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Article

# Synthesis of Alkynylselenides under Visible-Light Irradiation Using the Ionic Liquid [BMIm]$BF_4$ as a Solvent

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In this work, a visible-light-driven synthesis of alkynyl selenides using [BMIm]$BF_4$ as an environmentally friendly solvent and without the addition of metal catalysts, photosensitizers, directing-groups, or bases is reported. The target compounds were obtained in moderate to good yields with good functional group tolerance by the reaction of diorganoyldiselenides with 1-bromoalkynes proceeding through a radical mechanism.

**Keywords:** ionic liquids, environmentally friendly synthesis, visible-light, organochalcogen

## Introduction

Visible-light promoted reactions have emerged as a remarkable and powerful tool to provide greener and milder transformations in organic synthesis, leading to a wide range of organic reactions that are conducted at room temperature and easily operated.[1] Moreover, the light-emitting diodes that are able to promote photochemical reactions under visible-light are inexpensive, sustainable lighting sources with broad commercial availability,[2] which makes this approach very attractive from an environmental and economic perspective.

In this context, the continuous search for new synthetic routes that can reduce/minimize the generation of waste and side-products and that, in some way, fit within the principles of green chemistry is necessary.[3] In this way, for a long time, ionic liquids have attracted the interest of the scientific community and even industry,[4] as these organic salts can exhibit several applications in organic synthesis,[5] $CO_2$ capture,[6] catalysis,[7] biochemistry,[8] and others. In particular, they have often been used to replace conventional solvents in organic reactions[9] due to their unique physical properties such as high thermal stability, low volatility, low flammability, and negligible vapor pressure.[10] In addition, the fundamental structure of ionic liquids has offered many combinations of organic cations and organic or inorganic anions in order to specifically model them for different sustainable applications.[11]

As part of the sophisticated organochalcogen chemistry found in biological[12] and materials sciences,[13] alkynyl chalcogenides are useful and versatile synthetic intermediates in hydrohalogenation,[14] cycloaddition,[15] cross coupling,[16] A$^3$-coupling,[17] chalcogenoesters synthesis,[18] and cyclization reactions,[19] playing an important role in the synthesis of bioactive heterocyclic compounds described as anti-cancer,[15] anti-alzheimer's,[19] and antioxidant[19] agents (Scheme 1).

A convenient method for the synthesis of alkynyl chalcogenides involves the reaction between diorganoyl dichalcogenides and terminal alkynes. However, this approach often requires reducing agents[20] or metal catalysts, such as copper,[21] iron,[22] or silver[23] (Scheme 2a, *i*). Recently, some metal-free strategies under base-catalyzed conditions (catalytic $K_3PO_4$ or CsOH) were described,[24] but these methodologies are restricted to the synthesis of alkynyl tellurides (Scheme 2a, *ii*). Alternatively, considering the number of works about carbon-chalcogen bond formation under visible light irradiation,[25] photochemistry becomes a promising tool to expand the synthesis of alkynyl chalcogenides in an eco-friendly pathway. The first step toward the photoinduced synthesis of alkynyl chalcogenides was taken by Collins and co-workers,[26] who reported an elegant transition-metal photoredox catalysis for the synthesis of alkynyl sulfides using thiols and 1-bromoalkynes in the presence of a nickel catalyst and 4CzIPN as a photosensitizer under blue light emitting diode (LED) irradiation (Scheme 2b). Interestingly, the use of 1-bromoalkynes in this methodology was essential

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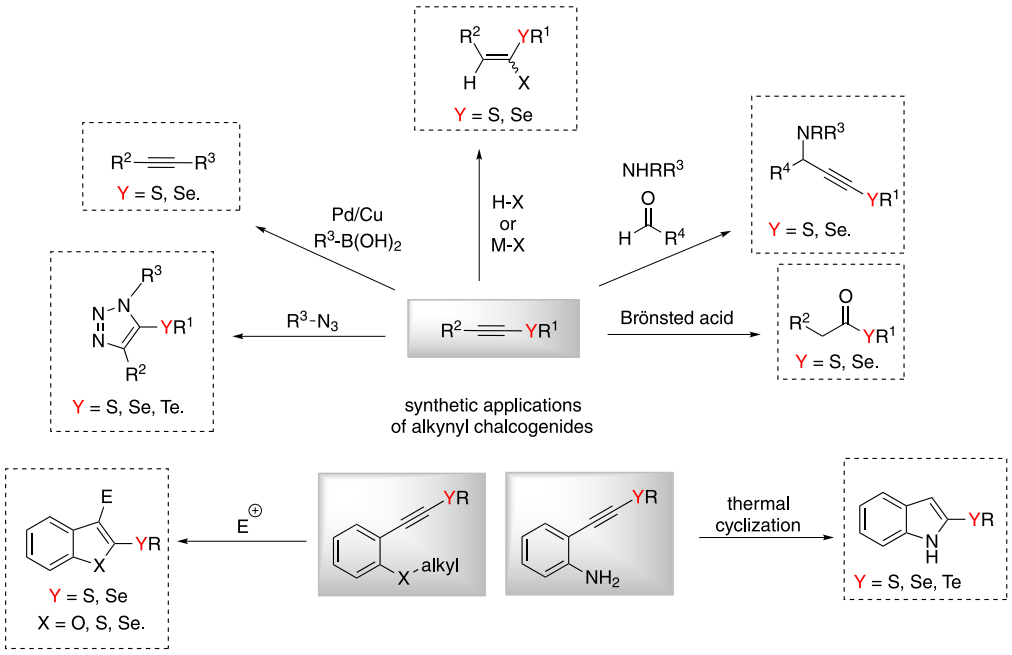



