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Synthesis of Alkynylated Selenophenes by Site-Selective Sonogashira Reactions of Tetrabromoselenophene

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Mono-, di-, and tetraalkynylated selenophenes were prepared by site-selective Sonogashira reactions of tetrabromoselenophene. Aryl-, alkyl-, and trimethylsilylacetylenes were suitable substrates for this procedure. The first attack occurred regioselectively at C-2 and C-5. In addition, differently diarylated dialkynylselenophenes were prepared using site-selective Suzuki and Sonogashira reactions.

Introduction

Selenium compounds are considerably relevant in pharmaceutical chemistry.[1] In fact, selenium is an essential element for humans, and various diseases result from an insufficient supply of selenium.[2,3] A number of drugs containing selenium heterocycles play an important role in the clinic.[4] For example, selenazofurin is an antitumor and antiviral agent (Figure 1).[5] Various pharmacological activities have been reported for selenophenes, including muscarinic antagonist activity,[6] antiviral activity,[7] and antiproliferative activity against human leukemia cells.[8,9] Selenophenes stabilize microtubules by polymerization of tubulin.[10] They are cytotoxic against colon carcinoma,[11] human cervical cancer, and hepatocellular carcinoma.[12] In addition, selenophenes show antifungal activity.[13]

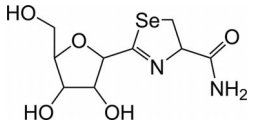


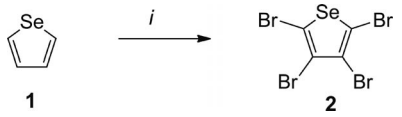
Figure 1. Structure of selenazofurin.

Moreover, conjugated selenophenes have received significant attention in the field of organic electronics.[14] It is notable that Polyselenophenes have lower band gaps than their sulfur analogues. This makes them excellent candidates for OFET (organic field-effect transistor) applications or polymer solar cells.[15] However, in contrast to their sulfur counterparts, selenophenes are little studied, due to a lack of suitable synthetic methods. Chemical transformations and syntheses of selenium heterocycles are, in general, more difficult to carry out than those of their sulfur analogues, because of the lower stability of selenium heterocycles. Synthetic procedures developed for sulfur heterocycles cannot usually simply be applied to their selenium analogues, and an individual development or optimization is usually required. In contrast to sulfur, oxygen, and nitrogen heterocycles, palladium-catalyzed cross-coupling reactions of selenium heterocycles are relatively rare.

In recent years, we have developed site-selective Suzuki–Miyaura reactions of tetrabromothiophene,[16] tetrabromo-*N*-methylpyrrole,[17] tetrabromofuran,[18] and tetrabromoselenophene.[19] We have also reported Heck reactions of tetrabromothiophene and tetrabromo-*N*-methylpyrrole.[20] Whitesides et al. have reported Sonogashira reactions of tetrabromothiophene.[21] We have reported Sonogashira reactions of tetrabromo-*N*-methylpyrrole[22] and of tetrabromofuran.[23] In this paper, we report what are, to the best of our knowledge, the first Sonogashira reactions[24] of tetrabromoselenophene. These reactions proceed with very good site-selectivity, and allow a convenient synthesis of hitherto unknown polyalkynylated selenophenes.

Results and Discussion

Tetrabromoselenophene was prepared according to the procedure of Helmholdt and co-workers by the reaction of selenophene with an excess of bromine (Scheme 1).[25]



Scheme 1. Synthesis of tetrabromoselenophene. *Conditions: i*) 1) Br_2 (7.0 equiv.), 0 °C, CH_2Cl_2; 2) reflux 72 h; 3) NaOH, H_2O (2 M), reflux, 6 h.

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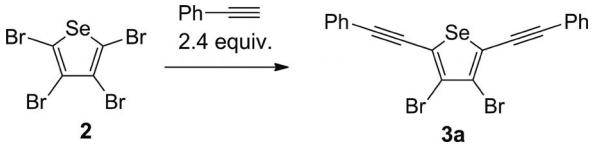
Table 1. Optimization of the synthesis of **3a**.

Entry	Catalyst	Ligand	Solvent/Base	CuI [mol-%]	*T* [°C]	Yield [%][a]
1	$PdCl_2(CH_3CN)_2$ (3 mol-%)	P(*t*Bu)$_3$ (6 mol-%)	dioxane/HN(*i*Pr)$_2$	2	20	90
2	$PdCl_2(CH_3CN)_2$ (3 mol-%)	P(*t*Bu)$_3$ (6 mol-%)	dioxane/HN(*i*Pr)$_2$	2	100	86
3	$PdCl_2(CH_3CN)_2$ (3 mol-%)	X-Phos (6 mol-%)	dioxane/HN(*i*Pr)$_2$	2	20	73
4	$Pd(PPh_3)_4$ (10 mol-%)		toluene + ethanol/HN(*i*Pr)$_2$	10	100	54
5[b]	$Pd(PPh_3)_4$ (10 mol-%)		DMF/NEt_3		20	61
6	$Pd(OAc)_2$ (10 mol-%)		$N(CH_2CH_2OH)_3$		100	66
7	10 mol-% $Pd(PPh_3)_4$ (10 mol-%)		HN(*i*Pr)$_2$	10	80	42

[a] Yields of isolated products. [b] Procedure developed by Zeni et al. (Ref.[26]).

Helmholdt used $CHCl_3$ as the solvent and obtained tetrabromoselenophene in 39% yield. We found that the yield could be dramatically improved to 84% by using CH_2Cl_2.

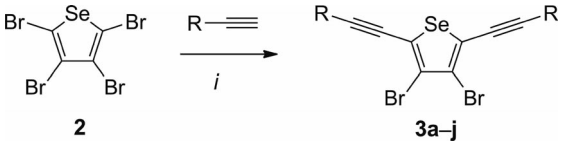
The reaction of tetrabromoselenophene (**2**) with 2.4 equiv. phenylacetylene gave 2,5-dialkynyl-3,4-dibromoselenophene **3a** (Scheme 2). The yield strongly depended on the conditions. To find the best conditions for the Sonogashira reaction, we tested different catalyst systems. The results are listed in Table 1.



Scheme 2. Optimization of the synthesis of **3a**.

After a thorough optimization, the yield could be improved to up to 90% [Table 1, entry 1, $PdCl_2(CH_3CN)_2$, P(*t*Bu)$_3$, dioxane, HN(*i*Pr)$_2$, 20 °C]. The catalyst and ligand proved to be the most important parameters in the optimization, while temperature and solvent also played a role. At first glance, it is surprising that the yield at 100 °C (Table 1, entry 2) is lower than that obtained at room temperature (Table 1, entry 1). This can be explained as follows: The reaction at positions 2 and 5 is favoured because of the electron-withdrawing effect of the selenium atom. At elevated temperatures, significant amounts of tri- and tetra-substituted selenophenes were formed.

