Supporting Information for

One Pot Catalytic Preparation of β -Selenyl Acrylamides

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General Comments.

Sulfenamides **1a-g** were synthesized according to the reported procedure.¹ Acetylenes were commercially obtained and used after distillation under nitrogen over calcium hydride or phosphorous pentoxide. All transition metal catalysts were commercially obtained and stored in a nitrogen filled glovebox. Carbon monoxide was purchased and used without further purification. Benzene and toluene were distilled under nitrogen from sodium. Methylene chloride and acetonitrile were distilled under nitrogen from calcium hydride.

¹H, ¹³C-NMR, 300 and 75 MHz respectively, and NOE difference spectra were recorded with Bruker spectrometers. Chemical shifts were referenced to residual ¹H signals in deuterated solvents. Column chromatography was performed using Sorbent 60 32-60 standard grade silica gel. Gas chromatography-mass spectrometry (GC/MS) was performed on a Hewlett Packard Series 5980 GC/5971 A MS with a Hewlett Packard Series 1 capillary column. Gas chromatography (GC) was performed on a Hewlett Packard Series 6850 GC with a Hewlett Packard Series 1 methyl siloxane column. IR spectra were obtained on a Perkin Elmer Spectrum BX FT-IR system. High-resolution mass spectra (HRMS) were obtained on a Fison VG Autospec in the Mass Spectral

Facility of the University of Pittsburgh. Elemental analysis was performed independently by Desert Analytics, Tucson, Arizona.

S-Phenyl-*N*-dimethyl-sulfenamide (1a): ^1H NMR (300 MHz, C_6D_6) δ 2.53 (s, 6 H), 6.93-7.37 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 48.3, 127.1, 128.8, 129.9, 137.2; MS (EI), m/z 153 (M^+), 138, 109, 77, 65.

S-Phenyl-*N*-benzyl-*N*-methyl-sulfenamide (1b): ^1H NMR (300 MHz, C_6D_6) δ 2.51 (s, 3 H), 3.87 (s, 2 H), 6.95-7.35 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 45.2, 65.1, 127.0, 128.6, 128.7, 128.9, 138.2, 138.8; MS (EI), m/z 229 (M^+), 138, 109, 91, 77, 65.

S-Phenyl-*N*-diethyl-sulfenamide (1c): ^1H NMR (300 MHz, C_6D_6) δ 1.08 (t, $J = 7.0\text{ Hz}$, 6 H), 2.79 (q, $J = 7.0\text{ Hz}$, 4 H), 6.92-7.35 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.8, 53.4, 125.0, 125.5, 128.8, 142.1; MS (EI), m/z 181 (M^+), 166, 109, 77, 65.

S-Phenyl-*N*-allyl-*N*-methyl-sulfenamide (1d): ^1H NMR (300 MHz, C_6D_6) δ 2.59 (s, 3), 3.34 (d, $J = 6.4\text{ Hz}$, 2 H), 4.98 (m, 2 H), 5.79 (dtd, $J = 10.0, 7.0, 2.4\text{ Hz}$, 1 H), 6.93-7.36 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 45.2, 63.3, 117.1, 126.4, 127.6, 128.7, 135.4; MS (EI), m/z 179 (M^+), 138, 109, 77, 65.

S-Phenyl-*N*-diallyl-sulfenamide (1e): ^1H NMR (300 MHz, C_6D_6) δ 3.44 (d, $J = 6.4\text{ Hz}$, 4 H), 5.04 (m, 4 H), 5.83 (dtd, $J = 10.5, 6.4, 2.6\text{ Hz}$, 2 H), 6.92-7.35 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 60.9, 117.5, 126.1, 128.9, 135.6, 140.6; MS (EI), m/z 205 (M^+), 164, 109, 77, 65, 41.

S-Phenyl-N-methyl-sulfenamide (1f): ^1H NMR (300 MHz, C_6D_6) δ 2.24 (br.s, 1 H), 2.42 (d, $J = 17.4\text{ Hz}$, 3 H), 6.93-7.35 (m, 5); ^{13}C NMR (75 MHz, C_6D_6) δ 38.4, 123.8, 125.2, 128.8, 129.1, 141.7; MS (EI), m/z 139 (M^+), 124, 109, 97, 65.

S-Phenyl-N-diisopropyl-sulfenamide (1g): ^1H NMR (300 MHz, C_6D_6) δ 1.07 (d, $J = 6.4\text{ Hz}$, 12 H), 3.12 (hpt, $J = 6.5\text{ Hz}$, 2 H), 6.89-7.36 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 21.9, 55.8, 122.1, 124.4, 128.6, 146.4; MS (EI), m/z 209 (M^+), 194, 152, 109, 77, 65.

