Supporting Information

Metal-free Difunctionalization of Alkynes to Access Tetrasubstituted Olefins through Spontaneous Selenosulfonylation of Vinylidene ortho-Quinone Methide (VQM)

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I. General information

$^1$H and $^{13}$C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer and Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: CDCl$_3$ ($^1$H NMR δ 0.00, $^{13}$C NMR δ 77.00). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Melting points were measured using SGWX-4A Microscopic melting point meter and are uncorrected. Enantiomeric excesses (ee) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6 mm \( \Phi \times 250 \text{ mmL} \). Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

II. General procedure for the synthesis of o-alkynynaphthols

The preparation of o-alkynynaphthols were followed the literature procedure.$^1$, $^2$

Method A: (1a, 1b, 1c, 1e, 1f, 1p, 1q, 1r, 1s)

![](image)

Sulfuric acid (208.0 mmol) was added to a solution of 2-naphthol S (20.0 g, 138.8 mmol) and potassium iodide (23.04 g, 138.8 mmol) in methanol (400 mL) at 0 °C. A precipitate formed, and hydrogen peroxide (30% aqueous solution, 277.6 mmol) was added. After 1.5 h of warming slowly to room temperature, the mixture was filtered, and the filtrate was concentrated. The residue was dissolved in CH$_2$Cl$_2$ (300 mL), washed with 25% sat.aq. Na$_2$S$_2$O$_3$ (250 mL) and water (200 mL), dried over Na$_2$SO$_4$, and concentrated to provide a solid (26.32 g). This material was purified by column chromatography on silica gel (PE:EA = 20:1) to provide an orange solid S1 (34.0 g, 91%).

Acetyl chloride (1.5 equiv.) was dropwise added to a solution of S1 (21.8 g, 80.7 mmol) and Et$_3$N (22.4 mL, 161.4 mmol) in CH$_2$Cl$_2$ (200 mL) at 0 °C under N$_2$. The reaction mixture was
stirred at 0 °C for 30 min and then quenched with sat. aq. NH₄Cl followed by extraction with CH₂Cl₂. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel to afford S2 (23.9 g, 95%).

To a dry flask under N₂ containing S2 (5 mmol) was sequentially added Et₃N (10 mL), appropriate alkynes (5 mmol), PdCl₂(PPh₃)$_2$ (70 mg, 0.1 mmol), CuI (47.6 mg, 0.25 mmol). The mixture was stirred for 6 h at 50 °C. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford S3.

Hydrazine monohydrate (10 mmol) was dropwise added to a solution of S3 (2 mmol) in CH₃CN (10 mL). After the resulted mixture was stirred at room temperature for 0.5 h, the mixture was treated with sat. aq. NH₄Cl and extracted with CH₂Cl₂ and dried over Na₂SO₄. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford the compound 1.

**Method B: (1d, 1g-1o)**

Trimethylsilylacetylene (5.9 mL, 41.7 mmol) was dropwise added to a solution of S2 (10 g, 32.1 mmol), PdCl₂(PPh₃)$_2$ (1.1 g, 1.6 mmol), CuI (609 mg, 3.2 mmol) and Et₃N (13.4 mL, 96.1 mmol) in THF (50 mL) at room temperature under N₂. Then, the mixture was stirred for 12 h. The reaction mixture was treated with sat. aq. NH₄Cl followed by extraction with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE:EA = 30:1) to afford S4 (7.3 g, 80% yield).

To a solution of S4 (7.0 g, 24.8 mmol) in THF (75 mL) was added TBAF in THF (1 M, 12.4 mL, 12.4 mmol) dropwise at 0 °C under N₂. Then the mixture was stirred for 1 h. The reaction mixture was treated with sat. aq. NH₄Cl followed by extraction with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE:EA = 100:1) to afford S5 (3.9 g, 75% yield).
To a dry flask under N₂ containing the appropriate iodebenzenes (2.4 mmol) was sequentially added Et₃N (5.0 mL), S₅ (500 mg, 2.4 mmol), PdCl₂(PPh₃)₂ (33.7 mg, 0.048 mmol) and CuI (22.9 mg, 0.12 mmol). The mixture was stirred for 6 h at 50 °C. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford S3.

Hydrazine monohydrate (10 mmol) was dropwise added to a solution of S3 (2 mmol) in CH₃CN (10 mL). After the resulted mixture was stirred at room temperature for 0.5 h, the mixture was treated with sat. aq. NH₄Cl and extracted with CH₂Cl₂, and dried over Na₂SO₄. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel afford the compound 1.

III. General procedure for the synthesis of o-alkynylphenols

\[
\begin{align*}
\text{I} & \quad \text{OH} & \quad \text{PdCl₂(PPh₃)₂, Cul} \\
& & \text{DIPA, THF, rt, 3 h} & \rightarrow & \text{R} & \quad \text{OH} \\
\end{align*}
\]

To a dry flask under N₂ containing 2-iodophenol (10.0 mmol) was sequentially added THF (25 mL), diisopropylamine (10.0 mmol), appropriate alkynes (12.0 mmol), PdCl₂(PPh₃)₂ (0.3 mmol), CuI (0.9 mmol). The resulting solution was stirred at room temperature for 3 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel to afford appropriate o-alkynylphenols.

IV. General procedure for the synthesis of selenosulfonates

\[
\begin{align*}
\text{S₆} & \quad \text{Se, CuO, KOH} & \quad \text{DMSO, 90 °C, 4 h} & \rightarrow & \text{R} & \quad \text{Se} & \quad \text{R} \\
& & & & \text{PhI(CF₃COO)₂} & \quad \text{CH₂Cl₂, 0 °C to rt, 4 h} & \rightarrow & \text{R} & \quad \text{O}_2\text{S} & \quad \text{R} \\
\end{align*}
\]

The preparation of compound S₆ were followed the literature procedure.³ To a stirred solution of Se⁰ metal (10 mmol, 2.0 equiv.) and halides (5 mmol, 1.0 equiv.) in DMSO (10 mL) was added CuO nanoparticles (0.5 mmol, 0.1 equiv.) followed by KOH (10 mmol, 2.0 equiv.) under nitrogen atmosphere. The resulting reaction mixture was stirred at 90 °C for 6 h. After the reaction was complete, the reaction mixture was allowed to cool, extraction with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE:EA = 100:1) to afford S₆.
The preparation of compound 2 were followed the literature procedure.\(^4\) A suspension of appropriate sodium benzenesulfonates (20 mmol, 4.0 equiv.) in CH\(_2\)Cl\(_2\) (50 mL) containing S6 (5 mmol, 1.0 equiv.) was cooled at 0 °C and [bis(trifluoroacetoxy)iodo]benzene (5.5 mmol, 1.1 equiv.) in CH\(_2\)Cl\(_2\) (20 mL) was added dropwise. Then the mixture was stirred at room temperature for 3 h. The reaction mixture was washed with H\(_2\)O, dried over anhydrous Na\(_2\)SO\(_4\). The solvent CH\(_2\)Cl\(_2\) was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EA = 6:1) to afford compound 2.
V. Optimization of the reaction conditions

