Synthesis, Structural Characterisation, and Synthetic Application of Stable Seleniranium Ions

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1. Experimental procedures

1.1 General experimental

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in dried glassware under an argon atmosphere and were performed using standard Schlenk techniques. Flash chromatography (FC) was carried out using Acros silica gel (0.035 - 0.070 mm; 60 Å) with pressure of about 1.1-1.5 bar. Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F254 plates; detection with UV light or by dipping into a solution of KMnO₄ (13.1 g K₂CO₃, 0.20 g KOH, 2.00 g KMnO₄, 200 mL H₂O) followed by heating. Exact mass spectrum with electrospray ionization (MS-ESI-ESI, m/z) were recorded on a Bruker MicroTof or a Thermo Scientific Orbitrap LTQ XL (Nanospray). IR spectra were recorded on a Digilab Varian 4000 FT-IR Excalibur Series with a MKII Golden Gate Single Reflection ATR unit. IR signals are reported as w (weak), m (middle), s (strong) or br (broad) in cm⁻¹. NMR spectrum were recorded on Bruker DPX 300 (300 MHz), Agilent DD2 500 (500 MHz) or Agilent DD2 600 (600 MHz)). ¹H-NMR and ¹³C-NMR chemical shifts (δ) are reported in ppm relative to TMS and referenced to the residual solvent signal (CDCl₃: 7.26 ppm/77.0 ppm, CD₂Cl₂: 5.33 ppm/54.24 ppm). ¹¹B-, ¹⁹F- and ⁷⁷Se- NMR signals are referenced to TMS according to the general chemical shift scale. The connectivity around the three membered ring was verified by H,Se-gHMOC-experiments (optimised on 10 Hz). Solvents for flash chromatography were distilled before use. Dichloromethane (CH₂Cl₂) for reactions was distilled from P₂O₅. Hexane (97%, AcroSeal® ExtraDry over Molecular Sieves) was purchased from Acros and used as received.

[Ad₂Br][BARF] (1)², dibutyl selenide³, homogeranyl benzene (5a)⁴, 4-iPr-homogeranyl benzene (5b)², homofarnesyl benzene (5c)⁵ and tert-butyl geranyl carbonate⁶ were prepared according to literature procedures. Diphenyl selenide, dibenzyl selenide and cyclooctene were purchased from Sigma Aldrich.
1.2 General procedures

General procedure for synthesis of seleniranium ions (GP 1)
A 10 mL Schlenk-tube was charged with the respective diselenide (1.00 eq., 0.10 mmol) and dry CH₂Cl₂ (1 mL). 1 (125 mg, 0.10 mmol) was added in one portion at room temperature. The tube was sealed, briefly shaken and the resulting mixture was overlayed with hexane (5 mL). Crystallisation at -20 °C for two days provided the respective seleniranium ions. Residual solvents were removed via cannula and the resulting crystals were washed with hexane (3 x 5 mL) and dried in vacuo.

General procedure for selenium-induced cyclisation (GP 2)
A 50 mL Schlenk-tube was charged with the respective cyclisation precursor (0.40 mmol, 1.00 eq.), HMDS (99 µL, 0.48 mmol, 1.20 eq.) and CH₂Cl₂ (6.0 mL). Thiiranium or seleniranium salts (0.48 mmol, 1.20 eq.) were added in CH₂Cl₂ (2.0 mL) at -78 °C (acetone/CO₂). The reaction mixture was allowed to reach room temperature over 15 min until complete consumption of the starting material was observed by TLC control. SiO₂ was added and solvents were removed in vacuo. The crude product was purified by flash column chromatography.
1.3 Preparation of thiiranium and seleniranium ions

[Ad$_2$SPh][BARF] (SI1)

A 10 mL Schlenk-tube was charged with diphenyl disulfide (33 mg, 0.15 mmol, 1.50 eq.) and dry CH$_2$Cl$_2$ (1 mL), after which 1 (125 mg, 0.10 mmol, 1.00 eq) was added in one portion at room temperature. The resulting yellow solution was stirred for 1 day and overlayed with hexane (5 mL). Crystallisation at -20 °C for two days provided the thiiranium ion SI1. The colourless crystals were washed with hexane (3 x 5 mL) and dried in vacuo (122 mg, 0.098 mmol, 98%).

$^1$H-NMR (600 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 7.79 – 7.75 (m, 8H, H-16/16'), 7.68 – 7.62 (m, 1H, H-14), 7.62 – 7.57 (m, 6H, H-12/12'/H-18), 7.58 – 7.51 (m, 2H, H-13/13'), 2.86 – 2.83 (m, 2H, H-2), 2.44 – 2.40 (m, 2H, CH)*, 2.31 – 2.27 (m, 2H, CH$_2$)*, 2.27 – 2.22 (m, 8H, 2 x CH$_2$)*, 2.19 – 2.12 (m, 7H, CH$_2$+2 x CH)*, 1.98 – 1.91 (m, 4H, 2 x CH$_2$)*, 1.91 – 1.87 (m, 2H, CH$_2$)*, 1.77 – 1.71 (m, 2H, CH$_2$)*.

$^{13}$C-NMR (151 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 162.5 (q, $^1$J$_{C:B}$ = 49.8 Hz, C-15), 135.5 (s, C-16/16'), 134.1 (s, C-14), 132.3 (s, C-12/12'), 131.9 (s, C-13/13'), 129.6 (qq, $^2$J$_{C:F}$ = 31.5 Hz, $^4$J$_{C:F}$ = 2.8 Hz, C-17/17'), 125.3 (q, $^1$J$_{C:F}$ = 272.4 Hz, C-19/19'), 120.4 (s, C-11), 118.1 (s, C-18), 105.5 (s, C-1/1'), 39.9 (s, CH$_2$)*, 39.3 (s, CH$_2$)*, 38.8 (s, CH$_2$)*, 38.2 (s, CH$_2$)*, 36.6 (s, CH$_2$)*, 35.7 (s, C-2), 32.0 (s, CH)*, 27.1 (s, 2 x CH)*.

$^{11}$B-NMR (192 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = -6.6 (s).

$^{19}$F-NMR (564 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = -62.8 (s).

MS-ESI-EM: $m/z = 377.2298$ calculated for C$_{26}$H$_{33}$S$^+$ ([M]$^+$), found: 377.2309.

For crystal structure analysis data, see page S45.
According to the GP I diphenyl diselenide (31 mg, 0.099 mmol) was treated with 1. Crystallisation provided 2a (126 mg, 0.098 mmol, 99%) as colourless solid.

$^1$H-NMR (600 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 7.76 – 7.73 (m, 8H, H-16/16’), 7.64 – 7.58 (m, 1H, H-14), 7.57 (s, 4H, H-18), 7.54 – 7.48 (m, 4H, H-12/12’+H-13/13’), 2.74 – 2.70 (m, 2H, H-2/2’), 2.53 – 2.49 (m, 2H, H-10/10’), 2.42 – 2.37 (m, 2H, H-8a/8’a), 2.38 – 2.35 (m, 4H, H-9/9’), 2.36 – 2.32 (m, 2H, H-7a/7’a), 2.30 – 2.25 (m, 2H, H-7b/7’b), 2.24 – 2.19 (m, 4H, H-8b/8’b+H-4/4’), 2.17 – 2.13 (m, 2H, H-6/6’), 2.09 – 2.05 (m, 2H, H-3a/3’a), 2.01 – 1.98 (m, 2H, H-3b/b’b), 1.98 – 1.95 (m, 2H, H-5a/5’a), 1.95 – 1.91 (m, 2H, H-5b/5’b).

