RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2023, **13**, 914

Silver-catalyzed direct selanylation of indoles: synthesis and mechanistic insights†

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Received 28th October 2022
Accepted 17th December 2022

DOI: 10.1039/d2ra06813c

rsc.li/rsc-advances

Herein we describe the Ag(I)-catalyzed direct selanylation of indoles with diorganoyl diselenides. The reaction gave 3-selanylindoles with high regioselectivity and also allowed direct access to 2-selanylindoles when the C3 position of the indole ring was blocked *via* a process similar to Plancher rearrangement. Experimental analyses and density functional theory calculations were carried out in order to picture the reaction mechanism. Among the pathways considered (*via* concerted metalation–deprotonation, Ag(III), radical, and electrophilic aromatic substitution), our findings support a classic electrophilic aromatic substitution *via* Lewis adducts between Ag(I) and diorganoyl diselenides. The results also afforded new insights into the interactions between Ag(I) and diorganoyl diselenides.

Introduction

Coinage metal (copper, silver, and gold) salts are among the major players in modern catalysis.[1] Although silver catalysts have long been believed to have low catalytic efficiency in comparison with other coinage metals, the rapid development of silver chemistry revealed several valuable synthetic transformations over the last two decades.[2] In addition, silver has been applied as homogeneous or heterogeneous mediators or catalysts in important industrial applications.[2e,3] In particular, Ag(I) salts are employed as σ-Lewis acids due to the availability of their empty f orbitals and relativistic contraction of the electron cloud[14,1a,b,2a] and as a π-Lewis acid as a result of the d^{10} electronic configuration which allows the back-donation of electron density to the antibonding π* orbitals.[1a,b,2a,4] These features offer numerous opportunities in organic synthesis. For instance, Ag(I) salts have been used in cycloadditions,[5] alkynylations,[2a,6] cycloisomerizations,[7] hydrofunctionalizations,[8] halogenations,[9] azidations,[10] C–H functionalizations,[2c,11] and chalcogenylations[12] and also as additives in transition metal-catalyzed reactions.[13]

Selenium-containing compounds are of great importance since they show numerous biological activities[14] and also play an important role in organic synthesis[12a,15] and materials science.[16] For instance, selenium or sulfur-functionalized indoles display promising therapeutic properties,[17] and some of them are already commercially-available drugs (Fig. 1).[18] In this scenario, the development of efficient and selective methods for the C–Se bond formation have become of paramount importance, which encourages studies on the direct conversion of an inert C–H bond to a C–Se bond that can eliminate pre-functionalized starting materials, resulting in more step- and atom-economical synthesis.[12a,19]

Generally, the direct selanylation of indole derivatives under transition metal-catalyzed[20] or transition metal-free conditions[21] relies on the nucleophilicity of the C3 position of this electron-rich heteroarene, and structurally diverse 3-selanylindoles were prepared using these methodologies. Despite the advantages of the transition-metal free methods, the use of stoichiometric amounts of catalysts or the synthesis of starting materials through multistep transformations limits their applications. With this in mind, we report the Ag(I)-catalyzed regioselective C3 selanylation of indoles without the addition of any external additive or ligand in a single step. The mechanism of this reaction was also further investigated by means of density functional theory (DFT) calculations.

Results and discussion

As shown in Table 1, 1-methylindole (**1a**) and diphenyl diselenide (**2a**) were employed to optimize the reaction conditions

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d2ra06813c

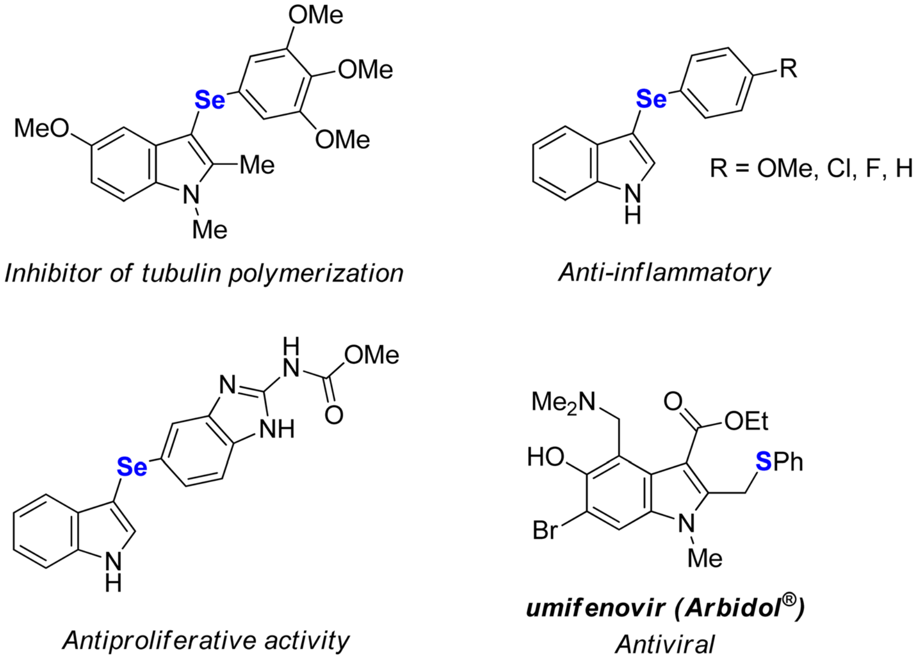


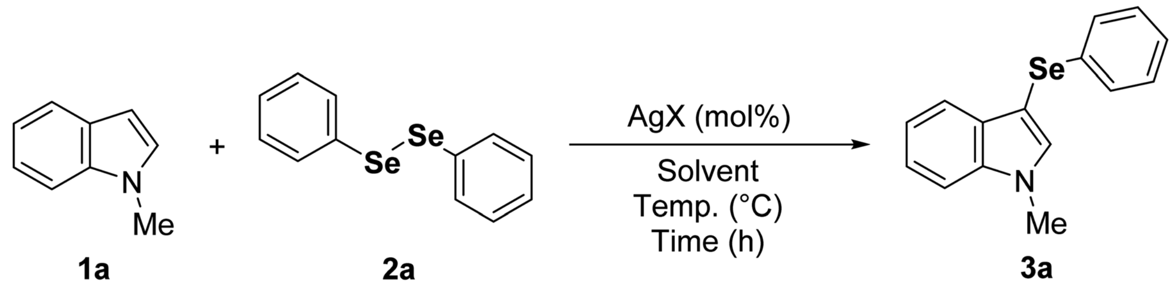
Fig. 1 Biologically relevant selenium or sulfur-functionalized indoles.

(Table 1). The first experiment was developed with 5.0 mol% Ag_2SO_4 in DMSO (dimethyl sulfoxide) as the solvent at 100 °C for 24 h, which furnished a 23% yield of the desired product **3a** (Table 1, entry 1). Under the same conditions of time and temperature, when the amount of Ag_2SO_4 was increased to 10 mol% and 20 mol% the product **3a** was obtained in 42% and 79% yields respectively (Table 1, entries 2 and 3). Additionally, the use of 30 mol% Ag_2SO_4 gave the expected product in 87% yield (Table 1, entry 4). Considering the good yields of the desired product obtained with 20 mol% Ag_2SO_4, the influence of the reaction time was evaluated under this condition. It was observed that a shorter reaction time slightly increased the yield of **3a** to 85% (Table 1, entry 5); however, an even shorter time provided the product in a 65% yield (Table 1, entry 6). Next, the reaction temperature was also evaluated (Table 1, entries 7 and 8), and when the experiments were performed at lower temperatures, the yields of **3a** were lower than that observed at 100 °C (Table 1, entry 5). On the other hand, when the temperature was 110 °C, the reaction yield was 83% (Table 1, entry 9). In addition, when the reaction was carried out under inert atmosphere, the yield was 56%, which suggests that O_2 could be involved in the reaction pathway (Table 1, entry 10). The screening of the catalyst revealed that other sources of Ag(I) were not effective even when the mol% amount of Ag(I) ions in the system were matched (Table 1, entries 11–15) to the reaction with Ag_2SO_4 (Table 1, entry 5). Finally, among the solvents examined (Table 1, entries 16–23), DMSO was still the most effective (Table 1, entry 5).

To further examine the efficiency of this reaction, the substrate scope was evaluated (Table 2) under the best reaction parameters (Table 1, entry 5). The results demonstrated that the indole **1a** was selanylated at the C3 position with moderate to good yields employing diaryl diselenides with either electron-donating or electron-withdrawing groups (**3a–e**). In general, higher yields were observed with diaryl diselenides bearing electron-donating groups (**3b** and **3c**), and longer times did not improve the yields of reactions employing diaryl diselenides with electron-withdrawing groups (**3d** and **3e**). Moreover, sterically-hindered diaryl diselenides were tolerated; however, only moderate reaction yields were obtained (**3f** and **3g**). The reaction also worked with dialkyl diselenides, but the compound **3h** was obtained in only 38% yield. On the other hand, the reaction of 1-benzylindole or indole afforded good yields of **3i** and **3j**, respectively. In these cases, longer times (24 h) slightly increased the reaction yields. Surprisingly, the protocol allows the direct access to 2-selanylindoles (**3l**) when the C3 position of the indole ring was blocked (escatol), probably *via* a process similar to Plancher rearrangement.[20b,22] In addition, the electron-richer 1,2-dimethylindole provided a good yield of **3k** despite its more sterically-hindered C3 position, and a low yield of **3m** was obtained when diphenyl disulfide was employed instead of diphenyl diselenide (**2a**). Finally, the method was not suitable for diaryl ditellurides, and the product **3n** was not detected under standard conditions.

