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Note	

Direct Synthesis of Benzoselenophene and Benzothiophene Derivatives from 1,1-Diarylethenes and Biaryls by Chalcogen Cation-Mediated Successive Bond Formation

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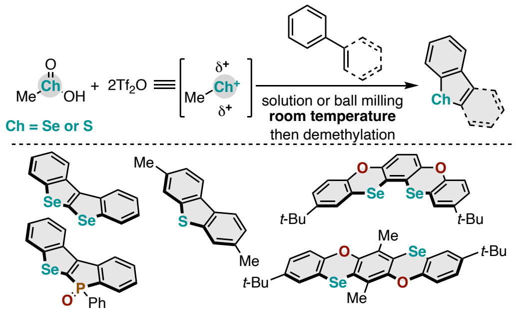
Supporting Information Placeholder

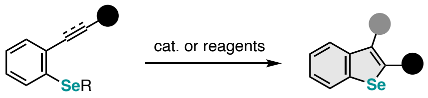


ABSTRACT: A Tf_2O-mediated sequential C–Se bond forming reaction of 1,1-diarylethenes and biaryls with methaneselenic acid has been developed. Upon demethylation workup with ethanolamine, the corresponding benzoselenophene derivatives are obtained directly. The related synthesis of benzothiophene derivatives with sodium methanesulfinate is also possible with the unique assistance of ball milling technique. The active species is considered to be a highly electrophilic chalcogen cation, which enables successive bond formation even at room temperature.

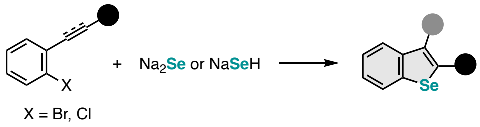
Because of its unique intrinsic electronic and physical characters, a selenophene has attracted a significant amount of attention in the fields of pharmaceuticals[1] and material science. In particular, the highly π-conjugated benzoselenophenes have been widely studied as the important structural cores in the design and synthesis of organic light-emitting diodes,[2] organic field effect transistors,[3] and organic solar cells.[4] Accordingly, numerous synthetic methods have been developed by synthetic chemists.[5] The reported procedures are briefly categorized into three types (Scheme 1): (a) the cyclization of *ortho*-alkynylated benzeneselenol derivatives, (b) the nucleophilic selenation of *ortho*-alkynylated halobenzenes, and (c) the electrophilic selenation of relatively simple alkynylbenzenes. Reactions of type a are simple and practical but suffer from the tedious and multistep preparation of complicated selenated starting substrates. Nucleophilic selenation reaction b with in situ-generated Na_2Se or NaHSe is more beneficial, but the multiply substituted halogenated starting substrates should still be prepared in advance. In the reaction of type c, the simple and abundant hydrocarbons can be directly used under mild conditions, which is the large advantage from a synthetic point of view. However, the applicable electrophilic selenation species is limited to $SeBr_4$ generated from SeO_2 and HBr.[6] Thus, further development of highly reactive electrophilic selenation reagents and its application to the synthesis of highly π-conjugated selenophene derivatives are strongly desired.

Scheme 1. Representative Approaches to Benzoselenophenes

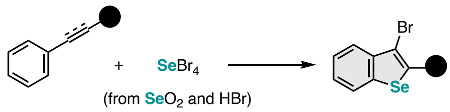
(a) Cyclization of ortho-alkynylated benzeneselenol derivatives