(Z)-3-Phenylselenyl-hex-2-enoic acid dimethylamide (3): To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (63.0 mg, 0.20 mmol), S-phenyl-N-dimethyl sulfenamide **1a** (31.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL , 0.30 mmol), 2.5% palladium tetraphenylphosphine (6.0 mg, 5.2 μmol) and benzene (4 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 68 h at 78 $^\circ\text{C}$ with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil that was analyzed by gas chromatography. GC showed the following percentages of starting material and byproducts in the reaction: diphenyl diselenide, **2a**, 25%; benzene thioselenic acid phenyl ester, **2b**, 2.1%; diphenyl disulfide, **2c**, 14.5%; (Z)-3-phenylsulfenyl-hex-2-enoic acid dimethylamide, **4**, 9.3%; N-dimethyl phenyl thiocarbamate, **5a**, 1.3%; N-dimethyl phenyl selenylcarbamate, **5b**, 2.5 %; (Z)-1,3-phenylthio-2-penten-1-one, **6a**, 1.8%; 3-phenylselenyl-hex-2-enoic acid S-phenyl ester, **6b**, 1.1%; (Z)-1,2-bis(phenylseleno)-1-pentene, **7**, 1.6%; diphenyl selenide, **8**, trace; selenium triphenylphosphine, **9**, 3%. The crude reaction mixture was purified via column chromatography using 20% ethyl

acetate/hexanes followed by methanol to yield the orange oil (Z)-3-phenylselenenyl-hex-2-enoic acid dimethylamide (**3**) (32.5 mg, 0.11 mmol) in 55% yield. The *E/Z* ratio was determined by NOE difference and ^1H NMR spectroscopy (*E/Z* = 0/100). ^1H NMR (300 MHz, C_6D_6) δ 0.61 (t, $J = 7.3\text{ Hz}$, 3 H), 1.34 (m, $J_1 = J_2 = 7.5\text{ Hz}$, 2 H), 2.16 (t, $J = 7.4\text{ Hz}$, 2 H), 2.31 (s, 3 H), 2.69 (s, 3 H), 6.29 (s, 1 H), 6.92-7.62 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 23.5, 34.9, 36.5, 40.1, 114.3, 128.5, 128.9, 130.6, 137.7, 157.5, 166.6; IR (NaCl) 3070, 2887, 2325, 1960, 1815, 1633 (C=O), 1438, 1034, 674 cm^{-1} ; MS (EI), m/z 297 (M^+), 253, 157, 140 (base), 72. HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{NOSe}$: 297.063927. Found 297.063185. Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NOSe}$: C, 56.55; H, 6.39; N, 4.71. Found: C, 56.90; H, 6.44; N, 4.67.

(Z)-3-Phenylselenenyl-hex-2-enoic acid methyl-benzyl-amide (10**):** To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (63.0 mg, 0.20 mmol), S-phenyl-N-benzyl-N-methyl sulfenamide **1b** (47.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL , 0.30 mmol), 3.5% palladium tetraphenylphosphine (8.0 mg, 6.9 μmol), benzene (4.0 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 44 h at 75 $^\circ\text{C}$ with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using 20% ethyl acetate/hexanes and methanol to yield the orange oil (Z)-3-phenylselenenyl-hex-2-enoic acid methyl-benzyl-amide (**10**) (32.0 mg, 0.09 mmol) in 45% yield. The *E/Z* ratio was determined ^1H NMR (*E/Z* = 0/100). Two distinct rotamers were observed by ^1H and ^{13}C NMR at room temperature. ^1H NMR (300 MHz, C_6D_6) δ 0.49 (t, $J = 7.1\text{ Hz}$, 3 H), 0.60 (t, $J = 7.0\text{ Hz}$, 3 H), 1.34 (m, 4 H), 2.07 (t, $J = 7.1\text{ Hz}$, 2 H), 2.19 (t, $J = 7.2\text{ Hz}$, 2 H), 2.39 (s, 3 H), 2.81 (s, 3 H), 4.06

(s, 2 H), 4.51 (s, 2 H), 6.35 (s, 1 H), 6.42 (s, 1 H), 6.95-7.69 (m, 20 H). ^{13}C NMR (75 MHz, C_6D_6) δ 13.3, 13.4, 23.5, 23.6, 33.6, 34.2, 39.9, 40.2, 50.8, 53.2, 113.9, 130.5, 132.3, 132.4, 134.5, 137.7, 138.4, 158.9, 159.1, 166.8, 167.2; MS (EI), m/z 373 (M^+), 296, 253, 216 (base), 157, 120, 91, 77, 65.

