Supporting Information

Synthesis of β -cyanoalkylsulfonylated vinyl selenides through a four-component reaction

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1. General Information

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 μ m, 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. X-ray single crystal diffraction data were recorded on Bruker D8 VENTURE. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 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.

2. General Experimental Procedure and Characterization Data



1,2-Dichloroethane (2.0 mL) was added to a sealed tube containing cycloketone oxime esters **1** (0.2 mmol), DABCO (SO₂)₂ (0.2 mmol), diselenides **2** (0.2 mmol), alkynes **3** (0.3 mmol) and Cu(OAc)₂ (10 mol%) under a nitrogen atmosphere via a syringe. The resulting mixture was stirred at 60 °C in an oil bath for 12 hours. After completion of reaction as monitored by TLC analysis, the mixture was diluted with DCM and washed with saturated aqueous NaHCO₃ (10 mL), brine (10 mL), and dried over anhydrous Na₂SO₄. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding products **4**, **5**, **6** or **7**.



(E)-4-((2-Phenyl-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4a)

Yellow solid, 70% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 7.8, 1.6 Hz, 2H), 7.52 – 7.40 (m, 8H), 5.88 (s, 1H), 2.73 (t, J = 7.2 Hz, 2H), 2.38 (t, J = 7.1 Hz, 2H), 2.17 – 1.84 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 136.8, 134.3, 130.6, 130.5, 130.2, 128.4, 128.3, 126.6, 122.2, 118.2, 53.3, 18.8, 16.1; HRMS (ESI) calcd for C₁₈H₁₇NO₂NaSSe⁺ (M+Na⁺): 414.0043, found: 414.0048.



(E)-4-((2-(Phenylselanyl)-2-(p-tolyl)vinyl)sulfonyl)butanenitrile (4b)

Yellow solid, 74% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.64 (m, 2H), 7.51 – 7.42 (m, 3H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.54 – 2.26 (m, 5H), 2.00 – 1.90 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 140.6, 136.7, 131.4, 130.5, 129.1, 128.3, 126.8, 121.9, 118.2, 53.2, 21.5, 18.8, 16.1; HRMS (ESI) calcd for C₁₉H₁₉NO₂NaSSe ⁺ (M+Na⁺): 428.0199, found: 428.0207.



(E)-4-((2-(4-Methoxyphenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4c)

Yellow solid, 68% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 2H), 7.52 – 7.42 (m, 5H), 7.00 – 6.89 (m, 2H), 5.85 (s, 1H), 3.83 (s, 3H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.01 – 1.89 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.2, 160.1, 136.6, 130.5, 130.4, 130.2, 127.0, 126.3, 121.7, 118.3, 113.9, 55.4, 53.0, 18.9, 16.1; HRMS (ESI) calcd for C₁₉H₁₉NO₃NaSSe⁺ (M+Na⁺): 444.0149, found: 444.0157.



(E)-4-((2-(3-Hydroxyphenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4d)

Yellow solid, 45% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.61 (m, 2H), 7.52 – 7.41 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.96 – 6.83 (m, 2H), 6.41 (s, 1H), 5.85 (s, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.93 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 155.9, 136.7, 135.4, 130.6, 130.5, 129.9, 126.5, 121.7, 120.3, 118.5, 117.7, 115.3, 53.3, 18.8, 16.1; HRMS (ESI) calcd for C₁₈H₁₇NO₃NaSSe⁺ (M+Na⁺): 429.9992, found: 429.9991.



(E)-4-((2-(2-Formylphenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4e)

Red brown solid, 50% yield; ¹H NMR (400 MHz, CDCl₃) δ 10.16 (s, 1H), 7.91 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H), 7.56 (td, *J* = 7.5, 1.2 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.35 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.08 (s, 1H), 2.90 – 2.78 (m, 2H), 2.45 – 2.38 (m, 2H), 2.05 – 1.93 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 190.8, 158.4, 136.8, 135.9, 133.4, 132.7, 131.2, 130.7, 130.5, 130.0, 129.5, 126.2, 122.8, 118.2, 53.4, 18.5, 16.1; HRMS (ESI) calcd for C₁₉H₁₇NO₃NaSSe⁺ (M+Na⁺): 441.9992, found: 442.0000.