**Scheme 1.** Selected synthetic applications of alkynyl chalcogenides.

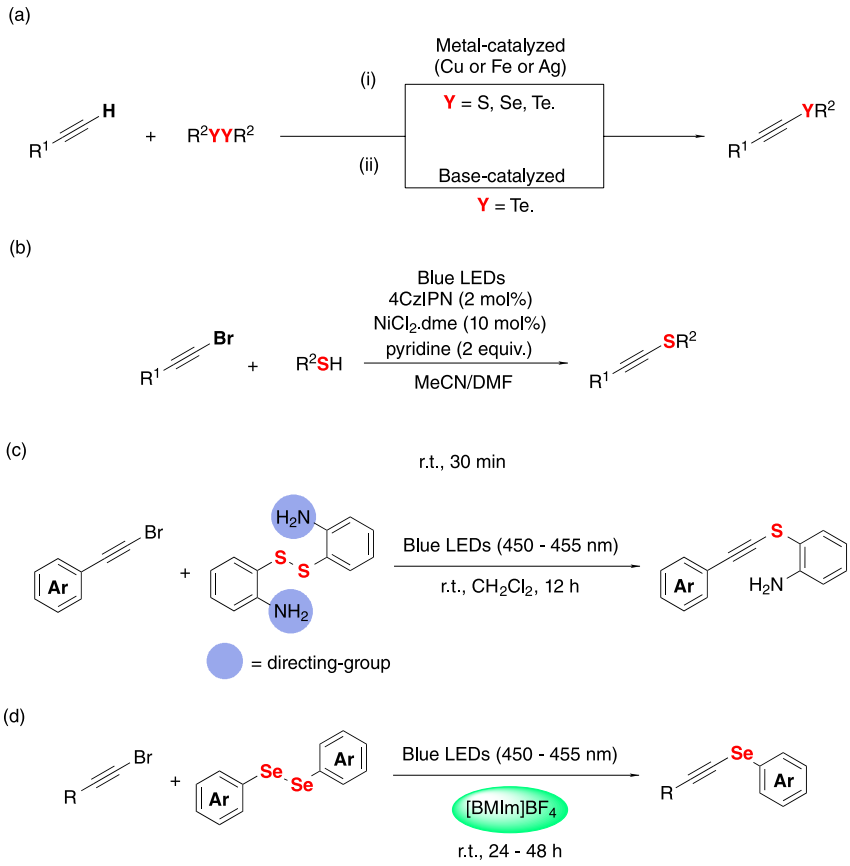
to avoid the reduction of the C≡C bond and the subsequent formation of vinyl chalcogenides as side-products, which are usually observed in previous photoinduced reactions of terminal alkynes with thiols[19] or diorganoyl dichalcogenides under visible light irradiation.[27] More recently, the amino group *ortho*-assisted synthesis of alkynyl sulfides using 2,2'-diaminodisulfides and terminal alkynes or 1-bromoalkynes proved to be an efficient strategy towards the formation of the Csp–S bond under visible light (Scheme 2c).[28]

In this context, considering the well-established homolytic cleavage of diorganoyl dichalcogenides under visible light to produce chalcogen centered-radicals[29] and the use of 1-bromoalkynes in order to maintain the valuable C≡C bond in photoinduced processes, herein, we report the synthesis of alkynylselenides under visible-light irradiation using the ionic liquid [BMIm]$BF_4$ as an environmentally friendly solvent (Scheme 2d). The developed methodology avoided the requirement of directing-group strategies and allowed the synthesis of alkynyl selenides in moderate to good yields. Furthermore, [BMIm]$BF_4$ played a crucial role as the reaction media to convert vinylic side-products into the desired alkynyl selenides.

