

Copper-catalyzed regio- and chemoselective selenosulfonation of 1,6-enynes from sulfur dioxide

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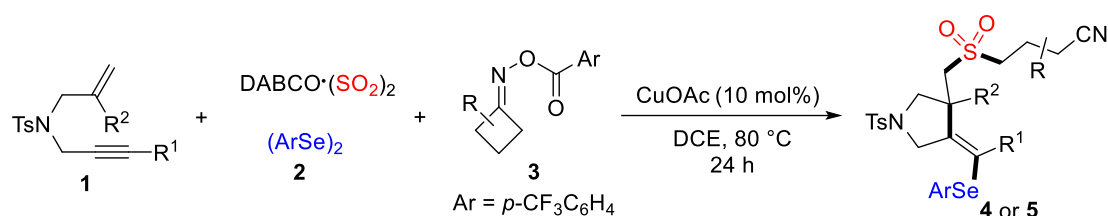
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S3-S18).
3. References (S18)
4. ¹H, ¹³C and ¹⁹F NMR spectra of compounds **4**, **5** and **6** (S19-S79).

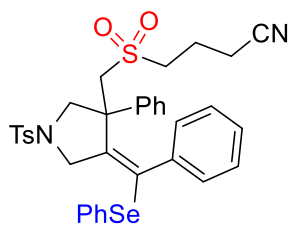
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H , ^{13}C and ^{19}F NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz, 100 MHz and 376 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument. All of 1,6-enynes **1**, diselenides **2**, and cycloketone oxime esters **3** were prepared according to the reported procedures.¹⁻³

*General experimental procedure for the reaction of 1,6-enyne **1**, $(\text{DABCO})\cdot(\text{SO}_2)_2$, diselenide **2**, and cycloketone oxime ester **3**.*

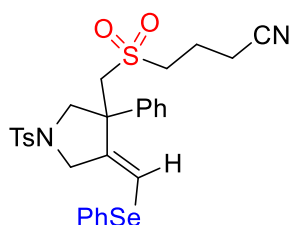


1,2-Dichloroethane (2.0 mL) was added to a sealed tube containing 1,6-enynes **1** (0.2 mmol), $(\text{DABCO})\cdot(\text{SO}_2)_2$ (0.2 mmol), diselenides **2a** (0.2 mmol), cycloketone oxime esters **3a** (0.4 mmol) and CuOAc (10 mol%) under N_2 atmosphere via a syringe. The resulting mixture was stirred at $80\text{ }^\circ\text{C}$ for 24 hours. After completion of reaction as monitored by TLC analysis, the mixture was diluted with ethyl acetate and washed with saturated aqueous NaHCO_3 (10 mL), brine (10 mL), and dried over anhydrous Na_2SO_4 . Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 2:1) to give the corresponding products **4** or **5**.



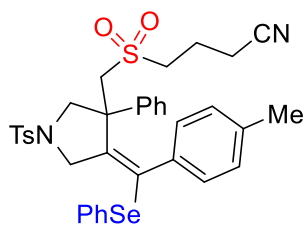
(Z)-4-(((3-Phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4a**)

Yellow solid, 86% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.19 – 7.14 (m, 3H), 7.14 – 7.09 (m, 5H), 7.00 (t, $J = 7.5$ Hz, 2H), 6.92 (t, $J = 7.4$ Hz, 1H), 6.84 (t, $J = 7.5$ Hz, 2H), 6.46 (d, $J = 6.7$ Hz, 2H), 4.32 (d, $J = 14.3$ Hz, 1H), 4.07 (d, $J = 14.3$ Hz, 1H), 3.87 (q, $J = 10.5$ Hz, 2H), 3.45 (d, $J = 15.0$ Hz, 1H), 3.35 (d, $J = 15.0$ Hz, 1H), 2.81 (t, $J = 7.3$ Hz, 2H), 2.50 (s, 3H), 2.47 (td, $J = 7.2, 2.7$ Hz, 2H), 2.06 – 1.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 141.1, 139.8, 137.1, 136.0, 131.5, 131.0, 130.0, 129.1, 128.7, 128.1, 128.3, 128.2, 127.6, 127.5, 127.4, 127.3, 126.7, 118.2, 59.2, 59.1, 54.3, 53.9, 52.9, 21.7, 18.2, 16.1; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{34}\text{N}_2\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 713.1023, found: 713.1031.



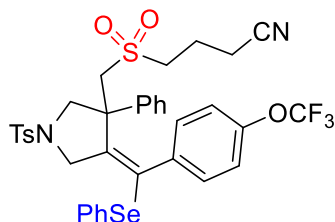
(Z)-4-(((3-Phenyl-4-((phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4b**)

Yellow oil, 34% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.66 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.27 (m, 10H), 6.73 – 6.41 (m, 1H), 4.67 (d, $J = 10.7$ Hz, 1H), 3.86 (d, $J = 15.1$ Hz, 1H), 3.79 – 3.68 (m, 2H), 3.25 (d, $J = 6.9$ Hz, 1H), 3.21 (d, $J = 2.5$ Hz, 1H), 2.45 (s, 3H), 2.36 – 2.19 (m, 3H), 2.17 – 2.05 (m, 1H), 1.94 – 1.78 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 143.2, 137.0, 132.5, 132.4, 132.1, 130.0, 129.6, 129.3, 128.5, 128.0, 127.8, 127.0, 117.9, 115.7, 61.7, 55.3, 52.5, 52.1, 50.5, 21.6, 18.0, 16.1; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 637.0710, found: 637.0723.