![Reaction Scheme](image)

Table 1. Screening of solvent\(^{[a]}\)

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>additive</th>
<th>yield (%)(^{[b]})</th>
<th>E:Z(^{[c]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_2)Cl(_2)</td>
<td>-</td>
<td>73</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)OH</td>
<td>-</td>
<td>69</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>-</td>
<td>85</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>m-xylene</td>
<td>-</td>
<td>60</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td>toluene</td>
<td>-</td>
<td>63</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>6(^{[d]})</td>
<td>toluene</td>
<td>-</td>
<td>64</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>7</td>
<td>CH(_3)CN</td>
<td>-</td>
<td>54</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8</td>
<td>CHCl(_3)</td>
<td>-</td>
<td>52</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>9</td>
<td>THF</td>
<td>-</td>
<td>&lt;5</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Reaction conditions: 1a (0.1 mmol), 2a (0.1 mmol) in solvent (1.0 mL) at room temperature for 10 h. \(^{[b]}\)Yield ratio was determined by column chromatography. \(^{[c]}\)Determined by \(^1\)H NMR analysis. \(^{[d]}\)The reaction were carried out at 80 °C.

Table 2. Screening of additive\(^{[a]}\)

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>additive</th>
<th>yield (%)(^{[b]})</th>
<th>E:Z(^{[c]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>Et(_3)N</td>
<td>67</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>K(_2)CO(_3)</td>
<td>69</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>KF</td>
<td>73</td>
<td>&gt;99:1</td>
</tr>
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<td>4</td>
<td>DCE</td>
<td>DABCO</td>
<td>70</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>malonic acid</td>
<td>72</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>benzoic acid</td>
<td>54</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>citric acid</td>
<td>57</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8</td>
<td>DCE</td>
<td>cinnamic acid</td>
<td>49</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>9</td>
<td>DCE</td>
<td>boric acid</td>
<td>&lt;5</td>
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</tr>
<tr>
<td>10</td>
<td>DCE</td>
<td>AIBN</td>
<td>48</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Reaction conditions: 1a (0.1 mmol), 2a (0.1 mmol), additive (0.1 mmol) in DCE (1.0 mL) at room temperature for 10 h. \(^{[b]}\)Yield ratio was determined by column chromatography. \(^{[c]}\)Determined by \(^1\)H NMR analysis.
Table 3. Screening of conditions for phenol derivatives\[^{[a]}\]

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>base</th>
<th>( T (°C) )</th>
<th>time (h)</th>
<th>yield (%)[^{[b]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>-</td>
<td>r.t</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>-</td>
<td>reflux</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>-</td>
<td>reflux</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>-</td>
<td>reflux</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>DMSO</td>
<td>-</td>
<td>reflux</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>r.t</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>KF</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>DCE</td>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
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<tr>
<td>9</td>
<td>DCE</td>
<td>KOH</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>DCE</td>
<td>NaOH</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>DCE</td>
<td>( t-\text{BuOK} )</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>DCE</td>
<td>EtONa</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>DCE</td>
<td>MeONa</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>DCE</td>
<td>NaOAc</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
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<tr>
<td>15</td>
<td>DCE</td>
<td>DABCO</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>DCE</td>
<td>DBU</td>
<td>r.t</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>DCE</td>
<td>Et\text{}_{3}N</td>
<td>r.t</td>
<td>24</td>
<td>trace</td>
</tr>
<tr>
<td>18</td>
<td>toluene</td>
<td>Et\text{}_{3}N</td>
<td>reflux</td>
<td>16</td>
<td>20</td>
</tr>
</tbody>
</table>

\[^{[a]}\]Unless otherwise noted, all reactions were carried out with \( 1\text{t} \) (0.2 mmol) and \( 2\text{a} \) (0.2 mmol) in 2.0 mL solvents loading at corresponding temperature and reaction time. \[^{[b]}\]Isolated yield of \( 3\text{t} \).
VI. General procedure for the synthesis of compounds 3 or 4

\[
\begin{align*}
\text{R}^1 & \quad \text{R}^2 \quad \text{R}^3 \quad \text{R}^4 \\
\text{O} & \quad \text{S} & \quad \text{O} \\
\text{1} & \quad \text{2} & \quad \text{3 or 4}
\end{align*}
\]

The substrate 1 (0.2 mmol) and selenosulfonate 2 (0.2 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. DCE (2.0 mL) was injected into the tube. After stirring at room temperature for 10 h, the mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the products 3 or 4.

VII. General procedure for the synthesis of compounds 3t and 3u

\[
\begin{align*}
\text{R} & \quad \text{Et}_3\text{N} \\
\text{O} & \quad \text{O} \\
\text{1t or 1u} & \quad \text{2a} \\
\text{3t or 3u}
\end{align*}
\]

The Et₃N (1.0 mmol) was added to a solution of substrate 1t or 1u (1.0 mmol) and selenosulfonate 2a (1.0 mmol) in toluene (10 mL). After reflux for 16 h, The mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the products 3t or 3u.

VIII. Mechanistic studies

\[
\begin{align*}
\text{R} ^1 \quad \text{R} ^2 \quad \text{R} ^3 \quad \text{R} ^4 \\
\text{O} & \quad \text{S} & \quad \text{O} \\
\text{1a} & \quad \text{2a} & \quad \text{3a}
\end{align*}
\]

The substrate 1a (0.1 mmol), selenosulfonate 2a (0.1 mmol) and (2,2,6,6-tetramethyl-1-piperidinyl)oxyI (TEMPO) (0.1 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. DCE (1.0 mL) was injected into the tube. After stirring at room temperature for 72 h, The mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product 3a.
The substrate 5 (0.1 mmol) and selenosulfonate 2a (0.1 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. DCE (1.0 mL) was injected into the tube. Then the mixture was stirring at room temperature for 72 h.

The substrate 1a (0.2 mmol), sodium 4-methy-benzensulfinate (0.2 mmol) and diphenyl diselenide (0.2 mmol) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. CH$_2$Cl$_2$ (2.0 mL) was injected into the tube. After stirring at room temperature for 12 h, the mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the compound 6 (20% yield).

