Highly Stereoselective one pot Procedure to Prepare bis- and tris-Chalcogenide Alkenes via Addition of Disulfides and Diselenides to Terminal Alkynes

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SUPPORTING INFORMATION

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Materials and Methods

Proton nuclear magnetic resonance spectra (^1H NMR) were obtained at 400 MHz. Spectra were recorded in CDCl_3 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl_3 or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 100 MHz. Spectra were recorded in CDCl_3 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl_3 . Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using silica gel (230-400 mesh) following the methods described by Still.¹ Thin layer chromatography (TLC) was performed using silica gel GF₂₅₄, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a controller.

General Procedure for the Preparation of the Bis-chalcogenide alkenes: *n*-Butyllithium (1.34 mL of a 1.567M solution in hexane, 2.1 mmol) was added, under argon, to a solution of alkyne (1 mmol) in THF (2 mL) previously cooled at 0 °C. The resulting solution was stirred for 30 min at room temperature. After this time, the mixture was cooled at 0 °C and the disulfide or diselenide (1.2 mmol) in THF (1 mL) was added. The reaction was warmed at room temperature, stirred for 3 h, and then treated with ethanol (0.5 mL). The mixture was then heated at reflux for 12 h. After this time, the mixture was cooled at room temperature, diluted with ethyl acetate (20 mL) and washed with brine (2x20 mL). The organic phase was separated, dried over MgSO_4 and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/ethyl acetate (80:20).

(Z)-2,3-bis(methylthio)prop-2-en-1-ol (2a): Yield: 0.147 g (98%). ^1H RMN: CDCl_3 , 400 MHz, δ (ppm): 6.40 (s, 1H), 4.21 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 2.16 (s, 1H). ^{13}C RMN: CDCl_3 , 100 MHz, δ (ppm): 130.8, 130.4, 64.8, 16.9, 14.3. MS (EI, 70 eV) m/z (relative intensity): 151 (7), 121 (100), 103 (14), 73 (14), 59 (40), 47 (13). HRMS Calcd. For $\text{C}_5\text{H}_{10}\text{OS}_2$: 150.0173. Found: 150.0178.

(Z)-2,3-bis(phenylthio)prop-2-en-1-ol (2b): Yield: 0.219 g (80%). ^1H RMN: CDCl_3 , 400 MHz, δ (ppm): 7.44-7.19 (m, 10H), 7.01 (t, $J = 1.02$ Hz, 1H), 4.12 (s, 2H), 2.15 (s, 1H). ^{13}C RMN: CDCl_3 , 100 MHz, δ (ppm): 134.8, 134.5, 133.1, 130.3, 129.9, 129.8, 129.2, 129.1,

¹ Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925

127.3, 126.9, 65.3. MS (EI, 70 eV) m/z (relative intensity): 274 (100), 186 (10), 167 (43), 147 (27), 135 (52), 91 (14), 77 (5). HRMS Calcd. For $C_{15}H_{14}OS_2$: 274.0486. Found: 274.0491.

(Z)-2,3-bis(4-methoxyphenylthio)prop-2-en-1-ol (2c): Yield: 0.264 g (79%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.38-7.35 (m, 4H), 6.86-6.81 (m, 4H), 6.72 (s, 1H), 4.02 (s, 2H), 3.77-3.75 (m, 6H), 2.15 (m, 1H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 159.4, 159.3, 133.2, 132.9, 132.9, 130.3, 125.3, 123.1, 114.7, 114.7, 64.9, 55.3, 55.2. MS (EI, 70 eV) m/z (relative intensity): 333 (1), 318 (91), 227 (95), 179 (90), 164 (100), 139 (85), 96 (25), 77 (10). HRMS Calcd. For $C_{17}H_{18}O_3S_2$: 334.0697. Found: 334.0703.