(E)-4-((2-(2-Fluorophenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4f)

Yellow oil, 80% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 2H), 7.51 – 7.40 (m, 3H), 7.40 – 7.29 (m, 2H), 7.20 – 7.15 (m, 1H), 7.08 (t, *J* = 9.0 Hz, 1H), 6.04 (s, 1H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 2.15 – 1.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 157.8 (d, *J* = 248.1 Hz), 154.1, 136.8, 131.7 (d, *J* = 8.2 Hz), 130.6,

130.4, 130.1 (d, J = 1.9 Hz), 126.1, 124.1 (d, J = 3.5 Hz), 123.2, 122.4 (d, J = 15.9 Hz), 118.2, 115.7 (d, J = 21.3 Hz), 53.1, 18.6, 16.2; HRMS (ESI) calcd for $C_{18}H_{16}NO_{2}FNaSSe^{+}$ (M+Na⁺): 431.9949, found: 431.9958.



(E)-4-((2-(4-Fluorophenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4g)

Yellow solid, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.64 (m, 2H), 7.53 – 7.43 (m, 5H), 7.15 – 7.07 (m, 2H), 5.91 (s, 1H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.93 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6 (d, *J* = 251.3 Hz), 159.5, 136.7, 130.6 (d, *J* = 4.3 Hz), 130.5, 130.5, 130.2 (d, *J* = 3.5 Hz), 126.5, 122.3, 118.1, 115.6 (d, *J* = 22.0 Hz), 53.3, 18.7, 16.1; HRMS (ESI) calcd for C₁₈H₁₆NO₂NaS-SeF⁺ (M+Na⁺): 431.9949, found: 431.9957.



(E)-4-((2-(4-Chlorophenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4h)

Yellow solid, 76% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.63 (m, 2H), 7.54 – 7.43 (m, 3H), 7.43 – 7.37 (m, 4H), 5.89 (s, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.93 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 136.7, 136.3, 132.8, 130.7, 130.6, 129.7, 128.7, 126.4, 122.3, 118.2, 53.4, 18.7, 16.1; HRMS (ESI) calcd for C₁₈H₁₆NO₂NaSClSe⁺ (M+Na⁺): 447.9653, found: 447.9656.



(E)-4-((2-(3-Bromophenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4i)

Yellow solid, 52% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 2H), 7.59 (t, *J* = 1.7 Hz, 1H), 7.56 – 7.44 (m, 4H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 5.88 (s, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.12 – 1.87 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 158.6, 136.8, 136.3, 133.0, 130.9, 130.7, 130.6, 129.8, 127.0, 126.3, 122.4, 122.2, 118.2, 53.5, 18.7, 16.1; HRMS (ESI) calcd for C₁₈H₁₆NO₂NaS-SeBr⁺ (M+Na⁺): 491.9148, found: 491.9154.



(E)-4-((2-(Phenylselanyl)-2-(pyridin-2-yl)vinyl)sulfonyl)butanenitrile (4j)

Brown solid, 54% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.70 – 8.63 (m, 1H), 7.79 – 7.73 (m, 1H), 7.70 – 7.67 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.35 – 7.30 (m, 1H), 5.95 (s, 1H), 3.23 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.14 – 2.05 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 153.4, 149.4, 136.8, 136.5, 130.6, 130.5, 125.8, 124.5, 124.3, 122.9, 118.3, 54.6, 18.7, 16.2; HRMS (ESI) calcd for C₁₇H₁₆N₂O₂NaSSe⁺ (M+Na⁺): 414.9995, found: 415.0002.



(*E*)-4-((2-(Phenylselanyl)-2-(pyridin-3-yl)vinyl)sulfonyl)butanenitrile (4k)

Yellow solid, 48% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.67 – 8.60 (m, 2H), 7.83 – 7.72 (m, 1H), 7.68 – 7.64 (m, 2H), 7.56 – 7.44 (m, 3H), 7.39 – 7.31 (m, 1H), 6.00 (s, 1H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.09 – 1.91 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 157.0, 150.8, 148.1, 136.7, 136.0, 130.8, 130.6, 126.1, 123.1, 122.9, 118.1, 53.7, 18.6, 16.1; HRMS (ESI) calcd for C₁₇H₁₆N₂O₂NaSSe⁺ (M+Na⁺): 414.9995, found: 415.0003.