(Z)-4-(((3-Phenyl-4-((phenylselanyl)(*p*-tolyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4c**)

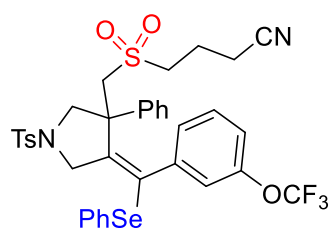
Yellow solid, 82% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.73 (m, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.10 (m, 8H), 7.01 (t, $J = 7.5$ Hz, 2H), 6.67 (d, $J = 7.8$ Hz, 2H), 6.39 (d, $J = 7.5$ Hz, 2H), 4.28 (d, $J = 14.4$ Hz, 1H), 4.06 (d, $J = 14.4$ Hz, 1H), 3.92 (d, $J = 10.5$ Hz, 1H), 3.83 (d, $J = 10.5$ Hz, 1H), 3.45 (d, $J = 15.0$ Hz, 1H), 3.33 (d, $J = 15.0$ Hz, 1H), 2.74 (t, $J = 7.1$ Hz, 2H), 2.50 (s, 3H), 2.45 (td, $J = 7.1, 5.0$ Hz, 2H), 2.14 (s, 3H), 2.04 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 141.2, 140.1, 137.2, 135.7, 134.4, 131.6, 131.0, 130.0, 129.0, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 127.5, 126.8, 118.1, 59.4, 58.9, 54.3, 53.8, 52.8, 21.7, 21.1, 18.2, 16.1; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{36}\text{N}_2\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 727.1179, found: 727.1186.



(Z)-4-(((3-Phenyl-4-((phenylselanyl)(4-(trifluoromethoxy)phenyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4d**)

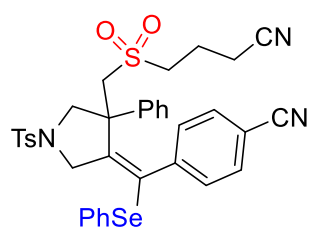
Yellow solid, 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.16 – 7.07 (m, 6H), 7.04 – 6.96 (m, 4H), 6.80 (t, $J = 7.5$ Hz, 1H), 6.71 (d, $J = 8.2$ Hz, 1H), 6.25 (d, $J = 61.7$ Hz, 2H), 4.37 (d, $J = 14.4$ Hz, 1H), 4.16 – 3.99 (m, 2H), 3.65 (d, $J = 10.5$ Hz, 1H), 3.52 (q, $J = 14.9$ Hz, 2H), 3.17 – 2.95 (m, 2H), 2.61 – 2.46 (m, 5H), 2.26 – 2.03 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 148.0, 144.5, 140.9, 140.4, 138.8, 136.2, 131.2, 130.1, 129.8, 128.8, 128.7, 128.6, 128.4, 128.2, 127.6, 127.5, 126.8, 126.5, 121.5, 120.1 (q, $J = 257.6$ Hz), 119.5, 118.2, 59.7, 58.7, 54.6, 54.4, 53.1, 21.7,

18.3, 16.2; ^{19}F NMR (376 MHz, CDCl_3) δ -57.7; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{33}\text{N}_2\text{O}_5\text{F}_3\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 797.0846, found: 797.0858.



(Z)-4-(((3-Phenyl-4-((phenylselanyl)(3-(trifluoromethoxy)phenyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4e**)

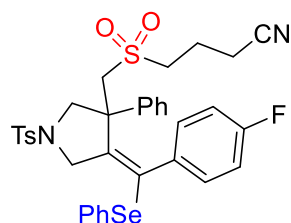
Yellow solid, 82% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.17 – 7.07 (m, 6H), 7.04 – 6.96 (m, 4H), 6.81 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.25 (d, J = 61.3 Hz, 2H), 4.37 (d, J = 14.4 Hz, 1H), 4.11 – 4.03 (m, 2H), 3.65 (d, J = 10.5 Hz, 1H), 3.55 (d, J = 15.0 Hz, 1H), 3.49 (d, J = 14.9 Hz, 1H), 3.05 (td, J = 7.1, 2.9 Hz, 2H), 2.54 (t, J = 7.2 Hz, 2H), 2.51 (s, 3H), 2.18 – 2.07 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 148.0, 144.5, 141.0, 140.4, 138.8, 136.2, 131.2, 130.1, 129.8, 128.8, 128.7, 128.6, 128.4, 128.2, 127.6, 127.5, 126.8, 126.5, 121.5, 120.2 (q, J = 257.6 Hz), 119.5, 118.3, 59.7, 58.7, 54.6, 54.4, 53.1, 21.7, 18.3, 16.2; ^{19}F NMR (376 MHz, CDCl_3) δ -57.7; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{33}\text{N}_2\text{O}_5\text{F}_3\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 797.0846, found: 797.0860.



(Z)-4-(((4-(((3-Cyanopropyl)sulfonyl)methyl)-4-phenyl-1-tosylpyrrolidin-3-ylidene)(phenylselanyl)methyl)benzonitrile (**4f**)

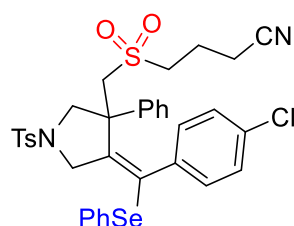
Yellow oil, 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.20 – 7.07 (m, 6H), 7.06 – 6.98 (m, 4H), 6.90 (d, J = 7.1 Hz, 2H), 6.35 (s, 2H), 4.48 (d, J = 14.4 Hz, 1H), 4.16 (d, J = 10.6 Hz, 1H), 4.07 (d, J = 14.4 Hz, 1H), 3.55 (d, J = 2.3 Hz, 2H), 3.50 (d, J = 10.6 Hz, 1H), 3.22 (td, J = 7.1, 2.4 Hz, 2H), 2.61 (t, J = 7.1 Hz,

2H), 2.52 (s, 3H), 2.28 – 2.17 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 141.9, 141.7, 141.1, 136.2, 130.9, 130.8, 130.1, 129.5, 129.4, 129.0, 128.9, 128.5, 128.3, 127.6, 126.6, 126.6, 118.3, 118.3, 110.4, 60.2, 58.7, 55.0, 54.6, 53.1, 21.7, 18.3, 16.3; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 738.0975, found: 738.0984.



