Supporting Information for

Synthesis of Phenanthroselenophenes via Pd-Catalyzed Successive C–H Bond Arylation and Annulation

Xinzhe Shi, Shuxin Mao, Thierry Roisnel, Henri Doucet* and Jean-François Soulé,*

Univ Rennes, CNRS UMR6226, F-3500 Rennes, France.

Corresponding Author :

*E-mail for H.D.: henri.doucet@univ-rennes1.fr

*E-mail for J.-F.S.: jean-francois.soule@univ-rennes1.fr,

Table of contents:

1. GENERAL INFORMATION 2
2. PREPARATION OF STARTING MATERIALS 2-ARYL SELENOPHENES 2
3. GENERAL PROCEDURES 4
4. OPTIMIZATION OF THE REACTIONS 5
5. PRODUCT CHARACTERIZATIONS 7
6. NMR CHARTS 32
7. REFERENCES 102
1. General information

All reactions were carried out under argon atmosphere with standard Schlenk techniques. 1,4-Dioxane and DMA were purchased from Acros Organics and were not purified before use. \( ^1 \text{H} \) and \( ^{13} \text{C} \) NMR spectra were recorded on Bruker AV III 400 MHz or 500 NMR spectrometer equipped with BBFO probehead. Chemical shifts (\( \delta \)) were reported in parts per million relatives to residual chloroform (7.26 ppm for \( ^1 \text{H} \); 77.16 ppm for \( ^{13} \text{C} \)), constants were reported in Hertz. \( ^1 \text{H} \) NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All reagents were weighed and handled in air. IR spectra were recorded on a Perkin-Elmer Spectrum BX instrument with an FT-IR system. HRMS were recorded on a Bruker Maxis 4G (ESI/APCI Q-TOF) mass spectrometer at the corresponding facilities of the CRMPO, Centre Régional de Mesures Physiques de l’Ouest, Université de Rennes 1.

Preparation of the \( \text{PdCl(dppb)(C_3H_5)} \) catalyst: An oven-dried 40-mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with \([\text{Pd(C}_3\text{H}_5\text{Cl}]}_2\) (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. \( ^{31} \text{P} \) NMR (81 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 19.3 (s).

2. Preparation of starting materials 2-aryl selenophenes

\[
\text{Se} \quad + \quad \text{Br} - \text{Ar} \xrightarrow{\text{PdCl(C}_3\text{H}_5\text{)}(\text{dppb}) \ (2 \text{ mol\%}) \quad \text{KOAc (2 equiv.)} \quad \text{DMA, 130 °C, 16 h}} \quad \text{Se} \quad \text{Ar} \\
\text{(2 equiv.)} \quad \text{KOAc (2 equiv.)} \quad \text{DMA, 130 °C, 16 h} \quad \text{Ar} = 4\text{-ClPh} \quad \text{S1} \quad 45\% \\
\text{4-Me} \quad \text{S2} \quad 42\% \\
\text{1-Napht} \quad \text{S3} \quad 48\% \\
\text{4-Py}^{[a]} \quad \text{S4} \quad 41\% \\
\]

[a] Reaction performed from 4-bromopyridine hydrochloride using 3 equivalents of KOAc.

Scheme 5.1. Pd-catalyzed C–H bond arylation of selenophene with aryl bromides

To a 15 mL oven dried Schlenk tube, selenophene (1310 mg, 10 mmol, 2 equiv.), aryl bromide (5 mmol, 1 equiv.), KOAc (980 mg, 10 mmol, 2 equiv.), DMA (20 mL) and PdCl(C\(_3\)H\(_5\))(dppb) (60 mg, 0.1 mmol, 2 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 130 °C for 16 h. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired arylated products.
2-(4-Chlorophenyl)selenophene (S1): Following the above procedure using selenophene (1310 mg, 10 mmol) and 1-bromo-4-chlorobenzene (957 mg, 5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound S1 (543 mg, 45%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.93 (d, $J = 5.6$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 3.6$ Hz, 1H), 7.30 (m, 3H).

The compound is known and the NMR data are identical to those reported in the literature.$^2$

2-(p-Tolyl)selenophene (S2): Following the procedure E using selenophene (1310 mg, 10 mmol) and 4-bromotoluene (855 mg, 5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound S2 (464 mg, 42%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): 7.87 (d, $J = 5.6$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 3.7$ Hz, 1H), 7.28 (m, 1H), 7.15 (d, $J = 7.9$ Hz, 2H), 2.33 (s, 3H).

The compound is known and the NMR data are identical to those reported in the literature.$^2$

2-(Naphthalen-1-yl)selenophene (S3): Following the procedure E using selenophene (1310 mg, 10 mmol) and 1-bromonaphthalene (1035 mg, 5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound S3 (617 mg, 48%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 – 8.32 (m, 1H), 8.16 (dd, $J = 5.5$, 1.3 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.64 (dd, $J = 7.1$, 1.2 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.49 – 7.45 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.1, 134.6, 134.0, 131.7, 131.5, 129.9, 129.7, 128.4 (2), 128.22, 126.5, 126.1, 126.0, 125.3.

Elemental analysis: calcd (%) for C$_{14}$H$_{10}$Se (257.19): C 65.38, H 3.92; found: C 65.61, H 4.08.
4-(Selenophen-2-yl)pyridine (S4): Following the procedure E using selenophene (1310 mg, 10 mmol) and 4-bromopyridine hydrochloride (972 mg, 5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound S4 (427 mg, 41%) as a white solid (mp = 77-79 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.58 (d, $J = 6.0$ Hz, 2H), 8.10 (dd, $J = 5.6$, 1.0 Hz, 1H), 7.69 (dd, $J = 3.9$, 1.0 Hz, 1H), 7.43 (dd, $J = 6.0$, 1.6 Hz, 2H), 7.38 (dd, $J = 5.6$, 3.9 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 147.4, 143.4, 132.7, 131.0, 127.7, 120.4.

Elemental analysis: calcd (%) for C$_9$H$_7$NSe (208.12): C 51.94, H 3.39; found: C 60.19, H 3.57.

3. General procedures

Procedure A (desulfitative arylation): To a 15 mL oven dried Schlenk tube, 2-bromobenzenesulfonyl chloride (1.5 mmol), 2-aryl(selenophene (1 mmol), Li$_2$CO$_3$ (440 mg, 6 mmol), 1,4-dioxane (5 mL) and Pd(OAc)$_2$ (2.2 mg, 0.1 mmol) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 140 °C (oil bath temperature) for 4 hours (see tables and schemes). After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired arylated products.

Procedure B (direct arylation annulation with aryl bromides): To a 15 mL oven dried Schlenk tube, 2-arylated 4-(2-bromoaryl)selenophene derivative (0.5 mmol), aryl bromide (1 mmol, 2 equiv.), KO$^+$Piv (210 mg, 1.5 mmol, 3 equiv.), DMA (2 mL) and PdCl(C$_3$H$_5$)(dppb) (6 mg, 0.01 mmol, 2 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 150 °C (oil bath temperature) for 16 hours (see tables and schemes). The solution was cool-down and concentrated until formation of a precipitate. Then, the solution was kept at room temperature over 1 h and the precipitate was collected by filtration, washed with methanol and dried under vacuo to afford the desired products. If no precipitate was formed, the crude mixture was purified by silica column chromatography to afford the desired arylated products.

Procedure C (annulation reaction): To a 15 mL oven dried Schlenk tube, 2,5-diaryled 4-(2-bromoaryl)selenophene derivative (0.25 mmol), KO$^+$Piv (80 mg, 0.5 mmol, 2 equiv.), DMA (1 mL) and PdCl(C$_3$H$_5$)(dppb) (3 mg, 0.005 mmol, 2 mol%) were successively added. The
reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 150 °C (oil bath temperature) for 16 hours (see tables and schemes). The solution was cool-down and concentrated until formation of a precipitate. Then, the solution was kept at room temperature over 1 h and the precipitate was collected by filtration, washed with methanol and dried under vacuo to afford the desired products.

**Procedure D (Double direct arylation and annulation with aryl bromides):** To a 15 mL oven dried Schlenk tube, 2-arylated 4-(2-bromoaryl)selenophene derivative (0.5 mmol), aryl bromide (1.5 mmol, 3 equiv.), KOPiv (210 mg, 2 mmol, 4 equiv.), DMA (2 mL) and PdCl(C₃H₅)(dpbb) (9 mg, 0.015 mmol, 3 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 150 °C (oil bath temperature) for 16 hours (see tables and schemes). The solution was cool-down and concentrated until formation of a precipitate. Then, the solution was kept at room temperature over 1 h and the precipitate was collected by filtration, washed with methanol and dried under vacuo to afford the desired products. If no precipitate was formed, the crude mixture was purified by silica column chromatography to afford the desired arylated products.