(Z)-2,3-bis(4-chlorophenylthio)prop-2-en-1-ol (2d): Yield: 0.215 g (63%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.38-7.26 (m, 8H), 6.97 (t, $J = 1.17$ Hz, 1H), 4.15 (d, $J = 5.11$ Hz, 2H), 1.85 (t, $J = 5.55$ Hz, 1H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 134.6, 133.8, 133.2, 133.1, 131.8, 131.6, 131.1, 130.1, 129.4, 129.4, 65.4. MS (EI, 70 eV) m/z (relative intensity): 257 (9), 168 (20), 111 (15), 97 (26), 83 (34), 69 (51), 67 (73), 55 (100). HRMS Calcd. For $C_{15}H_{12}Cl_2OS_2$: 341.9706. Found: 341.9712.

(Z)-2,3-bis(3-chlorophenylthio)prop-2-en-1-ol (2e): Yield: 0.202 g (59%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.43-7.19 (m, 8H), 7.07 (s, 1H), 4.19 (s, 2H), 1.93 (s, 1H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 136.4, 135.2, 135.0, 134.8, 134.5, 130.3, 130.2, 130.0, 129.9, 128.9, 128.3, 127.7, 127.4, 127.1, 65.5. MS (EI, 70 eV) m/z (relative intensity): 341 (3), 222 (100), 178 (23), 161 (11), 143 (6). HRMS Calcd. For $C_{15}H_{12}Cl_2OS_2$: 341.9707. Found: 341.9714.

(Z)-2,3-bis(2-chlorophenylthio)prop-2-en-1-ol (2f): Yield: 0.274 g (80%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.49-7.47 (m, 1H), 7.42-7.33 (m, 3H), 7.27-7.13 (m, 4H), 7.06 (s, 1H), 4.17 (s, 2H), 2.12 (s, 1H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 135.0, 134.3, 134.1, 133.6, 132.2, 131.6, 130.4, 130.1, 130.0, 129.8, 128.6, 127.7, 127.4, 127.3, 65.5. MS (EI, 70 eV) m/z (relative intensity): 342 (1), 326 (66), 291 (24), 235 (100), 183 (30), 148 (98), 108 (86), 69 (31). HRMS Calcd. For $C_{15}H_{12}Cl_2OS_2$: 341.9706. Found: 341.9814.

(Z)-2,3-bis(benzylthio)prop-2-en-1-ol (2i): Yield: 0.157 g (52%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.30-7.17 (m, 10H), 6.51 (s, 1H), 3.92 (s, 2H), 3.90 (s, 2H), 3.87 (s, 2H), 1.81 (s, 1H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 137.9, 137.6, 132.6, 129.5, 128.7, 128.7, 128.6, 128.3, 127.2, 127.0, 66.2, 37.7, 35.8. MS (EI, 70 eV) m/z (relative intensity): 284 (33), 162 (100), 147 (17), 128 (50), 115 (25), 91 (38). HRMS Calcd. For $C_{17}H_{18}OS_2$: 302.0799. Found: 302.0805.

(Z)-2,3-bis(dodecylthio)prop-2-en-1-ol (2j): Yield: 0.247 g (54%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 6.51 (s, 1H), 4.17 (s, 2H), 2.77-2.70 (m, 4H), 1.66-1.55 (m, 4H), 1.39-1.26 (m, 36H), 0.88 (t, $J = 7.02$ Hz, 6H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 132.3, 129.3, 65.8, 34.1, 34.1, 31.9, 31.9, 31.7, 31.7, 30.4, 30.0, 29.63, 29.62, 29.61, 29.58, 29.57, 29.51, 29.5, 29.3, 29.25, 29.2, 28.8, 28.6, 22.7, 22.7, 14.1, 14.1. MS (EI, 70 eV) m/z (relative intensity): 458 (3), 257 (97), 240 (35), 227 (39), 199 (90), 87 (100), 59 (70). HRMS Calcd. For $C_{27}H_{54}OS_2$: 458.3616. Found: 458.3621.