$^{13}$C-NMR (151 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 162.4 (q, $^1$J$_{C-B}$ = 49.8 Hz), 135.4 (s, C-16/16’), 133.7 (s, C-14), 133.3 (s, C-12/12’), 132.0 (s, C-13/13’), 129.5 (qq, $^2$J$_{C-F}$ = 31.6, $^4$J$_{C-F}$ = 2.9 Hz, C-17/17’), 125.2 (q, $^1$J$_{C-F}$ = 272.4 Hz, C-19/19’), 122.6 (s, C-11), 121.4 (s, C-1/1’), 118.1 (s, C-18), 41.1 (s, C-7/7’), 40.8 (s, C-8/8’), 40.3 (s, C-9/9’), 38.7 (s, C-3/3’), 37.1 (s, C-5/5’), 35.9 (s, C-10/10’), 33.4 (s, C-2/2’), 27.6 (s, C-4/4’), 27.5 (s, C-6/6’).

$^{11}$B-NMR (192 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = -6.6 (s).

$^{19}$F-NMR (564 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = -62.9 (s).

$^{77}$Se-NMR (114 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 131.3 (s).

MS-ESI-EM: $m/z = 425.1744$ calculated for C$_{26}$H$_{33}$Se$^+$ ([M]$^+$), found: 425.1754.

Elemental analysis: C: 54.10%, H: 3.52%, N: 0.00% calcd. for C$_{58}$H$_{45}$BF$_{24}$Se; found: C: 54.21%, H: 3.53%, N: 0.00%.

For crystal structure analysis data, see page S47.
According to the GP I dibutyl diselenide (27 mg, 0.099 mmol) was treated with 1. Crystallisation provided 2b (123 mg, 0.097 mmol, 97%) as colourless solid.

$^1$H-NMR (600 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 7.77 – 7.73 (m, 8H, H-16/16’), 7.59 (s, 4H, H-18), 2.47 (t, $^3$J$_{HH}$ = 7.7 Hz, 2H, H-11), 2.43 – 2.10 (m, 22H, H-2+H-3a+H-4+H-6+H-7 +H-8+H-9+H10)*, 1.97 – 1.93 (m, 4H, H-5), 1.91 – 1.83 (m, 2H, H-12), 1.78 – 1.72 (m, 2H, H-3b), 1.57 – 1.49 (m, 2H, H-13), 0.97 (t, $^3$J$_{HH}$ = 7.3 Hz, 3H, H-14).

$^{13}$C-NMR (151 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 162.4 (q, $^1$J$_{CB}$ = 49.8 Hz), 135.4 (s, C-16/16’), 129.5 (qq, $^2$J$_{CF}$ = 31.6 Hz, $^4$J$_{CF}$ = 2.9 Hz, C-17/17’), 125.3 (q, $^1$J$_{CF}$ = 272.4 Hz, C-19/19’), 118.1 (m, C-18), 111.4 (s, C-1/1’), 40.4 (s, CH$_2$)*, 40.3 (s, CH$_2$)*, 40.1 (s, CH$_2$)*, 39.0 (s, C-3), 37.0 (s, C-5), 34.9 (s, CH)$^*$, 32.1 (s, CH)$^*$, 30.0 (s, C-11), 29.7 (s, C-12), 27.4 (s, CH)$^*$, 27.4 (s, CH)$^*$, 23.8 (s, C-13), 13.7 (s, C-14).

$^{11}$B-NMR (192 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = -6.6 (s).

$^{19}$F-NMR (564 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = -62.9 (s).

$^{77}$Se-NMR (95 MHz, CD$_2$Cl$_2$, 299 K): $\delta$ (ppm) = 18.3 (s).

MS-ESI-EM: $m/z$ = 405.2056 calculated for C$_{24}$H$_{37}$S$^+$ ([M]$^+$), found: 405.2069.

For crystal structure analysis data, see page S49.
According to the GP I dibenzyl diselenide (34 mg, 0.100 mmol) was treated with 1. Crystallisation provided the product 2c (130 mg, 0.100 mmol, 99%) as colourless solid.

**1H-NMR** (600 MHz, CD$_2$Cl$_2$, 299 K):  $\delta$ (ppm) = 7.75 (s, 8H, H-17/17'), 7.58 (s, 4H, H-19), 7.49 – 7.44 (m, 3H, H-14/14'+H-15), 7.41 (dd, $^3J_{H,H}$ = 6.6 Hz, $^4J_{H,H}$ = 3.0 Hz, 2H, C-13/13'), 3.74 (s, 2H, H-11), 2.56 – 2.52 (m, 2H, H-2), 2.48 – 2.43 (m, 2H, H-8a), 2.43 – 2.38 (m, 4H, C-3a+CH)*, 2.38 – 2.33 (m, 2H, CH$_2$)*, 2.32 – 2.26 (m, 4H, CH+CH$_2$)*, 2.26 – 2.19 (m, 4H, C-8b+CH$_2$)*, 2.19 – 2.13 (m, 4H, CH+CH$_2$)*, 2.03 – 1.96 (m, 6H, H-3b+H-5).

**13C-NMR** (151 MHz, CD$_2$Cl$_2$, 299 K):  $\delta$ (ppm) = 162.4 (q, $^1J_{C,B}$ = 49.8 Hz), 135.4 (s, C-17/17'), 131.2 (s, C-15), 130.9 (C-14/14'), 130.5 (C-13/13'), 129.5 (qq, $^2J_{C,F}$ = 31.6 Hz, $^4J_{C,F}$ = 2.6 Hz, C-18/18'), 128.5 (s, C-12), 125.2 (q, $^1J_{C,F}$ = 272.4 Hz, C-20/20'), 118.5 – 117.8 (m, C-19/19'), 114.8 (s, C-1/1'), 40.6 (s, C-8/8'), 40.3 (s, CH$_2$)*, 40.3 (s, CH$_2$)*, 39.3 (s, C-3/3'), 37.0 (s, C-5/5'), 35.2 (s, C-11/11'), 34.9 (C-10/10'), 32.4 (C-2/2'), 27.4 (s, CH)*, 27.4 (s, CH)*.

**11B-NMR** (192 MHz, CD$_2$Cl$_2$, 299 K):  $\delta$ (ppm) = -6.6 (s).

**19F-NMR** (564 MHz, CD$_2$Cl$_2$, 299 K):  $\delta$ (ppm) = -62.9 (s).

**77Se-NMR** (114 MHz, CD$_2$Cl$_2$, 299 K):  $\delta$ (ppm) = 40.9 (s).

**MS-ESI-EM:** $m/z$ = 439.1900 calculated for C$_{27}$H$_{35}$Se$^+$ ([M]$^+$), found: 439.1908.

For crystal structure analysis data, see page S51.
1.4 Cyclisation experiments

*rac*-Phenyl-((2$S^*$,4$aS^*$,10$aR^*$)-1,1,4a-trimethyloctahydrophenanthren-2-yl)selane (6a)

According to the *GP 2 5a* (91 mg, 0.40 mmol) was cyclised using 2a. Column chromatography (pentane:CH$_2$Cl$_2$ = 80:20) provided the product 6a (120 mg, 0.31 mmol, 79%, *d.r.* = 96:4) as a colourless oil. Single crystals were obtained by crystallisation from isopropyl alcohol.

