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

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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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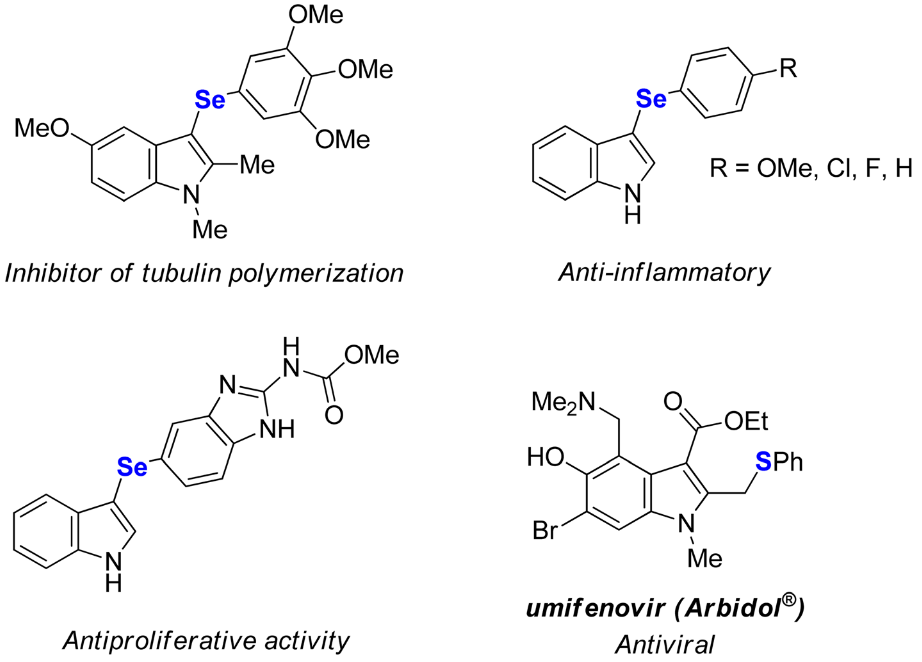


Inhibitor of tubulin polymerization

Anti-inflammatory

Antiproliferative activity

umifenovir (Arbidol®)
Antiviral

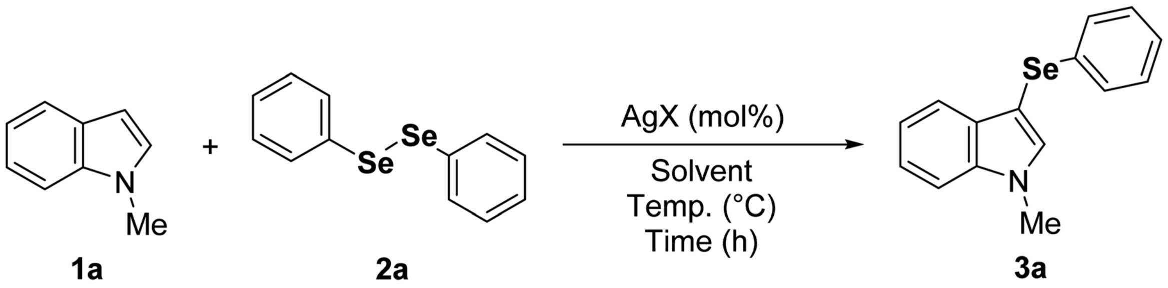
Fig. 1 Biologically relevant selenium or sulfur-functionalized indoles.

