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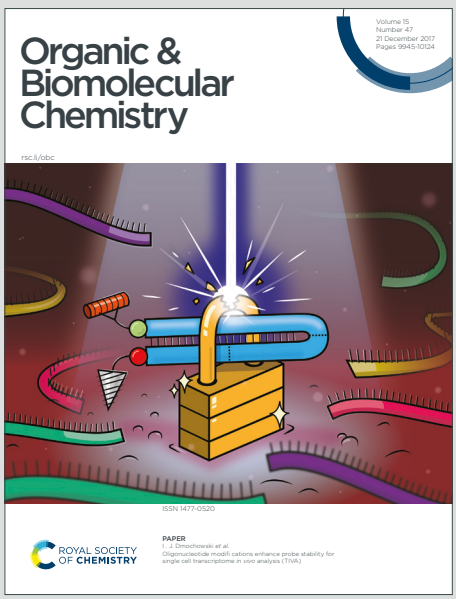

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ARTICLE

Synthesis of benzo[*b*]chalcogenophenes fused to selenophenes via intramolecular electrophilic cyclization of 1,3-diynes

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We describe herein an alternative and transition-metal-free procedure for the access of benzo[*b*]chalcogenophenes fused to selenophenes via intramolecular cyclization of 1,3-diynes. This efficient protocol involves a double cyclization of 1,3-diynyl chalcogen derivatives promoted by electrophilic species of organoselenium generated *in situ* by the oxidative cleavage of the Se-Se bond of dibutyl diselenide using Oxone® in acetonitrile as solvent in an open-flask at 80 °C. In this study, 15 selenophenes with broad substrate scope were prepared in moderate to excelent yields (55-98%) and short reaction times (0.5-3.0 h).

Introduction

Organoselenium compounds have received increased attention in recent years, due to their promising applications as catalysts,[1] as versatile synthetic intermediates[2] allowing selective transformations,[3] and to their biological activities.[4] In parallel, a number of selenophenes are known to display a wide range of biological activities, such as antibacterial,[5] antioxidant,[6] antidepressant,[7] antitumoral,[8] anticonvulsant,[9] hepatoprotective[10] and antinociceptive (Figure 1).[11] Apart from their biological activities, selenophenes have also been used in the preparation of materials that show potential as optical properties,[12] semiconductors,[13] solar cells[14] and film transistors.[15]

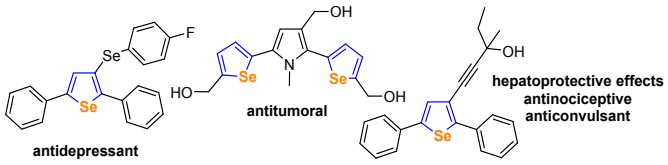

Figure 1 Some biologically active selenophenes.

Due to the growing importance and utility of these selenium heterocyclic in organic synthesis, different methodologies have been reported for their preparation. Traditional methods for the synthesis of selenophenes involve the addition of either nucleophilic or electrophilic selenium species to appropriate acyclic precursors containing the π-system, followed by an intramolecular cyclization[16] or by the cyclization of appropriate organoselenium substrates.[17] In this context, the iron-promoted tandem cyclization of 1,3-diynyl-chalcogen derivatives with dialkyl diselenides has been described for the synthesis of benzo[*b*]furan-fused selenophenes (Scheme 1a).[18] Subsequently, the same group reported the synthesis of chalcogenisochromene-fused chalcogenophenes by the cascade cyclization of *ortho*-diynyl benzyl chalcogenides promoted by iron(III) chloride in the presence of dialkyl dichalcogenides (Scheme 1b).[19] Moreover, Sonawane and co-workers[20] reported the synthesis of selenophene-fused quinoline-based heteroacenes by the intramolecular cascade cyclization of 1,3-diyne promoted by iron and dialkyl diselenides (Scheme 1c). Recently, our group synthesized 5*H*-selenopheno[3,2-*c*]isochromen-5-ones by the double intramolecular cyclization of methyl 2-(organyl-1,3-diynyl)benzoate promoted by electrophilic species of selenium, which were generated *in situ* by the reaction of dialkyl diselenides with Oxone® (Scheme 1d).[21]

Potassium peroxymonosulfate is commercially available as a stable triple salt ($2KHSO_5.KHSO_4.K_2SO_4$), sold under the trade name Oxone®. This reactant has been widely explored in organic synthesis due to its low cost, stability, water solubility and low toxicity.[22] Oxone® is also known as an oxidizing agent containing 50% active oxidant/mol in its formulation, the anion peroxymonosulfate HSO_5^-,[22] responsible for several classical synthetic transformations, such as functional group oxidation,[23] halogenation reactions,[24] cross coupling,[25] synthesis of heterocycles,[26] among others.[27] Regarding the combination of Oxone® with organoselenium chemistry,[28] our group and others have reported several useful reactions, including the oxidation of selenides to the corresponding selenones[28a,b] and the synthesis of several Se-containing heterocycles through electrophilic cyclization, like 4-organoselanyl-1*H*-pyrazoles from α,β-alkynyl hydrazones,[28c] 2,3-bis-organochalcogenylbenzo[*b*]chalcogenophenes from 2-functionalized chalcogenoalkynes,[28d] 1-aryl-4-(organylselanyl)-1*H*-pyrazoles by direct cyclocondensation and C–H bond selenylation reactions starting from hydrazines, 1,3-diketones and diorganyl diselenides[28e] and in the ultrasound-promoted radical synthesis of 5-methylselanyl-4,5-dihydroisoxazoles.[28f]

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† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: Figures of the NMR spectra of all the prepared compounds. See DOI: 10.1039/x0xx00000x