**IR** (neat): 2939 br, 1476$m$, 1437$m$, 1377*w*, 906*s*, 723*s*, 690*s*.

**$^1$H-NMR** (600 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 7.68 – 7.61 (m, 2H, H-19/19’), 7.33 – 7.30 (m, 3H, H-20/20’+H-21), 7.25 (d, $^3$J$_{H,H}$ = 7.8 Hz, 1H, H-6), 7.19 – 7.15 (m, 1H, H-7), 7.13 (ddd, $^3$J$_{H,H}$ = 8.4 Hz, $^3$J$_{H,H}$ = 4.9 Hz, $^4$J$_{H,H}$ = 1.4 Hz, 1H, H-8), 7.09 (d, $^3$J$_{H,H}$ = 7.4 Hz, 1H, H-9), 3.14 (dd, $^2$J$_{H,H}$ = 12.9 Hz, $^3$J$_{H,H}$ = 4.0 Hz, 1H, H-1), 3.01 (ddd, $^2$J$_{H,H}$ = 17.2 Hz, $^3$J$_{H,H}$ = 6.6 Hz, 1H, H-11a), 2.93 (ddd, $^3$J$_{H,H}$ = 17.9 Hz, $^3$J$_{H,H}$ = 11.4 Hz, $^3$J$_{H,H}$ = 7.4 Hz, 1H, H-11b), 2.37 – 2.32 (m, 1H, H-3a), 2.31 – 2.22 (m, 1H, H-2a), 2.19 – 2.14 (m, 1H, H-2b), 2.05 – 1.99 (m, 1H, H-12a), 1.85 (ddd, $^2$J$_{H,H}$ = 19.8 Hz, $^3$J$_{H,H}$ = 13.2 Hz, $^3$J$_{H,H}$ = 6.6 Hz, 1H, H-12b), 1.51 (d, $^3$J$_{H,H}$ = 12.2 Hz, 1H, H-13), 1.54 – 1.47 (m, 1H, H-3b), 1.39 (s, 3H, H-17), 1.30 (s, 3H, H-15), 1.12 (s, 3H, H-16).

**$^{13}$C-NMR** (151 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 149.3 (s, C-5), 134.9 (s, C-10), 134.4 (s, C-19/19’), 130.8 (s, C-18), 129.0 (s, C-20/20’), 129.0 (s, C-9), 127.1 (s, C-21), 125.8 (s, C-7), 125.5 (s, C-8), 124.5 (s, C-6), 60.0 (s, C-1), 52.1 (s, C-13), 40.2 (s, C-3), 39.0 (s, C-14), 38.0 (s, C-4), 31.2 (s, C-17), 30.9 (s, C-11), 29.2 (s, C-2), 24.9 (s, C-15), 20.2 (s, C-12), 19.0 (s, C-16).

**$^{77}$Se-NMR** (95 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 355.1 (s).

**MS-ESI-EM**: *m/z* = 491.0406 calculated for C$_{23}$H$_{28}$AgSe$^+$ ([M+Ag]$^+$), found: 491.0398.

For crystal structure analysis data, see page S55.
According to the GP 2 5a (119 mg, 0.40 mmol) was cyclised using 2b and stirred overnight at room temperature. Column chromatography (pentane → pentane:diethyl ether = 98:2) provided the product 6b (12 mg, 0.03 mmol, 8%, d.r. = 97:3) as a colourless oil.

**IR** (neat): 2961 br, 2930 br, 2872 br, 1487 m, 1449 m, 1377 m, 907 s, 724 s.

**1H-NMR** (600 MHz, CDCl₃, 299 K): δ (ppm) = 7.23 (dd, 3J_H,H = 7.9, 4J_H,H = 1.1 Hz, 1H, H-6), 7.14 – 7.11 (m, 1H, H-7), 7.09 – 7.06 (m, 1H, H-8), 7.05 – 7.03 (m, 1H, H-9), 2.97 – 2.92 (m, 1H, H-11a), 2.91 – 2.84 (m, 1H, H-11b), 2.64 – 2.61 (m, 1H, H-1), 2.59 (t, 5J_H,H = 7.5 Hz, 1H, H-18), 2.36 – 2.31 (m, 1H, H-3a), 2.19 – 2.11 (m, 2H, H-2), 1.94 1.97 – 1.92 (m, 1H, H-12a), 1.79 – 1.72 (m, 1H, H-12b), 1.69 – 1.62 (m, 2H, H-19), 1.53 – 1.48 (m, 1H, H-3b), 1.45 – 1.39 (m, 3H, H-13+H-20), 1.22 (s, 3H, H-15), 1.22 (s, 3H, H-17), 0.96 (s, 3H, H-16), 0.92 (t, 3J_H,H = 7.4 Hz, 3H, H-21).

**13C-NMR** (151 MHz, CDCl₃, 299 K): δ (ppm) = 149.6 (C-5), 135.1 (C-10), 129.1 (C-9), 125.9 (C-7), 125.5 (C-8), 124.6 (C-6), 55.2 (C-1), 51.9 (C-13), 40.4 (C-3), 38.9 (C-14), 38.1 (C-4), 33.1 (C-19), 31.0 (C-17), 30.9 (C-11), 29.7 (C-2), 25.0 (C-15), 24.2 (C-18), 23.3 (C-20) 20.4 (C-12), 18.9 (C-16), 13.8 (C-21).

**77Se-NMR** (95 MHz, CDCl₃, 299 K): δ (ppm) = 215.4 (s).

**GC-EI-MS:** m/z = 364.1665 calculated for C_{21}H_{32}Se⁺ ([M]^+), found: 364.1666.
rac-Phenyl((2S,4aS,10aR)-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl)sulfane (6c)

According to the GP 2 5a (119 mg, 0.40 mmol) was cyclised using [Ad₃SPh][BARF] and stirred overnight at room temperature. Column chromatography (pentane → pentane:diethyl ether = 98:2) provided the product 6c (35 mg, 0.11 mmol, 26%, d.r. = 98:2) as a colourless oil.

IR (neat): 2965 br, 2941 br, 1479 m, 1437 m, 1390 m, 1376 m, 756 s, 733 s, 722 s, 690 s.

¹H-NMR (600 MHz, CDCl₃, 299 K): δ (ppm) = 7.44 – 7.39 (m, 2H, C-19), 7.31 – 7.25 (m, 2H, H-20), 7.23 – 7.17 (m, 2H, H-21+H-6), 7.14 – 7.08 (m, 1H, H-7), 7.10 – 7.05 (m, 1H, H-8), 7.06 – 7.02 (m, 1H, H-9), 3.01 – 2.94 (m, 1H, H-11a), 2.91 (dd, 3J_H,H = 17.4 Hz, 3J_H,H = 7.6 Hz, 1H, H-1), 2.92 – 2.85 (m, 1H, H-11b), 2.35 – 2.28 (m, 1H, H-3a), 2.06 – 1.99 (m, 2H, H-2), 2.00 – 1.93 (m, 1H, H-12a), 1.85 – 1.74 (m, 1H, H-12b), 1.51 – 1.44 (m, 1H, H-3b), 1.45 (dd, 3J_H,H = 12.2 Hz, 3J_H,H = 2.2 Hz, 1H, H-13), 1.32 (s, 3H, H-17), 1.24 (s, 3H, H-15), 1.04 (s, 3H, H-16).

¹³C-NMR (151 MHz, CDCl₃, 299 K): δ (ppm) = 149.4 (C-5), 137.0 (C-18), 135.1 (C-10), 131.5 (C-19), 129.1 (C-9), 129.0 (C-20), 126.5 (C-21), 125.9 (C-7), 125.5 (C-8), 124.6 (C-6), 61.1 (C-1), 52.4 (C-13), 39.2 (C-3), 38.8 (C-14), 38.0 (C-4), 30.9 (C-11), 30.2 (C-17), 28.1 (C-2), 25.0 (C-15), 19.9 (C-12), 17.9 (C-16).

GC-EI-MS: m/z = 336.1906 calculated for C₂₃H₂₈S⁺ ([M⁺]), found: 336.1905.

Consistent with published data.⁷
**rac-Phenyl-(2S*,4aS*,10aR*)-6-isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-yl) selane (6d)**

According to the *GP 2* 5b (108 mg, 0.40 mmol) was cyclised using 2a. Column chromatography (pentane → pentane:diethyl ether = 98:2) provided the product 6d (73 mg, 0.17 mmol, 43%, d.r. = 94:6) as a colourless oil.