(Z)-4-(((4-((4-Fluorophenyl)(phenylselanyl)methylene)-3-phenyl-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4g**)

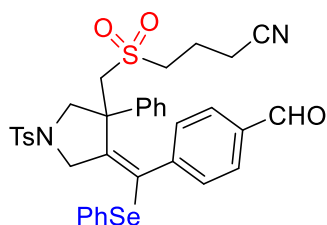
Yellow solid, 77% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.18 – 7.09 (m, 6H), 7.07 – 6.97 (m, 4H), 6.48 (t, $J = 8.5$ Hz, 2H), 6.32 (s, 2H), 4.37 (d, $J = 14.3$ Hz, 1H), 4.08 – 3.98 (m, 2H), 3.66 (d, $J = 10.6$ Hz, 1H), 3.53 (d, $J = 15.0$ Hz, 1H), 3.46 (d, $J = 15.0$ Hz, 1H), 3.03 (t, $J = 7.3$ Hz, 2H), 2.61 – 2.53 (m, 2H), 2.51 (s, 3H), 2.20 – 2.07 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.4 (d, $J = 248.4$ Hz), 144.4, 141.4, 140.6, 136.1, 133.1 (d, $J = 3.4$ Hz), 131.2, 130.7 (d, $J = 8.2$ Hz), 130.5, 130.0, 128.8, 128.5, 128.4, 128.2, 127.5, 127.3, 126.6, 118.2, 114.2 (d, $J = 21.7$ Hz), 59.7, 59.0, 54.7, 54.3, 53.0, 21.7, 18.2, 16.2; ^{19}F NMR (376 MHz, CDCl_3) δ -113.6; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{33}\text{N}_2\text{O}_4\text{NaS}_2\text{SeF}^+$ ($\text{M}+\text{Na}^+$): 731.0929, found: 731.0938.



(Z)-4-(((4-((4-Chlorophenyl)(phenylselanyl)methylene)-3-phenyl-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4h**)

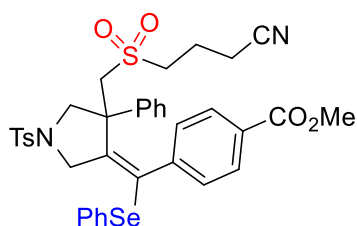
Brown solid, 83% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.09 (m, 6H), 7.08 – 6.97 (m, 4H), 6.75 (d, $J = 8.3$ Hz, 2H), 6.27 (d, $J = 7.1$ Hz, 2H), 4.38 (d, $J = 14.4$ Hz, 1H), 4.05 (t, $J = 12.2$ Hz, 2H), 3.65 (d, $J = 10.5$ Hz, 1H),

3.54 (d, $J = 15.0$ Hz, 1H), 3.46 (d, $J = 15.0$ Hz, 1H), 3.04 (t, $J = 7.3$ Hz, 2H), 2.56 (t, $J = 7.3$ Hz, 2H), 2.51 (s, 3H), 2.19 – 2.07 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 141.4, 141.1, 136.0, 135.6, 133.0, 131.2, 130.2, 130.1, 130.0, 129.0, 128.6, 128.5, 128.2, 127.5, 127.4, 127.3, 126.6, 118.3, 59.8, 58.9, 54.8, 54.3, 52.9, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{33}\text{N}_2\text{O}_4\text{NaS}_2\text{ClSe}^+$ ($\text{M}+\text{Na}^+$): 747.0633, found: 747.0640.



(*Z*)-4-(((4-((4-Formylphenyl)(phenylselanyl)methylene)-3-phenyl-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4i**)

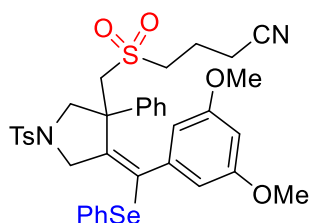
Yellow solid, 69% yield; ^1H NMR (400 MHz, CDCl_3) δ 9.75 (s, 1H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.26 (t, $J = 3.7$ Hz, 2H), 7.17 – 7.05 (m, 6H), 7.03 – 6.93 (m, 4H), 6.48 (s, 2H), 4.45 (d, $J = 14.4$ Hz, 1H), 4.23 – 4.04 (m, 2H), 3.68 – 3.41 (m, 3H), 3.11 (t, $J = 7.3$ Hz, 2H), 2.57 (t, $J = 7.1$ Hz, 2H), 2.51 (s, 3H), 2.21 – 2.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 144.6, 143.5, 141.3, 141.2, 136.1, 134.4, 131.1, 130.1, 129.9, 129.5, 128.9, 128.7, 128.5, 128.4, 128.2, 127.6, 126.9, 126.6, 118.3, 59.9, 58.8, 54.9, 54.4, 53.1, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}_5\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 741.0972, found: 741.0978.



Methyl (*Z*)-4-(((4-(((3-cyanopropyl)sulfonyl)methyl)-4-phenyl-1-tosylpyrrolidin-3-ylidene)(phenylselanyl)methyl)benzoate (**4j**)

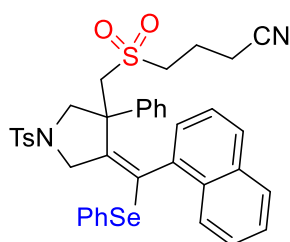
Yellow solid, 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 8.3$ Hz, 4H), 7.17 – 7.07 (m, 6H), 7.00 (t, $J = 8.3$ Hz, 4H), 6.43 (s, 2H), 4.40 (d, $J = 14.4$ Hz, 1H), 4.16 – 3.96 (m, 2H), 3.83 (s, 3H), 3.67 (d, $J = 10.5$ Hz, 1H), 3.48 (q, $J = 15.0$ Hz,

2H), 3.01 (t, $J = 7.3$ Hz, 2H), 2.60 – 2.48 (m, 5H), 2.20 – 2.06 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 144.5, 141.9, 141.1, 141.1, 136.0, 131.20, 130.1, 130.0, 128.9, 128.9, 128.7, 128.5, 128.4, 128.4, 128.2, 127.6, 127.1, 126.6, 118.2, 59.7, 58.9, 54.8, 54.3, 53.0, 52.1, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{36}\text{N}_2\text{O}_6\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 771.1078, found: 771.1083.



(*Z*)-4-(((4-((3,5-Dimethoxyphenyl)(phenylselanyl)methylene)-3-phenyl-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4k**)

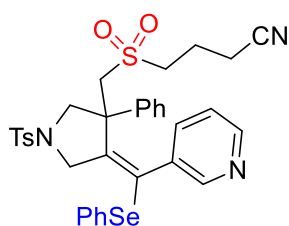
Yellow solid, 91% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.12 (m, 8H), 7.05 (t, $J = 7.5$ Hz, 2H), 6.02 (t, $J = 2.2$ Hz, 1H), 5.59 (s, 2H), 4.26 (d, $J = 14.3$ Hz, 1H), 4.15 (d, $J = 14.4$ Hz, 1H), 3.92 (d, $J = 10.4$ Hz, 1H), 3.78 (d, $J = 10.3$ Hz, 1H), 3.67 – 3.54 (m, 1H), 3.51 – 3.33 (m, 7H), 3.00 – 2.80 (m, 2H), 2.56 – 2.43 (m, 5H), 2.14 – 1.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 144.3, 142.0, 139.8, 139.0, 135.9, 131.5, 130.3, 130.0, 128.7, 128.4, 128.4, 128.1, 127.8, 127.5, 126.6, 118.2, 107.1, 100.1, 59.6, 58.7, 55.1, 54.7, 54.0, 52.7, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{38}\text{N}_2\text{O}_6\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 773.1234, found: 773.1245.



