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Efficient Synthesis of Substituted Selenophenes Based on the First Palladium(0)-Catalyzed Cross-Coupling Reactions of Tetrabromoselenophene

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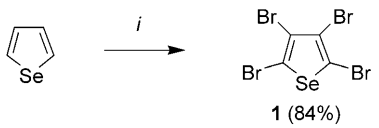
Abstract: Regioselective Suzuki cross-coupling reactions of tetrabromoselenophene allow a convenient synthesis of aryl-substituted selenophenes. High yields were obtained using a novel biarylmonophosphine ligand. The first tetra(1-alkynyl)selenophene was prepared in one step by a Sonogashira reaction of tetrabromoselenophene.

Keywords: cross-coupling; heterocycles; P ligands; palladium; selenium

Selenium represents an essential element for higher organisms.[1] In this context, the selenium-containing enzymes glutathione peroxidase and 5′-deiodase type 1 play an important role. In fact, a number of diseases can result from selenium deficiency.[2,3] In addition, selenium-containing molecules are of considerable pharmacological relevance.[4] A prominent example is the antitumor and antiviral active C-glycosylselenazole selenazofurin.[5] Selenophenes have also been reported to be of considerable pharmacological relevance. For example, they act as muscarinic antagonists,[6] show antiviral activity,[7] exert inhibitory activity against human myelogenous leukemia K562 cells, cytotoxicity against HT-29, HeLa, ACHN and 5637 cells,[8] and *in vitro* antiproliferative activity against human acute B-lymphoblastic leukemia and human acute T-lymphoblastic leukemia.[9] In addition, selenophenes promote the polymerization of tubulin and stabilize microtubules.[10] Selenophene-containing porphyrins have been shown to possess activity against murine colon carcinoma Colo-26 cells.[11] Selenophenes also exhibit antifungal activity[12] and are cytotoxic against human cervical cancer KB cells and human hepatocellular carcinoma HepG2 cells.[13]

Unfortunately, selenium compounds are in most cases less stable than their corresponding sulfur analogues. In addition, the methods and conditions available for the synthesis of organosulfur compounds can often not be applied to selenium. Therefore, the development of new methods for the synthesis of organoselenium compounds is of considerable current interest. Substituted selenophenes[14] have been mostly prepared so far based on cyclocondensation reactions. For example, 2,5-diarylselenophenes and tetraarylselenophenes are available by cyclocondensation of alkynes (2 equiv.) with selenium in the presence of lithium metal.[15] However, these reactions often suffer from the harsh reaction conditions. Kirsch and coworkers reported[16] the synthesis of 2,5-diarylselenophenes in which β-aryl-β-chloro acroleins, easily prepared from substituted acetophenones and Vilsmaier-Haack reagent, are condensed with appropriate benzyl bromide derivatives to give the title compounds. Heterocycles have been widely functionalized by palladium(0)-catalyzed cross-coupling reactions.[17] However, syntheses of functionalized selenophenes by such reactions are relatively rare. 2,5-Diarylselenophenes were prepared by Suzuki reactions of 2,5-dihaloselenophenes.[18] The Sonogashira reaction of 2-bromo- and 2-iodoselenophene with alkynes has been reported to give (1-alynyl)selenophenes.[19] The reaction of 2,5-diiodoselenophene with two equivalents of an alkyne has been reported to give 2,5-bis(1-alkynyl)selenophenes. The synthesis of tris- and tetrakis(1-alkynyl)selenophenes has, to the best of our knowledge, not been reported to date.

In recent years, it has been shown that polyhalogenated heterocycles can be regioselectively functionalized in palladium(0)-catalyzed cross-coupling reactions by selective activation of a single halogen atom. The regioselectivity is controlled by electronic and steric parameters.[20] Recently, we reported the synthesis of tetraarylthiophenes[21] and -pyrroles[22] based on regioselective Suzuki reactions of tetrabromothiophene and tetrabromo-*N*-methylpyrrole, respectively. Herein, we disclose our preliminary results related to Suzuki reactions of tetrabromoselenophene. These reactions allow a convenient and regioselective ap-

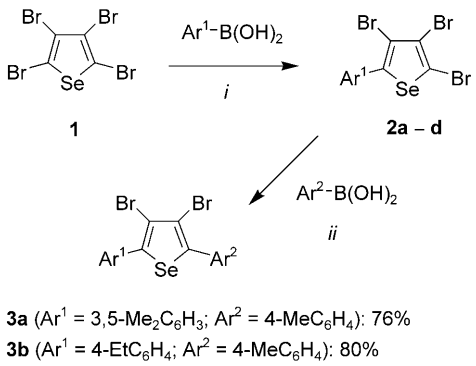


Scheme 1. Synthesis of tetrabromoselenophene (**1**); *conditions*: *i*, 1) Br_2 (7.0 equiv.), 0 °C, CH_2Cl_2; 2) reflux, 3 d; 3) NaOH, H_2O (2 M), reflux, 6 h.

proach to aryl-substituted selenophenes which are not readily available by other methods. In addition, we report the synthesis of what is, to the best of our knowledge, the first tetrakis(1-alkynyl)selenophene by a Sonogashira reaction of tetrabromoselenophene.

Helmholdt and co-workers have recently reported the synthesis of tetrabromoselenophene (**1**) in 39% yield by reflux of a $CHCl_3$ solution of selenophene with an excess of bromine.[23] We have been able to improve the yield to 84% by some modifications (Scheme 1). The solvent $CHCl_3$ was replaced by CH_2Cl_2. Due to the lower boiling point of CH_2Cl_2, the amount of bromine present in solution (and not in the gas phase) could be increased. The reaction time had to be extended from 12 to 72 h in order to make sure that the bromination is complete. Considerable amounts of di- and tribrominated selenophenes were formed when the reaction time was too short. Tetrabromoselenophene was isolated as a crystalline solid which can be stored under argon at −18 °C for several weeks.

The Suzuki reaction of **1** with various boronic acids (1.1 equiv.) afforded the 5-aryl-2,3,4-tribromoselenophenes **2a–d** in good yields and with very good regioselectivity (Scheme 2, Table 1). During the optimization, it was important to suppress the formation of 2,5-diaryl-3,4-dibromoselenophenes, as their separation from the desired products proved to be difficult. Therefore, the stoichiometry was an important parameter and only a slight excess of the boronic acid should be used. Products **2a**, **c**, **d** were best prepared using $Pd(PPh_3)_4$ (5 mol%) in dioxane/toluene/H_2O (2:2:1) (procedure A). For the reaction of **1** with sterically encumbered 3,5-dimethylphenylboronic acid (to give product **2b**) the application of procedure A gave unsatisfactory results (formation of a complex mixture). The problem was solved by employment of the new ligand **L** (Figure 1) which has been recently introduced by Buchwald and co-workers.[24] The reaction of a dioxane/toluene solution (1:1) of **1** with 3,5-dimethylphenylboronic acid, in the presence of $Pd(OAc)_2$ (5 mol%) and **L** (10 mol%), afforded **2b** in 85% yield (procedure B). The reaction of **2a**, **b** with 1.2 equiv. of (4-tolyl)boronic acid, following procedure B, resulted in the regioselective formation of the unsymmetrical 2,5-diaryl-3,4-dibromoselenophenes **3a**, **b** (Scheme 2).