To obtain more insights into the mechanism of the current reaction, radical scavenging experiments were conducted by adding 1.0 equivalent of 2,6-di-*tert*-butyl-4-methylphenol (BHT) or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The reaction with BHT proceeded smoothly to afford the product **3a** without affecting the yield (Scheme 1a), and the addition of TEMPO reduced the yield but did not completely suppress the reaction, which suggests that a radical pathway would not be dominant. The radical mechanism was further ruled out by an experiment employing 1.0 equivalent of diphenyl diselenide (**2a**) and

Table 1 Optimization of the reaction conditions



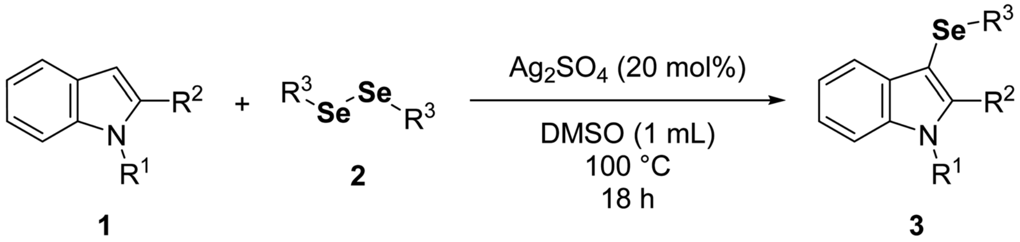
Entry[a]	Catalyst (mol%)	Solvent	Time (h)	Temp. (°C)	Yield[b,d] (%)
1	Ag_2SO_4 (5)	DMSO (1.0)	24	100	23
2	Ag_2SO_4 (10)	DMSO (1.0)	24	100	42
3	Ag_2SO_4 (20)	DMSO (1.0)	24	100	79
4	Ag_2SO_4 (30)	DMSO (1.0)	24	100	87
5	**Ag_2SO_4 (20)**	**DMSO (1.0)**	**18**	**100**	**85**
6	Ag_2SO_4 (20)	DMSO (1.0)	12	100	65
7	Ag_2SO_4 (20)	DMSO (1.0)	18	80	66
8	Ag_2SO_4 (20)	DMSO (1.0)	18	60	58
9	Ag_2SO_4 (20)	DMSO (1.0)	18	110	83
10[c]	Ag_2SO_4 (20)	DMSO (1.0)	18	100	56
11	$AgNO_3$ (20)	DMSO (1.0)	18	100	32
12	$AgNO_3$ (40)	DMSO (1.0)	18	100	60
13	$AgBF_4$ (40)	DMSO (1.0)	18	100	29
14	AgCl (40)	DMSO (1.0)	18	100	25
15	AgOAc (40)	DMSO (1.0)	18	100	36
16	Ag_2SO_4 (20)	DMF (1.0)	18	100	37
17	Ag_2SO_4 (20)	NMP (1.0)	18	100	45
18	Ag_2SO_4 (20)	1,4-Dioxane (1.0)	18	100	11
19	Ag_2SO_4 (20)	Isopropanol (1.0)	18	100	9
20	Ag_2SO_4 (20)	Water	18	100	33
21	Ag_2SO_4 (20)	THF	18	100	32
22	Ag_2SO_4 (20)	DCE	18	100	2
23	Ag_2SO_4 (20)	Toluene	18	100	20

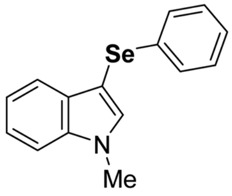
[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.25 mmol), AgX (mol%) and dry solvent (1.0 mL) under air atmosphere. [b] Isolated yields. [c] Under argon atmosphere. [d] In all reactions, we have not identified any side products.

TEMPO, which afforded a 70% yield of **3a** (Scheme 1a). In order to evaluate if Lewis adducts between Ag(I) and diorganoyl diselenides (**1**) are involved in the mechanism, we conducted an experiment using anions with a high affinity to Ag(I) that can compete with diorganoyl diselenides (**1**) (Scheme 1b). In this way, the reaction yield of **3a** was only 11% with KBr as an additive (1.0 equivalent) under optimized conditions, which indicates that these Lewis adducts could be involved. The yield of **3a** was 35% when the reaction was developed under inert atmosphere (Scheme 1c), which suggests an important role for O_2 from atmospheric air in this protocol. In addition, when the reaction was carried out in another polar aprotic solvent (*N*,*N*-dimethylformamide, DMF) under O_2 atmosphere, the yield of **3a** was increased to 45% (Scheme 1d) when compared to the reaction in DMF under air atmosphere (Table 1, entry 16; Scheme 1d). Regarding the role of O_2 from atmospheric air (Scheme 1d), given the reaction stoichiometry of **1** (0.50 mmol) and **2** (0.25 mmol), it seems that O_2 can restore the diorganoyl diselenides (**1**) by oxidation of the Ag(I)-organoselenolate.[23] It is well known that DMSO can also regenerate diorganoyl diselenides (**1**) by oxidation of organoselenolate anions;[24] however, an experiment using DMF and 5.0 equivalents of DMSO under inert atmosphere gave only 28% of **3a**, further supporting the role of O_2 in this reaction (Scheme 1d). Given the data obtained from the control experiments (Scheme 1), plus the reaction regioselectivity at C3 position of indoles (**1**), we believe that the favorable interaction between the soft Lewis acid Ag(I) and the soft Lewis base selenium on the diorganoyl diselenides (**2**) is crucial in reducing the diselenide bond order, then accelerating its nucleophilic cleavage by the indole derivatives (**1**) *via* electrophilic aromatic substitution.[23e,25]

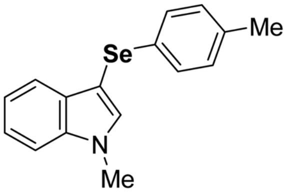
In order to further shed light on the reaction mechanism, calculations at the M06-2X/BS level of theory (BS: LANL2DZ for Ag atom and 6-311++G(d,p) for other atoms) were performed (computational details are provided in the Experimental section). Considering that a radical pathway does not have support based on the experimental results (Scheme 1), additional plausible mechanistic proposals were investigated

Table 2 Substrate scope for silver-catalyzed direct selanylation of indoles[a,b]

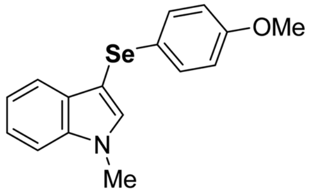




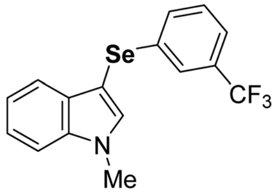
3a (85%)



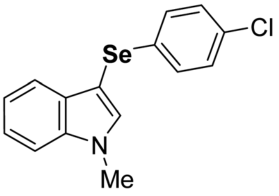
3b (80%)



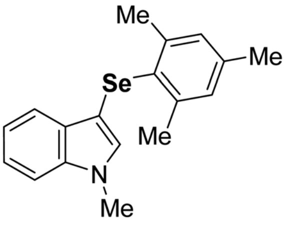
3c (88%)



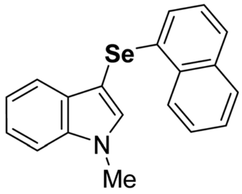
3d (62%), (60%)[c]



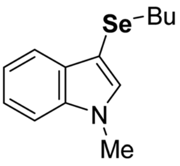
3e (68%), (65%)[c]



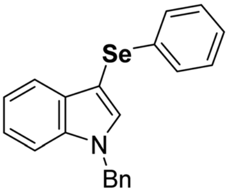
3f (65%)



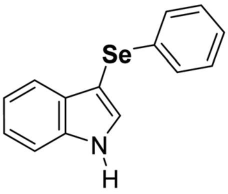
3g (62%)



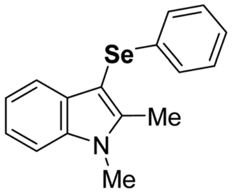
3h (38%)



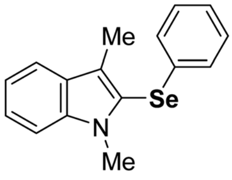
3i (72%), (92%)[c]



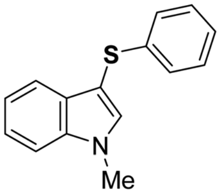
3j (72%), (82%)[c]



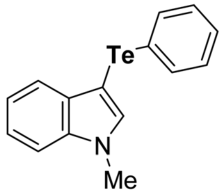
3k (58%), (84%)[c]



3l (37%), (64%)[c]