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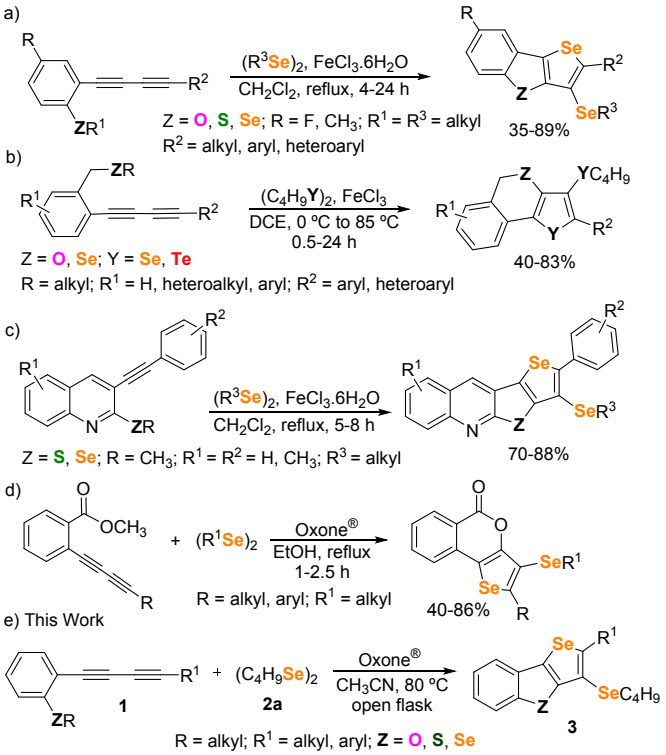


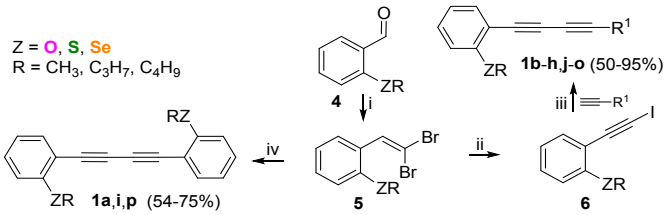
Scheme 1 Previously reported methods and our general reaction scheme.

Considering our interest in developing green protocols for the synthesis of organoselenium compounds and the importance of the selenophene nucleus, we report here an alternative and transition-metal-free procedure for the access of fused selenophenes. This protocol involves the electrophilic cyclization of 1,3-diynyl chalcogen derivatives **1** promoted by dibutyl diselenide **2a** and Oxone® for the synthesis of benzo[*b*]chalcogenophene-fused selenophenes **3** (Scheme 1e).

Results and discussion

Our investigations in this direction begun with the synthesis of the starting material 1,3-diynes **1** (Scheme 2). For this, previously synthesized[29,30] or commercially available 2-chalcogenbenzaldehydes **4** were subjected to the Corey-Fucks reaction, producing the respective dibromoalkenes **5**.[31] The dibromoalkenes, after reacting with butyllithium followed by the addition of iodine, provided the alkynyl iodides **6**,[32] which when reacting with terminal alkynes via Cadiot-Chodkiewicz coupling provided the unsymmetrical 1,3-diynes **1b**-**h**, **j**-**o**.[33] In addition, the symmetrical diynes **1a**, **1i** and **1p** were synthesized by copper-catalyzed homocoupling reaction of dibromoalkenes **5** using a DBU/DMSO system.[34]

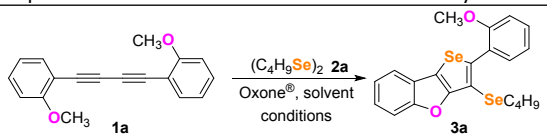
Thus, interested in obtaining the fused selenophenes **3**, the 1,4-bis(2-methoxyphenyl)buta-1,3-diyne **1a** and dibutyl diselenide **2a** were chosen as model substrates to perform the optimization studies in the reaction with Oxone® under air condition. Firstly, we added 1,3-diyne **1a** (0.25 mmol), dibutyl diselenide **2a** (0.38 mmol) and Oxone® (0.5 mmol) in ethanol at 70 °C for 1.5 h, and the desired 3-(butylselanyl)-2-(2-methoxyphenyl)selenopheno[3,2-*b*]benzofuran **3a** was obtained in 85% yield (Table 1, entry 1).



Scheme 2 Reaction conditions: i) CBr_4 (1.2 equiv), PPh_3 (2.5 equiv), CH_2Cl_2, 0 °C, 3.0 h, 80-95% yields; ii) BuLi (2.0 equiv), I_2 (1.0 equiv), THF, 0 °C, 1.5 h, 65-89% yields; iii) CuI (20 mol%), pyrrolidine, 0 °C, 0.2 h, 50-95% yields; iv) CuI (20 mol%), DBU (2 equiv), DMSO, 25 °C, 8-12 h, 54-75% yields.

The use of inert atmosphere was also examined, and a similar yield of compound **3a** was observed under this condition, indicating that it is not necessary in this reaction (Table 1, entry 2). Following, the effect of using different amounts of diselenide **2a** was evaluated (Table 1, entries 3 and 4). A decrease in the yield of **3a** was observed when the amount of **2a** was reduced to 0.25 mmol, and it was obtained in 50% yield after 2 h (Table 1, entry 3). By using 0.50 mmol of **2a**, the product **3a** was obtained in 89% yield after 1.5 h (Table 1, entry 4).

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



#	**2a** (mmol)	Oxone® (mmol)	Solvent	T (°C)	Time (h)	Yield **3a** (%)[b]
1	0.38	0.50	EtOH	70	1.5	85
2[c]	0.38	0.50	EtOH	70	1.5	82
3	0.25	0.50	EtOH	70	2.0	50
4	0.50	0.50	EtOH	70	1.5	89
5	0.38	0.75	EtOH	70	1.5	80
6	0.38	0.25	EtOH	70	1.5	74
7	**0.38**	**0.50**	**CH_3CN**	**80**	**1.5**	**95**
8	0.38	0.50	glycerol	100	24.0	30
9	0.38	0.50	PEG-400	100	2.5	58
10	0.38	0.50	DMF	140	2.5	84

[a] Reaction conditions: A mixture of 1,3-diyne **1a** (0.25 mmol), Oxone® and dibutyl diselenide **2a** in the solvent (3.0 mL) was stirred at the temperature and time indicated. [b] Isolated yields after purification by column chromatography. [c] Performed under inert atmosphere of nitrogen.