(Z)-1,2-bis(methylthio)pent-1-en-3-ol (2k): Yield: 0.172 g (97%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 6.52 (s, 1H), 4.10 (t, $J = 6.28$ Hz, 1H), 2.48 (s, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 1.77-1.57 (m, 2H), 0.91 (t, $J = 7.45$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 134.6, 132.8, 76.8, 28.7, 16.7, 15.9, 9.8. MS (EI, 70 eV) m/z (relative intensity): 160 (100), 145 (80), 130 (7), 112 (5), 97 (52). HRMS Calcd. For $C_7H_{14}OS_2$: 178.0486. Found: 178.0490.

(Z)-1,2-bis(phenylthio)pent-1-en-3-ol (2l): Yield: 0.242 g (80%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.43-7.16 (m, 10H), 7.11 (s, 1H), 4.12 (q, *J* = 6.43 Hz, 1H), 1.93 (s, 1H), 1.80-1.58 (m, 2H), 0.91 (t, *J* = 7.45 Hz, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 136.2, 134.8, 134.1, 132.0, 130.2, 129.0, 128.9, 128.6, 127.2, 126.2, 76.4, 29.0, 9.7. MS (EI, 70 eV) *m/z* (relative intensity): 284 (100), 269 (29), 175 (46), 167 (27), 143 (20), 77 (3). HRMS Calcd. For C₁₇H₁₈OS₂: 302.0799. Found: 302.0807.

(Z)-2-methyl-3,4-bis(methylthio)but-3-en-2-ol (2m): Yield: 0.160 g (90%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 6.70 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.27 (s, 1H), 1.43 (s, 6H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 137.2, 135.1, 74.6, 28.8, 16.9, 16.5. MS (EI, 70 eV) *m/z* (relative intensity): 130 (80), 82 (100), 71 (23), 67 (55), 59 (21). HRMS Calcd. For C₇H₁₄OS₂: 178.0486. Found: 178.0492.

(Z)-2-methyl-3,4-bis(phenylthio)but-3-en-2-ol (2n): Yield: 0.235 g (78%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.42-7.24 (m, 10H), 7.17-7.13 (m, 1H), 2.18 (s, 1H), 1.46 (s, 6H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 137.7, 135.0, 134.95, 134.9, 130.5, 129.1, 128.9, 127.4, 127.0, 125.6, 75.0, 29.3. MS (EI, 70 eV) *m/z* (relative intensity): 284 (100), 207 (18), 176 (99), 143 (62), 130 (14), 66 (8). HRMS Calcd. For C₁₇H₁₈OS₂: 302.0799. Found: 302.0808.

(Z)-1-(1,2-bis(methylthio)vinyl)cyclohexanol (2o): Yield: 0.185 g (85%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 6.70 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 1.97 (s, 1H), 1.79-1.56 (m, 10H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 138.1, 135.9, 75.5, 36.2, 25.4, 21.9, 17.3, 16.8. MS (EI, 70 eV) *m/z* (relative intensity): 200 (63), 185 (100), 137 (25), 110 (10). HRMS Calcd. For C₁₀H₁₈OS₂: 218.0799. Found: 218.0805.

(Z)-1-(1,2-bis(phenylthio)vinyl)cyclohexanol (2p): Yield: 0.239 g (70%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.40-7.24 (m, 10H), 7.15-7.11 (m, 1H), 1.92 (s, 1H), 1.82-1.53 (m, 10H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 138.0, 135.4, 135.1, 135.0, 130.3, 129.0, 128.7, 127.2, 126.7, 125.3, 75.7, 36.1, 25.1, 21.7. MS (EI, 70 eV) *m/z* (relative intensity): 342 (1), 324 (100), 247 (14), 215 (59), 182 (47), 147 (33), 109 (22), 77 (43). HRMS Calcd. For C₂₀H₂₂OS₂: 342.1112. Found: 342.1118.

