

Electrophilic Cyclization of (*Z*)-Selenoenynes: Synthesis and Reactivity of 3-Iodoselenophenes

*Diego Alves, Cristiane Luchese, Cristina W. Nogueira and Gilson Zeni**

Laboratório de Síntese, Reatividade, Avaliação Farmacológica e Toxicológica de
Organocalcogênicos, CCNE, UFSM, Santa Maria - Rio Grande do Sul – Brazil -

97105-900

gzeni@quimica.ufsm.br

SUPPORTING INFORMATION

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Materials and Methods

Proton nuclear magnetic resonance spectra (^1H NMR) were obtained at 200 MHz on a Bruker DPX-200 NMR spectrometer or at 400 MHz on a Bruker DPX-400 NMR spectrometer. 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 either at 50 MHz on a Bruker DPX-200 NMR spectrometer or at 100 MHz on a Bruker DPX-400 NMR spectrometer. 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), dt (double triplet), td (triple doublet) and m (multiplet). High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using Merck Silica Gel (230-400 mesh) following the methods described by Still.¹ Thin layer chromatography (TLC) was performed using Merck 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. Most reactions were monitored by TLC for disappearance of starting material. 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 Variac controller.

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

General Procedure for the Preparation of the (Z)-selenoenynes 1a-b and 1d-f.

To a solution of the 1,4-diphenyl-1,3-butadiyne (1.010g; 5.0 mmol) and appropriate diorganoyldiselenide (2.5 mmol) in 95% ethanol (50 mL) under a nitrogen atmosphere, NaBH₄ (0.472g; 12.5 mmol) was added at room temperature, under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 5 hours, allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3x30 mL) and water (3x30 mL). After drying the organic phase over anhydrous MgSO₄, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as eluent. **(Z)-1-(Methylseleno)-1,4-diphenylbut-1-en-3-yne (1a).** Yield: 1.039g (70%). H¹ NMR (CDCl₃, 200 MHz): δ 7.55-7.30 (m, 10H), 6.17 (s, 1H), 1.95 (s, 3H). C¹³ NMR (CDCl₃, 100 MHz): δ 148.58, 139.41, 131.37, 128.46, 128.45, 128.30, 128.29, 128.21, 123.44, 110.08, 96.98, 88.07, 7.05. MS (relative intensity) *m/z*: 297 (100), 203 (65), 173 (35), 96 (21), 77 (15), 47 (21). HRMS calcd for C₁₇H₁₄Se: 298.0261. Found: 298.0266.

(Z)-1-(Ethylseleno)-1,4-diphenylbut-1-en-3-yne (1b). Yield: 1.104g (71%). H¹ NMR (CDCl₃, 200 MHz): δ 7.54-7.30 (m, 10H), 6.22 (s, 1H), 2.59 (q, *J* = 7.50 Hz, 2H), 1.26 (t, *J* = 7.50 Hz, 3H). C¹³ NMR (CDCl₃, 100 MHz): δ 147.63, 140.03, 131.37, 128.42, 128.38, 128.27, 128.17, 128.13, 123.49, 111.25, 96.85, 88.32, 20.49, 15.56. MS (relative intensity) *m/z*: 312 (100), 204 (75), 127 (62), 106 (39), 102 (45), 77 (16). HRMS calcd for C₁₈H₁₆Se: 312.0417. Found: 312.0422.

(Z)-1-(*tert*-Butylseleno)-1,4-diphenylbut-1-en-3-yne (1d). Yield: 1.084g (64%). H¹ NMR (CDCl₃, 200 MHz): δ 7.67-7.62 (m, 2H), 7.54-7.49 (m, 2H), 7.39-7.31 (m, 6H), 6.56 (s, 1H), 1.36 (s, 9H). C¹³ NMR (CDCl₃, 100 MHz): δ 145.02, 142.72, 131.54, 128.31, 128.30, 128.25, 128.20, 128.19, 123.63, 118.68, 95.85, 89.87, 46.48, 32.93. MS (relative intensity) *m/z*: 339 (100), 283 (65), 204 (54), 127 (25), 77 (23), 56 (13), 42 (18). HRMS calcd for C₂₀H₂₀Se: 340.0730. Found: 340.0735.