Based on these results, the amount of dibutyl diselenide **2a** was fixed in 0.38 mmol and the effect of using different amounts of Oxone® was evaluated. However, using 0.75 mmol or 0.25 mmol of Oxone®, the yield of **3a** decreases to 80% and 74% after 1.5 h, respectively (Table 1, entries 5 and 6). In order to improve the performance of the reaction, other solvents were also evaluated including acetonitrile, glycerol, PEG-400 and DMF (Table 1, entries 7-10). Fortunately, using acetonitrile as solvent, the yield of product **3a** increased to 95% after 1.5 h (Table 1, entry 7). Thus, from the results presented on Table 1,

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the best reaction conditions to prepare fused selenophene **3a** involve stirring a mixture of 1,3-diyne **1a** (0.25 mmol), dibutyl diselenide **2a** (0.38 mmol) and Oxone® (0.50 mmol) using acetonitrile (3.0 mL) as the solvent at 80 °C for 1.5 h (Table 1, entry 7).

Once the best conditions were determined for the synthesis of benzo[*b*]furan fused selenophene **3a**, the scope and limitations of the methodology were explored by reacting different 1,3-diynyl chalcogen derivatives **1** with a variety of dialkyl dichalcogenides **2**, and the results are shown in Table 2. No product was observed when dibutyl telluride or dimethyl disulfide were used as substrates in the reaction with **1a**, even after 5 h of reaction, and the starting materials were recovered (Table 2, entries 2 and 3).

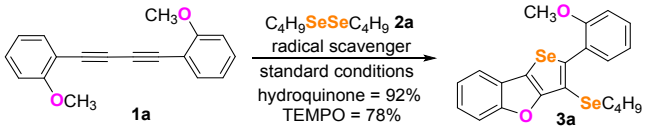
After that, the performance of the reaction using unsymmetrical 1-(buta-1,3-diyn-1-yl)-2-methoxybenzenes **1b**-**h** was evaluated. When the 1,3-diyne containing an electron-neutral substituent in the phenyl ring ($R^1 = C_6H_5$, **1b**) was used, the expected product **3d** was obtained in 93% yield after 1.0 h (Table 2, entry 4). The presence of an electron-donating substituent (R^1 = 4-$CH_3OC_6H_4$, **1c**) positively affected the reaction, affording the respective fused selenophene **3e** in 98% yield after 0.8 h (Table 2, entry 5). Additional analysis to prove the structure of the compound **3e** can be found in the SI (Figures 37-42). The presence of an electron-withdrawing substituent, however, decreased the reactivity of 1,3-diynes **1d** (R^1 = 4-ClC_6H_4) and **1e** (R = 2-ClC_6H_4), and the respective products **3f** and **3g** were obtained in 83% and 85% yields after 1.5 h and 2.5 h (Table 2, entries 6 and 7).

Additionally, when 1,3-diyne substituted with 2-naphthyl group **1f** was used in the reaction with Bu_2Se_2, the corresponding product **3h** was obtained in 89% yield after 0.5 h of reaction (Table 2, entry 8). The alkyl-substituted 1,3-diyne **1g** was also a suitable substrate for the reaction, affording the respective product **3i** in 55% yield after 1.0 h (Table 2, entry 9). The low yield could be attributed to its decomposition during the purification process by column chromatography. In order to extend the scope of this protocol, we tested the reactivity of the 1,3-diyne **1h**. However, after 1.5 h of reaction, an inseparable mixture of the first cyclization product, the second cyclization product and other byproducts was observed by GC/MS (Table 2, entry 10; see Fig. S67 in the ESI for experimental details and figures of chromatogram and mass spectra).

The effect of the presence of a nucleophilic heteroatom different of oxygen in the 1,3-diyne was evaluated. When the symmetric 1,3-diyne thio-substituted at the 2-position of the alkylated aryl ring **1i** was used in the reaction with **2a**, 3,3'-bis(butylselanyl)-2,2'-dibenzo[*b*]thiophene **3j** was surprisingly obtained in 77% yield after 3.0 h (Table 2, entry 11). Although the selenium atom is more nucleophilic than the sulfur one, we believe that the steric hindrance of the SeC_4H_9 group, inhibits the formation of the Se-cyclization product compared to the *S*-cyclization one.[35] The unsymmetrical [2-(phenylbuta-1,3-diyn-1-yl)phenyl](propyl)sulfide **1j** reacted with diselenide **2a** under the optimal conditions to afford the fused selenophene **3k** in 85% yield after 1.0 h (Table 2, entry 12). In contrast, the presence of substituents in the phenyl ring of the 1,3-diynes **1** negatively affects the reaction. The 1,3-diyne **1k**, containing electron-donating group (R^1 = 4-$CH_3C_6H_4$,) was more reactive than the electron-withdrawing analogue **1l** (R^1 = 4-ClC_6H_4), affording the respective products **3l** and **3m** in 80% and 70% yields after 2.0 h and 3.0 h, respectively (Table 2, entries 13 and 14). In addition, when the 2-naphthyl- and alkyl-substituted 1,3-diynes **1m** and **1n** were employed as substrates under the optimal conditions, the products **3n** and **3o** were obtained in moderate to good yields (65% and 83%) after 1.5 and 2.5 h, respectively (Table 2, entries 15 and 16). The low yield of the compound **3n** could be attributed to its decomposition during the purification process by column chromatography.

After, we evaluated the use of the unsymmetrical 1,3-diyne **1o** bearing two potential nucleophiles, i.e., a competitive cyclization reaction between nucleophilic oxygen and sulfur at the *ortho*-position of opposite aryl groups. Under this competitive condition, occurred the formation of the benzothiophene-fused selenophene **3p** in 79% yield after 0.5 h, due to the higher nucleophilicity of the sulfur atom compared to the oxygen one (Table 2, entry 17).[18] Lastly, the symmetric selenodiyne **1p** was used in the reaction with diselenide **2a**, affording the expected dibenzo[*b*]selenophene **3q** in 86% yield after 3.0 h (Table 2, entry 18).

In order to acquire substantial support to a possible reaction mechanism, some control experiments were designed. Firstly, the reaction was conducted in the presence of 3 equiv. of the radical inhibitors benzene-1,4-diol (hydroquinone) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). In these experiments, the product **3a** was formed in 92% yield using hydroquinone and in 78% yield using TEMPO (Scheme 3). These findings suggest that a radical pathway is not involved in the reaction.



Scheme 3 Reactions in the presence of radical scavengers hydroquinone and TEMPO.