## Results and Discussion

Our reaction study started by using (bromoethynyl) benzene (**1a**) and diphenyldiselenide (**2a**) as model substrates and the reaction was carefully monitored by gas chromatography mass spectrometry (GC-MS). Initially, the stoichiometric relationship between **1a** and **2a** was evaluated (for details, see Supplementary Information (SI) section, Table S1). The best condition was found when 3.0 equivalents of **1a** and 1.0 equivalent of **2a** reacted under blue LED irradiation (100 W) in dichloromethane (DCM) after 1 h, with 68% conversion of **2a** into the desired product phenyl(phenylethynyl)selane (**3a**) along with the vinylic side-product **4** (*m/z* = 418) in a 69:31 ratio, respectively (Table 1, entry 1). To improve the conversion of **2a** and the reaction selectivity, other lightning sources were evaluated (Table 1, entries 2-4), but unsatisfactory conversions of **2a** were obtained. Next, the reaction was performed under blue LED (100 W) irradiation in other polar aprotic solvents (Table 1, entries 5-9), such as tetrahydrofuran (THF), dimethylformamide (DMF), and dimethylsulfoxide (DMSO). A moderate conversion of **2a** was observed in DMF, with a good ratio of the desired product **3a** and the vinylic side-product **4** (Table 1, entry 5). Alternatively, the reaction performed in THF showed an excellent conversion of **2a**, but the reaction was not selective (Table 1, entry 6). Longer reaction times in DMF provided good conversions of **2a** with excellent selectivity (Table 1, entries 7 and 8). Similarly, a good conversion of **2a** was obtained in DMSO, but the selectivity was not improved (Table 1, entry 9).

In order to selectively produce **3a** under environmentally benign reaction conditions, we hypothesized that ionic liquids based on the imidazolium cation and tetrafluoroborate ($BF_4^-$) anion could serve as an ideal reaction media in our methodology. In 2005, Ranu and Jana[30] demonstrated that this class

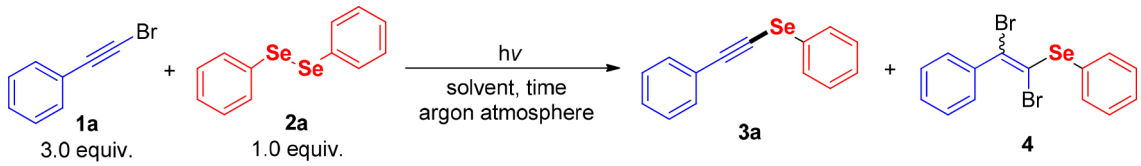



**Scheme 2.** Synthetic strategies for the synthesis of alknyl chalcogenides. (a) Typical synthesis of alkynyl chalcogenides from terminal alkynes; (b) photoinduced synthesis of alkynyl sulfides from 1-bromoalkynes and thiols; (c) photoinduced synthesis of alkynyl sulfides from 1-bromoalkynes and diorganoyl disulfides using directing-group strategy; (d) this work: photoinduced synthesis of alkynyl selenides from 1-bromoalkynes in ionic liquids.

of ionic liquids could effectively act as a catalyst and solvent in debromination reactions of alkyl and alkenyl *vicinal*-dibromides, affording the respective alkenes and alkynes in high yields.[31] With this in mind, and in order to convert the undesired vinylic side-product **4** into **3a** by debromination, we performed a reaction in the ionic liquid [BMIm]$BF_4$, which gratifyingly led to an excellent conversion of **2a** with high selectivity for the desired product **3a** (Table 1, entry 10). Furthermore, the use of the ionic liquid [BMIm]$PF_6$ as the solvent did not favor the reaction selectivity (Table 1, entry 11), indicating an important role of the $BF_4$ anion in our methodology. Finally, lower or higher amounts of [BMIm]$BF_4$ did not improve the reaction efficiency (Table 1, entries 12 and 13).

With the optimized reaction conditions in hand (Table 1, entry 10), we then evaluated the reaction scope of this photoinduced process. Unfortunately, although high conversion and selectivity were achieved during the reaction optimization study for the synthesis of **3a**, this compound could not be cleanly isolated by column chromatography from the remaining mixture of diphenyldiselenide **2a** and the vinylic side-product **4**, so we decided to use methoxy-substituted diaryl diselenides **2** during the reaction scope to benefit the purification processes (Scheme 3). Initially, bromoethynylbenzene (**1a**) and arylbromoalkyne derivatives bearing electron-donating or electron-withdrawing groups on the benzene ring successfully reacted with 1,2-bis(4-methoxyphenyl) diselane (**2b**), affording the respective alkynylselenides **3b**-**3h** in moderate to good yields. The reaction also tolerated bromoalkynes containing naphtalene derivatives or heteroaromatic groups in comparable yields (Scheme 3, **3i** and **3j**). Sterically hindered 1,2-bis(2-methoxyphenyl) diselane (**2c**) also proved to be a suitable reaction partner in this transformation (Scheme 3, **3k**). Also, vinyl or alkyl bromoalkyne derivatives were well tolerated, but modest yields and longer reaction times were required, which was probably related to a weakly radical stabilization on these substrates (Scheme 3, **3l**-**3n**). It is noteworthy that an alkynylsulfide derivative could also be synthesized through this photoinduced process (Scheme 3, **3o**). This reaction required the use of a 200 W blue LED to proceed well, which is a reasonable result considering the higher relative energy of the S–S bond in comparison to the Se–Se bond.[31] Finally, it is important to mention that the reaction did not work for bromoalkynes containing strong electron-donating

