Ultrasound-promoted synthesis of 2-organoselanyl-naphthalenes using Oxone® in aqueous medium as an oxidizing agent

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ABSTRACT

A green methodology to synthesize 2-organoselanyl-naphthalenes based on the reaction of alkynols with diaryl diselenides is described. The electrophilic species of selenium were generated in situ, by the oxidative cleavage of the Se–Se bond of diaryl diselenides by Oxone® using water as the solvent. The reactions proceeded efficiently under ultrasonic irradiation as an alternative energy source, using a range of alkynols and diorganyl diselenides as starting materials. Through this methodology, the corresponding 2-organoselanyl-naphthalenes were obtained in moderate to good yields (56–94%) and in short reaction times (0.25–2.3 h).

Subjects Natural Resource Management, Food, Water and Energy Nexus, Green Chemistry
Keywords Green chemistry, Organoselenium, Ultrasound, Oxone, Naphthalenes, Organic synthesis

Submitted 22 March 2018
Accepted 15 April 2018
Published 7 May 2018

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Academic editor
Gamal El-Hiti

Additional Information and Declarations can be found on page 10

DOI **10.7717/peerj.4706**

INTRODUCTION

Compounds containing chalcogen atoms (S, Se, Te) are versatile synthetic intermediates for the synthesis of complex molecules (*Mukherjee et al., 2010*; *Beletskaya & Ananikov, 2011*; *Godoi, Schumacher & Zeni, 2011*). Furthermore, the interest in organochalcogen compounds is connected to their well reported pharmacological activities (*Santi, 2014*), including antidepressant-like (*Brod et al., 2017*), antiviral (*Sartori et al., 2016*), antifungal (*Venturini et al., 2016*), anxiolytic (*Reis et al., 2017*), anticholinesterasic (*Peglow et al., 2017*), anti-inflammatory (*Pinz et al., 2017*), and antioxidant (*Nobre et al., 2017*).

The plethora of methods to incorporate organoselenium groups in organic substrates includes the use of nucleophilic (*Iwaoka, 2011*), radical (*Nomoto et al., 2013*), and electrophilic species of selenium (*Santi & Tidei, 2013*; *Sancineto et al., 2016*). The reaction of diorganyl diselenides with a halogen source is the most used method to access electrophilic selenium species (*Raucher, 1977*; *Azeredo et al., 2014*; *Shi, Yu & Yan, 2015*; *Rafique et al., 2016*; *Silva et al., 2017*). However, the obtained selanyl halides are unstable and difficult to prepare (*Santi, 2014*). Due to the disadvantages of the use of

halogenated selenium species, new alternatives have been described in the literature for the generation of electrophilic selenium species, such as the use of inorganic salts such as sodium (*Kibriya et al., 2017*), potassium (*Santi & Tidei, 2014*; *Prasad et al., 2013*), and ammonium (*Tiecco et al., 1989*; *Santi et al., 2008*; *Santoro et al., 2010*) persulfate through the in situ reaction with diorganyl diselenides. Naphthalenes and their derivatives are known for their countless biological properties reported in the literature, like anticancer (*Norton et al., 2008*), antifungal (*Iverson & Uetrecht, 2001*), and antiviral activities (*Yeo et al., 2005*). In addition, these compounds demonstrated a wide spectrum of applications in materials (*Lee, Noll & Smith, 2008*) and polymer chemistry (*Reddy et al., 2007*). The numerous methodologies to prepare this class of compounds include chemical modifications in functionalized naphtalenes (*Koz, Demic & Icli, 2016*; *Aksakal et al., 2017*), cyclization of alkynes and aldehydes using iron (*Zhu et al., 2013*) or boron (*Xiang et al., 2013*) catalysis, reaction of internal, and terminal alkynes with enamine and hypervalent iodine (*Gao, Liu & Wei, 2013*), cascade reaction of aldehydes and ketones catalyzed by trifluoromethanesulfonic acid (*Manojveer & Balamurugan, 2015*) and Claisen rearrangement using vanillin derivatives (*Chan et al., 2017*).