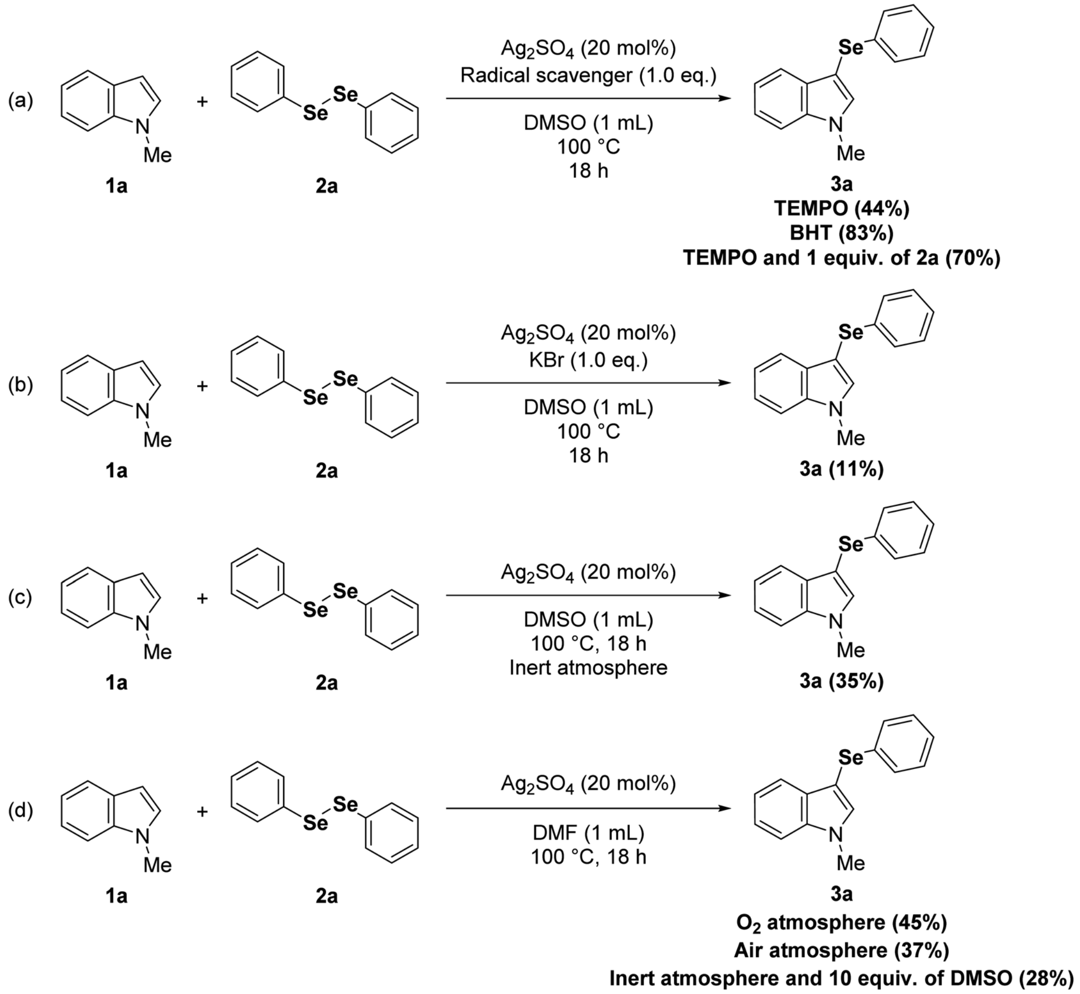


3m (35%)



3n (0%)

[a] Reaction conditions: **1** (0.50 mmol), **2** (0.25 mmol), Ag_2SO_4 (20 mol%) and dry DMSO (1.0 mL) under air atmosphere. [b] Isolated yields. [c] 24 h.



Scheme 1 Control experiments for mechanistic studies.

considering the reaction between **1a** and **2a** in the presence of Ag_2SO_4. In a recent work on the silver-catalyzed synthesis of diaryl selenides using arylboronic acids,[26] authors proposed that the reaction mechanism involves the formation of [RSe–Ag(III)–SeR]$^+$ as a key intermediate, leading to the final product R–Se–Ar after additional steps. We checked this hypothesis for the formation of **3a**; however, all of the attempts to optimize [PhSe–Ag(III)–SePh]$^+$ as a minimum failed, leading to **2a** coordinated with Ag(I). For that reason, we turned our attention to two other mechanisms: (i) concerted metalation–deprotonation (CMD) and (ii) electrophilic aromatic substitution. For mechanism (i), the transition state structure (TSS_1(i)) involved in a CMD process was located as presented in Fig. 2, consistent with the formation of a new Ag(I)–C bond concerted with the deprotonation of **1a** by SO_4^{2-}. For such event, an energy barrier of 28.7 kcal mol^{-1} was found. As mentioned, all attempts to optimize Ag(III)–phenylselenolate produced from an oxidative addition of **2a** to Ag(I) as a minimum failed; however, we found that the reaction proceeds to the rate determining step forming **3a** *via* nucleophilic attack of the C3 atom of Ag(I)–indole intermediate (INT(i)) to **2a** with a barrier of 35.0 kcal mol^{-1} in an overall endergonic process. The CMD mechanism is commonly observed for higher valency transition metals (*e.g.*, Pd(II), Rh(III), Ru(II)), therefore the barrier likely relies on low valence nature of Ag(I).

Regarding mechanism (ii), taking into account the solvated ions in DMSO (Ag(I) and SO_4^{2-}), a TSS consistent with the nucleophilic attack of indole C3 to **2a** forming a new Se–C bond was located (TSS_1(ii)). As shown in Fig. 3, an initial complex formed by **1a** and **2a** coordinated with Ag(I) was confirmed. A rate determining energy barrier of 25.3 kcal mol^{-1} was observed, emphasizing the key role of the catalyst supporting the phenylselenolate departure. On the basis of bond distances, results indicate that the first step of the reaction occurs asynchronously; in the TSS_1(ii), the Se–C bond formation is 87% completed, whereas the Se–Se bond is only 35% cleaved. Although we managed to locate the TSS involved in the deprotonation of the tetrahedral intermediate (INT(ii)) by the sulfate ion (TSS_2(ii)), calculations suggest that the formation of **3a**, along with the regeneration of the catalyst, occurs in a barrierless fashion, as TSS_2(ii) features a lower energy (17.9 kcal mol^{-1}) than the preceding stationary point (19.5 kcal mol^{-1}), as depicted in Fig. 3. We have also investigated the deprotonation of INT(ii) promoted by Ag(I)–phenylselenolate formed in the

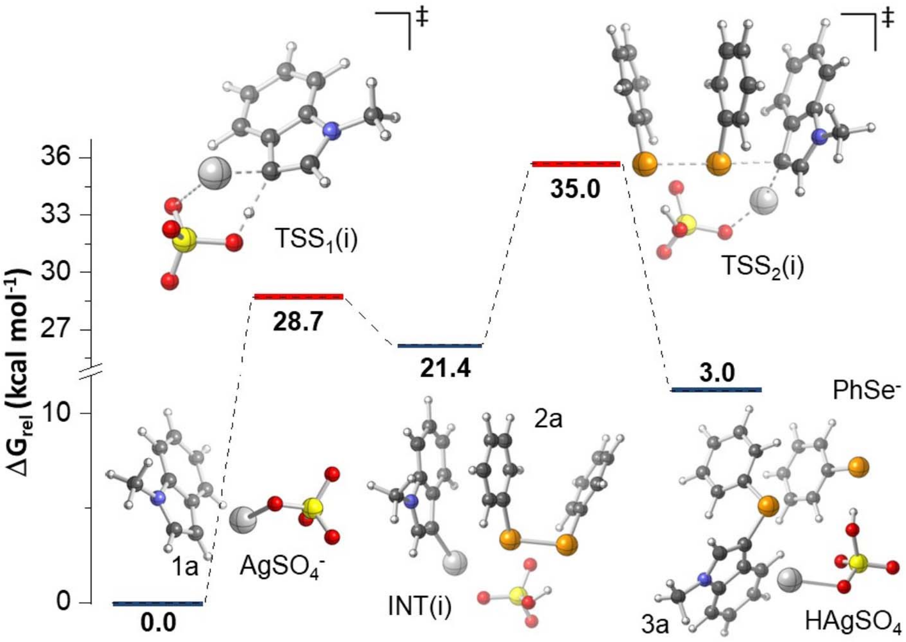


Fig. 2 Potential energy surface (PES) of the CMD mechanism (i) proposed for the formation of **3a** obtained using M062X functional combined with LANL2DZ (for Ag atom) and 6-311++G(d,p) (for additional atoms). Atom color: S-yellow, O-red, Se-orange, N-blue, C-gray, and H-white.

first step. In this case, however, the results indicated a much higher energy barrier of 30.9 kcal mol^{-1}, confirming that the reaction pathway involves sulfate ions acting as a base (details are provided in ESI†). Despite the well-known higher basicity of free phenylselenolate, it seems that the soft Lewis acid Ag(I) considerably reduces its basicity, therefore the deprotonation