### 4. Optimization of the reactions

**Table S1.** Optimization of Pd-Catalyzed Tandem C5-Arylation – Annulation of 4-(2-Bromophenyl)-2-(4-chlorophenyl)selenophene (1) with 4-bromobenzonitrile for the Synthesis of 10.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Base</th>
<th>Solvent, T (°C)</th>
<th>Conversion of 1 (%)</th>
<th>Isolated yield in 10 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td>DBU</td>
<td>DMA, 150 °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)₂</td>
<td>KOAc</td>
<td>DMA, 150 °C</td>
<td>100</td>
<td>43%[a],[b]</td>
</tr>
<tr>
<td>3</td>
<td>PdCl(C₃H₅)(dpbb)</td>
<td>KOAc</td>
<td>DMA, 150 °C</td>
<td>100</td>
<td>54%[a]</td>
</tr>
<tr>
<td>4</td>
<td>PdCl(C₃H₅)(dpbb)</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>100</td>
<td>57%[a]</td>
</tr>
<tr>
<td>5</td>
<td>PdCl(C₃H₅)(dpbb)</td>
<td>KOPiv</td>
<td>DMF, 130 °C</td>
<td>25</td>
<td>traces[a],[b]</td>
</tr>
<tr>
<td>6</td>
<td>PdCl(C₃H₅)(dpbb)</td>
<td>KOPiv</td>
<td>NMP, 140 °C</td>
<td>45</td>
<td>25%[a],[b]</td>
</tr>
</tbody>
</table>

[a] formation of [1,1'-biphenyl]-4,4'-dicarbonitrile, [b] formation of debrominated selenophene 45 and other unidentified products
**Table S2.** Optimization of Pd-Catalyzed One-Pot Three-Fold Direct Arylations of 3-(2-Bromophenyl)selenophene (8) with 1-Bromo-4-chlorobenzene for the Synthesis of 23i.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Base</th>
<th>Solvent, T (°C)</th>
<th>Conversion of 36 (%)</th>
<th>Isolated yield in 42 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td>DBU</td>
<td>DMF, 140 °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)₂</td>
<td>K₂CO₃</td>
<td>DMA, 150 °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>PdCl(C₃H₅)(dppb)</td>
<td>KOAc</td>
<td>DMA, 150 °C</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>PdCl(C₃H₅)(dppb)</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>PdCl(C₃H₅)(dppb)[a]</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>PdCl(C₃H₅)(dppb)[b]</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>49</td>
<td>42</td>
</tr>
</tbody>
</table>

[a] using 10 mol% of Pd catalyst loading, [b] using 20 mol% of Pd catalyst loading,

**Table S2.** Optimization of Pd-Catalyzed One-Pot Four-Fold Direct Arylations of 3,4-bis(4-(trifluoromethyl)phenyl)selenophene (36) with 1,2-Dibromobenzene for the Synthesis 42.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Base</th>
<th>Solvent, T (°C)</th>
<th>Conversion of 36 (%)</th>
<th>Isolated yield in 42 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td>DBU</td>
<td>DMA, 150 °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)₂</td>
<td>K₂CO₃</td>
<td>DMA, 150 °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Pd(C₃H₅)(dppb)</td>
<td>KOAc</td>
<td>DMA, 150 °C</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>Pd(C₃H₅)(dppb)</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Pd(C₃H₅)(dppb)[a]</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>Pd(C₃H₅)(dppb)[b]</td>
<td>KOPiv</td>
<td>DMA, 150 °C</td>
<td>49</td>
<td>42</td>
</tr>
</tbody>
</table>

[a] using 10 mol% of Pd catalyst loading, [b] using 20 mol% of Pd catalyst loading,
5. Product characterizations

4-(2-Bromophenyl)-2-(4-chlorophenyl)selenophene (1): Following the procedure A using 2-(4-chlorophenyl)selenophene S1 (241 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (383 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 1 (280 mg, 76%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 1.3$ Hz, 1H), 7.73 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.70 (d, $J = 1.3$ Hz, 1H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.46 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.24 (td, $J = 7.7$, 1.7 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.0, 144.2, 138.6, 134.7, 133.4, 133.3, 131.1, 129.0, 128.9, 128.8, 127.7, 127.4, 127.3, 122.4.

IR (neat): $\nu = 3053$, 1496, 1473, 1421, 1263, 1093, 825, 750 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{16}$H$_{10}$BrClSe (396.57): C 48.46, H 2.54; found: C 48.57, H 2.39.

4-(4-(2-Bromophenyl)selenophen-2-yl)pyridine (2): Following the procedure A using 4-(selenophen-2-y1)pyridine S4 (208 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (383 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 1:1) to afford the desired compound 2 (210 mg, 58%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.60 (d, $J = 5.7$ Hz, 2H), 8.06 (d, $J = 1.3$ Hz, 1H), 7.86 (d, $J = 1.3$ Hz, 1H), 7.67 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.40 (d, $J = 1.8$ Hz, 1H), 7.35 (td, $J = 7.5$, 1.2 Hz, 1H), 7.22 (ddd, $J = 8.0$, 7.2, 1.9 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.6, 146.2, 144.8, 143.3, 138.5, 133.5, 131.2, 130.9, 129.9, 129.3, 127.6, 122.5, 120.4.

IR (neat): $\nu = 3049$, 1490, 1474, 1421, 1223, 1083, 845 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{15}$H$_{10}$BrNSe (363.12): C 49.62, H 2.78; found: C 49.85, H 2.88.
4-(2-Bromophenyl)-2-(p-tolyl)selenophene (3): Following the procedure A using 2-(4-methylphenyl)selenophene S2 (221 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (383 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 3 (297 mg, 79%) as a yellow oil.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{: } \delta &\text{ 7.89 (d, } J = 1.3 \text{ Hz, 1H), 7.66 (dd, } J = 8.0, 1.0 \text{ Hz, 1H), 7.61 (d, } J = 1.3 \text{ Hz, 1H), 7.49 (d, } J = 8.1 \text{ Hz, 2H), 7.43 (dd, } J = 7.7, 1.7 \text{ Hz, 1H), 7.34 (td, } J = 7.5, 1.1 \text{ Hz, 1H), 7.21–7.17 } (m, \text{ 3H), 2.37 (s, 3H).} \\
\text{C NMR (100 MHz, CDCl}_3\text{: 149.8, 144.4, 139.2, 137.8, 133.6, 133.4, 131.3, 129.7, 128.9, 127.8, 127.5, 127.0, 126.3, 122.6, 21.3.} \\
\text{IR (neat): } \nu = 3049, 2859, 1494, 1468, 1443, 1216, 1099, 832 \text{ cm}^{-1} \\
\text{Elemental analysis: calcd (\%) for C}_{17}\text{H}_{13}\text{BrSe (376.16): C 54.28, H 3.48; found: C 54.37, H 3.67.}
\end{align*}
\]

4-(2-Bromophenyl)-2-(naphthalen-1-yl)selenophene (4): Following the procedure A using 2-(naphthalen-1-yl)selenophene S3 (257 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (383 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 4 (210 mg, 51%) as yellow oil.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{: } \delta &\text{ 8.49 – 8.46 } (m, \text{ 1H), 8.13 (d, } J = 1.4 \text{ Hz, 1H), 7.96 – 7.90 } (m, \text{ 2H), 7.74–7.67 } (m, \text{ 3H), 7.58 – 7.52 } (m, \text{ 4H), 7.39 (td, } J = 7.5, 1.2 \text{ Hz, 1H), 7.23 (td, } J = 7.8, 1.7 \text{ Hz, 1H).} \\
\text{C NMR (100 MHz, CDCl}_3\text{: 146.8, 143.6, 139.1, 134.4, 134.0, 133.4, 131.8, 131.6, 131.4, 129.7, 128.9, 128.5, 128.4, 128.2, 127.5, 126.6, 126.2, 126.0, 125.3, 122.6.} \\
\text{IR (neat): } \nu = 3023, 1512, 1497, 1455, 1263, 1083, 752 \text{ cm}^{-1} \\
\text{Elemental analysis: calcd (\%) for C}_{20}\text{H}_{13}\text{BrSe (412.19): C 58.28, H 3.18; found: C 58.10, H 3.27.}
\end{align*}
\]
4-(2-Bromo-4-(trifluoromethyl)phenyl)-2-(4-chlorophenyl)selenophene (5): Following the procedure A using 2-(4-chlorophenyl)selenophene S1 (241 mg, 1 mmol) and 2-bromo-4-(trifluoromethyl)benzenesulfonyl chloride (485 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 5 (311 mg, 67%) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.00 (d, J = 1.2 \text{ Hz}, 1H), 7.96 (s, 1H), 7.62 – 7.60 (m, 2H), 7.53 – 7.49 (m, 3H), 7.36 (d, J = 8.5 \text{ Hz}, 2H)\).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 148.9, 143.1, 142.4, 134.6, 133.9, 131.4, 131.1 (q, J = 33.0 \text{ Hz}), 130.4 (q, J = 3.8 \text{ Hz}), 129.8, 129.3, 127.5, 127.2, 124.4 (q, J = 3.5 \text{ Hz}), 123.3 (q, J = 272.6 \text{ Hz}), 122.7\).

\(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -62.7\).

IR (neat): \(\nu = 3058, 1532, 1489, 1189, 1017, 945, 821, 769 \text{ cm}^{-1}\)

Elemental analysis: calcd (%) for C\(_{17}\)H\(_9\)BrClF\(_3\)Se (464.57): C 43.95, H 1.95; found: C 44.12, H 2.19.

4-(2-Bromo-4-fluorophenyl)-2-(4-chlorophenyl)selenophene (6): Following the procedure A using 2-(4-chlorophenyl)selenophene S1 (241 mg, 1 mmol) and 2-bromo-4-fluorobenzenesulfonyl chloride (410 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 6 (290 mg, 70%) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.89 (d, J = 1.3 \text{ Hz}, 1H), 7.59 (d, J = 1.4 \text{ Hz}, 1H), 7.50 (d, J = 8.6 \text{ Hz}, 2H), 7.42 (dd, J = 8.3, 2.6 \text{ Hz}, 1H), 7.38 (dd, J = 6.0, 2.6 \text{ Hz}, 1H), 7.35 (d, J = 8.5 \text{ Hz}, 2H), 7.07 (td, J = 8.3, 2.6 \text{ Hz}, 1H)\).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 161.6 (d, J = 251.3 \text{ Hz}), 148.3, 143.4, 135.0 (d, J = 3.6 \text{ Hz}), 134.7, 133.6, 131.9 (d, J = 8.3 \text{ Hz}), 129.2, 128.9, 127.7, 127.4, 122.6 (d, J = 9.5 \text{ Hz}), 120.5 (d, J = 24.4 \text{ Hz}), 114.6 (d, J = 20.9 \text{ Hz})\).