(Z)-1-(Benzylseleno)-1,4-diphenylbut-1-en-3-yne (1e). Yield: 1.268g (68%). H¹ NMR (CDCl₃, 200 MHz): δ 7.52-7.12 (m, 15H), 6.23 (s, 1H), 3.87 (s, 2H). C¹³ NMR

(CDCl₃, 100 MHz): δ 147.64, 140.05, 138.35, 131.40, 128.92, 128.55, 128.46, 128.33, 128.29, 128.27, 128.26, 126.77, 123.38, 111.61, 97.26, 88.29, 30.57. MS (relative intensity) m/z : 374 (100), 283 (63), 204 (50), 127 (20), 91 (53), 77 (17). HRMS calcd for C₂₃H₁₈Se: 374.0573. Found: 374.0577.

(Z)-1-(Phenylseleno)-1,4-diphenyl-but-1-en-3-yne (1f).² Yield: 1.220g (68%). H¹ NMR (CDCl₃, 400 MHz): δ 7.50-7.40 (m, 4H), 7.38-7.22 (m, 5H), 7.19 (m, 3H), 7.07 (m, 3H), 6.40 (s, 1H). C¹³ NMR (CDCl₃, 100 MHz): δ 147.10, 139.40, 133.20, 133.00, 131.40, 129.90, 128.30, 128.20, 127.90, 126.90, 123.20, 112.60, 97.60, 88.30. MS (relative intensity) m/z : 359 (100), 282 (39), 203 (82), 156 (72), 126 (42), 101 (35), 77 (31). HRMS calcd for C₂₂H₁₆Se: 360.0417. Found: 360.0410.

General Procedure for the Preparation of the (Z)-selenoenynes 1c and 1g-m.

To a suspension of elemental selenium (0.395 g; 5 mmol) in dry THF (25 mL) under argon and with magnetic stirring was added *n*-butyllithium (2.0 mL of a 2.5 M solution in hexane; 5 mmol). A yellow solution was formed. To this solution was added the appropriate diyne (1 mmol) in deoxygenated ethanol (25 mL). The mixture was then heated at reflux for 24 h. After this time, the mixture was cooled to room temperature and diluted with ethyl acetate (60 mL) and washed with saturated aq NH₄Cl (30 mL) and water (3x30 mL). The organic phase was separated, dried over MgSO₄, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. **(Z)-1-(*n*-Butylseleno)-1,4-diphenyl-but-1-en-3-yne (1c).**³ Yield: 1.135g (67%). H¹ NMR (CDCl₃, 400 MHz): δ 7.53-7.45 (m, 4H), 7.38-7.30 (m, 6H), 6.21 (s, 1H), 2.58 (t, J = 7.44Hz, 2H), 1.53 (quint, J = 7.44Hz, 2H), 1.28 (sex, J = 7.44Hz, 2H), 0.78 (t, J = 7.44Hz, 3H). C¹³ NMR (CDCl₃, 100 MHz): δ 147.90, 140.09, 131.39, 128.43, 128.37, 128.28, 128.21, 128.16, 123.56, 111.15, 96.77, 88.39, 32.47, 26.55, 22.72, 13.47. MS (relative intensity) m/z : 339 (100), 283 (65), 204 (54), 127 (25), 77 (23), 56 (13), 42 (18). HRMS calcd for C₂₀H₂₀Se: 340.0730. Found: 340.0735.

⁽²⁾ Dabdoub, M. J.; Baroni, A. C. M.; Lenardão, E. J.; Gianeti, T. R.; Hurtado, G. R. *Tetrahedron* **2001**, 57, 4271.

⁽³⁾ Zeni, G.; Stracke, M. P.; Nogueira, C. W.; Braga, A. L.; Menezes, P. H.; Stefani, H. A. *Org. Lett.* **2004**, 6, 1135.

(Z)-1-(*n*-Butylseleno)-1,4-bis-(*p*-methylphenyl)-but-1-en-3-yne (1g). Yield: 1.266g (69%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.42-7.36 (m, 4H), 7.17-7.12 (m, 4H), 6.19 (s, 1H), 2.60 (t, $J = 7.44$ Hz, 2H), 2.36-2.35 (m, 6H), 1.54 (quint, $J = 7.44$ Hz, 2H), 1.29 (sex, $J = 7.44$ Hz, 2H), 0.79 (t, $J = 7.44$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.30, 138.37, 138.22, 137.26, 131.24, 129.05, 129.04, 128.08, 120.52, 110.72, 96.78, 87.94, 32.41, 26.55, 22.73, 21.50, 21.19, 13.48. MS (relative intensity) m/z : 368 (100), 311 (44), 232 (37), 141 (63), 136 (29), 91 (78), 57 (22), 43 (19). HRMS calcd for $\text{C}_{22}\text{H}_{24}\text{Se}$: 368.1043. Found: 368.1047.