**IX. Synthetic transformations**

The preparation of compound 7 were followed the literature procedure.$^5$ m-CPBA (0.6 mmol, 1.2 equiv.) was dissolved in 5 mL of CHCl$_3$ and added to a solution of 3a (0.5 mmol, 1 equiv.) in 20 mL of CHCl$_3$. After standing for 10 min at room temperature, the solvent CHCl$_3$ was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EA = 1:10) to afford compound 7 (254.0 mg, 89%).

A solution of KOH (6.34 mmol) in 5 mL of water was added dropwise to 7 (0.2 mmol) in 10 mL of THF. After 5 h at room temperature, the mixture was extracted with EA. The combined organic layers were dried with anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE:EA = 4:1) to afford 8.
m-CPBA (1.2 mmol, 2.4 equiv.) was dissolved in 5 mL of CHCl₃ and added to a solution of 3t (0.5 mmol, 1 equiv.) in 20 mL of CHCl₃. After standing for 10 min at room temperature, the solvent was removed under reduced pressure to afford a residue. Then the residue was dissolved by 20 mL of THF and 5 mL of 1 M aqueous KOH solution was added dropwise. After 1.5 h at room temperature, the mixture was extracted with EA. The combined organic layers were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford 9 (132.0 mg, 76%).

The substrate 1a (0.1 mmol), selenosulfonate 2a (0.1 mmol) and cat.-A (10 mol%) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. CH₂Cl₂ (1.0 mL) was injected into the tube. After stirring at 40 ºC for 5 h, the mixture was evaporated and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product 3a'.

X. ¹H, ¹³C NMR and HRMS data of compounds (1t, 1u, 3a-3u, 4a-4n, 7, 8, 9)

¹H NMR (600 MHz, CDCl₃): δ 7.55 – 7.51 (m, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.26 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 5.86 (s, 1H).

¹³C NMR (150 MHz, CDCl₃): δ 156.44, 131.63, 131.54, 130.43, 128.75, 128.43, 122.32, 120.38, 114.70, 109.54, 96.31, 83.01.


Physical properties: yellow solid; Yield: 95%, 1.84 g; M. p. 70–71 ºC
1 H NMR (600 MHz, CDCl₃): δ 7.44 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.89 – 6.83 (m, 3H), 5.93 (s, 1H), 3.78 (s, 3H).

13 C NMR (150 MHz, CDCl₃): δ 159.92, 156.30, 133.02, 131.48, 130.06, 120.29, 114.58, 114.33, 114.05, 109.87, 96.32, 81.66, 55.21.


Physical properties: yellow solid; Yield: 90%, 1.75 g; M. p. 67–68 °C

1 H NMR (400 MHz, CDCl₃): δ 7.82 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 8.3 Hz, 1H), 7.38 – 7.24 (m, 6H), 7.14 – 6.96 (m, 8H), 6.93 – 6.84 (m, 4H), 2.19 (s, 3H).

13 C NMR (100 MHz, CDCl₃): δ 160.15, 153.19, 144.00, 137.11, 135.87, 135.77, 135.11, 132.19, 132.12, 130.41, 130.27, 128.96, 128.87, 128.58, 128.49, 128.30, 127.86, 127.14, 127.01, 123.55, 122.95, 119.32, 114.29, 21.38.


Physical properties: white solid; Yield: 85%, 94.4 mg; M. p. 171–173 °C

1 H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.09 – 6.97 (m, 5H), 6.94 – 6.83 (m, 6H), 2.23 (s, 3H), 2.18 (s, 3H).

13 C NMR (100 MHz, CDCl₃): δ 160.55, 153.12, 143.95, 137.82, 136.99, 135.79, 132.22, 132.06, 130.11, 128.92, 128.78, 128.50, 128.45, 128.26, 127.81, 127.18, 126.95, 123.52, 123.00, 119.28, 114.43, 21.37, 21.28.


Physical properties: white solid; Yield: 76%, 89.0 mg; M. p. 189–190 °C
**1H NMR** (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.9$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.59 (d, $J = 8.3$ Hz, 1H), 7.40 – 7.23 (m, 6H), 7.02 (t, 3H), 6.98 – 6.89 (m, 4H), 6.85 (q, 4H), 2.20 (s, 3H), 1.21 (s, 9H).

**13C NMR** (100 MHz, CDCl$_3$): $\delta$ 160.70, 153.11, 150.88, 143.75, 137.15, 136.19, 132.27, 132.07, 131.93, 130.17, 129.02, 128.81, 128.47, 128.31, 128.29, 128.12, 127.34, 127.06, 123.98, 123.59, 123.14, 119.20, 114.25, 34.39, 31.20, 21.39.

**HRMS (ESI)** m/z Calcd for [C$_{35}$H$_{32}$NaO$_3$SSe, M + Na]$^+$: 635.1130, Found: 635.1126.

**Physical properties:** white solid; **Yield:** 53%, 61.4 mg; **M. p.:** 212–213 °C

**1H NMR** (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.9$ Hz, 1H), 7.73 (d, $J = 7.4$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.36 – 7.26 (m, 6H), 7.12 – 7.05 (m, 3H), 7.02 (d, $J = 7.1$ Hz, 2H), 6.98 – 6.86 (m, 4H), 6.78 (t, $J = 8.3$ Hz, 2H), 2.20 (s, 3H).

**13C NMR** (100 MHz, CDCl$_3$): $\delta$ 162.20 (d, $J = 258.0$ Hz), 158.78, 153.13, 144.17, 137.09, 135.74, 132.20, 132.10, 131.21, 131.18, 128.95, 128.90, 128.82, 128.51, 128.43, 128.34, 127.07, 126.90, 123.61, 122.86, 119.28, 114.40, 114.18, 21.39.

**HRMS (ESI)** m/z Calcd for [C$_{35}$H$_{32}$FNaO$_3$SSe, M + Na]$^+$: 597.0409, Found: 597.0412.

**Physical properties:** white solid; **Yield:** 81%, 92.9 mg; **M. p.:** 182–184 °C

**1H NMR** (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.9$ Hz, 1H), 7.73 (q, $J = 9.2$ Hz, 1H), 7.44 (d, $J = 8.1$ Hz, 1H), 7.41 – 7.20 (m, 7H), 7.16 – 7.00 (m, 6H), 6.99 – 6.84 (m, 4H), 2.20 (s, 3H).

**13C NMR** (100 MHz, CDCl$_3$): $\delta$ 158.40, 153.13, 144.17, 137.09, 135.74, 132.20, 132.10, 131.21, 131.18, 128.94, 128.58, 128.49, 128.35, 128.26, 127.41, 127.08, 126.69, 123.63, 122.78, 119.34, 118.98, 114.09, 21.42.