The scope of the reaction was studied next (Scheme 3, Table 2). For aryl- and TMS-substituted acetylenes, the best yields were obtained when the reactions were carried out under the optimized conditions outlined above (Table 1, entry 1). Only trace amounts of product were isolated when *p*-fluorophenylacetylene was used. This can be explained by the electron-withdrawing nature of the fluoride moiety. Substitution of one bromide by the *p*-fluorophenylacetylene moiety resulted in some activation, and the product reacted much more quickly with the second molecule of the alkyne than did the starting material. In fact, the tetra-substituted selenophene was the major product, and some starting material **2** was also recovered. In the case of 1-decyne, product **3e** was isolated in only 47% yield using the optimized conditions (Table 1, entry 1). But the yield increased to 87% when the reaction was carried out under similar conditions that we had developed for the Sonogashira reaction of tetrabromopyrrole[22] and tetrabromofuran[23] (Table 1, entry 7). The use of a less reactive catalyst system avoids the formation of products with higher degrees of alkynylation. Product **3h** could not be prepared, presumably because the free OH group of 2-methyl-3-butyn-2-ol underwent complexation to the metal centre, which led to inhibition of the reaction. However, the reaction could be successfully carried out in the more polar solvent DMF under conditions developed by Zeni and co-workers (Table 1, entry 5).[26] The reaction proceeds without the need of a copper co-catalyst. Unfortunately, 1-dimethylamino-2-propyne did not react under these conditions.



Scheme 3. Synthesis of **3a**–**j**. *Conditions: i*) **2** (1.0 equiv.), RC≡CH (2.4 equiv.), $PdCl_2(CH_3CN)_2$ (3 mol-%), CuI (2 mol-%), HP(*t*Bu)$_3$BF$_4$ (6 mol-%), 1,4-dioxane, HN(*i*Pr)$_2$, 20 °C, 20 h.

Table 2. Synthesis of **3a**–**j**.

3	R	Yield [%][a]
a	Ph	90
b	3-MeC_6H_4	83
c	Me_3Si	65
d	4-FC_6H_4	traces
e	Oct	47 (87)[b]
f	CH_2NMe_2	0
g	4-(MeO)C_6H_4	40
h	C(OH)Me_2	0 (48)[c]
i	4-tBuC_6H_4	32
j	CH_2OAc	71

[a] Yields of isolated products (conditions: Table 1, entry 1). [b] Yields of isolated products (conditions: Table 1, entry 7). [c] Yields of isolated products (conditions: Table 1, entry 5).

The structures of all products were confirmed by spectroscopic methods. The structure of **3b** was independently confirmed by X-ray crystal structure analysis (Figure 2).[27]

The synthesis of tetraalkynylselenophenes was studied next (Scheme 4, Table 3). In 2008, we described the synthesis of tetraalkynylselenophene **4a** in 77% yield.[19] However, the procedure required a very high palladium concentration, and was not catalytic with respect to CuI. Thus, it was our objective to develop a new procedure that would allow the synthesis of tetraalkynylselenophenes with a low catalyst concentration. The reactions were carried out under the

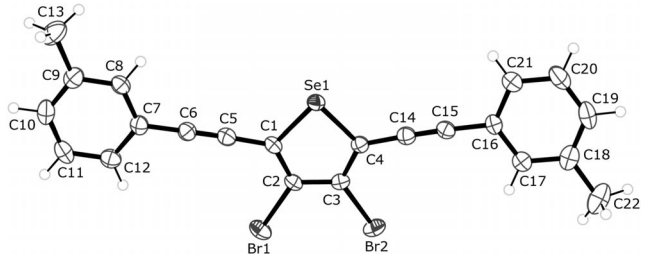
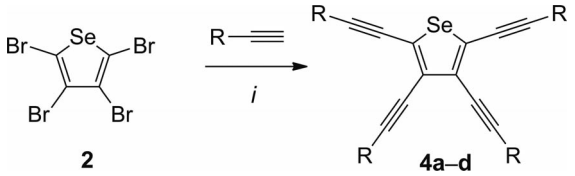


Figure 2. ORTEP plot of **3b**.

optimized conditions given in Table 1 (entries 1 and 3) with 6 equiv. acetylene. Products **4a**,**b** were prepared using X-Phos, and **4c**,**d** were prepared using $HP(tBu)_3BF_4$ as the ligand. The moderate yields of **4a**–**c** can be explained as being due to practical problems during the chromatographic purification.



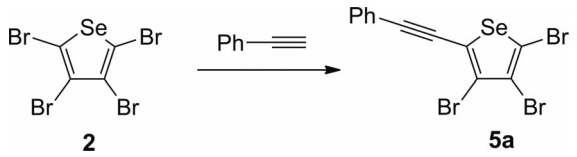
Scheme 4. Synthesis of tetraalkynylated selenophenes **4a**–**d**. *Conditions: i*) **2** (1.0 equiv.), RC≡CH (6.0 equiv.), $PdCl_2(CH_3CN)_2$ (3 mol-%), CuI (2 mol-%), $HP(tBu)_3BF_4$ or X-Phos (6 mol-%), $HN(iPr)_2$, 20 °C, 20 h.

Table 3. Synthesis of **4a**–**d**.

4	Ligand	R	Yield [%][a]
a	X-Phos	C_6H_5	34
b	X-Phos	4-$tBuC_6H_4$	28
c	$P(tBu)_3$	4-FC_6H_4	37
d	$P(tBu)_3$	4-MeC_6H_4	87

[a] Yields of isolated products.

The synthesis of 5-alkynyl-3,4,5-tribromoselenophenes proved to be impossible. Optimization of the synthesis of 5-phenylethynyl-3,4,5-tribromoselenophene (**5a**) showed that at least 38% isolated yield could be obtained (Table 4, Scheme 5). The structure of **5a** was independently confirmed by X-ray crystal structure analysis (Figure 3).[27]



Scheme 5. Synthesis of **5a**. *Conditions:* see Table 4.

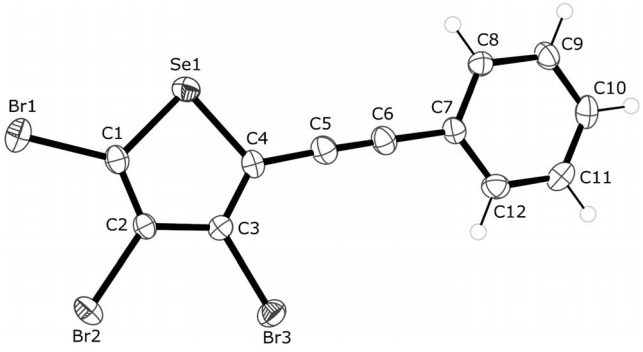
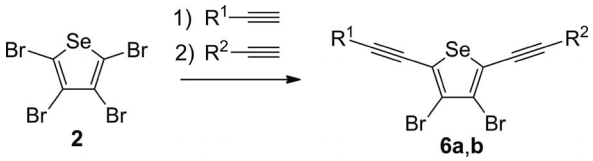


Figure 3. Crystal structure of **5a**.

Analysis of the crude mixture revealed that a high amount of the monoalkynylated product was formed, but it was difficult to isolate this product in good yield, presumably due to decomposition during chromatography. Therefore, we tried to trap the product by the addition of a second alkyne and isolation of a more stable (unsymmetrical) 2,5-dialkynylselenophene. The reaction of **2** with two different alkynes gave products **6a**,**b** in good yields (Scheme 6, Table 5). The reactions were carried out under the conditions given in Table 1, entry 1.