The synthesis of selenium-containing naphthalene derivatives, however, is scarcely described. Five main synthetic routes have been developed to construct selanyl naphthalenes: (i) annulation of aryl enynes (*Yang et al., 2014*), (ii) metal-catalyzed direct selenylation of naphthylboronic acids (*Mohan et al., 2015*), (iii) cyclization reactions of 4-arylbut-3-yn-2-ols with electrophilic selenium species, like PhSeBr (*Zhang, Sarkar & Larock, 2006*) or PhSeSePh/$FeCl_3$ system (*Recchi, Back & Zeni, 2017*), (iv) [4+2] cycloaddition reaction of chalcogenoalkynes with *o*-alkynylbenzaldehydes (*Mantovani, Back & Zeni, 2012*), and (v) oxidative C(sp^3)-/Se coupling in tetralones (*Prasad, Sattar & Kumar, 2017*). Despite these are efficient methodologies, chlorinated or high boiling point solvents, harsh base, transition metal catalysts, and/or halogenating reagents are involved in the synthesis.

On the other hand, Oxone® is an inexpensive, stable, water-soluble, and safe alternative oxidizing agent that has been used in numerous oxidation reactions (*Hussain, Green & Ahmed, 2013*). This green oxidant is a mixture of three inorganic salts ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), with potassium peroxymonosulfate ($KHSO_5$) being the active species. The synthesis of important heterocyclic compounds was accomplished using Oxone®, such as chromene and carbazoles (*Reddy, Kannaboina & Das, 2017*), benzimidazoles (*Daswani et al., 2016*), benzoxazoles (*Hati et al., 2016*), pyrazole (*Kashiwa et al., 2016*), and pyridine derivatives (*Swamy et al., 2016*). Furthermore, it was used in intramolecular cycloaddition (*More & Ramana, 2016*) and cyclization reactions (*Sharma et al., 2016*), in the synthesis of α-bromoketones (*Rammurthy et al., 2017*), in halogenation reactions of quinolines (*Wang et al., 2016*), oxidation of alcohols to carbonyl compounds (*Mishra & Moorthy, 2017*) and in the synthesis of iodohydrins and iodoarenes (*Soldatova et al., 2016*). However, to the best of our knowledge, no reactions using Oxone® to prepare electrophilic selenium species as substrate in cycloaddition reactions have been described so far.

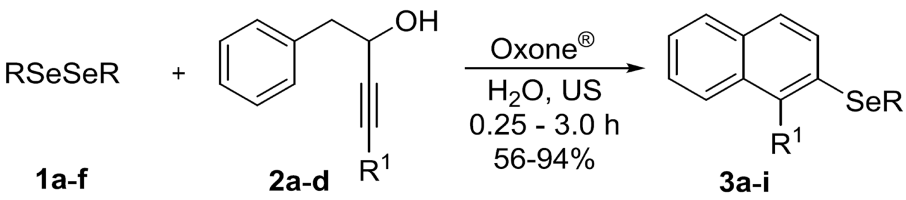


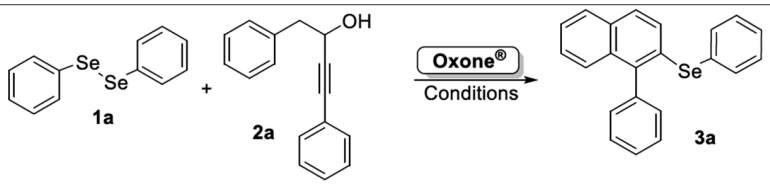
Figure 1 **Synthesis of 2-organochalcogenyl-naphtalenes.** Full-size DOI: 10.7717/peerj.4706/fig-1

In the last years, the use of ultrasonic waves as an alternative energy source in organic synthesis has exponentially increased. The so-called sonochemistry has the ability to accelerate, or even totally modify the reaction course, through the formation of new reactive intermediates that normally are not involved when conventional heating is used (*Nowak, 2010*; *Mojtahedi & Abaee, 2012*; *Schiel et al., 2015*). Recently, we have described new ultrasonic-promoted reactions, including the synthesis of 1,2,3-triazoyl carboxamides (*Xavier et al., 2017*), 3-selanylindoles (*Vieira et al., 2015*) and chrysin derivatives (*Fonseca et al., 2017*). Considering the importance of organoselenium compounds and naphthalene derivatives, and due our interest in green synthetic protocols associated to organochalcogen chemistry, we report herein a new ultrasound-promoted method to prepare 2-organoselanyl-naphthalenes **3a–i**. Our strategy involves the carbocyclization of alkynols **2a–d** using electrophilic selenium species, which were generated in situ by the reaction of diorganyl diselenides **1a–f** with Oxone® (Fig. 1).