(E)-4-((2-(Phenylselanyl)-2-(thiophen-2-yl)vinyl)sulfonyl)butanenitrile (4l)

Yellow solid, 65% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.65 (m, 2H), 7.61 – 7.54 (m, 2H), 7.52 – 7.43 (m, 3H), 7.14 – 7.10 (m, 1H), 5.92 (s, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.04 – 1.93 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 136.5, 134.7, 131.5, 130.6, 130.5, 130.2, 128.1, 127.2, 123.0, 118.1, 52.4, 18.9, 16.2; HRMS (ESI) calcd for C₁₆H₁₅NO₂NaS₂Se⁺ (M+Na⁺): 419.9607, found: 419.9604.



(E)-4-((2-Cyclohexyl-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4m)

White solid, 31% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.54 (m, 2H), 7.51 – 7.38 (m, 3H), 5.46 (s, 1H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.16-2.03 (m, 2H), 1.87 (t, *J* = 13.7 Hz, 4H), 1.75 (d, *J* = 12.8 Hz, 1H), 1.67 – 1.54 (m, 3H), 1.49 – 1.36 (m, 2H), 1.31 – 1.18 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 137.3, 130.4, 130.2, 125.4, 119.1, 118.2, 54.0, 42.1, 33.3, 25.9, 25.5, 18.8, 16.3; HRMS (ESI) calcd for C₁₈H₂₃NO₂NaSSe⁺ (M+Na⁺): 420.0512, found: 420.0515.



(E)-4-((5-Chloro-2-(phenylselanyl)pent-1-en-1-yl)sulfonyl)butanenitrile (4n)

Yellow oil, 69% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.59 (m, 2H), 7.52 – 7.43 (m, 3H), 5.67 (s, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 4H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.24 – 2.16 (m, 2H), 2.15 – 2.07 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 136.9, 130.5, 130.5, 125.3, 120.7, 118.2, 53.8, 44.0, 33.3, 31.0, 18.7, 16.3; HRMS (ESI) calcd for C₁₅H₁₈NO₂NaSClSe⁺ (M+Na⁺): 413.9810, found: 413.9809.

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(E)-4-((2-(Phenylselanyl)hex-1-en-1-yl)sulfonyl)butanenitrile (40)

Yellow oil, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.58 (m, 2H), 7.52 – 7.41 (m, 3H), 5.61 (s, 1H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.93 – 2.82 (m, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.16 – 2.00 (m, 2H), 1.78 – 1.64 (m, 2H), 1.57 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 137.0, 130.4, 130.3, 125.6, 119.8, 118.2, 53.9, 33.2, 32.8, 22.6, 18.8, 16.3, 13.8; HRMS (ESI) calcd for C₁₆H₂₁NO₂NaSSe⁺ (M+Na⁺): 394.0356, found: 394.0353.



(*E*)-4-((1-Phenyl-1-(phenylselanyl)prop-1-en-2-yl)sulfonyl)butanenitrile (4p)

Yellow solid, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.12 (m, 3H), 7.06 – 6.98 (m, 5H), 6.97 – 6.92 (m, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.46 – 2.35 (m, 5H), 2.07 – 1.94 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 137.1, 135.5, 130.5, 129.1, 129.0, 128.7, 128.2, 127.3, 126.8, 118.2, 52.6, 18.7, 18.6, 16.2; HRMS (ESI) calcd for C₁₉H₁₉NO₂NaSSe⁺ (M+Na⁺): 428.0199, found: 428.0202.



(E)-4-((1,2-Diphenyl-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (4q)

Yellow solid, 45% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.49 (m, 5H), 7.14 – 7.03 (m, 8H), 7.02 – 6.92 (m, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.09 – 1.97 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 137.2, 134.9, 134.7, 134.1, 130.6, 130.0, 129.4, 128.8, 128.6, 128.6, 128.2, 127.5, 127.3, 118.2, 52.0, 18.6, 16.1; HRMS (ESI) calcd for C₂₄H₂₁NO₂NaSSe⁺ (M+Na⁺): 490.0356, found: 490.0361.