Scheme 6. Synthesis of unsymmetrical 2,5-dialkynylselenophenes **6a**,**b**. *Conditions: i*) **2** (1.0 equiv.), $R^1C{\equiv}CH$ (1.05 equiv.) and $R^2C{\equiv}CH$ (1.05 equiv.), $PdCl_2(CH_3CN)_2$ (3 mol-%), CuI (2 mol-%), $HP(tBu)_3BF_4$ (6 mol-%), $HN(iPr)_2$, 20 °C, 20 h.

Table 4. Optimization of the synthesis of **5a**.

Entry	Catalyst	Ligand	Solvent/base	Equiv. alkyne	*T* [°C]	Yield [%][a]
1	$Pd(CH_3CN)_2Cl_2$	$P(tBu)_3$	dioxane/$HN(iPr)_2$	1.50	20	traces
2	$Pd(CH_3CN)_2Cl_2$	$P(tBu)_3$	dioxane/$HN(iPr)_2$	2.00	20	0
3	$Pd(CH_3CN)_2Cl_2$	$P(tBu)_3$	dioxane/$HN(iPr)_2$	1.20	20	traces
4	$Pd(CH_3CN)_2Cl_2$	$P(tBu)_3$	dioxane/$HN(iPr)_2$	1.05	20	traces
5	$Pd(CH_3CN)_2Cl_2$	$P(tBu)_3$	dioxane/$HN(iPr)_2$	1.05	0	0
6	$Pd(CH_3CN)_2Cl_2$	$P(tBu)_3$	dioxane/$HN(iPr)_2$	1.05[b]	0	6
7	$Pd(CH_3CN)_2Cl_2$	$P(Cy)_3$	dioxane/$HN(iPr)_2$	1.20	20	0
8	$Pd(CH_3CN)_2Cl_2$	$P(Cy)_3$	dioxane/$HN(iPr)_2$	1.20	60	traces
9	$Pd(CH_3CN)_2Cl_2$	X-Phos	dioxane/$HN(iPr)_2$	1.20	20	0
10	$Pd(CH_3CN)_2Cl_2$	$P(2\text{-}Tol)_3$	dioxane/$HN(iPr)_2$	1.05	20	traces
11	$Pd(PPh_3)_4$	–	DMF/NEt_3	1.50	80	38

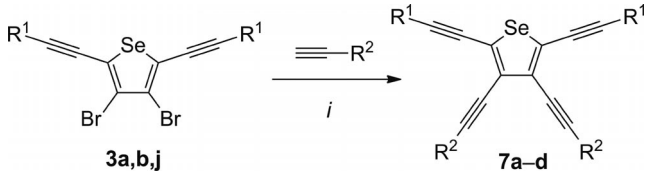
[a] Yields of isolated products. [b] Slow addition of the alkyne.

Table 5. Synthesis of unsymmetrical 2,5-alkynylated selenophenes.

6	R^1	R^2	Yield [%][a]
a	C_6H_5	3-MeC_6H_4	67
b	3-MeC_6H_4	4-*t*BuC_6H_4	54

[a] Yields of isolated products (small amounts of symmetrical disubstituted products could not be separated).

The reaction of 2,5-dialkynylselenophenes **3a**,**b**,**j** with 2.4 equiv. of alkynes gave tetraalkynylselenophenes **7a**–**d** (Scheme 7, Table 6). Products **7a**,**b**,**d** were isolated in good yields, but the yield of **7c** was low. This might be explained by complexation of the acetyl group to the catalyst and inhibition of the catalytic cycle. The reactions were carried out under the conditions reported in Table 1, entry 1.



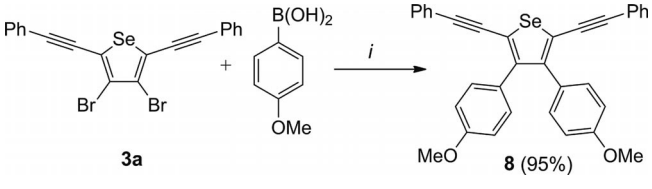
Scheme 7. Synthesis of compounds **7a**–**d**. *Conditions: i*) **2** (1.0 equiv.), $R^1C{\equiv}CH$ (2.4 equiv.), $PdCl_2(CH_3CN)_2$ (3 mol-%), CuI (2 mol-%), HP(*t*Bu)$_3BF_4$ (6 mol-%), HN(*i*Pr)$_2$, 20 °C, 20 h; *ii*) **4a**,**b**,**j** (1.0 equiv.), $R^2C{\equiv}CH$ (3.0 equiv.), $PdCl_2(CH_3CN)_2$ (5 mol-%), CuI (3 mol-%), HP(*t*Bu)$_3BF_4$ (10 mol-%), HN(*i*Pr)$_2$, 60 °C, 10 h.

Table 6. Synthesis of 7**a**–**d**.

4	7	R^1	R^2	Yield [%][a]
a	**a**	C_6H_5	CH_2OAc	93
a	**b**	C_6H_5	3-MeC_6H_4	60
j	**c**	CH_2OAc	3-MeC_6H_4	22
b	**d**	3-MeC_6H_4	CH_2OAc	82

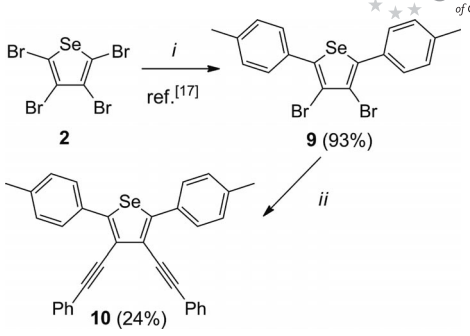
[a] Yields of isolated products.

A combination of Suzuki and Sonogashira reactions was investigated next. The reaction of **3a** with 4-(methoxyphenyl)boronic acid gave **8** in 95% yield (Scheme 8). The best yields were obtained when the ligand X-Phos was used.



Scheme 8. Synthesis of compound **8**. *Conditions: i*) **3a** (1.0 equiv.), boronic acid (3.0 equiv.), $Pd(OAc)_2$ (2 mol-%), X-Phos (3 mol-%), K_3PO_4 (3 equiv.), dioxane, water, 80 °C, 8 h.

Earlier, we reported the synthesis of 2,5-diarylselenophene **9**.[17] Its reaction with phenylacetylene gave **10**, albeit in only 24% yield (Scheme 9).



Scheme 9. Synthesis of compound **10**. *Conditions: i*) $Pd(PPh_3)_4$ (5 mol-%), K_3PO_4 (4.0 equiv.), boronic acid (2.2 equiv.), toluene, water, 20 h; *ii*) $PdCl_2(CH_3CN)_2$ (3 mol-%), X-Phos (6 mol-%), CuI (2 mol-%), dioxane, HN(*i*Pr)$_2$, alkyne (3.0 equiv.).