(b) Nucleophilic selenation of ortho-alkynylated halobenzenes

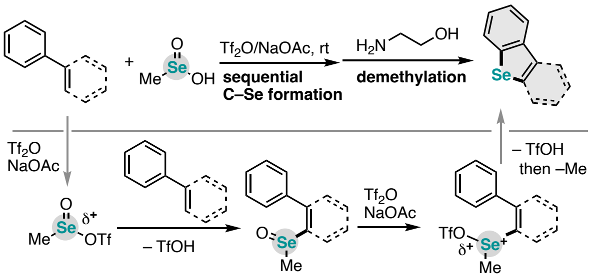


(c) Electrophilic selenation of simple alkynylbenzenes



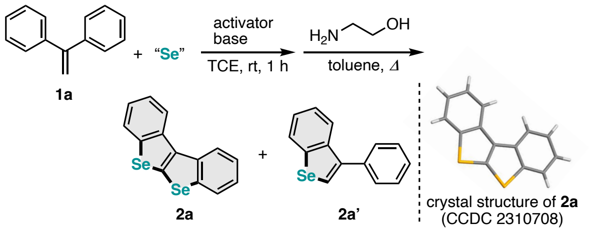
Herein, we report a sequential C–Se bond-forming reaction with commercially available methaneselenic acid and Tf_2O, where relatively simple 1,1-diarylethene and biaryl starting substrates are directly converted to the corresponding π-extended benzoselenophene derivatives (Scheme 2).[7] The key to success is the in situ generation of highly electrophilic selenium cation equivalents, which enables otherwise challenging stepwise C–Se bond formations even at room temperature. We note that during the preparation of this Letter, Zeng and co-workers reported the related double C–Se bond formation using a combination of Se powder and TMSCN, leading to the benzoselenophene derivatives.[8] However, the substrate was limited to the electron-rich enamine derivative, which is complementary to the study presented here. Moreover, our strategy is also applied to the benzothiophene synthesis with sodium methanesulfinate instead of methaneselenic acid with the unique assistance of ball milling.[9]

Scheme 2. Direct Synthesis of Benzoselenophenes from 1,1-Diarylethenes and Biaryls via Se Cation Equivalents



We began our optimization studies to identify suitable electrophilic selenation sources and conditions with 1,1-diarylethene (**1a**) as the model substrate (Table 1). In an early experiment, treatment of **1a** with MeSe(O)OH, Tf_2O, and NaOAc in a 1,1,2,2-tetrachloroethane (TCE) solvent at room temperature for 1 h afforded a mixture of doubly cyclized benzoselenophene derivative **2a** (3%) and monocyclized benzoselenophene **2a'** (48%, entry 1). The structure of **2a** was unambiguously confirmed by X-ray analysis (CCDC2310708).[10] We also tested other potential electrophilic selenation reagents such as MeSeSeMe (entry 2)[11] and SeO_2 (entry 3),[6] but the combined yield of **2a** and **2a'** was much lower. The choice of activator was also critical. $(CF_3CO)_2O$ promoted the reaction to some extent (entry 4), while other representative dehydrating reagents, including Ac_2O, Ts_2O, $PhNTf_2$, and Boc_2O, were totally ineffective (entry 5). The basic additive also affected the reaction efficiency. Both weaker and stronger bases decreased the yield (entries 6 and 7, respectively). The yield of **2a** eventually reached 53% for the prolonged reaction periods (10 h, entry 8), whereas the maximum yield of **2a'** was obtained with a 5 h reaction period (entry 9). Interestingly, mechanochemical conditions using ball milling (ZrO_2, 25 Hz)[9] gave a comparable reaction yield of **2a** even within 99 min (entry 10). Some additional observations should be noted: other halogenated solvents such as DCM and DCE were also effective, but TCE was the best for transforming **1a** into the doubly cyclized product **2a** convergently. A combined use of Se powder with TMSCN[8] or I_2[12] gave a much smaller amount of singly cyclized product **2a'** [<16% (see the Supporting Information for more detailed optimization studies)].

Table 1. Optimization of the Direct Synthesis of Benzoselenophene Derivatives from 1,1-Diphenylethene (1a)[a]



entry	"Se"	activator/base	yield (%)[b]	
			2a	**2a'**
1	MeSe(O)OH	Tf_2O/NaOAc	3	48
2	MeSeSeMe	Tf_2O/NaOAc	9	14
3	SeO_2	Tf_2O/NaOAc	trace	6
4	MeSe(O)OH	$(CF_3CO)_2O$/NaOAc	0	26
5	MeSe(O)OH	Ac_2O, Ts_2O, $PhNTf_2$, or Boc_2O/NaOAc	0	0
6	MeSe(O)OH	Tf_2O/Na_2CO_3	0	26
7	MeSe(O)OH	Tf_2O/NaOMe	0	26
8[c]	MeSe(O)OH	Tf_2O/NaOAc	53 (50)	trace
9[d]	MeSe(O)OH	Tf_2O/NaOAc	15	59 (49)
10[e]	MeSe(O)OH	Tf_2O/NaOAc	60 (53)	trace

