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Synthesis of Fused 4-Iodoselenophene[2,3-*b*]thiophenes by Electrophilic Cyclization of 3-Alkynylthiophenes

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Keywords: Fused-ring systems / Sulfur heterocycles / Cyclization / Cross-coupling / Alkynes / Chalcogens

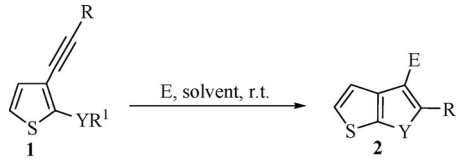
We present here our results on the electrophilic cyclization reaction of 3-alkynylthiophenes with different electrophiles such as I_2, ICl, and PhSeBr. The cyclization reaction proceeded cleanly under mild reaction conditions, giving fused 4-iodoselenophene[2,3-*b*]thiophenes in excellent yields. In addition, the obtained chalcogenophenes were readily transformed into more complex products through palladium- or copper-catalyzed cross-coupling reactions with thiols, boronic acids, and organozinc reagents.

Introduction

The derivatives of fused heterocycles are valued not only for their rich and varied chemistry, but also for many important biological properties.[1] The synthesis of fused heterocycles has also attracted considerable attention because of their use in the synthesis of a variety of functional materials for electronic devices.[2,3] However, little is known about fused Se-(S)-heterocycles with different features and applications in the literature, and there are only a few reports on generally useful syntheses of fused selenothiophenes, compounds which are of considerable interest as potentially biologically active compounds or pharmaceuticals.[4] In the context of heterocycles, electrophilic cyclization of unsaturated compounds has proved to be an efficient method for the one-step construction of a substituted heterocyclic unit.[5] Important heterocycles such as indoles,[5a,5b] benzo[*b*]furans,[5c,5d] benzo[*b*]thiophenes,[5e,5f] benzo[*b*]selenophenes,[5g] thiophenes,[5h] furans,[5i] and pyrroles[5j] among others[5k–5v] have been accessed using this protocol.[5]

Among chalcogenides, fused chalcogenophene derivatives play an important role in organic synthesis because of their excellent electrical properties and environmental stability. Chalcogenophene oligomers are compounds of current interest because many of them show photoenhanced biological activities,[6] and α-type chalcogenophene oligomers such as 5,2′:5′,2′′-thiophene produce crystalline, electroconductive polythiophenes in electrochemical polymerizations.[7] Thus, a wide variety of oligomers and related chalcogen compounds including mixed thiophene–pyrrole oligomers have been synthesized mainly with the expectation of obtaining excellent precursor compounds for molecular devices and electroconductive polymers.[8]

In addition, chalcogenophenes are widely studied agents with a diverse array of biological effects.[9] These include potent antitumor and antiviral activity, as well as efficacy as a maturation-inducing agent.[10] In this context, it is important to develop an effective synthetic method for fused selenothiophene rings as a key molecular framework for novel functional materials. The purpose of this study is to report the convenient one-step synthesis of novel fused heterocyclic ring systems containing selenothiophene moiety **2**, starting from 2-organochalcogen-3-alkynylthiophenes **1** (Scheme 1).



Scheme 1. General scheme.

Results and Discussion

For the preparation of 2-organochalcogen-3-alkynylthiophenes **1**, we chose the known Sonogashira reaction of 3-bromothiophene with terminal alkynes catalyzed by a palladium salt.[11] After that, for the introduction of the organochalcogen group, we first generated the 2-lithiothiophene intermediate by reaction of thiophene with *n*BuLi (1 equiv.)