In conclusion, we have reported the first Sonogashira cross-coupling reactions of tetrabromoselenophene. A large number of different alkynylated selenophenes were obtained in moderate to good yields. The optimized reaction conditions allow the site-selective synthesis of the mono-, di-, and tetraalkynylselenophenes. Furthermore, tetrasubstituted selenophenes derived from Suzuki- and Sonogashira cross-coupling reactions were obtained.

Experimental Section

General Remarks: ^1H NMR spectroscopy: Bruker AV 300 (300 MHz) and Bruker AV 400 (400 MHz). References: 0.00 for TMS, 7.26 for $CDCl_3$. Peak characterization: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, m = multiplet. The spectra were measured with a standard number of scans. Where the assignment was unclear, all possible proton assignments are stated. ^{13}C NMR spectroscopy: Bruker AV 300 (75 MHz) and Bruker AV 400 (100 MHz). References: 0.00 for TMS, 77.00 for $CDCl_3$. Peak characterization: q = quartet. The DEPT method was used for determining the presence of primary, secondary, teriary, and quaternary carbon atoms. Mass spectrometry (MS): Finnigan MAT 95 XP (electron ionisation EI, 70 eV). High-resolution MS (HRMS): Finnigan MAT 95 XP. Only measurements with an average deviation from the theoretical mass of ±2 mDa were considered to be correct. Infrared spectroscopy (IR): Nicolet 550 FTIR spectrometer with ATR sampling technique for both solids and liquids. Signal characterization: w = weak, m = medium, s = strong. X-ray crystallography: Bruker X8Apex diffractometer with CCD camera (Mo-K_α radiation and graphite monochromator, λ = 0.71073 Å). The space groups were determined by the XPREP program, and the structures were solved using the SHELX-97 program package. Refinements were carried out according to the minimum square error method. Elemental analysis (EA): Leco 932 C, H, N, S. Melting point determination: Micro-Hot-Stage GalenTM III Cambridge Instruments. Thin-layer chromatography (TLC): Merck Kieselgel 60 F254 on aluminium foil from Macherey–Nagel. Detection was carried out under UV light at 254 nm and 365 nm. The following mixtures were used as stains: 1–2% of either *p*-anisaldehyde or vanillin, glacial acetic acid (10%), sulfuric acid (5%), and methanol (83–84%). Column chromatography: performed with Merck Silica Gel 60 or Macherey–Nagel Silica Gel 60 (0.063–0.200 mm, 70–230 mesh). The finer Merck Silica Gel 60 (0.040–0.063 mm, 230–400 mesh) was used when appropriate.

General Procedure for Synthesis of 3a–j: The appropriate alkyne (2.4 equiv.) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** (0.5 mmol, 224 mg) in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. After completion of the reaction time, brine was added. The aqueous phase was extracted with CH_2Cl_2 (3 ×). The combined organic extracts were dried with Na_2SO_4 and filtered, and the solution was concentrated. The residue was purified by column chromatography (heptane) to obtain **3a**–**j**.

3,4-Dibromo-2,5-(phenylethynyl)selenophene (3a): Phenylacetylene (2.4 equiv., 0.132mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **3a** (220 mg, 90%) as a yellow solid, m.p. 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.39 (m, 6 H, Ph), 7.55–7.58 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 83.6, 101.0 (C≡C), 119.9, 122.4 (C_{Hetar}), 124.2 (C_{Ph}), 128.8, 129.6, 131.9 (CH_{Ph}) ppm. IR (ATR): $\tilde{\nu}$ = 3142 (w), 3053 (m), 3020 (w), 2957 (w), 2924 (w), 2858 (w), 2202 (w), 1511 (m), 1441 (m), 1292 (br., m), 912 (m), 743 (s), 682 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 491 (22) $[M(^{81}Br)]^+$, 490 (100) $[M]^+$, 330 (15), 250 (87), 125 (25). HRMS (EI, 70 eV): calcd. for $C_{20}H_{10}Br_2Se$ 487.83090; found 487.83051.

3,4-Dibromo-2,5-bis(*m*-tolylethynyl)selenophene (3b): *m*-Tolylacetylene (2.4 equiv., 0.154 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **3b** (198 mg, 83%) as a red solid, m.p. 132–133 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 6 H, CH_3), 7.18–7.26 (m, 4 H, Ar), 7.35–7.39 (m, 4 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 83.0, 101.0 (C≡C), 119.4, 121.9 (C_{Hetar}), 123.9 (C_{Ar}), 128.4, 128.7, 130.2, 132.1 (CH), 138.3 (C_{Ar}) ppm. IR (ATR): $\tilde{\nu}$ = 3018 (w), 2953 (w), 2920 (m), 2854 (w), 2729 (w), 2199 (w), 1508 (m), 1300 (m), 908 (m), 878 (m), 779 (s), 685 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 517 (100) $[M]^+$, 358 (15), 356 (11), 278 (60), 274 (13), 138 (17). $C_{22}H_{14}Br_2Se$ (517.11): calcd. C 51.10, H 2.73; found C 51.07, H 2.85.

(3,4-Dibromoselenophene-2,5-diyl)bis(ethyne-2,1-diyl)bis(trimethylsilane) (3c): (Trimethylsilyl)acetylene (2.4 equiv., 0.21 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **3c** (150 mg, 65%) as a brown solid, m.p. 128–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 18 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.3 (CH_3), 97.6, 108.0 (C≡C), 120.4, 124.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 2953 (m), 2896 (w), 2853 (w), 2784 (w), 2174 (m), 1494 (m), 1408 (br., w), 1275 (m), 1247 (s), 834 (br., s), 758 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 482 (88) $[M]^+$, 467 (100), 293 (29), 227 (24), 169 (21), 139 (16). HRMS (EI, 70 eV): calcd. for $C_{14}H_{18}Br_2SeSi_2$ 479.84735; found 479.847476.

3,4-Dibromo-2,5-di(dec-1-ynyl)selenophene (3e): 1-Decyne (2.4 equiv., 0.07 mL) was added to a solution of $Pd(PPh_3)_4$ (5 mol-%, 23 mg), CuI (10 mol-%, 15.2 mg), and **2** (0.5 mmol, 224 mg) in THF (5 mL) and NEt_3 (5 mL). The solution was stirred for 4 h at 80 °C. Purification gave **3e** as (243 mg, 87%) a brown liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88–0.93 (m, 6 H, CH_3), 1.27–1.36 (m, 20 H, CH_2), 1.44–1.49 (m, 4 H, CH_2), 1.57–1.69 (m, 4 H, CH_2), 2.48 (t, ^3J = 6.9 Hz, 4 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 20.1, 22.7, 28.2, 28.8, 29.0, 29.2, 31.8 (CH_2), 103.6, 112.2 (C≡C), 118.3, 127.6 (C_{Hetar}). IR (ATR): $\tilde{\nu}$ = 2953 (m), 2922 (s), 2853 (s), 2218 (w), 1709 (br., m), 1458 (m), 1377 (w), 1241 (w), 1113 (w), 722 (m) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 562 (76) $[M]^+$, 465 (100), 436 (12), 353 (24), 327 (28), 287 (23), 207 (69), 165 (63).