**Table 1.** Optimization of the reaction conditions for the synthesis of **3a**




| entry[a] | Lamp | Solvent | time / h | Conversion of **2a**[b] / % | Ratio (**3a**:**4**)[c] |
|---|---|---|---|---|---|
| 1 | blue 100 W | DCM | 1 | 68 | 69:31 |
| 2 | blue 50 W | DCM | 1 | 8 | 100:0 |
| 3 | white 100 W | DCM | 1 | 16 | 56:44 |
| 4 | UVA 50 W | DCM | 1 | 0 | – |
| 5 | blue 100 W | DMF | 1 | 47 | 89:11 |
| 6 | blue 100 W | THF | 1 | 94 | 62:38 |
| 7 | blue 100 W | DMF | 4 | 72 | 93:07 |
| 8 | blue 100 W | DMF | 24 | 72 | 97:03 |
| 9 | Blue 100 W | DMSO | 24 | 78 | 69:31 |
| 10[d] | blue 100 W | $[BMIm]BF_4$ | 24 | 98 | 90:10 |
| 11[d] | blue 100 W | $[BMIm]PF_6$ | 24 | 98 | 43:57 |
| 12[e] | blue 100 W | $[BMIm]BF_4$ | 24 | 82 | 81:19 |
| 13[f] | blue 100 W | $[BMIm]BF_4$ | 24 | 60 | 70:30 |

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), solvent (1 mL), under argon atmosphere; [b,c]determined by GC-MS of the crude reaction mixture; [d]reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), solvent (1 g); [e]reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), solvent (0.5 g); [f]reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), solvent (1.5 g). DCM: dichloromethane; THF: tetrahydrofuran; DMF: dimethylformamide; DMSO: dimethylsulfoxide.

or withdrawing groups such as amino, nitro, cyano, and pyridyl (Scheme 3, **3p**-**3s**).[32]

In order to give insights about the reaction mechanism, some control experiments were performed under the optimized reaction conditions for the synthesis of **3a** (Scheme 4). The addition of the radical inhibitor (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) almost completely inhibited the reaction, indicating a radical mechanism (Scheme 4a). Moreover, a reaction performed in the dark did not produce **3a**, which confirmed the fundamental effect of light irradiation in our methodology (Scheme 4b).

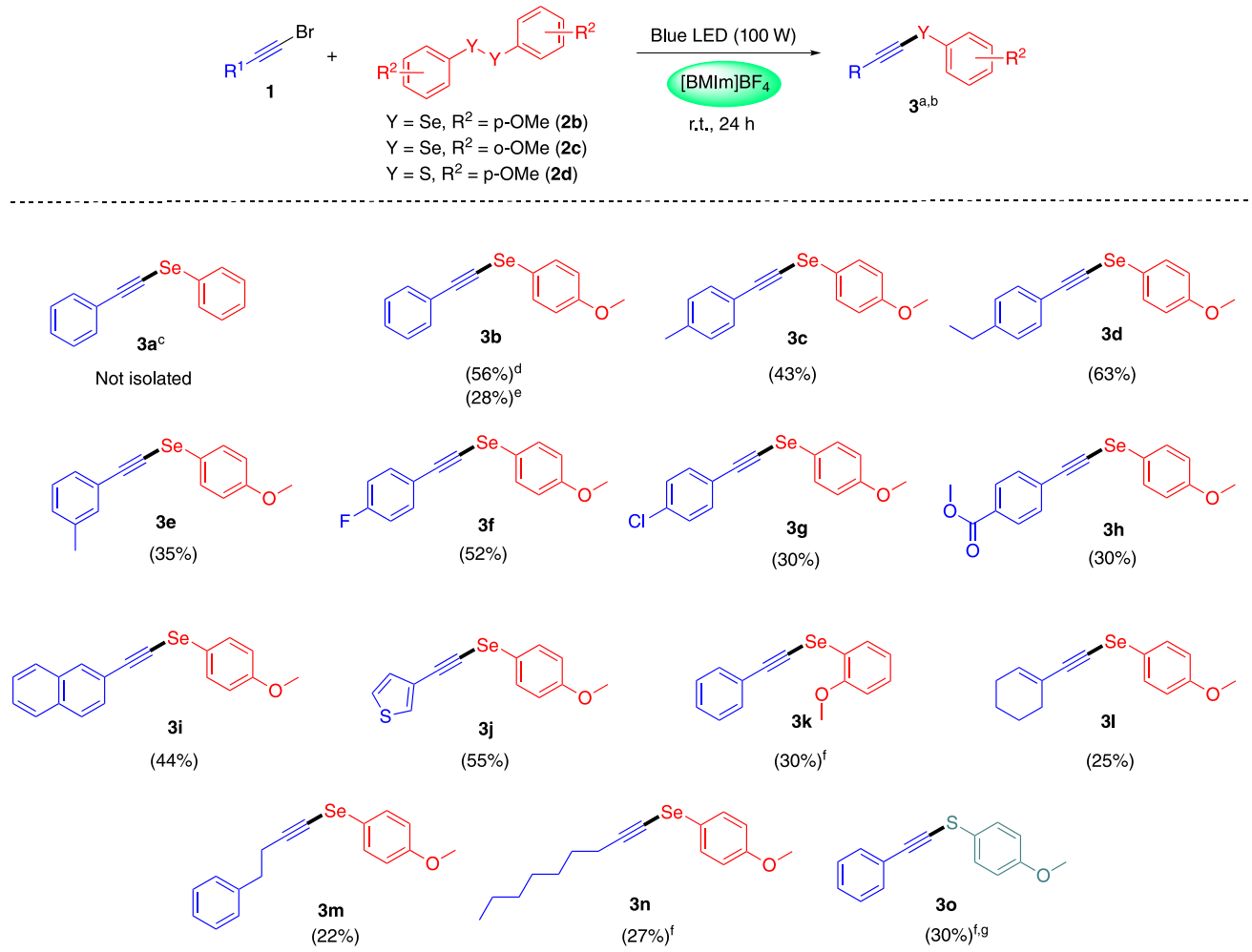
Based on these results, we proposed a plausible mechanism for the photoinduced synthesis of alkynylselenides **3** in $[BMIm]BF_4$ (Scheme 5). Initially, diaryldiselenide **2** undergoes a reversible Se–Se bond homolytic cleavage due to the light irradiation.[29] Then, a radical addition between arylselenium radical species and bromoalkyne **1** takes place to produce a vinylic radical intermediate **5**. At this point, the desired product **3** can be directly obtained by bromine radical elimination[31] from intermediate **5** (Scheme 5, pathway A). Conversely, this intermediate can undergo a bromine radical addition to generate the respective vinylic dibromide side-product **4** (Scheme 5, pathway B). Based on previous literature,[30] a debromination reaction can occur from **4** in the presence of $[BMIm]BF_4$, leading to vinylic carbanion species **6**, which is able to produce **3** with concomitant regeneration of $[BMIm]BF_4$.