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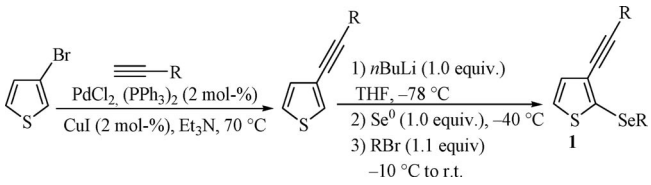
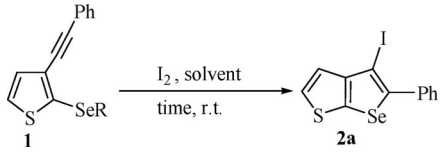
in THF at –78 °C for 1 h, followed by the addition of elemental chalcogen and alkylation with the use of an appropriate alkyl bromide (Scheme 2).[12]



Scheme 2. General procedure for the preparation of 2-organochalcogen-3-alkynylthiophenes **1**.

With the 2-organochalcogen-3-alkynylthiophenes **1** in hand, we then turned our attention to use these compounds in the electrophilic cyclization reactions. The model substrate, alkynylthiophene **1a**, was considered appropriate for studying an optimum set of electrophilic cyclization conditions. Thus, substrate **1a** (0.25 mmol) was treated with I_2 (1.1 equiv.) at room temperature with different solvents (Table 1). A comparison of the efficiencies of the solvents showed that all of them were effective, giving the cyclized product in good yields (Table 1, Entries 1–6); however, CH_2Cl_2 was the most efficient, as the product was obtained in 81% yield in a short time (Table 1, Entry 1).

Table 1. Optimization of the cyclization reaction conditions.[a]



1 **2a**

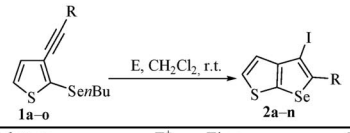
Entry	R	Solvent	Time [min]	Yield [%][b]
1	**1a**-*n*Bu	CH_2Cl_2	5	81
2	**1a**-*n*Bu	THF	120	87
3	**1a**-*n*Bu	Et_2O	90	66
4	**1a**-*n*Bu	MeOH	45	80
5	**1a**-*n*Bu	hexane	45	77
6	**1a**-*n*Bu	MeCN	10	76
7	**1p**-Et	CH_2Cl_2	15	84
8	**1q**-Bz	CH_2Cl_2	120	46
9	**1r**-Ph	CH_2Cl_2	120	n.r.

[a] Reaction performed in the presence of **1a** (0.25 mmol), I_2 (1.1 equiv.), and the solvent (5 mL). [b] Yields were determined by GC analysis.

Because the success of this reaction is probably dependent on the nature of the group directly linked to the selenium atom,[13] we decided to explore this influence by using different alkyl, aryl, and benzyl groups, and the results are shown in Table 1. Inspection of these results revealed that butyl and ethyl groups bonded at the selenium atom resulted in the formation of products in high yields after very short reaction times (Table 1, Entries 1 and 7). 2-Benzylseleno-3-alkynylthiophene also gave product **2a** in moderated yield, however, with longer reaction times (Table 1, Entry 8). Nonetheless, by performing the reaction with 3-alkynylthiophenes, having a phenyl group bonded at the selenium atom, the desired product was not observed, even under a long reaction time (Table 1, Entry 9). These results demonstrated that the efficiency of the cyclization reaction could significantly depend on steric effects and that this cyclization reaction occurs only with 3-alkynylthiophenes having a Se–C_{sp^3} bond.