3,4-Dibromo-2,5-(4-methoxyphenylacetylene)selenophene (3g): (4-Methoxyphenyl)acetylene (2.4 equiv., 0.159 mg) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **3g** (100 mg, 40%) as a yellow solid, m.p. 101–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 6 H, OCH_3), 6.89 (d, ^3J = 8.9 Hz, 4 H, Ar), 7.49 (d, ^3J = 8.9 Hz, 4 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 82.3, 100.9 (C≡C), 113.9 ($C_{Ar/Hetar}$) 114.2 (CH), 118.8, 123.7 ($C_{Ar/Hetar}$), 133.2 (CH), 160.4 (C_{Ar}). IR (ATR): $\tilde{\nu}$ = 3072 (w), 3049 (w), 3033 (w), 3005 (w) 2957 (w), 2938 (w), 2914 (w), 2836 (m), 2196 (m), 1600 (s), 1517 (s), 1453 (m), 1290 (s), 1245 (s), 1169 (s), 1021 (s), 822 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 550 (100) $[M]^+$, 535 (33), 316 (13), 295 (14), 280 (23), 262 (37), 247 (20), 235 (17), 223 (13), 112 (14). HRMS (EI, 70 eV): calcd. for $C_{22}H_{14}Br_2Se$ 547.85203; found 547.852633.

4,4′-(3,4-Dibromoselenophen-2,5-diyl)bis(2-methylbut-3-yn-2-ol) (3h): 2-Methyl-3-butyn-2-ol (2.5 equiv., 0.12 mL) was added to a solution of tetrakispalladium(0) (10 mol-%, 58 mg) and **2** (0.5 mmol, 224 mg) in DMF (3 mL) and NEt_3 (1 mL). The reaction mixture was stirred for 8 h at 80 °C. Purification resulted in **3h** (107 mg, 48%) as a brown solid, m.p. 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.64 (s, 12 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.1 (CH_3), 66.0 [*C*$(CH_3)_2$OH], 76.1, 105.0 (C≡C), 119.7, 123.3 (C_{Hetar}). IR (ATR): $\tilde{\nu}$ = 3274 (br., m), 2975 (m), 2926 (w), 1511 (m), 1454 (w), 1412 (w), 1377 (m), 1363 (s), 1155 (br., s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 454 (26) $[M]^+$, 439 (47), 418 (38), 379 (18), 336 (113), 315 (13), 279 (7), 218 (7). HRMS (EI, 70 eV): calcd. for $C_{14}H_{14}O_2Br_2Se$ 451.85203; found 451.851938.

3,4-Dibromo-2,5-bis[(4-*tert*-butylphenyl)ethynyl]selenophene (3i): (4-*tert*-Butylphenyl)acetylene (2.4 equiv., 0.159 mg) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **3i** (94 mg, 32%) as a red solid, m.p. 180–182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 18 H, CH_3), 7.38 (d, ^3J = 8.6 Hz, 4 H, Ar), 7.49 (d, ^3J = 8.7 Hz, 4 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.1 (CH_3), 34.9 [*C*$(CH_3)_3$], 82.8, 101.0 (C≡C), 119.1, 119.3, 123.9 ($C_{Ar/Hetar}$), 125.5, 131.4 (CH), 152.7 (C_{Ar}). IR (ATR): $\tilde{\nu}$ = 3084 (w), 3065 (w), 3032 (w), 2958 (br., m), 2901 (w), 2865 (w), 2202 (m), 1908 (w), 1523 (m), 1460 (m), 1406 (s), 1362 (m), 1115 (m), 828 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 602 (100) $[M]^+$, 587 (74), 557 (9), 522 (7), 286 (19), 258 (10), 138 (8). $C_{28}H_{26}Br_2Se$ (601.27): calcd. C 55.93, H 4.36; found C 55.87, H 4.475.

3,3′-(3,4-Dibromoselenophene-2,5-diyl)bis(prop-2-yne-3,1-diyl)-diacetate (3j): Propargyl acetate (2.4 equiv., 0.18 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **3j** (135 mg, 71%) as a brown solid, m.p. 112–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, CH_3), 4.95 (s, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7 (CH_3), 52.6 (CH_2), 79.7 (C≡C), 94.7 (C≡C), 120.5, (C_{Hetar}), 123.6 (C_{Hetar}), 170.0 (C=O). IR (ATR): $\tilde{\nu}$ = 3441 (w), 2961

(w), 2941 (w), 2709 (w), 2464 (w), 2225 (w), 1741 (s), 1722 (s), 1513 (m), 1449 (m), 1378 (m), 1361 (m), 1220 (br., s), 1024 (br., s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 482 (29) $[M]^+$, 439 (37), 422 (20), 380 (37), 299 (20), 123 (14). $C_{14}H_{10}Br_2O_4Se$ (480.99): calcd. C 34.98, H 2.28; found C 35.12, H 2.341.

General Procedure for Synthesis of 4a–d: The appropriate alkyne (6.0 equiv.) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), dicyclohexyl(2′,4′,6′-triisopropylbiphenyl-2-yl)phosphane (14 mg, 6 mol-%) or $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** (0.5 mmol, 224 mg) in dioxane (5 mL) and $HN(iPr)_2$ (1 mL). The reaction mixture was stirred for 20 h at room temperature. After the reaction time was over, it was quenched with brine. The aqueous phase was extracted with CH_2Cl_2 (3×). The combined organic extracts were dried with Na_2SO_4 and filtered, and the solution was concentrated. The residue was purified by column chromatography (hexane/dichloromethane = 10:1) to obtain **4a**–**d**.

2,3,4,5-Tetrakis(phenylethynyl)selenophene (4a): Phenylacetylene (6.0 equiv., 0.330 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), dicyclohexyl(2′,4′,6′-triisopropylbiphenyl-2-yl)phosphane (14 mg, 6 mol-%), and **2** in dioxane (5 mL) and $HN(iPr)_2$ (1 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **4a** (79 mg, 34%) as a yellow solid, m.p. 138–139 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.38 (m, 12 H, Ph), 7.53–7.62 (m, 8 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 84.1, 84.8, 95.1, 100.8 (C≡C), 122.6, 123.1 ($C_{Ar/Hetar}$), 128.4, 128.5, 128.6, 129.0 (CH), 129.2, 130.2 ($C_{Ar/Hetar}$), 131.5, 131.8 (CH). IR (ATR): $\tilde{\nu}$ = 3137 (w), 3077 (w), 3052 (w), 3017 (w), 2923 (w), 2852 (w), 2185 (w), 1596 (m), 1516 (w), 1490 (m), 1440 (m), 747 (s), 681 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 532 (100) $[M]^+$, 450 (21), 432 (4), 266 (10), 224 (19), 44 (9). $C_{36}H_{20}Se$ (531.50): calcd. C 81.35, H 3.79; found C 81.16, H 3.948.

