Supporting Information

Serendipitous Formation of Various Selenium Heterocycles Hidden in the Classical Synthesis of Selenophene

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1. General

All reactions were conducted under \( \text{N}_2 \) by using standard Schlenk techniques. Glassware was pre-dried at 120 °C. Solvents were treated as follows: \( \text{CH}_3\text{CN} \) was distilled from \( \text{P}_2\text{O}_5 \), \( \text{Et}_2\text{O} \) (pure for analysis), \( \text{CH}_2\text{Cl}_2 \) (pure for analysis), hexane (pure for analysis) were used as received. 1-Bromobutadiynes were obtained according to the known procedures.\(^1\) Piperidine (puriss p.a.), \( N \)-methylbenzylamine (97%), 2-methylaminomethyl-1,3-dioxolane (98%), morpholine (99%), diethyamine (99%), NaBH\(_4\) (96%), diphenyl diselenide (98%), Se (puriss p.a) and Te (99.5%) were used as received.

\(^1\)\(^H\) and \(^{13}\)C NMR spectra were recorded with a 500 MHz spectrometer with an inverse broadband probe. \(^{77}\)Se NMR spectra were recorded with a 600 MHz spectrometer with an inverse broadband probe. A solution of diphenyl diselenide in CDCl\(_3\) at 25 °C in a sealed capillary was used as an external standard (\( \delta = 463 \) ppm).\(^2\) For all the \(^1\)H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks (CDCl\(_3\), \(^1\)H: 7.26 ppm, \(^{13}\)C: 77.16 ppm). Coupling constants are given in Hz. HRMS spectra were recorded using a spectrometer with an ESI ion source and TOF or ICR ion analyser. For HRMS analysis the monoisotopic \( m/z \) values and isotope patterns were calculated using enviPat 2.4.\(^3\) \(^{80}\)Se was used for calculation of monoisotopic peaks.

Details of X-ray data collection and reduction

X-ray diffraction data were collected with the use of \( \omega \) scan technique. The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix, least-squares on \( F^2 \) by use of the SHELXTL Package.\(^4\) Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined.
2. Synthesis

Scheme S1. Test reactions.

A) [Chemical reaction diagram]

B) [Chemical reaction diagram]

C) [Chemical reaction diagram]
**Two-step procedure:** *Synthesis of ynamine.* Bromobutadiyne (1a, 0.138 g, 0.600 mmol) was dissolved in dry MeCN (10 mL) and placed in screw-sealed 20 mL vial. Next Na$_3$PO$_4$ (0.197 g, 1.20 mmol) and diethyl amine (0.093 mL, 0.90 mmol) were added. Mixture was stirred at 40 °C (aluminum heating block on magnetic stirrer with heating) for 1 h and after that time 10 mL of diethyl ether was added. Reaction mixture was passed through alumina plug (basic, Brockmann grade I, Et$_2$O) and next solvents were evaporated yielding ynamine as red oil. Crude ynamine was used without further purification.

*Reaction with Na$_2$Se.* NaBH$_4$ (0.120 g, 3.17 mmol), selenium (0.118 g, 1.49 mmol) and water (2 mL) were placed in N$_2$ purged Schlenk flask. The mixture was degassed with the use of freeze-pump-thaw technique and next stirred for 30 min. at room temperature. Next ynamine was dissolved in oxygen-free MeCN (30 mL) and added to the reaction mixture. Orange solution was stirred at 60 °C (oil bath on magnetic stirrer with heating) for 20 h under N$_2$ atmosphere. After that time solvent was removed under reduced pressure and crude product was purified with the use of column chromatography (Al$_2$O$_3$, basic, Brockmann grade I, CH$_2$Cl$_2$/Et$_2$O; v/v; 4/1 to pure Et$_2$O). Pure 3aa was obtained as red solid (0.153 g, 0.201 mmol), yield: 67%.