## Conclusions

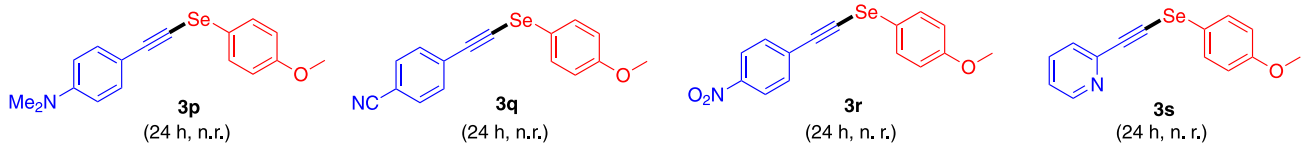
In conclusion, a low-cost, environmentally benign and easily workable methodology for the photoinduced synthesis of selenoalkynes was developed. Even if moderate to good yields were obtained in the reaction scope investigation, we highlight that this methodology benefits from mild conditions and the inherent absence of transition-metals, photosensitizers, or directing-groups to promote a challenging photoinduced Csp–Se bond formation. We also hope that this work may provide useful insights into the use of ionic liquids as sustainable catalysts/reaction media in organochalcogen chemistry.

## Experimental

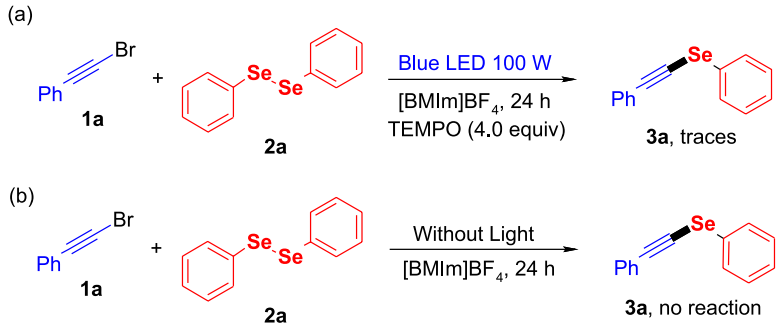
Unless otherwise stated, all reagents were purchased from commercial suppliers (Sigma-Aldrich, Steinheim, Germany) and used without further purification. DMF (*N*,*N*-dimethylformamide), DMSO (dimethyl sulfoxide), MeCN (acetonitrile), THF (tetrahydrofuran) and DCM (dichloromethane) were purified and dried under classical