Scheme 2. Synthesis of 5-aryl-2,3,4-tribromoselenophenes **2a–d** and of 2,5-diaryl-3,4-dibromoselenophenes **3a**, **b**; *conditions*: *i*, procedure A: **1** (1.0 equiv.), $Ar^1B(OH)_2$ (1.3 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene/H_2O (2:2:1), reflux, 8 h; procedure B: **1** (1.0 equiv.), $Ar^1B(OH)_2$ (1.1 equiv.), $Pd(OAc)_2$ (5 mol%), **L** (see Figure 1, 10 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene (1:1), reflux, 8 h; *ii*, **2a**, **b** (1.0 equiv.), $(4\text{-}MeC_6H_4)B(OH)_2$ (1.1 equiv.), $Pd(OAc)_2$ (5 mol%), **L** (see Figure 1, 10 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene (1:1), reflux, 8 h.

Table 1. Products and yields.

2	Ar^1	Yield [%] of **2**[a]
a	$4\text{-}EtC_6H_4$	50 (A)
b	$3,5\text{-}Me_2C_6H_3$	85 (B)
c	$4\text{-}(MeO)C_6H_4$	68 (A)
d	$3\text{-}PhC_6H_4$	47 (A)

[a] Isolated yields; in brackets: procedure (see legend of Scheme 1).

The Suzuki reaction of **1** with 2.5 equiv. of various arylboronic acids afforded the symmetrical 2,5-diaryl-3,4-dibromoselenophenes **4a–h** in good yields and with very good regioselectivity (Scheme 3, Table 2). The best yields of products **4b**, **c** were obtained by application of procedure B (using $Pd(OAc)_2$/**L**). In contrast, procedure A [using $Pd(PPh_3)_4$] gave better yields for halogenated arylboronic acids (products **4f**, **g**). This can be explained by the assumption that $Pd(OAc)_2$/**L** catalyzes a homo-coupling of the halogenated arylboronic acid which competes with the desired cross-coupling reaction.

The reaction of **4b** with (4-methoxyphenyl)boronic acid (3.0 equiv.) gave tetraarylselenophene **6** contain-

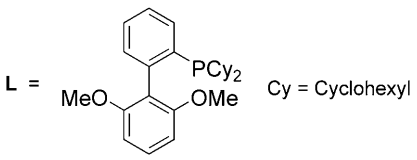
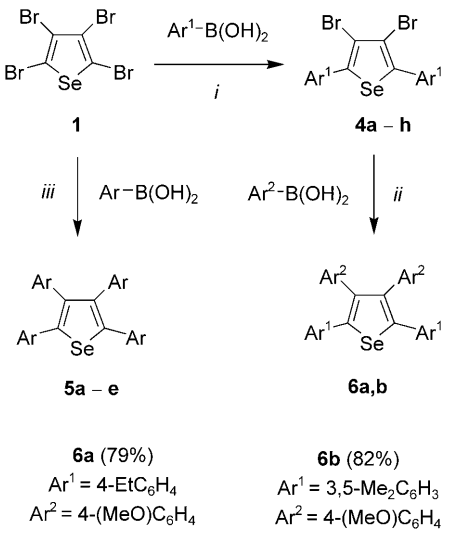


Figure 1. Biaryl-monophosphine ligand developed by Buchwald and co-workers (ref.[24]).



Scheme 3. Synthesis of 2,5-diaryl-3,4-dibromoselenophenes **4a–h** and tetraarylselenophenes **5a–e** and **6**; *conditions*: *i*, procedure A: **1** (1.0 equiv.), $Ar^1B(OH)_2$ (2.5 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene/H_2O (2:2:1), reflux, 14 h; procedure B: **1** (1.0 equiv.), $Ar^1B(OH)_2$ (2.1 equiv.), $Pd(OAc)_2$ (5 mol%), **L** (see Figure 1, 10 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene (1:1), reflux, 8 h; *ii*, **4b** (1.0 equiv.), $(4\text{-}(MeO)C_6H_4B(OH)_2$ (3.0 equiv.), $Pd(OAc)_2$ (5 mol%), **L** (see Figure 1, 10 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene (1:1), reflux, 8 h; *iii*, procedure A: **1** (1.0 equiv.), $Ar^1B(OH)_2$ (5.0 equiv.), $Pd(PPh_3)_4$ (10 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene/H_2O (2:2:1), reflux, 14 h; procedure B: **1** (1.0 equiv.), $Ar^1B(OH)_2$ (5.0 equiv.), $Pd(OAc)_2$ (10 mol%), **L** (see Figure 1, 20 mol%), K_3PO_4 (4.0 equiv.), dioxane/toluene (1:1), reflux, 8 h.

Table 2. Synthesis of **4a–h**.

4	Ar^1	Yield [%] of 4[a]
a	$4\text{-}MeC_6H_4$	83 (A)
b	$4\text{-}EtC_6H_4$	69 (A), 83 (B)
c	$3,5\text{-}Me_2C_6H_3$	65 (A), 79 (B)
d	$4\text{-}(MeO)C_6H_4$	82 (B)
e	$2\text{-}(MeO)C_6H_4$	42 (A), 68 (B)
f	$3\text{-}ClC_6H_4$	45 (A), 15 (B)
g	$4\text{-}BrC_6H_4$	55 (A)
h	$3\text{-}PhC_6H_4$	48 (A)

[a] Isolated yields; in brackets: procedure (see legend of Scheme 2).

ing two different types of aryl groups (Scheme 2). Tetraarylselenophene **5**, containing four identical aryl groups, was prepared by reaction of **1** with various arylboronic acid (5.0 equiv.) (Table 3). The sterically encumbered tetraarylselenophenes **5a–e** and **6** were isolated in very good yields when a) procedure B was employed, b) an excess of the respective boronic acid was employed and c) the amount of catalyst was increased (10 rather than 5 mol%). Considerable amounts of 2,3,5-triaryl-4-bromoselenophenes were formed when the amounts of boronic acid and catalyst were too low.

Table 3. Synthesis of **5a–e**.

5	Ar^1	Yield [%] of 5[a]
a	Ph	55 (A), 79 (B)
b	$4\text{-}MeC_6H_4$	89 (B)
c	$4\text{-}EtC_6H_4$	98 (B)
d	$3,5\text{-}Me_2C_6H_3$	74 (A)
e	$4\text{-}(MeO)C_6H_4$	89 (B)

[a] Isolated yields; in brackets: procedure (see legend of Scheme 2).

All products were characterized by spectroscopic methods. The structures of **4d** and **5d** were independently confirmed by X-ray crystal structure analyses (Figure 2 and Figure 3).[25]

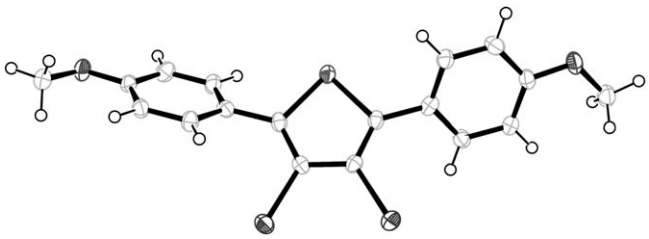


Figure 2. ORTEP plot of **4d** (50% probability level).