Methyl (E)-2-((3-cyanopropyl)sulfonyl)-3-phenyl-3-(phenylselanyl)acrylate (4r)

Yellow solid, 44% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.12 (m, 3H), 7.09 – 6.98 (m, 5H), 6.95 – 6.86 (m, 2H), 4.03 (s, 3H), 3.26 (t, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.20 – 2.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 163.9, 137.1, 134.4, 129.2, 128.7, 128.7, 127.8, 127.7, 127.6, 127.3, 118.3, 54.3, 53.4, 18.6, 16.2; HRMS (ESI) calcd for C₂₀H₁₉NO₄NaSSe⁺ (M+Na⁺): 472.0098, found: 472.0100.



tert-Butyl (*E*)-3-cyano-2-(((2-phenyl-2 (phenylselanyl)vinyl)sulfonyl)methyl)propanoate (5a)

Yellow solid, 46% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.65 (m, 2H), 7.54 – 7.39 (m, 8H), 5.91 (s, 1H), 3.34 – 3.15 (m, 1H), 3.05 – 2.96 (m, 1H), 2.93 – 2.82 (m, 1H), 2.80-2.65 (m, 2H), 1.44 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 161.4, 136.8, 134.2, 130.6, 130.5, 130.2, 128.4, 128.3, 126.5, 122.2, 116.6, 83.7, 54.5, 36.8, 27.8, 19.3; HRMS (ESI) calcd for C₂₃H₂₅NO₄NaSSe⁺ (M+Na⁺): 514.0567, found: 514.0571.



Benzyl (*E*)-3-cyano-2-(((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)methyl)propanoate (5b)

Yellow solid, 50% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.64 (m, 2H), 7.52 – 7.30 (m, 13H), 5.89 (s, 1H), 5.33 – 4.89 (m, 2H), 3.32 – 3.23 (m, 1H), 3.18 – 3.09 (m, 1H), 3.00 – 2.89 (m, 1H), 2.85-2.70 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 169.3,

161.9, 136.7, 134.6, 134.1, 130.6, 130.5, 130.2, 128.8, 128.8, 128.6, 128.4, 128.2, 126.5, 121.9, 116.5, 68.3, 54.3, 36.3, 19.1; HRMS (ESI) calcd for $C_{26}H_{23}NO_4NaSSe^+$ (M+Na⁺): 548.0411, found: 548.0414.



(E)-3-Phenyl-4-((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (5c)

Yellow solid, 71% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.59 (m, 2H), 7.51 – 7.31 (m, 11H), 7.12 – 7.06 (m, 2H), 5.83 (s, 1H), 3.48 – 3.38 (m, 1H), 3.14 – 3.06 (m, 1H), 3.00 – 2.94 (m, 1H), 2.82-2.66 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 139.3, 136.7, 134.3, 130.5, 130.5, 130.1, 129.3, 128.3, 128.3, 127.0, 126.5, 122.5, 117.3, 58.7, 36.2, 24.2; HRMS (ESI) calcd for C₂₄H₂₁NO₂NaSSe⁺ (M+Na⁺): 490.0356, found: 490.0356.



(E)-3-(Benzyloxy)-4-((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (5d)

Yellow solid, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.56 (m, 2H), 7.48 – 7.28 (m, 13H), 5.95 (s, 1H), 4.49 – 4.40 (m, 2H), 4.06 – 3.99 (m, 1H), 3.10 (dd, *J* = 14.3, 5.3 Hz, 1H), 2.87 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.62 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.46 (dd, *J* = 17.0, 5.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 136.7, 136.4, 134.4, 130.5, 130.4, 130.1, 128.7, 128.4, 128.0, 126.5, 123.2, 116.2, 72.2, 69.0, 58.3, 23.6; HRMS (ESI) calcd for C₂₅H₂₃NO₃NaSSe⁺ (M+Na⁺): 520.0462, found: 520.0466.