**Single step procedure:** Bromobutadiyne (1a, 0.138 g, 0.600 mmol) was dissolved in dry MeCN (10 mL) and placed in Schlenk flask. Next Na$_3$PO$_4$ (0.197 g, 1.20 mmol) and diethyl amine (0.093 mL, 0.90 mmol) were added. Reaction mixture was stirred at 40°C for 1 h and. At the same time NaBH$_4$ (0.120 g, 3.17 mmol), selenium (0.118 g, 1.49 mmol) and water (2 mL) were placed in second Schlenk flask, degassed by freeze-pump-thaw technique and stirred for 0.5 h. After that time the water solution of sodium selenide and 40 mL of degassed MeCN
were added to the first flask. Reaction mixture was heated to 60°C and stirred overnight at this temperature. After this time solvent was evaporated under reduced pressure and crude product was purified with the use of column chromatography (Al₂O₃, basic, Brockmann grade I, CH₂Cl₂) yielding pure product as a red solid (0.116 g, 0.152 mmol), yield: 51%

1H NMR (500 MHz, Chloroform-d) δ = 7.48 – 7.41 (m, 4H), 7.34 – 7.27 (m, 4H), 5.96 (s, 2H), 3.27 (q, J=7.2, 8H), 1.22 (t, J=7.1, 12H).

13C NMR (126 MHz, Chloroform-d) δ = 160.5, 141.0, 131.8, 129.2, 128.5, 124.5, 119.4, 109.8, 109.0, 48.3, 12.5.

77Se NMR (114 MHz, Chloroform-d) δ = 607.2 (selenophene), 446.8 (diselenide bridge).

FTIR (cm⁻¹, ATR, Ge): 697, 737, 1089, 1176, 1208, 1414, 1435, 1506, 1538, 1596, 2218, 2854, 2924.

HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₃₀H₃₀N₄NaSe₄ 788.9024; Found 788.9034.

Melting point range: 96-99 °C.

(3ab) 4,4'-(Diselanediylbis(5-(piperidin-1-yl)selenophene-3,2-diyl))dibenzonitrile

1-Bromobutadiyne (1a, 0.231 g, 1.00 mmol), piperidine (0.119 mL, 1.20 mmol), Na₃PO₄ (0.395 g, 2.40 mmol) and MeCN (10 mL) were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Selenium (0.238 g, 3.00 mmol), NaBH₄ (0.228 g, 6.02 mmol), water (2 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al₂O₃ (basic, Brockmann grade I, hexane/CH₂Cl₂; v/v; 1/2 to 0/1). Orange solid (0.172 g, 0.219 mmol), yield: 44%, new compound.
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta = 7.51 – 7.45$ (m, 4H), $7.33 – 7.28$ (m, 4H), $6.15$ (s, 2H), $3.12 – 3.07$ (m, 8H), $1.76 – 1.68$ (m, 8H), $1.62$ (tq, $J = 8.4, 4.4, 3.7, 4H$).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta = 163.9, 140.9, 131.9, 131.7, 129.6, 123.9, 119.3, 112.8, 109.7, 52.6, 25.3, 23.7$.

$^{77}$Se NMR (114 MHz, Chloroform-$d$) $\delta = 616.4$ (selenophene), $447.6$ (diselenide bridge).

FTIR (cm$^{-1}$, ATR, Ge): $825, 1119, 1237, 1377, 1457, 1505, 1529, 1597, 2220, 2853$.

HRMS (ESI-TOF) $m/z$: [M+Na]$^+$ Calcd for $C_{32}H_{30}N_4NaSe_8$ 812.9024; Found 812.9027.

Melting point range: 132-134 °C.

(3ac) 4,4''-(Diselenediylbis(5-(((1,3-dioxolan-2-yl)methyl)(methyl)amino)selenophene-3,2-diyl))dibenzonitrile