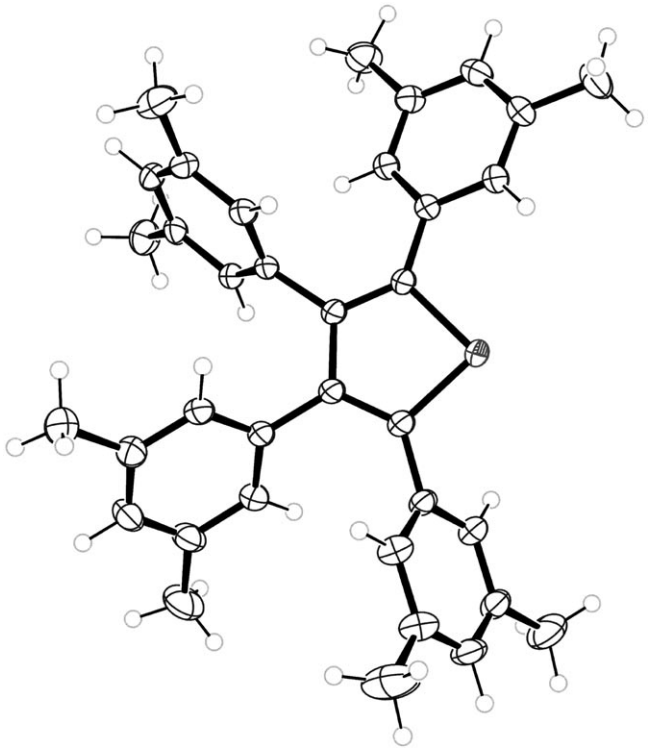
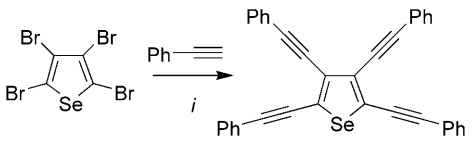


Figure 3. ORTEP plot of **5d** (50% probability level).



1 7 (77%)

Scheme 4. Synthesis of **7**; *conditions*: *i*, **1** (1.0 equiv.), PhC≡CH (6.0 equiv.), $Pd(PPh_3)_4$ (10 mol%), CuI (4.0 equiv.), *i*-Pr_2NH, 100 °C, 14 h.

The Sonogashira coupling of **1** with phenylacetylene afforded tetrakis(1-alkynyl)selenophene **7** in 77% yield (Scheme 4). During the optimization, the employment of an excess of alkyne (6.0 equiv.), a relatively high temperature (100 °C) and a long reaction time (14 h) proved to be important. The best results were obtained when $Pd(PPh_3)_4$ (10 mol%) was used as the catalyst. The use of an excess of CuI allowed us to significantly improve the yield compared to the use of only 10 mol%. Diisopropylamine was used as the solvent. To the best of our knowledge, the synthesis of a tetrakis(1-alkynyl)selenophene has not been reported to date.

In conclusion, we have reported a new strategy for the synthesis of 5-aryl-2,3,4-tribromoselenophenes, 2,5-diaryl-3,4-dibromoselenophenes, and tetraarylselenophenes based on regioselective Suzuki reactions of tetrabromoselenophene. The first tetrakis(1-alkynyl)-selenophene was prepared by Sonogashira reaction of tetrabromoselenophene with phenylacetylene.

Experimental Section

General Comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

Synthesis of Tetrabromoselenophene, C_4Br_4Se

Selenophene (2.50 g, 0.019 mol) was dissloved in CH_2Cl_2 (10 mL). This solution was cooled to 0 °C in an ice bath and subsequently an excess of bromine (13.00 g, 0.13 mol) was added dropwise during 2 h. The solution was stirred under reflux for 3 days. To the residue was added a saturated aqueous solution of NaOH and the solution was heated under reflux for 6 h. The aqueous layer and the organic layer were separated. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated under vacuum. The product was recrystallized from a 1:1-solution of chloroform and methanol at −18 °C. The product (in the form of yellow crystals) was washed with very cold ethyl acetate for several times to give the product as slightly yellow crystals; yield: 84%; mp 97–98 °C. ^{13}C NMR (75 MHz: $CDCl_3$): $\delta = 112.2$, 117.9 (CBr).

General Procedure A for the Synthesis of Aryl-Substituted Selenophenes 2a, c, d, 4a–h, and 5a, d

To a toluene/dioxane solution (1:1, 4 mL) of tetrabromoselenophene (0.134 g, 0.3 mmol) was added $Pd(PPh_3)_4$ at 20 °C. After stirring for 30 min, the arylboronic acid, K_3PO_4 and water (1 mL) were added. The mixture was stirred and heated under reflux for 8 h. After cooling to ambient temperature, the mixture was diluted with EtOAc, dried (Na_2SO_4), and filtered through a short Celite pad. The solution was concentrated under vacuum and the residue was purified by flash column chromatography (fine flash silica gel, heptanes).

Synthesis of 5-(4-Ethylphenyl)-2,3,4-tribromoselenophene (2a)

General procedure A was employed (reflux, 8 h). Starting with **1** (0.134 g, 0.3 mmol), 4-ethylphenylboronic acid (1.0 equiv., 0.33 mmol, 0.050 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **2a** was isolated as a slightly yellow solid; yield: 0.07 g (50%); mp 60–62 °C. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (t, 3 H, CH_3), 2.70 (q, 2 H, CH_2), 7.25, 7.44 (d, $^3J = 8.2$ Hz, 2 H, 2 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.3$ (CH_3), 28.7 (CH_2), 128.2, 129.0 (CH, Ar), 110.2, 111.3, 119.5 (C, CBr), 131.7, 144.8, 145.5 (C, Ar); IR (KBr,): $\tilde{\nu} = 3068$ (w), 3037 (w), 3019 (w), 2966 (w), 2925 (w), 2847 (w), 1905 (w), 1885 (w), 1660 (w), 1607 (w), 828 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 475 (M^+,[^{81}Br, ^{81}Br, ^{81}Br], 11), 473 (M^+,[^{81}Br, ^{81}Br, ^{79}Br], 16), 472 (100), 471 (M^+,[^{81}Br, ^{79}Br, ^{79}Br], 19), 469 (M^+,[^{79}Br, ^{79}Br, ^{79}Br], 13); HRMS (EI, 70 eV): calcd. for $C_{12}H_9Br_3Se$ (M^+,[^{81}Br, ^{81}Br, ^{79}Br]): 473.73732; found: 473.73826, (M^+,[^{81}Br, ^{79}Br, ^{79}Br]): 471.73936, found: 471.73943, (M^+,[^{79}Br, ^{79}Br, ^{79}Br]): 469.74141, found: 469.74065.