(*E*)-4-(Benzyloxy)-3-(((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)methyl)butanenitrile (5e)

Yellow oil, 69% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.61 (m, 2H), 7.52 – 7.41 (m, 5H), 7.40 – 7.29 (m, 6H), 7.27 – 7.24 (m, 2H), 5.89 (s, 1H), 4.45 (s, 2H), 3.47 – 3.32 (m, 2H), 2.82 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.74 – 2.42 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 137.4, 136.7, 134.3, 130.5, 130.5, 130.1, 128.6, 128.3, 128.0, 127.7, 126.6, 122.5, 117.4, 73.4, 70.0, 55.3, 31.2, 19.1; HRMS (ESI) calcd for C₂₆H₂₅NO₃NaSSe⁺ (M+Na⁺): 534.0618, found: 534.0624.



(*E*)-5-(((2-Phenyl-2-(phenylselanyl)vinyl)sulfonyl)methyl)cyclopent-2-ene-1-carbonitrile (5f)

White solid, 54% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.65 (m, 2H), 7.52 – 7.40 (m, 8H), 5.81 (s, 1H), 5.76 – 5.69 (m, 1H), 5.56 – 5.49 (m, 1H), 3.40 – 3.30 (m, 1H), 3.09 – 2.98 (m, 1H), 2.65 – 2.58 (m, 2H), 2.57 – 2.51 (m, 1H), 2.39 – 2.31 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 136.8, 134.5, 131.0, 130.5, 130.5, 130.2, 129.7, 128.4, 128.2, 126.8, 120.1, 117.2, 65.6, 42.7, 34.6, 23.2; HRMS (ESI) calcd for C₂₁H₁₉NO₂NaSSe⁺ (M+Na⁺): 452.0199, found: 452.0201.



tert-Butyl (*E*)-3-(cyanomethyl)-3-(((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)methyl)-azetidine-1-carboxylate (5g)

Yellow solid, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.66 (m, 2H), 7.54 – 7.42 (m, 8H), 5.90 (s, 1H), 3.74 (d, *J* = 9.4 Hz, 2H), 3.67 (d, *J* = 9.4 Hz, 2H), 3.09 (s, 2H), 2.86 (s, 2H), 1.42 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 155.8, 136.8, 134.1, 130.7, 130.6, 130.4, 128.5, 128.3, 126.3, 123.4, 116.5, 80.4, 59.2, 58.3, 33.4,

28.3, 25.6; HRMS (ESI) calcd for $C_{25}H_{28}N_2O_4NaSSe^+$ (M+Na⁺): 555.0833, found: 555.0836.



tert-Butyl (*E*)-4-(cyanomethyl)-4-(((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)methyl)pi -peridine-1-carboxylate (5h)

Yellow solid, 65% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.65 (m, 2H), 7.51 – 7.41 (m, 8H), 5.95 (s, 1H), 3.51 (d, *J* = 12.2 Hz, 2H), 2.98 – 2.82 (m, 4H), 2.67 (s, 2H), 1.77 – 1.59 (m, 3H), 1.55 – 1.38 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 154.6, 136.8, 134.4, 130.6, 130.5, 130.1, 128.4, 128.4, 126.4, 124.8, 116.9, 80.0, 57.7, 35.7, 34.3, 28.4, 27.1; HRMS (ESI) calcd for C₂₇H₃₂N₂O₄NaSSe⁺ (M+Na⁺): 583.1146, found: 583.1153.



Benzyl (*E*)-(1-cyano-3-((2-phenyl-2-(phenylselanyl)vinyl)sulfonyl)propan-2yl)carbamate (5i)

Yellow oil, 47% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 2H), 7.48 – 7.37 (m, 8H), 7.36 – 7.30 (m, 5H), 5.88 (s, 1H), 5.49 (d, *J* = 7.2 Hz, 1H), 5.09 (s, 2H), 4.18 (dd, *J* = 13.6, 6.2 Hz, 1H), 3.06 (dd, *J* = 14.3, 5.9 Hz, 1H), 2.90 (dd, *J* = 14.3, 5.8 Hz, 1H), 2.72 (d, *J* = 5.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 155.2, 136.8, 135.7, 134.1, 130.6, 130.5, 130.3, 128.7, 128.4, 128.3, 128.2, 126.5, 122.1, 116.4, 67.3, 56.7, 44.3, 22.8; HRMS (ESI) calcd for C₂₆H₂₄N₂O₄NaSSe⁺ (M+Na⁺): 563.0520, found: 563.0524.