Thus, careful analysis of the optimized reactions revealed that the optimum conditions for this electrophilic cyclization reaction was the combination of 2-butylseleno-3-alkynylthiophenes (1 equiv.) and electrophilic source (1.1 equiv.) by using CH_2Cl_2 (5 mL) as the solvent, at room temperature. In order to expand the applicability of our method, we applied these conditions to other 2-butylseleno-3-alkynylthiophenes **1a**–**o**. The results, summarized in Table 2, show that the reaction worked well for a variety of propargyl alcohols and aryl and alkyl alkynes bonded to the thiophene ring. A detailed analysis revealed that an aromatic ring connected to the alkyne having a neutral (Table 2, Entries 1–3), electron-donating (Table 2, Entries 4–6), or electron-withdrawing group (Table 2, Entries 8 and 9) formed the desired product in similar yields. These results revealed that the reaction does not significantly depend on the electronic effects of substituents in the aromatic ring bonded to the alkyne. When a substrate with a bulky group such as naphthalene (Table 2, Entry 7) was used, the reaction proceeded smoothly within 5 min, affording the corresponding fused heterocycle in 78% yield. In addition to aromatic rings, the reactions with alkyl (Table 2, Entries 10 and 11) and bulky alkyl groups (Table 2, Entries 12 and 13) directly bonded to the alkyne also led to the formation of the desired products with the use of either I_2 or ICl as the electrophilic source. We found that benzothiophenes derivatives **1h**–**n**, with an aryl group fused to the thiophene ring, had little influence on the cyclization reaction, as polyheterocyclic rings **2i**–**m** were obtained in similar yields to those obtained with the thiophene derivatives; however, an increase in the reaction time was required (Table 2, Entries 14–19). Concerning benzothiophenes with propargyl alkynyl alcohol or alkyl alkynes, we found some limitations in this methodology. For example, no reaction was observed with benzothiophenes **1m**,**n**, probably due to the electronic effect of the substituent on the benzothiophene ring (Table 2, Entries 20–22). Alternatively, under the same conditions described for 2-butylseleno-3-alkynylthiophenes, we were able to use tellurides. In this way, 2-butytelluro-3-alkynylthiophene **1o** underwent electrophilic cyclization with I_2, furnishing the tellurophene[2,3-*b*]thiophene in moderated yield (Table 2, Entry 23). Regarding selenium vs. oxygen cyclization, it is important to point out that we did not obtain any amount of benzofuran derivatives and the unique product obtained during the course of this cyclization was the selenophene derivatives (Table 2, Entries 18 and 19). This high selectivity can be attributed to the electronic effect (the relative nucleophilicity of the selenium atom, the cationic nature of the intermediate, and the methoxy group seems to be resistant to demethylation and ring closure).[14]

Table 2. Scope and generality of the electrophilic cyclization of 2-organochalcogen-3-alkynylthiophenes **1**.