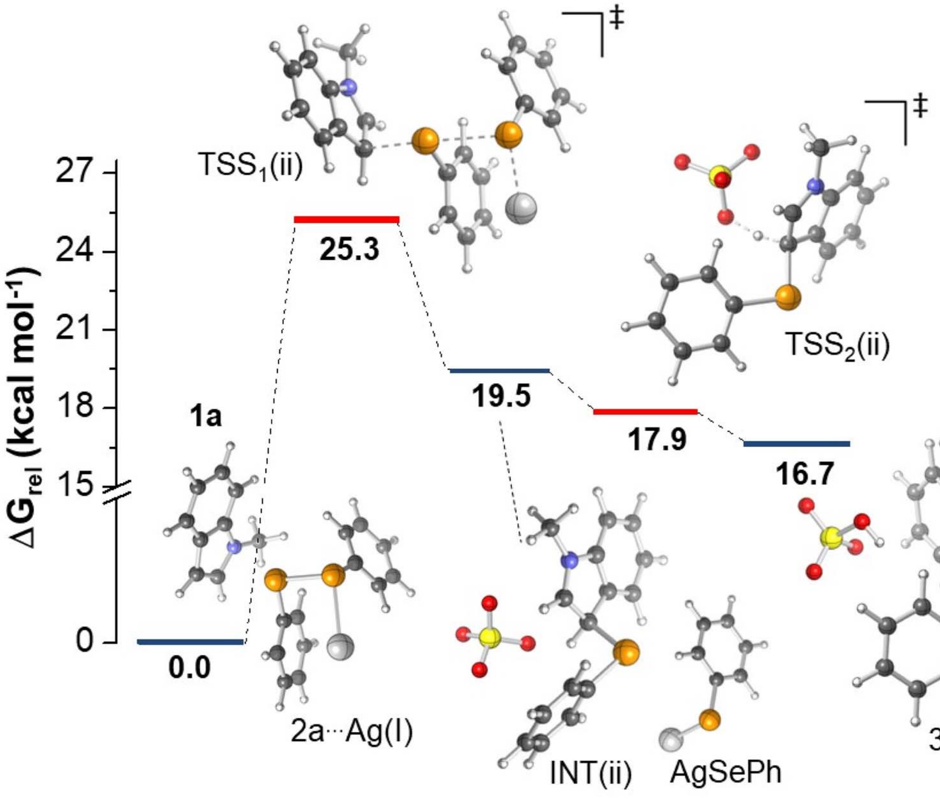
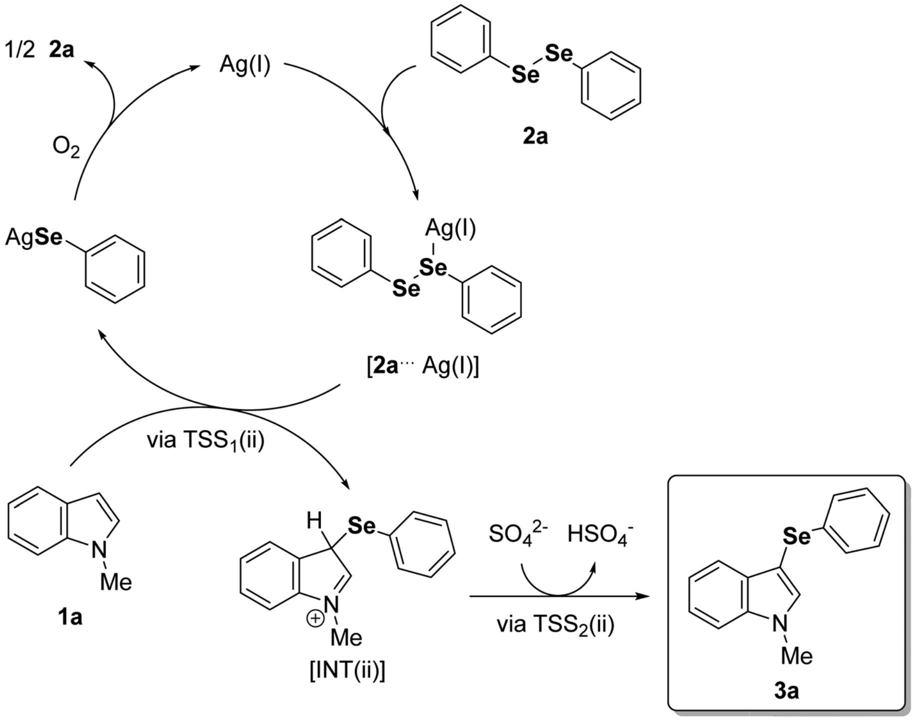


Fig. 3 Potential energy surface (PES) of the electrophilic substitution mechanism (ii) proposed for the formation of **3a** obtained using M062X functional combined with LANL2DZ (for Ag atom) and 6-311++G(d,p) (for additional atoms).



Scheme 2 Full catalytic cycle.

with free sulfate ion has a lower energy barrier. Although additional proposals could be envisioned, our calculations suggest that the classic electrophilic aromatic substitution mechanism for silver-catalyzed selanylation of indoles is predicted to be energetically feasible, considering the experimental conditions evaluated herein.

In view of the experimental data and theoretical calculations, we found that the energetically plausible mechanism follows a classic electrophilic aromatic substitution, where the interaction between the soft Lewis acid Ag(I) and the soft Lewis base selenium on the diorganoyl diselenides (**2**) is crucial to support the organoylselenolate departure (Fig. 3). Also, we obtained experimental data agreeing with O_2 from air atmosphere restoring the diorganoyl diselenides (**1**) by oxidation of the Ag(I)–organoselenolates.[23] Scheme 2 outlines the full catalytic cycle exemplified by **1a** and **2a**, which starts with the formation of a Lewis adduct between Ag(I) and diphenyl diselenide (**2a**) (Fig. 3, **2a**···Ag(I)). Then, the nucleophilic attack of the C3 position of 1-methylindole (**1a**) to the Se–Se bond *via* TSS_1(ii) releases the Wheland intermediate INT(ii) and Ag(I)–phenylselenolate. Finally, the aromaticity is restored *via* a barrierless deprotonation with a sulfate anion to afford **3a**.

Conclusions

In summary, we developed the Ag(I)-catalyzed direct selanylation of indoles with diorganoyl diselenides. The reaction gave 3-selanylindoles with high regioselectivity and also allowed the direct access to 2-selanylindoles when the C3 position of the indole ring was blocked *via* a process similar to Plancher rearrangement. DFT calculations failed to optimize Ag(III)–organoylselenolates to a minimum, ruling out these intermediates. Experimental and theoretical data supported an energetically plausible mechanism in which Lewis adducts between Ag(I) and diorganoyl diselenides follow an electrophilic aromatic substitution with subsequent barrierless deprotonation by a sulfate anion to afford 3-selanylindoles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior do Brasil (CAPES) – Finance Code 001 and the Federal University of Paraná (UFPR). D. S. R. thanks Fernando da Silveira Rampon from the Content Plus Digital Agency (https://agenciamaisconteudo.com/en/) for the graphical abstract art.

References

1 (*a*) C.-J. Li and X. Bi, *Silver Catalysis in Organic Synthesis*, Wiley, 1st edn, 2019, vol. 2; (*b*) M. Hermata, *Silver in Organic Chemistry*, Wiley, 1st edn, 2011; (*c*) A. M. Echavarren, N. Jiao and V. Gevorgyan, Coinage metals in organic synthesis, *Chem. Soc. Rev.*, 2016, **45**, 4445; (*d*) A. J. Jordan, G. Lalic and J. P. Sadighi, Coinage metal hydrides: synthesis, characterization, and reactivity,

Chem. Rev., 2016, **116**, 8318; (*e*) V. K.-Y. Lo, A. O.-Y. Chan and C.-M. Che, Gold and silver catalysis: from organic transformation to bioconjugation, *Org. Biomol. Chem.*, 2015, **13**, 6667; (*f*) M. M. Díaz-Requejo and P. J. Pérez, Coinage metal catalyzed C-H bond functionalization of hydrocarbons, *Chem. Rev.*, 2008, **108**, 3379; (*g*) B. H. Lipshutz and Y. Yamamoto, Introduction: coinage metals in organic synthesis, *Chem. Rev.*, 2008, **108**, 2793.

2 (*a*) G. Fang and X. Bi, Silver-catalysed reactions of alkynes: recent advances, *Chem. Soc. Rev.*, 2015, **44**, 8124; (*b*) H. Pelissier, Enantioselective silver-catalyzed transformations, *Chem. Rev.*, 2016, **116**, 14868; (*c*) S. Radhika, C. M. A. Abdulla, T. Aneeja and G. Anilkumar, Silver-catalysed C-H bond activation: a recent review, *New J. Chem.*, 2021, **45**, 15718; (*d*) K. Sekine and T. Yamada, Sylver-catalyzed carboxylation, *Chem. Soc. Rev.*, 2016, **45**, 4524; (*e*) M. Naodovic and H. Yamamoto, Asymmetric silver-catalyzed reactions, *Chem. Rev.*, 2008, **108**, 3132; (*f*) N. Kaur, N. Ahlawat, P. Bhardwaj, Y. Verma, P. Grewal and N. K. Jangid, Ag-mediated synthesis of six-membered *N*-heterocycles, *Synth. Commun.*, 2020, **50**, 753; (*g*) M. Neetha, T. Aneeja, C. M. A. Afsina and G. Anilkumar, An Overview of Ag-catalyzed Synthesis of Six-membered Heterocycles, *ChemCatChem*, 2020, **12**, 5330; (*h*) P. Li, W. Wu and H. Jiang, Recent Advances in Silver-Catalyzed Transformations of Electronically Unbiased Alkenes and Alkynes, *ChemCatChem*, 2020, **12**, 5034; (*i*) M. Álvarez-Corral, M. Muñoz-Dorado and I. Rodríguez-García, Silver-mediated synthesis of heterocycles, *Chem. Rev.*, 2008, **108**, 3174; (*j*) P. Sivaguru, S. Cao, K. R. Babu and X. Bi, Silver-catalyzed activation of terminal alkynes for synthesizing nitrogen-containing molecules, *Acc. Chem. Res.*, 2020, **53**, 662.

3 (*a*) C. Wen, A. Yin and W.-L. Dai, Recent advances in silver-based heterogeneous catalysts for green chemistry process, *Appl. Catal., B*, 2014, **160**, 730; (*b*) G. J. Millar and M. Collins, Industrial production of formaldehyde using polycrystalline silver catalyst, *Ind. Eng. Chem. Res.*, 2017, **56**, 9247.