Yellow solid, 36% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.56 (m, 2H), 7.51 – 7.46 (m, 4H), 7.45 – 7.41 (m, 3H), 5.92 (s, 1H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.36 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 154.1, 136.5, 134.4, 130.1, 128.4, 128.2, 127.7, 123.1, 121.9, 118.2, 53.3, 35.0, 31.2, 18.8, 16.1; HRMS (ESI) calcd for C₂₂H₂₅NO₂NaSSe⁺ (M+Na⁺): 470.0669, found: 470.0671.



(E)-4-((2-((2-Methoxyphenyl)selanyl)-2-phenylvinyl)sulfonyl)butanenitrile (5k)

Yellow solid, 57% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.60 (m, 1H), 7.54 – 7.45 (m, 3H), 7.44 – 7.37 (m, 3H), 7.05 – 6.97 (m, 2H), 5.86 (s, 1H), 3.92 (s, 3H), 2.71 (t, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.01 – 1.92 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 159.0, 138.5, 134.4, 132.9, 130.1, 128.5, 128.3, 122.2, 121.4, 118.2, 115.6, 111.9, 56.2, 53.3, 18.9, 16.1; HRMS (ESI) calcd for C₁₉H₁₉NO₃NaSSe⁺ (M+Na⁺): 444.0149, found: 444.0150.



(E)-4-((2-((4-Bromophenyl)selanyl)-2-phenylvinyl)sulfonyl)butanenitrile (5l)

Brown solid, 43% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 7.48 – 7.41 (m, 5H), 5.93 (s, 1H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.07 – 1.83 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 138.2, 134.0, 133.7, 130.3, 128.5, 128.3, 125.5, 125.2, 122.7, 118.2, 53.3, 18.7, 16.1; HRMS (ESI) calcd for C₁₈H₁₆NO₂NaSSeBr⁺ (M+Na⁺): 491.9148, found: 491.9149.



Methyl (E)-4-((2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)selanyl)benzoate (5m)

Yellow solid, 57% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.70 (m, 2H), 7.49 – 7.44 (m, 2H), 7.44 – 7.39 (m, 3H), 6.00 (s, 1H), 3.95 (s, 3H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.92 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 158.9, 136.449, 134.0, 132.1, 131.8, 131.2, 130.4, 128.5, 128.4, 123.1, 118.1, 53.2, 52.5, 18.7, 16.1; HRMS (ESI) calcd for C₂₀H₁₉NO₄NaSSeBr⁺ (M+Na⁺): 472.0098, found: 472.0105.



(*E*)-4-((2-(3-((6,7-Bis(2-methoxyethoxy)quinazolin-4-yl)amino)phenyl)-2-(phenylselanyl)vinyl)sulfonyl)butanenitrile (6)

Yellow solid, 68% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1H), 8.06 – 7.78 (m, 2H), 7.69 – 7.60 (m, 3H), 7.53 – 7.38 (m, 5H), 7.22 (d, *J* = 7.5 Hz, 2H), 5.85 (s, 1H), 4.22 (d, *J* = 21.3 Hz, 4H), 3.81 (d, *J* = 11.7 Hz, 4H), 3.49 – 3.40 (m, 6H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.47 (t, *J* = 6.7 Hz, 2H), 2.09 – 1.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 154.3, 149.0, 139.0, 138.9, 136.7, 134.9, 130.6, 130.6, 129.1, 128.9, 127.7, 126.5, 125.2, 124.2, 124.1, 122.6, 122.5, 121.8, 121.0, 118.9, 70.8, 70.4, 68.8, 68.4, 59.3, 59.2, 53.5, 19.0, 16.2; HRMS (ESI) calcd for C₃₂H₃₅N₄O₆SSe⁺ (M+H⁺): 683.1443, found: 683.1445.