\(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -112.4\).

IR (neat): \(\nu = 3058, 1532, 1511, 1489, 1189, 1017, 945, 821, 769 \text{ cm}^{-1}\)
Elemental analysis: calcd (%) for C_{16}H_9BrClFSe (414.56): C 46.36, H 2.19; found: C 46.21, H 2.00.

4-(2-Bromo-5-(trifluoromethyl)phenyl)-2-(4-chlorophenyl)selenophene (7): Following the procedure A using 2-(4-chlorophenyl)selenophene S1 (241 mg, 1 mmol) and 2-bromo-5-(trifluoromethyl)benzenesulfonyl chloride (485 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 7 (255 mg, 55%) as a yellow oil.

^1H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 1.3 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.62 (d, J = 1.3 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.47 – 7.45 (m, 1H), 7.37 – 7.35 (m, 2H).

^13C NMR (100 MHz, CDCl₃): δ 149.0, 143.1, 139.7, 134.6, 134.0, 133.9, 130.1 (q, J = 32.9 Hz), 129.7, 129.3, 127.8 (q, J = 3.8 Hz), 127.6, 127.3, 125.5 (q, J = 3.6 Hz), 123.8 (q, J = 272.7 Hz).

^19F NMR (376 MHz, CDCl₃): δ -62.7.

IR (neat): ν = 3056, 1541, 1509, 1458, 1252, 1021, 890, 867 cm⁻¹

Elemental analysis: calcd (%) for C_{17}H_9BrClF₃Se (464.57): C 43.95, H 1.95; found: C 44.23, H 1.78.

3-(2-Bromophenyl)selenophene (8) Following the procedure A using selenophene (131 mg, 1 mmol) and 2-bromobenzenesulfonyl chloride (383 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 8 (223 mg, 78%) as yellow oil.

The NMR data are identical to those reported in the literature (A. Skhiri, R. B. Salem, J.-F. Soulé, H. Doucet, Chem. Eur. J. 2017, 23, 2788-2791)

3-(2-Bromo-4-(trifluoromethyl)phenyl)selenophene (9): Following the procedure A selenophene (131 mg, 1 mmol) and 2-bromo-4-(trifluoromethyl)benzenesulfonyl chloride (485 mg, 1.5 mmol), the residue
was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 9 (287 mg, 81%) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.13 (s, 1H), 8.10 (dd, $J = 5.4$, 2.5 Hz, 1H), 7.98 (s, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.57 (d, $J = 5.4$ Hz, 1H), 7.52 (d, $J = 8.1$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.6, 142.2, 131.6, 131.3, 130.9 (q, $J = 33.1$ Hz), 130.4 (q, $J = 3.8$ Hz), 130.3, 130.2, 124.3 (q, $J = 3.6$ Hz), 123.3 (q, $J = 272.6$ Hz), 122.8.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.5.

IR (neat): $\nu = 3053$, 1512, 1489, 1272, 1023, 808, 657 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{11}$H$_6$BrF$_3$Se (354.03): C 37.32, H 1.71; found: C 37.41, H 1.54.

2-(4-Chlorophenyl)phenanthro[9,10-b]selenophene-9-carbonitrile (10): Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 4-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 10 (119 mg, 57%) as a yellow solid (mp = 210-212 °C).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 9.40 (s, 1H), 9.00 – 8.95 (m, 2H), 8.70 (d, $J = 8.2$ Hz, 1H), 8.16 (d, $J = 8.3$ Hz, 1H), 7.99 (dd, $J = 8.3$, 1.3 Hz, 1H), 7.92 (d, $J = 8.5$ Hz, 2H), 7.82 – 7.75 (m, 2H), 7.58 (d, $J = 8.5$ Hz, 2H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 148.5, 140.5, 138.4, 134.0, 133.3, 131.7, 129.5 (2), 129.2, 128.5, 128.1, 128.0, 127.9, 127.2, 127.0, 125.2, 124.3, 124.0, 119.2, 109.0.

IR (neat): $\nu = 2922$, 2222, 1602, 1477, 1091, 1049, 1006, 817, 611 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{23}$H$_{12}$ClNSe (416.77): C 66.28, H 2.90; found: C 66.53, H 3.12.

ESI HRMS: [M+H] $^+$, m/z theoretical 417.98962, found 417.9898 (0 ppm).
2-(4-Chlorophenyl)-9-(trifluoromethyl)phenanthro[9,10-b]selenophene (11): Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 4-bromobenzotrifluoride (225 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 11 (140 mg, 61%) as a brown solid (mp = 214-216 °C).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.86 (s, 1H), 8.65 – 8.63 (m, 1H), 8.34 – 8.28 (m, 2H), 7.94 (d, J = 8.3 Hz, 1H), 7.75 (dd, J = 8.4, 1.7 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)): δ 148.1, 139.8, 139.7, 134.5 (2), 132.0, 130.1, 129.4, 129.1, 128.2 (q, J = 32.7 Hz), 128.1 (2), 127.9, 126.8 (2), 124.8, 124.6 (q, J = 272.1 Hz), 123.7, 123.5 (q, J = 3.2 Hz), 122.4, 121.2 (q, J = 4.2 Hz).

\(^19\)F NMR (471 MHz, CDCl\(_3\)): δ -61.8.

IR (neat): \(\nu = 2920, 1489, 1257, 1097, 1049, 1008, 808, 750 \text{ cm}^{-1}\)

Elemental analysis: calcd (%) for C\(_{23}\)H\(_{12}\)ClF\(_3\)Se (459.75): C 60.09, H 2.63; found: C 60.27, H 2.87.

ESI HRMS: [M+H]+, m/z theoretical 460.98176, found 460.9819 (0 ppm).

1-(2-(4-Chlorophenyl)phenanthro[9,10-b]selenophen-9-yl)propan-1-one (12): Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 4-bromopropiophenone (213 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 12 (143 mg, 64%) as a yellow solid (mp = 223-225 °C).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 9.26 (s, 1H), 8.75 – 8.73 (m, 1H), 8.33 – 8.29 (m, 2H), 8.11 (dd, J = 8.3, 1.6 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.19 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 200.4, 148.3, 140.0, 139.9, 134.6, 134.5 (2), 132.9, 130.0, 129.7, 129.4, 128.1, 127.9, 127.8, 126.7, 126.30, 126.27, 124.7, 124.3, 123.8, 122.5, 32.1, 8.6.

IR (neat): \(\nu = 2922, 1678, 1236, 1093, 1010, 821, 744, 715 \text{ cm}^{-1}\)
Elemental analysis: calcd (%) for C_{25}H_{17}ClOSe (447.82): C 67.05, H 3.83; found: C 67.19, H 3.49.

2-(4-Chlorophenyl)-10-(trifluoromethyl)phenanthro[9,10-b]selenophene (13): Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 3-bromobenzotrifluoride (225 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 13 (136 mg, 59%) as a white solid (mp =226-228 °C).

\[
\begin{align*}
\text{H NMR (400 MHz, CD}_{2}\text{Cl}_{2}) &: \delta 8.80 (d, J = 8.7 \text{ Hz}, 1H), 8.73 (dd, J = 7.9, 1.6 \text{ Hz}, 1H), 8.44 – 8.38 (m, 2H), 8.21 (s, 1H), 7.84 (dd, J = 8.6, 1.9 \text{ Hz}, 1H), 7.78 – 7.73 (m, 2H), 7.71 (d, J = 8.5 \text{ Hz}, 2H), 7.46 (d, J = 8.5 \text{ Hz}, 3H). \\
\text{C NMR (126 MHz, CD}_{2}\text{Cl}_{2}) &: 147.9, 140.6, 139.5, 134.9, 134.7, 131.2, 130.8, 130.0, 129.7, 129.3 (q, J = 32.5 \text{ Hz}), 129.0, 128.9, 128.3, 127.1, 125.1, 125.0, 124.7 (q, J = 272.1 \text{ Hz}), 124.5, 123.6 (q, J = 4.1 \text{ Hz}), 122.9, 122.7 (q, J = 3.3 \text{ Hz}). \\
\text{F NMR (376 MHz, CD}_{2}\text{Cl}_{2}) &: -62.1.
\end{align*}
\]

IR (neat): \( \nu = 2918, 2848, 1477, 1278, 1157, 808, 692 \text{ cm}^{-1} \)

Elemental analysis: calcd (%) for C_{23}H_{12}ClF_{3}Se (459.75): C 60.09, H 2.63; found: C 60.27, H 2.51.