4 (*a*) D. J. Gorin and F. D. Toste, Relativistic effects in homogeneous gold catalysis, *Nature*, 2007, **446**, 395; (*b*) P. Pyykkö, Theoretical chemistry of gold, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412; (*c*) P. S. Bagus, Y. S. Lee and K. S. Pitzer, Effects of relativity and of the lanthanide contraction on the atoms from hafnium to bismuth, *Chem. Phys. Lett.*, 1975, **33**, 408.

5 Selected examples:(*a*) F. Jia and B. Zhang, Mechanistic insight into the silver-catalyzed cycloaddition synthesis of 1,4-disubstituted-1,2,3-triazoles: the key of the role of silver, *New J. Chem.*, 2019, **43**, 8634; (*b*) S. Wang, L.-J. Yang, J.-L. Zeng, Y. Zheng and J.-A. Ma, Silver-catalyzed [3+2] cycloaddition of isocyanides with diazo compounds: new regioselective access to 1,4-disubstituted-1,2,3-triazoles, *Org. Chem. Front.*, 2015, **2**, 1468; (*c*) J. McNulty, K. Keskar and R. Vemula, The First Well-Defined Silver (I)-Complex-Catalyzed Cycloaddition of Azides onto Terminal Alkynes at Room Temperature, *Chem.–Eur. J.*, 2011, **17**, 14727; (*d*) I. Nakamura, T. Nemoto, Y. Yamamoto and A. Meijere, Thermally induced and silver-salt-catalyzed [2+2] cycloadditions of imines to (alkoxymethylene) cyclopropanes, *Angew. Chem., Int. Ed.*, 2006, **45**, 5176; (*e*) S. Zhu, R. Liang, H. Jiang and W. Wu, An Efficient Route to Polysubstituted Tetrahydronaphtols: Silver-Catalyzed [4+2] Cyclization of 2-Alkylbenzaldehydes and Alkene, *Angew. Chem., Int. Ed.*, 2012, **51**, 10861; (*f*) M. Gao, H. Chen, R. Bai, B. Cheng and A. Lei, Synthesis of pyrroles by click reaction: silver-catalyzed cycloaddition of terminal alkynes with isocyanides, *Angew. Chem., Int. Ed.*, 2013, **52**, 6958.

6 Selected examples:(*a*) M. Meng, G. Wang, L. Yang, K. Cheng and C. Qi, Silver-Catalyzed Double Decarboxylative Radical Alkynylation/Annulation of Arylpropiolic Acid with α-keto Acids: Access to Ynones and Flavones under Mild Conditions, *Adv. Synth. Catal.*, 2018, **360**, 1218; (*b*) X. Liu, Z. Wang, X. Cheng and C. Li, Silver-Catalyzed Decarboxylative Alkynylation of Aliphatic Carboxylic Acids in Aqueous Solution, *J. Am. Chem. Soc.*, 2012, **134**, 14330; (*c*) F. Lazreg, M. Lesieur, A. J. Samson and C. S. J. Cazin, Light-Stable Silver N-Heterocyclic Carbene Catalysts for the Alkynylation ok Ketones in Air, *ChemCatChem*, 2016, **8**, 209; (*d*) U. Halbes-Letinois, J.-M. Weibel and P. Pale, The organic chemistry of silver acetylides, *Chem. Soc. Rev.*, 2007, **36**, 759.

7 Selected examples:(*a*) M. Abreu, Y. Tang, E. Brachet, M. Selkti, V. Michelet and P. Belmont, Silver-catalyzed tandem cycloisomerization/hydroarylation reactions and mechanistic investigations for an efficient access to 1,2-dihydroisoquinolines, *Org. Biomol. Chem.*, 2021, **19**, 1037; (*b*) X. Bantreil, A. Bourderioux, P. Mateo, C. E. Hagerman, M. Selkti, E. Brachet and P. Belmont, Phosphine-triggered selectivity switch in silver-catalyzed *o*-alkynylbenzohydroxamic acid cycloisomerizations, *Org. Lett.*, 2016, **18**, 4814; (*c*) P. Belmont and E. Parker, Silver and gold catalysis for cycloisomerization reactions, *Eur. J. Org. Chem.*, 2009, **2009**, 6075; (*d*) J. A. Marshall and G. S. Bartley, Observations regarding the Ag(I)-catalyzed conversion of allenones to furans, *J. Org. Chem.*, 1994, **59**, 7169; (*e*) D. S. Ermolat'ev, V. P. Mehta and E. V. V. Eycken, Ag^+-mediated synthesis of substituted furo[2,3-*b*]pyrazines, *Synlett*, 2007, **20**, 3117.

8 Selected examples:(*a*) M. Li, W. Wu and H. Jiang, Recent Advances in Silver-Catalyzed Transformations of Electronically Unbiased Alkenes and Alkynes, *ChemCatChem*, 2020, **12**, 5034; (*b*) A. Luna, F. Herrera, S. Higuera, A. Murillo, I. Fernandéz and P. Almendros, $AgNO_3$-SiO_2: convinient AgNPs source for the sustainable hydrofunctionalization of alllenyl-indoles using heterogeneous catalysis, *J. Catal.*, 2020, **389**, 432; (*c*) X. Hong, F. Ma, D. Zha and H. Li, Silver-Catalyzed Stereoselective *trans* Addition of 4-Hydrocoumarins to Haloalkynes and Late-Stage Nitration, *Asian J. Org. Chem.*, 2018, **7**, 2552; (*d*) Z. Chen, J. Li, H. Jiang, S. Zhu, Y. Li and C. Qi, Silver-catalyzed difunctionalization of terminal alkynes: highly regio- and stereoselective synthesis of (*Z*)-β-haloenol acetates, *Org. Lett.*, 2010, **12**, 3262; (*e*) G. Jiang,

C. Zhu, J. Li, W. Wu and H. Jiang, Silver-Catalyzed Regio- and Stereoselective Thiocyanation of Haloalkynes: Access to (*Z*)-Vinyl Thiocyanates, *Adv. Synth. Catal.*, 2017, **359**, 1208; (*f*) J. Zhang, L.-G. Meng, P. Li and L. Wang, The sequential reactions of tetrazoles with bromoalkynes for the synthesis of (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides and 2-arylindoles, *RSC Adv.*, 2013, **3**, 6807.

9 Selected examples:(*a*) R. Al-Zoubi and D. G. Hall, Mild silver(I)-mediated regioselective iodination and bromination of arylboronic acids, *Org. Lett.*, 2010, **12**, 2480; (*b*) T. Furuya and T. Ritter, Fluorination of boronic acids mediated by silver(I) triflate, *Org. Lett.*, 2009, **11**, 2860; (*c*) X. Tan, T. Song, Z. Wang, H. Chen, L. Cui and C. Li, Silver-catalyzed decarboxylative bromination of aliphatic carboxylic acids, *Org. Lett.*, 2017, **19**, 1634; (*d*) W. Wu, S. Yi, W. Huang, D. Luo and H. Jiang, Ag-catalyzed oxidative cyclization reaction of 1,6-enynes and sodium sulfinate: access to sulfonylated benzofurans, *Org. Lett.*, 2017, **19**, 2825; (*e*) Z. Wang, *Comprehensive Organic Name Reactions and Reagents*, Wiley, 1st edn, 2010, vol. 3.

10 Selected examples:(*a*) C. Liu, X. Wang, Z. Li, L. Cui and C. Li, Silver-catalyzed decarboxylative radical azidation of aliphatic carboxylic acids in aqueous solution, *J. Am. Chem. Soc.*, 2015, **137**, 9820; (*b*) Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song and X. Bi, Silver(I)-catalyzed hydroazidation of ethynyl carbinols: synthesis of 2-azidoallyl alcohols, *Angew. Chem., Int. Ed.*, 2014, **53**, 5305; (*c*) Y. Ning, N. Wu, H. Yu, P. Liao, X. Li and X. Bi, Silver-catalyzed tandem hydroazidation/alkyne-azide cycloaddition of dyines with TMS-N_3: an easy access to 1,5-fused 1,2,3-triazole frameworks, *Org. Lett.*, 2015, **17**, 2198; (*d*) G. R. Kumar, Y. K. Kumar, R. Kant and M. S. Reddy, Synthesis of benzofuranyl and indolyl methyl azides by tandem silver-catalyzed cyclization and azidation, *Org. Biomol. Chem.*, 2016, **14**, 4077; (*e*) Y. Zhu, X. Li, X. Wang, X. Huang, T. Shen, Y. Zhang, X. Sun, M. Zou, S. Song and N. Jiao, Silver-catalyzed decarboxylative azidation of aliphatic carboxylic acids, *Org. Lett.*, 2015, **17**, 4702.

