Electronic Supplementary Information

for

Electrochemical Selenocyclization of 2-Ethynylanilines with Diselenides: A Facile and Efficient Access to 3-Selenylindoles

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1. General and experimental details

1.1 General information

All commercially available reagents (AR grade) were directly used as received without further purification. The electrochemical reactions were performed on DJS-292B potentiostats (made in China) in constant current mode with high purity metal or graphite electrodes (> 99.99%). All yields of products refer to the isolated yields after chromatography that performed on 200 ~ 300 mesh silica gel with PE (petroleum ether) / EtOAc or PE / DCM (dichloromethane) as eluents. After each electrochemical reaction, the electrodes were washed with EtOAc, DCM and/or acetone, then deionized water and/or 1.0 M HCl, and wiped with lens tissue; if necessary, gentle polish was further conducted using 2000 and 8000 mesh sandpapers.

¹H NMR (400 MHz), ¹³C NMR (101 MHz) and ¹⁹F NMR (376 MHz) spectra were recorded on a Bruker AV-400 spectrometer with CDCl₃ as the solvent. For ¹H NMR, the signal of CDCl₃ (δ = 7.26 ppm) or tetramethylsilane (TMS, δ = 0.00 ppm) serves as the internal standard; for proton decoupled ¹³C {¹H} NMR, the signal of CDCl₃ (δ = 77.16 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration. GC-MS analysis was performed on a 7890A-5975C/Agilent. HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. Cyclic voltammetry studies were conducted on an IKA ElectraSyn 2.0 with a glassy carbon working electrode, a Pt plate counter electrode and an Ag/AgCl reference electrode (filled with 3.0 M KCl aq.).

2-Ethynylaniline substrates 1a - 38a were prepared by the methods described in our previous work (and the references therein)^[1]. Diselenide substrates 2b - 4b were synthesized by means of a reported method ^[2], while 1b, 5b, 6b, disulfide 7b, and ditelluride 8b were purchased form commercial sources. All the characterization data of known substrates were in good agreement with those reported previously: (1a - 4a, 6a - 16a, 18a - 24a, 26a, 28a - 38a)^[1], 5a ^[3], 17a ^[4], (2b - 4b) ^[2].

1.2 General procedure for the electrochemical selenocyclization



To a 10 mL reaction tube with a magnetic stir bar were added substrates **a** (0.2 mmol) and **b** (0.13 mmol, 0.65 equiv), followed by electrolyte ${}^{n}Bu_{4}NPF_{6}$ (15.5 mg, 0.04 mmol, 0.2 equiv) and solvent MeCN (5.0 mL, 0.04 M to **a**, 0.008 M to ${}^{n}Bu_{4}NPF_{6}$). For substrates **35a** and **38a** which showed poor solubility, additional 5.0 mL DCM and 0.2 equiv of ${}^{n}Bu_{4}NPF_{6}$ were added. Then the tube was equipped with two platinum plate electrodes ($10 \times 10 \times 0.2$ mm, 6 mm apart, the plates were totally immersed in the solution). The 5 mA (5 mA/cm²) constant current electrolysis was performed at room temperature under air atmosphere with 600 rpm magnetic stirring. After the indicated time as determined by TLC analysis (2 - 4 h, 1.87 - 3.73 F/mol, the voltages generally ranged from ~3.5 V to ~4.5 V during the electrolysis), the electrodes were detached from the power source and rinsed with EtOAc or DCM, and the resulting mixture was transferred to a flask to have the solvent removed under reduced pressure. Further purification by column chromatography on silica gel (eluted with EtOAc/PE or DCM/PE) afforded the desired product **c**.

For some substrates with distinct incomplete conversion (*in all these cases, no more obvious conversion of a was observed at 3 or 4 h, as monitored by TLC analysis*), the unreacted 2-ethynylanilines were recovered by column chromatography along with the isolation of desired products c.

On the basis of the isolated yield of **c** and the corresponding recovered **a**, the yields *b.r.s.m*. (based on the recovered starting material) were calculated as follows:

Yield b.r.s.m. of $c = \frac{\text{Isolated yield of } c}{1 - \text{Recovered yield of } a}$



Fig. S1 Setup for the electrochemical selenocyclization.

1.3 Procedure for the gram-scale electrosynthesis



Substrates **1a** (1.04 g, 3.0 mmol), **1b** (609 mg, 1.95 mmol, 0.65 equiv) and ${}^{n}Bu_{4}NPF_{6}$ (232 mg, 0.6 mmol, 0.2 equiv) were placed in a 50 mL beaker with a magnetic stir bar. Solvent MeCN (50 mL, 0.06 M to **1a**, 0.012 M to ${}^{n}Bu_{4}NPF_{6}$) was then added, after which the mixture was stirred for several minutes until the dissolution of all solid compounds. The beaker was equipped with two Pt

electrodes (20 x 20 x 0.2 mm, fixed on the paperboard, approximately 1 cm apart), and the system was electrolyzed with 30 mA (7.5 mA/cm²) constant current. The reaction was monitored by TLC, which revealed the disappearance of **1a** at 5 h (1.87 F/mol, the voltage ranged from ~5.5 V to ~6.5 V during the electrolysis). The resulting mixture was then transferred to a flask to have the solvent removed under reduced pressure. Further purification by column chromatography on silica gel afforded the desired product **1c** as a white solid (1.43g, 95%).





Fig. S2 Setup for the gram-scale electrosynthesis.

2. Characterization data

2.1 Characterization data for unreported substrates



25a: 4-iodo-N-(2-(phenylethynyl)phenyl)benzenesulfonamide

Light yellow solid, <u>m. p.</u>: 112 – 115 °C.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 7.76 – 7.65 (m, 2H), 7.62 (d, J = 8.3 Hz, 1H), 7.53 – 7.36 (m, 8H),

7.35 – 7.29 (m, 1H), 7.23 – 7.15 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 138.8, 138.4, 137.1, 132.3, 131.7, 129.9, 129.4, 128.8, 128.7, 125.4,

122.0, 121.4, 115.5, 101.0, 96.4, 83.7.

<u>HRMS</u> (ESI) calculated for C₂₀H₁₅INO₂S⁺ m/z [M+H]⁺: 459.9863, found: 459.9859.



27a: 1-phenyl-*N*-(2-(phenylethynyl)phenyl)methanesulfonamide

Light yellow solid, <u>m. p.</u>: 92 – 94 °C.