(Z)-3-methyl-1,2-bis(phenylthio)pent-1-en-3-ol (2q): Yield: 0.243 g (77%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.41-7.25 (m, 10H), 7.15 (t, *J* = 7.75 Hz, 1H), 2.02 (s, 1H), 1.84-1.66 (m, 2H), 1.41 (s, 3H), 0.88 (t, *J* = 7.45 Hz, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 138.1, 135.0, 134.8, 134.0, 130.3, 129.0, 128.8, 127.2, 125.6, 77.5, 33.8, 26.6, 8.1. MS (EI, 70 eV) *m/z* (relative intensity): 298 (100), 222 (34), 190 (42), 162 (39), 148 (18), 77 (7). HRMS Calcd. For C₁₈H₂₀OS₂: 316.0955. Found: 316.0960.

(Z)-2,3-bis(phenylselanyl)prop-2-en-1-ol (2r): Yield: 0.333 g (90%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.59-7.53 (m, 4H), 7.39 (s, 1H), 7.32-7.27 (m, 6H), 4.14 (s, 2H), 1.86 (s, 1H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 133.4, 133.2, 132.4, 132.2, 130.3, 129.4, 129.3, 128.6, 127.8, 127.5, 67.6. MS (EI, 70 eV) *m/z* (relative intensity): 369 (86), 312 (41), 212 (67), 195 (100), 181 (72), 155 (68), 78 (20). HRMS Calcd. For C₁₅H₁₄OSe₂: 369.9375. Found: 369.9382.

(Z)-2,3-bis(mesitylselanyl)prop-2-en-1-ol (2s): Yield: 0.363 g (80%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 6.95 (s, 2H), 6.94 (s, 2H), 6.71 (s, 1H), 3.78 (d, *J* = 5.70 Hz, 2H), 2.53 (s, 6H), 2.50 (s, 6H), 2.28 (s, 3H), 2.27 (s, 3H), 1.40 (t, *J* = 5.70 Hz, 1H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 143.3, 142.8, 138.8, 138.7, 132.7, 128.8, 128.7, 128.2, 127.0, 125.5, 66.8, 24.5, 24.3, 20.9, 20.9. MS (EI, 70 eV) *m/z* (relative intensity): 453 (5), 237 (32), 225 (100), 198 (29), 119 (46). HRMS Calcd. For C₂₁H₂₆OSe₂: 454.0314. Found: 454.0320.

(Z)-2,3-bis(4-methoxyphenylselanyl)prop-2-en-1-ol (2t): Yield: 0.301 g (70%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.54-7.51 (m, 4H), 7.16 (s, 1H), 6.86-6.83 (m, 4H), 4.06 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 2.00 (s, 1H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 159.8, 159.8, 135.5, 135.4, 134.2, 134.2, 132.6, 132.1, 115.1, 115.0, 67.2, 55.3, 55.3. MS (EI, 70 eV) *m/z* (relative intensity): 251 (100), 242 (94), 225 (53), 213 (91), 198 (39), 188 (48), 107 (19). HRMS Calcd. For C₁₇H₁₈O₃Se₂: 429.9586. Found: 429.9592.

(Z)-2,3-bis(4-chlorophenylselanyl)prop-2-en-1-ol (2u): Yield: 0.285 g (65%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.51-7.45 (m, 4H), 7.34 (s, 1H), 7.30-7.25 (m, 4H), 4.15 (d, *J* = 5.41 Hz, 2H), 1.83 (t, *J* = 6.28 Hz, 1H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 134.5, 134.3, 133.9, 133.6, 133.4, 132.3, 129.5, 129.5, 128.2, 126.7, 67.5. MS (EI, 70 eV) *m/z* (relative intensity): 438 (10), 379 (17), 251 (62), 228 (52), 216 (100), 190 (77), 156 (58), 111 (38). HRMS Calcd. For C₁₅H₁₂Cl₂OSe₂: 437.8596. Found: 437.8601.