11 F. Liu, Z. Zhang, H.-Y. Diao and Z.-J. Shi, Silver in C(sp^2)-H Functionalization, *ChemCatChem*, 2021, **13**, 1475.

12 (*a*) D. S. Rampon, E. Q. Luz, D. B. Lima, R. A. Balaguez, P. H. Schneider and D. Alves, Transition metal catalysed direct selenylation of arenes and heteroarenes, *Dalton Trans.*, 2019, **48**, 9851; (*b*) D. S. Rampon, D. Seckler, E. Q. Luz, D. B. Paixão, A. Larroza, P. H. Schneider and D. Alves, Transition metal catalysed direct sulfanylation of unreactive C-H bonds: an overview of the last two decades, *Org. Biomol. Chem.*, 2022, **20**, 6072; (*c*) M. C. D. F. Xavier, B. Goldani, R. F. Schumacher, G. Perin, P. H. Schneider and D. Alves, Silver-catalyzed direct selenylation of terminal alkynes through C-H bond functionalization, *Mol. Catal.*, 2017, **427**, 73; (*d*) A. M. Barcellos, M. Sacramento, G. P. Costa, G. Perin, E. J. Lenardão and D. Alves, Organoboron compounds as versatile reagents in the transition metal-catalyzed C-S, C-Se and C-Te bond formation, *Coord. Chem. Rev.*, 2021, **442**, 214012.

13 (*a*) M. D. Lotz, N. M. Camasso, A. J. Canty and M. S. Sanford, Role of silver salts in palladium-catalyzed arene and heteroarene C-H functionalization reaction, *Organometallics*, 2017, **36**, 165; (*b*) K. L. Bay, Y.-F. Yang and K. N. Houk, Multiple roles of silver salts in palladium-catalyzed C-H activations, *J. Organomet. Chem.*, 2018, **864**, 19; (*c*) T. Bhattacharya, S. Dutta and D. Maiti, Deciphering the Role of Silver in Palladium-Catalyzed C-H Functionalizations, *ACS Catal.*, 2021, **11**, 9702; (*d*) N. Kaplaneris, L. Ackermann and M. J. Johansson, Late-stage C-H functionalization offers new opportunities in drug discovery, *Nat. Rev. Chem.*, 2021, **5**, 522; (*e*) R. L. Carvalho, G. G. Dias, C. L. M. Pereira, P. Ghosh, D. Maiti and E. N. Silva, A Catalysis Guide Focusing on C-H Activation Processes, *J. Braz. Chem. Soc.*, 2021, **32**, 917.

14 (*a*) H. J. Reich and R. J. Hondal, Why nature chose selenium, *ACS Chem. Biol.*, 2016, **11**, 821; (*b*) C. W. Nogueira, G. Zeni and J. B. T. Rocha, Organoselenium and organotellurium compounds: toxicology and pharmacology, *Chem. Rev.*, 2004, **104**, 6255; (*c*) D. Manna, G. Roy and G. Mugesh, Antithyroid drugs and their analogues: synthesis, structure, and mechanism of action, *Acc. Chem. Res.*, 2013, **46**, 2706; (*d*) V. K. Jain, *An Overview of Organoselenium Chemistry: From Fundamentals to Synthesis in Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments*, Royal Society of Chemistry, 1st edn, 2017; (*e*) E. J. Lenardão, C. Santi and L. Sancineto, *New Frontiers in Organoselenium compounds*, Springer, Cham, 1st edn, 2018; (*f*) V. K. Jain and K. I. Priyadarsini, *Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments*, Royal Society of Chemistry, 1st edn, 2018; (*g*) C. W. Nogueira, N. V. Barbosa and J. B. T. Rocha, Toxicology and pharmacology of synthetic organoselenium compounds: an update, *Arch. Toxicol.*, 2021, **95**, 1179; (*h*) M. Liu, X. Zhang, S. Chu, Y. Ge, T. Huang, Y. Liu and L. Yu, Selenization of cotton products with NaHSe endowing the antibacterial activities, *Chin. Chem. Lett.*, 2022, **33**, 205; (*i*) H. Cao, R. Ma, S. Chu, J. Xi, L. Yu and R. Guo, Synergistic effect of T80/B30 vesicles and T80/PN320 mixed micelles with Se/C on nasal mucosal immunity, *Chin. Chem. Lett.*, 2021, **32**, 2761; (*j*) L. Xian, Q. Li, T. Li and L. Yu, Methylselenized glucose: An efficient organoselenium fertilizer enhancing the selenium content in wheat grains, *Chin. Chem. Lett.*, 2022, DOI: **10.1016/j.cclet.2022.107878**; (*k*) X. Xiao, Z. Shao and L. Yu, A perspective of the engineering applications of carbon-based selenium-containing materials, *Chin. Chem. Lett.*, 2021, **32**, 2933; (*l*) H. Cao, Y. Yang, X. Chen, J. Liu, C. Chen, S. Yuan and L. Yu, Synthesis of selenium-doped carbon from glucose: An efficient antibacterial material against Xcc, *Chin. Chem. Lett.*, 2020, **31**, 1887.

15 (*a*) G. Perin, E. J. Lenardão, R. G. Jacob and R. B. Panatieri, Synthesis of vinyl selenides, *Chem. Rev.*, 2009, **109**, 1277; (*b*) M. Godoi, M. W. Paixão and A. L. Braga, Chiral organoselenium-transition-metal catalysts in asymmetric transformation, *Dalton Trans.*, 2011, **40**, 11347; (*c*)

D. M. Freudendahl, S. Santoro, S. A. Shahzad, C. Santi and T. Wirth, Green chemistry with selenium reagents: development of efficient catalytic reactions, *Angew. Chem., Int. Ed.*, 2009, **48**, 8409; (*d*) S. Santoro, J. B. Azeredo, V. Nascimento, L. Sancineto, A. L. Braga and C. Santi, The green side of the moon: ecofriendly aspects of organoselenium chemistry, *RSC Adv.*, 2014, **4**, 31521; (*e*) T. Guo, Z. Li, L. Bi, L. Fan and P. Zhang, Recent advances in organic synthesis applying elemental selenium, *Tetrahedron*, 2022, **112**, 132752; (*f*) M. S. Silva, D. Alves, D. Hartwig, R. G. Jacob, G. Perin and E. J. Lenardão, Selenium-NMR Spectroscopy in Organic Synthesis: From Structural Characterization Towards New Investigations, *Asian J. Org. Chem.*, 2021, **10**, 91; (*g*) F. V. Singh and T. Wirth, Selenium and Tellurium Electrophiles in Organic Synthesis, *Phys. Sci. Rev.*, 2019, **4**, 20170131.

16 (*a*) S. M. Lee, H. R. Lee, G. Dutta, J. Lee, J. H. Oh and G. Yang, Furan-flanked diketopyrrolopyrrole-based chalcogenophene copolymers with siloxane hybrid side chains for organic field-effect transistors, *Polym. Chem.*, 2019, **10**, 2854; (*b*) C.-C. Liu, S.-W. Mao and M.-Y. Kuo, Cyanated pentaceno[2,3-*c*]chalcogenophenes for potential application in air-stable ambipolar organic thin-film transistors, *J. Phys. Chem. C*, 2010, **114**, 22316; (*c*) Z. Yi, S. Wang and L. Liu, Design of high-mobility diketopyrrolopyrrole-based π-conjugated copolymers for organic thin-film transistors, *Adv. Mater.*, 2015, **27**, 3589; (*d*) K. Takimiya, Y. Kunugi, Y. Konda, H. Ebata, Y. Toyoshima and T. Otsubo, 2,7-Diphenyl[1]benzoselenopheno[3,2-*b*][1]benzoselenophene as a stable organic semiconductor for a high performance field-effect transistor, *J. Am. Chem. Soc.*, 2006, **128**, 3044; (*e*) T. Yamamoto and K. Takimiya, Facile synthesis of highly π-extended heteroarenes, dinaphto[2,3-*b*: 2′, 3′-*f*] chalcogenophenes[3,2-*b*]chalcogenophenes, and their application to field-effect, *J. Am. Chem. Soc.*, 2007, **129**, 2224; (*f*) Y. An, J. Oh, S. Chen, B. Lee, S. M. Lee, D. Han and C. Yang, Effects of incorporating different chalcogenophene comonomers into random acceptor terpolymers on the morphology and performance of all-polymer solar cells, *Polym. Chem.*, 2018, **9**, 593; (*g*) S. Yamaguchi, C. Xu and T. Okamoto, Ladder π-conjugated materials with main group elements, *Pure Appl. Chem.*, 2006, **78**, 721; (*h*) P. Arsenyan, A. Petrenko, K. Leitonas, D. Volyniuk, J. Simokaitiene, T. Klinavičius, E. Skuodis, J.-H. Lee and J. V. Gražulevičius, Synthesis and performance in OLEDs of selenium-containing phosphorescent emitters with red emission color deeper than the corresponding NTSC standard, *Inorg. Chem.*, 2019, **58**, 10174; (*i*) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, Semiconducting π-conjugated systems in field-effect transistors: a material odyssey of organic electronics, *Chem. Rev.*, 2012, **112**, 2208; (*j*) B. Kim, H. R. Yeom, M. H. Yun, J. Y. Kim and C. Yang, A selenophene analogue of PCDTBT: selective fine-tuning of LUMO to lower of the bandgap for efficient polymer solar cells, *Macromolecules*, 2012, **45**, 8658; (*k*) S. Haid, A. Mishra, C. Uhrich, M. Pfeiffer and P. Bäuerle, Dicyanovinylene-substituted selenophene-thiophene co-oligomers for small-molecule organic solar cells, *Chem. Mater.*, 2011, **23**, 4435; (*l*) A. J. Kronemeijer, E. Gili, M. Shahid, J. Rivnay, A. Salleo, M. Heeney and H. Sirringhaus, A selenophene-based low-bandgap donor-acceptor polymer leading to fast ambipolar logic, *Adv. Mater.*, 2012, **24**, 1558; (*m*) K. Yamada, T. Okamoto, K. Kudoh, A. Wakamiya and S. Yamaguchi, Single-crystal field-effect transistors of benzoannulated fused oligothiphenes and oligoselenophenes, *Appl. Phys. Lett.*, 2007, **90**, 72102; (*n*) D. S. Rampon, F. S. Rodembusch, J. M. F. M. Schneider, I. H. Bechtold, P. F. B. Gonçalves, A. A. Merlo and P. H. Schneider, Novel selenoesters fluorescent liquid crystalline exhibiting a rich phase polymorfism, *J. Mater. Chem.*, 2010, **20**, 715.