1-Bromobutadiyne (1a, 0.061 g, 0.27 mmol), $I$-1,3-(dioxolan-2-yl)-N-methylmethanamine (0.046 mL, 0.40 mmol), $Na_3PO_4$ (0.090 g, 0.531 mmol) and MeCN were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Selenium (0.045 g, 0.57 mmol), $NaBH_4$ (0.045 g, 1.21 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: $Al_2O_3$ (basic, Brockmann grade I, CH$_2$Cl$_2$ to CH$_2$Cl$_2$/Et$_2$O; v/v; 1/1, Et$_2$O). yellow solid (0.075 g, 0.088 mmol), yield: 65%, new compound.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta = 7.47 – 7.45$ (m, 4H), $7.28 – 7.25$ (m, 4H), $6.00$ (s, 2H), $5.10$ (t, $J = 3.9$ Hz, 2H), $4.05 – 3.95$ (m, 4H), $3.93– 3.89$ (m, 4H), $4.05$ (d, $J = 3.9$ Hz, 4H), $3.02$ (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta = 161.9, 140.8, 131.8, 130.7, 129.5, 123.9, 119.4, 110.8, 109.3, 101.9, 65.3, 59.3, 42.1$. 

S7
Se NMR (114 MHz, Chloroform-\textit{d}) \( \delta = 611.2 \) (selenophene), 444.9 (diselenide bridge).

FTIR (cm\(^{-1}\), ATR, diamond): 734, 837, 1037, 1096, 1144, 1357, 1417, 1430, 1507, 1539, 1596, 2221, 2888, 3078.

HRMS (ESI-TOF) \( m/z \): [M+Na]\(^+\) Calcd for C\(_{32}\)H\(_{30}\)N\(_4\)O\(_4\)NaSe\(_4\) 876.8820; Found 876.8825.

Melting point range: 142-143 \(^\circ\)C.

\((3\text{ad})\) 4,4'-(Diselanediyldibis(5-(benzyl(methyl)amino)selenophene-3,2-diyl))dibenzonitrile

1-Bromobutadiyne (1\text{a}, 0.154 g, 0.669 mmol), \textit{N}-methylbenzylamine (0.13 mL, 1.01 mmol), Na\(_3\)PO\(_4\) (0.219 g, 1.34 mmol) and MeCN were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Selenium (132 mg, 1.67 mmol), NaBH\(_4\) (0.134 g, 3.48 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al\(_2\)O\(_3\) (basic, Brockmann grade I, CH\(_2\)Cl\(_2\) to CH\(_2\)Cl\(_2\)/THF; v/v; 5/1). Red solid (0.177 g, 0.206 mmol), yield: 62%, new compound.

\(^1\)H NMR (500 MHz, Chloroform-\textit{d}) \( \delta = 7.45 - 7.42 \) (m, 4H), 7.38 - 7.27 (m, 14H), 6.06 (s, 2H), 4.39 (s, 4H), 2.93 (s, 6H).

\(^{13}\)C NMR (126 MHz, Chloroform-\textit{d}) \( \delta = 162.0, 140.7, 136.4, 131.7, 129.9, 129.3, 128.9, 127.9, 127.5, 124.2, 119.2, 110.8, 109.3, 60.4, 40.5.

\(^{77}\)Se NMR (114 MHz, Chloroform-\textit{d}) \( \delta = 612.2 \) (selenophene), 447.3 (diselenide bridge).

FTIR (cm\(^{-1}\), ATR, Ge): 732, 827, 1100, 1113, 1357, 1378, 1448, 1510, 1539, 1598, 2222, 2929, 2971.

HRMS (ESI-TOF) \( m/z \): [M+Na]\(^+\) Calcd for C\(_{38}\)H\(_{30}\)N\(_4\)NaSe\(_4\) 884.9029; Found 884.9030.

Melting point range: 137-140 \(^\circ\)C.
(3bb) 1,2-Bis(2-(4-fluorophenyl)-5-(piperidin-1-yl)selenophen-3-yl)diselane

1-Bromobutadiyne (1b, 0.063 g, 0.24 mmol), piperidine (0.04 mL, 0.28 mmol), Na₃PO₄ (0.096 g, 0.57 mmol) and MeCN (10 mL) were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Selenium (0.054 g, 0.69 mmol), NaBH₄ (0.051 g, 1.38 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al₂O₃ (basic, Brockmann grade I, Et₂O). Orange solid (0.058 g, 0.075 mmol), yield: 63%, new compound.

