

# Synthesis and Reactivity of 3-Alkynyldihydroselenophene Derivatives

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We present herein our results on the synthesis of 3-alkynyldihydroselenophenes by palladium-catalyzed Sonogashira cross-coupling of 3-iododihydroselenophenes with different alkynes under mild conditions in good to excellent yields. The developed protocol tolerated a wide range of functional groups in the dihydroselenophenes and alkynes. These 3-alkynyldihydroselenophenes, bearing the chalcogen group,

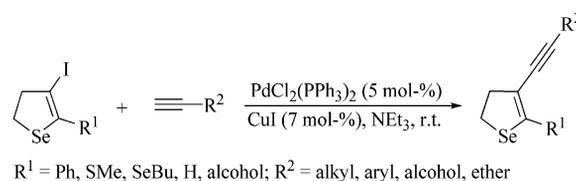
underwent highly selective intramolecular cyclizations when treated with I<sub>2</sub> to afford fused dihydroselenophene[2,3,*b*]-selenophene rings. In addition, 3-alkynyldihydroselenophene obtained by this methodology was also submitted to an oxidative reaction by using DDQ to give the aromatic selenophene in moderated yields.

## Introduction

Organoselenium chemistry is a very broad and exciting field with many opportunities for research and development of applications. Organoselenium compounds have become attractive synthetic targets because of their chemo-, regio-, and stereoselective reactions and their useful biological activities.<sup>[1]</sup> Furthermore, organoselenium compounds can usually be used in the presence of a wide variety of functional groups, thus avoiding protecting group chemistry.<sup>[2]</sup> Among organoselenium compounds, selenophene derivatives are widely studied agents with a diverse array of biological effects, including antioxidant,<sup>[3]</sup> antinociceptive,<sup>[4]</sup> and anti-inflammatory properties,<sup>[5]</sup> as well as efficacy as maturation inducing agents.<sup>[6]</sup> A great number of these heterocycles have been synthesized and their chemistry has attracted a good deal of interest and activity from a variety of standpoints such as structure, stereochemistry, reactivity, and applications to organic synthesis.<sup>[7]</sup> However, the synthetic study of a partially saturated version, 2,3-dihydrosele- nophene derivatives of selenophenes, has been surprisingly limited.<sup>[8]</sup> In the context of heterocycles, the transition-metal-catalyzed cyclization reaction of simple acyclic pre- cursors is one of the most attractive ways to directly con- struct complicated molecules under mild conditions.<sup>[9]</sup> In this way, palladium is one of the most common transition

metals used,<sup>[10]</sup> although it sometimes displays intolerance to some functionalities or proceeds with a lack of regio- selectivity. On the other hand, the electrophilic cyclization appears as an alternative route to generate highly func- tionalized heterocycles. This methodology takes advantage, in most cases, by the presence of a halogen atom suitable to suffer further transformations. This cyclization has been used as an efficient tool in the synthesis of highly sub- stituted indoles,<sup>[11]</sup> furans,<sup>[12]</sup> thiophenes,<sup>[13]</sup> selenophenes,<sup>[14]</sup> benzo[*b*]furans,<sup>[15]</sup> benzo[*b*]thiophenes,<sup>[16]</sup> benzo[*b*]seleno- phenes,<sup>[17]</sup> lactones,<sup>[18]</sup> and pyrroles<sup>[19]</sup> by employing elec- trophiles like I<sub>2</sub>, ICl, or chalcogen derivatives.<sup>[20]</sup>

These and especially the knowledge that 3-alkynyldihyd- roselenophenes are promising candidates for electrophilic cyclization reactions to form fused selenophenes prompted us to develop a complete investigation on the synthesis of 3-alkynyldihydroselenophenes from 3-iododihydroseleno- phenes as the sequence showed in Scheme 1.



Scheme 1. General scheme for the cross-coupling of 3-iododihydrosele- nophene derivatives with terminal alkynes.