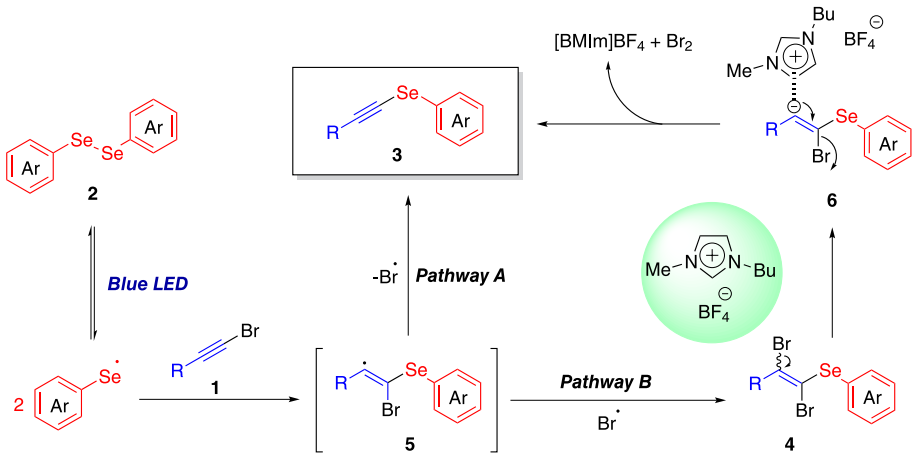

No reaction for the following products:




**Scheme 3.** Scope of the photoinduced synthesis of selenoalkynes. [a]Reaction conditions: **1** (0.3 mmol), **2** (0.1 mmol), [BMIm]$BF_4$ (1.0 g), under blue LED (100 W) and argon atmosphere for the respective reaction times indicated. [b]Isolated yields. [c]Product observed by GC-MS in a 90:10 (**3a**/**4a**) ratio after 98% conversion of **2a**. [d]Isolated yield after 100% conversion of **2b**, in a 100:0 ratio of **3b**:**4b** determined by GC-MS of the crude reaction mixture. [e]Reaction carried out with 2.7 mmol of **2b** and 8.1 mmol of **1a** in [BMIm]$BF_4$ (27.0 g). [f]Reactions carried out during 48 h. [g]Blue LED (200 W).




**Scheme 4.** Control experiments for the synthesis of **3a**. (a) Radical trapping experiment. Reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), TEMPO (4.0 equiv.), [BMIm]$BF_4$ (1.0 g), under blue LED (100 W) and argon atmosphere for 24 h. (b) Reaction performed in dark. **1a** (0.3 mmol), **2a** (0.1 mmol), [BMIm]$BF_4$ (1.0 g) under argon atmosphere (reaction flask covered with aluminum foil) for 24 h.




**Scheme 5.** Plausible mechanism for the photoinduced synthesis of alkynylselenides **3** in $[BMIm]BF_4$.

methods.[1] Solvents used in liquid-liquid extraction and as eluents for chromatographic purification were distilled before use. The reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 $F_{254}$ aluminum sheets, and the visualization of the spots were done under UV light (254 nm), stained with iodine, or by the mixture between 5% of vanillin in 10% of $H_2SO_4$ and heat as developing agents. Column chromatography was performed on silica gel (230-400 mesh). $^1H$ and $^{13}C$ nuclear magnetic resonance (NMR) were recorded on 400 MHz spectrometer Varian Inova 400 and Bruker Avance 400. Chemical shifts ($\delta$) are expressed in ppm downfield from tetramethylsilane (TMS) as internal standard in spectra made in $CDCl_3$. Coupling constants are reported in Hz. Hydrogen coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), multiplet (m) and broad signal (bs) as soon as appears. Melting points were recorded on a Stuart Scientific melting point apparatus SMP3. High resolution mass spectra (HMRS) were recorded on a Micromass Q-Tof spectrometer (Milford, United States), using electrospray ionization (ESI).

### General procedure for the synthesis of alkynylselenides **3a-3n** and alkynylsulfide **3o**

In a dried glass tube under argon atmosphere, $[BMIm]BF_4$ (1.0 g) was added and degassed for 20 min at room temperature. After this time, bromoalkyne **1** (0.3 mmol) and diaryldichalcogenide **2** (0.1 mmol) were added. Under argon atmosphere, the reaction mixture was stirred in the photoreactor (blue LED, 100 W) at room temperature for 24 h for the synthesis of **3a**-**3j**, **3l** and **3m** and 48 h for the synthesis of **3k**, **3n** and **3o** (the respective synthesis of alkynylsulfide **3o** was performed using a blue LED 200 W). After the completion of the reaction, hexane/ethyl acetate (90:10 v:v, 5.0 mL) was added to the glass tube. After vigorous stirring, two layers were generated, and the upper layer containing the organic solvents was collected and this process was repeated until complete extraction of the desired product **3** (monitored by TLC). The collected organic phase was concentrated under reduced pressure and further purified by preparative thin layer chromatography on silica gel to give the desired products **3b**-**3o**.