Based on the control experiments and in the literature,[18,28c-e] a plausible mechanism for the formation of the benzo[*b*]chalcogenophenes fused selenophene **3a-i, k-p** from the reaction of 1,3-diyne **1a** with dibutyl diselenide **2a** promoted by Oxone® is presented in Scheme 4. Firstly, dibutyl diselenide **2a** reacts with Oxone® to affords two electrophilic selenium species, **A** and **B**. In the cyclization step, the 1,3-diyne **1a** reacts with the electrophilic species **A** or **B** to form the seleniranium intermediate **C**, releasing the sulfate anion (KSO_4^-) and water (H_2O) to the medium. After an intramolecular attack by the electron pair of the oxygen, the cation benzofuran intermediate **D** is formed. Then, the displacement of the methyl group from intermediate **D** occurs after an attack by nucleophilic species present in the reaction medium, affording

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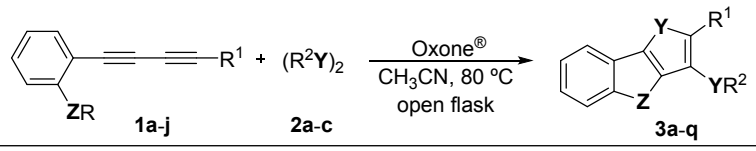
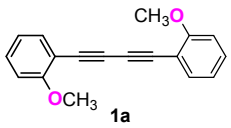
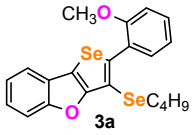
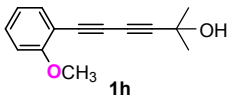
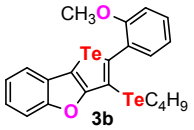
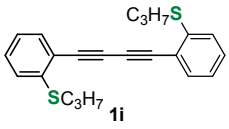
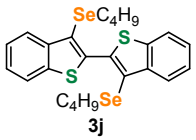
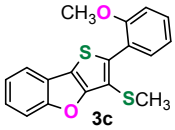
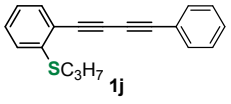
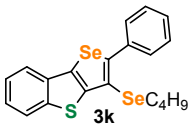
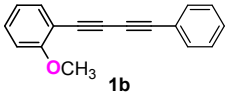
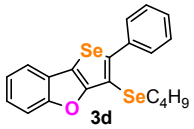
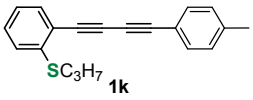
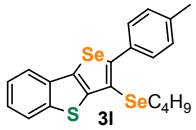
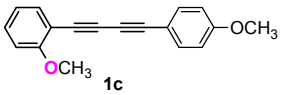
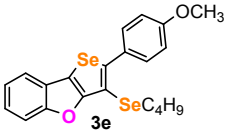
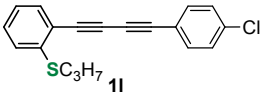
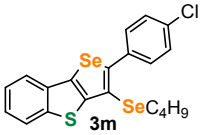
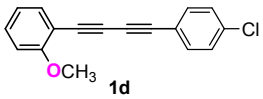
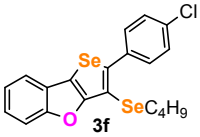
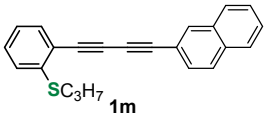
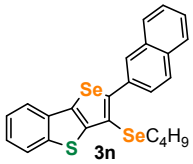
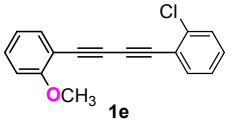
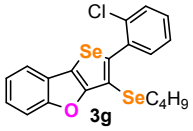
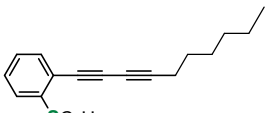
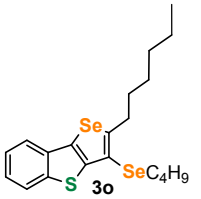
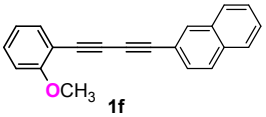
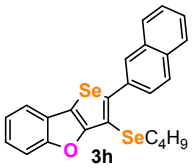
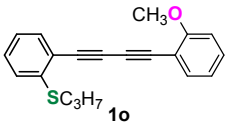
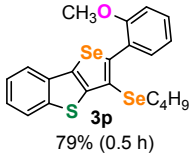
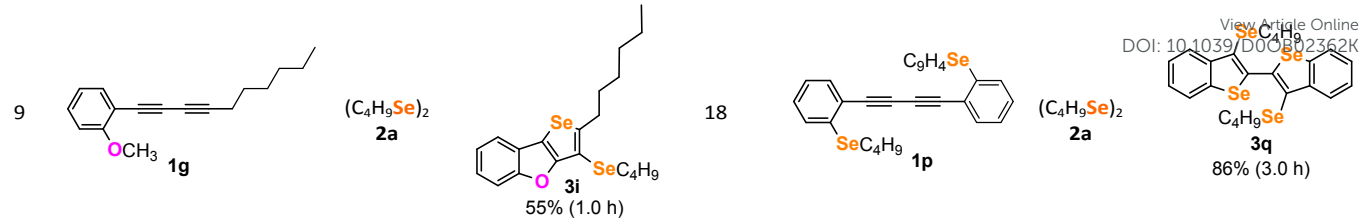
Table 2 Scope of the reaction to prepare the benzo[*b*]chalcogenophene-fused chalcogenophenes **3a-q**.[a,b]