Synthesis of 5-(3,5-Dimethylphenyl)-2,3,4-tribromoselenophene (2b)

An oven-dried Schlenk flask was charged with $Pd(OAc)_2$, ligand **L**, tetrabromoselenophene, boronic acid and powdered, anhydrous K_3PO_4. The Schlenk flask was capped with a rubber septum and then evacuated and filled with argon. A toluene/dioxane mixture (1:1, 4 mL) was added by syringe through a septum. The septum was replaced by a condenser in an argon stream. The reaction mixture was stirred at 100 °C for 6 h under argon. The solution was allowed to cool to ambient temperature and water (5 mL) was added. The aqueous and the organic layer were separated and the latter was dried (Na_2SO_4). The solution was filtered and the filtrate was concentrated under vacuum. The residue was purified by flash column chromatography (fine flash silica gel, heptanes). Starting with **1** (0.134 g, 0.3 mmol) and 3,5-dimethylphenylboronic acid (1.1 equiv., 0.33 mmol, 0.050 g), $Pd(OAc)_2$ (3.4 mg, 5 mol%), and **L** (12.3 mg, 10 mol%), **2b** was isolated as a white solid; yield: 1.2 g (85%); mp 130–132 °C. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.36$ (s, 6 H, $2CH_3$),

7.04 (s, 1H, CH, Ar), 7.12 (s, 2H, 2 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.3$ (CH_3), 126.8, 130.8 (CH, Ar), 110.2, 111.4, 119.4 (C, CBr), 134.1, 138.4, 145.1 (C, Ar); IR (KBr): $\tilde{\nu} = 2909$ (w), 2851 (w), 2721 (w), 1796 (w), 1769 (w), 1746 (w), 1722 (w), 1592 (w), 1453 (w), 1229 (w), 848 (w), 722 (w), 690 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 475 (M^+,[^{81}Br, ^{81}Br, ^{81}Br], 10), 473 (M^+,[^{81}Br, ^{81}Br, ^{79}Br], 17), 472 (100), 471 (M^+,[^{81}Br, ^{79}Br, ^{79}Br], 19), 469 (M^+,[^{79}Br, ^{79}Br, ^{79}Br], 13); HR-MS (EI, 70 eV): calcd. for $C_{12}H_9Br_3Se$ (M^+,[^{81}Br, ^{81}Br, ^{79}Br]): 473.73732; found: 473.73824, (M^+,[^{81}Br, ^{79}Br, ^{79}Br]): 471.73936, found: 471.73962, (M^+,[^{79}Br, ^{79}Br, ^{79}Br]): 469.74141, found: 469.74110.

Synthesis of 5-(4-Methoxyphenyl)-2,3,4-tribromoselenophene (2c)

General procedure A was employed (reflux, 8 h). Starting with **1** (0.134 g, 0.3 mmol), 4-methoxyphenylboronic acid (1.1 equiv., 0.33 mmol, 0.051 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **2c** was isolated as a yellow solid; yield: 0.96 g (68%); mp 125–127 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.84$ (s, 3H, CH_3), 6.94, 7.44 (d, 2H, CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.4$ (CH_3), 114.1, 130.4 (d, ^3J = 8.2 Hz, CH, Ar), 110.0, 110.9, 119.4 (C, CBr), 126.7, 144.6, 160.2 (C, Ar); IR (KBr): $\tilde{\nu} = 3026$ (w), 2953 (w), 2895 (w), 2830 (w), 2546 (w), 2090 (w), 1884 (w), 1601 (w), 1492 (w), 1245 (w), 1029 (w), 826 (w), 690 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 477 (M^+,[^{81}Br, ^{81}Br, ^{81}Br], 7), 475 (M^+,[^{81}Br, ^{81}Br, ^{79}Br], 14), 474 (100), 473 (M^+,[^{81}Br, ^{79}Br, ^{79}Br], 18), 471 (M^+,[^{79}Br, ^{79}Br, ^{79}Br], 12); HR-MS (EI, 70 eV): calcd. for $C_{11}H_7Br_3OSe$ (M^+,[^{81}Br, ^{79}Br, ^{79}Br]): 473.71863, found: 473.72001, (M^+,[^{79}Br, ^{79}Br, ^{79}Br]): 471.72068, found: 471.72235.

Synthesis of 5-(3-Biphenyl)-2,3,4-tribromoselenophene (2d)

General procedure A was employed (reflux, 8 h). Starting with **1** (0.134 g, 0.3 mmol), 4-methoxyphenylboronic acid (1.1 equiv., 0.33 mmol, 0.065 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv, 0.254 g), and water (1 mL), **2d** was isolated as a yellow solid; yield: 0.73 g (47%); mp 90–93 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.38–7.74 (m, 9H, CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.21, 127.91, 128.93 (CH, 2CH, Ar), 127.79, 127.85, 129.2 (CH, 1 CH, Ar), 110.9, 111.9, 119.7 (C, CBr), 134.8, 140.2, 141.8, 144.5 (C, Ar); IR (KBr): $\tilde{\nu} = 3057$ (w), 3024 (w), 1926 (w), 1874 (w), 1798 (w), 1693 (w), 1568 (w), 1468 (w), 1233 (w), 745 (w), 689 (w), 619 (w), 588 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 523 (M^+,[^{81}Br, ^{81}Br, ^{81}Br], 6), 521 (M^+,[^{81}Br, ^{81}Br, ^{79}Br], 10), 519 (M^+,[^{81}Br, ^{79}Br, ^{79}Br], 9), 517 (M^+,[^{79}Br, ^{79}Br, ^{79}Br], 7); HR-MS (EI, 70 eV): calcd. for $C_{16}H_9Br_3Se$ (M^+,[^{81}Br, ^{81}Br, ^{79}Br]): 521.73732; found: 521.73765, (M^+,[^{81}Br, ^{79}Br, ^{79}Br]): 519.73936, found: 519.73924, (M^+,[^{79}Br, ^{79}Br, ^{79}Br]): 517.74141, found: 517.74031.

General Procedure for the Synthesis of Unsymmetrical 2,5-Diaryl-3,4-dibromoselenophenes 3a, b

An oven-dried Schenk flask was charged with $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%), **3a, b** (0.3 mmol), the boronic acid (1.1 equiv., 0.33 mmol) and powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g). The Schlenk flask was evacuated and subsequently flushed with argon. A mixture of toluene and dioxane (1:1, 4 mL) was added by syringe. The reaction mixture was heated under reflux for 6 h. The mixture was allowed to cool to ambient temperature and water (5 mL) was added. The aqueous and the organic layer were separated. The latter was dried (Na_2SO_4), filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash column chromatography (fine silica gel, heptanes).

Synthesis of 2-Ethylphenyl-5-(*p*-tolyl)-3,4-dibromoselenophene (3a)

Starting with **2a** (0.141 g, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12.3 mg, 10 mol%), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g) and 4-methylphenylboronic acid (1.0 equiv., 0.33 mmol, 0.041 g, **3a** was isolated as an orange highly viscous oil after reflux for 8 h; yield: 0.11 g (76%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$ (t, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.67 (q, 2H, CH_2), 7.19, 7.25, 7.42, 7.47 (d, $^3J = 8.2$ Hz, 2H, 2 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.6$, 21.1 (CH_3), 28.5 (CH_2), 126.79, 126.90, 128.2, 129.4 (CH, Ar), 132.06, 132.28, 136.7, 138.6, 143.0, 145.0 (C, Ar), 112.0 (overlap of two CBr, Ar); IR (KBr): $\tilde{\nu} = 3020$ (w), 2961 (w), 2927 (w), 2968 (w), 1901 (w), 1605 (w), 1490 (m), 940 (w), 817 (m), 799 (m), 718 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 485 (M^+,[^{81}Br, ^{81}Br], 11), 484 (100), 483 (M^+,[^{81}Br, ^{79}Br], 19), 481 (M^+,[^{79}Br, ^{79}Br], 22); HR-MS (EI, 70 eV): calcd. for $C_{19}H_{16}Br_2Se$ (M^+,[^{81}Br, ^{81}Br]): 485.87425; found: 485.87411, (M^+,[^{81}Br, ^{79}Br]): 483.87635, found: 483.87642, (M^+,[^{79}Br, ^{79}Br]): 481.87840, found: 481.87849.