(Z)-5-(*n*-Butylseleno)-dodec-5-en-7-yne (1h). Yield: 0.956g (64%). ^1H NMR (CDCl_3 , 400 MHz): δ 5.76-5.74 (m, 1H), 2.81 (t, $J = 7.44$ Hz, 2H), 2.39-2.30 (m, 4H), 1.70-1.29 (m, 12H), 0.94-0.89 (m, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 146.41, 108.66, 96.29, 78.41, 37.45, 32.58, 31.21, 30.84, 24.04, 24.03, 23.03, 22.00, 21.96, 19.40, 13.84, 13.57. MS (relative intensity) m/z : 299 (100), 242 (15), 163 (75), 136 (25), 106 (45), 56 (19). HRMS calcd for $\text{C}_{16}\text{H}_{28}\text{Se}$: 300.1356. Found: 300.1361.

(Z)-9-(*n*-Butylseleno)-icos-9-en-11-yne (1i). Yield: 1.274g (62%). ^1H NMR (CDCl_3 , 400 MHz): δ 5.74 (s, 1H), 2.81 (t, $J = 7.44$ Hz, 2H), 2.38-2.29 (m, 4H), 1.70-1.28 (m, 28H), 0.94-0.86 (m, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 146.56, 108.50, 96.39, 78.43, 37.72, 32.56, 31.83, 29.37, 29.36, 29.21, 29.19, 29.13, 29.09, 28.94, 28.91, 28.78, 24.01, 23.05, 22.64, 22.63, 19.73, 14.08, 14.07, 13.59. MS (relative intensity) m/z : 411 (100), 354 (11), 275 (87), 261 (15), 247 (21), 233 (17), 219 (11), 136 (51), 112 (52), 56 (31), 42 (24). HRMS calcd for $\text{C}_{24}\text{H}_{44}\text{Se}$: 412.2608. Found: 412.2613.

(Z)-3-(*n*-Butylseleno)-2,7-dimethyl-oct-3-en-5-yne-2,7-diol (1j). Yield: 1.060g (70%). ^1H NMR (CDCl_3 , 200 MHz): δ 6.35 (s, 1H), 3.04 (t, $J = 7.50$ Hz, 2H), 2.53-2.45 (m, 2H), 1.74-1.33 (m, 16H), 0.92 (t, $J = 7.50$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 154.42, 112.19, 100.72, 80.11, 74.54, 65.55, 32.34, 31.21, 28.98, 28.20, 22.96, 13.57. MS (relative intensity) m/z : 267 (100), 210 (23), 136 (78), 131 (56), 56 (21), 42 (23). HRMS calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Se}$: 304.0942. Found: 304.0948.

(Z)-2-(*n*-Butylseleno)-hex-2-en-4-yne-1,6-diol (1k).³ Yield: 0.852g (69%). ¹H NMR (CDCl₃, 400 MHz): δ 6.16 (s, 1H), 4.44 (s, 2H), 4.30 (s, 2H), 2.92 (t, *J* = 7.50 Hz, 2H), 2.75 (m, 2H), 1.67 (quint, *J* = 7.50 Hz, 2H), 1.42 (sex, *J* = 7.50 Hz, 2H), 0.93 (t, *J* = 7.50 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 146.26, 109.08, 94.54, 82.81, 66.07, 51.51, 32.54, 24.36, 22.87, 13.51. MS (relative intensity) *m/z*: 230 (40), 212(15), 191 (34), 112 (100), 94 (22), 76 (31). HRMS calcd for C₁₀H₁₆O₂Se: 248.0365. Found: 248.0378.

(Z)-1-(*n*-Butylseleno)-1-phenyl-oct-1-en-3-yne (1l).³ Yield: 1.052g (66%). ¹H NMR (CDCl₃, 400 MHz): δ 7.47-7.45 (m, 2H), 7.35-7.25 (m, 3H), 5.97 (s, 1H), 2.88 (t, *J* = 7.44 Hz, 2H), 2.40 (t, *J* = 7.44 Hz, 2H), 1.69 (quint, *J* = 7.44 Hz, 2H), 1.54 (quint, *J* = 7.44 Hz, 2H), 1.48-1.32 (m, 4H), 0.95-0.90 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 149.54, 131.20, 128.19, 127.87, 123.68, 107.90, 95.01, 87.56, 37.75, 32.54, 31.27, 24.39, 23.01, 22.02, 13.87, 13.59. MS (relative intensity) *m/z*: 319 (100), 213 (76), 184 (48), 127 (10), 102 (29), 77 (38), 57 (47), 43 (32). HRMS calcd for C₁₈H₂₄Se: 320.1043. Found: 320.1048.