(*Z*)-4-(((4-(Naphthalen-1-yl)(phenylselanyl)methylene)-3-phenyl-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4l**)

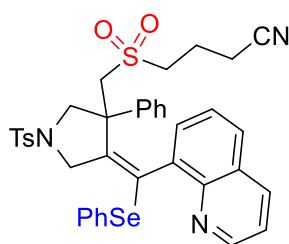
Yellow solid, 81% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (t, $J = 8.4$ Hz, 2H), 7.72 – 7.61 (m, 1.38H), 7.55 – 7.36 (m, 6H), 7.23 – 7.11 (m, 4H), 7.05 – 6.62 (m, 9H), 6.27 (dd, $J = 7.1, 0.68$ Hz, 1H), 4.50 (d, $J = 14.3$ Hz, 0.38H), 4.38 (d, $J = 14.2$ Hz, 0.68H), 4.22 (d, $J =$

14.2 Hz, 0.68H), 4.13 – 4.05 (m, 1H), 3.92 (q, $J = 10.8$ Hz, 0.68H), 3.80 (d, $J = 10.6$ Hz, 0.68H), 3.65 (m, 1H), 2.96 (q, $J = 14.6$ Hz, 1.38H), 2.87 – 2.59 (m, 1H), 2.54 (d, $J = 3.8$ Hz, 3H), 2.46 – 2.19 (m, 4H), 2.07 – 1.92 (m, 1H), 1.69 – 1.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 144.2, 141.0, 139.6, 139.5, 137.5, 136.5, 136.5, 133.3, 133.1, 133.0, 132.9, 132.1, 131.4, 131.1, 130.1, 130.0, 129.3, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.8, 126.7, 126.6, 126.5, 126.3, 126.1, 125.8, 125.6, 125.2, 124.5, 123.7, 118.1, 117.9, 60.5, 58.5, 58.3, 58.0, 54.1, 53.6, 53.5, 53.3, 52.9, 21.7, 18.2, 18.0, 16.1, 16.0; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{36}\text{N}_2\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 763.1179, found: 763.1193.



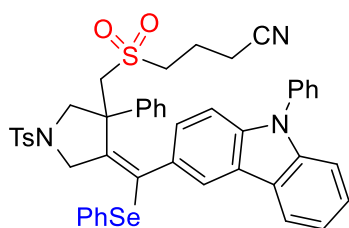
(Z)-4-(((3-Phenyl-4-((phenylselanyl)(pyridin-3-yl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4m**)

Yellow oil, 54% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 3.9$ Hz, 1H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.59 (s, 1H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.07 (m, 6H), 7.06 – 6.92 (m, 4H), 6.69 – 6.50 (m, 2H), 4.44 (d, $J = 14.4$ Hz, 1H), 4.12 (dd, $J = 17.1, 12.5$ Hz, 2H), 3.70 – 3.45 (m, 3H), 3.15 (t, $J = 7.3$ Hz, 2H), 2.63 – 2.54 (m, 2H), 2.51 (s, 3H), 2.22 – 2.13 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.0, 147.7, 144.6, 142.4, 141.1, 136.2, 135.8, 133.2, 131.1, 130.1, 129.0, 128.8, 128.5, 128.2, 127.8, 127.7, 126.8, 126.5, 121.9, 118.3, 60.0, 58.6, 54.9, 54.6, 53.2, 21.7, 18.3, 16.2; HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{34}\text{N}_3\text{O}_4\text{S}_2\text{Se}^+$ ($\text{M}+\text{H}^+$): 692.1156, found: 692.1159.



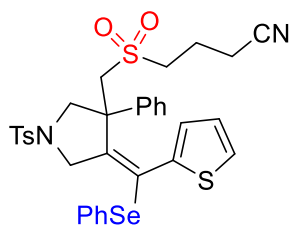
(Z)-4-(((3-Phenyl-4-((phenylselanyl)(quinolin-8-yl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4n**)

Yellow solid, 68% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.79 – 8.74 (m, 1H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.24 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.13 – 7.08 (m, 3H), 7.07 – 6.94 (m, 5H), 6.89 (t, $J = 7.5$ Hz, 3H), 6.53 (s, 1H), 4.41 (d, $J = 14.3$ Hz, 1H), 4.23 (d, $J = 14.4$ Hz, 1H), 4.06 (d, $J = 10.4$ Hz, 1H), 3.66 (d, $J = 10.4$ Hz, 1H), 3.51 (d, $J = 14.8$ Hz, 1H), 3.43 (d, $J = 14.8$ Hz, 1H), 3.01 (t, $J = 7.3$ Hz, 2H), 2.57 – 2.45 (m, 5H), 2.19 – 2.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.8, 146.6, 144.4, 141.8, 136.0, 135.8, 135.2, 131.2, 130.3, 130.2, 130.0, 128.7, 128.5, 128.4, 128.2, 128.1, 127.5, 127.5, 126.6, 126.4, 121.4, 118.2, 59.9, 58.7, 55.1, 54.3, 52.7, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{38}\text{H}_{36}\text{N}_3\text{O}_4\text{S}_2\text{Se}^+$ ($\text{M}+\text{H}^+$): 742.1312, found: 742.1317.