MATERIAL AND METHODS

General remarks

Pre-coated TLC sheets (ALUGRAM® Xtra SIL G/UV_{254}; Macherey-Nagel GmbH & Co-KG, Düren, Germany). using UV light and acidic ethanolic vanillin solution (5% in 10% H_2SO_4) were used to follow the reaction progress. Aldrich technical grade silica gel (pore size 60 Å, 230–400 mesh) was used for flash chromatography. Carbon-13 nuclear magnetic resonance (^{13}C NMR) and hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained on Bruker Ascend 400 spectrometers at 100 MHz at 400 MHz, respectively. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the internal reference, for ^{1}H NMR and the solvent peak of $CDCl_3$ for ^{13}C NMR. Coupling constant (*J*) are reported in hertz. Abbreviations to denote the multiplicity of a particular signal are brs (broad signal), s (singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). A Shimadzu GC-MS-QP2010 was used to obtain the low-resolution mass spectra (MS), while a LTQ Orbitrap Discovery mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was employed to obtain the high-resolution mass spectra (HRMS), the experiments were performed via direct infusion of sample (flow: 10 μL/min) in the positive-ion mode using electrospray ionization. A (Cole Parmer CPX 130; Cole-Parmer Instrument Company, Chicago, IL, USA) operating with an amplitude of 60%, maxim power of 130 W at 20 KHz, was used to generate the ultrasonic waves. The temperature of the reactions under US was monitored with a Incoterm digital infrared thermometer (Infraterm, São Paulo, Brazil). Melting point (m.p.) values were



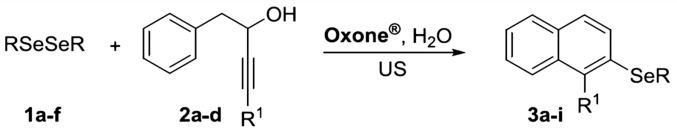
Entry	Oxone® (mmol)	Time	Amplitude	Solvent	Yield (%)[b]
1	0.25	72 h	-	ethanol	78[c]
2	0.25	50 min	60%	ethanol	84
3	0.25	40 min	60%	PEG-400	76
4	0.25	2 h	60%	glycerol	73
5	0.25	30 min	60%	H_2O	86
6	0.25	2 h	60%	DMSO	traces
7	0.25	2 h	60%	acetonitrile	traces
8	0.25	2 h	60%	DMF	62
9	0.25	3 h	40%	H_2O	63
10	0.25	30 min	60%	H_2O	85[d]
11	0.125	2 h	60%	H_2O	42
12	-	2 h	60%	H_2O	NR
13[e]	0.25	10 min	60%	H_2O	92

Figure 2 Optimization of reaction conditions to prepared compound 3a[a]. [a]A mixture of **1a** (0.125 mmol), **2a** (0.25 mmol), Oxone®, and the solvent (2.0 mL) in a glass tube was sonicated for the time indicated in the figure; the final temperature was 65 °C. [b]Isolated yields after column chromatography. [c]Reaction performed under conventional heating (oil bath at 60 °C) under magnetic stirring. [d]It was used 0.30 mmol of **2a**. [e]$KHSO_4$ (0.25 mmol) was added to the reaction mixture. NR, no reaction.
Full-size DOI: 10.7717/peerj.4706/fig-2

measured in a Marte PFD III instrument with a 0.1 °C precision. Oxone® was purchased from (Sigma-Aldrich, St. Louis, MO, USA).

General procedure for the synthesis of 2-organoselanyl-naphthalenes 3

To a 10 mL round bottomed glass tube, the appropriate diorganyl diselenide **1a–f** (0.125 mmol), alkynol **2a–d** (0.25 mmol), water (2.0 mL), and Oxone® (0.077 g; 0.25 mmol) were added. The US probe was placed in the reaction vial, which was sonicated (20 KHz, 60% of sonic amplitude) for the time indicated in Figs. 2 and 3. The reaction temperature was monitored and after 5 min it was around 64–65 °C, which was maintained until the end of the reaction. The reaction progress was monitored by TLC in order to evaluate the starting materials consumption. After the reaction was completed, the reaction mixture was extracted with ethyl acetate (15.0 mL), the organic phase was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The product was purified by column chromatography using hexanes as the eluent