 (8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cy

 clopenta[a]phenanthren-3-yl
 4-((E)-2-((3-cyanopropyl)sulfonyl)-1-(phenylse

 lanyl)vinyl)benzoate (7)

Yellow solid, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 6.5 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.45 (m, 3H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.02 – 6.92 (m, 2H), 5.94 (s, 1H), 3.01 – 2.91 (m, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.58 – 2.40 (m, 4H), 2.37 – 2.28 (m, 1H), 2.21 – 2.12 (m, 1H), 2.11 – 1.95 (m, 5H), 1.70 – 1.55 (m, 4H), 1.52 – 1.41 (m, 2H), 0.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 159.3, 148.7, 139.6, 138.2, 137.6, 136.7, 130.9, 130.8, 130.6, 130.0, 128.5, 126.5, 126.1, 122.3, 121.6, 118.8, 118.1, 53.6, 50.4, 48.0, 44.2, 38.0, 35.9, 31.6, 29.4, 26.3, 25.8, 21.6, 18.7, 16.1, 13.8; HRMS (ESI) calcd for C₃₇H₃₇NO₅NaSSe⁺ (M+Na⁺): 710.1455, found: 710.1459.

3. General Procedure for the Synthesis of Alkynyl Sulfone



Tetrahydrofuran (4.0 mL) was added to a sealed round bottomed flask containing β -selenovinyl sulfone **4** (0.1 mmol) under air atmosphere *via* a syringe and H₂O₂ aqueous solution (30 wt%, 2.0 mL) was added into the solution slowly. The resulting mixture was stirred at room temperature for 2 hours. After completion of reaction as monitored by TLC analysis, the mixture was diluted with chloroform (10 mL) and washed with water (10 mL), brine (10 mL), and dried over anhydrous Na₂SO₄. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to give the corresponding product **8**.



4-((Phenylethynyl)sulfonyl)butanenitrile (8a)

Yellow oil, 57% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.59 (m, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.47 (t, J = 7.2 Hz, 2H), 2.69 (t, J = 7.1 Hz, 2H), 2.51 – 2.25 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 133.0, 132.1, 128.9, 118.0, 117.1,

93.6, 82.7, 56.3, 19.6 16.1; HRMS (ESI) calcd for C₁₂H₁₁NO₂NaS⁺ (M+Na⁺): 256.0408, found: 256.0414.



4-(((4-Chlorophenyl)ethynyl)sulfonyl)butanenitrile (8b)

Yellow solid, 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 3.47 (t, J = 7.2 Hz, 2H), 2.69 (t, J = 7.0 Hz, 2H), 2.46 – 2.22 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 134.2, 129.5, 118.0, 115.6, 92.2, 83.6, 56.3, 19.5, 16.0; HRMS (ESI) calcd for C₁₂H₁₀NO₂NaSCl⁺ (M+Na⁺): 290.0018, found: 290.0024.

4. Radical Trapping Experiment



To a solution of cycloketone oxime ester **1a** (0.2 mmol), DABCO (SO₂)₂ (0.2 mmol), diphenyl diselenide **2a** (0.2 mmol), phenylacetylene **3a** (0.3 mmol) and Cu(OAc)₂ (10 mol%) in 1,2-dichloroethane (2.0 mL) was added BHT (0.4 mmol, 2.0 equiv) under a nitrogen atmosphere. The resulting mixture was stirred at 60 °C in an oil bath for 12 hours. After completion of reaction as monitored by TLC analysis, the mixture was diluted with DCM and washed with saturated aqueous NaHCO₃ (10 mL), brine (10 mL), and dried over anhydrous Na₂SO₄. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to give the corresponding products **4a** and **9** in 35% and 18% yields, respectively.

4-((3,5-Di-tert-butyl-4-hydroxybenzyl)sulfonyl)butanenitrile (9)

Light yellow solid, 18% yield; ¹H NMR (400 MHz, CDCl₃) δ 6.66 (s, 2H), 2.86 (t, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.19 – 2.11 (m, 2H), 1.71 (s, 2H), 1.26 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 184.2, 152.3, 135.1, 117.7, 65.4, 44.2, 35.6, 29.1, 18.2, 18.1, 16.4; HRMS (ESI) calcd for C₁₉H₂₉NO₃NaS⁺ (M+Na⁺): 374.1766, found: 374.1767.

5. X-Ray Single Crystal Diffraction Data

The crystals of compound **4i** were grown in a mixed solution of CH₂Cl₂ and petroleum ether as the solution slowly volatilized. X-ray single crystal diffraction data were recorded on Bruker D8 VENTURE. This crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2102437).