1 <u>H NMR</u> (400 MHz, CDCl₃) δ 7.68 (dd, J = 8.4, 1.1 Hz, 1H), 7.51 (dd, J = 7.8, 1.6 Hz, 1H), 7.39 –

7.30 (m, 6H), 7.29 – 7.20 (m, 5H), 7.12 (td, *J* = 7.6, 1.1 Hz, 1H), 6.98 (s, 1H), 4.39 (s, 2H).

¹³<u>C NMR</u> (101 MHz, CDCl₃) *δ* 138.1, 132.4, 131.7, 130.9, 130.1, 129.2, 129.0, 128.5, 128.2, 124.1,

121.9, 117.5, 113.2, 97.2, 83.4, 57.8.

<u>HRMS</u> (ESI) calculated for $C_{21}H_{18}NO_2S^+$ m/z [M+H]⁺: 348.1053, found: 348.1049.

2.2 Characterization data for products



1c: 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **1a** and **1b** as the substrates (in 0.2 mmol scale); the gram-scale reaction was run with 30 mA CCE for 5 h (1.87 F/mol) with **1a** and **1b** (in 3.0 mmol scale).

White solid, <u>m. p.</u>: 164 – 165 °C.

93.5 mg, 0.186 mmol, <u>93% isolated yield</u>.

Gram-scale: 1.43g, 2.85 mmol, 95% isolated yield.

 $\underline{^{1}\text{H NMR}} (400 \text{ MHz}, \text{CDCl}_{3}) \delta 8.42 - 8.33 \text{ (m, 1H)}, 7.49 - 7.36 \text{ (m, 5H)}, 7.36 - 7.30 \text{ (m, 4H)}, 7.29 \text{ (m, 2H)}, 7.29 \text{ (m, 2H)}$

- 7.23 (m, 1H), 7.13 - 7.00 (m, 5H), 6.98 - 6.89 (m, 2H), 2.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.0, 137.7, 135.2, 132.3, 132.0, 131.8, 131.1, 129.6, 129.4, 129.3,

129.2, 127.3, 127.1, 126.2, 125.9, 124.8, 121.4, 116.4, 110.7, 110.7, 21.8.



2c: 3-(phenylselanyl)-2-(p-tolyl)-1-tosyl-1H-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **2a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 161 – 162 °C.

101.6 mg, 0.196 mmol, <u>98% isolated yield</u>.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.36 (dt, J = 8.5, 1.0 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.11 – 7.06 (m, 3H), 7.05 – 7.00 (m, 2H), 6.97 – 6.89 (m, 2H), 2.43 (s, 3H), 2.34 (s, 3H).

<u>13C NMR</u> (101 MHz, CDCl₃) δ 145.3, 145.0, 139.3, 137.7, 135.1, 132.4, 132.1, 131.6, 129.5, 129.3, 129.1, 128.1, 127.0, 126.1, 125.7, 124.8, 121.3, 116.5, 110.4, 21.7, 21.7.



3c: 2-(4-methoxyphenyl)-3-(phenylselanyl)-1-tosyl-1H-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **3a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 169 – 171 °C.

102.4 mg, 0.192 mmol, 96% isolated yield.

 $\frac{^{1}\text{H NMR}}{^{1}\text{H OMR}}$ (400 MHz, CDCl₃) δ 8.37 (d, J = 8.4 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.33 – 7.21 (m, 5H), 7.12 – 7.00 (m, 5H), 6.97 – 6.86 (m, 4H), 3.86 (s, 3H), 2.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.4, 145.1, 144.9, 137.7, 135.1, 133.1, 132.4, 132.1, 129.5, 129.2, 129.1, 127.0, 126.1, 125.7, 124.8, 123.1, 121.2, 116.5, 112.8, 110.2, 77.5, 77.2, 76.8, 55.4, 21.7.



4c: 2-(4-fluorophenyl)-3-(phenylselanyl)-1-tosyl-1*H*-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **4a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 140 – 141 °C.

59.4 mg, 0.114 mmol, <u>57% isolated yield</u>.

Recovered substrate 4a:19.7 mg (0.054 mmol, 27%), 78% yield b.r.s.m.

 $\frac{^{1}\text{H NMR}}{^{5}\text{H}} (400 \text{ MHz, CDCl}_{3}) \delta 8.37 (\text{dt}, J = 8.5, 0.9 \text{ Hz}, 1\text{H}), 7.51 - 7.38 (\text{m}, 2\text{H}), 7.33 - 7.22 (\text{m}, 5\text{H}), 7.13 - 7.00 (\text{m}, 7\text{H}), 6.96 - 6.87 (\text{m}, 2\text{H}), 2.34 (\text{s}, 3\text{H}).$

 $\frac{^{13}\text{C NMR}}{^{13}\text{C NMR}}$ (101 MHz, CDCl₃) δ 163.4 (d, J = 249.3 Hz), 145.2, 143.9, 137.7, 135.1, 133.7 (d, J = 8.3 Hz), 132.2, 131.8, 129.6, 129.4, 129.2, 127.0 (d, J = 4.4 Hz), 126.3, 126.0, 124.9, 121.4, 116.4, 114.5 (d, J = 21.9 Hz), 111.0, 21.8.



5c: 2-(3-chlorophenyl)-3-(phenylselanyl)-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 3 h (2.80 F/mol) with **5a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, m. p.: 138 - 141 °C.

89.1 mg, 0.166 mmol, <u>83% isolated yield</u>.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.36 (d, J = 8.4 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H), 7.35 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 7.15 – 7.02 (m, 6H), 7.00 – 6.92 (m, 2H), 2.35 (s, 3H). ¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 145.3, 143.0, 137.6, 135.1, 133.2, 132.8, 132.0, 131.6, 130.0, 129.8, 129.7, 129.3, 129.2, 128.6, 127.0, 126.5, 126.2, 124.9, 121.5, 116.3, 111.4, 21.8. <u>HRMS</u> (ESI) calculated for C₂₇H₂₁ClNO₂SSe⁺ m/z [M+H]⁺: 538.0141, found: 538.0143.



6c: 2-(2-chlorophenyl)-3-(phenylselanyl)-1-tosyl-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 3 h (2.80 F/mol) with **6a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 145 – 148 °C.

96.6 mg, 0.180 mmol, 90% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃)) δ 8.32 (d, J = 8.4 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.41 (td, J = 7.4, 1.4 Hz, 2H), 7.30 (td, J = 7.4, 1.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.12 – 7.03 (m, 5H), 2.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.3, 140.7, 137.0, 136.2, 135.6, 133.5, 131.2, 131.1, 130.9, 130.8, 130.2, 129.7, 129.3, 129.1, 127.3, 126.4, 125.9, 125.8, 124.3, 121.5, 115.4, 110.9, 21.8.
 <u>HRMS</u> (ESI) calculated for C₂₇H₂₁ClNO₂SSe⁺ m/z [M+H]⁺: 538.0141, found: 538.0141.