2-(3-(2-Bromophenyl)-5-(4-chlorophenyl)selenophen-2-yl)benzonitrile (14i): Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 2-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 14i (159 mg, 64%) as a yellow oil.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_{3}) &: \delta 7.63 – 7.61 (m, 1H), 7.57 – 7.51 (m, 4H), 7.45 – 7.41 (m, 1H), 7.37 – 7.33 (m, 4H), 7.24 – 7.18 (m, 2H), 7.14 – 7.11 (m, 1H). \\
\text{C NMR (100 MHz, CDCl}_{3}) &: \delta 149.3, 143.4, 140.4, 139.5, 137.7, 134.3, 134.1, 133.5, 133.1, 132.4, 132.2, 131.7, 129.4, 129.3, 129.0, 128.3, 127.6, 127.3, 123.7, 118.2, 113.1.
\end{align*}
\]
2-(4-Chlorophenyl)phenanthro[9,10-b]selenophene-11-carbonitrile (14): Following the procedure C using 2-(3-(2-bromophenyl)-5-(4-chlorophenyl)selenophen-2-yl)benzonitrile (14i) (124 mg, 0.25 mmol), the residue was purified by precipitation to afford the desired compound 14 (78 mg, 75%) as a yellow solid (mp = 260-262 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.96 (d, $J$ = 8.3 Hz, 1H), 8.66 (dd, $J$ = 7.5, 2.0 Hz, 1H), 8.43 – 8.41 (m, 2H), 8.02 (dd, $J$ = 7.3, 1.2 Hz, 1H), 7.75 – 7.64 (m, 5H), 7.43 (d, $J$ = 8.5 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.8, 141.5, 136.5, 135.0, 134.7, 134.3, 131.4, 130.1, 129.6, 129.5, 128.7 (2), 128.5, 128.1, 127.1, 125.3, 124.9, 123.7, 121.5, 120.9, 108.0.

IR (neat): $\nu$ = 2924, 2212, 1492, 1479, 1095, 817, 789 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{23}$H$_{12}$ClNSe (416.77): C 66.28, H 2.90; found: C 66.19, H 3.03.

2-(4-Chlorophenyl)-11-(trifluoromethyl)phenanthro[9,10-b]selenophene (15): Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 2-bromobenzotrifluoride (225 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 15 (120 mg, 52%) as a white solid (mp =148-150 °C).

$^1$H NMR (500 MHz, CDCl$_3$): δ 8.99 (d, $J$ = 8.3 Hz, 1H), 8.68 – 8.66 (m, 1H), 8.42 – 8.40 (m, 2H), 8.09 (d, $J$ = 7.5 Hz, 1H), 7.71 – 7.64 (m, 5H), 7.41 (d, $J$ = 8.4 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.7 (q, $J$ = 4.7 Hz), 141.2, 134.9, 134.8, 134.5, 134.3, 131.0, 129.8, 129.4, 128.9, 128.6, 128.2, 128.0, 127.0 (q, $J$ = 7.9 Hz), 126.9, 125.2 (q, $J$ = 273.2 Hz), 124.7, 124.6, 124.2 (q, $J$ = 29.9 Hz), 124.0, 121.4.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -56.4.

IR (neat): $\nu$ = 2920, 2850, 1477, 1303, 1091, 780, 719 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{23}$H$_{12}$ClF$_3$Se (459.75): C 60.09, H 2.63; found: C 60.11, H 2.68.
2-(p-Tolyl)phenanthro[9,10-b]selenophene-9-carbonitrile (16): Following the procedure B using 4-(bromophenyl)-2-(p-tolyl)selenophene (3) (188 mg, 0.5 mmol) and 4-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 16 (129 mg, 65%) as a pale yellow solid (mp = 252-254 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.89 (s, 1H), 8.59 – 8.56 (m, 1H), 8.35 – 8.33 (m, 1H), 8.29 (s, 1H), 7.92 (d, $J$ = 8.2 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.62 (d, $J$ = 8.2 Hz, 2H), 7.27 (d, $J$ = 8.2 Hz, 2H), 2.43 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 151.1, 140.7, 139.1, 138.7, 133.1, 132.6, 130.2, 130.0, 129.3, 128.9, 128.42, 128.36, 128.2, 127.0, 126.9, 126.8, 124.9, 123.6, 121.4, 119.7, 109.3, 21.5.

IR (neat): $\nu$ = 2070, 2922, 2222, 1606, 1502, 1487, 1242, 800 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{24}$H$_{15}$NSe (396.35): C 72.73, H 3.81; found: C 72.54, H 3.90.

2-(Naphthalen-1-yl)phenanthro[9,10-b]selenophene-9-carbonitrile (17): Following the procedure B using 4-(bromophenyl)-2-(naphthalen-1-yl)selenophene (4) (206 mg, 0.5 mmol) and 4-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 17 (134 mg, 62%) as a yellow solid (mp = 228-230 °C).

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 9.50 (s, 1H), 9.06 – 9.04 (m, 1H), 8.72 (s, 1H), 8.71 – 8.69 (m, 1H), 8.36 – 8.34 (m, 1H), 8.27 (d, $J$ = 8.3 Hz, 1H), 8.10 – 8.08 (m, 2H), 8.04 (dd, $J$ = 8.4, 1.5 Hz, 1H), 7.82 – 7.78 (m, 3H), 7.68 – 7.62 (m, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 147.9, 140.0, 139.8, 133.5, 133.2, 131.8, 130.7, 129.7 (2), 129.6, 129.2, 128.7, 128.5, 128.4, 128.0, 127.8, 127.6, 127.2 (3), 126.5, 125.5, 125.3, 125.1, 124.4, 119.3, 109.1.

IR (neat): $\nu$ = 1956, 1918, 2228, 1457, 1089, 1024, 756 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{27}$H$_{15}$NSe (432.38): C 75.00, H 3.50; found: C 74.79, H 3.49.
**2-(Pyridin-4-yl)phenanthro[9,10-b]selenophene-9-carbonitrile (18):**

Following the procedure B using 4-(4-(2-bromophenyl)selenophene-2-yl)pyridine (2) (182 mg, 0.5 mmol) and 4-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 18 (111 mg, 58%) as a yellow solid (mp = 264-266 °C).

$^1$H NMR (500 MHz, CDCl$_3$): δ 9.00 (s, 1H), 8.72 (d, $J$ = 5.3 Hz, 2H), 8.67 – 8.66 (m, 1H), 8.63 (s, 1H), 8.43 – 8.41 (m, 1H), 8.04 (d, $J$ = 8.2 Hz, 1H), 7.82 (d, $J$ = 8.3 Hz, 1H), 7.78 – 7.77 (m, 2H), 7.62 (d, $J$ = 5.6 Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): 150.9, 147.1, 142.9, 140.8, 140.3, 132.4, 130.2, 129.3, 129.1, 128.9, 128.8, 128.5, 127.5, 127.2, 124.9, 124.6, 123.8, 120.9, 119.4, 110.3.

IR (neat): $\nu = 3041, 2222, 1591, 1245, 810, 789$ cm$^{-1}$

Elemental analysis: calcd (%) for C$_{22}$H$_{12}$N$_2$Se (383.31): C 68.94, H 3.16; found: C 68.99, H 3.04.

**1-(9-(4-Chlorophenyl)selenopheno[2',3':3,4]naphtho[2,1-b]thiophen-2-yl)ethan-1-one (19):**

Following the procedure B using 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (1) (198 mg, 0.5 mmol) and 1-(5-bromothiophen-2-yl)ethan-1-one (205 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 19 (99 mg, 45%) as a yellow solid (mp = 204-206 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.55 (s, 1H), 8.42 – 8.35 (m, 3H), 7.74 – 7.62 (m, 4H), 7.43 (d, $J$ = 8.6 Hz, 2H), 2.75 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.4, 148.0, 141.9, 139.9, 139.6, 134.7, 134.4, 133.8 (2), 129.5, 129.0, 128.6, 128.1, 128.1, 127.4, 126.8, 125.0, 124.3, 121.9, 27.0.

IR (neat): $\nu = 1089, 2920, 1639, 1489, 1359, 1276, 1012, 812$ cm$^{-1}$

Elemental analysis: calcd (%) for C$_{22}$H$_{13}$ClOSSe (439.82): C 60.08, H 2.98; found: C 60.27, H 3.12.

ESI HRMS: [M+H]$^+$, m/z theoretical 440.96136, found 440.9612 (0 ppm).
2-(4-Chlorophenyl)-6-(trifluoromethyl)phenanthro[9,10-b]selenophene-9-carbonitrile (20): Following the procedure B using 4-(2-bromo-4-(trifluoromethyl)phenyl)-2-(4-chlorophenyl)selenophene (5) (232 mg, 0.5 mmol) and 4-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 20 (138 mg, 57%) as pale yellow solid (mp = 250-252 °C).

\[ ^1\text{H NMR} \ (500 \text{ MHz, DMSO-}d_6) \delta 9.52 \ (s, 1\text{H}), 9.23 \ (s, 1\text{H}), 8.88 \ (s, 1\text{H}), 8.73 \ (d, J = 8.5 \text{ Hz}, 1\text{H}), 8.04 \ (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.98 - 7.93 \ (m, 2\text{H}), 7.83 \ (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.53 \ (d, J = 8.4 \text{ Hz}, 2\text{H}). \]

\[ ^{13}\text{C NMR} \ (126 \text{ MHz, DMSO-}d_6): \delta 148.9, 140.7, 139.5, 133.7, 133.4, 131.8, 131.4, 130.2, 130.1, 129.2, 128.0, 127.8, 127.2 (q, J = 32.2 \text{ Hz}), 127.1, 126.9, 126.4, 124.4 (q, J = 272.5 \text{ Hz}), 124.0 (q, J = 3.2 \text{ Hz}), 123.9, 122.0 (q, J = 3.9 \text{ Hz}), 119.0, 109.5. \]

\[ ^{19}\text{F NMR} \ (376 \text{ MHz, DMSO-}d_6): \delta -60.0. \]

IR (neat): \( v = 2005, 2922, 2223, 1606, 1315, 1111, 1012, 812 \ \text{ cm}^{-1} \)

Elemental analysis: calcld (%) for C_{24}H_{11}ClF_{3}NSe (484.76): C 59.46, H 2.29; found: C 59.41, H 2.39.