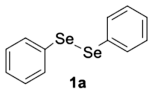
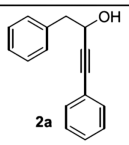
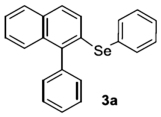
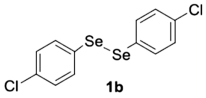
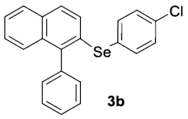
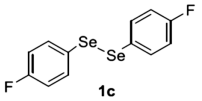
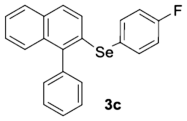
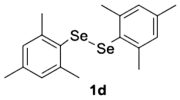
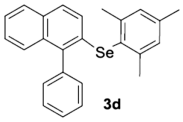
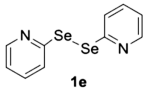
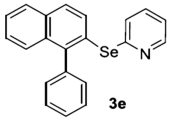
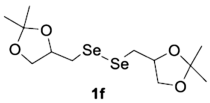
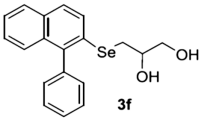
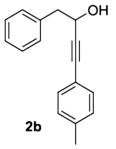
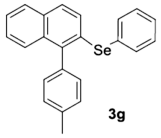
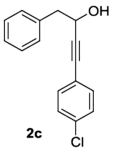
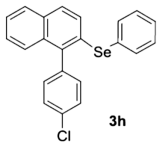
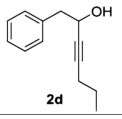
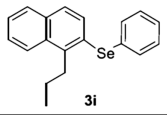
Entry	Diselenide **1**	Alkynol **2**	Product **3**	Time (h)	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	0.5	86
2	 **1b**	**2a**	 **3b**	1.3	63
3	 **1c**	**2a**	 **3c**	1.4	71
4	 **1d**	**2a**	 **3d**	0.5	78
5	 **1e**	**2a**	 **3e**	0.25	84
6	 **1f**	**2a**	 **3f**	0.5	56
7	**1a**	 **2b**	 **3g**	1.7	63
8	**1a**	 **2c**	 **3h**	2.3	72
9	**1a**	 **2d**	 **3i**	1.0	94

Figure 3 Synthesis of 2-organochalcogenyl-naphthalenes 3a–i[a]. [a]The mixture of reagents **1** (0.125 mmol), **2** (0.25 mmol), Oxone® (0.25 mmol) and 2.0 mL of water was added to the glass tube and sonicated for the time indicated in the figure. [b]Yields of isolated products after column chromatography.
Full-size DOI: 10.7717/peerj.4706/fig-3

(except for **3f**, where a mixture EtOAc/hexane (40/60) was used). All the compounds were properly characterized by MS, ^{1}H NMR, ^{13}C NMR, and HRMS (for the new ones).

*1-Phenyl-2-phenylselanyl-naphthalene (**3a**)* (*Recchi, Back & Zeni, 2017*): yield: 0.077 g (86%); yellowish solid; m.p. = 100–101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.80-7.78

(m, 1H); 7.64 (d, J = 8.8 Hz, 1H); 7.54-7.23 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.7, 139.6, 135.0, 133.1, 132.2, 131.0, 130.5, 130.2, 129.4, 128.5, 128.1, 127.9, 127.86, 127.8, 126.4, 126.1, 125.5. MS: *m*/*z* (rel. int., %) 360 (92.4), 280 (66.2), 202 (100.0), 126 (2.8), 77 (7.6).

*2-(4-Chlorophenylselanyl)-1-phenyl-naphthalene (**3b**)* (*Recchi, Back & Zeni, 2017*): yield: 0.062 g (63%); yellowish solid; m.p. = 117–118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.81 (d, J = 8.1 Hz, 1H); 7.68 (d, J = 8.7 Hz, 1H); 7.54-7.24 (m, 13H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 140.2, 139.5, 136.0, 134.2, 133.1, 132.3, 130.3, 130.1, 129.6, 128.9, 128.5, 128.3, 128.2, 127.9, 126.6, 126.2, 125.7. MS: *m*/*z* (rel. int., %) 394 (68.9), 314 (45.1), 202 (100.0), 126 (3.5), 77 (3.5).