2,3,4,5-Tetrakis[(4-*tert*-butylphenyl)ethynyl]selenophene (4b): (4-*tert*-Butylphenyl)acetylene (6.0 equiv., 475 mg) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), dicyclohexyl(2′,4′,6′-triisopropylbiphenyl-2-yl)phosphane (14 mg, 6 mol-%), and **2** in dioxane (5 mL) and $HN(iPr)_2$ (1 mL). The reaction mixture was stirred for 14 h at 80 °C. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **4b** (103 mg, 28%) as a red solid, m.p. 206–207 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 18 H, CH_3), 1.34 (s, 18 H, CH_3), 7.37 (d, ^3J = 2.3 Hz, 4 H, Ar), 7.40 (d, ^3J = 2.4 Hz, 4 H, Ar), 7.51 (d, ^3J = 8.5 Hz, 4 H, Ar), 7.54 (d, ^3J = 8.5 Hz, 4 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.2, 31.2 (CH_3), 34.9, 34.9 [$C(CH_3)_3$], 83.7, 84.3, 95.1, 100.8 (C≡C), 119.7, 120.3 ($C_{Ar/Hetar}$), 125.4, 125.5 (CH), 128.8, 130.1 ($C_{Ar/Hetar}$), 131.3, 131.5 (CH), 151.8, 152.3 (C_{Ar}). IR (ATR): $\tilde{\nu}$ = 3083 (w), 3034 (w), 2957 (m), 2902 (w), 2865 (w), 2188 (w), 1461 (m), 1406 (m), 1392 (w), 1266 (m), 1106 (m), 1016 (m), 831 (s), 558 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 756 (38) $[M]^+$, 741 (6), 669 (2), 363 (6), 207 (5), 91 (5), 60 (9). HRMS (EI, 70 eV): calcd. for $C_{52}H_{52}Se$ 756.32287; found 756.323101.

2,3,4,5-Tetrakis[(4-fluorophenyl)ethynyl]selenophene (4c): (4-Fluorophenyl)acetylene (6.0 equiv., 0.360 mg) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (5 mL) and $HN(iPr)_2$ (1 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **4c** (110 mg, 37%) as a yellow solid, m.p. 190–191 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.01–7.08 (m, 8 H, Ar), 7.49–7.55 (m, 8 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 83.8 (d, ^5J = 1.4 Hz, C≡C), 84.6 (d, ^5J = 1.4 Hz, C≡C), 94.2 (C≡C), 100.0 (C≡C), 116.1 (d, ^2J = 21.9 Hz, CH), 116.3 (d, ^2J = 21.9 Hz, CH), 118.9 (d, ^4J = 3.9 Hz, C), 119.4 (d, ^4J = 3.9 Hz, C), 129.4 (C_{Hetar}), 130.2 (C_{Hetar}), 133.8 (d, ^3J = 8.4 Hz, CH), 133.9 (d, ^3J = 8.4 Hz, CH), 163.1 (d, ^1J = 251.0 Hz, C), 163.3 (d, ^1J = 250.9 Hz, C). IR (ATR): $\tilde{\nu}$ = 3108 (w), 3058 (w), 2853 (w), 2192 (w), 1886 (w), 1600 (m), 1518 (s), 1228 (br., s), 1151 (s), 1091 (m), 824 (s), 522 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 604 (100) $[M]^+$, 522 (17), 429 (6), 302 (7), 262 (18), 44 (32). HRMS (EI, 70 eV): calcd. for $C_{36}H_{16}F_4Se$ 604.03479; found 604.036296.

2,3,4,5-Tetrakis(*m*-tolylethynyl)selenophene (4d): *m*-Tolylacetylene (6.0 equiv., 0.384 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (5 mL) and $HN(iPr)_2$ (1 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **4d** (254 mg, 87%) as a red solid, m.p. 99–100 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 6 H, CH_3), 2.36 (s, 6 H, CH_3), 7.16–7.28 (m, 8 H, Ar), 7.37–7.45 (m, 8 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3, 55.4 (CH_3), 72.9, 81.2, 82.3, 100.9 (C≡C), 113.9 ($C_{Ar/Hetar}$), 114.1, 114.2 (CH), 118.8, 123.7 ($C_{Ar/Hetar}$), 133.2, 134.0 (CH), 160.2, 160.4 ($C_{Ar/Hetar}$). IR (ATR): $\tilde{\nu}$ = 3091 (w), 2029 (w), 2918 (m), 2854 (w), 2730 (w), 2184 (w), 1598 (m), 1578 (m), 1507 (m), 1473 (m), 776 (s), 684 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 588 (100) $[M]^+$, 477 (5), 401 (3), 237 (15), 200 (6), 149 (7), 129 (9), 111 (16). $C_{40}H_{28}Se$ (587.61): calcd. C 81.76, H 4.80; found C 81.45, H 4.85.

2,3,4-Tribromo-5-(phenylethynyl)selenophene (5a): Phenylacetylene (1.2 equiv., 0.07 mL) was added to a solution of $Pd(PPh_3)_4$ (5 mol-%, 23 mg), CuI (10 mol-%, 15.2 mg), and **2** (0.5 mmol, 224 mg) in THF (5 mL) and NEt_3 (5 mL). The solution was stirred for 4 h at 80 °C. The reaction was quenched with brine. The aqueous phase was extracted with CH_2Cl_2 (3×). The combined organic extracts were dried with Na_2SO_4 and filtered, and the solution was concentrated. The residue was purified by column chromatography (heptane) to obtain **5a** (87 mg, 38%) as an unstable yellow solid, m.p. 97–98 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.39 (m, 3 H, Ph), 7.53–7.56 (m, 2 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 82.7, 100.7 (C≡C), 113.0, 118.5, 118.8, 122.0, 127.6 ($C_{Ar/Hetar}$), 128.5, 129.3, 131.6 (CH). IR (ATR): $\tilde{\nu}$ = 3057 (w), 3034 (w), 3018 (w), 2950 (w), 2918 (w), 2873 (w), 2848 (w), 1513 (m), 1430 (m), 1249 (m), 745 (s), 683 (s) cm^{-1}. MS (EI, = 70 eV): *m*/*z* (%) = 467 (100) $[M]^+$, 389 (8), 229 (22), 183 (8), 149 (16), 112 (14). HRMS (EI, 70 eV): calcd. for $C_{12}H_5Br_3Se$ 465.71011; found 465.709024.

General Procedure for the Synthesis of 6a,b: The appropriates alkynes (1.2 equiv.) were added simultaneously to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** (0.5 mmol, 224 mg) in dioxane (2 mL) and $HN(iPr)_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. After the reaction time was over, the reaction was quenched with brine. The aqueous phase was extracted with CH_2Cl_2 (3×). The combined organic extracts were dried with Na_2SO_4 and filtered, and the solution was concentrated. The residue was purified by column chromatography (heptane) to obtain **6a**,**b**.

