Reveal Opportunities for Drug Design and Discovery. *J. Med. Chem.* **2014**, *57*, 2832–2842. [CrossRef] [PubMed]
- Nogueira, C.W.; Zeni, G.; Rocha, J.B.T. Organoselenium and Organotellurium Compounds: Toxicology and Pharmacology. *Chem. Rev.* 2004, 104, 6255–6286. [CrossRef] [PubMed]
- 3. Cinar, M.E.; Ozturk, T. Thienothiophenes, Dithienothiophenes, and Thienoacenes: Syntheses, Oligomers, Polymers, and Properties. *Chem. Rev.* 2015, *115*, 3036–3140. [CrossRef] [PubMed]
- Xianyu, B.; Xu, H. Dynamic covalent bond-based materials: From construction to biomedical applications. Supramolecular Materials 2024, 3, 100070. [CrossRef]
- Xia, J.; Li, T.; Lu, C.; Xu, H. Selenium-Containing Polymers: Perspectives toward Diverse Applications in Both Adaptive and Biomedical Materials. *Macromolecules* 2018, *51*, 7435–7455. [CrossRef]
- Wang, N.; Saidhareddy, P.; Jiang, X. Construction of Sulfur-containing Moieties in the Total Synthesis of Natural Products. *Nat. Prod. Rep.* 2020, *37*, 246–275. [CrossRef] [PubMed]
- Sansom, C.E.; Jones, V.S.; Joyce, N.I.; Smallfield, B.M.; Perry, N.B.; van Klink, J.W. Flavor, Glucosinolates, and Isothiocyanates of Nau (Cook's Scurvy Grass, *Lepidium oleraceum*) and Other Rare New Zealand *Lepidium* Species. *J. Agric. Food Chem.* 2015, 63, 1833–1838. [CrossRef] [PubMed]
- 8. Rotruck, J.T.; Pope, A.L.; Ganther, H.E.; Swanson, A.B.; Hafeman, D.G.; Hoekstra, W.G. Selenium: Biochemical Role as a Component of Glutathione Peroxidase. *Science* **1973**, *179*, 588–590. [CrossRef] [PubMed]

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