17 (*a*) S. Zhang, B. An, J. Li, J. Hu, L. Huang, X. Li and A. S. C. Chan, Synthesis and evaluation of selenium-containing indole chalcone and diarylketone derivatives as tubulin polymerization inhibition agents, *Org. Biomol. Chem.*, 2017, **15**, 7404; (*b*) P. T. Birmann, F. S. S. Sousa, D. H. Oliveira, M. Domingues, B. M. Vieira, E. J. Lenardão and L. Savegnago, 3-(4-Chlorophenylselanyl)-1-methyl-1*H*-indole, a new selenium compound elicits an antinociceptive and anti-inflammatory effects in mice, *Eur. J. Pharmacol.*, 2018, **827**, 71; (*c*) A. M. Casaril, M. T. Ignasiak, C. Y. Chuang, B. Vieira, N. B. Padilha, L. Carroll, E. J. Lenardão, L. Savegnago and M. J. Davies, Selenium-containing indolyl compounds: kinetics of reactions with inflammation-associated oxidants and protective effect against oxidation of extracellular matrix proteins, *Free Radical Biol. Med.*, 2017, **113**, 395; (*d*) Z. Wen, J. Xu, Z. Wang, H. Qi, Q. Xu, Z. Bai, Q. Zhang, K. Bao, Y. Wu and W. Zhang, 3-(3,4,5-Trimethoxyphenylselenyl)-1*H*-indoles and their selenoxides as combretastatin A-4 analogs: microwave-assisted synthesis and biological evaluation, *Eur. J. Med. Chem.*, 2015, **90**, 184; (*e*) Q. Guan, C. Han, D. Zuo, M. Zhai, Z. Li, Q. Zhang, Y. Zhai, X. Jiang, K. Bao, Y. Wu and W. Zhang, Synthesis and evaluation of benzimidazole carbamates bearing indole moieties for antiproliferative and antitubulin activities, *Eur. J. Med. Chem.*, 2014, **87**, 306; (*f*) G. La Regina, R. Bai, W. M. Rensen, E. Di Cesare, A. Coluccia, F. Piscitelli, V. Famiglini, A. Reggio, M. Nalli, S. Pelliccia, E. Pozzo, B. Costa, I. Granata, A. Porta, B. Maresca, A. Soriani, M. L. Iannitto, A. Santoni, J. Li, M. M. Cona, F. Chen, Y. Ni, A. Brancale, G. Dondio, S. Vultaggio, M. Varasi, C. Mercurio, C. Martini, E. Hamel, P. Lavia, E. Novellino and R. Silvestri, Toward highly potent cancer agents by modulating the C-2 group of the arylthioindole class of tubulin polymerization inhibitors, *J. Med. Chem.*, 2013, **56**, 123; (*g*) M. Nuth, H. Guan, N. Zhukovskaya, Y. L. Saw and R. P. Ricciardi, Design of potent poxvirus inhibitor of the heterodimeric processivity factor required for viral replication, *J. Med. Chem.*, 2013, **56**, 3235.

18 (*a*) D. Huang, H. Yu, T. Wang, H. Yang, R. Yao and Z. Liang, Efficacy and safety of umifenovir for coronavirus disease 2019 (COVID19): a systematic and meta-analysis, *J. Med.*

Virol., 2020, **93**, 481; (*b*) J. Haviernik, M. Stefánik, M. Fojtíková, S. Kali, N. Tordo, I. Rudolf, Z. Hubalék, L. Eyer and D. Ruzek, Arbidol (Umifenovir): a broad-spectrum antiviral drug that inhibits medically impotant arthropod-borne flaviviruses, *Viruses*, 2018, **10**, 184; (*c*) A. M. Rapoport, M. E. Bigal, M. Volcy, F. D. Sheftell, M. Fellepa and S. J. Tepper, Naratriptan in the preventive treatment of refractory chronic migraine: a review of 27 cases, *Headache*, 2003, **43**, 482; (*d*) B. Casolla, L. Lionetto, S. Candela, L. D'Alonzo, A. Negro, M. Simmaco and P. Martelletti, Treatment of perimenstural migraine with triptans: un update, *Curr. Pain Headache Rep.*, 2012, **16**, 445; (*e*) N. T. Mathew, Naratriptan: a review, *Expert Opin. Invest. Drugs*, 2005, **8**, 687.

19 (*a*) W. Ma, N. Kaplaneris, X. Fang, L. Gu, R. Mei and L. Ackermann, Chelation-assisted transition metal-catalysed C-H chalcogenylations, *Org. Chem. Front.*, 2020, **7**, 1022; (*b*) M. Iwasaki and Y. Nishihara, Palladium-catalysed direct thiolation and selenation of aryl C-H bonds assisted by directing groups, *Dalton Trans.*, 2016, **45**, 15278; (*c*) J. Rafique, D. S. Rampon, J. B. Azeredo, F. L. Coelho, P. H. Schneider and A. L. Braga, Light-Mediated Seleno-Functionalization of Organic Molecules: Recent Advances, *Chem. Rec.*, 2021, **21**, 2739; (*d*) G. M. Martins, A. G. Meirinho, N. Ahmed, A. L. Braga and S. R. Mendes, Recent advances in electrochemical chalcogen (S/Se)-functionalization of organic molecules, *ChemElectroChem*, 2019, **6**, 5928.

20 (*a*) Y. Cao, J. Liu, F. Liu, L. Jiang and W. Yi, Copper-catalyzed direct and odorless selenylation with a sodium selenite-based reagent, *Org. Chem. Front.*, 2019, **6**, 825; (*b*) E. Q. Luz, D. Seckler, J. S. Araújo, L. Angst, D. B. Lima, E. A. M. Rios, R. R. Ribeiro and D. S. Rampon, Fe(III)-Catalyzed direct C3 chalcogenylation of indoles: the effect of iodide ions, *Tetrahedron*, 2019, **75**, 1258; (*c*) B. M. Vieira, S. Thurow, M. da Costa, A. M. Casaril, M. Domingues, R. F. Schumacher, G. Perin, D. Alves, L. Savegnano and E. J. Lenardão, Ultrasound-assisted synthesis and antioxidant activity of 3-selanyl-1H-indole and 3-selanylimidazo[1,2-*a*]pyridine derivatives, *Asian J. Org. Chem.*, 2017, **6**, 1635; (*d*) L. Dongping, G. Wu, H. Yang, M. Liu, W. Gao, X. Huang, J. Chen and H. Wu, Copper-catalyzed three-component reaction for regioselective aryl- and heteroarylselenation of indoles using selenium powder, *J. Org. Chem.*, 2016, **81**, 4485; (*e*) T. Guo, Z. Dong, P. Zhang, W. Xing and L. Li, Direct selenation of imidazoheterocycles and indoles with selenium powder in a copper-catalyzed three-component one-pot system, *Tetrahedron Lett.*, 2018, **59**, 2554; (*f*) B. M. Vieira, S. Thurow, J. S. Brito, G. Perin, D. Alves, R. G. Jacob, C. Santi and E. J. Lenardão, Sonochemistry: an efficient alternative to the synthesis of 3-selanylindoles using CuI as catalyst, *Ultrason. Sonochem.*, 2015, **27**, 192; (*g*) N. Mukherjee, D. Kundu and B. C. Ranu, Copper-Silver Dual Catalyzed Decyanative C-Se Cross-Coupling, *Adv. Synth. Catal.*, 2017, **359**, 329; (*h*) S. Guan, Y. Chen, H. Wu and R. Xu, Iron-catalyzed tandem reaction of C-Se bond coupling/selenosulfonation of indoles with benzeneselenols, *RSC Adv.*, 2020, **10**, 27058.