¹H NMR (500 MHz, Chloroform-d) δ 7.22 – 7.18 (m, 4H), 6.97 – 6.92 (m, 4H), 6.17 (s, 2H), 3.08 – 3.04 (m, 8H), 1.73 – 1.68 (m, 8H), 1.61 – 1.56 (m, 4H).
¹³C NMR (126 MHz, Chloroform-d) δ 162.8, 162.1 (C-F, J_CF = 247.4 Hz), 133.4, 132.4 (C-F, J_CF = 3.4 Hz), 131.3 (C-F, J_CF = 7.9 Hz), 122.0 , 115.1 (C-F, J_CF = 21.6 Hz), 112.4, 52.9, 25.4, 23.8.
⁷⁷Se NMR (114 MHz, Chloroform-d) δ = 615.3, 441.0.
FTIR (cm⁻¹, ATR, diamond): 826, 1233, 1381, 1447, 1509, 2855, 2938.
HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C₃₀H₃₁F₂N₂Se₄ 776.9116; Found 776.9111.
Melting point range: 134-137 °C.

(4cb) Ethyl (Z)-2-(5-(piperidin-1-yl)-3H-1,2-diselenol-3-ylidene)acetate

1-Bromobutadiyne (1c, 0.050 g, 0.276 mmol), piperidine (0.041 mL, 0.414 mmol), Na₃PO₄ (0.094 g, 0.552 mmol) and MeCN were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Selenium (0.054 g, 0.69 mmol), NaBH₄ (0.054 g, 1.46 mmol), water (1 mL) and degassed MeCN (20 mL) were used
for the second step according to the procedure for 3aa. Purification: Al₂O₃ (basic, Brockmann grade I, Et₂O). Orange solid (0.043 g, 0.118 mmol), yield: 43%, new compound.

¹H NMR (500 MHz, Chloroform-d) δ = 6.57 (s, 1H), 6.12 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.45 – 3.40 (m, 4H), 1.68 (dd, J = 10.7, 5.8 Hz, 4H), 1.65 – 1.61 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ = 172.2, 170.1, 168.7, 102.1, 96.9, 60.2, 53.0, 25.6, 23.9, 14.8.

⁷⁷Se NMR (114 MHz, Chloroform-d) δ = 644.0, 391.6.

FTIR (cm⁻¹, ATR, diamond): 1045, 1119, 1143, 1301, 1403, 1443, 1483, 1607, 1730, 2854, 2933.

HRMS (ESI-TOF) m/z: [M+H]^+ Calcd for C₁₂H₁₈NO₂Se₂ 367.9668; Found 367.9660.

Melting point range: 139 -142 ℃.

(4cc) Ethyl (Z)-2-((5-(((1,3-dioxolan-2-yl)methyl)(methyl)amino)-3H-1,2-diselenol-3-ylidene)acetate

1-Bromobutadiyne (1c, 0.074 g, 0.40 mmol), 1-(1,3-dioxolan-2-yl)-N-methylmethanamine (0.69 mL, 0.60 mmol), Na₃PO₄ (0.137 g, 0.806 mmol) and MeCN were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Selenium (0.066 g, 0.841 mmol), NaBH₄ (0.064 g, 1.749 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al₂O₃ (basic, Brockmann grade I, Et₂O). Orange oil (0.062 g, 0.16 mmol), yield: 40%, new compound.

¹H NMR (500 MHz, Chloroform-d) δ = 6.52 (s, 1H), 6.14 (s, 1H), 5.09 (t, J = 4.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.99 (dd, J = 8.8, 5.2 Hz, 2H), 3.89 (dd, J = 7.7, 6.2 Hz, 2H), 3.57 (d, J = 4.0 Hz, 2H), 3.19 (s, 3H), 1.30 (t, J = 7.1 Hz, 4H).
$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 172.4, 170.1, 168.3, 102.3, 102.2, 96.8, 65.3, 60.3, 59.6, 43.1, 14.8.

$^{77}$Se NMR (114 MHz, Chloroform-$d$) $\delta = 668.4, 388.1$.

FTIR (cm$^{-1}$, ATR, diamond): 1041, 1142, 1245, 1315, 1393, 1476, 1603, 1690, 2891.