(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



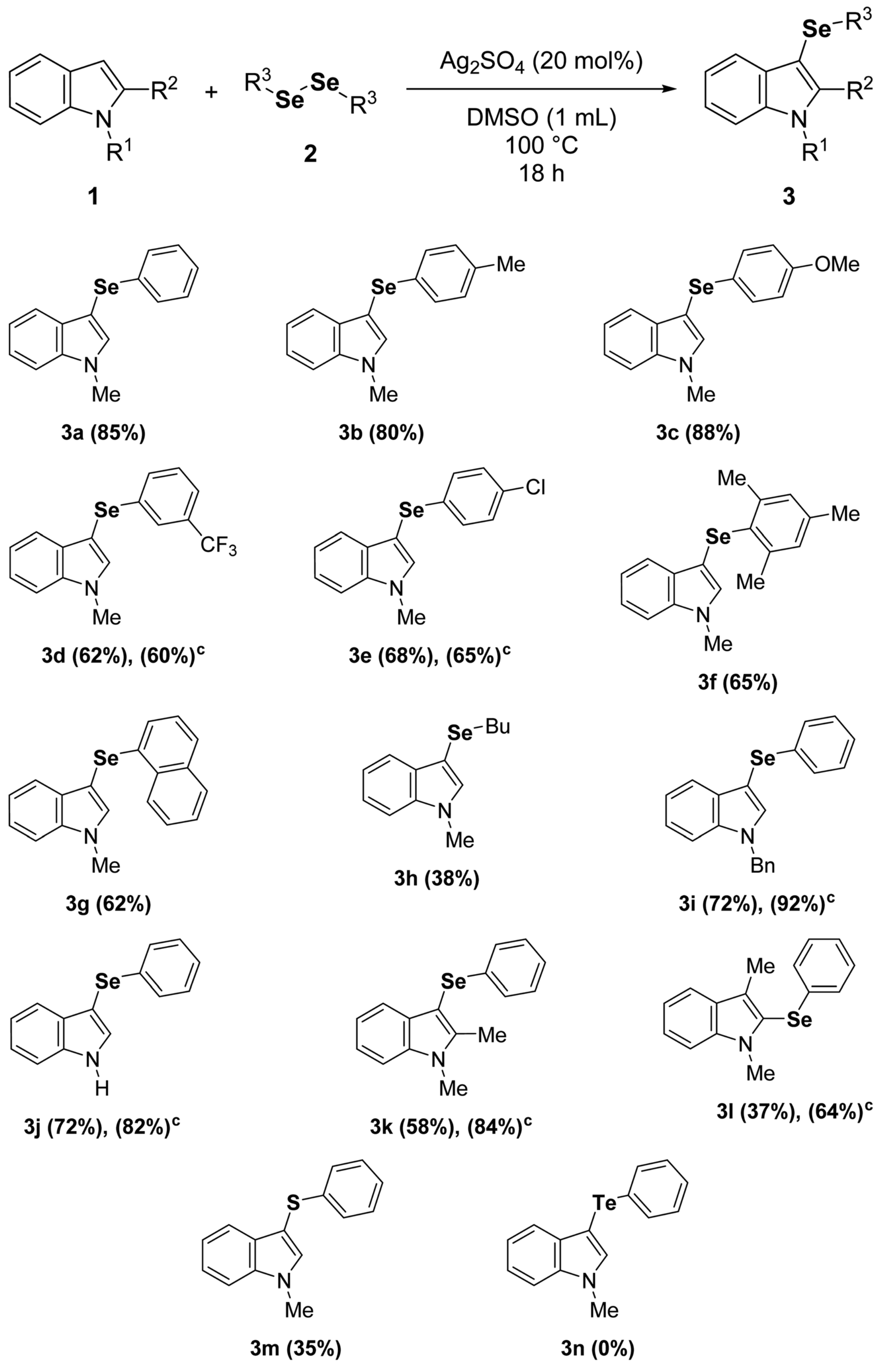
Entry[a]	Catalyst (mol%)	Solvent	Time (h)	Temp. (°C)	Yield[b,d] (%)
1	Ag_2SO_4 (5)	DMSO (1.0)	24	100	23
2	Ag_2SO_4 (10)	DMSO (1.0)	24	100	42
3	Ag_2SO_4 (20)	DMSO (1.0)	24	100	79
4	Ag_2SO_4 (30)	DMSO (1.0)	24	100	87
5	**Ag_2SO_4 (20)**	**DMSO (1.0)**	**18**	**100**	**85**
6	Ag_2SO_4 (20)	DMSO (1.0)	12	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]



1 + **2** → **3**

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]