1a–o **2a–n**

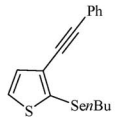
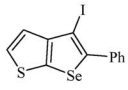
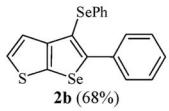
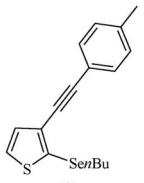
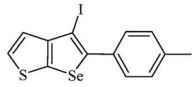
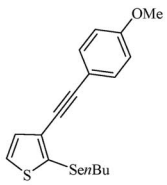
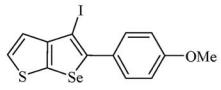
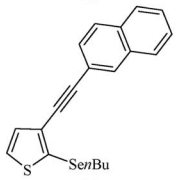
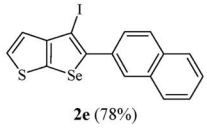
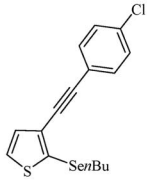
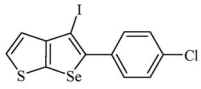
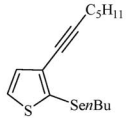
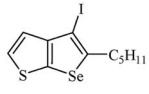
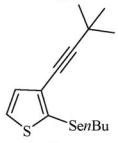
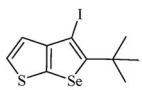
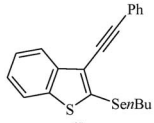
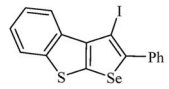
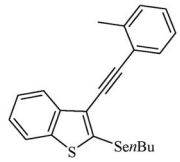
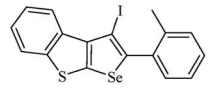
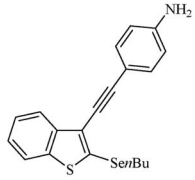
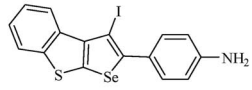
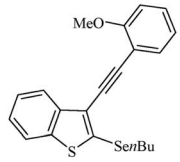
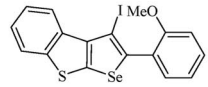
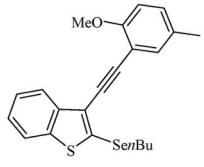
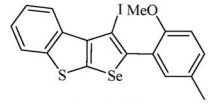
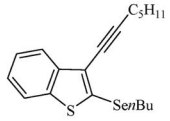
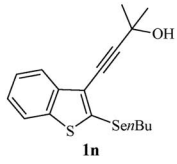
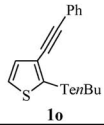
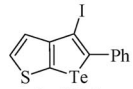
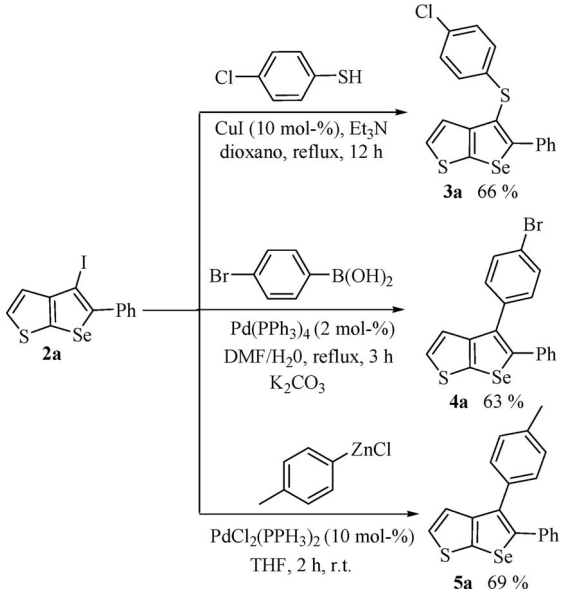
Entry	Substrate	E^+	Time [min]	Product (Yield[a,b])
1	 **1a**	I_2	5	 **2a** (81%)
2	**1a**	ICl	5	**2a** (89%)
3	**1a**	PhSeBr	10	 **2b** (68%)
4	 **1b**	I_2	5	 **2c** (86%)
5	**1b**	ICl	5	**2c** (80%)
6	 **1c**	I_2	7	 **2d** (62%)
7	 **1d**	I_2	5	 **2e** (78%)
8	 **1e**	I_2	7	 **2f** (73%)
9	**1e**	ICl	7	**2f** (76%)
10	 **1f**	I_2	5	 **2g** (71%)
11	**1f**	ICl	5	**2g** (62%)
12	 **1g**	I_2	30	 **2h** (67%)
13	**1g**	ICl	7	**2h** (71%)

Table 2. *(Continued)*.

Entry	Substrate	E^+	Time [min]	Product (Yield[a,b])
14	 **1h**	I_2	15	 **2i** (60%)
15	**1h**	ICl	60	**2i** (63%)
16	 **1i**	I_2	15	 **2j** (38%)
17	 **1j**	I_2	30	 **2k** (68%)
18	 **1k**	I_2	15	 **2l** (65%)
19	 **1l**	I_2	20	 **2m** (62%)
20	 **1m**	I_2	120	n.r.
21	 **1n**	I_2	120	n.r.
22	**1n**	ICl	120	n.r.
23	 **1o**	I_2	15	 **2n** (48%)

[a] Yields of **2a**–**m** and **2n** are given for isolated products. [b] All products were easy purified by column chromatography; however, a few were unstable and reliable elemental analyses could not be obtained.