ESI HRMS: [M+H] +, m/z theoretical 485.97701, found 485.9769 (0 ppm).

2-(4-Chlorophenyl)-6-fluorophenanthro[9,10-b]selenophene-11-carbonitrile (21): Following the procedure B using 4-(2-bromo-4-fluorophenyl)-2-(4-chlorophenyl)selenophene (6) (207 mg, 0.5 mmol) and 2-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 21 (104 mg, 48%) as a pale yellow solid (mp = 264-266 °C).

\[ ^1\text{H NMR} \ (500 \text{ MHz, CDCl}_3): \delta 8.82 \ (d, J = 8.1 \text{ Hz}, 1\text{H}), 8.42 \ (dd, J = 9.1, 5.7 \text{ Hz}, 1\text{H}), 8.38 \ (s, 1\text{H}), 8.28 \ (dd, J = 11.0, 2.5 \text{ Hz}, 1\text{H}), 8.07 \ (dd, J = 7.4, 1.0 \text{ Hz}, 1\text{H}), 7.72 \ (d, J = 8.5 \text{ Hz}, 2\text{H}), 7.68 \ (dd, J = 8.3, 7.4 \text{ Hz}, 1\text{H}), 7.50 - 7.46 \ (m, 1\text{H}), 7.45 \ (d, J = 8.5 \text{ Hz}, 2\text{H}). \]

\[ ^{13}\text{C NMR} \ (126 \text{ MHz, CDCl}_3): \delta 161.6 \ (d, J = 246.7 \text{ Hz}), 150.4, 141.0, 135.7 \ (d, J = 1.8 \text{ Hz}), 135.6, 134.9, 134.2, 131.8, 130.5 \ (d, J = 8.1 \text{ Hz}), 129.5, 129.4, 128.9, 128.2, 127.2 \ (d, J = 8.9 \text{ Hz}), 126.9 \ (d, J = 1.9 \text{ Hz}), 125.4, 121.3, 120.7, 117.3 \ (d, J = 23.5 \text{ Hz}), 109.2 \ (d, J = 22.9 \text{ Hz}), 108.2. \]
\(^{19}\)F NMR (471 MHz, CDCl\(_3\)): δ -112.6.

IR (neat): \(\nu = 2918, 2850, 2224, 1477, 1095, 764\) cm\(^{-1}\)

Elemental analysis: calcd (%) for C\(_{23}\)H\(_{11}\)ClFNSe (434.76): C 63.54, H 2.55; found: C 63.86, H 2.67.

2-(4-Chlorophenyl)-5-(trifluoromethyl)phenanthro[9,10-b]selenophene-11-carbonitrile (22): Following the procedure B using 4-(2-bromo-3(trifluoromethyl)phenyl)-2-(4-chlorophenyl)selenophene (7) (232 mg, 0.5 mmol) and 2-bromobenzonitrile (182 mg, 1 mmol), the residue was purified by precipitation to afford the desired compound 22 (153 mg, 63%) as a pale yellow solid (mp = 266-268 °C).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.97 (d, \(J = 8.3\) Hz, 1H), 8.76 (d, \(J = 8.7\) Hz, 1H), 8.65 (s, 1H), 8.43 (s, 1H), 8.09 (d, \(J = 7.0\) Hz, 1H), 7.89 (d, \(J = 8.5\) Hz, 1H), 7.75 (d, \(J = 8.5\) Hz, 2H), 7.71 (d, \(J = 7.8\) Hz, 1H), 7.46 (d, \(J = 8.5\) Hz, 2H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ 150.9, 141.0, 137.7, 136.0, 135.1, 133.9, 132.1, 130.9, 130.2 (q, \(J = 32.8\) Hz), 129.6 (2), 129.1, 128.6, 128.2, 125.8, 124.7, 124.3 (q, \(J = 272.3\) Hz), 122.9 (q, \(J = 3.6\) Hz), 122.3 (q, \(J = 4.0\) Hz), 121.0, 120.5, 108.4.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -62.2.

IR (neat): \(\nu = 3056, 2216, 1489, 1471, 1327, 1112, 1053, 796\) cm\(^{-1}\)

Elemental analysis: calcd (%) for C\(_{24}\)H\(_{11}\)ClF\(_3\)NSe (484.76): C 59.46, H 2.29; found: C 59.31, H 2.01.

3-(2-Bromophenyl)-2,5-bis(4-chlorophenyl)selenophene (23i): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 1-bromo-4-chlorobenzene (383 mg, 2 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 23i (134 mg, 53%) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.67 (dd, \(J = 8.0, 1.5\) Hz, 1H), 7.52 (d, \(J = 8.5\) Hz, 2H), 7.48 (s, 1H), 7.37 (d, \(J = 8.5\) Hz, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.19 (m, 4H), 7.14 (d, \(J = 8.5\) Hz, 2H).
13C NMR (100 MHz, CDCl₃): δ 146.7, 144.7, 140.5, 138.7, 134.5, 134.3, 133.8, 133.6, 133.2, 132.0, 129.9, 129.4, 129.3, 128.8, 127.6, 127.3, 123.9.

9-Chloro-2-(4-chlorophenyl)phenanthro[9,10-b]selenophene (23): Following the procedure C using 3-(2-bromophenyl)-2,5-bis(4-chlorophenyl)selenophene (23i) (127 mg, 0.25 mmol), the residue was purified by precipitation to afford the desired compound 23 (77 mg, 72%) as a yellow solid (mp = 208-210 °C).

1H NMR (400 MHz, DMSO-d₆): δ 8.95 (s, 1H), 8.92 – 8.88 (m, 2H), 8.67 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 8.5 Hz, 2H), 7.79 – 7.69 (m, 3H), 7.57 (d, J = 8.5 Hz, 2H).

13C NMR (100 MHz, DMSO-d₆): δ 146.3, 139.0, 138.5, 134.2, 133.0, 131.9, 129.6, 129.4, 129.2, 128.3, 128.1, 128.0, 127.9 (2), 126.9, 125.2, 124.3, 124.0, 123.5.

IR (neat): ν = 3055, 1492, 1435, 1091, 789, 755 cm⁻¹

Elemental analysis: calcd (%) for C₂₂H₁₂Cl₂Se (426.20): C 62.00, H 2.84; found: C 62.28, H 2.98.

ESI HRMS: [M+H] +, m/z theoretical 426.9554, found 426.9554 (0 ppm).

4,4’-(3-(2-Bromophenyl)selenophene-2,5-diyl)dibenzonitrile (24i): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 4-bromobenzonitrile (364 mg, 2 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 24i (142 mg, 58%) as a yellow oil.

1H NMR (400 MHz, CDCl₃): δ 7.69 – 7.64 (m, 5H), 7.60 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.30 – 7.21 (m, 4H), 7.18 (dd, J = 7.3, 2.0 Hz, 1H).

13C NMR (100 MHz, CDCl₃): δ 147.2, 145.5, 142.1, 140.1, 139.8, 137.9, 133.4, 133.0, 132.4, 131.8, 131.7, 129.9, 129.1, 127.8, 126.5, 123.6, 118.7, 118.7, 111.4, 111.3.
2-(4-Cyanophenyl)phenanthro[9,10-b]selenophene-9-carbonitrile (24): Following the procedure C using 4,4’-(3-(2-bromophenyl)selenophene-2,5-diyl)dibenzonitrile (24i) (122 mg, 0.25 mmol), the residue was purified by precipitation to afford the desired compound 24 (72 mg, 71%) as a yellow solid (mp = 220-222 °C).

1H NMR (500 MHz, DMSO-d6): δ 9.46 (d, J = 1.1 Hz, 1H), 9.22 (s, 1H), 9.02 (d, J = 7.9 Hz, 1H), 8.75 (dd, J = 8.1, 1.1 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), 8.04 (dd, J = 8.3, 1.5 Hz, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.85 – 7.78 (m, 2H).

13C NMR (126 MHz, DMSO-d6): δ 147.6, 140.5, 139.8, 139.4, 133.2, 131.6, 129.7 (2), 129.6, 128.7, 128.1, 128.0, 127.4, 127.3, 127.1, 126.1, 125.3, 124.4, 119.2, 118.7, 110.8, 109.5.

IR (neat): ν = 3066, 2222, 1600, 1467, 1478, 804 cm⁻¹

Elemental analysis: calcd (%) for C24H12N2Se (407.33): C 70.77, H 2.97; found: C 70.89, H 3.10.

1,1’-((3-(2-Bromophenyl)selenophene-2,5-diyl)bis(4,1-phenylene))bis(propan-1-one) (25i): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 4-bromopiophenone (426 mg, 2 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 25i (154 mg, 56%) as a yellow oil.

1H NMR (400 MHz, CDCl₃): δ 7.99 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.67 – 7.64 (m, 3H), 7.61 (s, 1H), 7.28 – 7.20 (m, 5H), 3.02 (q, J = 7.2 Hz, 2H), 2.94 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H).