7c: 4-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)benzonitrile^[5]

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with 7a and 1b as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 218 – 220 °C.

70.6 mg, 0.134 mmol, <u>67% isolated yield</u>.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.35 (dd, J = 8.5, 1.8 Hz, 1H), 7.67 (dd, J = 8.2, 2.0 Hz, 2H), 7.53 – 7.40 (m, 4H), 7.35 – 7.21 (m, 3H), 7.15 – 7.07 (m, 3H), 7.04 (td, J = 7.5, 7.1, 1.9 Hz, 2H), 6.89 (dd, J = 7.6, 2.1 Hz, 2H), 2.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.5, 142.5, 137.8, 135.9, 134.6, 132.3, 132.3, 131.4, 131.0, 129.7, 129.5, 129.3, 126.9, 126.6, 126.6, 125.2, 121.7, 118.8, 116.5, 112.8, 112.6, 21.8.



8c: tert-butyl (3-(3-(phenylselanyl)-1-tosyl-1H-indol-2-yl)phenyl)carbamate

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **8a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 71 - 74 °C.

69.2 mg, 0.112 mmol, 56% isolated yield.

Recovered substrate 8a: 37.0 mg (0.08 mmol, 40%), <u>93% yield b.r.s.m.</u>

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.35 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.47 – 7.35 (m, 4H), 7.33 – 7.23 (m, 2H), 7.23 – 7.18 (m, 1H), 7.14 – 7.01 (m, 5H), 7.00 – 6.91 (m, 3H), 6.48 (s, 1H), 2.34 (s, 3H), 1.52 (s, 9H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 152.6, 145.0, 144.3, 137.6, 135.1, 132.1, 131.9, 131.8, 129.8, 129.7, 129.6, 129.1, 128.0, 127.2, 126.3, 126.2, 125.8, 124.7, 121.9, 121.4, 119.2, 116.3, 110.7, 80.7, 28.5, 21.7.

<u>HRMS</u> (ESI) calculated for $C_{32}H_{31}N_2O_4SSe^+$ m/z [M+H]⁺: 619.1164, found: 619.1160.



9c: 2-(naphthalen-2-yl)-3-(phenylselanyl)-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **9a** and **1b** as the substrates (in 0.2 mmol scale).

Light brown solid, m. p.: 157 – 159 °C.

88.4 mg, 0.160 mmol, 80% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.41 (d, J = 8.4 Hz, 1H), 7.94 – 7.83 (m, 2H), 7.75 (dd, J = 7.5, 1.7 Hz, 1H), 7.64 (s, 1H), 7.58 – 7.48 (m, 4H), 7.45 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.14 – 7.02 (m, 5H), 7.01 – 6.93 (m, 2H), 2.34 (s, 3H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 145.1, 144.9, 137.8, 135.1, 133.6, 132.4, 132.3, 132.1, 131.2, 129.6, 129.5, 129.3, 129.2, 128.7, 128.5, 128.0, 127.1, 127.0, 126.7, 126.4, 126.3, 125.9, 124.8, 121.4, 116.5, 111.4, 21.7.

HRMS (ESI) calculated for C₃₁H₂₄NO₂SSe⁺ m/z [M+H]⁺: 554.0687, found: 554.0684.



10c: 3-(phenylselanyl)-2-(thiophen-2-yl)-1-tosyl-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with 10a and 1b as

the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 135 – 137 °C.

80.3 mg, 0.158 mmol, 79% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.36 (d, J = 8.5 Hz, 1H), 7.52 – 7.36 (m, 5H), 7.30 – 7.21 (m, 2H),

7.14 – 6.97 (m, 9H), 2.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.1, 137.9, 137.4, 135.2, 132.4, 131.9, 131.7, 130.7, 129.8, 129.6, 129.2, 128.8, 127.1, 126.4, 126.4, 126.2, 124.7, 121.5, 116.3, 113.1, 21.8.
 <u>HRMS</u> (ESI) calculated for C₂₅H₂₀NO₂S₂Se⁺ m/z [M+H]⁺: 510.0095, found: 510.0094.



11c: 2-(ferrocen-1-yl)-3-(phenylselanyl)-1-tosyl-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **11a** and **1b** as the substrates (in 0.2 mmol scale).

Red viscous oil.

12.1 mg, 0.020 mmol, 10% isolated yield.

Recovered substrate 11a: 45.5 mg (0.100 mmol, 50%), 20% yield b.r.s.m.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.24 (d, J = 8.3 Hz, 1H), 7.40 – 7.18 (m, 3H), 7.12 – 6.90 (m, 7H),

6.76 (d, *J* = 7.7 Hz, 2H), 5.02 (s, 2H), 4.43 (s, 2H), 4.16 (s, 5H), 2.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.7, 144.5, 139.1, 134.6, 133.3, 132.3, 129.2, 129.1, 128.9, 127.4,

126.0, 125.5, 125.2, 120.6, 118.5, 112.0, 72.7, 70.5, 68.3, 21.8.

<u>HRMS</u> (ESI) calculated for $C_{31}H_{26}FeNO_2SSe^+ m/z$ [M+H]⁺: 612.0193, found: 612.0192.



12c: 2-(cyclohex-1-en-1-yl)-3-(phenylselanyl)-1-tosyl-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **12a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 125 – 127 °C.

74.7 mg, 0.148 mmol, 74% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.27 (d, J = 8.3 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.38 – 7.30 (m, 2H), 7.22 – 7.13 (m, 3H), 7.08 (d, J = 3.2 Hz, 5H), 5.45 (tt, J = 3.8, 1.6 Hz, 1H), 2.85 – 2.54 (m, 1H), 2.34 (s, 3H), 2.25 – 2.16 (m, 2H), 2.10 – 1.93 (m, 1H), 1.88 – 1.56 (m, 4H). <u>¹³C NMR</u> (101 MHz, CDCl₃) δ 147.3, 144.9, 137.1, 135.6, 132.5, 132.2, 132.1, 130.9, 129.6, 129.5, 129.1, 127.0, 126.1, 125.3, 124.3, 121.3, 115.6, 108.4, 30.8, 25.7, 22.7, 21.9, 21.7. <u>HRMS</u> (ESI) calculated for C₂₇H₂₆NO₂SSe⁺ m/z [M+H]⁺: 508.0844, found: 508.0847.