In order to complete our investigation and to further prove the potential of 4-iodoselenophene[2,3-*b*]thiophene derivatives as precursors for increasing molecular complexity, we tested the reactivity of these compounds toward Suzuki, Negishi, and thiol cross-coupling by palladium- and copper-catalyzed reactions. In this way, the reaction of **2a** with aryl thiols by using just CuI as the catalyst in dioxane afforded the resultant products **3a** in 66% isolated yields. In addition, the reaction of **2a** with organoboron and organozinc species gave the corresponding Suzuki **4a** and Negishi **5a** products in 63 and 69% yield, respectively (Scheme 3).



Scheme 3. Reactivity of **2a** toward Suzuki, Negishi and thiol cross-coupling.

Conclusions

In summary, we have demonstrated the electrophilic cyclization reaction of 2-alkylchalcogen-3-alkynylthiophenes with different electrophilic sources under exceptionally mild conditions and established a route to obtain fused 4-iodoselenophene[2,3-*b*]thiophenes in good yields. The fused chalcogenophenes obtained by electrophilic cyclization appear highly promising as intermediates for the preparation of more highly substituted structures. In fact, by using palladium- or copper-catalyzed cross-coupling reactions with thiols, boronic acids, and organozinc reagents, we were able to convert 4-iodoselenophene[2,3-*b*]thiophenes into highly substituted, fused chalcogenophenes in good yields. We believe that this approach to fused chalcogenophenes should prove quite useful in synthesis, particularly when one considers that there are many ways to transform the resulting halogen and selenium functionalities into other substituents.

Experimental Section

General Procedure for the Preparation of 2-Alkylselanyl-3-alkynylthiophenes 1a–n, 1p, and 1q: To a two-necked round-bottomed flask under an argon atmosphere was added *n*-butyllithium (1.5 M in hexane, 13.5 mL, 20 mmol) dropwise to a solution of the appropriate 3-alkynylthiophene (20 mmol) in freshly distilled dry THF (100 mL) at –78 °C. The reaction mixture was then stirred for 30 min at this temperature and then warmed to –40 °C and elemental selenium (1.58 g, 20 mmol) was added in one portion. The reaction was then stirred for an additional 1 h at this temperature. The appropriate alkyl bromide (25 mmol) was added at –10 °C, and the reaction mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH_4Cl (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was dried with $MgSO_4$ and concentrated under vacuum. Purification was carried out by flash chromatography on silica gel (hexane).

2-(Ethylselenyl)-3-(phenylethynyl)thiophene (1p): ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.52 (m, 2 H, C*H*-Ar), 7.38–7.34 (m, 3 H, C*H*-Ar), 7.32 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th), 7.14 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th), 2.98 (q, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2-CH_3), 1.46 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 131.5, 130.6, 128.5, 128.3, 128.2, 99.9, 92.5, 84.6, 24.3, 15.6 ppm. MS: *m*/*z* (%) = 289 (100), 274 (34), 259 (59), 216 (21), 182 (16), 137 (41), 112 (15), 87 (8).

General Procedure for the Preparation of 3-(Phenylselanyl)(phenylethynyl)thiophene (1r): To a two-necked round-bottomed flask under an argon atmosphere was added *n*-butyllithium (1.5 M in hexane, 13.5 mL, 20 mmol) dropwise to a solution of 3-phenylethynyllthiophene (3.68 g, 20 mmol) in freshly distilled dry THF (100 mL) at –78 °C. The reaction mixture was then stirred for 30 min at this temperature and was then warmed to –40 °C. PhSeBr (5.9 g, 25 mmol) was added in one portion, and the reaction mixture was then stirred for an additional 2 h at room temperature, quenched with saturated NH_4Cl (50 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was dried with $MgSO_4$ and concentrated under vacuum. Purification was carried out by flash chromatography on silica gel (hexane). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.43 (m, 4 H, C*H*-Ar), 7.36–7.22 (m, 7 H, 6*H*-Ar, 1*H*-Th), 7.17 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 132.5, 131.6, 130.9, 130.7, 129.7, 129.2, 128.3, 128.2, 127.3, 123.0, 92.9, 84.3 ppm. MS: *m*/*z* (%) = 340 (17), 260 (100), 215 (31), 129 (26), 77 (1), 51 (9).