**HRMS (ESI)** m/z Calcd for [C$_{35}$H$_{32}$ClNaO$_3$SSe, M + Na]$^+$: 613.0114, Found: 613.0118.

**Physical properties:** white solid; **Yield:** 47%, 55.5 mg; **M. p.:** 171–172 °C

**1H NMR** (400 MHz, CDCl$_3$): $\delta$ 7.99 (s, 2H), 7.85 (d, $J = 8.5$ Hz, 1H), 7.78 – 7.70 (m, 1H), 7.40 (s, 1H), 7.36 – 7.22 (m, 8H), 7.14 – 7.00 (m, 3H), 6.99 – 6.84 (m, 4H), 2.21 (s, 3H).

**13C NMR** (100 MHz, CDCl$_3$): $\delta$ 156.40, 153.25, 146.83, 144.79, 142.40, 137.25, 134.74, 132.54, 131.83, 131.57, 129.42, 129.11, 128.95, 128.84, 128.56, 128.44, 127.18, 125.95, 123.74, 122.43, 119.53, 113.54, 21.43.
**HRMS (ESI) m/z** Calcd for \([C_{31}H_{23}NNaO_5S_e, M + Na]^+\): 624.0354, Found: 624.0355.

**Physical properties:** yellow solid; **Yield:** 61%, 73.3 mg; **M. p.** 120–123 °C

![Chemical structure](image)

**1H NMR** (400 MHz, CDCl₃): δ 7.85 (d, J = 8.9 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.43 – 7.28 (m, 4H), 7.26 – 7.15 (m, 5H), 7.15 – 7.07 (m, 2H), 6.94 (t, J = 7.5 Hz, 3H), 6.87 (d, J = 8.0 Hz, 2H), 2.16 (s, 3H).

**13C NMR** (100 MHz, CDCl₃): δ 158.79, 153.18, 144.45, 137.58, 136.00, 134.24, 132.40, 132.33, 131.90, 131.10, 129.62, 129.28, 129.07, 128.97, 128.80, 128.24, 127.97, 126.72, 126.45, 125.86, 123.62, 123.58, 121.32, 119.71, 113.73, 21.38.

**HRMS (ESI) m/z** Calcd for \([C_{31}H_{23}BrNaO_3S_e, M + Na]^+\): 656.9609, Found: 656.9614.

**Physical properties:** white solid; **Yield:** 47%, 59.6 mg; **M. p.** 175–177 °C

![Chemical structure](image)

**1H NMR** (400 MHz, CDCl₃): δ 7.85 (d, J = 9.4 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 8.9 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.26 – 7.15 (m, 3H), 7.09 (t, J = 8.3 Hz, 3H), 6.93 (t, J = 7.5 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 2.13 (s, 3H).

**13C NMR** (100 MHz, CDCl₃): δ 156.55, 153.12, 144.52, 137.77, 133.98, 133.25, 132.53, 132.47, 131.27, 130.84, 129.95, 129.11, 129.01, 128.83, 128.76, 128.34, 128.22, 127.93, 126.93, 126.18 (q, J = 30.0 Hz), 126.15 (q, J = 5.0 Hz), 125.90, 124.06 (q, J = 272.0 Hz), 123.64, 122.78, 122.77, 119.80, 113.90, 21.34.

**HRMS (ESI) m/z** Calcd for \([C_{32}H_{23}F_3NaO_3S_e, M + Na]^+\): 647.0377, Found: 647.0374.

**Physical properties:** white solid; **Yield:** 30%, 37.4 mg; **M. p.** 201–204 °C

![Chemical structure](image)

**1H NMR** (400 MHz, CDCl₃): δ 7.84 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 10.0 Hz, 2H), 7.43 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.9 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.06 (m, 6H), 7.05 – 6.98 (m, 2H), 6.94 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 2.16 (s, 3H).

**13C NMR** (100 MHz, CDCl₃): δ 154.24, 153.36, 144.79, 144.53, 137.35, 134.12, 132.41, 132.04, 131.26, 130.69, 129.51, 129.09, 128.85, 128.82, 128.75, 128.41, 127.94, 126.75, 126.39, 126.08, 124.56, 123.60, 123.16, 120.56 (q, J = 258.0 Hz), 119.62, 115.77, 113.71, 21.35.

**HRMS (ESI) m/z** Calcd for \([C_{32}H_{23}F_3NaO_4S_e, M + Na]^+\): 663.0327, Found: 663.0330.

**Physical properties:** white solid; **Yield:** 55%, 70.4 mg; **M. p.** 161–163 °C

![Chemical structure](image)

**1H NMR** (400 MHz, CDCl₃): δ 7.81 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.39 – 7.25 (m, 6H), 7.09 – 6.93 (m, 5H), 6.93 – 6.79 (m, 5H), 6.67 (s, 1H), 2.20 (s, 3H), 2.11 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.21, 153.21, 143.80, 137.11, 136.55, 136.20, 134.73, 132.04, 130.34, 128.97, 128.82, 128.55, 128.46, 128.29, 128.08, 127.17, 127.04, 123.54, 123.08, 119.20, 114.21, 21.37, 21.02.

HRMS (ESI) m/z Calcd for [C$_{32}$H$_{26}$NaO$_3$SSe, M + Na]$^+$: 593.0660, Found: 593.0657.

Physical properties: white solid; Yield: 51%, 56.7 mg; M. p. 175–178 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 – 7.79 (m, 2H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.43 (s, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.07 (m, 9H), 6.97 (t, $J = 7.4$ Hz, 2H), 6.85 (d, $J = 7.8$ Hz, 2H), 2.13 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.00, 153.04, 144.72, 137.74, 134.31, 133.74, 132.63, 132.55, 132.37, 131.97, 130.94, 130.79, 129.44, 128.99, 128.90, 128.75, 128.60, 127.99, 127.63 (q, $J = 31.0$ Hz), 126.99, 126.48 (q, $J = 5.0$ Hz), 125.62, 123.70, 123.20 (q, $J = 273.0$ Hz) 122.59, 119.82, 113.73, 21.35.

HRMS (ESI) m/z Calcd for [C$_{32}$H$_{22}$ClF$_3$NaO$_3$SSe, M + Na]$^+$: 680.9988, Found: 680.9989.

Physical properties: white solid; Yield: 31%, 40.8 mg; M. p. 182–184 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 8.9$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.44 – 7.37 (m, 1H), 7.36 – 7.24 (m, 5H), 7.04 (t, $J = 7.3$ Hz, 1H), 7.01 – 6.95 (m, 2H), 6.91 (d, $J = 7.8$ Hz, 4H), 6.63 (s, 1H), 6.57 (s, 2H), 2.22 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): 160.28, 153.24, 143.62, 137.11, 136.57, 136.40, 134.46, 132.36, 131.94, 130.42, 129.17, 128.97, 128.75, 128.50, 128.29, 127.87, 127.29, 127.06, 125.90, 123.52, 123.19, 119.12, 114.17, 21.35, 20.92.