## Results and Discussion

We initially focused on experiments to find a route that would give the required starting materials, 3-alkynyldihyd- roselenophenes, in good yields. We envisioned that this route could start with the introduction of an iodine group

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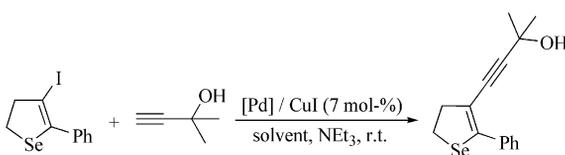
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in the C-3 position of the dihydroselenophenes and subsequent functionalization by using palladium-catalyzed Sonogashira cross-coupling<sup>[21]</sup> with terminal alkynes. For the introduction of the iodine group, we chose the electrophilic cyclization of homopropargyl selenides by using iodine as the electrophilic source.<sup>[22]</sup>

Thus, the reaction of homopropargyl selenides (0.5 mmol) and I<sub>2</sub> (1.1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at room temperature gave 3-iododihydroselenophenes in high yields. By this method, we prepared a number of 3-iododihydroselenophenes **1a–e** and applied these compounds as starting materials in palladium-catalyzed Sonogashira cross-couplings.

Our initial studies on the preparation of 3-alkynyldihydroselenophenes focused on the development of an optimum set of reaction conditions. For this purpose, 2-phenyl-3-iododihydroselenophene (**1a**) and 2-methyl-3-butyn-2-ol (**2a**) were used as standard substrates. Thus, a mixture of 3-iododihydroselenophene **1a** (0.25 mmol) and alkyne **2a** (0.375 mmol) was treated with a variety of palladium catalysts and various solvents by using NEt<sub>3</sub> as a base in the presence of CuI (Table 1). Careful analysis of the optimized reaction revealed that the optimum condition for this coupling involved the use of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol-%), NEt<sub>3</sub> (2 mL), 3-iododihydroselenophene **1a** (0.25 mmol), propargyl alcohol **2a** (0.375 mmol), and CuI (7 mol-%) at room temperature for 12 h.

Table 1. Optimization of reaction conditions.

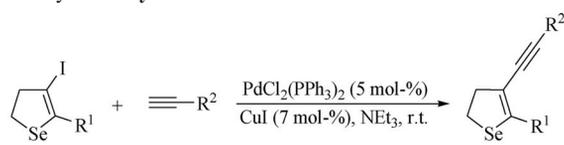


Entry	Catalyst (mol-%)	Solvent	Yield [%] <sup>[a]</sup>
1	PdCl <sub>2</sub> (5)	DMF	46
2	Pd(OAc) <sub>2</sub> (5)	DMF	26
3	Pd(PPh <sub>3</sub> ) <sub>4</sub> (5)	DMF	37
4	Pd(PhCN) <sub>2</sub> Cl <sub>2</sub> (5)	DMF	18
5	Pd(acac) <sub>2</sub> (5)	DMF	25
6	Pd(dppe) <sub>2</sub> (5)	DMF	–
7	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	DMF	93
8	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	NEt <sub>3</sub>	95
9	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	MeOH	78
10	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	dioxane	65
11	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	THF	31
12	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	toluene	50
13	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (1)	NEt <sub>3</sub>	67
14	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (10)	NEt <sub>3</sub>	24
15	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5) <sup>[b]</sup>	NEt <sub>3</sub>	54
16	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5) <sup>[c]</sup>	NEt <sub>3</sub>	traces

[a] Yields were calculated by GC analysis. [b] Reaction was performed in the presence of 5 mol-% of CuI. [c] Reaction was performed in the absence of CuI.

To demonstrate the efficiency of this reaction, we explored the generality of our method by extending the best conditions to other terminal alkynes and different 3-iodo-

Table 2. Cross-coupling reaction of 3-iododihydroselenophenes **1a–e** and alkynes **2a–y**.