*2-(4-Fluorophenylselanyl)-1-phenyl-naphthalene (**3c**)* (*Recchi, Back & Zeni, 2017*): yield: 0.067 g (71%); yellowish solid; m.p. = 123–124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.80-7.78 (m, 1H); 7.65 (d, J = 8.7 Hz, 1H); 7.55-7.48 (m, 5H); 7.44-7.40 (m, 2H); 7.36-7.34 (m, 3H); 7.18 (d, J = 8.2 Hz, 1H); 7.00 (t, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.9 (d, J = 246.6 Hz), 139.4, 139.2, 137.5 (d, J = 7.9 Hz), 133.0, 132.0, 131.1, 130.1, 128.5, 128.2, 127.9, 127.87, 127.4, 126.5, 126.0, 125.5, 124.7 (d, J = 3.5 Hz), 116.7 (d, J = 21.2 Hz). MS: *m*/*z* (rel. int., %) 378 (74.2), 298 (65.2), 202 (100.0), 126 (2.3), 77 (1.9).

*2-Mesitylselanyl-1-phenyl-naphthalene (**3d**)* (*Recchi, Back & Zeni, 2017*): yield: 0.078 g (78%); yellowish solid; m.p. = 111–112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.74 (d, J = 8.1 Hz, 1H); 7.58-7.31 (m, 9H); 6.99 (s, 2H); 6.82 (d, J = 8.7 Hz, 1H); 2.37 (s, 6H); 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.8, 139.7, 139.0, 137.9, 133.2, 132.0, 131.7, 130.0, 128.9, 128.6, 128.0, 127.9, 127.8, 127.7, 126.3, 125.5, 125.2, 124.9, 24.2, 21.1. MS: *m*/*z* (rel. int., %) 402 (100.0), 202 (55.9), 198 (57.3), 91 (18.4), 77 (9.3).

*1-Phenyl-2-(2-pyridylselanyl)-naphthalene (**3e**)*: yield: 0.076 g (84%); yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.42-8.40 (m, 1H); 7.87-7.85 (m, 1H); 7.79 (d, J = 8.6 Hz, 1H); 7.73 (d, J = 8.6 Hz, 1H); 7.50-7.35 (m, 7H); 7.29-7.27 (m, 2H); 7.10 (d, J = 8.0 Hz, 1H); 7.03-7.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 150.0, 143.5, 139.9, 136.5, 133.3, 133.1, 131.9, 130.0, 128.5, 128.1, 127.9, 127.7, 127.6, 127.0, 126.4, 126.2, 126.0, 120.7. MS: *m*/*z* (rel. int., %) 361 (56.7), 284 (100.0), 278 (13.8), 202 (74.8), 79 (16.4). HRMS calcd. for $C_{21}H_{15}NSe$: $[M+H]^+$ 362.0448; found: 362.0443.

*1-Phenyl-2-(propanyl-2,3-diolselanyl)-naphthalene (**3f**)*: yield: 0.050 g (56%); yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.83 (d, J = 8.4 Hz, 1H); 7.79 (d, J = 8.6 Hz, 1H); 7.66 (d, J = 8.6 Hz, 1H); 7.54-7.28 (m, 8H); 3.73-3.63 (m, 3H); 3.48 (dd, J = 11.1 and 5.9 Hz, 1H); 3.01 (dd, J = 12.8 and 4.7 Hz, 1H); 2.89 (dd, J = 12.8 and 8.0 Hz, 1H); 2.59 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.6, 139.8, 133.0, 132.3, 130.3, 130.0, 128.5, 128.4, 128.37, 128.2, 127.9, 127.2, 126.6, 126.3, 125.8, 70.2, 65.5, 31.5. MS: *m*/*z* (rel. int., %) 358 (55.9), 280 (46.8), 202 (100.0). HRMS calcd. for $C_{19}H_{18}O_2Se$: $[M]^+$ 358.0472; found: 358.0467.

*2-Phenylselanyl-1-(4-tolyl)-naphthalene (**3g**)* (*Recchi, Back & Zeni, 2017*): yield: 0.059 g (63%); yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.78 (d, J = 8.0 Hz, 1H); 7.63 (d, J = 8.8 Hz, 1H); 7.53-7.51 (m, 2H); 7.46-7.39 (m, 2H); 7.36-7.23 (m, 9H); 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 139.5, 137.5, 136.5, 135.1, 133.2, 132.1, 131.1, 130.4,

130.0, 129.4, 129.2, 128.0, 127.9, 127.89, 127.8, 126.4, 126.1, 125.4, 21.4. MS: *m/z* (rel. int., %) 374 (100.0), 282 (18.5), 202 (52.3), 91 (2.0).