HRMS (ESI) m/z Calcd for [C$_{33}$H$_{28}$NaO$_3$SSe, M + Na]$^+$: 607.0817, Found: 607.0818.

Physical properties: white solid; Yield: 43%, 50.2 mg; M. p. 192–193 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (t, $J = 7.8$ Hz, 2H), 7.57 – 7.50 (m, 2H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.40 – 7.30 (m, 5H), 7.22 (d, $J = 8.9$ Hz, 1H), 7.08 (t, $J = 7.2$ Hz, 1H), 7.00 – 6.89 (m, 6H), 2.25 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.88, 153.39, 144.80, 137.39, 137.27, 135.91, 133.70, 132.44, 131.96, 130.46 (q, $J = 33.0$ Hz), 129.36, 129.29, 129.03, 128.88, 128.55, 128.26, 127.48, 126.18, 123.82, 123.29 (q, $J = 270.0$ Hz), 122.71, 121.13 (t, $J = 4.0$ Hz), 118.75, 113.32, 21.39.

HRMS (ESI) m/z Calcd for [C$_{33}$H$_{22}$F$_6$NaO$_3$SSe, M + Na]$^+$: 715.0251, Found: 715.0249.

Physical properties: white solid; Yield: 46%, 63.6 mg; M. p. 179–182 ºC
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85 (d, $J = 8.9$ Hz, 1H), 7.70 (d, $J = 7.9$ Hz, 1H), 7.43 – 7.14 (m, 10H), 7.11 (t, $J = 7.4$ Hz, 2H), 6.93 (d, $J = 7.9$ Hz, 2H), 2.20 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.23, 145.19, 143.37, 137.00, 134.15, 133.54, 132.88, 131.26, 130.16, 129.20, 128.99, 128.83, 128.21, 127.23, 125.57, 123.74, 122.53, 119.49, 112.45, 21.43.

HRMS (ESI) m/z Calcd for [C$_{31}$H$_{19}$F$_5$NaO$_3$SSe, M + Na]$^+$: 669.0032, Found: 669.0030.

Physical properties: white solid; Yield: 61%, 78.8 mg; M. p. 211–213 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 8.2$ Hz, 1H), 7.45 – 7.34 (m, 3H), 7.33 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.16 (d, $J = 4.5$ Hz, 1H), 7.15 – 7.06 (m, 3H), 7.03 – 6.93 (m, 3H), 6.90 (d, $J = 7.5$ Hz, 2H), 6.77 – 6.70 (m, 1H), 2.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.99, 150.76, 143.93, 136.39, 136.39, 136.38, 135.89, 135.89, 135.38, 134.57, 132.29, 132.04, 130.64, 128.83, 128.58, 128.44, 128.42, 128.29, 128.05, 127.73, 127.18, 126.16, 123.61, 123.16, 119.02, 114.63, 21.40.

HRMS (ESI) m/z Calcd for [C$_{29}$H$_{22}$NaO$_3$SSe, M + Na]$^+$: 585.0068, Found: 585.0070.

Physical properties: white solid; Yield: 46%, 51.7 mg; M. p. 97–99 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (dd, $J = 8.1$, 4.6 Hz, 2H), 7.66 (d, $J = 8.3$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 3H), 7.31 (t, $J = 7.4$ Hz, 1H), 7.25 (d, $J = 6.3$ Hz, 1H), 7.20 (d, $J = 8.9$ Hz, 1H), 7.16 – 7.00 (m, 4H), 7.01 – 6.84 (m, 5H), 6.67 (d, $J = 4.8$ Hz, 1H), 2.21 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.16, 153.04, 143.73, 136.56, 136.51, 134.52, 132.63, 132.27, 131.97, 128.93, 128.84, 128.49, 128.42, 128.38, 128.32, 128.17, 127.45, 127.15, 125.97, 124.15, 123.59, 123.25, 118.96, 114.31, 21.40.

HRMS (ESI) m/z Calcd for [C$_{29}$H$_{22}$NaO$_3$SSe, M + Na]$^+$: 585.0068, Found: 585.0070.

Physical properties: white solid; Yield: 62%, 69.6 mg; M. p. 188–189 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89 (s, 1H), 7.69 (d, $J = 8.9$ Hz, 1H), 7.52 (s, 1H), 7.46 – 7.38 (m, 2H), 7.32 – 7.23 (m, 3H), 7.15 – 7.00 (m, 6H), 6.99 (d, $J = 7.5$ Hz, 2H), 6.95 – 6.80 (m, 4H), 2.23 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.42, 153.67, 144.17, 137.04, 135.91, 134.80, 131.04, 130.84, 130.25, 130.22, 130.11, 130.04, 129.01, 128.66, 128.38, 128.35, 127.91, 127.13, 126.80, 124.86, 120.48, 117.22, 114.41, 21.45.

S15
HRMS (ESI) m/z Calcd for [C_{31}H_{23}BrNaO_{3}SSe, M + Na]^+ : 656.9609, Found: 656.9607.

Physical properties: white solid; Yield: 76%, 94.4 mg; M. p. 172–175 °C

\[ ^{1}H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) : \delta \ 8.07 \ (d, \ J = 8.3 \text{ Hz, 1H}), 7.75 \ (d, \ J = 8.0 \text{ Hz, 1H}), 7.47 \ (t, \ J = 7.4 \text{ Hz, 1H}), 7.40 \ (t, \ J = 7.4 \text{ Hz, 1H}), 7.32 \ (d, \ J = 7.7 \text{ Hz, 2H}), 7.25 \ (s, 2H), 7.07 - 6.94 \ (m, 5H), 6.94 - 6.78 \ (m, 6H), 6.56 \ (s, 1H), 4.06 \ (s, 3H), 2.28 \ (s, 3H). \]

\[ ^{13}C \text{ NMR} \ (100 \text{ MHz, CDCl}_3) : \delta 157.06, 146.81, 144.91, 142.92, 138.53, 136.94, 134.93, 133.52, 129.46, 129.00, 128.54, 128.33, 128.23, 128.21, 128.17, 127.80, 127.52, 127.35, 127.08, 126.81, 125.34, 124.40, 123.94, 114.54, 107.61, 55.99, 21.46. \]

HRMS (ESI) m/z Calcd for [C_{32}H_{26}NaO_{4}SSe, M + Na]^+ : 609.0605, Found: 609.0605.