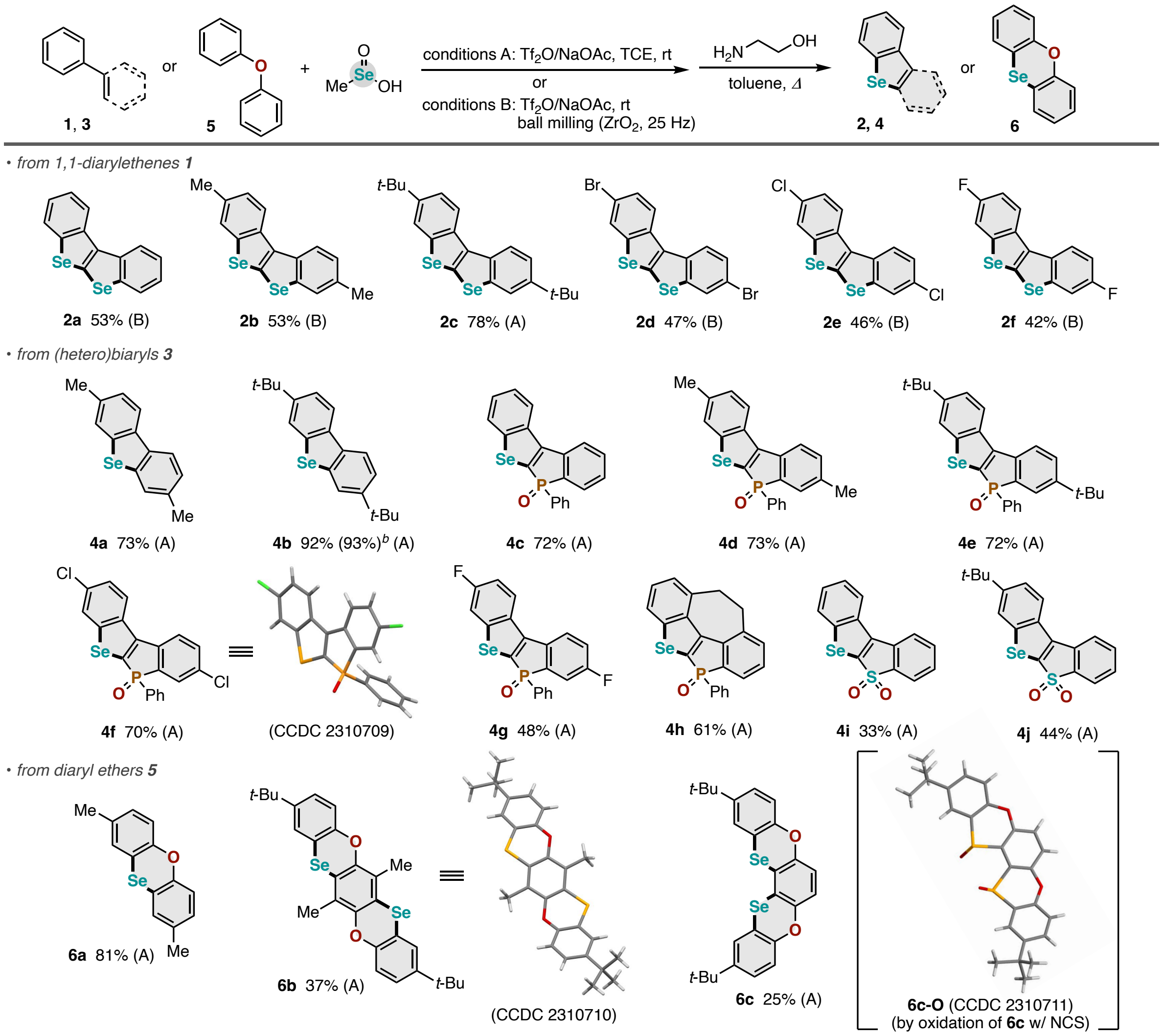
[a] Conditions: **1a** (0.10 mmol), "Se" (0.50 mmol), activator (1.0 mmol), base (1.0 mmol), TCE (1.0 mL), rt, 1 h, then $H_2N(CH_2)_2OH$ (1.0 mL), toluene (1.5 mL), 120 °C, 2 h. [b] Estimated by ^1H NMR with dibenzyl ether as the internal standard. Isolated yields in parentheses. [c] For 10 h. [d] For 5 h. [e] Without TCE. Ball milling (ZrO_2, 25 Hz, 99 min).