Entry	Substrate	Alkyne	Product	Yield [%] <sup>[a]</sup>
1	<b>1a</b>	<b>2a</b>	<b>3a</b>	95
2	<b>1a</b>	<b>2b</b>	<b>3b</b>	70
3	<b>1a</b>	<b>2c</b>	<b>3c</b>	95
4	<b>1a</b>	<b>2d</b>	<b>3d</b>	72
5	<b>1a</b>	<b>2e</b>	<b>3e</b>	91
6	<b>1a</b>	<b>2f</b>	<b>3f</b>	77
7	<b>1a</b>	<b>2g</b>	<b>3g</b>	81
8	<b>1a</b>	<b>2h</b>	<b>3h</b>	76
9	<b>1a</b>	<b>2i</b>	<b>3i</b>	80
10	<b>1a</b>	<b>2j</b>	<b>3j</b>	75

Table 2. (Continued).

Entry	Substrate	Alkyne	Product	Yield [%] <sup>[a]</sup>
11	<b>1a</b>	<b>2k</b>	<b>3k</b>	80
12	<b>1a</b>	<b>2l</b>	<b>3l</b>	40
13	<b>1b</b>	<b>2j</b>	<b>3m</b>	90
14	<b>1b</b>	<b>2a</b>	<b>3n</b>	41
15	<b>1b</b>	<b>2i</b>	<b>3o</b>	72
16	<b>1c</b>	<b>2a</b>	<b>3p</b>	n.r.
17	<b>1c</b>	<b>2j</b>	<b>3q</b>	98
18	<b>1c</b>	<b>2i</b>	<b>3r</b>	80
19	<b>1d</b>	<b>2a</b>	<b>3s</b>	65
20	<b>1d</b>	<b>2j</b>	<b>3t</b>	97
21	<b>1d</b>	<b>2i</b>	<b>3u</b>	87

Table 2. (Continued).

Entry	Substrate	Alkyne	Product	Yield [%] <sup>[a]</sup>
22	<b>1e</b>	<b>2a</b>	<b>3v</b>	92
23	<b>1e</b>	<b>2j</b>	<b>3w</b>	73
24	<b>1e</b>	<b>2i</b>	<b>3x</b>	94
25	<b>1e</b>	<b>2g</b>	<b>3y</b>	82

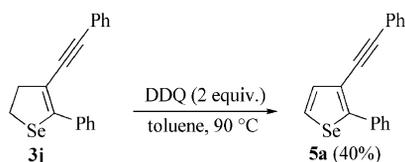
[a] Yields of **3a–y** are given for isolated products.

dihydroselenophenes; the results are summarized in Table 2. First, to determine the real influence of the terminal alkynes, we used 2-phenyl-3-iododihydroselenophene (**1a**) for all experiments. The results demonstrated that the reaction worked well for both hindered and nonhindered propargyl alcohols (Table 2, Entries 1–3). We observed that the reaction also worked well with long-chain and protected propargyl alcohols (Table 2, Entries 4 and 5). In addition to propargyl alcohols, the reaction with aliphatic alkynes also led to the formation of the desired products in good yields (Table 2, Entries 6–9). We observed that the reaction is not sensitive to electronic effects of the aromatic ring directly bonded to the alkyne. For example, alkynes having an aryl- or an aryl-substituted group gave similar yields (Table 2, Entries 10 and 11). By contrast, when the reaction was carried out with 1,3-diyne a decrease in the yield was observed and the Sonogashira product was obtained in 40% yield (Table 2, Entries 12). Finally, we then explored the possibility of expanding our methodology to 3-iododihydroselenophenes **1b–e** having a hydrogen, alcohol chain, sulfur, and selenium groups in the C-2 position. It was found that the reaction worked well, affording 3-alkynyl-dihydroselenophenes derivatives **3m–y** in moderate to excellent yields under the same reaction conditions (Table 2, Entries 13–25). The limitation in our method was observed when compound **1c** (Table 2, Entry 16), which has a hindered alcohol in the C-2

Table 3. Electrophilic cyclization with iodine.<sup>[a]</sup>

Entry	3-Alkynyl-dihydroselenophenes	Product (% yield)
1		
2		
3		
4		
5		

[a] Yields of **4a–e** are given for isolated products.