13C NMR (100 MHz, CDCl₃): δ 200.2, 200.0, 147.6, 145.9, 141.4, 140.2, 140.0, 138.6, 136.1, 135.7, 133.3, 131.9, 131.2, 129.5, 129.0, 128.7, 128.4, 127.7, 126.1, 123.8, 31.9, 31.9, 8.4, 8.3.
1-(4-(9-Propionylphenanthro[9,10-b]selenophen-2-yl)phenyl)propan-1-one (25): Following the procedure C using 1,1’-((3-(2-bromophenyl)selenophene-2,5-diyl)bis(4,1-phenylene))bis(propan-1-one) (25i) (138 mg, 0.25 mmol), the residue was purified by precipitation to afford the desired compound 25 (77 mg, 66%) as a yellow solid (mp = 250-252 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.32 (s, 1H), 8.82 – 8.78 (m, 1H), 8.51 (s, 1H), 8.41 – 8.38 (m, 1H), 8.17 (dd, J = 8.4, 1.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.75 – 7.70 (m, 2H), 3.22 (q, J = 7.2 Hz, 2H), 3.06 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 200.5, 200.1, 148.3, 140.9, 140.2, 140.0, 136.5, 134.8, 132.9, 130.1, 129.8, 129.1, 128.4, 128.0, 126.9, 126.8, 126.5, 126.4, 124.8, 124.4, 123.9, 123.7, 32.2, 32.0, 8.6, 8.4.

IR (neat): ν = 1978, 1939, 1615, 1598, 1355, 1236, 956, 792 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{28}$H$_{22}$O$_2$Se (469.44): C 71.64, H 4.72; found: C 71.53, H 5.06.

ESI HRMS: [M+H$^+$], m/z theoretical 471.08578, found 471.0860 (0 ppm).

9-Fluoro-2-(4-fluorophenyl)phenanthro[9,10-b]selenophene (26): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 1-bromo-4-fluorobenzene (350 mg, 2 mmol), the residue was purified by precipitation to afford the desired compound 26 (94 mg, 48%) as a white solid (mp = 176-178 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.55 (dd, J = 7.5, 1.9 Hz, 1H), 8.34 (dd, J = 7.3, 2.2 Hz, 1H), 8.29 – 8.26 (m, 2H), 7.92 (dd, J = 8.8, 5.7 Hz, 1H), 7.71 – 7.64 (m, 4H), 7.36 (td, J = 8.7, 2.5 Hz, 1H), 7.21 – 7.10 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): 162.9 (d, J = 248.6 Hz), 161.7 (d, J = 245.6 Hz), 146.5, 140.3, 137.6, 132.6 (d, J = 3.4 Hz), 130.3 (d, J = 8.1 Hz), 130.2, 129.0 (d, J = 3.9 Hz), 128.4 (d, J = 8.1 Hz), 128.1 (d, J = 8.8 Hz), 128.0, 127.0 (d, J = 1.8 Hz), 126.3, 124.8, 123.9, 122.1, 116.4 (d, J = 24.0 Hz), 116.2 (d, J = 21.9 Hz), 109.1 (d, J = 22.7 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -113.4, -113.5.
IR (neat): ν = 2920, 2850, 1504, 1440, 1228, 1178, 789, 715 cm⁻¹

Elemental analysis: calcd (%) for C₂₂H₁₂F₂Se (393.29): C 67.19, H 3.08; found: C 67.28, H 3.01.

9-(Trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)phenanthro[9,10-b]selenophene (27): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 4-bromobenzotrifluoride (450 mg, 2 mmol), the residue was purified by precipitation to afford the desired compound 27 (141 mg, 57%) as a white solid (mp =197-199 °C).

¹H NMR (500 MHz, CDCl₃): δ 8.91 (s, 1H), 8.70 – 8.68 (m, 1H), 8.44 (s, 1H), 8.40 – 8.34 (m, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.83 – 7.79 (m, 3H), 7.73 – 7.70 (m, 4H).

¹³C NMR (126 MHz, CDCl₃): δ 147.5, 140.6, 139.7, 139.4, 132.0, 130.4 (q, J = 32.7 Hz), 130.1, 129.2, 128.5 (q, J = 32.4 Hz), 128.4, 128.3, 127.0 (2), 126.9, 126.3 (q, J = 3.7 Hz), 124.8, 124.6 (q, J = 272.1 Hz), 124.2 (q, J = 272.0 Hz), 123.8, 123.6 (2), 121.3 (q, J = 4.0 Hz).

¹⁹F NMR (471 MHz, CDCl₃): δ -61.9, -62.6.

IR (neat): ν = 1850, 1568, 1487, 1178, 1147, 1087, 756, 715 cm⁻¹

Elemental analysis: calcd (%) for C₂₄H₁₂F₆Se (493.31): C 58.43, H 2.45; found: C 58.21, H 2.78.

2-(2-Cyanophenyl)phenanthro[9,10-b]selenophene-11-carbonitrile (28): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 4-bromobenzonitrile (364 mg, 2 mmol), the residue was purified by precipitation to afford the desired compound 28 (104 mg, 51%) as a pale yellow solid (mp = 250-252 °C).

¹H NMR (500 MHz, DMSO-d₆): δ 9.33 (d, J = 8.5 Hz, 1H), 9.00 (s, 1H), 8.97 (dd, J = 7.7, 1.8 Hz, 1H), 8.68 (dd, J = 7.4, 1.8 Hz, 1H), 8.32 (dd, J = 7.3, 1.0 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.91 – 7.81 (m, 4H), 7.68 (td, J = 7.8, 1.0 Hz, 1H).

¹³C NMR (126 MHz, DMSO-d₆): δ 144.9, 140.4, 137.9, 136.9, 135.2, 134.2, 133.5, 130.4, 129.8, 129.4, 129.2, 129.0, 128.6, 128.1, 127.3, 126.8, 126.3, 124.8, 124.0, 120.0, 118.1, 109.6, 106.7.
IR (neat): \( \nu = 2918, 2330, 2220, 1591, 1408, 1284, 1182, 850, 756 \) cm\(^{-1}\)

Elemental analysis: calcd (%) for \( \text{C}_{24}\text{H}_{12}\text{N}_{2}\text{Se} \) (407.33): C 70.77 H 2.97; found: C 70.89, H 2.51.

**11-(Trifluoromethyl)-2-(2-(trifluoromethyl)phenyl)phenanthro[9,10-b]selenophene** (29): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 2-bromobenzotrifluoride (450 mg, 2 mmol), the residue was purified by precipitation to afford the desired compound 29 (131 mg, 53%) as a white solid (mp = 248-250 °C).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 9.00 (d, \( J = 8.3 \) Hz, 1H), 8.68 – 8.66 (m, 1H), 8.39 – 8.37 (m, 1H), 8.31 (s, 1H), 8.09 (d, \( J = 7.5 \) Hz, 1H), 7.84 (d, \( J = 7.8 \) Hz, 1H), 7.70 – 7.60 (m, 5H), 7.54 (t, \( J = 7.6 \) Hz, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 146.1 (q, \( J = 4.9 \) Hz), 140.2, 136.5, 135.0 (q, \( J = 2.0 \) Hz), 133.3, 131.5, 131.0, 130.0, 129.4 (q, \( J = 4.0 \) Hz), 129.0 (q, \( J = 30.0 \) Hz), 128.9, 128.6, 128.2, 128.0, 126.9 (q, \( J = 7.8 \) Hz), 126.8, 126.7 (q, \( J = 5.5 \) Hz), 126.1 (q, \( J = 2.2 \) Hz), 125.2 (q, \( J = 273.2 \) Hz), 124.8, 124.7, 124.3 (q, \( J = 29.9 \) Hz), 124.2 (q, \( J = 273.9 \) Hz), 123.9.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -56.51, -57.12.

IR (neat): \( \nu = 3078, 1602, 1571, 1307, 1116, 789, 694 \) cm\(^{-1}\)

Elemental analysis: calcd (%) for \( \text{C}_{24}\text{H}_{12}\text{F}_{6}\text{Se} \) (493.31): C 58.43, H 2.45; found: C 58.52, H 2.31.

**2-(Pyridin-4-yl)benzo[h]selenopheno[2,3-f]isoquinoline** (30): Following the procedure D using 3-(2-bromophenyl)selenophene (8) (143 mg, 0.5 mmol) and 4-bromopyridine hydrochloride (389 mg, 2 mmol), the residue was purified by precipitation to afford the desired compound 30 (101 mg, 56%) as a yellow solid (mp = 190-192 °C).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.01 (s, 1H), 8.81 – 8.79 (m, 1H), 8.73 – 8.70 (m, 3H), 8.58 (s, 1H), 8.40 – 8.37 (m, 1H), 7.75 – 7.72 (m, 3H), 7.61 – 7.59 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 150.8, 147.4 (2), 146.1, 142.9, 141.2, 139.4, 134.2, 130.2, 128.4, 128.3, 127.5, 124.8, 124.5, 123.5, 123.1, 120.9, 119.0.
IR (neat): $\nu = 2926, 1595, 1215, 908, 734 \text{ cm}^{-1}$

Elemental analysis: calcd (%) for $C_{20}H_{12}N_2Se$ (359.29): C 66.86, H 3.37; found: C 66.98, H 3.46.

4-(4-(2-Bromophenyl)selenophen-3-yl)benzonitrile (31): Following the procedure A using 3-(2-bromophenyl)selenophene (8) (286 mg, 1 mmol) and 4-cyanobenzenesulfonyl chloride (302 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 31 (162 mg, 42%) as a yellow solid (mp = 210-212 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (d, $J = 2.7$ Hz, 1H), 7.98 (d, $J = 2.7$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.29 – 7.16 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.1, 142.7, 142.5, 138.8, 133.0, 132.0, 131.9, 131.1, 129.9, 129.4, 129.0, 127.4, 124.0, 119.0, 110.5.

IR (neat): $\nu = 2987, 2226, 1473, 1108, 876 \text{ cm}^{-1}$

Elemental analysis: calcd (%) for $C_{17}H_{10}BrNSe$ (387.14): C 52.74, H 2.60; found: C 52.96, H 2.92.