(Z)-1,2-bis(phenylselanyl)pent-1-en-3-ol (2y): Yield: 0.330 g (83%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.57-7.53 (m, 4H), 7.46 (s, 1H), 7.30-7.24 (m, 6H), 4.07 (q, *J* = 5.99 Hz, 1H), 1.89 (d, *J* = 5.55 Hz, 1H), 1.76-1.56 (m, 2H), 0.89 (t, *J* = 7.45 Hz, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 135.9, 135.2, 133.2, 131.4, 130.5, 129.6, 129.3, 127.8, 127.1, 78.5, 29.4, 9.9. MS (EI, 70 eV) *m/z* (relative intensity): 397 (1), 380 (27), 223 (60), 157 (33), 142 (100), 128 (32), 77 (31). HRMS Calcd. For C₁₇H₁₈OSe₂: 397.9688. Found: 397.9693.

(Z)-2-methyl-3,4-bis(phenylselanyl)but-3-en-2-ol (2z): Yield: 0.298 g (75%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.61 (s, 1H), 7.56-7.49 (m, 4H), 7.30-7.19 (m, 6H), 2.13 (s, 1H), 1.45 (s, 6H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 139.1, 136.8, 133.3, 130.7, 130.4, 130.0, 129.3, 129.3, 127.8, 126.6, 75.9, 29.4. MS (EI, 70 eV) *m/z* (relative intensity): 380 (46), 314 (14), 222 (41), 157 (31), 142 (100), 128 (23), 77 (13). HRMS Calcd. For C₁₇H₁₈OSe₂: 397.9688. Found: 397.9695.

General Procedure for the Preparation of the Tris-chalcogenides alkenes: *n*-Butyllithium (0.7 mL of a 1.567M solution in hexane, 1.1 mmol) was added, under argon, to a solution of alkyne (1 mmol) in THF (2 mL) previously cooled at 0 °C. The resulting solution was stirred for 30 min at room temperature. After this time, the mixture is cooled at 0 °C and the disulfide or diselenide (3 mmol) in THF (1 mL) was added. The mixture was then heated at reflux for 12 h, cooled at room temperature, diluted with ethyl acetate (20 mL) and washed with brine (2x20 mL). The organic phase was separated, dried over MgSO₄ and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/ethyl acetate (80:20) or hexane.

1-(1,2,2-tris(methylthio)vinyl)benzene (3a): Yield: 0.206 g (85%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.40-7.18 (m, 5H), 2.44 (s, 3H), 2.14 (s, 3H), 1.83 (s, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 145.2, 138.2, 129.2, 128.1, 127.7, 127.3, 18.3, 17.0, 16.7. MS (EI, 70 eV) *m/z* (relative intensity): 242 (100), 194 (7), 179 (17), 160 (11), 147 (7). HRMS Calcd. For C₁₁H₁₄S₃: 242.0258. Found: 242.0263.

1-(1-phenyl-2,2-bis(phenylselanyl)vinylselanyl)benzene (3b): Yield: 0.435 g (76%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.44-6.97 (m, 20H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 148.9, 140.5, 135.8, 133.4, 132.7, 132.3, 131.8, 130.6, 129.0, 128.8, 128.5, 128.4, 127.8, 127.4, 127.35, 127.3, 127.2, 117.3. MS (EI, 70 eV) *m/z* (relative intensity): 334 (26),

312 (13), 258 (89), 179 (100), 153 (15). HRMS Calcd. For $C_{26}H_{20}Se_3$: 571.9061. Found: 571.9068.

3-ethoxy-1,1,2-tris(methylthio)prop-1-ene (3e): Yield: 0.199 g (89%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 4.59 (s, 2H), 3.51 (q, $J = 7.02$ Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H), 1.23 (t, $J = 7.02$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 141.5, 130.2, 68.7, 64.8, 18.3, 16.7, 15.2, 15.1. MS (EI, 70 eV) m/z (relative intensity): 224 (100), 179 (48), 161 (9), 128 (9). HRMS Calcd. For $C_8H_{16}OS_3$: 224.0363. Found: 224.0369.