Scheme 2. Oxidation of 3-alkynyl-dihydroselenophene **3j** with DDQ.

position of the selenophene ring, was treated with propargylic alcohol **2a**. Unfortunately, in this case the reaction conditions failed to give the desired product. The starting material was recovered in its entirety, even under forcing conditions.

Because chalcogenophene derivatives exhibit a broad range of biological activities and applications as intermediates in organic synthesis, we wondered if it would be possible to prepare fused chalcogenophenes directly from 3-alkynyl-dihydrochalcogenophenes previously prepared. Recently, Larock and co-workers reported that 2,3-disubstituted benzo[*b*]selenophenes were obtained in good yields by the electrophilic cyclization of 2-(1-alkynyl)selenoanisoles by using  $I_2$  as an electrophilic source.<sup>[17]</sup>

Inspired by Larock's reaction, we extended this method to access new fused chalcogenophenes **4a–e**. Gratifyingly, we found that the electrophilic cyclization of 3-alkynyl-dihydroselenophenes with  $I_2$  in  $CH_2Cl_2$  as the solvent at room temperature afforded the desired fused chalcogenophenes **4a–e** in moderated to good yields (Table 3).

Recently, it was reported that 2,3-dichloro-5,6-dicyanobenzquinone (DDQ) is a useful promoter for the oxidation of 2,3-dihydrothiophene<sup>[23]</sup> or 2,3-dihydrofuran<sup>[24]</sup> to aromatic thiophene or furan. As demonstrated in Scheme 2, the reaction of DDQ with 3-alkynyl-dihydrochalcogenophene **3j** also proceeded smoothly to give the corresponding 2,3-disubstituted selenophene **5a** in moderate yield.

## Conclusions

We described herein an efficient methodology for the synthesis of 3-alkynyl-dihydroselenophene derivatives through Sonogashira cross-coupling of 3-iododihydroselenophenes with different alkynes. This cross-coupling reaction proceeded cleanly under mild conditions and was performed with propargylic alcohols, propargylic ethers, as well as aliphatic and aryl alkynes. The products obtained were effective for subsequent electrophilic cyclization reactions by using iodine as the electrophilic source, giving the fused chalcogenophenes in moderate yields. A 3-alkynyl-dihydroselenophene obtained by this methodology was also submitted to an oxidative reaction by using DDQ to give the aromatic selenophene in moderate yield.

## Experimental Section

**General Procedure for the Formation of 3-Alkynyl-dihydroselenophenes:** To a Schlenk tube, under an argon atmosphere, containing the appropriate 3-iododihydroselenophene (0.25 mmol) in  $Et_3N$  (1.5 mL) was added  $Pd(PPh_3)_2Cl_2$  (0.0087 g, 0.0124 mmol). After that, the appropriate terminal alkyne (0.3 mmol) dissolved in  $Et_3N$  (0.5 mL) was then added. The resulting solution was stirred for 5 min at room temperature. After this time,  $CuI$  (0.0033 g, 0.0017 mmol) was added, and the reaction mixture was stirred at room temperature for the required time. The mixture was then diluted with ethyl acetate (20 mL) and washed with brine ( $3 \times 10$  mL). The organic phase was separated, dried with  $MgSO_4$ , and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, ethyl acetate/hexane).

**2-Methyl-4-(2-phenyl-4,5-dihydroselenophen-3-yl)but-3-yn-2-ol (3a):** Yield: 0.069 g (95%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.74–7.71 (m, 2 H,  $CH-Ar$ ), 7.35–7.25 (m, 3 H,  $CH-Ar$ ), 3.30 (t,  $J_{H,H}$  = 7.6 Hz, 2 H,  $CH_2CH_2$ ), 3.16 (t,  $J_{H,H}$  = 7.3 Hz, 2 H,  $CH_2CH_2$ ), 2.18 (s, 1 H,  $OH$ ), 1.51 (s, 6 H,  $CH$ ) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 135.58, 128.48, 128.75, 127.98, 114.50, 99.94, 96.83, 79.98, 65.76, 44.06, 32.21, 24.01 ppm. MS:  $m/z$  (%) = 291 (100), 276 (56), 211 (30), 181 (21), 167 (40), 153 (51), 141 (31), 115 (37), 77 (22).  $C_{15}H_{16}OSe$  (292.04): calcd. C 61.86, H 5.54; found C 62.10, H 5.56.