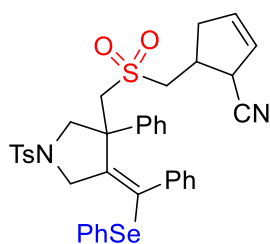
(Z)-4-(((3-Phenyl-4-((9-phenyl-9H-carbazol-3-yl)(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4o**)

Yellow solid, 66% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 7.2$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.45 – 7.38 (m, 5H), 7.37 – 7.31 (m, 2H), 7.26 – 7.19 (m, 2H), 7.16 (d, $J = 4.7$ Hz, 7H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.93 (t, $J = 7.4$ Hz, 3H), 6.65 (s, 1H), 4.36 – 4.21 (m, 2H), 3.93 (d, $J = 10.3$ Hz, 1H), 3.86 (d, $J = 10.3$ Hz, 1H), 3.44 (d, $J = 14.8$ Hz, 1H), 3.34 (d, $J = 14.8$ Hz, 1H), 2.74 (t, $J = 7.3$ Hz, 2H), 2.49 (s, 3H), 2.32 (t, $J = 6.8$ Hz, 2H), 2.00 – 1.84 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 142.5, 141.1, 140.9, 139.5, 137.2, 135.5, 131.6, 131.4, 130.0, 130.0, 129.0, 128.7, 128.5, 128.3, 128.2, 128.0, 127.7, 127.5, 127.2, 126.8, 126.5, 126.3, 122.9, 122.1, 121.2, 120.3, 120.2, 118.1, 110.0, 108.7, 59.5, 58.8, 54.9, 53.9, 52.6, 21.7, 18.1, 16.1; HRMS (ESI) calcd for $\text{C}_{47}\text{H}_{41}\text{N}_3\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 878.1601, found: 878.1623.



(Z)-4-(((3-Phenyl-4-((phenylselanyl)(thiophen-2-yl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**4p**)

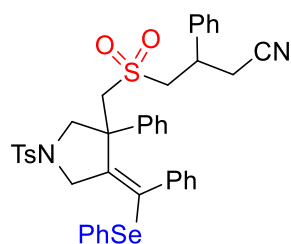
Yellow oil, 74% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.27 – 7.16 (m, 8H), 7.09 (t, $J = 7.4$ Hz, 2H), 6.98 (dd, $J = 5.1, 0.8$ Hz, 1H), 6.47 (dd, $J = 5.0, 3.7$ Hz, 1H), 6.03 (dd, $J = 3.4, 0.8$ Hz, 1H), 4.22 (s, 2H), 3.93 (d, $J = 10.3$ Hz, 1H), 3.86 (d, $J = 10.2$ Hz, 1H), 3.61 (d, $J = 14.9$ Hz, 1H), 3.50 (d, $J = 14.8$ Hz, 1H), 2.86 (t, $J = 7.3$ Hz, 2H), 2.56 – 2.35 (m, 5H), 2.11 – 1.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 144.1, 141.7, 139.0, 135.1, 131.5, 130.0, 129.0, 128.9, 128.8, 128.4, 128.3, 128.1, 127.7, 126.8, 126.6, 126.0, 123.2, 118.2, 59.5, 58.1, 55.3, 53.8, 53.2, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2\text{O}_4\text{NaS}_3\text{Se}^+$ ($\text{M}+\text{Na}^+$): 719.0587, found: 719.0600.



(Z)-5-(((3-Phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)methyl)cyclopent-2-ene-1-carbonitrile (**5a**)

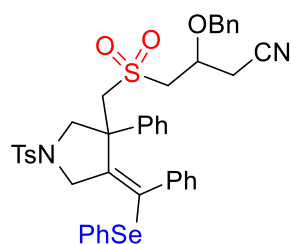
Yellow solid, 92% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.73 (m, 3H), 7.40 (t, $J = 7.0$ Hz, 4H), 7.23 (s, 4H), 7.18 – 7.09 (m, 9H), 7.03 – 6.89 (m, 7H), 6.84 (t, $J = 7.5$ Hz, 1H), 6.59 (d, $J = 7.2$ Hz, 1H), 6.44 (d, $J = 6.2$ Hz, 1H), 5.80 – 5.47 (m, 3H), 4.30 – 4.13 (m, 3H), 4.04 (dd, $J = 12.3, 7.0$ Hz, 2H), 3.80 (d, $J = 10.3$ Hz, 1H), 3.70 (d, $J = 10.4$ Hz, 1H), 3.49 – 3.09 (m, 6H), 2.82 – 2.53 (m, 5H), 2.50 (d, $J = 5.2$ Hz, 5H), 2.45 – 2.28 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 144.1, 141.5, 140.5, 140.1, 139.6, 137.2, 137.2, 136.0, 135.8, 131.9, 131.6, 130.8, 130.8, 130.6, 130.6, 129.9, 129.8, 129.8, 129.3, 129.0, 128.7, 128.6, 128.3, 128.3, 128.1, 127.9, 127.6, 127.5, 127.4, 127.2, 126.8, 126.6, 117.4, 117.2, 66.4,

65.6, 59.2, 58.4, 58.3, 56.4, 54.3, 53.8, 53.0, 52.9, 42.4, 42.2, 34.6, 23.2, 21.7; HRMS (ESI) calcd for $C_{38}H_{36}N_2O_4NaS_2Se^+$ ($M+Na^+$): 751.1179, found: 751.1193.



(Z)-3-Phenyl-4-(((3-phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**5b**)

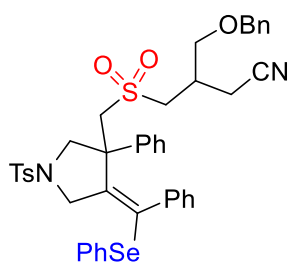
Yellow solid, 75% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.45 – 7.37 (m, 3H), 7.37 – 7.27 (m, 3H), 7.17 – 6.94 (m, 10H), 6.93 – 6.84 (m, 1H), 6.83 – 6.72 (m, 3H), 6.43 (d, $J = 6.9$ Hz, 1H), 6.21 (d, $J = 3.0$ Hz, 1H), 4.32 – 4.20 (m, 1H), 4.10 – 4.00 (m, 1H), 3.82 (m, 1H), 3.67 – 3.57 (m, 1H), 3.53 – 3.35 (m, 2H), 3.33 – 3.24 (m, 1H), 3.20 – 2.92 (m, 2H), 2.90 – 2.77 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 144.3, 141.5, 141.4, 140.4, 139.7, 139.0, 138.5, 137.1, 135.9, 135.8, 131.5, 131.2, 130.9, 130.7, 130.0, 130.0, 129.5, 129.3, 129.1, 128.8, 128.7, 128.5, 128.5, 128.3, 128.3, 128.2, 127.7, 127.7, 127.5, 127.3, 127.2, 127.2, 127.0, 126.6, 126.6, 117.4, 117.2, 60.5, 60.5, 59.4, 59.0, 58.6, 54.7, 54.5, 53.1, 52.7, 37.1, 36.0, 24.4, 24.3, 21.7; HRMS (ESI) calcd for $C_{41}H_{38}N_2O_4NaS_2Se^+$ ($M+Na^+$): 789.1336, found: 789.1351.