1-(3-ethoxy-1,1-bis(phenylselanyl)prop-1-en-2-ylselanyl)benzene (3f): Yield: 0.482 g (87%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.33-7.15 (m, 15H), 4.26 (s, 2H), 3.21 (q, $J = 7.02$ Hz, 2H), 1.07 (t, $J = 7.02$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 144.1, 135.4, 133.9, 132.4, 132.3, 131.4, 130.0, 128.9, 128.7, 128.6, 128.3, 127.6, 127.1, 124.0, 72.6, 65.2, 15.0. MS (EI, 70 eV) m/z (relative intensity): 312 (29), 270 (58), 234 (34), 195 (81), 155 (35), 114 (100). HRMS Calcd. For $C_{23}H_{22}OSe_3$: 553.9166. Found: 553.9171.

1-(1,1-bis(4-chlorophenylselanyl)-3-ethoxyprop-1-en-2-ylselanyl)-4-chlorobenzene (3g): Yield: 0.439 g (67%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.61-7.12 (m, 12H), 4.23 (s, 2H), 3.24 (q, $J = 7.02$ Hz, 2H), 1.11 (t, $J = 7.02$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 144.1, 136.7, 135.2, 135.0, 134.4, 134.3, 133.8, 133.7, 130.0, 129.2, 129.0, 128.9, 127.9, 123.8, 72.6, 65.5, 15.1. MS (EI, 70 eV) m/z (relative intensity): 656 (4), 460 (22), 381 (19), 273 (33), 228 (100), 188 (81), 154 (65). HRMS Calcd. For $C_{23}H_{19}Cl_3OSe_3$: 655.7997. Found: 655.8004.

1-(3-ethoxy-1,2-bis(4-methoxyphenylselanyl)prop-1-enylselanyl)-4-methoxybenzene (3h): Yield: 0.322 g (50%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.63-6.72 (m, 12H), 4.21 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.21 (q, $J = 7.02$ Hz, 2H), 1.10 (t, $J = 7.02$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 160.1, 159.6, 159.3, 143.3, 137.8, 135.9, 134.7, 123.9, 122.6, 122.0, 120.3, 114.5, 114.4, 114.3, 72.0, 65.1, 55.2, 55.2, 55.2, 15.1. MS (EI, 70 eV) m/z (relative intensity): 642 (3), 371 (53), 293 (58), 267 (27), 187 (100), 145 (65). HRMS Calcd. For $C_{26}H_{28}O_4Se_3$: 643.9483. Found: 643.9490.

3-ethoxy-1,1,2-tris(methylthio)pent-1-ene (3i): Yield: 0.184 g (73%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 4.99 (t, $J = 7.16$ Hz, 1H), 3.54-3.28 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H), 1.86-1.59 (m, 2H), 1.19 (t, $J = 7.02$ Hz, 3H), 0.89 (t, $J = 7.16$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 143.6, 138.6, 82.7, 64.0, 27.5, 18.4, 17.8, 17.1, 15.2, 10.2. MS (EI, 70 eV) m/z (relative intensity): 251 (100), 222 (24), 206 (83), 195 (9). HRMS Calcd. For $C_{10}H_{20}OS_3$: 252.0676. Found: 252.0682.

1-(3-ethoxy-1,1-bis(phenylselanyl)pent-1-en-2-ylselanyl)benzene (3j): Yield: 0.413 g (71%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 7.31-7.10 (m, 15H), 4.67 (m, 1H), 3.51-3.26 (m, 2H), 1.88-1.44 (m, 2H), 1.10 (t, $J = 6.87$ Hz, 3H), 0.88 (t, $J = 7.31$ Hz, 3H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 144.6, 135.5, 132.7, 132.3, 131.9, 131.7, 131.6, 129.2, 129.0, 128.7, 128.3, 127.9, 127.1, 127.0, 85.1, 64.5, 27.8, 15.2, 10.3. MS (EI, 70 eV) m/z (relative intensity): 578 (18), 426 (44), 334 (76), 312 (100), 256 (60), 176 (64), 154 (33). HRMS Calcd. For $C_{25}H_{26}OSe_3$: 581.9479. Found: 581.9485.