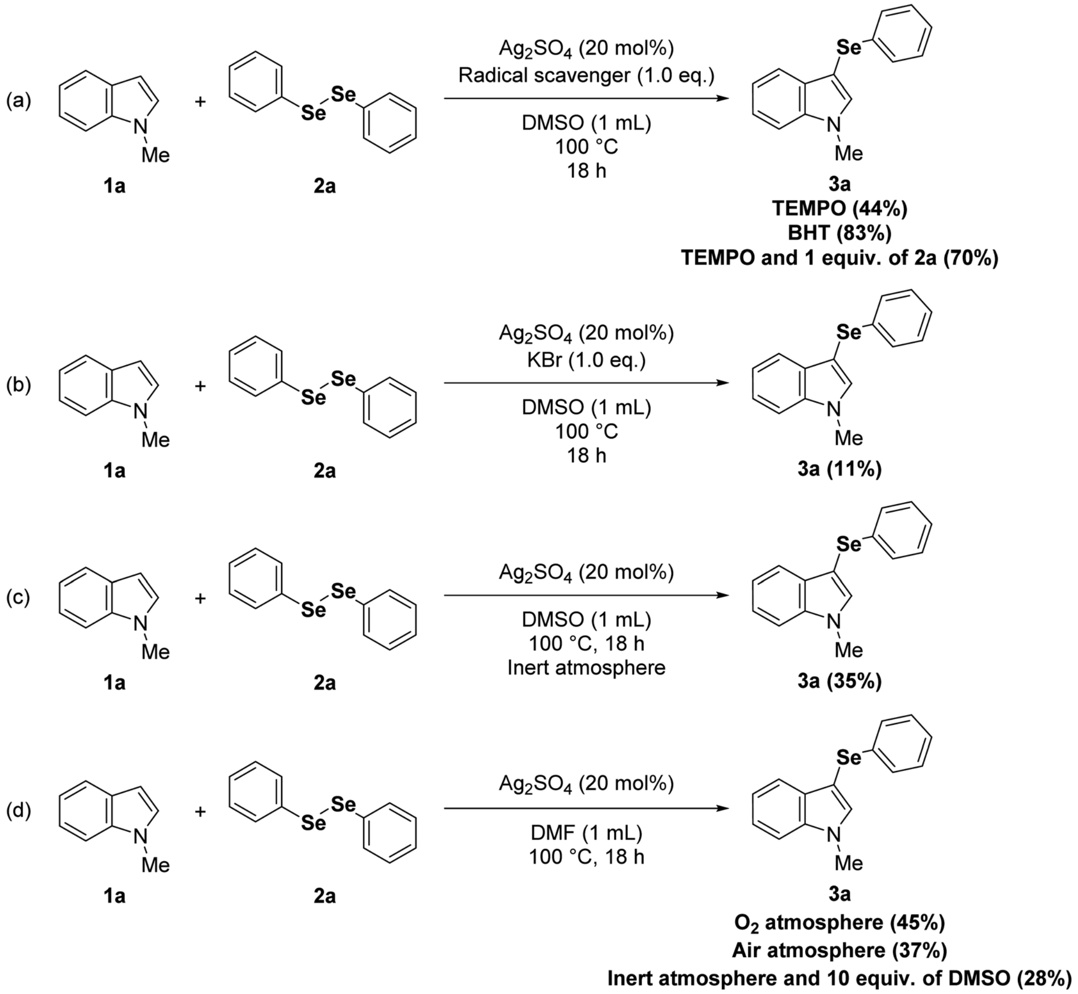
3k (58%), (84%)[c]

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

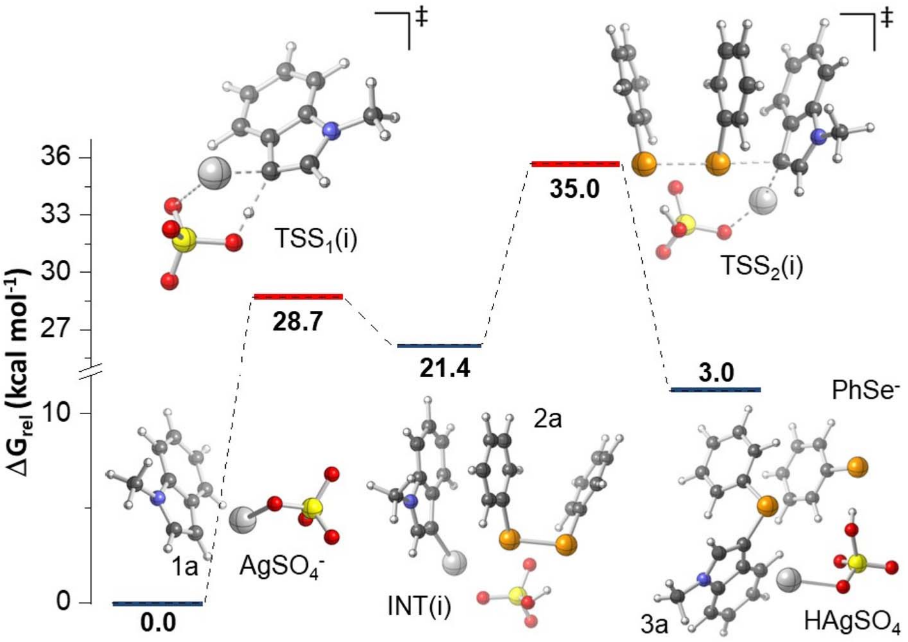


Fig. 2 Potential energy surface (PES) of the CMD mechanism (i) proposed for the formation of **3a** obtained using M062X functional combined with LANL2DZ (for Ag atom) and 6-311++G(d,p) (for additional atoms). Atom color: S-yellow, O-red, Se-orange, N-blue, C-gray, and H-white.