3,4-Dibromo-2-(phenylethynyl)-5-(*m*-tolylethynyl)selenophene (6a): Phenylacetylene (1.2 equiv., 0.07 mL) and *m*-tolylacetylene (1.2 equiv., 0.08 mL) were added simultaneously to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), $HP(tBu)_3BF_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and HN-

(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **6a** (168 mg, 67%) as a brown solid that also contained a small amount of the symmetrical product, m.p. 122–123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 7.16–7.27 (m, 2 H, Ph/Ar), 7.34–7.37 (m, 5 H, Ph/Ar), 7.53–7.56 (m, 2 H, Ph/Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 83.1, 83.1, 83.3, 83.3, 100.7, 100.8, 101.0, 101.1 (C≡C), 119.4, 119.4, 119.6, 119.6, 121.9, 121.9, 122.1, 122.1, 123.7, 123.9, 124.0 ($C_{Ar/Hetar}$), 128.4, 128.5, 128.7, 129.2, 130.2, 131.6, 132.1 (CH), 138.2 ($C_{Ar/Hetar}$). IR (ATR): $\tilde{\nu}$ = 3051 (w), 3017 (w), 2919 (m), 2850 (w), 2197 (m), 1510 (m), 1440 (m), 1298 (br., m), 751 (s), 684 (s) cm^{-1}. MS (EI, = 70 eV): m/z (%) = 504 (100) [M]$^+$, 424 (1), 344 (9), 264 (58), 252 (8), 132 (27). HRMS (EI, 70 eV): calcd. for $C_{21}H_{12}Br_2Se$ 501.84655; found 501.846370.

3,4-Dibromo-2-[(4-*tert*-butylphenyl)ethynyl]-5-(*m*-tolylethynyl)-selenophene (6b):[1] (4-*tert*-Butylphenyl)acetylene (1.2 equiv., 120 mg) and *m*-tolylacetylene (1.2 equiv., 0.08 mL) were added at the same time to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 3 mol-%), CuI (2 mg, 2 mol-%), HP(tBu)$_3$BF$_4$ (9 mg, 6 mol-%), and **2** in dioxane (2 mL) and HN(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Purification resulted in **6b** (168 mg, 67%) as a brown solid, m.p. 79–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, C(CH_3)$_3$], 2.37 (s, 3 H, CH_3), 7.19–7.29 (m, 2 H, Ar), 7.38–7.41 (m, 4 H, Ar), 7.46–7.52 (m, 2 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 31.1 [C(CH_3)$_3$], 34.9 [C(CH_3)$_3$], 82.8, 82.8, 83.0, 83.0, 100.6, 100.7, 100.7, 100.8 (C≡C), 119.1, 119.1, 119.3, 119.4, 121.9, 123.7, 123.9, 124.0 ($C_{Ar/Hetar}$), 125.4, 125.5, 128.4, 128.7, 130.1, 130.2, 131.4, 132.1, 132.2, 132.9 (CH), 138.2, 152.7, 152.7 ($C_{Ar/Hetar}$). IR (ATR): $\tilde{\nu}$ = 3083 (w), 3053 (w), 3033 (w), 2958 (s), 2903 (m), 2865 (m), 2196 (m), 1521 (m), 1266 (m), 832 (s), 780 (s), 687 (s), 559 (s) cm^{-1}. MS (EI, = 70 eV): m/z (%) = 560 (93) [M]$^+$, 545 (57), 515 (13), 368 (11), 304 (15), 273 (83), 256 (100), 207 (14). HRMS (EI, 70 eV): calcd. for $C_{25}H_{20}Br_2Se$ 557.90915; found 557.909427.

General Procedure for the Synthesis of 7a–d: The appropriate alkyne (3.0 equiv.) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 6 mol-%), CuI (2 mg, 4 mol-%), HP(tBu)$_3$BF$_4$ (9 mg, 6 mol-%), and **3** (0.25 mmol) in dioxane (2 mL) and HN(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. After the reaction time was over, the reaction was quenched with brine. The aqueous phase was extracted with CH_2Cl_2 (3×). The combined organic extracts were dried with Na_2SO_4 and filtered, and the solution was concentrated. The residue was purified by column chromatography to obtain **7a**–**d**.

3,3′-[2,5-Bis(phenylethynyl)selenophene-3,4-diyl]bis(prop-2-yne-3,1-diyl) Diacetate (7a): Propargyl acetate (3.0 equiv., 0.074 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 6 mol-%), CuI (2 mg, 4 mol-%), HP(tBu)$_3$BF$_4$ (9 mg, 6 mol-%), and **3a** (0.25 mmol, 112 mg) in dioxane (2 mL) and HN(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **7a** (83 mg, 60%) as a red solid, m.p. 130–131 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 6 H, CH_3), 7.36 7.38 (m, 6 H, Ph), 7.55–7.58 (m, 4 H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (CH_3), 52.8 (CH_2), 80.9, 83.4, 88.5, 101.1 (C≡C), 122.4 ($C_{Ph/Hetar}$), 128.5 (CH), 128.8 ($C_{Ph/Hetar}$), 129.1 (CH), 130.8 ($C_{Ph/Hetar}$), 131.7 (CH), 170.2 (C=O). IR (ATR): $\tilde{\nu}$ = 3065 (w), 3034 (w), 2977 (w), 2924 (w), 2852 (w), 2218 (w), 2192 (m), 1745 (s), 1365 (m), 1267 (m), 1209 (s), 755 (s), 688 (s) cm^{-1}. MS (EI, = 70 eV): m/z (%) = 524 (100) [M]$^+$, 464 (9), 422 (37), 393 (44), 313 (76), 300 (9), 162 (14). HRMS (ESI): calcd. for $C_{30}H_{20}NaO_4Se$ [M + Na]$^+$ 547.04212; found 547.04168.

2,5-Bis(phenylethynyl)-3,4-bis(*m*-tolylethynyl)selenophene (7b): *m*-Tolylacetylene (3.0 equiv., 0.09 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 6 mol-%), CuI (2 mg, 4 mol-%), HP(tBu)$_3$BF$_4$ (9 mg, 6 mol-%), and **3a** (0.25 mmol, 112 mg) in dioxane (2 mL) and HN(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **7b** (83 mg, 60%) as a red solid, m.p. 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 6 H, CH_3), 7.13–7.25 (m, 4 H, Ph/Ar), 7.33–7.36 (m, 6 H, Ph/Ar), 7.39–7.42 (m, 4 H, Ph/Ar), 7.54–7.57 (m, 4 H, Ph/Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 84.1, 84.5, 95.6, 100.7 (C≡C), 122.7, 123.0 ($C_{Ph/Ar}$), 128.3, 128.5, 128.8, 128.9, 129.5 ($CH_{Ph/Ar}$), 130.4 ($C_{Ph/Ar}$), 131.6, 132.4 ($CH_{Ph/Ar}$), 138.0 ($C_{Ph/Ar}$). IR (ATR): $\tilde{\nu}$ = 3054 (w), 3017 (w), 2945 (w), 2916 (w), 2853 (w), 1595 (m), 1484 (m), 1440 (m), 776 (s), 751 (s), 685 (s) cm^{-1}. MS (EI, = 70 eV): m/z (%) = 560 (100) [M]$^+$, 544 (4), 463 (6), 280 (7), 231 (6), 178 (6), 149 (6). HRMS (EI, 70 eV): calcd. for $C_{38}H_{24}Se$ 560.10377; found 560.107147.