**IR (neat):** 2960 br, 2933 br, 1579 w, 1448 m, 1475 m, 1389 m, 1376 m, 732 s, 690 s.

**1H-NMR** (600 MHz, CDCl₃, 299 K): δ (ppm) = 7.63 – 7.58 (m, 2H, H-21/21’), 7.29 – 7.27 (m, 3H, H-22/22’+H-23), 7.08 (dd, 3J_H,H = 1.3 Hz, 1H, H-6), 7.02 – 6.98 (m, 2H, H-8+H-9), 7.02 – 6.98 (m, 2H, H-11b), 3.10 (dd, 3J_H,H = 12.9 Hz, 3J_H,H = 4.1 Hz, 1H), 2.95 (dd, 2J_H,H = 16.9 Hz, 3J_H,H = 6.5 Hz, 3J_H,H = 1.6 Hz, 1H, H-11a), 2.90 – 2.86 (m, 1H, H-11b), 2.86 – 2.83 (m, 1H, H-18), 2.35 (dt, 2J_H,H = 13.1 Hz, 3J_H,H = 3.4 Hz, 1H, H-3a), 2.28 – 2.19 (m, 1H, H-2a), 2.15 – 2.10 (m, 1H, H-2b), 2.00 – 1.95 (m, 1H, H-12a), 1.86 – 1.75 (m, 1H, H-12b), 1.53 – 1.44 (m, 1H, H-3b), 1.48 (dd, 3J_H,H = 12.1 Hz, 3J_H,H = 2.1 Hz, 1H, H-13), 1.34 (s, 3H, H-17), 1.27 (s, 3H, H-15), 1.24 (d, 3J_H,H = 6.9 Hz, 3H, H-19/19’), 1.24 (d, 3J_H,H = 6.9 Hz, 3H, H-19/19’), 1.08 (s, 3H, H-16).

**13C-NMR** (151 MHz, CDCl₃, 299 K): δ (ppm) = 149.2 (C-5), 146.3 (C-7), 134.3 (C-21/21’), 132.4 (C-10), 130.9 (C-20), 129.1 (C-22/22’), 129.0 (C-9), 127.1 (C-23), 123.6 (C-8), 122.6 (C-6), 60.1 (C-1), 52.2 (C-13), 40.3 (C-3), 39.1 (C-14), 38.1 (C-4), 34.2 (C-18), 31.2 (C-17), 30.5 (C-11), 29.3 (C-2), 25.0 (C-15), 24.3 (C-19/19’), 24.3 (C-19/19’), 20.3 (C-12), 19.0 (C-16).

**77Se-NMR** (114 MHz, CDCl₃, 299 K): δ (ppm) = 354.5 (s).

**MS-ESI-EM:** m/z = 533.0876 calculated for C₂₆H₃₄SeAg⁺ ([M+Ag]⁺), found: 533.0875.
rac-Phenyl-((2S*,4aR*,4bR*,10bR*,12aR*)-1,1,4a,10b-tetramethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysen-2-yl)selane (6e)

According to the GP 2 5c (119 mg, 0.40 mmol) was cyclised using 2a. Column chromatography (pentane → pentane:diethyl ether = 98:2) provided the product 6e (127 mg, 0.28 mmol, 70%, d.r. = 98:2) as a colourless oil.

IR (neat): 2939 br, 2850 br, 1578 w, 1476 m, 1437 m, 1387 m, 1367 m, 759 s, 734 s.

$^{1}H$-NMR (600 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 7.59 – 7.57 (m, 2H, H-24/24'), 7.28 – 7.25 (m, 4H, H-12+H-25/25'+H-26), 7.17 – 7.11 (m, 1H, H-11), 7.08 (ddd, $^3$J$_{H,H}$ = 7.4 Hz, $^3$J$_{H,H}$ = 7.4 Hz, $^4$J$_{H,H}$ = 1.3 Hz, 1H, H-10), 7.04 – 7.02 (m, 1H, H-9), 3.03 (dd, $^3$J$_{H,H}$ = 13.0 Hz, $^3$J$_{H,H}$ = 4.3 Hz, $^4$J$_{H,H}$ = 17.0 Hz, $^3$J$_{H,H}$ = 5.4 Hz, 1H, H-7a), 2.80 (ddd, $^2$J$_{H,H}$ = 17.4 Hz, $^3$J$_{H,H}$ = 11.6 Hz, $^3$J$_{H,H}$ = 7.4 Hz, 1H, H-7b), 2.45 – 2.41 (m, 1H, H-15a), 2.17 – 2.07 (m, 1H, H-2a), 1.99 – 1.94 (m, 1H, H-2b), 1.86 – 1.77 (m, 3H, H-3a+H-6a+H-16a), 1.72 – 1.62 (m, 2H, H-6b+H-16b), 1.56 – 1.49 (m, 1H, H-15b), 1.26 (s, 3H, H-22), 1.26 (dd, $^3$J$_{H,H}$ = 12.1 Hz, $^4$J$_{H,H}$ = 2.2 Hz, 1H, H-5), 1.22 (s, 3H, H-19), 1.02 – 1.00 (m, 1H, H-17), 0.99 (s, 3H, H-20), 0.99 (s, 3H, H-21), 0.98 – 0.90 (m, 1H, H-3b).

$^{13}C$-NMR (151 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 150.1 (C-13), 135.1 (C-8), 134.4 (C-24/24'), 130.9 (C-23), 129.0 (C-25/25'), 128.9 (C-9), 127.1 (C-26), 125.9 (C-11), 125.3 (C-10), 124.7 (C-12), 60.7 (C-1), 57.7 (C-17), 55.3 (C-5), 41.4 (C-3), 40.7 (C-15), 38.9 (C-18), 38.0 (C-14), 37.8 (C-4), 31.1 (C-22), 30.9 (C-7), 28.7 (C-2), 26.2 (C-19), 20.2 (C-16), 18.9 (C-20), 18.1 (C-6), 16.3 (C-21).

$^{77}$Se-NMR (114 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 356.8 (s).

MS-ESI-EM: $m/z = 559.1033$ calculated for C$_{28}$H$_{36}$SeAg$^+$ ([M+Ag]$^+$), found: 559.1024.
According to the GP 27 (119 mg, 0.40 mmol) was cyclised using 2a. Column chromatography (pentane → pentane:diethyl ether = 98:2) provided the product 8 (21 mg, 0.06 mmol, 15%, d.r. = 96:4) as a colourless oil.

IR (neat): 2966br, 2939br, 1746s, 1578w, 1393m, 1221s, 1142s, 1126s, 1084s, 744m, 692m.

$^1$H-NMR (600 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 7.59 – 7.54 (m, 2H, H-13/13’), 7.33 – 7.26 (m, 3H, H-14/14’+H-15), 4.49 (dd, $^2$J$_{H,H}$ = 10.8 Hz, $^3$J$_{H,H}$ = 5.6 Hz, 1H, H-6a), 4.40 (dd, $^2$J$_{H,H}$ = 10.8 Hz, $^3$J$_{H,H}$ = 12.8 Hz, 1H, H-6b), 2.99 (dd, $^3$J$_{H,H}$ = 12.7 Hz, $^3$J$_{H,H}$ = 4.0 Hz, 1H, H-1), 2.19 – 2.12 (m, 1H, H-2a), 2.01 (dd, $^3$J$_{H,H}$ = 12.8 Hz, $^3$J$_{H,H}$ = 5.6 Hz, 1H, H-7), 1.96 – 1.92 (m, 1H, H-3a), 1.91 – 1.85 (m, 1H, H-2b), 1.65 – 1.58 (m, 1H, H-3b), 1.50 (s, 3H, H-9), 1.30 (s, 3H, H-11), 0.96 (s, 3H, H-10).