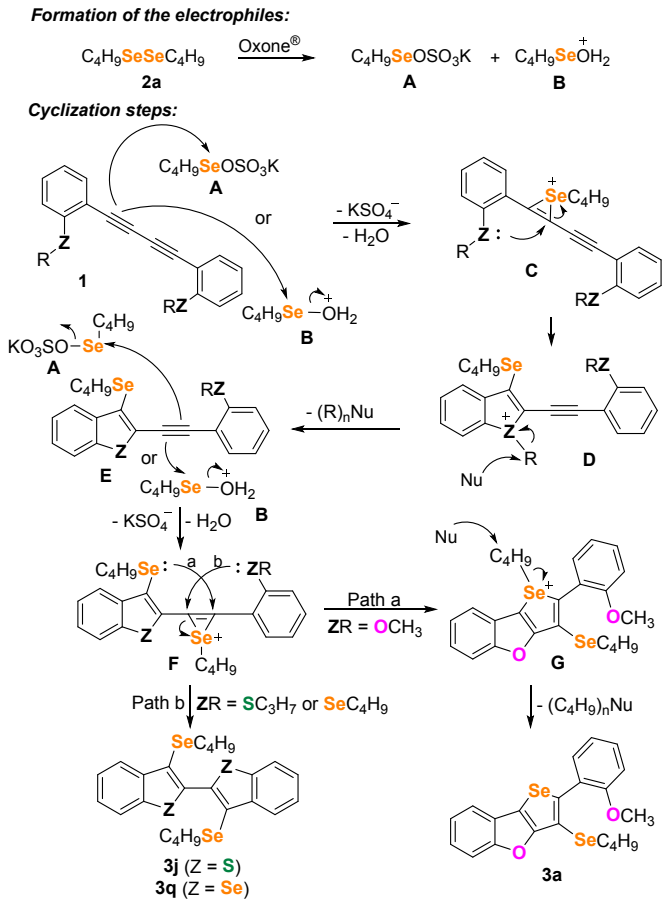


#	1,3-diyne **1**	$(R^2Y)_2$	Product **3** (Yield %) - reaction time	#	1,3-diyne **1**	$(R^2Y)_2$	Product **3** (Yield %) - reaction time
1	 **1a**	$(C_4H_9Se)_2$ **2a**	 **3a** 95% (1.5 h)	10	 **1h**	$(C_4H_9Se)_2$ **2a**	_d
2	**1a**	$(C_4H_9Te)_2$ **2b**	 **3b** NR[c] (5.0 h)	11	 **1i**	$(C_4H_9Se)_2$ **2a**	 **3j** 77% (3.0 h)
3	**1a**	$(CH_3S)_2$ **2c**	 **3c** NR[c] (5.0 h)	12	 **1j**	$(C_4H_9Se)_2$ **2a**	 **3k** 85% (1.0 h)
4	 **1b**	$(C_4H_9Se)_2$ **2a**	 **3d** 93% (1.0 h)	13	 **1k**	$(C_4H_9Se)_2$ **2a**	 **3l** 80% (2.0 h)
5	 **1c**	$(C_4H_9Se)_2$ **2a**	 **3e** 98% (0.8 h)	14	 **1l**	$(C_4H_9Se)_2$ **2a**	 **3m** 70% (3.0 h)
6	 **1d**	$(C_4H_9Se)_2$ **2a**	 **3f** 83% (1.5 h)	15	 **1m**	$(C_4H_9Se)_2$ **2a**	 **3n** 65% (1.5 h)
7	 **1e**	$(C_4H_9Se)_2$ **2a**	 **3g** 85% (2.5 h)	16	 **1n**	$(C_4H_9Se)_2$ **2a**	 **3o** 83% (2.5 h)
8	 **1f**	$(C_4H_9Se)_2$ **2a**	 **3h** 89% (0.5 h)	17	 **1o**	$(C_4H_9Se)_2$ **2a**	 **3p** 79% (0.5 h)



[a] Reactions performed using 1,3-diynes **1** (0.25 mmol), dialkyl dichalcogenide **2** (0.38 mmol), acetonitrile (3.0 mL) and Oxone® (0.50 mmol) at 80 °C. [b] Isolated yields. [c] The product was not formed and the starting materials were recovered. [d] An inseparable mixture of the first cyclization product and second cyclization product, besides other byproducts, was obtained.

the intermediate **E**. Following, **E** reacts in the same way with **A** or **B** to give the seleniranium intermediate **F**, and after an intramolecular attack (Path a) by the selenium electron pair, the fused selenophene cation intermediate **G** is formed. The displacement of the butyl group from the selenonium cation affords the expected product **3a**. In contrast, the formation of the dibenzo[*b*]thiophene **3j** or -selenophene **3q** can be attributed to the intermolecular attack (Path b) by the electron pair of the chalcogen atom (Z = S or Se) in the seleniranium intermediate **F**, generated from the symmetric 1,3-diyne sulfur- or selenium-substituted at the 2-position of the alkylated aryl ring **1i** and **1p** (Scheme 4).



Scheme 4 Proposed mechanism for the synthesis of benzo[*b*]calcogenophene-fused selenophenes **3a**-**i**,**k**-**p** and dibenzo[*b*]chalcogenophenes **3j** and **3q**.

Conclusions

In summary, we have developed an alternative and transition-metal-free procedure for the access of fused selenophenes and dibenzo[*b*]chalcogenophenes. This protocol involves a double cyclization of 1,3-diynyl chalcogen-derivatives promoted by electrophilic species of selenium generated *in situ* by the reaction of dibutyl diselenide with Oxone®. The synthetic feasibility and versatility were demonstrated by the good yields (55-98%) and short reaction times (0.5-3.0 h) for the preparation of 15 compounds, with broad substrate scope.

Experimental

General remarks

The reactions were monitored by thin TLC sheets ALUGRAM® Xtra SIL G/UV$_{254}$. For visualization, TLC plates were either placed under UV light, stained with iodine vapor and 5% vanillin in 10% H_2SO_4 and heat. Column chromatography was performed using Merck Silica Gel (pore size 60 Å, 230-400 mesh). Carbon-13 nuclear magnetic resonance (^{13}C NMR) and hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained on Bruker Avance III HD 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 constants (*J*) are reported in Hertz and chemical shift (δ) in ppm. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet), t (triplet), td (triplet of dublet), quint (quintet), sext (sextet) and m (multiplet). Low-resolution mass spectra (MS) were measured on a Shimadzu GC-MS-QP2010 mass spectrometer. The HRMS analyses were performed in a Bruker micrOTOF-QII spectrometer equipped with an APCI source operating in positive mode. The samples were solubilized in acetonitrile and analyzed by direct infusion. Melting point (m.p.) values were measured in a Marte PFD III instrument with a 0.1 °C precision. Oxone® was purchased from Sigma-Aldrich. The 1,3-diynes **1** were previously prepared as described in the Support Information.