General Procedure for the Preparation of 2-(Butyltellanyl)-3-(phenylethynyl)thiophene (1o): To a two-necked round-bottomed flask under an argon atmosphere was added *n*-butyllithium (1.5 M in hexane, 13.5 mL, 20 mmol) dropwise to a solution of 3-phenylethynylthiophene (3.68 g, 20 mmol) in freshly distilled dry THF (100 mL) at –78 °C. The reaction mixture was then stirred for 30 min at this temperature and was then warmed to –40 °C. Elemental tellurium (2.56 g, 20 mmol) was added in one portion, and the reaction was then stirred for an additional 1 h at this temperature. 1-Bromobutane (3.43 g, 25 mmol) was added at –10 °C, and the reaction mixture was stirred for 2 h at room temperature, quenched with saturated NH_4Cl (50 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was dried with $MgSO_4$ and concentrated under vacuum. Purification was carried out by flash chromatography on silica gel (hexane). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.58–7.52 (m, 2 H, C*H*-Ar), 7.42 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th), 7.38–7.32 (m, 3 H, C*H*-Ar), 7.12 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th), 2.98 (t, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2-CH_2), 1.79 (quint., $J_{H,H}$ = 7.3 Hz, 2 H, CH_2-CH_2-CH_2), 1.39 (sext., $J_{H,H}$ = 7.3 Hz, 2 H, CH_2-CH_2-CH_3), 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3 H,

CH_2-CH_3) ppm. ^{13}C NMR (50 MHz, CDCl3, 25 °C): δ = 132.5, 131.5, 130.4, 128.2, 128.3, 128.2, 123.2, 104.2, 91.9, 86.2, 36.5, 24.8, 13.3, 8.1 ppm. MS: *m*/*z* (%) = 370 (35), 312 (10), 184 (100), 139 (49), 57 (9).

General Procedure for the Cyclizations Reactions: To a solution of the appropriate 2-(alkylchalcogen)-3-(alkynyl)thiophene (0.25 mmol) in CH_2Cl_2 (2 mL) was added gradually the electrophilic source (1.1 equiv.) in CH_2Cl_2 (3 mL). The reaction mixture was allowed to stir at room temperature for the desired time showed in Table 2. The organic phase was extracted with CH_2Cl_2 (20 mL) and washed with saturated aqueous $Na_2S_2O_3$. The combined organic layer was dried with anhydrous Mg_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel (hexane).

4-Iodo-5-phenylseleno[2,3-*b*]thiophene (2a): Yield: 0.074 g (76%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.61–7.57 (m, 2 H, C*H*-Ar), 7.48–7.41 (m, 4 H, 3*H*-Ar, 1*H*-Th), 7.33 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.8, 136.5, 129.7, 128.5, 128.5, 127.9, 124.2, 73.6 ppm. MS: *m*/*z* (%) = 385 (100), 260 (69), 216 (20), 169 (31), 137 (36), 86 (19), 50 (6). $C_{12}H_7ISSe$ (389.11): calcd. C 37.04, H 1.81; found C 37.29, H 2.12.

General Procedure for the Copper-Catalyzed Coupling Reaction of Intermediate 2a with 4-Chlorobenzenethiol: To a Schlenk tube, under an argon atmosphere, containing 4-iodo-5-phenylselenopheno[2,3-*b*]thiophene (**2a**; 0.5 mmol) in dry dioxane (3 mL) was added the appropriate thiol (0.6 mmol). After this, Et_3N (1 mmol) was added dropwise, followed by CuI (0.0095 g, 10 mol-%). The reaction mixture was stirred at reflux temperature for 6 h. After this, the solution was cooled to room temperature, diluted with dichloromethane (20 mL), and washed with saturated aqueous NH_4Cl (3 × 20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated under vacuum. Purification was carried out by flash chromatography on silica gel (hexane).