*1-(4-Chlorophenyl)-2-phenylselanyl-naphthalene (**3h**)* (*Recchi, Back & Zeni, 2017*): yield: 0.071 g (72%); yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.80 (d, J = 8.1 Hz, 1H); 7.66 (d, J = 8.7 Hz, 1H); 7.49-7.27 (m, 13H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 138.6, 138.0, 134.9, 133.9, 133.0, 132.2, 131.6, 131.0, 130.3, 129.4, 128.7, 128.5, 128.4, 128.0, 127.99, 126.7, 125.8, 125.7. MS: *m/z* (rel. int., %) 394 (100.0), 282 (25.4), 202 (69.6), 126 (2.5), 77 (5.4).

*2-Phenylselanyl-1-propyl-naphthalene (**3i**)*: yield: 0.094 g (94%); yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.05 (d, J = 8.7 Hz, 1H); 7.79-7.77 (m, 1H); 7.54-7.42 (m, 5H); 7.27-7.25 (m, 3H); 3.34-3.30 (m, 2H); 1.76-1.66 (m, 2H); 1.09 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 140.6, 133.2, 132.8, 132.3, 131.8, 131.5, 131.4, 129.31, 129.26, 129.2, 127.7, 127.1, 127.0, 126.4, 125.6, 124.4, 34.6, 24.1, 14.5. MS: *m/z* (rel. int., %) 326 (61.5), 216 (100.0), 202 (10.9), 77 (3.4). HRMS calcd. for $C_{19}H_{18}Se$: $[M+H_2O+H]^+$ 345.0758; found: 345.0753.

RESULTS AND DISCUSSION

The selenocyclization of alkynols with electrophilic selenium species is an efficient strategy to prepare organoselanyl-naphthalenes (*Recchi, Back & Zeni, 2017*). In our preliminary studies on the use of Oxone® as an oxidant to cleavage of Se–Se bond, we have observed that its reaction with diselenides generates highly reactive species in situ (*Perin et al., 2018*). Thus, by combining the selenocyclization strategy with the environmental and economic advantages of using Oxone® as an oxidizing agent, a study was carried out to evaluate the possibility of using it in selenocyclization reactions to prepare organoselanyl-naphthalenes. In our preliminary experiments, we choose diphenyl diselenide **1a** and 1,4-diphenylbut-3-in-2-ol **2a** as model substrates to establish the best conditions for the cyclization reaction promoted by Oxone® to synthesize the respective 2-organoselanyl-naphthalene **3a**.

Initially, the reaction was performed using 0.25 mmol of alkynol **2a**, 0.125 mmol of diphenyl diselenide **1a** and 0.25 mmol of Oxone®, using ethanol (2.0 mL) as the solvent at 60 °C under magnetic stirring. The desired product **3a** was obtained in 78% yield after 72 h (Fig. 2, entry 1). To improve this result, some experiments were performed with the purpose of increasing the isolated yield and reducing the reaction time. The same reaction was then performed under ultrasonic irradiation (amplitude of 60%) and after 50 min, product **3a** was obtained in 84% yield (Fig. 2, entry 2). Aiming to improve the yield of **3a**, parameters as the nature of the solvent, quantities of the starting material 2a, amounts of Oxone®, and amplitude of the US were evaluated (Fig. 2, entries 3–12).

Regarding the influence of the solvent in the reaction, a range of solvents were tested and in reactions using polyethylene glycol-400 (PEG-400, Labsynth, Diadema, Brazil), glycerol, and DMF, product **3a** was obtained in good yields (Fig. 2, entries 3, 4, and 8). To our satisfaction, a very good yield of 86% was obtained after sonication of the reaction mixture

for 30 min in water (Fig. 2, entry 5). However, using dimethyl sulfoxide (DMSO) or acetonitrile as the solvent, only trace amounts of **3a** were observed (Fig. 2, entries 6 and 7).

After water was defined as the best solvent for the reaction, the amplitude used in the ultrasound apparatus was evaluated. When the reaction was performed at 40% of amplitude, the desired product **3a** was obtained in only 63% yield (Fig. 2, entry 9). It was observed that at this lower amplitude, the homogenization of the mixture was incomplete, what could negatively affect the reaction yield.