General procedure for the synthesis of 3-(butylselanyl)-2-organylselenofeno[3,2-*b*]benzochalcogenophenes 3

To a 25.0 mL two-necked round-bottomed flask equipped with magnetic stirring and a reflux system containing the appropriate 1,3-diynes **1a**-**p** (0.25 mmol), a solution of dibutyl diselenide **2a** (0.38 mmol, 0.104 g) in acetonitrile (3.0 mL) and Oxone®

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($KHSO_5.{}^1/_2KHSO_4.{}^1/_2K_2SO_4$, FW = 307 g.mol^{-1}, 0.50 mmol, 0.15 g) were added under air atmosphere. The resulting mixture was stirred at 80 °C for the time indicated in Table 2. The reactions were monitored by TLC until total disappearance of the 1,3-diyne **1**. After this time, the resulting solution was received in water (10.0 mL) and the product was extracted with ethyl acetate (3x 10.0 mL). The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using silica gel and hexane/ethyl acetate (95:05) as the eluent. Yield: 55-98%.

3-(Butylselanyl)-2-(2-methoxyphenyl)selenopheno[3,2-*b*]benzofuran 3a:[18] Yield: 0.110 g (95%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.62-7.60 (m, 2H); 7.42 (dd, *J* = 7.5, 1.4 Hz, 1H); 7.38-7.25 (m, 3H); 7.01 (t, *J* = 7.4 Hz, 1H); 6.95 (d, *J* = 8.3 Hz, 1H); 3.81 (s, 3H); 2.94 (t, *J* = 7.4 Hz, 2H); 1.53 (quint, *J* = 7.4 Hz, 2H); 1.27 (sext, *J* = 7.4 Hz, 2H); 0.78 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.4, 157.0, 156.6, 144.8, 131.9, 130.0, 126.6, 125.3, 124.2, 123.0, 120.2, 119.5, 117.2, 112.3, 111.0, 109.2, 55.4, 32.2, 26.9, 22.6, 13.4. MS (rel. int., %) *m/z*: 464 (M^+, 68.9), 407 (10.9), 376 (12.9), 327 (98.9), 312 (68.8), 285 (13.7), 256 (17.7), 247 (100.0), 218 (32.2), 189 (56.2), 176 (42.4), 77 (11.3), 57 (20.5), 41 (77.6).

3-(Butylselanyl)-2-phenylselenopheno[3,2-*b*]benzofuran 3d:[18] Yield: 0.101 g (93%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.67-7.62 (m, 4H); 7.46-7.29 (m, 5H); 2.97 (t, *J* = 7.4 Hz, 2H); 1.58-1.51 (m, 2H); 1.28 (sext, *J* = 7.4 Hz, 2H); 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 161.0, 157.1, 149.5, 136.6, 129.5, 128.4, 128.3, 126.4, 124.5, 123.2, 119.6, 116.5, 112.4, 106.8, 32.2, 27.8, 22.6, 13.4. MS (rel. int., %) *m/z*: 434 (M^+, 71.2), 427 (15.0), 377 (54.5), 375 (28.5), 298 (100.0), 268 (36.7), 189 (36.7), 163 (11.5), 57 (10.2), 41 (25.9).

3-(Butylselanyl)-2-(4-methoxyphenyl)selenopheno[3,2-*b*]benzofuran 3e: Yield: 0.114 g (98%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.62-7.60 (m, 2H); 7.54 (d, *J* = 8.8 Hz, 2H); 7.32-7.25 (m, 2H); 6.94 (d, *J* = 8.8 Hz, 2H); 3.82 (s, 3H); 2.94 (t, *J* = 7.4 Hz, 2H); 1.53 (quint, *J* = 7.4 Hz, 2H); 1.28 (sext, *J* = 7.4 Hz, 2H); 0.78 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.9, 159.7, 156.9, 149.6, 130.7, 129.1, 126.4, 124.2, 123.1, 119.4, 115.7, 113.8, 112.2, 106.0, 55.2, 32.2, 27.7, 22.5, 13.4. ^{77}Se NMR ($CDCl_3$, 76 MHz) δ (ppm) = 502.1, 183.0. MS (rel. int., %) *m/z*: 464 (M^+, 100.0), 407 (30.2), 376 (18.8), 328 (43.8), 313 (13.6), 256 (15.1), 176 (34.1), 57 (7.9), 41 (25.4). HRMS (APCI-QTOF) calculated mass for $C_{21}H_{21}O_2Se_2$ $[M+H]^+$: 464.9872, found: 464.9858.

3-(Butylselanyl)-2-(4-chlorophenyl)selenopheno[3,2-*b*]benzofuran 3f:[18] Yield: 0.097 g (83%); white solid; m.p. = 104-105 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.65 (t, *J* = 8.3 Hz, 2H); 7.55 (d, *J* = 8.5 Hz, 2H); 7.41 (d, *J* = 8.5 Hz, 2H); 7.37-7.30 (m, 2H); 2.97 (t, *J* = 7.3 Hz, 2H); 1.54 (quint, *J* = 7.3 Hz, 2H); 1.29 (sext, *J* = 7.3 Hz, 2H); 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.9, 157.1, 147.8, 135.1, 134.4, 130.7, 128.6, 126.2, 124.7, 123.3, 119.7, 116.8, 112.4, 107.4, 32.3, 27.9, 22.6, 13.4. MS (rel. int., %) *m/z*: 468 (M^+, 100.0), 412 (66.6), 374 (45.5), 332 (85.2), 302 (18.8), 267 (11.0), 252 (21.7), 223 (27.8), 187 (49.9), 57 (15.6), 41 (40.6).

3-(Butylselanyl)-2-(2-chlorophenyl)selenopheno[3,2-*b*]benzofuran 3g:[18] Yield: 0.100 g (85%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.67-7.63 (m, 2H); 7.50 (dd, *J* = 7.7, 1.5 Hz, 1H); 7.45-7.42 (m, 1H); 7.38-7.29 (m, 4H); 2.93 (t, *J* = 7.3 Hz, 2H); 1.55 (quint, J = 7.3 Hz, 2H); 1.29 (sext, *J* = 7.3 Hz, 2H); 0.81 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.0, 157.1, 145.6, 135.3, 134.4, 132.7, 130.0, 129.7, 126.4, 126.3, 124.7, 123.2, 119.6, 118.0, 112.5, 110.2, 32.3, 27.4, 22.6, 13.4. MS (rel. int., %) *m/z*: 468 (M^+, 50.9), 412 (10.3), 374 (78.1), 332 (31.7), 302 (11.2), 267 (15.0), 252 (20.9), 223 (23.3), 187 (63.5), 57 (23.7), 44 (100.0).