Synthesis of 2-(3,5-Dimethylphenyl)-5-(*p*-tolyl)-3,4-dibromoselenophene (3b)

Starting with **2b** (0.141 g, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g) and 4-methylphenylboronic acid (1.1 equiv., 0.33 mmol, 0.041 g), **3b** was isolated as an orange highly viscous oil after reflux for 8 h; yield: 0.116 g (80%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$ (s, 6H, $2CH_3$), 1.30 (s, 3H, CH_3), 7.19, 7.28 (d, $^3J = 8.2$ Hz, 2H, 2 CH, Ar), 7.51 (s, 1H, CH, Ar), 7.59 (s, 2H, 2 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.1$, 21.4 (CH_3), 125.1 (C, 1 CH, Ar), 126.8, 129.1, 129.4 (C, 2 CH, Ar), 132.1, 136.7, 138.1, 138.8, 141.4, 142.9 (C, Ar), 112.1 (overlap of two CBr, Ar); IR (KBr): $\tilde{\nu} = 3019$ (w), 2914 (w), 2857 (w), 2729 (w), 1666 (w), 1597 (m), 1490 (m), 1239 (m), 840 (m), 799 (m), 693 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%) = 485 (M^+,[^{81}Br, ^{81}Br], 12), 484 (100), 483 (M^+,[^{81}Br, ^{79}Br], 21), 481 (M^+,[^{79}Br, ^{79}Br], 22). HR-MS (EI, 70 eV): calcd for $C_{19}H_{16}Br_2Se$ (M^+,[^{81}Br, ^{81}Br]): 485.87425; found: 485.87431, (M^+,[^{81}Br, ^{79}Br]): 483.87635, found: 483.87649, (M^+,[^{79}Br, ^{79}Br]): 481.87840, found: 481.87836.

Synthesis of 2,5-Ditolyl-3,4-dibromoselenophene (4a)

General procedure A was employed (reflux, 8 h). Starting with **1** (0.134 g, 0.3 mmol), *p*-tolylboronic acid (2.2 equiv., 0.66 mmol, 0.09 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water

(1 mL), **4a** was isolated as a yellow solid; yield: 0.117 g (83%); mp 98–102 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.25$ (s, 6H, $2CH_3$), 7.22, 7.39 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.3$ (CH_3), 129.5, 129.8 (CH, Ar), 132.1, 138.8, 142.9 (C, Ar), 112.1 (CBr, Ar); IR (KBr): $\tilde{\nu} = 3019$ (w), 2914 (w), 2725 (w), 1894 (w), 1565 (w), 1488 (m), 1246 (w), 1178 (w), 1021 (w), 957 (w), 809 (m), 719 (m), 637 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 471 (M^+,[^{81}Br, ^{81}Br], 20), 469 (M^+,[^{81}Br, ^{79}Br], 23), 470 (100), 467 (M^+,[^{79}Br, ^{79}Br], 19); HR-MS (EI, 70 eV): calcd. for $C_{18}H_{14}Br_2Se$ (M^+,[^{81}Br, ^{81}Br]): 471.85811; found: 471.85951, (M^+,[^{81}Br, ^{79}Br]): 469.86015, found: 469.86074, (M^+,[^{79}Br, ^{79}Br]): 467.86220, found: 467.86196.

Synthesis of 2-(2,5-Diethylphenyl)-3,4-dibromoselenophene (4b)

General procedure A (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *p*-ethylphenylboronic acid (2.2 equiv., 0.66 mmol, 0.099 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **4b** was isolated as a yellow solid; yield: 0.103 g (69%).

General procedure B (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *p*-ethylphenylboronic acid (2.2 equiv., 0.66 mmol, 0.099 g), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%), and powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), **4b** was isolated as a yellow solid; yield: 0.124 g (83%); mp 68–72 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.19$ (t, 6H, $2CH_3$), 2.56 (q, 4H, $2CH_2$), 7.12, 7.41 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.3$ (CH_3), 28.6 (CH_2), 128.2, 129.1 (CH, Ar), 132.2, 143.0, 145.0 (C, Ar), 112.1 (CBr, Ar); IR (KBr): $\tilde{\nu} = 2959$ (w), 2926 (w), 2867 (w), 1906 (w), 1668 (w), 1607 (w), 1522 (w), 1490 (m), 1453 (w), 834 (m), 796 (m), 769 (m), 688 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 499 (M^+,[^{81}Br, ^{81}Br], 21), 498 (100), 497 (M^+,[^{81}Br, ^{79}Br], 23), 495 (M^+,[^{79}Br, ^{79}Br], 19); HRMS (EI, 70 eV): calcd for $C_{20}H_{18}Br_2Se$ (M^+,[^{81}Br, ^{81}Br]): 499.88941; found: 499.88998, (M^+,[^{81}Br, ^{79}Br]): 497.89145, found: 497.89169, (M^+,[^{79}Br, ^{79}Br]): 495.89350, found: 495.89277.

Synthesis of 2,5-Bis(3,5-dimethylphenyl)-3,4-dibromoselenophene (4c)

General procedure A (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), 3,5-dimethylboronic acid (2.2 equiv., 0.66 mmol, 0.099 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **4c** was isolated as a yellow solid; yield: 0.097 g (65%).

General procedure B (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), 3,5-dimethylboronic acid (2.2 equiv., 0.66 mmol, 0.099 g), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%), and powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), **4c** was isolated as a yellow solid; yield: 0.118 g (79%); mp 162–164 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.29$ (s, 12H, $4CH_3$), 6.97 (s, 2H, 2 CH, Ar), 7.12 (s, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.3$ (CH_3), 126.9, 130.4 (CH, Ar), 134.8, 138.2, 143.1 (C, Ar), 112.0 (CBr, Ar); IR (KBr): $\tilde{\nu} = 2995$ (w), 2911 (w), 2857 (w), 2725 (w), 1737 (w), 1595 (w), 1444 (w), 1228 (m), 888 (w), 843 (m), 784 (m), 691 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 499 (M^+,[^{81}Br, ^{81}Br], 21), 498 (100), 497 (M^+,[^{81}Br, ^{79}Br], 25), 495 (M^+,[^{79}Br, ^{79}Br], 20); HR-MS (EI, 70 eV): calcd. for $C_{20}H_{18}Br_2Se$ (M^+,[^{81}Br, ^{81}Br]): 499.88941; found: 499.89033 (M^+,[^{81}Br, ^{79}Br]): 497.89145, found: 497.89246, (M^+,[^{79}Br, ^{79}Br]): 495.89350, found: 495.89365.