### (4-Methoxyphenyl)(phenylethynyl)selane (**3b**)[33]

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 56% yield; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (d, 2H, *J* 8.9 Hz), 7.47-7.44 (m, 2H), 7.32-7.29 (m, 3H), 6.88 (d, 2H, *J* 8.9 Hz), 3.79 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.5, 131.9, 131.7, 128.4, 128.3, 123.1, 118.3, 115.4, 101.5, 70.4, 55.4.

### (4-Methoxyphenyl)(*p*-tolylethynyl)selane (**3c**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 43% yield; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, 2H, *J* 8.9 Hz), 7.36 (d, 2H, *J* 7.9 Hz), 7.11 (d, 2H, *J* 7.9 Hz), 6.88 (d, 2H, *J* 8.9 Hz), 3.79 (s, 3H), 2.34 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.3, 138.6, 131.66, 131.65, 129.0, 120.2, 118.5, 115.3, 101.6, 69.2, 55.3, 21.5; $^{77}Se$ NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 260.83; HRMS (ESI) *m/z* [$M^+$] calcd. for $C_{16}H_{14}OSe$, 302.0210; found, 302.0201.

### ((4-Ethylphenyl)ethynyl)(4-methoxyphenyl)selane (**3d**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 63% yield; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, *J* 8.9 Hz, 2H), 7.38 (d, *J* 8.2 Hz, 2H), 7.14 (d, *J* 8.2 Hz,

2H), 6.87 (d, *J* 8.9 Hz, 2H), 3.79 (s, 3H), 2.64 (q, *J* 7.6 Hz, 2H), 1.22 (t, *J* 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.3, 144.9, 131.8, 131.6, 127.8, 120.4, 118.5, 115.3, 101.7, 69.2, 55.3, 28.8, 15.3; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 260.90; HRMS (ESI) *m/z* [M$^+$] calcd. for $C_{17}H_{17}OSe$, 316.0361; found, 316.0351.

(4-Methoxyphenyl)(*m*-tolylethynyl)selane (**3e**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 35% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (d, *J* 8.8 Hz, 2H), 7.31-7.24 (m, 2H), 7.23-7.17 (m, 1H), 7.18-7.10 (m, 1H), 6.88 (d, *J* 8.8 Hz, 2H), 3.80 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.4, 138.0, 132.2, 131.7, 129.3, 128.7, 128.2, 123.0, 118.4, 115.3, 101.7, 69.8, 55.4, 21.2; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 261.33; HRMS (ESI) *m/z* [M$^+$] calcd. for $C_{17}H_{16}OSe$, 302.0210; found, 302.0200.

((4-Fluorophenyl)ethynyl)(phenyl)selane (**3f**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 52% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, *J* 8.8 Hz, 2H), 7.46-7.42 (m, 2H), 7.02-6.98 (m, 2H), 6.88 (d, *J* 8.8 Hz, 2H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.5 (d, $^1J_{C\text{-}F}$ 250.0 Hz), 159.5, 133.7 (d, $^3J_{C\text{-}F}$ 8.4 Hz), 132.0, 119.4 (d, $^4J_{C\text{-}F}$ 3.5 Hz), 118.1, 115.6 (d, $^2J_{C\text{-}F}$ 22.1 Hz), 115.3, 100.2, 70.1, 55.3; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 261.44; HRMS (ESI) *m/z* [M$^+$] calcd. for $C_{16}H_{14}OSe$, 305.9959; found, 305.9951.

((4-Chlorophenyl)ethynyl)(phenyl)selane (**3g**)[34]

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a pale-yellow solid in 30% yield; melting point 81-83 ºC; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (d, *J* 8.9 Hz, 2H), 7.37 (d, *J* 8.7 Hz, 2H), 7.28 (d, *J* 8.7 Hz, 2H), 6.89 (d, *J* 8.9 Hz, 2H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.6, 134.3, 132.8, 132.1, 128.6, 121.7, 117.9, 115.4, 100.1, 71.8, 55.4.

4-(((4-Methoxyphenyl)selanyl)ethynyl)benzoate (**3h**)

The product was isolated by a preparative thin layer chromatography (hexane 95:5 ethyl acetate) as a yellow solid in 30% yield; mp 72-74 ºC; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.98 (d, *J* 8.4 Hz, 2H), 7.54 (d, *J* 8.8 Hz, 2H), 7.48 (d, *J* 8.4 Hz, 2H), 6.90 (d, *J* 8.8 Hz, 2H), 3.91 (s, 3H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.5, 159.7, 132.3, 131.1, 129.4, 129.3, 127.9, 117.7, 115.4, 100.7, 74.8, 55.4, 52.2; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 266.27; HRMS (ESI) *m/z* [M$^+$] calcd. for $C_{17}H_{14}O_3Se$, 346.0108; found, 346.0101.