4-(4-Chlorophenylthio)-5-phenylselenopheno[2,3-*b*]thiophene (3a): Yield: 0.134 g (66%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.52 (m, 3 H, C*H*-Ar, C*H*-Th), 7.41–7.32 (m, 4 H, C*H*-Ar, C*H*-Th), 7.14 (d, $J_{H,H}$ = 8.1 Hz, 2 H, C*H*-*p*-Cl-C_6H_4), 7.00 (d, $J_{H,H}$ = 8.1 Hz, 2 H, C*H*-*p*-Cl-C_6H_4) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 135.8, 135.1, 133.4, 131.2, 129.4, 129.0, 128.8, 128.6, 128.5, 127.9, 122.4 ppm. MS: *m*/*z* (%) = 408 (11), 406 (100), 326 (57), 290 (58), 171 (43), 145 (44), 89 (8), 45 (3).

General Procedure for the Palladium-Catalyzed Coupling Reaction of 2a with 4-Bromophenylboronic Acid: A solution of 4-iodo-5-phenylselenopheno[2,3-*b*]thiophene (**2a**; 0.5 mmol) in DMF/H_2O (5:1, 5 mL) was added to $Pd(PPh_3)_4$ (2 mol-%) and K_2CO_3 (2 equiv.). After this, the boronic acid (1.5 equiv.) in DMF (0.5 mL) was added dropwise, and the reaction mixture was stirred at reflux temperature for 8 h. The organic phase was separated, dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography (hexane/ethyl acetate, 9:1).

4-(4-Bromophenyl)-5-phenylselenopheno[2,3-*b*]thiophene (4a): Yield: 0.131 g (63%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, $J_{H,H}$ = 8.1 Hz, 2 H, C*H*-*p*-Br-C_6H_4), 7.39 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th), 7.27–7.17 (m, 7 H, C*H*-Ar, C*H*-*p*-Br-C_6H_4), 7.08 (d, $J_{H,H}$ = 5.3 Hz, 1 H, C*H*-Th) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.7, 146.4, 135.9, 131.7, 131.3, 129.4, 128.5, 128.5, 127.6, 122.1, 121.3 ppm. MS: *m*/*z* (%) = 421 (15), 418 (100), 338 (24), 258 (70), 169 (30), 129 (58), 51 (2).

General Procedure for the Palladium-Catalyzed Negishi Coupling of 2a with *p*-Tolylzinc Chloride: A 10-mL Schlenk tube, equipped with a magnetic bar and a rubber septum, under an argon atmosphere, containing the previously prepared organozinc compound (1.5 mmol) was charged sequentially with **2a** (0.5 mmol) and $Pd(PPh_3)_4$ (0.057 g, 10 mol-%). The yellow mixture was stirred at room temperature for 3 h. After this, the solution was diluted with dichloromethane (20 mL) and washed with saturated aqueous NH_4Cl (3 × 20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography (hexane).

5-Phenyl-4-*p*-tolylselenopheno[2,3-*b*]thiophene (5a): Yield: 0.121 g (69%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.62–7.11 (m, 11 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 138.3, 136.6, 129.4, 128.9, 128.6, 127.8, 126.8, 126.1, 121.7, 118.3, 21.1 ppm. $C_{19}H_{14}SSe$ (353.34): calcd. C 64.58, H 3.99; found C 64.71, H 4.20.

Supporting Information (see footnote on the first page of this article): Experimental procedures, additional experimental details for the preparation of all compounds, and ^{1}H and ^{13}C NMR spectra for all reaction products.

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[13] For a mechanistic hypothesis, see the Supporting Information.

[14] For other relative reactivities of various functional groups toward alkyne electrophilic cyclization reactions, see: S. Mehta, J. P. Waldo, R. C. Larock, *J. Org. Chem.* **2009**, *74*, 1141.

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