Figure S1. X-ray structure of 4i (displacement ellipsoids are drawn at the 30% probability level).

4i
$C_{18}H_{16}BrNO_2SSe$
469.25
173(2) K
1.34138 Å

Table S1. Crystal data and structure refinement for 4i.

Crystal system	Monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 10.3416(9) Å	a= 90 °.	
	b = 18.4062(16) Å	b= 112.267(3) °.	
	c = 10.3029(9) Å	g = 90 °.	
Volume	1814.9(3) Å ³		
Z	4		
Density (calculated)	1.717 Mg/m ³		
Absorption coefficient	4.329 mm ⁻¹		
F(000)	928		
Crystal size	0.100 x 0.080 x 0.030 mm ³		
Theta range for data collection	4.019 to 59.490 °.		
Index ranges	-11<=h<=13, -17<=k<=23, -13<=l<=13		
Reflections collected	15494		
Independent reflections	3975 [R(int) = 0.0744]		
Completeness to theta = 53.594 $^{\circ}$	98.6 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.752 and 0.314		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	3975 / 0 / 217		
Goodness-of-fit on F ²	1.042		
Final R indices [I>2sigma(I)]	R1 = 0.0474, $wR2 = 0.1178$		
R indices (all data)	R1 = 0.0525, $wR2 = 0.1231$		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.903 and -0.836 e.Å ⁻³		

6. Copies of ¹H and ¹³C NMR Spectra

¹H NMR spectrum of compound 4a (400 MHz, CDCl₃)





^{13}C NMR spectrum of compound 4a (100 MHz, CDCl_3)





^{13}C NMR spectrum of compound 4b (100 MHz, CDCl_3)



¹H NMR spectrum of compound 4c (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 4c (100 MHz, CDCl_3)



¹H NMR spectrum of compound 4d (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 4d (100 MHz, CDCl_3)



¹H NMR spectrum of compound **4e** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **4e** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **4f** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 4f (100 MHz, CDCl_3)



¹H NMR spectrum of compound 4g (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 4g (100 MHz, CDCl_3)



¹H NMR spectrum of compound **4h** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 4h (100 MHz, CDCl_3)







^{13}C NMR spectrum of compound 4i (100 MHz, CDCl_3)


¹H NMR spectrum of compound **4j** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 4j (100 MHz, CDCl_3)



¹H NMR spectrum of compound 4k (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 4k (100 MHz, CDCl_3)



¹H NMR spectrum of compound **4l** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 4l (100 MHz, CDCl_3)



¹H NMR spectrum of compound **4m** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **4m** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **4n** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound **4n** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **40** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **40** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **4p** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **4p** (100 MHz, CDCl₃)



¹H NMR spectrum of compound 4q (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 4q (100 MHz, CDCl₃)



¹H NMR spectrum of compound **4r** (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 4r (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5a** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **5a** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **5b** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **5b** (100 MHz, CDCl₃)



^1H NMR spectrum of compound 5c (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 5c (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5d** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 5d (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5e** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 5e (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5f** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound 5f (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5g** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **5g** (100 MHz, CDCl₃)







^{13}C NMR spectrum of compound **5h** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **5i** (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 5i (100 MHz, CDCl_3)


¹H NMR spectrum of compound **5j** (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 5j (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5k** (400 MHz, CDCl₃)







¹H NMR spectrum of compound **5l** (400 MHz, CDCl₃)



^{13}C NMR spectrum of compound **51** (100 MHz, CDCl_3)



¹H NMR spectrum of compound **5m** (400 MHz, CDCl₃)











¹³C NMR spectrum of compound 6 (100 MHz, CDCl₃)



¹H NMR spectrum of compound 7 (400 MHz, CDCl₃)



¹³C NMR spectrum of compound 7 (100 MHz, CDCl₃)



¹H NMR spectrum of compound 8a (400 MHz, CDCl₃)



 ^{13}C NMR spectrum of compound 8a (100 MHz, CDCl_3)



¹H NMR spectrum of compound **8b** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **8b** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **9** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **9** (100 MHz, CDCl₃)