(4-Methoxyphenyl)(naphtalen-2-ylethynyl)selane (**3i**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 44% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.31 (d, *J* 8.2 Hz, 1H), 7.85-7.79 (m, 2H), 7.68 (d, *J* 7.2 Hz, 1H), 7.59 (d, *J* 8.8 Hz, 2H), 7.57-7.48 (m, 2H), 7.44-7.39 (m, 1H), 6.90 (d, *J* 8.8 Hz, 2H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.5, 133.4, 133.1, 131.9, 130.6, 128.8, 128.2, 126.8, 126.4, 126.2, 125.1, 120.9, 118.5, 115.3, 99.6, 75.2, 55.3; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 264.64; HRMS (ESI) *m/z* [M + H]$^+$ calcd. for $C_{19}H_{15}OSe$, 339.0283; found, 339.0271.

3-(((4-Methoxyphenyl)selanyl)ethynyl)thiophene (**3j**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 55% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, 2H, *J* 8.9 Hz), 7.48 (dd, 1H, *J* 3.0, 1.2 Hz), 7.25 (dd, 1H, *J* 5.0, 3.0 Hz), 7.13 (dd, 1H, *J* 5.0, 1.2 Hz), 6.87 (d, 2H, *J* 8.9 Hz), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.4, 131.9, 130.0, 129.6, 125.2, 122.3, 118.2, 115.3, 96.2, 69.8, 55.3; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 261.56; HRMS (ESI) *m/z* [M$^+$] calcd. for $C_{13}H_{10}OSSe$, 293.9613; found, 293.9606.

(2-Mmethoxyphenyl)(phenylethynyl)selane (**3k**)[35]

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 30% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.74 (dd, 1H, *J* 7.6, 1.6 Hz), 7.57-7.51 (m, 2H), 7.38-7.32 (m, 3H), 7.27-7.21 (m, 1H), 7.01 (td, 1H, *J* 7.6, 1.2 Hz), 6.87-6.81 (m, 1H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 155.7, 131.7, 128.5, 128.4, 128.3, 127.7, 123.3, 122.2, 118.5, 110.2, 104.2, 68.7, 55.9.

(Cyclohex-1-en-1-ylethynyl)(4-methoxyphenyl)selane (**3l**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 25% yield; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46 (d, 2H, *J* 8.9 Hz), 6.87 (d, 2H, *J* 8.9 Hz), 6.18-6.12 (m, 1H), 3.80 (s, 3H), 2.23-2.05 (m, 4H), 1.71-1.52 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.2, 135.7, 131.3, 120.9, 118.8, 115.2, 103.7, 66.5, 55.3, 29.1, 25.6, 22.2, 21.4; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 258.56; HRMS (ESI) *m/z* [M$^+$] calcd. for $C_{17}H_{14}O_3Se$, 292.0361; found, 292.0352.

(4-Methoxyphenyl)(4-phenylbut-1-yn-1-yl)selane (**3m**)

The product was isolated by a preparative thin layer chromatography (petroleum ether) as a yellow oil in 22%. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.38 (d, 2H, *J* 8.9 Hz), 7.32-7.28 (m, 2H), 7.25-7.19 (m, 3H), 6.83 (d, 2H, *J* 8.9 Hz), 3.80 (s, 3H), 2.88 (t, 2H, *J* 7.5 Hz), 2.71 (t, 2H, *J* 7.5 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.2, 140.4, 131.4, 128.5, 128.4, 126.3, 118.5, 115.1, 102.1, 59.6, 55.4, 35.0, 22.6; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 256.91; HRMS (ESI) *m/z* [$M^+$] calcd. for $C_{17}H_{16}OSe$, 316.0361; found, 316.0352.

(4-Methoxyphenyl)(oct-1-yn-1-yl)selane (**3n**)

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 27% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.46 (d, 2H, *J* 8.9 Hz), 6.86 (d, 2H, *J* 8.9 Hz), 3.80 (s, 3H), 2.40 (t, 2H, *J* 7.1 Hz), 1.63-1.51 (m, 2H), 1.46-1.36 (m, 2H), 1.35-1.21 (m, 4H), 0.89 (t, 3H, *J* 7.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.2, 131.3, 118.8, 115.2, 103.2, 58.4, 55.4, 31.3, 28.7, 28.6, 22.6, 20.5, 14.1; $^{77}$Se NMR (76 MHz, $CDCl_3$, $(PhSe)_2$ as internal standard $\delta$ = 463.00 ppm) $\delta$ 256.09; HRMS (ESI) *m/z* [$M^+$] calcd. for $C_{15}H_{20}OSe$, 296.0674; found, 296.0668.

(4-Methoxyphenyl)(phenylethynyl)sulfane (**3o**)[36]

The product was isolated by a preparative thin layer chromatography (hexane 97:3 ethyl acetate) as a yellow oil in 30% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52-7.46 (m, 2H), 7.43 (d, 2H, *J* 8.8 Hz), 7.36-7.31 (m, 3H), 6.91 (d, 2H, *J* 8.8 Hz), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.0, 131.6, 128.9, 128.4, 128.3, 123.0 (2C), 115.0, 96.2, 77.2, 55.4.

## Supplementary Information

Supplementary information (supplementary tables, NMR spectra) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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