$^{13}$C-NMR (151 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 148.7 (C-5), 135.0 (C-13/13’), 129.4 (C-14/14’), 129.4 (C-12), 128.0 (C-15), 81.4 (C-4), 67.6 (C-6), 57.3 (C-1), 48.3 (C-7), 39.8 (C-3), 37.7 (C-8), 29.9 (C-11), 29.3 (C-2), 20.8 (C-9), 18.1 (C-10).

$^{77}$Se-NMR (114 MHz, CDCl$_3$, 299 K): $\delta$ (ppm) = 346.9 (s).

MS-ESI-EM: $m/z$ = 377.0627. calculated for C$_{17}$H$_{22}$O$_3$SeNa$^+$ ([M+Na]$^+$), found: 377.0628.
1.5 Further experiments using cyclization products

(1S,2R,4S)-2-(hydroxymethyl)-1,3,3-trimethyl-4-(phenylselanyl)cyclohexan-1-ol (SI2)

To 8 (21 mg, 0.06 mmol, 1.00 eq.) dissolved in MeOH (10 mL), K$_2$CO$_3$ (25 mg, 0.18 mmol, 3.00 eq.) was added and heated to 40 °C over 3 h. After cooling to room temperature, aqueous, saturated NH$_4$Cl solution (10 mL) was added and the organic phase was separated. The aqueous phase was extracted with ethyl acetate and the combined organic layers were dried over Na$_2$SO$_4$. The solvents were removed in vacuo.

Purification by column chromatography (pentane:ethyl acetate = 50:50) provided the protected product SI2 as colorless oil (19 mg, 0.06 mmol, 98%).

**IR** (neat): 3317 br, 2966 br, 2939 br, 2870 br, 1476 m, 1437 m, 1376 m, 1141 s, 1022 s, 740 s, 691 s.

**$^1$H-NMR** (600 MHz, CDCl$_3$, 299 K): δ (ppm) = 7.57 – 7.54 (m, 2H, H-12/12’), 7.28 – 7.26 (m, 2H, H-13/13’), 7.26 – 7.25 (m, 1H, H-14), 3.97 – 3.95 (m, 2H, H-7), 3.33 (br s, 2H, OH), 3.01 (dd, $^3$J$_{H,H}$ = 12.9 Hz, $^3$J$_{H,H}$ = 3.9 Hz, 1H, H-1), 2.04 – 1.99 (m, 1H, H-2a), 1.88 – 1.79 (m, 1H, H-2b), 1.77 – 1.72 (m, 1H, H-3a), 1.69 (dd, $^3$J$_{H,H}$ = 8.5 Hz, $^3$J$_{H,H}$ = 4.7 Hz, 1H, H-5), 1.46 (ddd, $^3$J$_{H,H}$ = 13.9 Hz, $^3$J$_{H,H}$ = 12.9 Hz, $^3$J$_{H,H}$ = 3.8 Hz, 1H, H-3b), 1.36 (s, 3H, H-10), 1.35 (s, 3H, H-8), 0.86 (s, 3H, H-9).

**$^{13}$C-NMR** (151 MHz, CDCl$_3$, 299 K): δ (ppm) = 134.7 (C-12/12’), 130.2 (C-11), 129.2 (C-13/13’), 127.5 (C-14), 74.3 (C-4), 62.5 (C-7), 59.4 (C-1), 57.2 (C-5), 43.9 (C-3), 38.6 (C-6), 31.1 (C-10), 30.1 (C-2), 23.5 (C-8), 18.7 (C-9).

**$^{77}$Se-NMR** (114 MHz, CDCl$_3$, 299 K): δ (ppm) = 352.1 (s).

**MS-ESI-EM**: $m/z$ = 351.0834 calculated for C$_{16}$H$_{24}$O$_2$SeNa$^+$ ([M+Na]$^+$), found: 351.0841.
To 6a (80 mg, 0.21 mmol, 1.00 eq.) dissolved in THF/H₂O (3:1, 6 mL), NaIO₄ (135 mg, 0.63 mmol, 3.00 eq.) was added at 0 °C and stirred overnight at room temperature. Water (10 mL) was added, the reaction mixture was diluted with Et₂O and the organic phase was separated. The aqueous phase was extracted with Et₂O and the combined organic layers were washed with aqueous, saturated NaCl solution and dried over Na₂SO₄. The solvents were removed in vacuo. Purification by column chromatography (pentane:CH₂Cl₂ = 90:10) provided the product SI3 as colorless solid (16 mg, 0.07 mmol, 34%).

**¹H-NMR** (300 MHz, CDCl₃, 299 K): δ (ppm) = 7.29 (d, ³J_H,H = 7.6 Hz, 1H, ArH), 7.20 – 7.08 (m, 2H, 2 x ArH), 7.08 – 7.04 (m, 1H, ArH), 5.62 (ddd, ³J_H,H = 10.0 Hz, ³J_H,H = 5.9 Hz, ³J_H,H = 1.8 Hz, 1H, C=CH), 5.51 (dd, ³J_H,H = 10.1, ³J_H,H = 2.6 Hz, 1H, C=CH), 2.99 – 2.79 (m, 2H, CH₂), 2.55 (dd, ³J_H,H = 16.8, ³J_H,H = 6.0 Hz, 1H, CH₃H₆), 2.13 (d, ³J_H,H = 16.8 Hz, 1H, CH₃H₆), 1.92 – 1.64 (m, 3H, CH₂+CH), 1.28 (s, 3H, CH₃), 1.06 (s, 3H, CH₃), 1.01 (s, 3H, CH₃).

**¹³C-NMR** (75 MHz, CDCl₃, 299 K): δ (ppm) = 148.1 (Cₚ), 138.3 (CH), 135.63 (Cₚ), 129.13 (CH), 126.23 (CH), 126.13 (CH), 125.43 (CH), 122.03 (CH), 48.33 (CH), 39.93 (CH₂), 37.23 (Cₚ), 35.33 (Cₚ), 32.03 (CH₂), 31.33 (CH₃), 25.43 (CH₃), 22.53 (CH₃), 20.13 (CH₂).

**MS-ESI-EM**: m/z = 333.0767 calculated for C₁₇H₂₂Ag⁺ ([M+Ag⁺]), found: 333.0772.

Consistent with published data.⁸
1.6  Crossover experiments

1.6.1  Reaction of 2a with cis-cyclooctene

To a solution of 2a (60 mg, 0.05 mmol, 1.00 eq.) in CD$_2$Cl$_2$ (1.0 mL) cyclooctene (6.5 µL, 0.05 mmol, 1.00 eq.) was added at -78 °C (acetone/CO$_2$). The reaction mixture was transferred into a pre-cooled NMR-tube (-78 °C) and directly measured at -70 °C (500 MHz). During measurements the temperature was allowed to reach room temperature.

Supporting figure 1: $^1$H-NMR-spectra of 2a and cis-cyclooctene at different temperatures.
Supporting figure 2: $^{77}$Se-NMR-spectra of 2a and cis-cyclooctene at different temperatures.
1.6.2 Reaction of 2b with cis-cyclooctene

To a solution of 2b (60 mg, 0.05 mmol, 1.00 eq.) in CDCl₂ (1.0 mL) cyclooctene (6.5 µL, 0.05 mmol, 1.00 eq.) was added at -78 °C (acetone/CO₂). The reaction mixture was transferred into a pre-cooled NMR-tube (-78 °C) and directly measured at -70 °C (500 MHz). During measurements the temperature was allowed to reach room temperature.

Supporting figure 3: \(^1\)H-NMR-spectra of 2b and cis-cyclooctene at different temperatures.
Supporting figure 4: $^{77}$Se-NMR-spectra of 2b and cis-cyclooctene at different temperatures.
2. NMR spectra

Supporting figure 5: $^1$H-NMR-spectrum of [Ad$_2$SPh][BArF] (SII).