When an excess of alkynol **2a** was used, total consumption of diphenyl diselenide **1a** occurred after 30 min of reaction (monitored by TLC), however the yield of **3a** was maintained (Fig. 2, entry 10). By using a lower amount of Oxone® (0.125 mmol), there was no total consumption of the starting materials after 2 h of reaction, and the desired product **3a** was obtained in only 42% yield (Fig. 2, entry 11). Finally, the reaction was carried out in the absence of Oxone® and after 2 h none of product was formed (Fig. 2, entry 12). In order to verify the influence of the $KHSO_4$ species present in the reaction medium, a test was performed using 0.25 mmol of Oxone® together with 0.25 mmol of $KHSO_4$ and, after only 10 min of reaction, the starting materials were totally consumed, and the desired product **3a** was obtained in 92% isolated yield, showing the need of generation of this species in the reaction medium (Fig. 2, entry 13). Thus, the best condition was defined as the sonication of a mixture of 0.125 mmol of diphenyl diselenide **1a** and 0.25 mmol of alkynol **2a** in the presence of 0.25 mmol of Oxone® in water (2.0 mL) for 30 min (Fig. 2, entry 5).

Once the best reaction conditions were determined, the methodology was extended to different substrates, in order to evaluate its generality and robustness in the synthesis of different 2-organoselanyl-naphthalenes **3a–i** (Fig. 3). Firstly, the effect of electron-donor (EDG) and electron-withdrawing groups (EWG) attached to the aromatic ring of diselenide **1a–d** was evaluated (Fig. 3, entries 1–4). It was observed that both EDG and EWG negatively affect the reaction, affording lower yields of the respective products. When diselenide **1b**, containing a chlorine atom at the *para* position was used, there was a significant decrease in yield when compared to diphenyl diselenide **1a**, and the respective naphthalene **3b** was obtained in 63% yield (Fig. 3, entry 2). Similarly, the electron-poor diselenide **1c**, with a fluorine atom at the *para* position, afforded the respective naphthalene **3c** in a moderate yield of 71% after 1.4 h (Fig. 3, entry 3).

The sterically hindered dimesityl diselenide **1d** was also a suitable substrate for the reaction, affording the expected product **3d** in 78% yield after 0.5 h of sonication (Fig. 3, entry 4). Heteroaromatic bis-pyridyl diselenide **1e** was successfully used as substrate in the reaction with alkynol **2a**, affording the respective 2-heteroarylselanyl-naphthalene **3e** in 84% yield (Fig. 3, entry 5).

Interestingly, when diselenide derived from protected glycerol (solketal) **1f** was used, deprotected naphthalene diol **3f** was obtained in 56% yield after 0.5 h of reaction (Fig. 3, entry 6). This may be associated with the ketal deprotection ability of Oxone®, which has already been reported in the literature (*Mohammadpoor-Baltork, Amini & Farshidipoor, 2000*).