13c: 2-(*tert*-butyl)-3-(phenylselanyl)-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **13a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 93 – 96 °C.

25.8 mg, 0.054 mmol, 27% isolated yield.

Recovered substrate 13a: 30.1 mg (0.092 mmol, 46%), 50% yield b.r.s.m.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.06 (d, J = 8.3 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.20 (dt, J = 8.4, 4.3 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.06 – 6.98 (m, 6H), 6.91 (d, J = 7.7 Hz, 2H), 2.30 (s, 3H), 1.79 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.7, 144.3, 140.1, 134.9, 133.0, 132.0, 129.7, 129.1, 128.9, 127.4, 126.3, 125.2, 125.1, 121.2, 118.4, 116.2, 37.5, 32.5, 21.7.

HRMS (ESI) calculated for C₂₅H₂₆NO₂SSe⁺ m/z [M+H]⁺: 484.0844, found: 508.0847.



14c: *tert*-butyl 4-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)piperidine-1-carboxylate Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **14a** and **1b** as the substrates (in 0.2 mmol scale). Light yellow solid, m. p.: 77 - 80 °C.

48.8 mg, 0.080 mmol, 40% isolated yield.

Recovered substrate 14a: 39.2 mg (0.086 mmol, 43%), 70% yield b.r.s.m.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.32 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.29 – 7.24 (m, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.13 – 7.08 (m, 3H), 7.04 – 6.98 (m, 2H), 4.11 (d, J = 13.1 Hz, 2H), 3.80 (tt, J = 12.1, 3.4 Hz, 1H), 2.65 (t, J = 13.0 Hz, 2H), 2.40 (s, 3H), 2.31 (qd, J = 12.5, 4.2 Hz, 2H), 1.48 – 1.36 (m, 11H). ¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 155.1, 147.5, 145.5, 137.2, 137.0, 132.3, 131.9, 130.2, 129.3, 128.5, 126.5, 126.0, 125.4, 124.2, 120.6, 115.4, 105.9, 79.7, 44.9, 36.1, 30.9, 28.6, 21.8.

HRMS (ESI) calculated for C₃₁H₃₅N₂O₄SSe⁺ m/z [M+H]⁺: 611.1477, found: 611.1473.



15c: 2-butyl-3-(phenylselanyl)-1-tosyl-1*H*-indole^[6]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **15a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 74 - 76 °C.

90.7 mg, 0.188 mmol, 94% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.21 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.7 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.24 – 7.14 (m, 3H), 7.10 – 6.97 (m, 5H), 3.30 – 3.20 (m, 2H), 2.34 (s, 3H), 1.70 – 1.58 (m, 2H), 1.38 (h, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H). <u>¹³C NMR</u> (101 MHz, CDCl₃) δ 147.3, 145.0, 137.2, 136.0, 132.1, 132.0, 129.9, 129.2, 129.0, 128.9,

 $128.9,\,126.4,\,126.1,\,125.0,\,124.3,\,120.7,\,115.4,\,108.1,\,33.4,\,28.4,\,22.8,\,21.7,\,13.9.$



16c: 5-methyl-2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole^[7]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **16a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 157 – 160 °C.

96.7 mg, 0.192 mmol, 96% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.23 (d, J = 8.4 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.34 (m, 2H), 7.34 – 7.27 (m, 4H), 7.27 – 7.20 (m, 2H), 7.12 – 6.99 (m, 5H), 6.91 (dt, J = 7.8, 1.1 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 145.3, 144.9, 135.9, 135.1, 134.6, 132.6, 132.2, 131.7, 131.1, 129.5, 129.3, 129.1, 129.1, 127.3, 127.2, 127.0, 126.0, 121.1, 116.2, 110.4, 21.7, 21.5.



17c: 5-methoxy-2-phenyl-3-(phenylselanyl)-1-tosyl-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **17a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 114 – 116 °C.

104.4 mg, 0.196 mmol, <u>98% isolated yield</u>.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.25 (dd, J = 9.0, 1.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.27 (td, J = 7.6, 6.6, 1.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 3H), 7.07 – 6.97 (m, 3H), 6.93 (d, J = 7.8 Hz, 2H), 6.86 (s, 1H), 3.72 (s, 3H), 2.35 (s, 3H). ¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 157.5, 145.8, 144.9, 134.9, 133.7, 132.1, 131.9, 131.7, 131.1, 129.5, 129.4, 129.3, 129.2, 127.3, 127.0, 126.2, 117.7, 114.9, 110.9, 103.4, 55.7, 21.8. <u>HRMS</u> (ESI) calculated for C₂₈H₂₄NO₃SSe⁺ m/z [M+H]⁺: 534.0637, found: 534.0640.



18c: 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole-5-carbonitrile

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **18a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 141 – 143 °C.

87.1 mg, 0.166 mmol, <u>83% isolated yield</u>.

 $\frac{1}{14} \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 8.48 (dd, J = 8.8, 1.8 \text{ Hz}, 1\text{H}), 7.81 (d, J = 1.8 \text{ Hz}, 1\text{H}), 7.65 (dd, J = 8.7, 1.8 \text{ Hz}, 1\text{H}), 7.52 - 7.45 (m, 1\text{H}), 7.39 (td, J = 7.7, 1.9 \text{ Hz}, 2\text{H}), 7.32 - 7.21 (m, 4\text{H}), 7.16 - 7.05 (m, 5\text{H}), 7.00 - 6.94 (m, 2\text{H}), 2.37 (s, 3\text{H}).$ $\frac{1^{3}\text{C NMR}}{101} (101 \text{ MHz, CDCl}_3) \delta 146.9, 145.8, 139.5, 135.0, 132.3, 131.8, 130.8, 130.0, 129.9, 129.8, 130.8, 130.0, 129.9, 129.8, 130.8, 130.0, 129.9, 129.8, 130.8, 130.0, 129.9, 129.8, 130.8, 130.8, 130.0, 129.9, 129.8, 130.8, 130.8, 130.0, 129.9, 129.8, 130.8$

129.4, 128.7, 127.5, 127.1, 126.9, 126.2, 119.3, 117.1, 109.9, 108.2, 21.8.

HRMS (ESI) calculated for C₂₈H₂₁N₂O₂SSe⁺ m/z [M+H]⁺: 529.0483, found: 529.0487.