**3-(2-Phenyl-4,5-dihydroselenophen-3-yl)prop-2-yn-1-ol (3b):** Yield: 0.046 g (70%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.73–7.68 (m, 2

H, CH-Ar), 7.39–7.28 (m, 3 H, CH-Ar), 4.37 (s, 2 H, CH), 3.37–3.14 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 1.84 (s, 1 H, OH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 145.53, 135.49, 128.54, 128.31, 128.13, 114.37, 90.33, 83.22, 51.69, 44.09, 24.04 ppm. MS: *m/z* (%) = 261 (65), 163 (59), 151 (100), 139 (25), 126 (52), 114 (31).

**3-Methyl-1-(2-phenyl-4,5-dihydroselenophen-3-yl)pent-1-yn-3-ol (3c):** Yield: 0.073 g (95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ = 7.74–7.70 (m, 2 H, CH-Ar), 7.38–7.26 (m, 3 H, CH-Ar), 3.37–3.28 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 3.22–3.13 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 1.97 (s, 1 H, OH), 1.75–1.64 (q, *J*<sub>H,H</sub> = 6.1 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 1.47 (s, 3 H, CH), 1.02–0.95 (t, *J*<sub>H,H</sub> = 7.5 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 144.76, 135.53, 128.46, 128.35, 127.97, 114.61, 95.79, 80.97, 69.28, 44.14, 36.39, 29.09, 24.00, 8.98 ppm. MS: *m/z* (%) = 306 (100), 225 (37), 199 (20), 151 (15), 112 (18). C<sub>16</sub>H<sub>18</sub>OSe (306.05): calcd. C 62.95, H 5.94; found C 62.69, H 5.91.

**4-(2-Phenyl-4,5-dihydroselenophen-3-yl)but-3-yn-1-ol (3d):** Yield: 0.050 g (72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.74–7.70 (m, 2 H, CH-Ar), 7.38–7.26 (m, 3 H, CH-Ar), 3.72–3.66 (t, *J*<sub>H,H</sub> = 6.1 Hz, CH<sub>2</sub>CH<sub>2</sub>), 3.35–3.12 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 2.61–2.45 (t, *J*<sub>H,H</sub> = 6.2 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 1.86 (s, 1 H, OH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 135.81, 128.41, 128.25, 128.11, 115.29, 89.76, 80.25, 60.97, 44.21, 24.15, 23.94 ppm. MS: *m/z* (%) = 275 (97), 229 (30), 163 (100), 151 (64), 138 (37), 114 (22).

**3-(Hex-1-ynyl)-2-phenyl-4,5-dihydroselenophene (3f):** Yield: 0.056 g (77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.77–7.75 (m, 2 H, CH-Ar), 7.33–7.24 (m, 3 H, CH-Ar), 3.32–3.25 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 3.18–3.14 (t, *J*<sub>H,H</sub> = 7.3 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 2.34–2.31 (t, *J*<sub>H,H</sub> = 7.1 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 1.55–1.37 (m, 5 H, CH<sub>2</sub>CH<sub>2</sub>), 0.920–0.88 (t, *J*<sub>H,H</sub> = 7.3 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 135.85, 128.30, 127.91, 120.06, 115.91, 99.92, 94.26, 78.28, 44.63, 30.59, 23.62, 21.89, 19.40, 13.54 ppm. MS: *m/z* (%) = 288 (91), 270 (44), 231 (24), 208 (15), 176 (29), 151 (100), 139 (22), 115 (25), 88 (13). C<sub>16</sub>H<sub>18</sub>Se (290.06): calcd. C 66.43, H 6.27; found C 66.70, H 6.30.