HRMS (ESI-TOF) $m/z$: [M+Na]$^+$ Calcd for C$_{12}$H$_{17}$NO$_4$NaSe$_2$ 421.9386; Found 421.9383.

(5ab) 4-(5-(Piperidin-1-yl)tellurophen-2-yl)benzonitrile

![Chemical Structure](image)

1-Bromobutadiyne (1a, 0.069 g, 0.30 mmol), piperidine (0.042 mL, 0.36 mmol), Na$_3$PO$_4$ (0.123 g, 0.750 mmol) and MeCN (10 mL) were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Tellurium (0.084 g, 0.66 mmol), NaBH$_4$ (0.059 g, 1.56 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al$_2$O$_3$ (basic, Brockmann grade I, hexane/CH$_2$Cl$_2$; v/v; 2/1 to 0/1). Yellow solid (0.045 g, 0.12 mmol), yield: 40%, new compound.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta = 7.61$ (d, $J = 4.8$ Hz, 1H), 7.51 – 7.48 (m, 2H), 7.33 – 7.30 (m, 2H), 6.24 (d, $J = 4.8$ Hz, 1H), 3.18 – 3.14 (m, 4H), 1.73 – 1.70 (m, 4H), 1.62 – 1.60 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta = 165.2, 145.3, 135.8, 132.6, 126.7, 125.4, 119.6, 112.0, 107.9, 55.1, 25.5, 23.9$.

FTIR (cm$^{-1}$, ATR, diamond): 765, 824, 1118, 1234, 1444, 1375, 1596, 2213, 2857, 2940.

HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for C$_{16}$H$_{17}$N$_2$Te 367.0454; Found 367.0440.

Melting point range: 184-186 °C
(5ac) 4-(5-(((1,3-Dioxolan-2-yl)methyl)(methyl)amino)tellurophen-2-yl)benzonitrile

1-Bromobutadiyne (1a, 0.069 g, 0.30 mmol), 1-(1,3-dioxolan-2-yl)-N-methylmethanamine (0.041 mL, 0.36 mmol), Na$_3$PO$_4$ (0.118 g, 0.72 mmol) and MeCN (10 mL) were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Tellurium (0.084 g, 0.66 mmol), NaBH$_4$ (0.059 g, 1.56 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al$_2$O$_3$ (basic, Brockmann grade I, hexane/CH$_2$Cl$_2$; v/v; 2/1 to 0/1). Yellow solid (0.061 g, 0.15 mmol), yield: 50%, new compound.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ = 7.62 (d, $J = 4.8$ Hz, 1H), 7.49 – 7.46 (m, 2H), 7.31 – 7.27 (m, 2H), 6.07 (d, $J = 4.8$ Hz, 1H), 5.13 (t, $J = 3.8$ Hz, 1H), 4.03 – 3.98 (m, 2H), 3.89 – 3.87 (m, 2H), 3.45 (d, $J = 3.8$ Hz, 2H), 3.10 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 162.6, 145.4, 136.1, 132.7, 125.3, 125.2, 119.7, 110.3, 107.7, 102.5, 65.3, 61.5, 44.2.

FTIR (cm$^{-1}$, ATR, diamond): 753, 829, 1036, 1283, 1409, 1503, 1598, 2219, 2897, 2963.

HRMS (ESI-TOF) $m/z$: [M+Na]$^+$ Calcd for C$_{16}$H$_{16}$N$_2$O$_2$NaTe 421.0172; Found 421.0169.

Melting point range: 175-178 °C

(5ad) 4-(5-(Benzyl(methyl)amino)tellurophen-2-yl)benzonitrile

1-Bromobutadiyne (1a, 0.231 g, 1.00 mmol), N-benzylmethylamine (0.155 mL, 1.20 mmol), Na$_3$PO$_4$ (0.412 g, 2.51 mmol) and MeCN (10 mL) were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Tellurium (0.282 g, 2.21 mmol), NaBH$_4$ (0.198 g, 5.22 mmol), water (2 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al$_2$O$_3$
(basic, Brockmann grade I, hexane/CH₂Cl₂; v/v; 2/1 to 0/1). Orange oil (0.143 g, 0.357 mmol), yield: 36%, new compound.