19c: 2-phenyl-3-(phenylselanyl)-1-tosyl-5-(trifluoromethyl)-1H-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 3 h (2.80 F/mol) with **19a** and **1b** as the substrates (in 0.2 mmol scale).

Colorless viscous oil.

105.0 mg, 0.184 mmol, <u>92% isolated yield</u>.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.49 (d, J = 8.8 Hz, 1H), 7.77 (s, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.33 – 7.21 (m, 4H), 7.13 – 7.02 (m, 5H), 6.99 – 6.91 (m, 2H), 2.34 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 146.5 145.6 139.1, 135.1 132.1, 131.8 131.3 130.4 129.9 129.8, 129.6, 129.3, 127.4, 127.1, 127.0 (q, J = 32.6 Hz), 126.6, 124.5 (q, J = 271.9 Hz), 122.4 (q, J = 3.5 Hz), 118.8 (q, J = 4.1 Hz), 116.6, 110.4, 21.8.



20c: 6-bromo-2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **20a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 161 – 164 °C.

94.2 mg, 0.162 mmol, 81% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.57 (d, J = 1.9 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.41 – 7.33 (m,

3H), 7.33 - 7.22 (m, 5H), 7.15 - 7.01 (m, 5H), 6.97 - 6.88 (m, 2H), 2.36 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.4, 145.3, 138.2, 135.0, 131.8, 131.5, 131.0, 130.6, 129.7, 129.5,

129.2, 128.1, 127.3, 127.1, 126.4, 122.5, 119.4, 119.3, 110.2, 21.8.

HRMS (ESI) calculated for C₂₇H₂₁BrNO₂SSe⁺ m/z [M+H]⁺: 581.9636, found: 581.9641.



21c: methyl 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole-6-carboxylate

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **21a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 134 – 136 °C.

91.9 mg, 0.164 mmol, 82% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 9.07 (d, J = 1.5 Hz, 1H), 7.97 (dd, J = 8.4, 1.6 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.35 – 7.28 (m, 4H), 7.14 – 7.08 (m, 3H), 7.07 – 7.02 (m, 2H), 6.97 – 6.91 (m, 2H), 3.99 (s, 3H), 2.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.4, 147.7, 145.4, 137.1, 135.9, 135.0, 131.7, 131.5, 130.6, 129.7,
129.6, 129.2, 127.6, 127.4, 127.2, 126.5, 125.9, 121.1, 118.1, 110.5, 52.5, 21.8.

<u>HRMS</u> (ESI) calculated for $C_{29}H_{24}NO_4SSe^+ m/z [M+H]^+$: 562.0586, found: 562.0590.



22c: 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-pyrrolo[2,3-b]pyridine^[6]

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **22a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 185 – 186 °C.

62.0 mg, 0.124 mmol, <u>62% isolated yield</u>.

Recovered substrate 22a: 20.9 mg (0.060 mmol, 30%), 89% yield b.r.s.m.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.52 (q, J = 2.1 Hz, 1H), 7.85 (d, J = 7.9 Hz, 2H), 7.71 (dd, J = 7.7, 2.0 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.40 (d, J = 7.3 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.14 – 7.02 (m, 5H), 2.37 (s, 3H).

<u>13C NMR</u> (101 MHz, CDCl₃) δ 149.5, 145.7, 145.2, 144.9, 135.9, 131.4, 131.3, 131.0, 130.1, 130.0, 129.6, 129.5, 129.4, 129.3, 128.1, 127.6, 126.6, 124.4, 120.1, 106.6, 21.8.



23c: 1-((4-methoxyphenyl)sulfonyl)-2-phenyl-3-(phenylselanyl)-1H-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **23a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 141 – 142 °C.

80.9 mg, 0.156 mmol, 78% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.37 (d, J = 8.4 Hz, 1H), 7.49 – 7.30 (m, 9H), 7.30 – 7.23 (m, 1H),

7.11 - 6.99 (m, 3H), 6.97 - 6.89 (m, 2H), 6.79 - 6.69 (m, 2H), 3.78 (s, 3H).

¹³<u>C NMR</u> (101 MHz, CDCl₃) *δ* 163.9, 145.1, 137.7, 132.3, 132.0, 131.8, 131.1, 129.7, 129.3, 129.3,

129.2, 127.3, 126.2, 125.8, 124.8, 121.3, 116.5, 114.1, 110.6, 55.8.



24c: 1-((4-nitrophenyl)sulfonyl)-2-phenyl-3-(phenylselanyl)-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **24a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 213 – 215 °C.

101.4 mg, 0.190 mmol, 95% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.35 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.53 – 7.37 (m, 5H), 7.36 – 7.28 (m, 3H), 7.11 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.4 Hz, 2H), 6.97 (d, J = 7.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 150.7, 144.3, 142.9, 137.4, 132.5, 131.8, 131.3, 130.5, 129.9, 129.8, 129.3, 128.3, 127.6, 126.7, 126.4, 125.6, 124.1, 121.9, 116.4, 112.6.

HRMS (ESI) calculated for C₂₆H₁₉N₂O₄SSe⁺ m/z [M+H]⁺: 535.0225, found: 535.0222.



25c: 1-((4-iodophenyl)sulfonyl)-2-phenyl-3-(phenylselanyl)-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **25a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 175 – 177 °C.

110.6 mg, 0.180 mmol, 90% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.34 (d, J = 8.6 Hz, 1H), 7.65 (dd, J = 8.6, 2.0 Hz, 2H), 7.49 – 7.36

(m, 5H), 7.34 - 7.24 (m, 3H), 7.14 - 7.04 (m, 5H), 6.93 (d, <math>J = 6.9 Hz, 2H).

 $\frac{^{13}\text{C NMR}}{(101 \text{ MHz, CDCl}_3)} \delta 144.7, 138.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 137.4, 132.5, 131.8, 130.8, 129.5, 129.3, 128.2, 137.6, 130.8, 129.5, 129.3, 128.2, 137.6, 130.8, 129.5,$

127.4, 126.4, 126.1, 125.2, 121.6, 116.5, 111.6, 101.9.

<u>HRMS</u> (ESI) calculated for C₂₆H₁₉INO₂SSe⁺ m/z [M+H]⁺: 615.9341, found: 615.9342.



26c: 2-phenyl-3-(phenylselanyl)-1-(pyridin-3-ylsulfonyl)-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **26a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 158 – 160 °C.

53.4 mg, 0.109 mmol, <u>55% isolated yield</u>.