With solution (entry 8 in Table 1, conditions A) and mechanochemical conditions (entry 10 in Table 1, conditions B), we tested the reaction with some 1,1-diarylethenes **1** (Scheme 3). In general, the mechanochemical conditions gave better results. Methyl-, bromo-, chloro-, and fluoro-substituted substrates were directly converted into doubly cyclized selenophene derivatives **2b** and **2d**–**f**, respectively, in 42–53% yields. Because of the transition-metal-free conditions, the Br and Cl functions remained untouched, which can be additional synthetic handles for further π-extension by cross-coupling chemistry. Exceptionally, *tert*-butyl-substituted **2c** was formed in a better yield under solution conditions. Several (hetero)biaryls **3** were also viable for affording the corresponding single Se-incorporated dibenzoselenophenes **4**. In these cases, the reaction proceeded smoothly under solution conditions rather than under mechanochemical conditions. The relatively simple 4,4'-dimethylbiphenyl (**3a**) and 4,4'-di(*tert*-butyl)biphenyl (**3b**) were amenable to the reaction (**4a** and **4b**, respectively). Phosphorus-containing biaryls **3c**–**h** were also promising substrates for affording phosphole-selenophene-fused aromatics **4c**–**h**, respectively, in good yields, which showed strong fluorescence properties (see the Supporting Information for details). The 3-arylbenzothiophene dioxides could also be employed to furnish the corresponding tetracyclic systems **4i** and **4j** in acceptable yields. Moreover, diaryl ether **5a** participated in the reaction (**6a**). Particularly notable is the successful double cyclization reaction. The linear- and bent-type benzobisoxaselenines **6b** and **6c** were directly obtained from the corresponding 1,4-diphenoxybenzenes **5b** and **5c**, respectively. Single-crystal X-ray analysis determined the structures of **4f** and **6b**, while **6c** was analyzed after the oxidation to selenoxide **6c-O**, where the second cyclization event was confirmed to occur selectively at the more sterically congested position (CCDC 2310709–2310711).[13] The preliminary optoelectronic data of **6b** are included in the Supporting Information.

To gain some insight into the reaction mechanism, we attempted isolation of a selenium cation intermediate (Scheme 4). We conducted the reaction of 4,4'-di(*tert*-butyl)biphenyl (**3b**) with PhSe(O)(OH) instead of MeSe(O)OH to prevent the spontaneous demethylation reaction leading to the neutral selenophene. Pleasingly, the corresponding dibenzoselenonium salt **7b•OTf** was successfully obtained in 77% yield. Its X-ray analysis revealed that the O atom in the OTf anion was binding to both the cationic Se center and the ortho C–H group (CCDC 2310712), which is consistent with the literature.[14] Subsequent treatment with $H_2N(CH_2)_2OH$ afforded dibenzoselenophene **4b** in 95% yield, which can support our initial working hypothesis in Scheme 2.

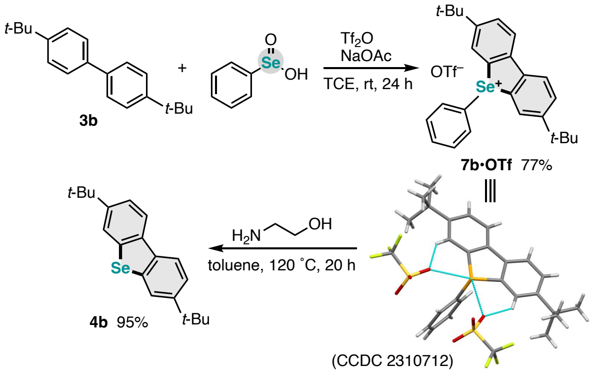
We finally applied this protocol to the dibenzothiophene synthesis by replacing MeSe(O)OH/NaOAc with MeS(O)ONa.[15] In this case, we observed the more

Scheme 3. Direct Synthesis of Benzoselenophene Derivatives from 1,1-Diarylethenes, (Hetero)biaryls, or Diaryl Ethers with MeSe(O)OH[a]



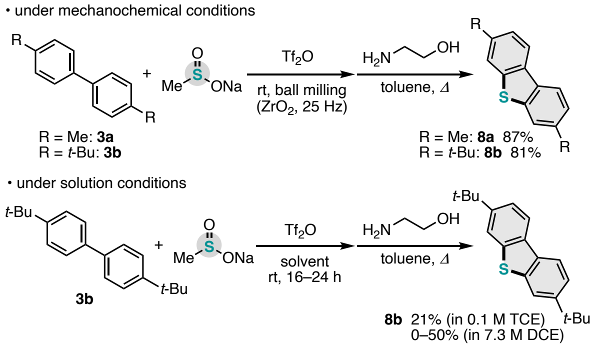
[a] Reaction conditions: Conditions A: **1**, **3,** or **5**, MeSe(O)(OH), Tf_2O, NaOAc, TCE, rt–40 ˚C. Conditions B: **1**, **3,** or **5**, MeSe(O)(OH), Tf_2O, NaOAc, ball milling (ZrO_2, 25 Hz), rt, 99 min. The conditions employed (A or B) are in parentheses. See the Supporting Information for detailed conditions and reagent stoichiometry dependent on each substrate. Isolated yields are shown. The formed bonds are drawn with bold lines. [b] On a 1.0 mmol scale.