Physical properties: white solid; Yield: 72%, 84.3 mg; M. p. 171–172 °C

\[ ^{1}H \text{ NMR} \ (600 \text{ MHz, CDCl}_3) : \delta 7.48 \ (s, 4H), 7.40 \ (s, 1H), 7.26 \ (d, \ J = 8.4 \text{ Hz, 2H}), 7.13 \ (d, \ J = 7.7 \text{ Hz, 2H}), 7.10 - 7.05 \ (m, 3H), 6.95 - 6.88 \ (m, 3H), 6.58 \ (d, \ J = 8.1 \text{ Hz, 1H}), 6.54 \ (d, \ J = 7.5 \text{ Hz, 1H}), 6.50 \ (t, \ J = 7.4 \text{ Hz, 1H}), 5.62 \ (s, 1H), 2.35 \ (s, 3H). \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3) : \delta 151.88, 151.78, 143.78, 139.38, 137.47, 136.91, 134.33, 129.88, 129.79, 129.59, 129.11, 128.86, 128.77, 128.30, 128.12, 127.13, 119.96, 116.95, 21.55. \]

HRMS (ESI) m/z Calcd for [C_{27}H_{22}NaO_{3}SSe, M + Na]^+ : 529.0347, Found: 529.0351.

Physical properties: white solid; Yield: 20%, 101.2 mg; M. p. 76–78 °C

\[ ^{1}H \text{ NMR} \ (600 \text{ MHz, CDCl}_3) : \delta 7.42 - 7.29 \ (m, 2H), 7.27 - 7.23 \ (m, 2H), 7.13 \ (d, \ J = 7.6 \text{ Hz, 2H}), 7.07 \ (t, \ J = 7.2 \text{ Hz, 3H}), 7.00 \ (d, \ J = 8.3 \text{ Hz, 2H}), 6.92 \ (dt, \ J = 18.7, 7.1 \text{ Hz, 3H}), 6.59 \ (d, \ J = 8.1 \text{ Hz, 1H}), 6.50 \ (q, \ J = 7.7 \text{ Hz, 2H}), 5.52 \ (s, 1H), 3.88 \ (s, 3H), 2.35 \ (s, 3H). \]

\[ ^{13}C \text{ NMR} \ (150 \text{ MHz, CDCl}_3) : \delta 160.54, 151.99, 151.75, 143.68, 139.20, 137.59, 136.92, 131.83, 129.86, 129.79, 129.10, 128.75, 128.30, 128.07, 127.27, 126.30, 123.78, 120.01, 116.99, 114.32, 55.30, 21.56. \]

HRMS (ESI) m/z Calcd for [C_{28}H_{24}NaO_{4}SSe, M + Na]^+ : 559.0453, Found: 559.0449.

Physical properties: white solid; Yield: 26%, 139.3 mg; M. p. 183–184 °C

\[ ^{1}H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) : \delta 7.79 \ (d, \ J = 8.9 \text{ Hz, 1H}), 7.73 \ (d, \ J = 7.9 \text{ Hz, 1H}), 7.55 \ (d, \ J = 8.3 \text{ Hz, 1H}), 7.50 - 7.38 \ (m, 3H), 7.34 \ (t, \ J = 7.5 \text{ Hz, 1H}), 7.30 - 7.22 \ (m, 3H), 7.18 - 6.94 \ (m, 10H), 6.89 \ (t, \ J = 7.5 \text{ Hz, 2H}). \]
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.49, 153.27, 138.97, 137.06, 134.97, 132.92, 132.16, 130.32, 128.93, 128.58, 128.38, 128.31, 128.22, 127.89, 127.17, 127.11, 126.96, 123.60, 122.89, 119.21, 114.02.

HRMS (ESI) m/z Calcd for [C$_{30}$H$_{22}$NaO$_3$Se, M + Na$^+$]: 565.0347, Found: 565.0349.

Physical properties: white solid; Yield: 59%, 63.9 mg; M. p. 121–123 °C

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J$ = 8.9 Hz, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.48 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 7.25 (d, $J$ = 8.5 Hz, 1H), 7.18 – 6.95 (m, 8H), 6.90 (t, $J$ = 7.6 Hz, 2H), 6.75 (t, $J$ = 8.4 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.20 (d, $J$ = 254.0 Hz), 160.49, 153.24, 137.04, 135.32 (d, $J$ = 2.0 Hz), 134.89, 132.24, 132.11, 131.21, 131.11, 130.51, 128.95, 128.63, 128.48, 128.34, 127.98, 127.32, 127.20, 126.90, 123.76, 122.84, 119.06, 115.43 (d, $J$ = 22.0 Hz), 113.81.

HRMS (ESI) m/z Calcd for [C$_{30}$H$_{21}$FNaO$_3$Se, M + Na$^+$]: 583.0253, Found: 583.0250.

Physical properties: white solid; Yield: 64%, 71.6 mg; M. p. 158–159 °C

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J$ = 8.9 Hz, 1H), 7.77 (d, $J$ = 8.0 Hz, 1H), 7.60 (d, $J$ = 8.4 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.27 – 7.23 (m, 1H), 7.18 (s, 1H), 7.13 – 7.03 (m, 7H), 7.01 (d, $J$ = 7.7 Hz, 3H), 6.90 (t, $J$ = 7.5 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.00, 153.20, 139.58, 137.82, 137.07, 134.85, 132.33, 132.10, 130.27, 129.79, 129.01, 128.68, 128.52, 128.46, 128.38, 128.05, 127.38, 127.22, 126.88, 123.82, 122.84, 119.07, 113.75.

HRMS (ESI) m/z Calcd for [C$_{30}$H$_{21}$ClNaO$_3$Se, M + Na$^+$]: 598.9957, Found: 598.9960.

Physical properties: white solid; Yield: 76%, 87.6 mg; M. p. 166–169 °C

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (t, $J$ = 7.7 Hz, 2H), 7.66 (d, $J$ = 8.4 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.35 (t, $J$ = 7.5 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.19 (m, 3H), 7.13 – 6.92 (m, 8H), 6.88 (t, $J$ = 7.5 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.78, 153.31, 138.66, 137.03, 134.78, 132.24, 132.17, 131.43, 130.64, 129.79, 128.97, 128.63, 128.51, 128.34, 128.10, 127.99, 127.41, 127.17, 126.90, 123.77, 122.91, 118.98, 113.63.

HRMS (ESI) m/z Calcd for [C$_{30}$H$_{21}$BrNaO$_3$Se, M + Na$^+$]: 642.9452, Found: 642.9449.