¹H NMR (500 MHz, Chloroform-d) δ = 7.62 (d, J = 4.8 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.35 – 7.33 (m, 3H), 7.29 – 7.25 (m, 4H), 6.08 (d, J = 4.8 Hz, 1H), 4.47 (s, 2H), 3.06 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 162.4, 145.3, 136.6, 136.0, 132.7, 129.0, 128.0, 127.5, 125.5, 125.2, 119.7, 110.4, 107.7, 62.8, 42.7.

FTIR (cm⁻¹, ATR, diamond): 740, 826, 1068, 1291, 1410, 1503, 1598, 1626, 2217, 2938, 3030.

HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₉H₁₆N₂TeNa 425.0273; Found 425.0260.

(5ae) 4-(5-Morpholinotellurophen-2-yl)benzonitrile

![Chemical structure](image)

1-Bromobutadiyne (1a, 0.088 g, 0.38 mmol), morpholine (0.051 mL, 0.57 mmol), Na₃PO₄ (0.131 g, 0.772 mmol) and MeCN (10 mL) were used in a first step according to the procedure for 3aa and next crude ynamine was used without further purification. Tellurium (0.120 g, 0.940 mmol), NaBH₄ (0.074 g, 1.99 mmol), water (1 mL) and degassed MeCN (20 mL) were used for the second step according to the procedure for 3aa. Purification: Al₂O₃ (basic, Brockmann grade I, Et₂O). Yellow solid (0.103 g, 0.282 mmol), yield: 74%, new compound.

¹H NMR (500 MHz, Chloroform-d) δ = 7.62 (d, J = 4.7 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.37 – 7.34 (m, 2H), 6.37 (d, J = 4.8 Hz, 1H), 3.85 – 3.82 (m, 4H), 3.16 – 3.13 (m, 4H).

¹³C NMR (126 MHz, Chloroform-d) δ = 164.8, 144.9, 135.2, 132.6, 129.1, 125.8, 119.4, 113.4, 108.7, 66.4, 53.7.

FTIR (cm⁻¹, ATR, diamond): 548, 760, 1110, 1205, 1492, 1595, 2213, 2846, 2918, 2983.

HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₁₅H₁₄N₂OTe 368.0168; Found 368.0170.

Melting point range: 191-194°C.
3. X-Ray Crystallography Details

All monocrystals used for X-ray measurements were grown by slow evaporation of CH$_2$Cl$_2$/n-hexane solutions placed in 10 mL vials. Vials were closed using polypropylene caps with short needle pierced through the cap.

Table S1. X-ray crystallography details.

|                | 3aa                      | 3ab                      | 4cb                      |
|----------------|--------------------------|--------------------------|--------------------------|
| Chemical formula | C$_{30}$H$_{30}$N$_4$Se$_4$ | C$_{32}$H$_{34}$N$_4$Se$_4$ | C$_{12}$H$_{17}$NO$_2$Se$_2$ |
| $M_r$          | 762.42                   | 786.44                   | 365.18                   |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/c$ |
| Temperature (K) | 100                      | 100                      | 100                      |
| $a$, $b$, $c$ (Å) | 14.742 (4), 7.523 (2), 26.893 (7) | 5.4827 (2), 27.7015 (6), 19.6107 (5) | 7.915 (2), 15.836 (4), 11.278 (3) |
| $α$, $β$, $γ$ (°) | 90, 95.83 (3), 90        | 90, 95.339 (2), 90       | 90, 109.84 (3), 90      |
| $V$ (Å$^3$)    | 2967.1 (14)              | 2965.53 (15)             | 1329.7 (6)               |
| $Z$            | 4                        | 4                        | 4                        |
| Radiation type | Mo $Kα$                  | Mo $Kα$                  | Mo $Kα$                  |
| $μ$ (mm$^{-1}$) | 4.97                     | 4.98                     | 5.55                     |
| Crystal size (mm) | 0.9 × 0.8 × 0.34       | 0.71 × 0.13 × 0.10       | 0.50 × 0.32 × 0.06       |
| Diffractometer | Kuma KM-4 CCD            | Kuma KM-4 CCD            | Kuma KM4 CCD             |
| Absorption correction | Analytical               | Analytical               | Analytical               |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 20533, 7278, 3552 | 26724, 6728, 5482 | 17242, 5595, 3996 |
| $R_{int}$      | 0.163                    | 0.069                    | 0.078                    |
| (sin θ/λ)$_{max}$ (Å$^{-1}$) | 0.678                     | 0.651                    | 0.845                    |
| $R(F^2 > 2σ(F^2))$, $wR(F^2)$, $S$ | 0.097, 0.280, 1.03 | 0.058, 0.157, 1.11 | 0.058, 0.166, 1.01 |
| No. of reflections | 7278                      | 6728                     | 5595                     |
| No. of parameters | 350                       | 361                      | 155                      |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained | H-atom parameters constrained |
| $Δρ_{max}$, $Δρ_{min}$ (e Å$^{-3}$) | 1.50, −1.37               | 1.26, −0.70              | 1.86, −2.34              |
**Figure S1.** Molecular structure of 3aa; thermal ellipsoids set at 50% probability.