Recovered substrate 26a: 26.1 mg (0.078 mmol, 39%), 90% yield b.r.s.m.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.71 (d, J = 4.8 Hz, 1H), 8.63 (d, J = 2.4 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.67 (dt, J = 8.2, 2.0 Hz, 1H), 7.51 – 7.37 (m, 5H), 7.36 – 7.27 (m, 3H), 7.26 – 7.20 (m, 1H), 7.12 – 7.02 (m, 3H), 6.96 (d, J = 7.3 Hz, 2H).

 $\frac{^{13}\text{C NMR}}{(101 \text{ MHz, CDCl}_3)} \delta 154.4, 147.8, 144.4, 137.4, 134.6, 134.5, 132.4, 131.8, 131.4, 130.6, 134.5,$

 $129.8,\,129.7,\,129.3,\,127.6,\,126.5,\,126.3,\,125.4,\,123.5,\,121.7,\,116.3,\,112.0.$

<u>HRMS</u> (ESI) calculated for $C_{25}H_{19}N_2O_2SSe^+ m/z [M+H]^+$: 491.0327, found: 491.0322.



27c: 1-(benzylsulfonyl)-2-phenyl-3-(phenylselanyl)-1H-indole

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **27a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, m. p.: 89 – 91 °C.

93.2 mg, 0.186 mmol, 93% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.03 (dd, J = 8.2, 1.0 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.40 – 7.33 (m, 2H), 7.32 – 7.21 (m, 4H), 7.18 – 7.07 (m, 7H), 6.87 (dt, J = 7.0, 1.4 Hz, 2H), 6.72 (dd, J = 8.1, 1.4 Hz, 2H), 4.36 (s, 2H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 145.4, 136.9, 131.5, 131.3, 131.2, 130.8, 130.3, 129.4, 129.2, 129.1, 128.8, 127.1, 126.6, 126.5, 125.7, 124.5, 121.6, 114.8, 108.8, 59.5.

<u>HRMS</u> (ESI) calculated for $C_{27}H_{22}NO_2SSe^+ m/z [M+H]^+: 504.0531$, found: 504.0526.



28c: 2-phenyl-3-(*p*-tolylselanyl)-1-tosyl-1*H*-indole^[5]

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **1a** and **2b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 181 – 183 °C.

95.0 mg, 0.184 mmol, <u>92% isolated yield</u>.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.36 (dt, J = 8.4, 0.9 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 7.35 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 7.09 (d, J = 8.2 Hz, 2H), 6.86 (s, 4H), 2.34 (s, 3H), 2.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.0, 144.7, 137.7, 136.1, 135.2, 132.3, 131.8, 131.1, 130.0, 129.8, 129.5, 129.3, 127.9, 127.3, 127.0, 125.8, 124.7, 121.4, 116.4, 111.1, 21.7, 21.1.



29c: 3-((4-methoxyphenyl)selanyl)-2-phenyl-1-tosyl-1*H*-indole ^[5] Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **1a** and **3b** as the substrates (in 0.2 mmol scale). Light yellow solid, m. p.: 106 - 108 °C.

103.3 mg, 0.194 mmol, <u>97% isolated yield</u>.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.34 (d, J = 8.4 Hz, 1H), 7.50 – 7.35 (m, 5H), 7.35 – 7.27 (m, 4H), 7.27 – 7.21 (m, 1H), 7.06 (d, J = 7.9 Hz, 2H), 6.95 (dd, J = 8.7, 1.9 Hz, 2H), 6.65 – 6.54 (m, 2H), 3.69 (s, 3H), 2.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.8, 144.9, 144.1, 137.5, 135.2, 132.3, 132.2, 131.9, 131.2, 129.5,
129.2, 127.2, 127.0, 125.7, 124.6, 121.3, 121.3, 116.3, 114.9, 111.8, 55.3, 21.7.



30c: 3-((4-fluorophenyl)selanyl)-2-phenyl-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **1a** and **4b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 128 – 130 °C.

92.6 mg, 0.178 mmol, 89% isolated yield.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.36 (d, J = 8.4 Hz, 1H), 7.49 – 7.35 (m, 5H), 7.34 – 7.21 (m, 5H), 7.07 (d, J = 8.0 Hz, 2H), 6.94 (dd, J = 8.3, 5.2 Hz, 2H), 6.74 (t, J = 8.5 Hz, 2H), 2.32 (s, 3H). ¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 161.8 (d, J = 245.7 Hz), 145.1, 144.7, 137.5, 135.2, 131.9, 131.9 (d, J = 7.4 Hz), 131.8, 131.0, 129.5, 129.3, 127.3, 127.0, 126.0 (d, J = 3.1 Hz), 125.9, 124.7, 121.1, 116.3, 116.3 (d, J = 21.7 Hz), 111.0, 21.7.

<u>HRMS</u> (ESI) calculated for $C_{27}H_{21}FNO_2SSe^+ m/z [M+H]^+$: 522.0437, found: 522.0433.



31c: 3-(methylselanyl)-2-phenyl-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **1a** and **5b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 102 – 104 °C.

84.5 mg, 0.192 mmol, 96% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.36 (d, J = 8.3 Hz, 1H), 7.66 (dd, J = 7.7, 1.6 Hz, 1H), 7.52 – 7.40 (m, 4H), 7.40 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H), 1.91 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 144.9, 143.0, 137.3, 135.4, 132.2, 132.0, 131.5, 129.5, 129.2, 127.3, 127.0, 125.6, 124.4, 121.0, 116.2, 111.5, 21.7, 8.1.

HRMS (ESI) calculated for C₂₂H₂₀NO₂SSe⁺ m/z [M+H]⁺: 442.0374, found: 442.0371.



32c: 3-(benzylselanyl)-2-phenyl-1-tosyl-1*H*-indole

Following the General Procedure, the 5 mA CCE was kept for 4 h (3.73 F/mol) with **1a** and **6b** as the substrates (in 0.2 mmol scale).

Light yellow oil.

79.6 mg, 0.154 mmol, 77% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.36 (dd, J = 8.3, 1.0 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.47 – 7.39 (m, 2H), 7.37 – 7.28 (m, 5H), 7.13 – 7.06 (m, 3H), 7.05 – 6.99 (m, 2H), 6.99 – 6.94 (m, 2H), 6.76 – 6.68 (m, 2H), 3.71 (s, 2H), 2.34 (s, 3H).

 $\frac{13}{C}$ NMR (101 MHz, CDCl₃) δ 144.9, 144.6, 138.7, 137.1, 135.5, 132.4, 131.9, 131.1, 129.5, 129.0,

128.7, 128.3, 127.0, 127.0, 126.7, 125.5, 124.4, 121.0, 116.0, 110.2, 31.0, 21.7.