Synthesis of 2,5-Bis(*p*-methoxyphenyl)-3,4-dibromoselenophene (4d)

General procedure A was employed (reflux, 8 h). Starting with **1** (0.134 g, 0.3 mmol), *p*-methoxyphenylboronic acid (2.2 equiv., 0.66 mmol, 0.09 g), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%), and powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), **4d** was isolated as a yellow solid; yield: 0.123 g (82%); mp 157–161 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.75$ (s, 6H, $2OCH_3$), 6.84, 7.45 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.3$ (OCH_3), 114.0, 130.4 (CH, Ar), 127.3, 142.3, 159.9 (C, Ar), 111.7 (CBr, Ar); IR (KBr): $\tilde{\nu} = 2983$ (w), 2965 (w), 2832 (w), 1605 (m), 1491 (m), 1242 (m), 1174 (m), 1028 (m), 827 (m), 783 (w), 728 (w), 685 (w), 656 (w), 631 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 503 (M^+,[^{81}Br, ^{81}Br], 11), 502 (100), 501 (M^+,[^{81}Br, ^{79}Br], 21), 500 (100), 499 (M^+,[^{79}Br, ^{79}Br], 17); HR-MS (EI, 70 eV): calcd. for $C_{18}H_{14}Br_2O_2Se$ (M^+,[^{81}Br, ^{81}Br]): 503.84794; found: 503.84884, (M^+,[^{81}Br, ^{79}Br]): 501.84998, found: 501.84986, (M^+,[^{79}Br, ^{79}Br]): 499.85203, found: 499.85235.

Synthesis of 2,5-Bis(*o*-methoxyphenyl)-3,4-dibromoselenophene (4e)

General procedure A (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *o*-methoxyphenylboronic acid (2.2 equiv., 0.66 mmol, 0.09 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **4e** was isolated as a yellow solid; yield: 0.063 g (42%).

General procedure B (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *o*-methoxyphenylboronic acid (2.2 equiv., 0.66 mmol, 0.09 g), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%) and powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), **4e** was isolated as a yellow solid; yield: 0.102 g (68%); mp 85–87 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.76$ (s, 6H, $2OCH_3$), 6.89, 6.98 (t, $^3J = 8.2$ Hz, 2H, 2 CH, Ar), 7.29, 7.35 (d, $^3J = 8.2$ Hz, 2H, 2 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.6$ (OCH_3), 111.2, 120.3, 130.3, 131.8 (CH, Ar), 123.8, 139.2, 156.5 (C, Ar), 113.6 (CBr, Ar); IR (KBr): $\tilde{\nu} = 3011$ (w), 2936 (w), 2833 (w), 1472 (m), 1428 (m), 1256 (m), 1237 (m), 1113 (m), 1017 (m), 805 (w), 747 (w), 681 (w), 565 (w), 537 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 503 (M^+,[^{81}Br, ^{81}Br], 14), 502 (100), 501 (M^+,[^{81}Br, ^{79}Br], 23), 500 (100), 499 (M^+,[^{79}Br, ^{79}Br], 19); HR-MS (EI, 70 eV): calcd. for $C_{18}H_{14}Br_2O_2Se$ (M^+,[^{81}Br, ^{81}Br]): 503.84794; found: 503.84889, (M^+,[^{81}Br, ^{79}Br]): 501.84998, found: 501.84990, (M^+,[^{79}Br, ^{79}Br]): 499.85203, found: 499.85213.

Synthesis of 2,5-Bis(*m*-chlorophenyl)-3,4-dibromoselenophene (4f)

General procedure A (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *m*-chlorophenylboronic acid (2.2 equiv., 0.66 mmol, 0.103 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water

(1 mL), **4f** was isolated as a white solid; yield: 0.069 g (45%).

General procedure B (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *m*-chlorophenylboronic acid (2.2 equiv., 0.66 mmol, 0.103 g), $Pd(OAc)_2$ (3.4 mg, 5 mol%), **L** (12,3 mg, 10 mol%) and powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), **4f** was isolated as a white solid; yield: 0.023 g (15%); mp 170–171 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.37$, 7.39 (d, $^3J = 8.2$ Hz, 4 H, 4 CH, Ar), 7.46 (t, $^3J = 8.2$ Hz, 2 H, 2 CH, Ar), 7.58 (s, 2 H, 2CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 127.4$, 129.0, 129.2, 129.9 (CH, Ar), 134.6, 136.3, 141.8 (C, Ar), 113.4 (CBr, Ar); IR (KBr): $\tilde{\nu} = 3154$ (w), 3097 (w), 3045 (w), 1942 (w), 1874 (w), 1802 (w), 1757 (w), 1693 (w), 1590 (m), 1557 (m), 1545 (m), 878 (m), 767 (m), 688 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 515 (M^+,[^{81}Br, ^{81}Br, ^{37}Cl, ^{37}Cl], 6), 513 (M^+,[^{81}Br, ^{79}Br, ^{37}Cl, ^{37}Cl], 32), 511 (M^+,[^{79}Br, ^{79}Br, ^{37}Cl, ^{37}Cl], 77), 509 (M^+,[^{79}Br, ^{79}Br, ^{35}Cl, ^{37}Cl], 100), 507 (M^+,[^{79}Br, ^{79}Br, ^{35}Cl, ^{35}Cl], 65); HR-MS (EI, 70 eV): calcd. for $C_{16}H_8Br_2Cl_2Se$ (M^+,[^{81}Br, ^{81}Br, ^{35}Cl, ^{35}Cl]): 511.74886; found: 511.74944, (M^+,[^{81}Br, ^{79}Br, ^{37}Cl, ^{37}Cl]): 509.75091, found: 509.75133, (M^+,[^{79}Br, ^{79}Br, ^{35}Cl, ^{35}Cl]): 507.75295, found: 507.75284.

Synthesis of 2,5-Bis(*p*-bromophenyl)-3,4-dibromoselenophene (4g)

General procedure A (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *p*-bromophenylboronic acid (2.2 equiv., 0.66 mmol, 0.185 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **4g** was isolated as a white solid; yield: 0.099 g (55%); mp 207–209 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 7.47, 7.56 (d, $^3J = 8.2$ Hz, 4 H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 130.71$, 131.89, (CH, Ar), 123.2, 133.6, 142.0 (C, Ar), 113.2 (CBr, Ar); IR (KBr): $\tilde{\nu} = 3083$ (w), 3044 (w), 3017 (w), 2923 (w), 2295 (w), 1895 (w), 1584 (w), 1472 (m), 1391 (m), 1071 (m), 1008 (m), 820 (m), 733 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 603 (M^+,[^{81}Br, ^{81}Br, ^{81}Br, ^{81}Br], 10), 601 (M^+,[^{79}Br, ^{81}Br, ^{81}Br, ^{81}Br], 17), 599 (M^+,[^{79}Br, ^{79}Br, ^{81}Br, ^{81}Br], 19), 597 (M^+,[^{79}Br, ^{79}Br, ^{79}Br, ^{81}Br], 16), 595 (M^+,[^{79}Br, ^{79}Br, ^{79}Br, ^{79}Br], 9); HR-MS (EI, 70 eV): calcd. for $C_{16}H_8Br_4Se$ (M^+,[^{79}Br, ^{81}Br, ^{81}Br, ^{81}Br]): 601.64578; found: 601.64663, (M^+,[^{79}Br, ^{79}Br, ^{81}Br, ^{81}Br]): 599.64783, found: 599.64887, (M^+,[^{79}Br, ^{79}Br, ^{79}Br, ^{79}Br]): 595.65192, found: 595.65151.