Physical properties: white solid; Yield: 70%, 86.9 mg; M. p. 110–111 °C
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 8.9$ Hz, 1H), 7.72 (d, $J = 7.9$ Hz, 1H), 7.54 (d, $J = 8.3$ Hz, 1H), 7.45 (s, 1H), 7.36 – 7.23 (m, 5H), 7.07 (s, 5H), 6.86 (d, $J = 7.6$ Hz, 4H), 6.68 (d, $J = 7.7$ Hz, 2H), 2.18 (s, 3H), 2.11 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.30, 153.22, 143.84, 138.68, 136.93, 136.03, 135.15, 132.22, 131.98, 130.30, 129.07, 129.07, 128.89, 128.82, 128.40, 128.40, 128.24, 127.74, 127.05, 126.97, 123.48, 123.41, 123.02, 119.19, 114.21, 21.36, 21.04.

HRMS (ESI) m/z Calcd for [C$_{32}$H$_{26}$NaO$_3$SSe, M + Na]$^+$: 593.0660, Found: 593.0659.

Physical properties: white solid; Yield: 56%, 63.8 mg; M. p. 179 – 181 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 8.9$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.55 (d, $J = 8.3$ Hz, 1H), 7.48 (s, 1H), 7.38 – 7.26 (m, 4H), 7.24 (s, 1H), 7.19 – 6.99 (m, 5H), 6.99 – 6.92 (m, 2H), 6.88 (d, $J = 7.9$ Hz, 2H), 6.57 (t, $J = 8.5$ Hz, 2H), 2.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.91 (d, $J = 248.0$ Hz), 159.30, 153.29, 143.93, 139.13, 139.05, 136.01, 134.91, 132.16, 132.07, 131.01, 128.87, 128.39, 128.30, 127.94, 127.21, 127.06, 123.53, 122.91, 121.95 (d, $J = 3.0$ Hz), 119.18, 115.49 (d, $J = 22.0$ Hz), 115.38, 113.97, 21.36.

HRMS (ESI) m/z Calcd for [C$_{31}$H$_{23}$FNaO$_3$SSe, M + Na]$^+$: 597.0409, Found: 597.0411.

Physical properties: white solid; Yield: 65%, 74.6 mg; M. p. 159 – 161 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 8.9$ Hz, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.56 – 7.47 (m, 2H), 7.37 – 7.22 (m, 5H), 7.18 – 7.00 (m, 5H), 6.99 – 6.78 (m, 6H), 2.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.98, 153.28, 144.02, 138.22, 135.89, 135.19, 134.94, 132.16, 132.14, 131.71, 128.89, 128.48, 128.45, 128.32, 128.12, 127.30, 127.08, 125.22, 123.57, 128.27, 119.24, 114.03, 21.38.

HRMS (ESI) m/z Calcd for [C$_{31}$H$_{23}$ClNaO$_3$SSe, M + Na]$^+$: 613.0114, Found: 613.0115.

Physical properties: white solid; Yield: 75%, 88.5 mg; M. p. 158 – 160 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 8.9$ Hz, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.69 (d, $J = 8.1$ Hz, 1H), 7.40 (s, 1H), 7.35 – 7.28 (m, 2H), 7.18 – 7.15 (m, 5H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 3H), 6.71 (t, $J = 7.6$ Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.95, 153.16, 143.91, 142.74, 138.89, 135.88, 135.28, 132.37, 131.97, 130.95, 129.48, 128.89, 128.83, 128.43, 128.27, 128.03, 127.94, 126.98, 126.93, 125.79, 123.52, 123.02, 119.27, 114.54, 23.21, 21.37.

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HRMS (ESI) m/z Calcd for [C$_{32}$H$_{26}$Na$_3$O$_3$Se, M + Na]$^+$: 593.0660, Found: 593.0662.

Physical properties: white solid; Yield: 61%, 69.5 mg; M. p. 188–191 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J$ = 8.8 Hz, 1H), 7.72 (d, $J$ = 7.8 Hz, 1H), 7.59 (d, $J$ = 8.2 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.17 (m, 7H), 7.17 – 7.01 (m, 5H), 6.97 (t, $J$ = 7.7 Hz, 1H), 6.87 (d, $J$ = 7.9 Hz, 2H), 6.77 (t, $J$ = 7.5 Hz, 1H), 2.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.25, 153.23, 143.97, 140.06, 139.59, 135.82, 134.96, 132.25, 132.12, 131.43, 130.57, 129.04, 128.84, 128.44, 128.23, 128.15, 127.79, 127.02, 126.48, 123.60, 123.13, 119.17, 114.11, 21.38.

HRMS (ESI) m/z Calcd for [C$_{31}$H$_{23}$ClNa$_3$O$_3$Se, M + Na]$^+$: 613.0114, Found: 613.0113

Physical properties: white solid; Yield: 66%, 77.9 mg; M. p. 197–199 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J$ = 8.9 Hz, 1H), 7.72 (d, $J$ = 7.6 Hz, 1H), 7.58 (d, $J$ = 8.0 Hz, 1H), 7.37 – 7.23 (m, 9H), 7.15 (d, $J$ = 7.6 Hz, 1H), 7.12 – 7.05 (m, 3H), 6.87 (d, $J$ = 7.9 Hz, 3H), 6.82 (t, $J$ = 7.5 Hz, 1H), 2.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.42, 153.18, 144.03, 139.59, 135.75, 134.97, 132.42, 132.29, 132.16, 131.72, 131.32, 130.51, 130.28, 128.90, 128.85, 128.49, 128.25, 128.21, 127.12, 127.06, 127.00, 123.61, 123.19, 119.23, 114.12, 21.38.

HRMS (ESI) m/z Calcd for [C$_{31}$H$_{23}$BrNa$_3$O$_3$Se, M + Na]$^+$: 656.9609, Found: 656.9610

Physical properties: white solid; Yield: 54%, 68.5 mg; M. p. 189–191 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J$ = 8.9 Hz, 1H), 7.72 (d, $J$ = 7.8 Hz, 1H), 7.52 (d, $J$ = 8.1 Hz, 1H), 7.39 (s, 1H), 7.36 – 7.22 (m, 5H), 7.07 (s, 5H), 6.92 – 6.71 (m, 6H), 2.18 (s, 3H), 2.02 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.27, 153.20, 143.90, 137.99, 137.73, 135.94, 135.04, 133.87, 132.18, 132.04, 130.25, 129.25, 128.92, 128.84, 128.44, 128.25, 128.05, 127.77, 126.97, 126.94, 126.73, 123.51, 123.00, 119.23, 114.18, 21.36, 20.79.

HRMS (ESI) m/z Calcd for [C$_{32}$H$_{26}$Na$_3$O$_3$Se, M + Na]$^+$: 593.0660, Found: 593.0663.