N,N-diethyl-2,3,3-tris(methylthio)prop-2-en-1-amine (3k): Yield: 0.161 g (64%). 1H RMN: $CDCl_3$, 400 MHz, δ (ppm): 3.68 (s, 2H), 2.54 (q, $J = 7.16$ Hz, 4H), 2.50 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H), 1.03 (t, $J = 7.16$ Hz, 6H). ^{13}C RMN: $CDCl_3$, 100 MHz, δ (ppm): 144.8, 127.4, 54.8, 45.7, 18.2, 16.8, 15.5, 11.4. MS (EI, 70 eV) m/z (relative intensity): 251 (100), 204 (27), 179 (18), 156 (7), 86 (39). HRMS Calcd. For $C_{10}H_{21}NS_3$: 251.0836. Found: 251.0841.

N,N-diethyl-2,3,3-tris(phenylselanyl)prop-2-en-1-amine (3l): Yield: 0.331 g (57%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.31-7.15 (m, 15H), 3.45 (s, 2H), 2.44 (q, *J* = 7.02 Hz, 4H), 0.88 (t, *J* = 7.02 Hz, 6H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 135.0, 133.5, 133.3, 132.9, 132.3, 131.2, 128.9, 128.6, 128.6, 128.4, 127.8, 127.3, 127.2, 127.1, 59.5, 45.2, 11.1. MS (EI, 70 eV) *m/z* (relative intensity): 263 (17), 177 (190), 148 (100), 115 (33), 85 (43). HRMS Calcd. For C₂₅H₂₇NSe₃: 580.9639. Found: 580.9645.

4-(2,3,3-tris(methylthio)allyl)morpholine (3m): Yield: 0.204 g (77%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 3.69 (t, *J* = 4.53 Hz, 4H), 3.63 (s, 2H), 2.50 (s, 3H), 2.48 (t, *J* = 4.53 Hz, 4H), 2.35 (s, 3H), 2.24 (s, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 142.2, 128.0, 67.1, 58.9, 52.8, 17.9, 16.7, 15.2. MS (EI, 70 eV) *m/z* (relative intensity): 265 (100), 252 (34), 218 (85), 170 (58) 100 (67). HRMS Calcd. For C₁₀H₁₉NOS₃: 265.0629. Found: 265.0634.

3-(2,3,3-tris(methylthio)allyloxy)-1,1,2-tris(methylthio)prop-1-ene (3o): Yield: 0.198 g (53%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 4.61 (s, 2H), 2.46 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 140.7, 131.8, 68.4, 18.4, 16.8, 15.4. MS (EI, 70 eV) *m/z* (relative intensity): 373 (8), 327 (9), 195 (22), 177 (62), 160 (100). HRMS Calcd. For C₁₂H₂₂OS₆: 373.9995. Found: 374.0002.

1-(3-(2,3,3-tris(phenylselanyl)allyloxy)-1,1-bis(phenylselanyl)prop-1-en-2-ylselanyl)benzene (3p): Yield: 0.465 g (45%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 7.30-7.11 (m, 15H), 4.18 (s, 2H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 142.4, 134.8, 134.2, 132.5, 132.4, 131.6, 130.4, 129.1, 128.7, 128.6, 128.1, 127.6, 127.1, 127.1, 72.6. HRMS Calcd. For C₄₂H₃₄OSe₆: 1033.7601. Found: 1033.7609.

(Z)-1-deutero-1,2-bis(methylthio)pent-1-en-3-ol (4): Yield: 0.170 g (95%). ¹H RMN: CDCl₃, 400 MHz, δ(ppm): 4.11 (t, *J* = 6.28 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 2.04 (s, 1H), 1.76-1.60 (m, 2H), 0.92 (t, *J* = 7.45 Hz, 3H). ¹³C RMN: CDCl₃, 100 MHz, δ(ppm): 134.7 (t, *J* = 25.4 Hz), 132.9, 76.6, 29.02, 16.8, 16.2, 10.00. MS (EI, 70 eV) *m/z* (relative intensity): 179 (22), 163 (93), 159 (100), 154 (16). HRMS Calcd. For C₇H₁₃DOS₂: 179.0549. Found: 179.0554.

SELECTED SPECTRA