Synthesis of 2,5-Bis(3-biphenyl)-3,4-dibromoselenophene (4h)

General procedure A (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), 3-biphenylboronic acid (2.2 equiv., 0.66 mmol, 0.131 g), $Pd(PPh_3)_4$ (5 mol%, 17 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv, 0.254 g), and water (1 mL), **4h** was isolated as a yellow solid; yield: 0.085 g (48%); mp 90–93 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.35$–7.87 (m, 18 H, 18 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 125.2$, 125.5, 125.7, 125.0, 126.9, 127.1 (CH, Ar), 133.3, 138.4, 139.7, 141.1 (C, Ar), 110.7 (CBr, Ar); IR (KBr): $\tilde{\nu} = 3054$ (w), 3027 (w), 2961 (w), 1945 (w), 1878 (w), 1799 (w), 1594 (m), 1467 (m), 1261 (m), 1238 (m), 904 (m), 749 (m), 692 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 595 (M^+,[^{81}Br, ^{81}Br], 24), 593 (M^+,[^{81}Br, ^{79}Br], 24), 591 (M^+,[^{79}Br, ^{79}Br], 19); HR-MS (EI, 70 eV): calcd. for $C_{28}H_{18}Br_2Se$ (M^+,[^{81}Br, ^{81}Br]): 595.88941; found: 595.89002, (M^+,[^{81}Br, ^{79}Br]): 593.8914, found: 593.89108, (M^+,[^{79}Br, ^{79}Br]): 591.89350, found : 591.89212.

General Procedure C for the Synthesis of Tetraarylselenophenes 5a–e

An oven-dried Schenk flask was charged with $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%), **1** (0.3 mmol), the boronic acid (5 equiv., 1. 5 mmol) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g). The Schlenk flask was evacuated and subsequently flushed with argon. A 1:1-mixture (4 mL) of toluene and dioxane was added by syringe. The reaction mixture was heated under reflux for 8 h. The mixture was allowed to cool to ambient temperature and water (5 mL) was added. The aqueous and the organic layer were separated. The latter was dried (Na_2SO_4), filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash column chromatography (fine silica gel, heptanes).

Synthesis of Tetraphenylselenophene (5a)

General procedure A (reflux, 14 h): Starting with **1** (0.134 g, 0.3 mmol), phenylboronic acid (5.0 equiv., 1.5 mmol, 0.183 g), $Pd(PPh_3)_4$ (10 mol%, 34 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **5a** was isolated as a yellow solid; yield: 0.072 g (55%).

General procedure C (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), phenylboronic acid (5.0 equiv, 1.5 mmol, 0.183 g), $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g), **5a** was isolated as a yellow solid; yield: 0.103 g (79%); mp 158–162 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.94$–7.21 (m, 20 H, 12 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 124.4$, 125.0, 125.7, 126.2, 127.4, 128.9 (CH, Ar), 124.2, 135.9, 139.7, 142.6 (C, Ar); IR (KBr): $\tilde{\nu} = 3056$ (w), 3020 (w), 2962 (w), 1948 (w), 1876 (w), 1806 (w), 1596 (m), 1440 (m), 1068 (m), 1025 (m), 789 (m), 758 (m), 690 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 435 (M^+, 11), 434 (52), 434 (19), 433 (15), 150 (12); HR-MS (EI, 70 eV): calcd. for $C_{28}H_{20}Se$ (M^+): 436.07302; found: 436.07311.

Synthesis of Tetra(*p*-tolyl)selenophene (5b)

General procedure C (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol) and tolylboronic acid (5.0 equiv., 1.5 mmol, 0.205 g), $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g), **5b** was isolated as a yellow solid; yield: 0.131 g (89%); mp 240–244 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.26$, 2.31 (s, 6 H, 2CH_3), 6.86, 6.90, 7.03, 7.10 (d, $^3J =$ 8.2 Hz, 4 H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 21.13, 21.22 (CH_3), 128.4, 128.9, 129.3, 130.7 (CH, Ar), 133.6, 135.2, 135.7, 136.6, 141.4, 144.0 (C, Ar); IR (KBr): $\tilde{\nu} =$ 3021 (w), 2917 (w), 2860 (w), 1907 (w), 1738 (w), 1511 (m), 1495 (m), 1181 (m), 1110 (m), 857 (m), 831 (m), 813 (m), 731 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 491 (M^+, 15), 490 (47), 489 (17), 488 (15), 206 (9); HR-MS (EI, 70 eV): calcd. for $C_{32}H_{28}Se$ (M^+): 492.13507; found: 492.13510.

Synthesis of Tetra(*p*-ethylphenyl)selenophene (5c)

General procedure C (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *p*-ethylphenylboronic acid (5.0 equiv., 1.5 mmol, 0.225 g), $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g), **5c** was isolated as a yellow solid; yield: 0.161 g (0.98%); mp 101–103 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.20$, 1.25 (t, 6H, $2CH_3$), 2.57, 2.64 (q, 4H, $2CH_2$), 6.90, 6.93, 7.06, 7.14 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 15.16$, 15.27 (CH_3), 28.43 (overlap of two carbons) (CH_2), 127.0, 127.6, 129.3, 130.8 (CH, Ar), 133.9, 135.5, 141.6, 142.0, 142.8, 144.0 (C, Ar); IR (KBr): $\tilde{\nu} = 2961$ (m), 2930 (w), 2871 (w), 1903 (w), 1789 (w), 1510 (m), 1494 (m), 1453 (m), 1019 (m), 830 (m), 800 (m), 680 (m), 546 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 547 (M^+, 13), 546 (50), 547 (14), 546 (19), 262 (13); HR-MS (EI, 70 eV): calcd. for $C_{36}H_{36}Se$ (M^+): 548.49767; found: 548.19767.

Synthesis of Tetra(3,5-dimethylphenyl)selenophene (5d)

General procedure A (reflux, 14 h): Starting with **1** (0.134 g, 0.3 mmol), 3,5-dimethylphenylboronic acid (5.0 equiv, 1.5 mmol, 0.225 g), $Pd(PPh_3)_4$ (10 mol%, 34 mg), powdered, anhydrous K_3PO_4 (1.2 mmol, 4.0 equiv., 0.254 g), and water (1 mL), **5d** was isolated as a yellow solid; yield: 0.122 g (74%); mp 158–160 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 2.11, 2.19 (s, 12H, $4CH_3$), 6.72, 6.81 (s, 2H, 2 CH, Ar), 6.61, 6.86 (s, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 21.1, 21.2 (CH_3), 127.2, 128.7, 136.6, 137.3 (CH, Ar), 127.7 (overlap of two quaternary carbons), 128.5, 138.1, 142.1, 143.7 (C, Ar); IR (KBr): $\tilde{\nu} = 2997$ (w), 2947 (w), 2915 (w), 2858 (w), 1593 (m), 1463 (m), 1375 (m), 847 (m), 810 (m), 693 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 547 (M^+, 13), 546 (51), 547 (13), 546 (20), 262 (12); HR-MS (EI, 70 eV): calcd. for $C_{36}H_{36}Se$ (M^+): 548.49767; found: 548.19747.