(Z)-3-(Benzyloxy)-4-(((3-phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**5c**)

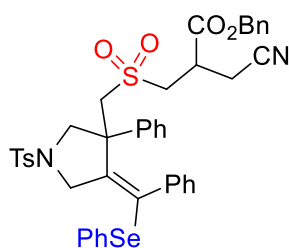
Yellow oil, 81% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.44 – 7.27 (m, 8H), 7.17 – 7.04 (m, 6H), 7.02 – 6.94 (m, 3H), 6.93 – 6.85 (m, 2H), 6.82 – 6.74 (m, 2H), 6.34 (m, 2H), 4.64 – 4.58 (m, 1H), 4.51 (t, $J = 10.8$ Hz, 1H), 4.30 (d, $J = 14.2$ Hz, 0.59H), 4.25 – 4.16 (m, 2H), 4.03 (m, 1H), 3.84 (s, 1H), 3.63 (d, $J = 10.3$ Hz, 0.51H), 3.51 – 3.33

(m, 2H), 3.32 – 3.16 (m, 1H), 3.02 – 2.90 (m, 1H), 2.76 – 2.67 (m, 1H), 2.65 – 2.55 (m, 1H), 2.48 (d, $J = 3.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 144.2, 142.5, 141.6, 140.3, 139.9, 137.2, 137.1, 136.2, 135.9, 135.6, 131.7, 131.5, 130.7, 130.3, 129.9, 129.2, 128.9, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.3, 127.3, 127.2, 127.1, 126.5, 126.4, 116.1, 116.0, 72.8, 72.5, 70.0, 69.9, 61.4, 59.7, 59.6, 59.6, 59.5, 59.0, 54.8, 54.5, 52.6, 52.6, 22.8, 22.8, 21.7, 21.7; HRMS (ESI) calcd for $\text{C}_{42}\text{H}_{40}\text{N}_2\text{O}_5\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 819.1442, found: 819.1455.



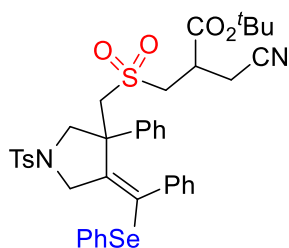
(*Z*)-4-(Benzyloxy)-3-(((3-phenyl-4-(phenyl(phenylselenanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)methyl)butanenitrile (**5d**)

Brown oil, 92% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (dd, $J = 8.2, 3.5$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 2H), 7.36 – 7.33 (m, 2H), 7.30 (t, $J = 8.0$ Hz, 3H), 7.15 – 7.12 (m, 4H), 7.11 – 7.06 (m, 4H), 7.00 (t, $J = 7.5$ Hz, 2H), 6.91 – 6.86 (m, 1H), 6.80 (dd, $J = 16.9, 8.0$ Hz, 2H), 6.44 (s, 2H), 4.49 (s, 2H), 4.30 (dd, $J = 14.3, 7.0$ Hz, 1H), 4.13 – 4.06 (m, 1H), 3.91 (dd, $J = 10.4, 4.2$ Hz, 1H), 3.82 (dd, $J = 10.4, 3.1$ Hz, 1H), 3.57 – 3.52 (m, 1H), 3.50 – 3.42 (m, 2H), 3.36 (dd, $J = 14.9, 3.0$ Hz, 1H), 2.96 – 2.84 (m, 1H), 2.81 – 2.71 (m, 1H), 2.70 – 2.53 (m, 3H), 2.51 – 2.49 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 141.5, 141.4, 139.9, 139.8, 137.5, 137.2, 135.9, 131.6, 131.0, 130.9, 130.0, 129.1, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 127.7, 127.5, 127.4, 127.3, 127.3, 127.2, 126.7, 117.4, 73.5, 70.1, 70.0, 59.8, 59.7, 59.3, 55.8, 55.7, 54.5, 52.9, 52.9, 30.7, 30.7, 21.7, 19.3, 19.2; HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{42}\text{N}_2\text{O}_5\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 833.1598, found: 833.1617.



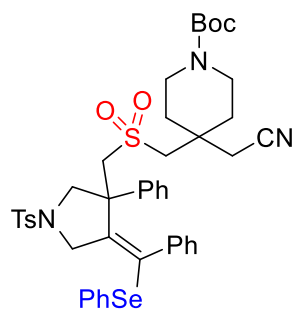
(Z)-Benzyl-3-cyano-2-((((3-phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)methyl)propanoate (**5e**)

Brown oil, 68% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.9$ Hz, 2H), 7.40 – 7.34 (m, 8H), 7.19 – 7.14 (m, 3H), 7.13 – 7.08 (m, 4H), 7.00 (t, $J = 7.6$ Hz, 2H), 6.93 – 6.77 (m, 3H), 6.45 (d, $J = 7.0$ Hz, 2H), 5.26 – 5.11 (m, 2H), 4.36 – 4.08 (m, 2H), 3.93 – 3.80 (m, 2H), 3.47 (dd, $J = 14.8, 7.7$ Hz, 1H), 3.40 – 3.18 (m, 3H), 3.03 – 2.89 (m, 1H), 2.87 – 2.76 (m, 2H), 2.48 (d, $J = 3.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 169.3, 144.2, 144.2, 141.8, 141.5, 139.6, 139.5, 137.2, 137.1, 135.9, 135.3, 134.6, 132.1, 131.7, 131.6, 131.0, 130.9, 130.0, 129.7, 129.1, 129.1, 128.8, 128.8, 128.8, 128.7, 128.7, 128.6, 128.3, 128.2, 127.7, 127.6, 127.4, 127.4, 127.3, 126.6, 126.5, 68.4, 68.4, 60.0, 59.8, 59.3, 59.2, 54.7, 54.6, 54.5, 54.5, 52.8, 52.7, 35.8, 35.7, 21.7, 19.4; HRMS (ESI) calcd for $\text{C}_{43}\text{H}_{40}\text{N}_2\text{O}_6\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 847.1391, found: 847.1406.