**Figure S2.** Molecular structure of 3ab; thermal ellipsoids set at 50% probability.
Figure S3. Molecular structure of 4cb; thermal ellipsoids set at 50% probability.
4. NMR spectra

(3aa) 4,4'-(Diselanediylbis(5-(diethylamino)selenophene-3,2-diyl))dibenzonitrile

\[
\text{NMR spectra}
\]

\[
\begin{align*}
\text{ppm} & \quad 7.44 & \quad 7.48 & \quad 7.50 & \quad 7.36 & \quad 7.32 & \quad 7.28 \\
\end{align*}
\]

\[
\text{ppm} & \quad 9.5 & \quad 9.0 & \quad 8.5 & \quad 8.0 & \quad 7.5 & \quad 7.0 & \quad 6.5 & \quad 6.0 & \quad 5.5 & \quad 5.0 & \quad 4.5 & \quad 4.0 & \quad 3.5 & \quad 3.0 & \quad 2.5 & \quad 2.0 & \quad 1.5 & \quad 1.0 & \quad 0.5 & \quad 0.0 \\
\end{align*}
\]

\[
\begin{align*}
\text{ppm} & \quad 190 & \quad 180 & \quad 170 & \quad 160 & \quad 150 & \quad 140 & \quad 130 & \quad 120 & \quad 110 & \quad 100 & \quad 90 & \quad 80 & \quad 70 & \quad 60 & \quad 50 & \quad 40 & \quad 30 & \quad 20 & \quad 10 & \quad 0 \\
\end{align*}
\]
(3ab) 4,4’-(Diselenediylbis(5-(piperidin-1-yl)selenophene-3,2-diyl))dibenzonitrile
(3ac) 4,4’-(Diselanediylbis(5-(((1,3-dioxolan-2-yl)methyl)(methyl)amino)selenophene-3,2-diyl))dibenzonitrile
(3ad) 4,4’-(Diselanediylbis(5-(benzyl(methyl)amino)selenophene-3,2-diyl))dibenzonitrile
(3bb) 1,2-Bis(2-(4-fluorophenyl)-5-(piperidin-1-yl)selenophen-3-yl)diselane
(4cb) Ethyl (Z)-2-(5-(piperidin-1-yl)-3H-1,2-diselenol-3-ylidene)acetate
(4cc) Ethyl (Z)-2-((1,3-dioxolan-2-yl)methyl)(methyl)amino)-3H-1,2-diselenol-3-ylidene)acetate
(5ab) 4-(5-(Piperidin-1-yl)tellurophen-2-yl)benzonitrile
(5ac) 4-(5-(((1,3-Dioxolan-2-yl)methyl)(methyl)amino)tellurophen-2-yl)benzonitrile
(5ad) 4-(5-(Benzyl(methyl)amino)tellurophen-2-yl)benzonitrile
(5ae) 4-(5-Morpholinotellurophen-2-yl)benzonitrile
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