Supporting figure 6: $^{13}$C-NMR-spectrum of [Ad$_2$SPh][BArF] (SII).
Supporting figure 7: $^{11}$C-NMR-spectrum of $[\text{Ad}_2\text{SPh}][\text{BArF}]$ (SII).

Supporting figure 8: $^{19}$F-NMR-spectrum of $[\text{Ad}_2\text{SPh}][\text{BArF}]$ (SII).
Supporting figure 9: $^1$H-NMR spectrum of [Ad$_2$SePh][BArF] (2a).

Supporting figure 10: $^{13}$C-NMR spectrum of [Ad$_2$SePh][BArF] (2a).
Supporting figure 11: $^{11}$B-NMR-spectrum of [Ad$_2$SePh][BArF] (2a).

Supporting figure 12: $^{19}$F-NMR-spectrum of [Ad$_2$SePh][BArF] (2a).
Supporting figure 13: $^{77}\text{Se}$-NMR-spectrum of $[\text{Ad}_2\text{SePh}]\text{[BArF]}$ (2a).

Supporting figure 14: H,Se-gHMQC-NMR-spectrum of $[\text{Ad}_2\text{SePh}]\text{[BArF]}$ (2a).
Supporting figure 15: $^1$H-NMR-spectrum of [Ad$_2$SeBu][BArF] (2b).

Supporting figure 16: $^{13}$C-NMR-spectrum of [Ad$_2$SeBu][BArF] (2b).
Supporting figure 17: $^{11}$B-NMR-spectrum of [Ad$_2$SeBu][BArF] (2b).

Supporting figure 18: $^{19}$F-NMR-spectrum of [Ad$_2$SeBu][BArF] (2b).
Supporting figure 19: $^{77}$Se-NMR-spectrum of [Ad$_2$SeBu][BArF] (2b).

Supporting figure 20: H,Se-gHMOC-NMR-spectrum of [Ad$_2$SeBu][BArF] (2b).
Supporting figure 21: $^1$H-NMR-spectrum of [Ad$_2$SeBn][BArF] (2c).

Supporting figure 22: $^{13}$C-NMR-spectrum of [Ad$_2$SeBn][BArF] (2c).
Supporting figure 23: $^{11}$B-NMR-spectrum of [Ad$_2$SeBn][BArF] (2c).

Supporting figure 24: $^{19}$F-NMR-spectrum of [Ad$_2$SeBn][BArF] (2c).
Supporting figure 25: $^{77}\text{Se}-\text{NMR}$-spectrum of [Ad$_2$SeBn][BArF] (2c).

Supporting figure 26: $^{1}$H,Se-$\text{gHMOC}$-NMR-spectrum of [Ad$_2$SeBn][BArF] (2c).
Supporting figure 27: $^1$H-NMR-spectrum of 6a.

Supporting figure 28: $^{13}$C-NMR-spectrum of 6a.
Supporting figure 29: $^{77}\text{Se-NMR}$-spectrum of 6a.

Supporting figure 30: $\text{H,Se-gHMQC-NMR}$-spectrum of 6a.
Supporting figure 31: $^1$H-NMR-spectrum of 6b.

Supporting figure 32: $^{13}$C-NMR-spectrum of 6b.
Supporting figure 33: $^{77}\text{Se}$-NMR-spectrum of $6b$.

Supporting figure 34: $^1\text{H,Se}$-gHMOC-NMR-spectrum of $6b$. 

S35
Supporting figure 35: $^1$H-NMR-spectrum of $6d$.

Supporting figure 36: $^{13}$C-NMR-spectrum of $6d$. 

S36
Supporting figure 37: $^{77}$Se-NMR-spectrum of 6d.

Supporting figure 38: H,Se-gHMQC-NMR-spectrum of 6d.
Supporting figure 39: $^1$H-NMR-spectrum of 6e.

Supporting figure 40: $^{13}$C-NMR-spectrum of 6e.
Supporting figure 41: $^{77}$Se-NMR-spectrum of 6e.

Supporting figure 42: H,Se-gHMOC-NMR-spectrum of 6e.
Supporting figure 43: $^1$H-NMR-spectrum of 8.

Supporting figure 44: $^{13}$C-NMR-spectrum of 8.
Supporting figure 45: $^{77}$Se-NMR-spectrum of 8.

Supporting figure 46: H,Se-gHMQC-NMR-spectrum of 8.
Supporting figure 47: $^1$H-NMR-spectrum of (SI2).

Supporting figure 48: $^{13}$C-NMR-spectrum of (SI2).
Supporting figure 49: $^{77}$Se-NMR-spectrum of (S12).

Supporting figure 50: H,Se-gHMGC-NMR-spectrum of (S12).
3. X-ray crystal structures

3.1 X-Ray diffraction, general information

Data sets for \([\text{Ad}_2\text{SPh}][\text{BArF}]\) and compounds 2a, 2b, 2c and \(\text{Bn}_2\text{SeBr}_2\) were collected with a D8 Venture CMOS diffractometer. Data sets for compound 6a were collected with an APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., 2016); cell refinement: SAINT V8.37A (Bruker AXS Inc., 2015); data reduction: SAINT V8.37A (Bruker AXS Inc., 2015); absorption correction, SADABS V2014/7 (Bruker AXS Inc., 2014);\(^{10}\) structure solution SHELXT-2015 (Sheldrick, 2015);\(^{11}\) structure refinement SHELXL-2015 (Sheldrick, 2015).\(^{11}\) \(R\)-values are given for observed reflections, and \(wR^2\) values are given for all reflections.

*Exceptions and special features:* For compound 2a three \(\text{CF}_3\) groups, for compound 2b four \(\text{CF}_3\) groups and for the phenyl thiiranium two \(\text{CF}_3\) groups and one dichloromethane molecule were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.
3.2 X-ray crystal structure analysis of [Ad$_2$SPh][BArF]

A colorless prism-like specimen of C$_{58}$H$_{45}$BF$_{24}$S · CH$_2$Cl$_2$, approximate dimensions 0.091 mm x 0.152 mm x 0.172 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1053 frames were collected. The total exposure time was 16.29 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 86233 reflections to a maximum θ angle of 68.45° (0.83 Å resolution), of which 10342 were independent (average redundancy 8.338, completeness = 99.4%, R$_{int}$ = 4.96%, R$_{sig}$ = 2.64%) and 8966 (86.70%) were greater than 2σ(F$^2$). The final cell constants of \( \mathbf{a} = 20.0832(7) \) Å, \( \mathbf{b} = 17.7513(6) \) Å, \( \mathbf{c} = 17.4707(6) \) Å, \( \mathbf{β} = 114.8110(10)^\circ \), volume = 5653.5(3) Å$^3$, are based upon the refinement of the XYZ-centroids of 9837 reflections above 20σ(I) with 6.950° < 2θ < 136.7°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.867. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6770 and 0.8070. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group \( P2_1/c \), with Z = 4 for the formula unit, C$_{58}$H$_{45}$BF$_{24}$S · CH$_2$Cl$_2$. The final anisotropic full-matrix least-squares refinement on F$^2$ with 850 variables converged at R$_1$ = 4.59%, for the observed data and wR$_2$ = 10.92% for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.824 e/Å$^3$ and the largest hole was -0.591 e/Å$^3$ with an RMS deviation of 0.056 e/Å$^3$. On the basis of the final model, the calculated density was 1.558 g/cm$^3$ and F(000), 2688 e$^\circ$. 
Supporting figure 37: Crystal structure of [Ad₂SPh][BArF] (Thermals ellipsoids are shown with 30% probability).