21 (*a*) I. D. Lemir, W. D. Castro-Godoy, A. A. Heredia, L. C. Schmidt and J. E. Arguello, Metal- and photocatalyst-free synthesis of 3-selenylindoles and asymmetric diarylselenides promoted by visible light, *RSC Adv.*, 2019, **9**, 22685; (*b*) N. L. Ferreira, J. B. Azeredo, B. L. Fiorentin and A. L. Braga, Synthesis of 3-Selenylindoles under Eco-friendly Conditions, *Eur. J. Org. Chem.*, 2015, **2015**, 5070; (*c*) X. Zhang, C. Wang, H. Jiang and L. Sun, Convenient synthesis of selenyl-indoles via iodide ion-catalyzed electrochemical C-H selenation, *Chem. Commun.*, 2018, **54**, 8781; (*d*) W. Zhang, S. Li, X. Tang, J. Tang, C. Pan and Y. Guipeng, Phenothiazine core promoted charge transfer in conjugated microporous polymers for photocatalytic Ugi-type reaction and aerobic selenation of indoles, *Appl. Catal., B*, 2020, **272**, 118982; (*e*) R. Jamal, S. Sumbal, M. S. Franco, L. Bettanin, A. R. Schneider, L. T. Silva and A. L. Braga, Direct, Metal-free C(sp^2) Chalcogenation of Indoles and Imidazopyridines with Dichalcogenides Catalysed by KIO$_3$, *Chem.–Eur. J.*, 2018, **24**, 4173; (*f*) H. Li, J. Wang, X. Wang and J. Yan, NaBr mediated regioselective synthesis of 3-selanylindoles, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2018, **193**, 394; (*g*) V. Rathore and S. Kumar, Visible-light-induced metal and reagent-free oxidative coupling of sp^2 C-H bond with organodichalcogenides: synthesis of 3-organochalcogenyl indoles, *Green Chem.*, 2019, **21**, 2670; (*h*) F. L. Coelho, E. S. Gil, P. F. B. Gonçalves, L. F. Campo and P. H. Schneider, Intramolecular Hydroamination of Selenoalkynes to 2-Selenylindoles in the Absence of Catalyst, *Eur. J. Chem.*, 2019, **25**, 8157; (*i*) X. Zhang, C. Wang, H. Jiang and L. Sun, A low-cost electrochemical thio- and selenocyanation strategy for electron-rich arenes under catalyst- and oxidant-free condition, *RSC Adv.*, 2018, **8**, 22042; (*j*) J. B. Azevedo, M. Godoi, G. M. Martins, C. C. Silveira and A. L. Braga, A solvent- and metal-free synthesis of 3-chalcogenyl-indoles employing DMSO/I$_2$ as an eco-friendly catalytic oxidation system, *J. Org. Chem.*, 2014, **79**, 4125.

22 Plancher's Rearrangement:(*a*) Z. Wang, *Comprehensive Organic Name Reactions and Reagents*, 1st edn, Wiley, vol. 3, 2010; (*b*) M. Mari, S. Lucarini, F. Bartoccini, G. Piersanti and G. Spadoni, Synthesis of 2-substituted tryptophans via a C3- to C2-alkyl migration, *Beilstein J. Org. Chem.*, 2014, **10**, 1991; (*c*) A. H. Jackson and P. Smith, Electrophilic substitution in indoles–III: rearrangement of 3,3-dialkylindolenines, *Tetrahedron*, 1968, **24**, 2227; (*d*) A. H. Jackson, B. Naidoo and P. Smith, Electrophilic substitution in indoles – IV: The cyclization of indolylbutanol to tetrahydrocarbazole, *Tetrahedron*, 1968, **24**, 6119; (*e*) K. M. Biswas and A. H. Jackson, Electrophilic substitution in indoles-V: Indolenine as intermediates in the benzylation of 3-substituted indoles, *Tetrahedron*, 1969, **25**, 227; (*f*) K. G. Liu, A. J. Robichaud, J. R. Lo, J. F. Mattes and Y. Cai, Rearrangement of 3,3-disubstituted indolenine and synthesis of 2,3-substituted indoles, *Org. Lett.*, 2006, **8**, 5769; (*g*) P. Hamel and P. Preville, Regioselective synthesis

of mixed indole 2,3-bis(sulfides). A study of the mechanism of the second sulfenylation of Indoles, *J. Org. Chem.*, 1996, **61**, 1573.

23 (*a*) M. Hirano, M. Monobe, S. Yakabe and T. Morimoto, Hydrotalcite clay-catalyzed air oxidation of thiols, *J. Chem. Res., Synop.*, 1999, **6**, 374; (*b*) J. Xan, E. A. Wilson, L. D. Roberts and N. H. Norton, The absorption of oxygen by mercaptans in alkaline solution, *J. Am. Chem. Soc.*, 1941, **63**, 1139; (*c*) C. F. Cullis, J. D. Hopton and D. L. Trimm, Oxidation of thiols in gas-liquid systems. Reaction in the presence of added metal catalysts, *J. Appl. Chem.*, 1968, **18**, 335; (*d*) P. C. B. Page, R. D. Wilkes and D. Reynolds, *Comprehensive Organic Functional Group Transformations*, vol. 2, Pergamon Oxford, 1995; (*e*) D. B. Lima, P. H. V. Santos, P. Fiori, G. Badshah, E. Q. Luz, D. Seckler and D. S. Rampon, Base-Promoted Direct Chalcogenylation of 2-Naphtols, *ChemistrySelect*, 2019, **13**, 13558; (*f*) Y. Ni, H. Zuo, Y. Li, Y. Wu and F. Zhong, Cooper-catalyzed regioselective intramolecular electrophilic sulfenoamination via Lewis acid activation of disulfides under aerobic conditions, *Org. Lett.*, 2018, **20**, 4350.

24 (*a*) C. N. Yiannios and J. V. Karabinos, Oxidation of thiols by dimethyl sulfoxide, *J. Org. Chem.*, 1963, **11**, 3246; (*b*) J.-G. Sun, W.-Z. Weng, P. Li and B. Zhang, Dimethyl sulfoxide as a mild oxidant in S-P(O) bond construction: simple and metal-free approaches to phosphinothioates, *Green Chem.*, 2017, **19**, 1128; (*c*) E. Q. Luz, G. L. Silvério, D. Seckler, D. B. Lima, F. S. Santana, R. V. Barbosa, C. R. M. D'Oca and D. S. Rampon, One-Pot Synthesis of 3-Halo-2-organochalcogenylbenzo[*b*]chalcogenophenes from 1-(2,2-Dibromovinyl)-2-organochalcogenylbenzenes, *Adv. Synth. Catal.*, 2021, **363**, 2610; (*d*) M. Iwasaki, Y. Tsuchiya, K. Nakajima and Y. Nishihara, Chelate-assisted direct selenation of aryl C-H bonds with diselenides catalyzed by palladium, *Org. Lett.*, 2014, **16**, 4920; (*e*) K. S. Santos, E. M. A. Sandagorda, R. Cargnelutti, T. Barcellos, R. G. Jacob, D. Alves and R. F. Schumacher, Copper-Catalyzed Selective Synthesis of 5-Selanyl-imidazo[2,1-*b*] thiazoles, *ChemistrySelect*, 2017, **2**, 10793; (*f*) S. F. Fonseca, N. B. Padilha, S. Thurow, J. A. Roehrs, L. Svegnago, M. N. Souza, M. G. Fronza, T. Collares, J. Buss, F. K. Seixas, D. Alves and E. J. Lenardão, Ultrasound-promoted copper-catalyzed synthesis of bis-arylselanyl chrysin derivatives with boosted antioxidant and anticancer activities, *Ultrason. Sonochem.*, 2017, **39**, 827; (*g*) M. Iwasaki, M. Iyanaga, Y. Tsuchiya, Y. Nishimura, W. Li, Z. Li and Y. Nishihara, Palladium-Catalyzed Direct Thiolation of Aryl C-H Bonds with Disulfides, *Chem.–Eur. J.*, 2014, **20**, 2459; (*h*) W. E. Fristad and J. R. Peterson, Oxidative coupling of arylthiols to diaryl disulfides, *Synth. Commun.*, 1985, **15**, 1; (*i*) T. J. Wallace, Reactions of thiols with sulfoxides. Scope of the reaction and synthetic applications, *J. Am. Chem. Soc.*, 1964, **86**, 2018; (*j*) T. Zhang, G. Deng, H. Li, B. Liu, Q. Tan and B. Xu, Cyclization of 2-Biphenylthiols to Dibenzothiophenes under $PdCl_2$/DMSO Catalysis, *Org. Lett.*, 2018, **20**, 5439; (*k*) C. Zhang, J. McClure and J. Chou, Silver-catalyzed direct thiolation of quinones by activation of aryl disulfides to synthesize quinonyl aryl thioethers, *J. Org. Chem.*, 2015, **80**, 4919; (*l*) A. Gupta, A. Rahaman and S. Bhadra, Direct α-chalcogenation of aliphatic carboxylic acid equivalents, *Org. Lett.*, 2019, **21**, 6164; (*m*) J.-M. Li, Y. Yu, J. Weng and G. Lu, Nickel-catalyzed direct C-H bond sulfenylation of acylhydrazines, *Org. Biomol. Chem.*, 2018, **16**, 6047.

25 (*a*) P. Gogoi, S. R. Gogoi, M. Kalita and P. Barman, Silver ion mediated in situ synthesis of mixed diaryl sulfides from diaryl disulfides, *Synlett*, 2013, **24**, 873; (*b*) A. Thupyai, C. Pimpasri and S. Yotphan, DABCO-catalyzed silver-promoted direct thiolation of pyrazolones with diaryl disulfides, *Org. Biomol. Chem.*, 2018, **16**, 424; (*c*) M. Bortoli, L. P. Wolters, L. Orian and F. M. Bickelhaupt, Addition-elimination or nucleophilic substitution? Understanding the energy profiles for the reaction of chalcogenolates with dichalcogenides, *J. Chem. Theory Comput.*, 2016, **12**, 2752; (*d*) G. S. Heverly-Coulson, R. J. Boyd, O. Mó and M. Yanez, Revealing Unexpected Mechanisms for Nucleophilic Attack on S-S and Se-Se Bridges, *Chem.–Eur. J.*, 2013, **19**, 3629.

26 B. Goldani, V. G. Ricordi, N. Seus, E. J. Lenardão, R. F. Schumacher and D. Alves, Silver-catalyzed synthesis of diaryl selenides by reaction of diaryl diselenides with aryl boronic acids, *J. Org. Chem.*, 2016, **81**, 11472.