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

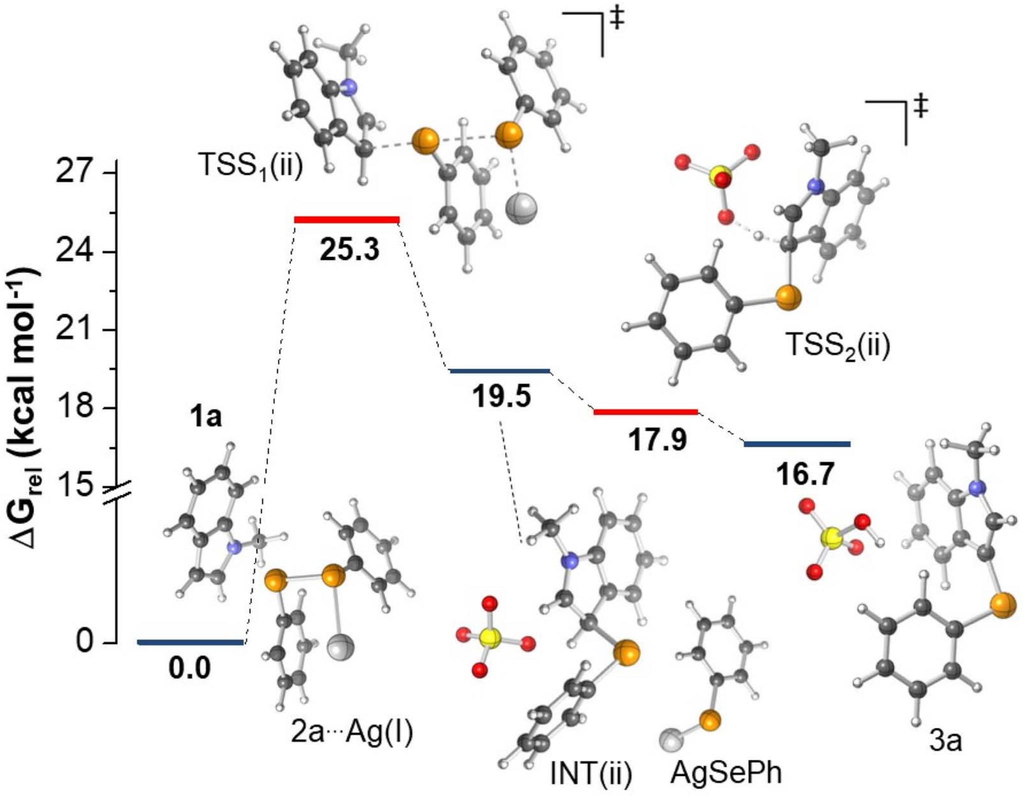
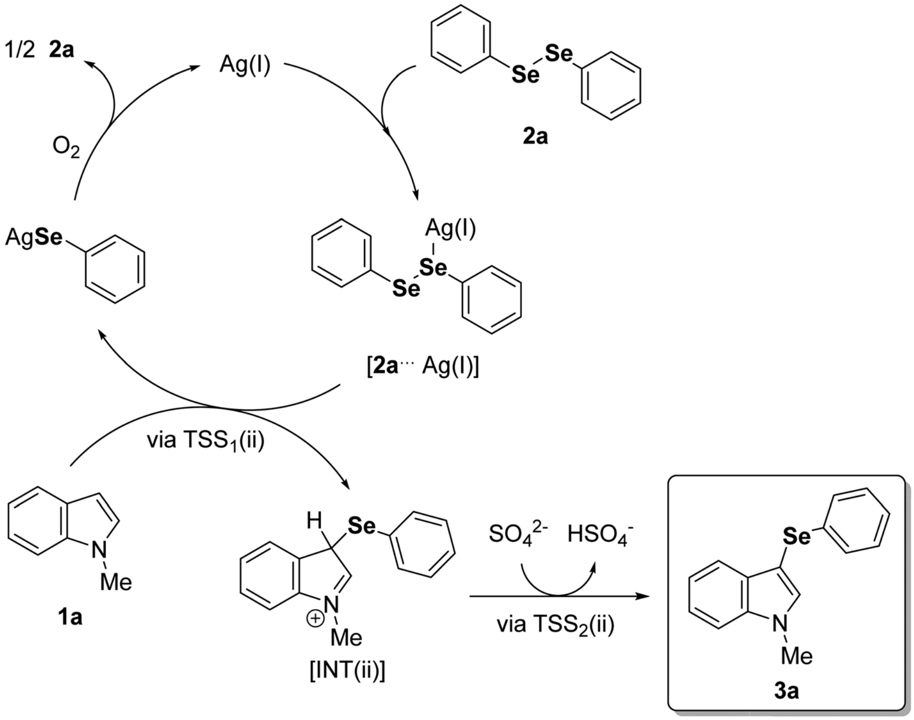


Fig. 3 Potential energy surface (PES) of the electrophilic substitution mechanism (ii) proposed for the formation of **3a** obtained using M062X functional combined with LANL2DZ (for Ag atom) and 6-311++G(d,p) (for additional atoms).



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.

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