Supporting figure 38: Crystal structure of [Ad₂SPh][BArF] (Thermals ellipsoids are shown with 30% probability).
3.3 X-ray crystal structure analysis of 2a

A colorless prism-like specimen of C₅₈H₄₅BF₂₄Se·CH₂Cl₂, approximate dimensions 0.122 mm x 0.265 mm x 0.343 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 742 frames were collected. The total exposure time was 6.18 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 151170 reflections to a maximum θ angle of 27.17° (0.78 Å resolution), of which 12504 were independent (average redundancy 12.090, completeness = 99.6%, Rint = 6.31%, Rsig = 2.73%) and 10271 (82.14%) were greater than 2σ(F²). The final cell constants of a = 16.7865(6) Å, b = 18.0322(8) Å, c = 18.9289(7) Å, β = 99.8880(10)°, volume = 5644.6(4) Å³, are based upon the refinement of the XYZ-centroids of 9965 reflections above 20σ(I) with 4.517° < 2θ < 54.19°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.931. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7520 and 0.9000. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/c, with Z = 4 for the formula unit, C₅₈H₄₅BF₂₄Se·CH₂Cl₂. The final anisotropic full-matrix least-squares refinement on F² with 897 variables converged at R1 = 3.26%, for the observed data and wR2 = 7.50% for all data. The goodness-of-fit was 1.043. The largest peak in the final difference electron density synthesis was 0.524 e/Å³ and the largest hole was -0.472 e/Å³ with an RMS deviation of 0.063 e/Å³. On the basis of the final model, the calculated density was 1.615 g/cm³ and F(000), 2760 e⁻.
Supporting figure 39: Crystal structure of compound 2a (Thermals ellipsoids are shown with 50% probability).

Supporting figure 40: Crystal structure of compound 2a (Thermals ellipsoids are shown with 30% probability).
3.4 X-ray crystal structure analysis of 2b

A colorless prism-like specimen of C\textsubscript{56}H\textsubscript{49}BF\textsubscript{24}Se, approximate dimensions 0.137 mm x 0.230 mm x 0.313 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2280 frames were collected. The total exposure time was 24.71 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 41540 reflections to a maximum θ angle of 70.41° (0.82 Å resolution), of which 9959 were independent (average redundancy 4.171, completeness = 98.2%, R\text{int} = 2.96%, R\text{sig} = 2.61%) and 9411 (94.50%) were greater than 2σ(F\textsuperscript{2}). The final cell constants of \( a = 12.6757(5) \) Å, \( b = 13.1647(5) \) Å, \( c = 16.7688(6) \) Å, \( α = 84.7820(10)^\circ \), \( β = 73.3120(10)^\circ \), \( γ = 82.5740(10)^\circ \), volume = 2653.63(17) Å\textsuperscript{3}, are based upon the refinement of the XYZ-centroids of 9923 reflections above 20 σ(I) with 6.782° < 2θ < 140.8°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.871. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5630 and 0.7640. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group \( P-1 \), with \( Z = 2 \) for the formula unit, C\textsubscript{56}H\textsubscript{49}BF\textsubscript{24}Se. The final anisotropic full-matrix least-squares refinement on F\textsuperscript{2} with 872 variables converged at R1 = 3.63%, for the observed data and wR2 = 9.19% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 0.765 e/Å\textsuperscript{3} and the largest hole was -0.504 e/Å\textsuperscript{3} with an RMS deviation of 0.057 e/Å\textsuperscript{3}. On the basis of the final model, the calculated density was 1.587 g/cm\textsuperscript{3} and F(000), 1280 e\textsuperscript{\textdegree}.
Supporting figure 41: Crystal structure of compound 2b (Thermals ellipsoids are shown with 30% probability).

Supporting figure 42: Crystal structure of compound 2b (Thermals ellipsoids are shown with 30% probability).
3.5 X-ray crystal structure analysis of 2c

A colorless plate-like specimen of C_{59}H_{47}BF_{24}Se, approximate dimensions 0.068 mm x 0.138 mm x 0.164 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1215 frames were collected. The total exposure time was 8.44 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 171064 reflections to a maximum θ angle of 27.54° (0.77 Å resolution), of which 12518 were independent (average redundancy 13.665, completeness = 99.7%, R_{int} = 7.74%, R_{sig} = 3.32%) and 10076 (80.49%) were greater than 2σ(F^2). The final cell constants of a = 13.7859(5) Å, b = 28.6706(10) Å, c = 14.2244(5) Å, β = 104.5350(10)°, volume = 5442.3(3) Å^3, are based upon the refinement of the XYZ-centroids of 9591 reflections above 20 σ(I) with 4.754° < 2θ < 54.93°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.943. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8780 and 0.9470. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2_1/n, with Z = 4 for the formula unit, C_{59}H_{47}BF_{24}Se. The final anisotropic full-matrix least-squares refinement on F^2 with 766 variables converged at R1 = 4.18%, for the observed data and wR2 = 8.78% for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 0.834 e/Å^3 and the largest hole was -0.395 e/Å^3 with an RMS deviation of 0.066 e/Å^3. On the basis of the final model, the calculated density was 1.589 g/cm^3 and F(000), 2624 e\('.
Supporting figure 43: Crystal structure of compound 2c (Thermals ellipsoids are shown with 50% probability).

Supporting figure 44: Crystal structure of compound 2c (Thermals ellipsoids are shown with 30% probability).
3.6 X-ray crystal structure analysis of Bn$_2$SeBr$_2$

A yellow prism-like specimen of C$_{14}$H$_{14}$Br$_2$Se, approximate dimensions 0.117 mm x 0.124 mm x 0.219 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 246 frames were collected. The total exposure time was 1.37 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 13517 reflections to a maximum $\theta$ angle of 27.51° (0.77 Å resolution), of which 1761 were independent (average redundancy 7.676, completeness = 99.4%, $R_{int} = 3.07\%$, $R_{exp} = 1.82\%$) and 1579 (89.66%) were greater than 2$\sigma$(F$^2$). The final cell constants of $a = 7.9846(3)$ Å, $b = 15.1323(5)$ Å, $c = 12.2645(4)$ Å, volume = 1481.86(9) Å$^3$, are based upon the refinement of the XYZ-centroids of 6801 reflections above 20 $\sigma$(I) with $6.088^\circ < 2\theta < 54.92^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.722. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2760 and 0.4580. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $Pnma$, with Z = 4 for the formula unit, C$_{14}$H$_{14}$Br$_2$Se. The final anisotropic full-matrix least-squares refinement on F$^2$ with 82 variables converged at R$_1 = 1.87\%$, for the observed data and wR$^2 = 4.34\%$ for all data. The goodness-of-fit was 1.064. The largest peak in the final difference electron density synthesis was 0.571 e/Å$^3$ and the largest hole was -0.821 e/Å$^3$ with an RMS deviation of 0.081 e/Å$^3$. On the basis of the final model, the calculated density was 1.887 g/cm$^3$ and F(000), 808 e$^\cdot$. 

S53
Supporting figure 45: Crystal structure of Bn₂SeBr₂ (Thermals ellipsoids are shown with 50% probability).