Synthesis of Tetra(*p*-methoxyphenyl)selenophene (5e)

General procedure C (reflux, 8 h): Starting with **1** (0.134 g, 0.3 mmol), *p*-ethylphenylboronic acid (5.0 equiv., 1.5 mmol, 0.228 g), $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%), and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g), **5e** was isolated as a yellow solid; yield: 0.148 g (89%); mp 188–193 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.72$, 3.76 (s, 6H, OCH_3), 6.66, 6.75, 6.83, 7.10 (d, $^3J =$ 8.2 Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 54.9, 55.1 (CH_3), 113.1, 113.6, 130.5, 132.0 (CH, Ar), 129.0, 130.6, 140.7, 143.1, 157.9, 158.4 (C, Ar); IR (KBr): $\tilde{\nu} = 3002$ (w), 2955 (w), 2838 (w), 1891 (w), 1601 (m), 1494 (m), 1281 (m), 1236 (m), 1110 (m), 1027 (m), 830 (m), 779 (m), 547 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 555 (M^+, 18), 554 (51), 553 (21), 542 (16), 539 (10), 223 (15), 195 (15), 152 (11), 44 (20); HR-MS (EI, 70 eV): calcd. for $C_{32}H_{28}O_4Se$ (M^+): 556.11339; found: 556.11393.

General Procedure D for the Synthesis of Tetraarylselenophenes (6a, b)

An oven-dried Schlenk flask was charged with $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%), **4b**, **c** (0.3 mmol), the boronic acid (3 equiv., 0.9 mmol) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g). The Schlenk flask was evacuated and subsequently flushed with argon. A mixture (1:1, 4 mL) of toluene and dioxane was added by syringe. The reaction mixture was heated under reflux for 8 h. The mixture was allowed to cool to ambient temperature and water (5 mL) was added. The aqueous and the organic layers were separated. The latter was dried (Na_2SO_4), filtered, and the filtrate was concentrated under vacuum. The residue was purified by flash column chromatography (fine silica gel, heptanes).

Synthesis of 2,5-Bis(*p*-ethylphenyl-3,4-bis(*p*-methoxyphenyl)selenophene (6a)

General procedure D (reflux, 8 h): Starting with **4b** (0.149 g, 0.3 mmol), *p*-methoxyboronic acid (3 equiv., 0.9 mmol, 0.137 g), $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g), **6a** was isolated as a yellow solid; yield: 0.13 g (79%); mp 182–185 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.22$ (t, 6H, $2CH_3$), 2.60 (q, 4H, $2CH_2$), 3.73 (s, 6H, OCH_3), 6.66, 6.84, 7.04, 7.10 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$), $\delta = 15.2$, 55.0 (CH_3), 28.4 (CH_2), 113.1, 127.7, 129.3, 132.0 (CH, Ar), 130.7, 133.9, 141.1, 142.7, 143.9, 157.9 (C, Ar); IR (KBr): $\tilde{\nu} = 2962$ (w), 2930 (w), 2834 (w), 2058 (w), 1894 (w), 1604 (m), 1506 (m), 1493 (m), 1241 (m), 1029 (m), 807 (m), 779 (m), 554 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 551 (M^+, 16), 550 (47), 549 (11), 549 (16), 266 (17); HR-MS (EI, 70 eV): calcd. for $C_{34}H_{32}O_2Se$ (M^+): 552.15620; found: 552.15502.

Synthesis of 2,5-Bis(3,5-dimethylphenyl)-3,4-bis(*p*-methoxyphenyl)selenophene (6b)

General procedure D (reflux, 8 h): Starting with **4c** (0.149 g, 0.3 mmol), *p*-methoxyboronic acid (3.0 equiv., 0.9 mmol, 0.137 g), $Pd(OAc)_2$ (6.8 mg, 10 mol%), **L** (24.6 mg, 20 mol%) and powdered, anhydrous K_3PO_4 (2.4 mmol, 8.0 equiv., 0.508 g), **6b** was isolated as a yellow solid; yield: 0.135 g (82%); mp 238–240 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.19$ (s, 12H, 4 CH_3), 3.73 (s, 6H, 2 OCH_3), 6.66, 6.81 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar), 6.83 (s, 4H, 4 CH, Ar), 6.87 (s, 2H, 2 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.2$ (CH_3), 55.1(OCH_3), 130.1, 127.7, 128.7, 131.9 (CH, Ar), 130.8, 136.4, 141.2, 144.1, 157.8, 158.0 (C, Ar); IR (KBr): $\tilde{\nu} = 2959$ (w), 2913 (w), 2836 (w), 2532 (w), 1727 (w), 1599 (m), 1495 (m), 1462 (m), 1242 (m), 1105 (m), 1032 (m), 1011 (m), 800 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 551 (M^+, 15), 550 (49), 549 (10), 549 (18), 266 (12); HR-MS (EI, 70 eV): calcd. for $C_{34}H_{32}O_2Se$ (M^+): 552.15620; found: 552.15655.

Procedure for the Synthesis of Tetra(phenylethynyl)-selenophene (7)

An oven-dried Schenk flask was charged with $Pd(Ph_3)_4$ (35 mg, 10 mol%), **1** (0.3 mmol), phenyacetylene (5.0 equiv., 1.5 mmol, 153 mg) and CuI (1.2 mmol, 4.0 equiv., 229 mg). The Schlenk flask was evacuated and subsequently flushed with argon. To the mixture was added *i*-Pr_2NH (12 mL) by syringe. After stirring of the solution at 0 °C for 4 h, the reaction mixture was heated under reflux for 8 h. The mixture was allowed to cool to ambient temperature and the solvent

was removed under vacuum. The residue was purified by flash column chromatography (fine silica gel, heptanes). Product **7** was isolated as a yellow solid; yield: 0.123 g (77%); mp 80–81 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.33$, 7.36 (t, $^3J = 8.2$ Hz, 4H, 4 CH, Ar), 7.38, 7.39 (t, $^3J = 8.2$ Hz, 2H, 2 CH, Ar), 7.52, 7.55 (d, $^3J = 8.2$ Hz, 4H, 4 CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 128.4$, 128.5, 129.2, 1231.6, 132.5 (overlap of two CH) (CH, Ar), 73.9, 81.6, 83.3, 100.8 (C, acetylene), 119.6, 122.1, 132.9 (C, Ar); IR (KBr): $\tilde{\nu} =$ 2959 (w), 2913 (w), 2836 (w), 2532 (w), 1727 (w), 1599 (m), 1495 (m), 1462 (m), 1242 (m), 1105 (m), 1032 (m), 1011 (m), 800 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%) = 531 (M^+, 15), 530 (100), 529 (37), 528 (22), 452 (17), 389 (15); HR-MS (EI, 70 eV): calcd. for $C_{36}H_{20}Se$ (M^+): 532.07302; found: 532.070312.

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