3-(2-Bromophenyl)-4-(4-nitrophenyl)selenophene (32): Following the procedure A using 3-(2-bromophenyl)selenophene (8) (286 mg, 1 mmol) and 4-nitrobenzenesulfonyl chloride (332 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 32 (143 mg, 35%) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J = 2.8$ Hz, 1H), 8.05 – 8.03 (m, 2H), 7.99 (d, $J = 2.8$ Hz, 1H), 7.52 (d, $J = 8.1$ Hz, 1H), 7.29 – 7.25 (m, 4H), 7.20 – 7.17 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.5, 144.4, 142.69, 142.66, 138.7, 133.0, 131.9, 131.1, 130.2, 129.4, 128.9, 127.3, 123.9, 123.3.

IR (neat): $\nu = 1922, 1593, 1504, 1375, 1109, 852, 738 \text{ cm}^{-1}$
Elemental analysis: calcd (%) for C_{16}H_{10}BrNO_{2}Se (407.13): C 47.20, H 2.48; found: C 47.36, H 2.31.

3-(2-Bromophenyl)-4-(4-methoxyphenyl)selenophene (33): Following the procedure A using 3-(2-bromophenyl)selenophene (8) (286 mg, 1 mmol) and 4-methoxybenzenesulfonyl chloride (310 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 33 (145 mg, 37%) as a yellow oil.

^1H NMR (400 MHz, CDCl₃): δ 7.94 – 7.90 (m, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.16 – 7.12 (m, 1H), 7.07 – 7.04 (m, 2H), 6.74 – 6.72 (m, 2H), 3.75 (s, 3H).

^13C NMR (100 MHz, CDCl₃): δ 158.6, 144.6, 143.2, 139.8, 132.8, 132.1, 130.5, 130.0, 129.7, 128.8, 127.0, 126.9, 124.2, 113.5, 55.2.

IR (neat): ν = 2833, 1606, 1510, 1462, 1174, 1019, 838, 786 cm⁻¹

Elemental analysis: calcd (%) for C_{17}H_{13}BrOSe (392.15): C 52.07, H 3.34; found: C 52.22, H 2.98.

3-(2-Bromo-4-(trifluoromethyl)phenyl)-4-(4-(trifluoromethyl)phenyl)selenophene (34): Following the procedure A using 3-(2-bromo-4-(trifluoromethyl)phenyl)selenophene (9) (354 mg, 1 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (267 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 34 (159 mg, 32%) as a white solid (mp = 262-264 °C).

^1H NMR (400 MHz, CDCl₃): δ 8.10 (d, J = 2.8 Hz, 1H), 8.02 (d, J = 2.8 Hz, 1H), 7.81 (d, J = 0.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H).

^13C NMR (100 MHz, CDCl₃): δ 143.3, 143.0, 141.6, 141.1, 132.3, 131.7, 131.4 (d, J = 33.3 Hz), 130.1 (q, J = 3.9 Hz), 129.9, 129.2 (d, J = 32.4 Hz), 128.7, 125.3 (q, J = 3.9 Hz), 124.4, 124.3 (q, J = 272.1 Hz), 124.2 (q, J = 3.7 Hz), 123.2 (q, J = 272.7 Hz).
IR (neat): $\nu = 2955, 1258, 1098, 1007, 809, 756 \text{ cm}^{-1}$

Elemental analysis: calcd (%) for C$_{18}$H$_9$BrF$_6$Se (498.12): C 43.40, H 1.82; found: C 43.58, H 1.63.

**4-(4-Phenylselenophen-3-yl)benzonitrile (35):** Following the procedure A using 3-phenylselenophene$^3$ (207 mg, 1 mmol) and 4-cyanobenzenesulfonyl chloride (302 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane-EtOAc, 90:10) to afford the desired compound 35 (151 mg, 49%) as a white solid (mp = 115-117 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J = 2.8$ Hz, 1H), 8.00 (d, $J = 2.8$ Hz, 1H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.28 – 7.23 (m, 5H), 7.12 – 7.10 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.2, 142.9, 142.7, 137.6, 132.0, 130.8, 129.9, 129.7, 129.2, 128.4, 127.4, 119.1, 110.6.

IR (neat): $\nu = 2958, 2218, 1253, 1045, 850, 720 \text{ cm}^{-1}$

Elemental analysis: calcd (%) for C$_{17}$H$_{11}$NSe (308.24): C 66.24, H 3.60; found: C 66.02, H 3.87.

**3,4-Bis(4-(trifluoromethyl)phenyl)selenophene (36):** Following the procedure A using selenophene (131 mg, 1 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (734 mg, 3 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 36 (130 mg, 31%) as a white solid (mp = 171-173 °C)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (s, 2H), 7.54 (d, $J = 8.4$ Hz, 4H), 7.27 (d, $J = 8.4$ Hz, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.9, 141.4, 130.9, 129.4, 125.4 (q, $J = 3.8$ Hz), 129.3 (q, $J = 32.5$ Hz), 124.3 (q, $J = 272.0$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.5.
IR (neat): $\nu = 2986, 1467, 1489, 1103, 856 \text{ cm}^{-1}$

Elemental analysis: calcd (%) for $C_{18}H_9F_6Se$ (419.23): C 51.57, H 2.40; found: C 51.84 H 2.63.

3,4-Diphenylselenophene (37): Following the procedure A using selenophene (131 mg, 1 mmol) and benzenesulfonyl chloride (530 mg, 3 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 37 (85 mg, 30%) as a white solid (mp = 109-111 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (s, 2H), 7.26 – 7.23 (m, 6H), 7.17 – 7.15 (m, 4H).

The compound is known and the NMR data are identical to those reported in the literature.$^4$

Phenanthro[9,10-c]selenophene-6-carbonitrile (38): Following the procedure C using 4-(4-(2-bromophenyl)selenophen-3-yl)benzonitrile (31) (97 mg, 0.25 mmol), the residue was by flash chromatography on silica gel (pentane-EtOAc, 80:20) to afford the desired compound 38 (50 mg, 65%) as an orange solid (mp = 189-191 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.94 (d, $J = 2.6$ Hz, 1H), 8.85 (d, $J = 2.6$ Hz, 1H), 8.66 (d, $J = 1.3$ Hz, 1H), 8.33 – 8.29 (m, 1H), 8.27 (d, $J = 8.3$ Hz, 1H), 8.24 – 8.21 (m, 1H), 7.72 (dd, $J = 8.3, 1.5$ Hz, 1H), 7.61 – 7.54 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.6, 136.3, 132.6, 130.3, 129.8, 129.7, 128.9, 128.5, 127.9, 127.7, 126.6, 125.4, 124.7, 124.4, 123.6, 119.5, 110.5.

IR (neat): $\nu = 1918, 2229, 1454, 1226, 1107, 755 \text{ cm}^{-1}$

Elemental analysis: calcd (%) for $C_{17}H_8NSe$ (306.23): C 66.68, H 2.96; found: C 66.86, H 3.12.

ESI HRMS: [M+H] $^+$, m/z theoretical 307.99729, found 307.9971 (1 ppm).
6-Nitrophenanthro[9,10-c]selenophene (39): Following the procedure C using 3-(2-bromophenyl)-4-(4-nitrophenvyl)selenophene (32) (102 mg, 0.25 mmol), the residue was by flash chromatography on silica gel (pentane-EtOAc, 80:20) to afford the desired compound 39 (51 mg, 63%) as an orange solid (mp = 193-195 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.27 (s, 1H), 9.01 (d, $J = 2.6$ Hz, 1H), 8.87 (d, $J = 2.6$ Hz, 1H), 8.45 – 8.42 (m, 1H), 8.32 (s, 1H), 8.32 (s, 1H), 8.26 – 8.23 (m, 1H), 7.63 – 7.58 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.6, 137.7, 136.2, 134.2, 130.5, 129.7, 129.1, 128.3, 127.8, 127.5, 125.5, 124.7, 124.5, 124.0, 121.8, 119.7.

IR (neat): ν = 3097, 2922, 1585, 1506, 1334, 1101, 885, 789 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{16}$H$_9$NO$_2$Se (326.21): C 58.91, H 2.78; found: C 59.06, H 2.55.

6-Methoxyphenanthro[9,10-c]selenophene (40): Following the procedure C using 3-(2-bromophenyl)-4-(4-methoxyphenyl)selenophene (33) (98 mg, 0.25 mmol), the residue was by flash chromatography on silica gel (pentane-EtOAc, 80:20) to afford the desired compound 40 (49 mg, 63%) as an orange solid (mp = 241-243 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.78 (d, $J = 2.7$ Hz, 1H), 8.63 (d, $J = 2.7$ Hz, 1H), 8.30 (d, $J = 6.1$, 3.4 Hz, 1H), 8.22 (dd, $J = 6.1$, 3.2 Hz, 1H), 8.14 (d, $J = 8.8$ Hz, 1H), 7.81 (d, $J = 2.5$ Hz, 1H), 7.54 – 7.48 (m, 2H), 7.12 (dd, $J = 8.8$, 2.6 Hz, 1H), 3.98 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.9, 137.6, 137.4, 131.1, 129.8, 129.6, 127.8, 127.1, 126.0, 124.7, 123.6, 123.41, 123.36, 121.2, 115.3, 107.1, 55.6.