3-(Butylselanyl)-2-(naphthalen-2-yl)selenopheno[3,2-*b*]benzofuran 3h:[18] Yield: 0.108 g (89%); yellow solid; m.p. = 69-71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.05 (s, 1H); 7.89-7.83 (m, 3H); 7.77 (dd, *J* = 8.5, 1.8 Hz, 1H); 7.66-7.63 (m, 2H); 7.51-7.48 (m, 2H); 7.35-7.28 (m, 2H); 2.97 (t, *J* = 7.4 Hz, 2H); 1.54 (quint, *J* = 7.4 Hz, 2H); 1.27 (sext, *J* = 7.4 Hz, 2H); 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 161.0, 157.0, 149.3, 134.1, 133.1, 132.9, 128.6, 128.2, 127.9, 127.7, 127.2, 126.5, 126.4, 124.5, 123.2, 119.6, 118.2, 116.7, 112.4, 107.1, 32.2, 27.8, 22.6, 13.4. MS (rel. int., %) *m/z*: 484 (M^+, 97.2), 478 (20.3), 427 (100.0), 398 (25.1), 347 (26.6), 319 (34.7), 268 (25.1), 239 (74.2), 237 (50.3), 212 (7.9), 207 (52.0), 163 (5.6), 119 (9.0), 73 (21.1), 57 (9.3), 41 (29.9).

3-(Butylselanyl)-2-hexylselenopheno[3,2-*b*]benzofuran 3i: Yield: 0.061 g (55%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.61-7.58 (m, 2H); 7.29-7.26 (m, 2H); 3.12 (t, *J* = 7.4 Hz, 2H); 2.94 (t, *J* = 7.4 Hz, 2H); 1.72 (quint, *J* = 7.4 Hz, 2H); 1.62 (quint, *J* = 7.4 Hz, 2H); 1.45-1.38 (m, 4H); 1.35-1.32 (m, 4H); 0.92-0.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.4, 157.0, 155.7, 126.6, 123.8, 123.0, 119.1, 114.0, 112.3, 106.9, 33.4, 32.6, 32.5, 31.6, 28.8, 27.9, 22.7, 22.6, 14.1, 13.5. MS (rel. int., %) *m/z*: 442 (M^+, 51.0), 385 (21.9), 371 (40.0), 367 (20.5), 340 (14.0), 315 (51.3), 313 (46.2), 305 (74.2), 281 (40.0), 235 (100.0), 207 (26.4), 115 (11.5), 57 (11.1), 41 (40.1). HRMS (APCI-QTOF) calculated mass for $C_{20}H_{27}OSe_2$ $[M+H]^+$: 443.0392, found: 443.0388.

3,3'-Bis(butylselanyl)-2,2'-dibenzo[*b*]thiophene 3j: Yield: 0.104 g (77%); yellow solid, m.p. = 108-109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.07 (d, *J* = 7.9 Hz, 2H); 7.85 (d, *J* = 7.9 Hz, 2H); 7.49-7.44 (m, 2H); 7.43-7.39 (m, 2H); 2.70 (t, *J* = 7.4 Hz, 4H); 1.46 (quint, *J* = 7.4 Hz, 4H); 1.22 (sext, *J* = 7.4 Hz, 4H); 0.74 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 141.6, 140.3, 138.5, 125.4, 125.2, 124.9, 122.8, 122.1, 32.5, 28.9, 22.7, 13.4. MS (rel. int., %) *m/z*: 538 (M^+, 4.1), 481 (5.8), 424 (6.1), 401 (10.7), 346 (28.7), 344 (100.0), 342 (53.7), 320 (15.5), 264 (19.7), 207 (10.7), 73 (14.2), 41 (87.0). HRMS (APCI-QTOF) calculated mass for $C_{24}H_{27}S_2Se_2$ $[M+H]^+$: 538.9885, found: 538.9880.

3-(Butylselanyl)-2-phenylbenzo[*b*]selenopheno[2,3-*d*]thiophene 3k:[18] Yield: 0.096 g (85%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.86 (d, *J* = 7.7 Hz, 1H); 7.73 (d, *J* = 7.7 Hz, 1H); 7.64 (d, *J* = 6.9

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Hz, 2H); 7.43-7.30 (m, 5H); 2.76 (t, *J* = 7.4 Hz, 2H); 1.46 (quint, *J* = 7.4 Hz, 2H); 1.21 (sext, *J* = 7.4 Hz, 2H); 0.73 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 151.9, 147.4, 140.3, 136.4, 136.0, 131.9, 129.7, 128.3, 124.7, 124.3, 123.6, 121.8, 114.0, 32.2, 28.5, 22.5, 13.4. MS (rel. int., %) *m/z*: 450 (M^+, 56.6), 396 (16.9), 392 (61.9), 314 (100.0), 309 (36.4), 234 (46.8), 207 (22.3), 187 (12.3), 73 (13.5), 57 (8.9), 41 (23.5).

3-(Butylselanyl)-2-(4-tolylphenyl)benzo[*b*]selenopheno[2,3-*d*]thiophene 3l:[18] Yield: 0.093 g (80%); yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.88 (d, *J* = 8.1 Hz, 1H); 7.75 (d, *J* = 7.6 Hz, 1H); 7.55 (d, *J* = 8.1 Hz, 2H); 7.39 (td, *J* = 7.6, 1.2 Hz, 1H); 7.34 (td, *J* = 7.6, 1.2 Hz, 1H); 7.24 (d, *J* = 7.9 Hz, 2H); 2.79 (t, *J* = 7.3 Hz, 2H); 2.40 (s, 3H); 1.48 (quint, *J* = 7.3 Hz, 2H); 1.25 (sext, *J* = 7.3 Hz, 2H); 0.76 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 152.2, 147.4, 140.3, 138.3, 136.1, 133.6, 131.6, 129.6, 129.0, 124.7, 124.3, 123.6, 121.7, 113.6, 32.2, 28.5, 22.6, 21.3, 13.4. MS (rel. int., %) *m/z*: 464 (M^+, 49.3), 392 (20.3), 328 (66.0), 312 (17.6), 248 (25.0), 202 (13.7), 44 (100.0).