Supporting figure 46: Crystal structure of compound Bn₂SeBr₂ (Thermals ellipsoids are shown with 30% probability).
3.7 X-ray crystal structure analysis of 6a

A colorless prism-like specimen of C$_{23}$H$_{28}$Se, approximate dimensions 0.030 mm x 0.060 mm x 0.080 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1625 frames were collected. The total exposure time was 37.31 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 27577 reflections to a maximum $\theta$ angle of 66.76° (0.84 Å resolution), of which 3305 were independent (average redundancy 8.344, completeness = 98.2%, $R_{int}$ = 9.32%, $R_{sig}$ = 4.82%) and 2567 (77.67%) were greater than 2$\sigma$(F$^2$). The final cell constants of $a$ = 22.6370(13) Å, $b$ = 8.9594(5) Å, $c$ = 18.7848(11) Å, $\beta$ = 95.800(4)°, volume = 3790.3(4) Å$^3$, are based upon the refinement of the XYZ-centroids of 4144 reflections above 20 $\sigma$(I) with 7.851° < 2$\theta$ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.867. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8160 and 0.9250. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C2/c, with Z = 8 for the formula unit, C$_{23}$H$_{28}$Se. The final anisotropic full-matrix least-squares refinement on F$^2$ with 220 variables converged at R1 = 4.11%, for the observed data and wR2 = 10.92% for all data. The goodness-of-fit was 0.960. The largest peak in the final difference electron density synthesis was 0.435 e/Å$^3$ and the largest hole was -0.355 e/Å$^3$ with an RMS deviation of 0.075 e/Å$^3$. On the basis of the final model, the calculated density was 1.344 g/cm$^3$ and F(000), 1600 e$^-$.

Supporting figure 47: Crystal structure of compound 6a (Thermals ellipsoids are shown with 30% probability).
4. DFT calculations

4.1 Methods

All calculations were performed with the TURBOMOLE 7.2.1 program. The structures were optimized without any geometry constraints using the TPSS functional and an atom-pairwise dispersion correction (D3). A flexible triple zeta basis set (def2-TZVP) was used in all calculations. All structures were confirmed to be minima on the potential energy surface by calculation of the harmonic vibrational frequencies, which were all real (positive). Single point electronic energies were calculated with the PW6B95 functional using the same basis set and the D3 correction. Solvation energies were calculated with COSMO-RS (BLYP/TZVP) for CH$_2$Cl$_2$ as solvent.
4.2 Energies

Supporting Table S1: DFT-calculated electronic energies after geometry optimization with TPSS-D3. Single point electronic energies obtained with PW6B95-D3. \( G(\text{RRHO})_{298} \): Free energy corrections with the rigid rotor/harmonic oscillator model obtained with TPSS-D3. \( G(\text{SOLV})_{298} \): COSMO-RS calculated free energy of solvation in \( \text{CH}_2\text{Cl}_2 \). The def2-TZVP basis set was used in all calculations.

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The two diastereoisomers of 4 have very similar free energies, the trans-isomer \textit{trans}-4 being slightly more stable: (cis\(\rightarrow\)trans, \( \Delta G_{298} \) = -0.3 kcal/mol).

With these energies, we obtain a free (Gibbs) energy of the reaction depicted in Scheme 2:

\[
2a + \text{cyclooctene} \rightarrow \text{Ad}=\text{Ad} + \textit{trans-4a} \quad \Delta G_{298} = +3.95 \text{ kcal/mol}
\]
4.3 NMR chemical shifts

The NMR isotropic shielding for the selenium cations 2a, trans-4a and cis-4a were calculated\textsuperscript{20,21} with Turbomole using the BP86 functional\textsuperscript{22,23} (def2-TZVP) and transferred into chemical shifts using Me\textsubscript{2}Se as reference (δ = 0 ppm).

Supporting Table S2: DFT-calculated NMR chemical shifts (BP96/def2-TZVP) after geometry optimization with TPSS-D3. (δ\textsubscript{X} = σ(Me\textsubscript{2}Se)-σ\textsubscript{X})

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4.4 Cartesian Coordinates, Molecular Structures and Electronic Energies

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\]

Lowest Freq. = 42.81 cm\(^{-1}\)

2a (001/c1/tpps-d3.def2-TZVP)

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E(TPSS-D3/def2-TZVP) = -2946.501289560 (conv)
Lowest Freq. = 33.17 cm\(^{-1}\)

PhSeCyOcten_Conf1 (003/c1/tpss-d3.def2-TZVP)

C \(-0.9389347, -0.7298005, 0.4748106\)
C \(0.4448091, -0.2690581, 0.8233514\)
C \(1.6649192, -1.0720791, 0.8854761\)
C \(1.8693825, -2.5438183, 0.6028523\)
C \(0.6953335, -3.4527094, 0.2043155\)
C \(0.1832530, -3.2599541, -1.2449196\)
C \(-1.1123854, -2.4599894, -1.4326075\)
C \(-1.0680626, -0.9747869, -1.0604352\)
H \(-1.6342014, 0.0536472, 0.7879916\)
H \(-1.2074221, -1.6405253, 1.0113412\)
H \(2.4030665, -2.9783019, 1.4553678\)
H \(2.6041800, -2.5575344, -0.2155701\)
H \(-0.1210319, -3.3920938, 0.9304462\)
H \(0.0086869, -4.2526988, -1.6720881\)
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H \(-1.9196662, -2.9403988, -0.8627758\)
H \(-1.3981686, -2.5314074, -2.4883232\)
H \(-1.9937930, -0.4965608, -1.3935770\)
H \(-0.2548318, -0.4717105, -1.5997531\)
Se \(1.0763514, -0.4588565, 2.8047832\)
H \(0.6840878, -5.1094407, 4.6151111\)
C \(0.1357417, -4.2209341, 4.3190375\)
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C \(-1.2834539, -1.9110538, 3.5962548\)
H \(-1.8244212, -1.0062287, 3.3401356\)
C \(0.1022367, -1.9919877, 3.4207999\)
C \(0.8257744, -3.1286928, 3.7963736\)
H \(1.9061259, -3.1585407, 3.6987995\)
H \(2.5734302, -0.4861953, 0.7523212\)
H \(0.6269591, 0.7861441, 0.6200391\)
E(TPSS-D3/def2-TZVP) = -2946.500966893 (conv)
Lowest Freq. = 24.45 cm⁻¹

trans-4

PhSeCyOcten_Conf2 (003/c2/tpss-d3.def2-TZVP)

C  -0.7185658  -0.5205574  0.0673888
C   0.6703347  -0.1574233  0.5190682
C   1.7698327  -1.0985377  0.7337642
C   1.8318932  -2.5825901  0.4745082
C   0.5597600  -3.4448893  0.3558939
C  -0.0391520  -3.5434007 -1.0670863
C  -1.1096996  -2.5267084 -1.4875202
C  -0.7287621  -1.0432533 -1.4006600
H   -1.3425254  0.3711079  0.1656443
H  -1.1550985  -1.2815844  0.7189390
H   2.4971127  -3.0028276  1.2367994
H   2.3984292  -2.6636715  -0.4672890
H  -0.1957899  -3.1480077  1.0933033
H   0.8649496  -4.4541598  0.6482453
H  -0.4878234  -4.5371289  -1.1692675
H   0.7868323  -3.5143676  -1.7889855
H  -2.0183908  -2.6844994  -0.8909435
H  -1.3832287  -2.7515237  -2.5245797
H  -1.4552883  -0.4521215  -1.9650205
H   0.2434520  -0.8691961  -1.8805554
Se  0.9836911  -0.4370502  2.5436705
H   2.3791086  4.3305423  3.2687790
C   2.7063095  3.2957501  3.2668187
C   4.0223451  2.9727250  3.6027376
C   4.7200790  3.7614541  3.8655195
C   4.4461426  1.6423649  3.6099071
H   5.4680366  1.3949190  3.8788855
C   3.5563310  0.6222066  3.2767742
H   3.8779216  -0.4146823  3.2906168
C   2.2461526  0.9643379  2.9313455
C   1.8017863  2.2891282  2.9316061
H   0.7746389  2.5335737  2.6788488
H   2.7511023  -0.6259996  0.7174118
H   0.9891854  0.8611795  0.3049207
Me₂Se

E(TPSS-D3/def2-TZVP) = -2481.360268784 (conv)
Lowest Freq. = 146.29 cm⁻¹

Me₂Se (002/c1/tpss-d3.def2-TZVP)

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5. References