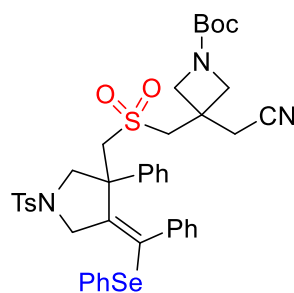
(Z)-tert-Butyl-3-cyano-2-((((3-phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)methyl)propanoate (**5f**)

Brown oil, 57% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, $J = 8.2, 2.2$ Hz, 2H), 7.40 (dd, $J = 8.0, 3.2$ Hz, 2H), 7.19 (t, $J = 5.3$ Hz, 3H), 7.15 – 7.10 (m, 5H), 7.00 (t, $J = 7.7$ Hz, 2H), 6.96 – 6.90 (m, 1H), 6.89 – 6.82 (m, 2H), 6.46 (d, $J = 18.8$ Hz, 2H), 4.36 – 4.07 (m, 2H), 3.96 – 3.84 (m, 2H), 3.48 (dd, $J = 14.8, 4.1$ Hz, 1H), 3.36 (dd, $J = 14.8, 10.4$ Hz, 1H), 3.21 (ddd, $J = 20.9, 13.9, 4.5$ Hz, 1H), 3.09 (dd, $J = 6.6, 4.6$ Hz, 1H), 2.96 – 2.69 (m, 3H), 2.50 (d, $J = 2.1$ Hz, 3H), 1.48 (d, $J = 4.3$ Hz, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 144.2, 144.1, 141.9, 141.4, 139.7, 139.6, 137.2, 137.1, 136.0, 135.9, 131.7, 131.0, 130.8, 130.0, 129.1, 128.7, 128.6, 128.5, 128.3, 128.3, 128.2, 127.7, 127.6, 127.6, 127.4, 127.4, 127.3, 126.6, 126.5, 116.6, 116.5, 83.9, 60.2, 59.8, 59.3, 59.1, 54.9, 54.5, 54.4, 52.8, 52.6, 36.5, 36.4, 27.8, 21.7, 19.6, 19.6; HRMS (ESI) calcd for $\text{C}_{40}\text{H}_{42}\text{N}_2\text{O}_6\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 813.1547, found: 813.1557.



(*Z*)-*tert*-Butyl-4-(cyanomethyl)-4-((((3-phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)methyl)piperidine-1-carboxylate (**5g**)

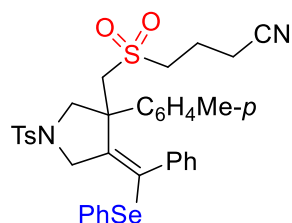
Yellow solid, 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.15 – 7.08 (m, 6H), 7.07 – 6.96 (m, 4H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.80 (t, $J = 7.5$ Hz, 2H), 6.42 (d, $J = 5.8$ Hz, 2H), 4.38 (d, $J = 14.3$ Hz, 1H), 4.07 – 3.94 (m, 2H), 3.76 (d, $J = 10.5$ Hz, 1H), 3.67 – 3.44 (m, 4H), 3.30 – 3.12 (m, 2H), 3.03 (d, $J = 14.3$ Hz, 1H), 2.94 (d, $J = 14.2$ Hz, 1H), 2.82 (q, $J = 16.9$ Hz, 2H), 2.50 (s, 3H), 1.87 – 1.69 (m, 2H), 1.62 – 1.50 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 144.3, 139.7, 137.0, 136.0, 131.4, 131.4, 130.0, 129.0, 128.7, 128.4, 128.3, 128.2, 127.5, 127.4, 127.3, 127.1, 126.8, 117.0, 80.0, 62.1, 59.3, 58.3, 54.4, 53.2, 36.1, 34.3, 34.3, 28.4, 27.1, 21.7; HRMS (ESI) calcd for $\text{C}_{44}\text{H}_{49}\text{N}_3\text{O}_6\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 882.2126, found: 882.2140.



(*Z*)-*tert*-Butyl-3-(cyanomethyl)-3-((((3-phenyl-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)methyl)azetidine-1-carboxylate (**5h**)

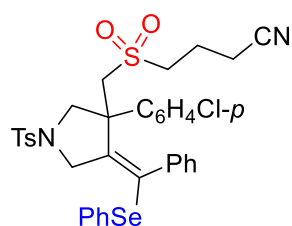
Yellow solid, 63% yield; ^1H NMR (400 MHz, CDCl_3) 7.77 (d, $J = 8.1$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.16 – 7.08 (m, 6H), 7.07 – 6.98 (m, 4H), 6.90 (t, $J = 7.4$ Hz, 1H), 6.81 (t, $J = 7.4$ Hz, 2H), 6.42 (d, $J = 6.3$ Hz, 2H), 4.40 (d, $J = 14.3$ Hz, 1H), 4.09 – 3.89 (m, 4H), 3.79 – 3.70 (m, 3H), 3.49 (q, $J = 15.2$ Hz, 2H), 3.34 (d, $J = 13.9$ Hz, 1H), 3.10 (d, $J = 13.9$ Hz, 1H), 2.99 (s, 2H), 2.51 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 144.4,

140.5, 139.4, 137.0, 136.1, 131.6, 131.4, 130.1, 129.0, 128.7, 128.4, 128.4, 128.2, 127.5, 127.5, 127.3, 127.2, 126.8, 116.5, 80.4, 61.4, 59.1, 58.4, 58.3, 54.4, 53.2, 33.4, 28.3, 25.9, 21.7; HRMS (ESI) calcd for $C_{42}H_{45}N_3O_6NaS_2Se^+$ ($M+Na^+$): 854.1813, found: 854.1829.