3-(Butylselanyl)-2-(4-chlorophenyl)benzo[*b*]selenopheno[2,3-*d*]thiophene 3m:[18] Yield: 0.085 g (70%); white solid; m.p. = 63-65 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.88-7.86 (m, 1H); 7.74-7.72 (m, 1H); 7.57 (d, *J* = 8.5 Hz, 2H); 7.40-7.36 (m, 3H); 7.33 (dd, *J* = 7.3, 1.3 Hz, 1H); 2.77 (t, *J* = 7.3 Hz, 2H); 1.46 (quint, *J* = 7.3 Hz, 2H); 1.23 (sext, *J* = 7.3 Hz, 2H); 0.75 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 150.2, 147.4, 140.4, 135.9, 134.8, 134.3, 132.1, 130.9, 128.5, 124.8, 124.5, 123.7, 121.8, 114.6, 32.2, 28.6, 22.5, 13.4. MS (rel. int., %) *m/z*: 484 (M^+, 18.6), 482 (15.5), 479 (8.2), 427 (15.6), 389 (12.6), 347 (26.0), 206 (12.3), 44 (100.0).

3-(Butylselanyl)-2-(naphthalen-2-yl)benzo[*b*]selenopheno[2,3-*d*]thiophene 3n: Yield: 0.081 g (65%); orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.12 (s, 1H); 7.92-7.87 (m, 4H); 7.84 (dd, *J* = 8.5, 1.7 Hz, 1H); 7.80 (d, *J* = 8.0 Hz, 1H); 7.54-7.52 (m, 2H); 7.43 (td, *J* = 7.6, 1.3 Hz, 1H); 7.38 (td, *J* = 7.6, 1.3 Hz, 1H); 2.80 (t, *J* = 7.3 Hz, 2H); 1.49 (quint, *J* = 7.3 Hz, 2H); 1.27-1.27 (m, 2H); 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 151.8, 147.6, 140.4, 136.1, 133.9, 133.1, 132.9, 132.2, 128.9, 128.3, 127.9, 127.7, 127.5, 126.6, 126.5, 124.8, 124.4, 123.7, 121.8, 114.3, 32.2, 28.6, 22.5, 13.4. MS (rel. int., %) *m/z*: 500 (M^+, 55.4), 443 (54.3), 363 (57.4), 362 (100.0), 282 (57.5), 237 (23.6). HRMS (APCI-QTOF) calculated mass for $C_{24}H_{21}SSe_2$ $[M+H]^+$: 500.9692, found: 500.9692.

3-(Butylselanyl)-2-hexylbenzo[*b*]selenopheno[2,3-*d*]thiophene 3o: Yield: 0.095 g (83%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.87-7.84 (m, 1H); 7.71-7.69 (m, 1H); 7.37 (td, *J* = 7.6, 1.2 Hz, 1H); 7.31 (td, *J* = 7.6, 1.2 Hz, 1H); 3.15 (t, *J* = 7.4 Hz, 2H); 2.84 (t, *J* = 7.4 Hz, 2H); 1.73 (quint, *J* = 7.4 Hz, 2H); 1.61 (sext, *J* = 7.4 Hz, 2H); 1.44-1.32 (m, 8H); 0.92-0.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 157.5, 146.0, 140.3, 136.2, 129.9, 124.6, 123.9, 123.7, 121.4, 114.3, 33.7, 32.9, 32.7, 31.6, 28.9, 28.3, 22.8, 22.6, 14.1, 13.5. MS (rel. int., %) *m/z*: 458 (M^+, 44.4), 400 (20.2), 386 (18.5), 331 (39.6), 321 (46.2), 251 (100.0), 171 (31.7), 41 (42.0). HRMS (APCI-QTOF) calculated mass for $C_{20}H_{27}SSe_2$ $[M+H]^+$: 459.0161, found: 459.0159.

3-(Butylselanyl)-2-(2-methoxyphenyl)benzo[*b*]selenopheno[2,3-*d*]tiophene 3p:[18] Yield: 0.095 g (79%); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.87 (d, *J* = 7.7 Hz, 1H); 7.75 (d, *J* = 7.7 Hz, 1H); 7.45 (d, *J* = 7.4 Hz, 1H); 7.40-7.31 (m, 3H); 7.05-6.96 (m, 2H); 3.82 (s, 3H); 2.77 (t, *J* = 7.3 Hz, 2H); 1.47 (quint, *J* = 7.3 Hz, 2H); 1.23 (sext, *J* = 7.3 Hz, 2H); 0.76 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 156.7, 147.4, 145.9, 140.5, 136.2, 133.0, 132.2, 130.1, 125.3, 124.6, 124.2, 123.6, 121.7, 120.2, 116.4, 111.0, 55.4, 32.2, 27.7, 22.6, 13.5. MS (rel. int., %) *m/z*: 480 (M^+, 100.0), 424 (39.4), 392 (20.4), 344 (90.5), 328 (60.0), 312 (15.7), 207 (34.3), 41 (41.7).

3,3'-Bis(butylselanyl)-2,2'-dibenzo[*b*]selenophene 3q: Yield: 0.136 g (86%); yellow solid, m.p. = 53-55 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.13 (d, *J* = 7.7 Hz, 2H); 7.87 (d, *J* = 7.7 Hz, 2H); 7.46 (t, *J* = 7.7 Hz, 2H); 7.34 (t, *J* = 7.7 Hz, 2H); 2.71 (t, *J* = 7.4 Hz, 4H); 1.48 (quint, *J* = 7.4 Hz, 4H); 1.28-1.19 (m, 4H); 0.75 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) = 143.5, 143.1, 142.2, 127.6, 125.6, 125.13, 125.1, 125.0, 32.5, 29.0, 22.8, 13.5. MS (rel. int., %) *m/z*: 634 (M^+, 2.5), 631 (13.2), 497 (21.0), 438 (100.0), 360 (20.8), 317 (5.0), 200 (34.5), 180 (4.3), 137 (8.7), 91 (13.9), 83 (44.4). HRMS (APCI-QTOF) calculated mass for $C_{24}H_{27}Se_4$ $[M+H]^+$: 634.8774, found: 634.8763.

Conflicts of interest

There are no conflicts to declare.

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