HRMS (ESI) calculated for C₂₈H₂₄NO₂SSe⁺ m/z [M+H]⁺: 518.0687, found: 518.0686.



35c: (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-3-(3-

(phenylselanyl)-1-tosyl-1H-indol-2-yl)benzoate

Following the General Procedure, with additional 5.0 mL DCM as co-solvent (10 mL solvent in total) and 0.2 equiv of ${}^{n}\text{Bu}_{4}\text{NPF}_{6}$ (0.4 equiv in total), the 5 mA CCE was kept for 4 h (3.73 F/mol) with **35a** and **1b** as the substrates (in 0.2 mmol scale).

White solid, <u>m. p.</u>: 172 – 174 °C.

155.6 mg, 0.170 mmol, 85% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.38 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 7.7 Hz, 1H), 7.89 (s, 1H), 7.58 – 7.39 (m, 4H), 7.33 – 7.23 (m, 3H), 7.13 – 6.99 (m, 5H), 6.94 (dd, J = 7.6, 2.6 Hz, 2H), 5.42 (s, 1H), 4.85 (tt, J = 10.8, 4.8 Hz, 1H), 2.47 – 2.28 (m, 5H), 2.08 – 1.88 (m, 4H), 1.87 – 1.79 (m, 1H), 1.71 – 1.43 (m, 7H), 1.41 – 1.30 (m, 3H), 1.27 – 0.96 (m, 14H), 0.93 (d, J = 6.5 Hz, 3H), 0.88 (s, 3H), 0.86 (s, 3H), 0.69 (s, 3H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 165.6, 145.2, 143.8, 139.8, 137.7, 136.0, 135.1, 132.6, 132.2, 131.7, 131.4, 130.4, 130.1, 129.7, 129.5, 129.2, 127.4, 127.0, 126.3, 126.1, 124.9, 122.9, 121.5, 116.4, 111.2, 74.8, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.8, 21.2, 19.6, 18.9, 12.0.

HRMS (ESI) calculated for C₅₅H₆₆NO₄SSe⁺ m/z [M+H]⁺: 916.3872, found: 916.3873.



36c: 2-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)ethyl 2-(4-isobutylphenyl)propanoate Following the General Procedure, the 5 mA CCE was kept for 3 h (2.80 F/mol) with **36a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow viscous oil.

94.8 mg, 0.144 mmol, 72% isolated yield.

Recovered substrate 36a:12.1 mg (0.024 mmol, 12%), 82% yield b.r.s.m.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.19 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.16 – 7.00 (m, 7H), 6.97 (d, J = 7.5 Hz, 4H), 4.44 (dt, J = 11.8, 6.3 Hz, 1H), 4.28 (dt, J = 11.4, 6.4 Hz, 1H), 3.63 (hept, J = 8.0, 7.2 Hz, 2H), 3.54 (q, J = 7.2 Hz, 1H), 2.39 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.80 (hept, J = 6.7 Hz, 1H), 1.41 (d, J = 7.1 Hz, 3H), 0.87 (s, 3H), 0.86 (s, 3H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 174.5, 145.2, 141.8, 140.5, 137.7, 137.3, 135.7, 131.7, 131.6, 130.0, 129.3, 129.2, 129.0, 127.3, 126.4, 126.2, 125.5, 124.4, 121.0, 115.4, 110.8, 64.1, 45.1, 45.1, 30.2, 28.1, 22.5, 21.7, 18.6.

<u>HRMS</u> (ESI) calculated for C₃₆H₃₈NO₄SSe⁺ m/z [M+H]⁺: 660.1681, found: 660.1680.



37c: 3-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)propyl (S)-2-(6-methoxynaphthalen-2-

yl)propanoate

Following the General Procedure, the 5 mA CCE was kept for 2 h (1.87 F/mol) with **37a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow viscous oil.

110.1 mg, 0.158 mmol, <u>79% isolated yield</u>.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.19 (d, J = 8.4 Hz, 1H), 7.70 – 7.60 (m, 3H), 7.53 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.20 (q, J = 7.3 Hz, 1H), 7.13 – 6.97 (m, 7H), 6.93 (d, J = 7.5 Hz, 2H), 4.17 (dt, J = 11.5, 5.9 Hz, 1H), 4.08 (dt, J = 11.4, 5.8 Hz, 1H), 3.93 – 3.79 (m, 4H), 3.28 (td, J = 8.5, 4.3 Hz, 2H), 2.30 (s, 3H), 1.99 (td, J = 13.4, 6.6 Hz, 2H), 1.57 (d, J = 7.2 Hz, 3H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 174.8, 157.7, 145.6, 145.1, 137.2, 135.9, 135.7, 133.8, 131.9, 131.7, 130.0, 129.5, 129.2, 129.1, 129.0, 127.2, 126.5, 126.4, 126.2, 126.1, 125.2, 124.4, 120.8, 119.0, 115.4, 108.9, 105.7, 64.3, 55.4, 45.6, 30.1, 25.6, 21.7, 18.7.

<u>HRMS</u> (ESI) calculated for C₃₈H₃₆NO₅SSe⁺ m/z [M+H]⁺: 698.1474, found: 698.1470.



38c: 5-(2-ethoxy-5-((2-phenyl-3-(phenylselanyl)-1*H*-indol-1-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one

Following the General Procedure, with additional 5.0 mL DCM as co-solvent (10 mL solvent in total) and 0.2 equiv of ${}^{n}Bu_{4}NPF_{6}$ (0.4 equiv in total), the 5 mA CCE was kept for 4 h (3.73 F/mol) with **38a** and **1b** as the substrates (in 0.2 mmol scale).

Light yellow solid, <u>m. p.</u>: 177 – 179 °C.

125.0 mg, 0.173 mmol, 87% isolated yield.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 10.71 (s, 1H), 8.56 (t, J = 2.0 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.54 (dt, J = 8.8, 1.9 Hz, 1H), 7.49 – 7.35 (m, 7H), 7.31 – 7.22 (m, 1H), 7.05 – 6.94 (m, 5H), 6.92 (dd, J = 9.0, 1.4 Hz, 1H), 4.34 – 4.21 (m, 5H), 2.90 (t, J = 7.5 Hz, 2H), 1.83 (h, J = 7.3 Hz, 2H), 1.62 – 1.57 (m, 4H), 1.03 (td, J = 7.4, 1.4 Hz, 3H).