Physical properties: white solid; Yield: 79%, 90.0 mg; M. p. 187–189 ºC

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J$ = 8.9 Hz, 1H), 7.74 (d, $J$ = 6.8 Hz, 1H), 7.47 (d, $J$ = 8.0 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.25 (m, 5H), 7.18 – 7.07 (m, 5H), 7.02 (d, 1H), 6.96 (s, 1H), 6.89 (t, $J$ = 8.4 Hz, 3H), 6.83 (t, $J$ = 7.8 Hz, 1H), 2.20 (s, 3H).

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\[ {^1}H\text{ NMR (400 MHz, CDCl}_3\text{):} \delta 7.81 (d, J = 8.9 \text{ Hz, 1H}), 7.73 (d, J = 7.8 \text{ Hz, 1H}), 7.51 (d, J = 8.1 \text{ Hz, 1H}), 7.42 - 7.24 (m, 6H), 7.24 - 7.07 (m, 5H), 6.89 (d, J = 7.9 \text{ Hz, 2H}), 6.82 - 6.69 (m, 2H), 6.69 - 6.60 (m, 1H), 2.20 (s, 3H). \]

\[ {^13}C\text{ NMR (100 MHz, CDCl}_3\text{):} \delta 158.58 (d, J = 241.0 \text{ Hz}), 158.30, 157.28 (d, J = 244.0 \text{ Hz}), 153.34, 153.52, 153.77, 132.37, 132.01, 131.75, 128.94, 128.54, 128.39, 128.30, 124.98, 124.74, 123.70, 122.83, 119.31, 118.31 (d, J = 8.0 \text{ Hz}), 118.08 (d, J = 7.8 \text{ Hz}), 115.97 (d, J = 8.0 \text{ Hz}), 115.70 (d, J = 8.0 \text{ Hz}), 113.86, 21.41. \]

HRMS (ESI) m/z Calcd for \([\text{C}_{31}\text{H}_{24}\text{F}_{2}\text{NaO}_{4}\text{SSe, M + Na}^+]\): 615.0315, Found: 615.0313.

Physical properties: white solid; Yield: 64%, 75.7 mg; M. p. 203–204 °C

\[ {^1}H\text{ NMR (400 MHz, CDCl}_3\text{):} \delta 8.01 (d, J = 8.3 \text{ Hz, 1H}), 7.80 (d, J = 8.1 \text{ Hz, 1H}), 7.74 (d, J = 8.8 \text{ Hz, 1H}), 7.63 (t, J = 7.6 \text{ Hz, 1H}), 7.48 - 7.30 (m, 7H), 7.30 - 7.20 (m, 5H), 6.94 (d, J = 8.0 \text{ Hz, 3H}), 6.80 (d, J = 7.7 \text{ Hz, 2H}), 2.25 (s, 3H). \]

\[ {^13}C\text{ NMR (100 MHz, CDCl}_3\text{):} \delta 155.60, 154.16, 146.43, 143.96, 137.63, 136.64, 134.25, 132.34, 131.66, 130.73, 129.34, 129.13, 128.68, 128.47, 128.32, 127.88, 127.66, 127.14, 126.78, 126.05, 124.35, 123.55, 118.61, 111.07, 21.52. \]

HRMS (ESI) m/z Calcd for \([\text{C}_{31}\text{H}_{24}\text{NaO}_{4}\text{SSe, M + Na}^+]\): 595.0453, Found: 595.0458.

Physical properties: white solid; Yield: 89%, 254.0 mg; M. p. 123–126 °C
$^1$H NMR (400 MHz, CDCl$_3$): δ 9.15 (d, $J = 8.5$ Hz, 1H), 7.92 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.9$ Hz, 1H), 7.80 – 7.68 (m, 4H), 7.66 (d, $J = 8.9$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.55 – 7.44 (m, 4H), 7.14 (d, $J = 8.0$ Hz, 2H), 2.29 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 160.35, 151.91, 143.89, 139.45, 131.43, 130.82, 130.41, 129.55, 129.15, 129.01, 128.41, 127.74, 127.07, 126.99, 126.61, 126.11, 125.25, 119.95, 118.93, 111.82, 21.47.

HRMS (ESI) m/z Calcd for [C$_{25}$H$_{18}$NaO$_3$S, M + Na]$^+$: 421.0869, Found: 421.0862.

Physical properties: white solid; Yield: 95%, 76.0 mg; M. p. 167–168 ºC

$^1$H NMR (600 MHz, CDCl$_3$): δ 8.09 – 8.03 (m, 1H), 7.82 (d, $J = 7.1$ Hz, 2H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.43 – 7.37 (m, 4H), 7.29 – 7.25 (m, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 2.21 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): δ 158.70, 153.16, 144.08, 139.43, 130.78, 130.05, 129.51, 128.14, 128.10, 126.66, 125.87, 125.47, 124.51, 121.62, 118.72, 111.36, 21.44.


Physical properties: white solid; Yield: 76%, 132.0 mg; M. p. 112–114 ºC

XI. HPLC traces of compound 3a’

(3a’) HPLC analysis: Chiralcel AD-H (Hexane/i-PrOH = 80:20), flow rate = 1.0 mL/min, wave length = 254 nm, $t_R$ = 13.251 min (minor), $t_R$ = 19.035 min (major).
XII. $^1$H and $^{13}$C NMR spectra of compounds (1t, 1u, 3a-3u, 4a-4n, 7, 8, 9)
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XIII. X-Ray Crystallographic information

Bond precision: C-C = 0.0049 Å
Wavelength = 0.71073 Å

Cell:
\[ a = 14.8543 (4) \quad b = 12.8156 (3) \quad c = 16.9743 (5) \]
\[ \alpha = 90 \quad \beta = 105.20 (3) \quad \gamma = 90 \]

Temperature: 295 K

Volume:
Calculated: 3120.95 (15)
Reported: 3120.94 (15)

Space group:
P 21/c
P 1 21/c 1

Hall group:
P 2ybc
-P 2ybc

Moiety formula:
C31 H23 Br O3 S Se [+ solvent]
C31 H23 Br O3 S Se

Sum formula:
C31 H23 Br O3 S Se [+ solvent]
C24 H17 Br O3 S Se

Mr:
634.41
634.42

Dx, g cm\(^{-3}\):
1.350
1.350

Z:
4
4

Mu (mm\(^{-1}\)):
2.577
2.577

F000:
1272.0
1272.0

F000’:
1271.47

h, k, l max:
18, 16, 21
18, 16, 21

Nref:
6391
6378

Tmin, Tmax:
0.352, 0.366
0.691, 1.000

Tmin’:
0.326

Correction method = MULTI
AbsCorr = MULTI-SCAN

T Limits: Tmin=0.691  Tmax=1.000

Data completeness = 0.998
Theta(max) = 26.372

R(reflections) = 0.0435 (4724)
wR2(reflections) = 0.1184 (6378)
Npar = 336
XIV. Reference