Scheme 4. Isolation and Conversion of the Selenonium Salt Intermediate



remarkable positive effects of mechanochemical conditions (Scheme 5). Dibenzothiophenes **8a** and **8b** were formed in high yields by using ball milling, whereas solution conditions in TCE (0.1 M) led to an only 21% ^{1}H NMR yield of **8b**. This is probably attributed to the higher concentration associated with the mechanochemical mixing. Actually, the highly concentrated conditions using DCE (7.3 M) improved the yield to 50% even without ball milling, but a longer reaction time (16–24 h) was necessary. Additionally, the heterogeneous mixture caused poor reproducibility. This finding clearly demonstrates the large advantage of mechanochemical conditions for organic synthesis needed to be conducted in highly concentrated reaction conditions.

Scheme 5. Direct Synthesis of Dibenzothiophenes from Biaryls with MeS(O)Ona (Mechanochemical vs Solution Conditions)



In conclusion, we have developed a Tf$_2$O-mediated sequential C–chalcogen bond-forming reaction of relatively simple 1,1-diarylethenes and (hetero)biaryls with MeCh(O)OH (Ch = Se or S) to form the corresponding benzoselenophene and -thiophene derivatives directly. The key to success is the generation of highly electrophilic chalcogen cations, which enable otherwise challenging successive bond formation even at room temperature. Moreover, the unique acceleration effect of mechanochemical conditions using ball milling is observed. Further expansion of substrate scope, application to synthesis of more largely π-conjugated chalcogen-containing heteroaromatics, and development of related chemical transformations with highly reactive heteroatom cations are ongoing in our laboratory.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are openly available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.xxxx.

^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, ^{31}P{^{1}H}, and ^{77}Se{^{1}H} NMR spectra, ORTEP drawing, detailed optimization studies, substrate limitation, and photoluminescence data (PDF)

Accession Codes

CCDC 2310708–2310712 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(12) For related cyclization reactions with S_8 and I_2, see: (a) Bennett, G. M.; Lesslie, M. S.; Turner, E. E. The configuration of heterocyclic compounds. Part V. Thianthren and phenoxthionine derivatives. *J. Chem. Soc.* **1937**, 444–446. (b) Smith, N. L. SYNTHESIS OF PHENOTHIAZINE DERIVATIVES FOR USE AS ANTIOXIDANTS. *J. Org. Chem.* **1950**, *15*, 1125–1130. (c) Sakai, S.; Sato, K.; Yoshida, K. Synthesis of [1]benzothiopheno[2,3-b][1]benzothiophene derivatives through iodine-mediated sulfuration reaction of 1,1-diarylethylenes. *Tetrahedron Lett.* **2020**, *61*, No 151476. (d) Ito, K.; Sakai, S.; Yoshida, K. Synthesis of [1]Benzothieno[2,3-b][1]benzothiophenes from 3-Arylbenzo[b]thiophenes through Iodine-Mediated Sulfur Insertion Reaction. *J. Org. Chem.* **2023**, *88*, 14797–14802.

(13) Unsuccessful results were obtained with substrates bearing strongly electron-donating methoxy and electron-withdrawing trifluoromethyl groups. The former gave a complicated mixture, and the latter showed much lower conversion. Attempts to apply more condensed naphthalene derivatives and electron-rich heteroaromatics such as indole and thiophene also remained unsuccessful. See the Supporting Information for details.

(14) Il’in, M. V.; Novikov, A. S.; Bolotin, D. S. Sulfonium and Selenonium Salts as Noncovalent Organocatalysts for the Multicomponent Groebke−Blackburn−Bienaymé Reaction. *J. Org. Chem.* **2022**, *87*, 10199–10207. We also preliminary tried the Suzuki-Miyaura cross-coupling reaction of selenonium salt **7b•OTf** under conditions for a related coupling with sulfonium salts. However, the targeted product was not detected. Further optimization studies are essential. See the Supporting Information for details.

(15) For related double C–S bond formation with $CF_3S(O)ONa$, see: (a) Magnier, E.; Blazejewski, J.-C.; Tordeux, M.; Wakselman, C. Straightforward One-Pot Synthesis of Trifluoromethyl Sulfonium Salts. *Angew. Chem., Int. Ed.* **2006**, *45*, 1279–1282. (b) Umemoto, T.; Zhou, X.; Li, Y. A new version of Umemoto's reagents: A three-step one-pot preparation of 2, 3,7,8-tetrafluoro-S-(trifluoromethyl)dibenzothiophenium triflate. *J. Fluorine Chem.* **2019**, *226*, No 109347. We also tried the reaction of **3b** with S_8 under the reported I_2-promoted conditions (refs 11). However, the targeted **8b** was not detected at all.