IR (neat): ν = 2972, 1453, 1174, 1039, 821 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{17}$H$_{12}$NOSe (311.24): C 65.60, H 3.89; found: C 65.72, H 4.00.
6,9-Bis(trifluoromethyl)phenanthro[9,10-c]selenophene  (41):
Following the procedure C using 3-(2-bromo-4-(trifluoromethyl)phenyl)-4-(4-(trifluoromethyl)phenyl)selenophene (34) (125 mg, 0.25 mmol), the residue was by flash chromatography on silica gel (pentane, 100) to afford the desired compound 41 (68 mg, 65%) as a white solid (mp = 251-253 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.97 (s, 2H), 8.61 (s, 2H), 8.34 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 136.4, 132.0, 129.2 (q, J = 32.4 Hz), 128.7, 126.1, 125.2, 124.6 (q, J = 3.6 Hz), 124.3 (q, J = 272.4 Hz), 120.9 (q, J = 3.9 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.2.

IR (neat): $\nu$ =2987, 1457, 1178, 875 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{18}$H$_8$F$_6$Se (417.21): C 51.82, H 1.93; found: C 51.64, H 1.63.

3,15-Bis(trifluoromethyl)diphenanthro[9,10-b:9',10'-d]selenophene (42):
Following the procedure D using 3,4-bis(4-(trifluoromethyl)phenyl)selenophene (36) (71 mg, 0.25 mmol), and 1,2-dibromobenzene (177 mg, 0.75 mmol), the residue was purified by precipitation to afford the desired compound 42 (59 mg, 42%) as a white solid (mp = 255-257 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.98 (s, 2H), 8.74 (d, J = 7.9 Hz, 2H), 8.53 (d, J = 8.6 Hz, 2H), 8.08 (d, J = 7.2 Hz, 2H), 7.80 – 7.68 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 143.6, 133.6, 131.8, 130.3, 130.1, 129.3, 128.7, 128.2, 128.0 (q, J = 32.6 Hz), 127.7, 126.8, 124.6 (q, J = 272.0 Hz), 123.6, 121.54 (d, J = 4.4 Hz), 121.48 (d, J = 3.8 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -61.9.

IR (neat): $\nu$ = 2987, 1620, 1608, 1352, 1217, 1101, 1082, 883, 720 cm$^{-1}$
Elemental analysis: calcd (%) for C$_{30}$H$_{14}$F$_6$Se (567.39): C 63.51, H 2.49; found: C 63.89, H 2.74.

Diphenanthro[9,10-b:9',10'-d]selenophene (43): Following the procedure D using 3,4-diphenylselenophene (37): (105 mg, 0.25 mmol), and 1,2-dibromobenzene (177 mg, 0.75 mmol), the residue was purified by precipitation to afford the desired compound 43 (40 mg, 37%) as a brown solid (mp = 195-197 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.74 (d, $J = 8.7$ Hz, 4H), 8.57 (d, $J = 8.4$ Hz, 2H), 8.10 – 8.07 (m, 2H), 7.73 – 7.64 (m, 6H), 7.49 (t, $J = 7.3$ Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.1, 134.8, 130.44, 130.3, 129.8, 127.7, 127.5, 127.3, 126.6, 126.1, 125.2, 123.9, 123.5.

IR (neat): $\nu$ = 2960, 2850, 1431, 1259, 1082, 1016, 796 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{28}$H$_{16}$Se (431.39): C 77.96, H 3.74; found: C 78.14, H 3.55.

Diphenanthro[9,10-b:9',10'-d]selenophene-3-carbonitrile (44): Following the procedure D using 4-(4-phenylselenophen-3-yl)benzonitrile (35) (77 mg, 0.25 mmol), and 1,2-dibromobenzene (177 mg, 0.75 mmol), the residue was purified by precipitation to afford the desired compound 44 (48 mg, 42%) as a brown solid (mp = 213-215 °C).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.99 (s, 1H), 8.73 – 8.71 (m, 2H), 8.64 – 8.62 (m, 1H), 8.57 (d, $J = 8.6$ Hz, 1H), 8.33 (d, $J = 8.2$ Hz, 1H), 8.06 – 8.00 (m, 2H), 7.75 – 7.65 (m, 5H), 7.61 (dd, $J = 8.6$, 1.4 Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.4, 141.6, 134.0, 133.8, 132.4, 130.6, 130.5, 130.1, 129.9, 129.8, 129.2, 128.9, 128.3, 128.1, 128.0, 127.9, 127.7, 126.9, 126.77, 126.76, 126.6, 126.5, 125.5, 124.2, 123.5, 123.4, 119.6, 109.1.

IR (neat): $\nu$ = 3069, 2223, 1598, 1433, 827 cm$^{-1}$

Elemental analysis: calcd (%) for C$_{29}$H$_{15}$NSe (456.41): C 76.32, H 3.31; found: C 76.49, H 3.54.
**2-(4-Chlorophenyl)-4-phenylselenophene (45):** Following the procedure A using 2-(4-chlorophenyl)selenophene S1 (241 mg, 1 mmol) and benzenesulfonyl chloride (265 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (pentane, 100) to afford the desired compound 45 (200 mg, 63%) as a yellow solid (mp = 121-123 °C).

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } \delta 8.02 (d, J = 1.3 Hz, 1H), 7.78 (d, J = 1.3 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.55 – 7.52 (m, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.38 – 7.32 (m, 3H).\]

\[\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta 149.4, 145.7, 137.2, 135.0, 133.7, 129.2, 128.9, 127.5, 127.4, 126.6, 125.8, 125.2.\]

IR (neat): \( \nu = 3028, 2922, 1479, 1398, 1093, 819 \text{ cm}^{-1} \)

Elemental analysis: calcd (%) for C\textsubscript{16}H\textsubscript{11}ClSe (317.57): C 60.49, H 3.49; found: C 60.58, H 3.24.

**2-(4-Chlorophenyl)phenanthro[9,10-b]selenophene (46):** Following the procedure D using 2-(4-chlorophenyl)-4-phenylselenophene (45) (79 mg, 0.25 mmol) and 1,2-dibromobenzene (118 mg, 0.5 mmol), the residue was purified by precipitation to afford the desired compound 46 (63 mg, 65%) as a brown solid (mp = 171-173 °C).

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{): } \delta 8.71 – 8.66 (m, 2H), 8.36 – 8.34 (m, 2H), 7.96 – 7.94 (m, 1H), 7.67 – 7.59 (m, 6H), 7.41 (d, J = 8.5 Hz, 2H).\]

\[\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta 146.2, 141.2, 138.1, 134.9, 134.0, 130.2, 129.9, 129.5, 129.3, 128.7, 127.8, 127.5, 127.3, 126.8, 126.24, 126.22, 124.6, 123.69, 123.67, 122.6.\]

IR (neat): \( \nu = 2954, 2852, 1462, 1381, 1093, 815, 742 \text{ cm}^{-1} \)

Elemental analysis: calcd (%) for C\textsubscript{22}H\textsubscript{13}ClSe (391.76): C 67.45, H 3.34; found: C 67.71, H 3.58.
6. NMR Charts
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<th>8.5</th>
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<th>9.5</th>
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<td>9.70</td>
<td>9.80</td>
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<td>11.1</td>
<td>11.2</td>
<td>11.3</td>
<td>11.4</td>
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</tr>
</tbody>
</table>

**Poor solubility in DMSO-d6**

![NMR spectrum of DMSO-d6](image)

**acetone**

---

| 13C ppm | 0.0 | 10.0 | 20.0 | 30.0 | 40.0 | 50.0 | 60.0 | 70.0 | 80.0 | 90.0 | 100.0 | 110.0 | 120.0 | 130.0 | 140.0 | 150.0 | 160.0 | 170.0 | 180.0 | 190.0 | 200.0 |
|---------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 13C ppm | 110.92| 113.92| 116.92| 119.92| 122.92| 125.92| 128.92| 131.92| 134.92| 137.92| 140.92| 143.92| 146.92| 149.92| 152.92| 155.92| 158.92| 161.92| 164.92| 167.92|

**Poor solubility in DMSO-d6**

![NMR spectrum of DMSO-d6](image)

**acetone**
Poor solubility in CDCl3
Poor solubility in CD2Cl2
Poor solubility in CD2Cl2
Poor solubility in CDCl₃
Poor solubility in CDC13
Poor solubility in CDCl3

1H (ppm)

13C (ppm)

5 – 58
Poor solubility in DMSO-d6

DMSO

H$_2$O

dichloromethane

$^{1}H$ ppm

1.0  9.5  9.0  8.5  8.0  7.5  7.0  6.5  6.0  5.5  5.0  4.5  4.0  3.5  3.0  2.5  2.0  1.5  1.0  0.5  0.0  -0.5

$^{13}C$ ppm

135  130  125  120  115  110  105  100  95  90  85  80  75  70  65  60  55  50  45  40  35  30  25  20  15  10  5  0
Poor solubility in DMSO–d6
Poor solubility in CDC13
Poor solubility in CDCl₃

Poor solubility in CDCl₃

H₂O

dichloromethane

silicone grease

silicone grease

5 – 66
Poor solubility in CDC13
23i

[Image of NMR spectra with chemical shifts and peak assignments]
Poor solubility in CDC3

Poor solubility in CDC3
Poor solubility in CDC13
Poor solubility in CDC13
Poor solubility in CDC13
Poor solubility in CDC3
Poor solubility in CDCl3
Poor solubility in CDCI3

Poor solubility in CDCI3
Poor solubility in CDC13

Poor solubility in CDC13
Poor solubility in CDC13

Poor solubility in CDC13
Poor solubility in CDCl3
Poor solubility in CDC13
Poor solubility in CDCl3

Poor solubility in CDCl3
Poor solubility in CDCl3
7. References