6-Chloro-(Z)-3-phenylselenyl-hex-2-enoic acid benzyl-methyl-amide (11): To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (62.0 mg, 0.19 mmol), S-phenyl-N-benzyl-N-methyl sulfenamide **1b** (46.0 mg, 0.20 mmol), 5-chloro-1-pentyne, (38.0 μL , 0.30 mmol), 4.6% palladium tetraphenylphosphine (10.8 mg, 9.3 μmol) and benzene (2.5 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 64 h at 78 $^\circ\text{C}$ with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using hexanes, 20% ethyl acetate/hexanes, methanol to yield the orange oil 6-chloro-(Z)-3-phenylselenyl-hex-2-enoic acid benzyl-methyl-amide (**11**) (50.0 mg, 0.12 mmol) in 60% yield. The *E/Z* ratio was determined by NOE difference and ^1H NMR spectroscopy (*E/Z* = 0/100). Two distinct rotamers were observed by ^1H and ^{13}C NMR at room temperature. ^1H NMR (300 MHz, C_6D_6) δ 1.44 (m, $J_1 = J_2 = 7.5\text{ Hz}$, 2 H), 1.54 (m, $J_1 = J_2 = 7.1\text{ Hz}$, 2 H), 2.19 (t, $J = 7.0\text{ Hz}$, 2 H), 2.30 (t, $J = 7.3\text{ Hz}$, 2 H), 2.38 (s, 3 H), 2.80 (m, 5 H), 2.91 (t, $J = 7.0\text{ Hz}$, 2 H), 4.05 (s, 2 H), 4.50 (s, 2 H), 6.38 (s, 1 H), 6.46 (s, 1 H), 6.94-7.55 (m, 20 H). ^{13}C NMR (75 MHz, C_6D_6) δ 32.2, 32.4, 33.7, 34.2, 34.9, 35.1, 43.4, 43.7, 50.8, 53.3, 115.1, 115.2, 126.6, 130.1, 137.5, 138.2, 156.5, 156.8, 166.5, 167.1; MS (EI), m/z 407 (M^+), 287, 250 (base), 157, 91, 77, 65.

(Z)-3-Phenylselenyl-undec-2-enoic acid benzyl-methyl-amide (12): To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (62.0 mg, 0.19 mmol), S-phenyl-*N*-benzyl-*N*-methyl sulfenamide **1b** (45.0 mg, 0.19 mmol), 1-decyne, (54.0 μ L, 0.30 mmol), 4.5% palladium tetraphenylphosphine (10.0 mg, 8.6 μ mol) and benzene (3 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 64 h at 78 °C with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using hexanes, 20% ethyl acetate/hexanes, methanol to yield the orange oil (Z)-3-phenylselenyl-undec-2-enoic acid benzyl-methyl-amide (**12**) (50.5 mg, 0.11 mmol) in 60% yield. The *E/Z* ratio was determined by ^1H NMR spectroscopy (*E/Z* = 0/100). Two distinct rotamers were observed by ^1H and ^{13}C NMR at room temperature. The rotamers were resolved into one species at 350 K. ^1H NMR (300 MHz, C_6D_6) δ 0.87 (t, $J = 6.9\text{ Hz}$, 6 H), 1.03-1.40 (m, 24 H), 2.19 (t, $J = 7.1\text{ Hz}$, 2 H), 2.28 (t, $J = 7.3\text{ Hz}$, 2 H), 2.41 (s, 3 H), 2.81 (s, 3 H), 4.09 (s, 2 H), 4.52 (s, 2 H), 6.42 (s, 1 H), 6.48 (s, 1 H), 6.94-7.73 (m, 20 H); ^{13}C NMR (75 MHz, $\text{d}_8\text{-tol}$) δ 14.4, 23.1, 29.6, 30.5, 30.7, 32.3, 33.6, 34.2, 38.3, 38.5, 50.8, 53.4, 113.6, 113.7, 130.7, 131.6, 132.3, 132.5, 133.6, 133.9, 134.6, 135.0, 138.5, 159.2, 159.6, 167.1, 167.7; MS (EI), m/z 443 (M^+), 323, 286 (base), 157, 120, 91, 77, 65.

(Z)-3-Phenylselenyl-hex-2-enoic acid diethylamide (13): To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (61.0 mg, 0.19 mmol), S-phenyl-*N*-diethyl sulfenamide **1c** (37.0 mg, 0.20 mmol), 1-pentyne (30.0 μ L, 0.30 mmol), 4.2% palladium tetraphenylphosphine (9.8 mg, 8.4 μ mol), benzene (1.5 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 63 h at 85 °C with

stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using hexanes, 5% ethyl acetate/hexanes and ethyl acetate to yield the light yellow oil (*Z*)-3-phenylselenenyl-hex-2-enoic acid diethylamide (**13**) (35.0 mg, 0.11 mmol) in 55% yield. The *E/Z* ratio was determined by NOE difference and ^1H NMR spectroscopy (*E/Z* = 0/100). ^1H NMR (300 MHz, C_6D_6) δ 0.59 (t, $J = 7.3\text{ Hz}$, 3 H), 0.77 (br.s, 3 H), 0.99 (br.s, 3 H), 1.33 (m, $J_1 = J_2 = 7.3\text{ Hz}$, 2 H), 2.18 (t, $J = 7.0\text{ Hz}$, 2 H), 2.84 (br.s, 2 H), 3.26 (br.s, 2 H), 6.37 (s, 1 H), 6.94-7.00 (m, 3 H), 7.61-7.63 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 13.6, 14.8, 23.6, 40.1, 40.7, 42.1, 114.0, 128.5, 128.9, 130.8, 137.8, 157.8, 166.0; MS (EI), m/z 325 (M^+), 253, 168 (base), 157, 100.

(Z)-3-Phenylselenenyl-hex-2-enoic acid allyl-methyl-amide (14): To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (63.0 mg, 0.20 mmol), S-phenyl-*N*-allyl-*N*-methyl-sulfenamide **1d** (36.0 mg, 0.20 mmol), 1-pentyne (30.0 μL , 0.30 mmol), 5.0% palladium tetraphenylphosphine (12 mg, 10.3 μmol), benzene (3.0 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 64 h at 82 $^\circ\text{C}$ with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was partially purified via column chromatography using hexanes, 5% ethyl acetate/hexanes, methanol yielding a mixture of diphenyl diselenide and (*Z*)-3-phenylselenenyl-hex-2-enoic acid allyl-methyl-amide (**14**). The *E/Z* ratio was determined by NOE difference and ^1H NMR spectroscopy (*E/Z* = 0/100). Two distinct rotamers were observed by ^1H and ^{13}C NMR at room temperature. ^1H NMR (300 MHz, C_6D_6) δ 0.59 (m, 6 H), 1.22 (br.s, 4 H),

2.16 (m, 4 H), 2.45 (s, 3 H), 2.78 (s, 3 H), 3.40 (br.s, 2 H), 3.92 (br.s, 2 H), 4.91 (m, 4 H), 5.40 (m, 1 H), 5.60 (m, 1 H), 6.35 (s, 2 H), 6.88-6.99 (m, 6 H), 7.58-7.62 (m, 4 H); ^{13}C NMR (75 MHz, C_6D_6) 13.4, 23.6, 33.5, 34.2, 40.1, 50.0, 52.0, 114.0, 116.0, 116.9, 130.5, 133.5, 134.1, 158.0, 158.6, 166.4, 166.9; MS (EI), m/z 323 (M^+), 253, 166 (base), 157, 77, 41.

(Z)-3-Phenylselenenyl-hex-2-enoic acid diallylamide (15): To a glass bomb in a nitrogen filled glovebox were added diphenyl diselenide (62.0 mg, 0.19 mmol), S-phenyl-N-diallyl sulfenamide **1e** (41.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL , 0.30 mmol), 8.0% palladium tetraphenylphosphine (17.5 mg, 15.1 μmol), benzene (2.5 mL). The reaction was charged with 0.5 atmospheres of carbon monoxide gas and heated for 43 h at 103 $^\circ\text{C}$ with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using hexanes, 5% ethyl acetate/hexanes, methanol to yield the orange oil (Z)-3-phenylselenenyl-hex-2-enoic acid diallylamide (**15**) (41.8 mg, 0.12 mmol) in 60% yield. The *E/Z* ratio was determined by NOE and ^1H NMR difference spectroscopy (*E/Z* = 0/100). ^1H NMR (300 MHz, C_6D_6) δ 0.57 (t, $J = 7.3\text{ Hz}$, 3 H), 1.31 (m, $J_1 = J_2 = 7.4\text{ Hz}$, 2 H), 2.15 (t, $J = 7.4\text{ Hz}$, 2 H), 3.55 (s, 2 H), 4.00 (d, $J = 5.3\text{ Hz}$, 2 H), 4.94 (m, 4 H), 5.44 (m, 1 H), 5.73 (m, 1 H), 6.38 (s, 1 H), 6.95-7.81 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 21.4, 23.5, 40.1, 48.4, 49.1, 113.8, 116.1, 117.1, 130.5, 131.7, 132.3, 133.5, 133.9, 137.8, 159.2, 166.7; MS (EI), m/z 349 (M^+), 272, 253, 192 (base), 157, 77, 41.

¹ Davis, F.A.; Friedman, A.J.; Kluger, E.W.; Skibo, E.B.; Fretz, R.E.; Milicia, A.P.; LeMasters, W.C. *J. Org. Chem.* **1977**, 42, 967-972.