<u>1³C NMR</u> (101 MHz, CDCl₃) δ 160.0, 153.6, 147.2, 146.0, 144.8, 138.4, 137.5, 132.2, 131.7, 131.6, 131.2, 131.1, 131.1, 130.5, 129.7, 129.3, 129.1, 127.4, 126.3, 125.9, 124.9, 124.5, 121.5, 121.1, 116.2, 112.8, 111.1, 66.3, 38.4, 27.6, 22.4, 14.6, 14.2.

<u>HRMS</u> (ESI) calculated for C₃₇H₃₄N₅O₄SSe⁺ m/z [M+H]⁺: 724.1491, found: 724.1495.

3. Mechanistic studies

3.1 Control experiments



Three additives (2 equiv, usually used as "radical trapping reagents") were added to the reaction systems of **1a** and **1b** before electrolysis. After standard electrochemical procedures (5 mA CCE for 2 h, 1.87 F/mol), the desired product **1c** was isolated from the mixtures. The reaction efficiencies were affected to different degree (5% isolated yield of **1c** with TEMPO, 69% with BHT, and 74% with 1,1-diphenylethylene) with incomplete conversion of substrate **1a**. However, no radical adduct were detected in all these reaction systems.

Since electrochemical reactions are based on net redox processes on electrodes, we further measured the oxidation potentials of these additives as well as the substrates (see Section **3.2** below), to see whether competitive oxidations at anode would occur (for the most effective TEMPO, the answer should be yes).



The control reaction with 2 equiv of TEMPO was carried out once again, this time under a prolonged 5 mA CCE for 5 h (4.66 F/mol). However, the isolated yield of **1c** (7%) did not improve

obviously, and substrate **1a** was recovered in 90% yield. Such a result indicated that the preferentially oxidized TEMPO at anode might be continuously regenerated by cathodic reduction.



The selenocyclization carried out with phenylselenenyl halides (1.3 equiv) as PhSe⁺ equivalents proceeded smoothly under non-electrochemical conditions. The reaction with PhSeCl provided the desired product **1c** in higher yield (while the system of PhSeBr showed a bit incomplete conversion of **1a**), which was exactly in accordance with the reactivity of two reagents (Se-Cl bond is more polarized than the corresponding Se-Br bond). This result suggest such an electrochemical selenocyclization is very like to proceed via RSe⁺ intermediates.

3.2 Cyclic voltammetry studies

The electrolyte solution for CV studies was prepared with $^{n}Bu_{4}NPF_{6}$ (0.1 M) in MeCN. The samples were prepared with 0.05 mmol of corresponding compound in 5 mL electrolyte solution (0.01 M). Measurements employed a glassy carbon working electrode, platinum plate counter electrode and an Ag/AgCl reference electrode. The applied scan rate was 100 mV/s, and the scans started from 0 V (initial E) to +2.5 V (high E), then back to 0 V (low E).



Fig S3. CV plots of 1a and 1b

The oxidation peak of **1a** appeared at +1.99 V; while for **1b**, clear oxidation peaks were observed at +1.64 V and +1.98 V. These results indicated that diselenide **1b** would be more easily oxidized at anode than 2-ethynylaniline **1a**, and a two-stage oxidation process of **1b** could be conceived.



Fig S4. CV plots of TEMPO, BHT and 1,1-diphenylethylene

The oxidation peaks of TEMPO, BHT and 1,1-diphenylethylene appeared at + 0.84 V, +1.65 V and +2.18 V, respectively. The results revealed that TEMPO with significantly lower oxidation potential would be preferentially oxidized at anode when it was added to the model reaction, thereby suppressing the conversion.



Fig S5. CV plots of 2-ethynylanilines 28a - 31a



Fig S6. CV plots of 2-ethynylanilines 32a - 34a

The CV plots of unproductive 2-ethynylanilines 28a - 34a were then recorded, aiming to account for their inertness under the standard electrochemical conditions. From the plots, we can speculate that in the presence of 1b (oxidation peak at +1.64 V), 2-ethynylanilines 32a - 34a that possessing lower oxidation potentials (oxidation peaks at +1.34 V, +1.28 V and +1.37 V, respectively) would get oxidized preferentially at the anode. Consequently, the key intermediate PhSe⁺ would not be generated from 1b in these systems to trigger the desired selenocyclization. While for other 2ethynylanilines that possess close potentials (28a - 31a, oxidation peaks at +2.05 V, +2.06 V, +1.93 V and +1.94 V, respectively) to 1a (oxidation peak at +1.99 V), the inertness should be explained from other aspects (e.g. the reactivity of the alkyne part, etc.).



Fig S7. CV plots of PhSeSePh (1b), PhSSPh (7b) and PhTeTePh (8b)

The CV plots of PhSSPh (7b) and PhTeTePh (8b) were also recorded. The oxidation peak of 7b appeared at +1.89 V, higher than the +1.64 V of 1b; while the first oxidation peak of 8b appeared at +1.44 V, lower than that of 1b. Unfortunately, from these results, we could not reach any reasonable explanation for the incompatibility of these dichalcogenides.

4. References

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27a, ¹H



27a, ¹³C


1c, ¹H



1c, ¹³C



2c, ¹H



2c, ¹³C



3c, ¹H







4c, ¹H



4c, ¹³C



5c, ¹H



5c, ¹³C



6c, ¹H



6c, ¹³C







7c, ¹³C



8c, ¹H



8c, ¹³C



9c, ¹H



9c, ¹³C



10c, ¹H



10c, ¹³C



11c, ¹H







12c, ¹H











13c, ¹³C



14c, ¹H



14c, ¹³C



15c, ¹H







16c, ¹H



16c, ¹³C



17c, ¹H



17c, ¹³C



18c, ¹H



18c, ¹³C


19c, ¹H



19c, ¹³C



20c, ¹H



20c, ¹³C



21c, ¹H







22c, ¹H



22c, ¹³C



23c, ¹H



23c, ¹³C



24c, ¹H



24c, ¹³C



25c, ¹H



25c, ¹³C



26c, ¹H



26c, ¹³C



27c, ¹H



27c, ¹³C



28c, ¹H



28c, ¹³C



29c, ¹H



29c, ¹³C



30c, ¹H



30c, ¹³C



31c, ¹H



31c, ¹³C



32c, ¹H



32c, ¹³C



35c, ¹H



35c, ¹³C



36c, ¹H



36c, ¹³C



37c, ¹H



37c, ¹³C



38c, ¹H



38c, ¹³C