**4-(2-Phenylethynyl)-2,3-dihydroselenophene (3m):** Yield: 0.053 g (90%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 7.45–7.25 (m, 5 H, CH-Ar), 7.07 (t, *J*<sub>H,H</sub> = 1.91 Hz, CH-vin), 3.36 (t, *J*<sub>H,H</sub> = 8.31 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 2.98 (t, *J*<sub>H,H</sub> = 8.31 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 131.31, 130.02, 128.27, 127.99, 123.29, 121.36, 99.95, 89.21, 86.53, 40.60, 25.52 ppm. MS: *m/z* (%) = 304 (55), 246 (52), 231 (17), 181 (21), 165 (100), 152 (50), 141 (24), 115 (19). C<sub>12</sub>H<sub>10</sub>Se (233.99): calcd. C 61.80, H 4.32; found C 62.10, H 4.37.

**4-(3,3-Dimethylbut-1-ynyl)-2,3-dihydroselenophene (3o):** Yield: 0.039 g (72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.80 (t, *J*<sub>H,H</sub> = 1.95 Hz, 1 H, CH-vin), 3.27 (t, *J*<sub>H,H</sub> = 8.31 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 2.83 (t, *J*<sub>H,H</sub> = 8.31 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 1.23 (s, 9 H, CH) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 127.05, 121.91, 98.40, 75.96, 40.98, 30.95, 30.56, 25.13 ppm. MS (%) *m/z* (%) = 215 (77), 200 (100), 172 (14), 135 (72), 122 (51), 91 (49), 77 (45). C<sub>10</sub>H<sub>14</sub>Se (214.03): calcd. C 56.34, H 6.62; found C 56.51, H 6.75.

**General Procedure for Iodocyclizations:** To a Schlenk tube, under an argon atmosphere, containing the appropriate 3-alkynyl-dihydroselenophene in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added gradually I<sub>2</sub> (1.1 equiv.) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The reaction mixture was allowed to stir at room temperature for the required time. The excess amount of I<sub>2</sub> was removed by washing with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The product was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic layer was dried with anhydrous MgSO<sub>4</sub> and concentrated under vacuum to yield the crude product, which was purified by flash chromatography (silica gel, ethyl acetate/hexane).

**3-Iodo-2-phenyl-4,5-dihydroselenopheno[2,3-*b*]thiophene (4a):** Yield: 0.069 g (70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.57–7.35 (m, 5 H), 3.84 (t, *J*<sub>H,H</sub> = 7.8 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 3.22 (t, *J*<sub>H,H</sub> = 7.8 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ = 149.32, 144.02, 137.73, 129.06, 128.44, 128.36, 128.15, 128.85, 35.41, 31.31 ppm. MS (%) *m/z* (%) = 391 (54), 281 (31), 207 (62), 184 (48), 115 (13), 73 (43), 44 (100).

**General Procedure for Aromatization:** To a Schlenk tube, under an argon atmosphere, containing the appropriate 3-alkynyl-dihydroselenophene (0.25 mmol) in toluene (2 mL) was added DDQ (0.5 mmol), and the reaction mixture was heated at 90 °C for 12 h. After this time, the mixture was diluted with ethyl acetate (20 mL) and washed with brine (3 × 10 mL). The combined organic layer was dried with anhydrous MgSO<sub>4</sub> and concentrated under vacuum. The residue was purified by flash chromatography (silica gel, ethyl acetate/hexane).

**2-Phenyl-3-(2-phenylethynyl)selenophene (5a):** Yield: 0.031 g (40%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 7.87 (d, *J*<sub>H,H</sub> = 5.9 Hz, 2 H, CH-Ar), 7.48–7.31 (m, 7 H, CH-Ar) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ = 152.73, 135.69, 134.20, 131.36, 128.54, 128.32, 128.30, 128.21, 128.07, 123.40, 119.81, 102.34, 90.41, 86.66 ppm. MS (%) *m/z* (%) = 307 (98), 228 (100), 215 (20), 200 (17), 153 (21), 113 (48), 101 (14). C<sub>18</sub>H<sub>12</sub>Se (308.01): calcd. C 70.36, H 3.94; found C 70.49, H 4.02.

**Supporting Information** (see footnote on the first page of this article) Spectroscopic data for all compounds **3**, **4**, and **5**.

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