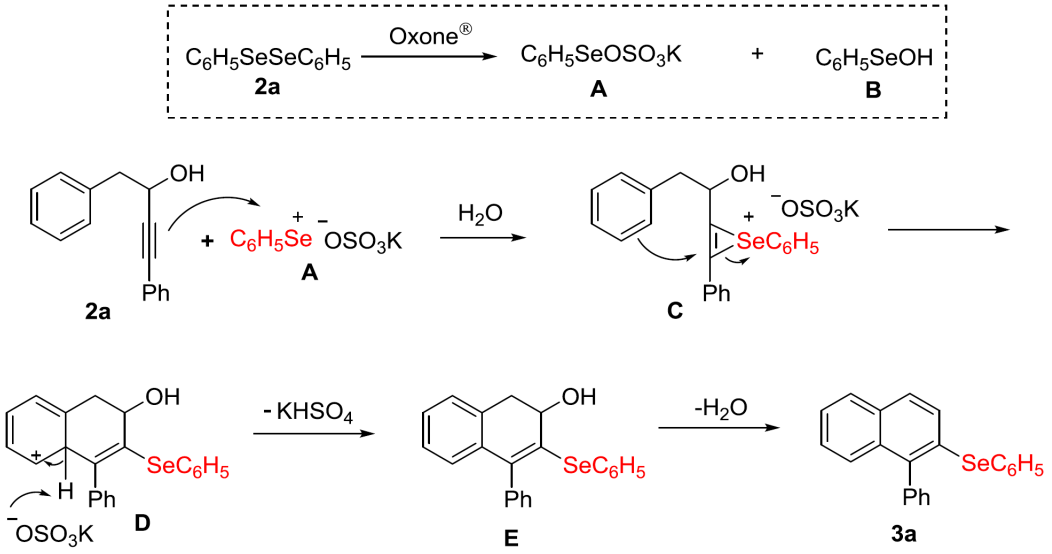


Figure 4 **Proposed mechanism.** Full-size DOI: 10.7717/peerj.4706/fig-4

The possibility of performing these reactions with other alkynols **2b–d** was also investigated. Alkynols derived from phenylacetylene **2b** and **2c**, containing EDG and EWG at the aromatic ring, efficiently reacted with diphenyl diselenide **1a**/Oxone®, affording the respective products **3g** and **3h** in 63 and 72% yields after 1.7 and 2.3 h, respectively (Fig. 3, entries 7 and 8). This result shows that the reaction is not sensitive the electronic effects of the substituents on the aromatic ring of the alkynols **2b** and **2c**. A remarkable positive effect was observed when an alkyl group was connected to the C_{sp} of the alkynol, as in **2d** and an excellent 94% yield of the expected naphthalene **3i** was obtained after 1.0 h (Fig. 3, entry 9).

Based on our results and those from the literature (*Zhang, Sarkar & Larock, 2006*; *Recchi, Back & Zeni, 2017*; *Perin et al., 2018*), a plausible mechanism for the carbocyclization of alkynol **1a** with $(C_6H_5Se)_2$ **2a**/Oxone® in aqueous medium is depicted in Fig. 4. The first step in the reaction is the oxidative cleavage of the Se–Se bond in diphenyl diselenide **2a** by Oxone®, forming intermediates **A** and **B** (*Perin et al., 2018*). Once the electrophilic selenium species **A** is formed, it reacts with the carbon–carbon triple bond of the alkynol **1a** to produce the seleniranium intermediate **C**. Following, an intramolecular 6-*endo-dig* cyclization occurs, giving intermediate **D**, which undergoes deprotonation to restoring the aromaticity of the system, forming the dihydronaphthalene **E**. Ultimately, water is eliminated to give the desired product **3a** (Fig. 4).

CONCLUSION

A convenient, selective and eco-friendly methodology was developed for the synthesis of 2-organoselanyl-naphthalenes **3**, using water as the solvent. The use of ultrasound as alternative energy source drastically reduces the reaction time, while increasing the reaction yield. This method involves the cyclization of properly

substituted alkynols in the presence of electrophilic selenium species. Oxone® was shown to be an efficient and mild oxidizing agent for the oxidative cleavage of the Se–Se bond of diselenides in situ.

ADDITIONAL INFORMATION AND DECLARATIONS

Funding

This work was supported by The Brazilian Council for Research and Technology (CNPq), CAPES and FAPERGS. The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Grant Disclosures

The following grant information was disclosed by the authors:
The Brazilian Council for Research and Technology (CNPq).
CAPES.
FAPERGS.

Competing Interests

Eder J Lenardao is an Academic Editor for PeerJ.

Author Contributions

- Gelson Perin conceived and designed the experiments, analyzed the data, contributed reagents/materials/analysis tools, authored or reviewed drafts of the paper, approved the final draft.
- Daniela Rodrigues Araujo performed the experiments, prepared figures and/or tables.
- Patrick Carvalho Nobre performed the experiments, prepared figures and/or tables.
- Eder João Lenardao conceived and designed the experiments, analyzed the data, contributed reagents/materials/analysis tools, authored or reviewed drafts of the paper, approved the final draft.
- Raquel Guimarães Jacob analyzed the data, contributed reagents/materials/analysis tools, authored or reviewed drafts of the paper.
- Marcio Santos Silva performed the experiments, analyzed the data, contributed reagents/materials/analysis tools, authored or reviewed drafts of the paper.
- Juliano Alex Roehrs performed the experiments, prepared figures and/or tables.

Data Availability

The following information was supplied regarding data availability:
The raw data are provided in the Supplemental File.

Supplemental Information

Supplemental information for this article can be found online at http://dx.doi.org/10.7717/peerj.4706#supplemental-information.

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