(Z)-4-(((4-(Phenyl(phenylselanyl)methylene)-3-(*p*-tolyl)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**5i**)

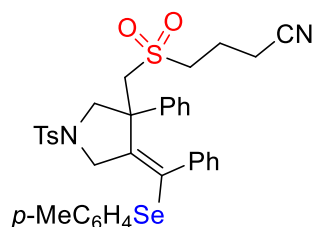
Light yellow solid, 76% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.16 – 7.09 (m, 3H), 7.05 – 6.91 (m, 7H), 6.86 (t, $J = 7.5$ Hz, 2H), 6.52 (d, $J = 7.1$ Hz, 2H), 4.28 (d, $J = 14.3$ Hz, 1H), 4.06 (d, $J = 14.4$ Hz, 1H), 3.91 (d, $J = 10.4$ Hz, 1H), 3.81 (d, $J = 10.4$ Hz, 1H), 3.39 (d, $J = 14.9$ Hz, 1H), 3.29 (d, $J = 14.9$ Hz, 1H), 2.73 (t, $J = 7.3$ Hz, 2H), 2.50 (s, 3H), 2.44 (td, $J = 7.2, 3.2$ Hz, 2H), 2.28 (s, 3H), 2.01 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.9, 137.8, 137.4, 137.3, 135.9, 131.7, 130.6, 130.0, 129.2, 128.7, 128.3, 128.1, 127.7, 127.3, 126.6, 118.2, 59.4, 58.9, 54.2, 53.7, 52.7, 21.7, 20.9, 18.2, 16.1; HRMS (ESI) calcd for $C_{36}H_{36}N_2O_4NaS_2Se^+$ ($M+Na^+$): 727.1179, found: 727.1188.



(Z)-4-(((3-(4-Chlorophenyl)-4-(phenyl(phenylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**5j**)

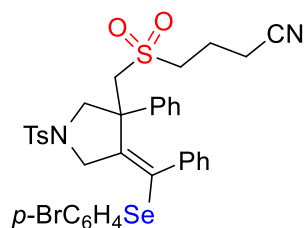
Yellow oil, 86% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.18 – 7.05 (m, 5H), 7.04 – 6.89 (m, 5H), 6.83 (t, $J = 7.5$ Hz, 2H), 6.39 (s, 2H), 4.32 (d, $J = 14.3$ Hz, 1H), 4.03 (m, 2H), 3.65 (d, $J = 10.6$ Hz, 1H), 3.46 (d, $J = 1.2$ Hz,

2H), 3.00 (t, $J = 7.3$ Hz, 2H), 2.56 – 2.46 (m, 5H), 2.13 – 2.02 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 139.6, 139.2, 136.9, 136.1, 133.3, 131.9, 131.3, 130.1, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 127.4, 127.3, 127.3, 118.2, 59.3, 58.5, 54.3, 54.2, 52.8, 21.7, 18.3, 16.2; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{33}\text{N}_2\text{O}_4\text{NaS}_2\text{ClSe}^+$ ($\text{M}+\text{Na}^+$): 747.0633, found: 747.0641.



(*Z*)-4-(((3-Phenyl-4-(phenyl(*p*-tolylselanyl)methylene)-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**5k**)

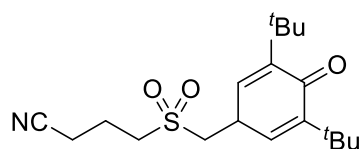
Yellow solid, 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.18 – 7.08 (m, 5H), 7.00 – 6.78 (m, 7H), 6.46 (d, $J = 6.7$ Hz, 2H), 4.32 (d, $J = 14.3$ Hz, 1H), 4.11 – 4.00 (m, 1H), 3.94 – 3.83 (m, 2H), 3.53 – 3.27 (m, 2H), 2.80 (t, $J = 7.3$ Hz, 2H), 2.52 – 2.43 (m, 5H), 2.20 (s, 3H), 2.05 – 1.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 140.8, 139.3, 138.5, 137.2, 136.0, 131.5, 131.4, 130.0, 129.5, 129.1, 128.4, 128.1, 127.5, 127.3, 127.2, 126.8, 123.9, 118.1, 59.4, 59.0, 54.2, 53.9, 53.0, 21.7, 21.1, 18.2, 16.1; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{36}\text{N}_2\text{O}_4\text{NaS}_2\text{Se}^+$ ($\text{M}+\text{Na}^+$): 727.1179, found: 727.1188.



(*Z*)-4-(((4-(((4-Bromophenylselanyl)(phenyl)methylene)-3-phenyl-1-tosylpyrrolidin-3-yl)methyl)sulfonyl)butanenitrile (**5l**)

Brown solid, 81% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.18 – 7.06 (m, 7H), 6.99 – 6.93 (m, 3H), 6.91 – 6.84 (m, 2H), 6.46 (d, $J = 6.1$ Hz, 2H), 4.27 (d, $J = 14.3$ Hz, 1H), 4.09 (d, $J = 14.3$ Hz, 1H), 3.92 (d, $J = 10.4$ Hz, 1H),

3.80 (d, $J = 10.4$ Hz, 1H), 3.46 (d, $J = 14.9$ Hz, 1H), 3.36 (d, $J = 14.9$ Hz, 1H), 2.85 (dd, $J = 10.8, 4.1$ Hz, 2H), 2.59 – 2.34 (m, 5H), 2.17 – 1.87 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 141.3, 140.7, 137.2, 137.1, 131.8, 131.4, 130.3, 130.0, 129.0, 128.5, 128.1, 127.6, 127.5, 126.6, 126.5, 123.0, 118.2, 59.4, 59.0, 54.5, 53.9, 52.8, 21.7, 18.2, 16.2; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{33}\text{N}_2\text{O}_4\text{NaS}_2\text{BrSe}^+$ ($\text{M}+\text{Na}^+$): 791.0128, found: 791.0133.



4-((3,5-Di-*tert*-butyl-4-hydroxybenzyl)sulfonyl)butanenitrile (**6**)

Light yellow solid, 21% yield; ^1H NMR (400 MHz, CDCl_3) δ 6.67 (s, 2H), 2.87 (t, $J = 7.1$ Hz, 2H), 2.58 (t, $J = 7.0$ Hz, 2H), 2.22 – 2.00 (m, 2H), 1.72 (s, 2H), 1.27 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.2, 152.3, 135.1, 117.8, 65.4, 44.3, 35.6, 29.2, 18.2, 18.1, 16.4; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_3\text{NaS}^+$ ($\text{M}+\text{Na}^+$): 374.1766, found: 374.1774.

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