3,3′-[3,4-Bis(*m*-tolylethynyl)selenophene-2,5-diyl]bis(prop-2-yne-3,1-diyl) Diacetate (7c): *m*-Tolylacetylene (3.0 equiv., 0.096 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 6 mol-%), CuI (2 mg, 4 mol-%), HP(tBu)$_3$BF$_4$ (9 mg, 6 mol-%), and **3j** (0.25 mmol, 120 mg) in dioxane (2 mL) and HN(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **7c** (30 mg, 22%) as a red solid, m.p. 82–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.16, 2.37 (s, 6 H, CH_3), 5.02 (s, 4 H, CH_2), 7.18–7.29 (m, 4 H, Ar), 7.41–7.43 (m, 4 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.2 (CH_3), 52.8 (CH_2), 80.4, 83.9, 94.2, 95.5 (C≡C), 122.6 ($C_{Ar/Hetar}$), 128.3, 129.0, 129.7 (CH), 131.4 ($C_{Ar/Hetar}$), 132.5 (CH), 138.0 ($C_{Ar/Hetar}$), 170.1 (C=O). IR (ATR): $\tilde{\nu}$ = 3021 (w), 2954 (w), 2921 (m), 2852 (m), 2202 (w), 1740 (br., s), 1373 (br., m), 1211 (br., s), 1021 (br., s), 782 (m), 688 (m) cm^{-1}. MS (EI, = 70 eV): m/z (%) = 552 (100) [M]$^+$, 493 (5), 450 (25), 421 (13), 407 (9), 341 (11), 326 (13), 163 (4). HRMS (ESI): calcd. for $C_{32}H_{24}NaO_4Se$ [M + Na]$^+$ 575.07345; found 547.07341.

3,3′-[2,5-Bis(*m*-tolylethynyl)selenophene-3,4-diyl]bis(prop-2-yne-3,1-diyl) Diacetate (7d): *m*-Tolylacetylene (3.0 equiv., 0.096 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (4 mg, 6 mol-%), CuI (2 mg, 4 mol-%), HP(tBu)$_3$BF$_4$ (9 mg, 6 mol-%), and **3b** (0.25 mmol, 129 mg) in dioxane (2 mL) and HN(iPr)$_2$ (0.5 mL). The reaction mixture was stirred for 20 h at room temperature. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **7d** (109 mg, 82%) as a red solid, m.p. 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.16, 2.36 (s, 6 H, CH_3), 4.99 (s, 4 H, CH_2), 7.17–7.28 (m, 4 H, Ar), 7.35–7.38 (m, 4 H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 21.2 (CH_3), 52.8 (CH_2), 81.0, 83.1, 88.4, 101.3 (C≡C), 122.2 ($C_{Ar/Hetar}$), 128.4 (CH), 128.7 ($C_{Ar/Hetar}$), 128.8, 130.1 (CH), 130.8 ($C_{Ar/Hetar}$), 132.2 (CH), 138.2 ($C_{Ar/Hetar}$), 170.2 (C=O). IR (ATR): $\tilde{\nu}$ = 3020 (w), 2975 (w), 2945 (w), 2920 (w), 2854 (w), 2218 (w), 2189 (w), 1743 (s), 1425 (m), 1366 (m), 1212 (s) cm^{-1}. MS (EI, = 70 eV): m/z (%) = 552 (100) [M]$^+$, 492 (6), 492 (6), 450 (28), 421 (14), 407 (11), 341 (13), 326 (17), 163 (6). HRMS (ESI): calcd. for $C_{32}H_{24}NaO_4Se$ [M + Na]$^+$ 575.07345; found 547.07317.

3,4-Bis(4-methoxyphenyl)-2,5-bis(phenylethynyl)selenophene (8): (4-Methoxyphenyl)boronic acid (3.0 equiv., 114 mg) was added to a solution of $Pd(OAc)_2$, dicyclohexyl(2′,4′,6′-triisopropylbiphenyl-2-yl)phosphane (3.6 mg, 6 mol-%), K_3PO_4 (3.0 equiv., 160 mg), and **3a** (0.25 mmol, 122 mg) in dioxane (1 mL) and water (0.1 mL). The reaction was stirred for 8 h at 80 °C. After this time, the reaction

was quenched with brine and extracted with ethyl acetate, and the crude material was purified by column chromatography. Product **8** (128 mg, 95%) was isolated as a yellow solid, m.p. 149–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 6 H, OCH_3), 6.80 (d, ^3J = 8.8 Hz, 4 H, Ph/Ar), 7.18 (d, ^3J = 8.9 Hz, 4 H, Ph/Ar), 7.28–7.30 (m, 6 H, Ph/Ar), 7.35–7.38 (m, 4 H, Ph/Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 85.6,97.0 (C≡C), 113.1 (CH), 123.1, 123.6 ($C_{Ar/Hetar}$), 128.3 (CH), 129.0 ($C_{Ar/Hetar}$), 131.2, 131.5 (CH), 147.2 (C_{Ar}), 158.7 (C_{Ar}). IR (ATR): $\tilde{\nu}$ = 3056 (w), 3004 (w), 2963 (w), 2929 (w), 2835 (w), 2536 (w), 1605 (m), 1504 (br., m), 1245 (s), 1174 (s), 1029 (s) cm^{-1}. MS (EI, = 70 eV): *m/z* (%) = 544 (100) $[M]^+$, 512 (4), 469 (3), 376 (4), 272 (3), 187 (5), 69 (9). HRMS (EI, 70 eV): calcd. for $C_{34}H_{24}O_2Se$ 544.09360; found 544.094275.

3,4-Bis(phenylethynyl)-2,5-di(*p*-tolyl)selenophene (10): Phenylacetylene (3.0 equiv., 0.08 mL) was added to a solution of $PdCl_2(CH_3CN)_2$ (2 mg, 3 mol-%), CuI (1 mg, 2 mol-%), dicyclohexyl(2′,4′,6′-triisopropylbiphenyl-2-yl)phosphane (7 mg, 6 mol-%), and **9** (0.25 mmol, 117 mg) in dioxane (5 mL) and $HN(iPr)_2$ (1.0 mL). The reaction mixture was stirred for 10 h at 80 °C. Quenching with brine, extraction with CH_2Cl_2, and purification by column chromatography resulted in **10** (30 mg, 24%) as a yellow solid, m.p. 195–197 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 6 H, CH_3), 7.26 (d, ^3J = 8.1 Hz, 4 H, Ph/Ar), 7.31–7.34 (m, 6 H, Ph/Ar), 7.50–7.53 (m, 4 H, Ph/Ar), 7.82 (d, ^3J = 8.1 Hz, 4 H, Ph/Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 86.7, 92.7 (C≡C), 122.7, 123.6 ($C_{Ar/Hetar}$), 128.1, 128.4, 129.4, 131.5 ($CH_{Ar/Ph}$), 132.6, 138.5, 149.9 ($C_{Ar/Hetar}$). IR (ATR): $\tilde{\nu}$ = 3055 (w), 3018 (w), 2918 (w), 2852 (w), 1596 (w), 1499 (m), 1458 (m), 1440 (m), 818 (m), 749 (s), 684 (s) cm^{-1}. MS (EI, = 70 eV): *m/z* (%) = 512 (100) $[M]^+$, 494 (5), 432 (24), 416 (13), 339 (5), 200 (15). HRMS (EI, 70 eV): calcd. for $C_{34}H_{24}Se$ 512.104981; found 512.104981.

Supporting Information (see footnote on the first page of this article): Copies of NMR spectra.

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[27] CCDC-913709 (for **3b**) and -913710 (for **5a**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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