(Z)-3-(*n*-Butylseleno)-2-methyl-6-phenyl-hex-3-en-5-yn-2-ol (1m).³ Yield: 1.011g (63%). ¹H NMR (CDCl₃, 400 MHz): δ 7.48-7.45 (m, 2H), 7.34-7.32 (m, 3H), 6.55 (s, 1H), 3.12 (t, *J* = 7.60 Hz, 2H), 2.32 (s, 1H), 1.70 (quint, *J* = 7.60 Hz, 2H), 1.51-1.36 (m, 8H), 0.89 (t, *J* = 7.60 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 155.00, 131.27, 128.35, 128.34, 123.31, 112.49, 96.19, 87.57, 74.54, 32.42, 29.09, 28.55, 22.96, 13.55. MS (relative intensity) *m/z*: 304 (21), 265 (44), 186 (100), 168 (75), 77 (11). HRMS calcd for C₁₇H₂₂OSe: 322.0858. Found: 322.0877.

(Z)-1-(*n*-Butylseleno)-4-phenyl-but-1-en-3-yne (1n). Powdered NaOH (0.220g, 5.5 mmol) was added to a two-neck round bottomed flask equipped with a reflux condenser, containing a solution of 2-hydroxy-2-methyl-6-phenyl-3,5-hexadiyne (0.830g; 5.0 mmol) in dry toluene (10 mL) under argon atmosphere. The mixture was slowly heated to reach reflux temperature, at this time the reaction mixture became dark brown and was refluxed until all the starting material was transformed (followed by TLC). The solution of the 1-phenyl-1,3-butadiyne obtained was cooled to room temperature and then a solution of dibutylselenide (0.680g; 2.5 mmol) in

95% ethanol (50 mL) was added. NaBH₄ (0.472g; 12.5 mmol) was added under vigorous stirring and gas evolution was observed during addition. The reaction mixture was stirred under reflux for 4h, allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3x30 mL) and water (3x30 mL). After drying the organic phase over anhydrous MgSO₄, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as the eluent. Yield: 0.841g (64%). ¹H NMR (CDCl₃, 400 MHz): δ 7.48-7.47 (m, 2H), 7.31-7.29 (m, 3H), 6.95 (d, *J* = 9.76 Hz, 1H), 6.12 (d, *J* = 9.76 Hz, 1H), 2.83 (t, *J* = 7.44 Hz, 2H), 1.74 (quint, *J* = 7.44 Hz, 2H), 1.44 (sex, *J* = 7.44 Hz, 2H), 0.93 (t, *J* = 7.44 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 136.90, 131.35, 128.23, 128.12, 123.34, 109.15, 96.77, 87.04, 33.07, 26.43, 22.73, 13.53. MS (relative intensity) *m/z*: 263 (100), 206 (31), 127 (76), 136 (71), 77 (34), 56 (31), 42 (13). HRMS calcd for C₁₄H₁₆Se: 264.0417. Found: 264.0422.

(Z)-1-(*n*-Butylseleno)-oct-1-en-3-yne (1o). The same procedure as for **1n** was followed. Yield: 0.802g (66%). ¹H NMR (CDCl₃, 400 MHz): δ 6.74 (d, *J* = 9.46 Hz, 1H), 5.90 (dt, *J* = 9.46, 2.17 Hz, 1H), 2.77 (t, *J* = 7.44 Hz, 2H), 2.37 (td, *J* = 2.17, 7.44 Hz, 2H), 1.72 (quint, *J* = 7.44 Hz, 2H), 1.58-1.38 (m, 6H), 0.94-0.91 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 134.33, 109.89, 98.23, 78.14, 33.08, 30.76, 26.04, 22.74, 21.90, 19.37, 13.58, 13.52. MS (relative intensity) *m/z*: 243 (100), 186 (52), 136 (58), 107 (79), 56 (35), 42 (21). HRMS calcd for C₁₂H₂₀Se: 244.0730. Found: 244.0724.

General Procedure for the Iodocyclizations. To a solution of 0.50 mmol of the appropriate (*Z*)-selenoenyne in 3 mL of CH₂Cl₂ was added gradually 1.1 equiv of I₂ or ICl dissolved in 7 mL of CH₂Cl₂. The reaction mixture was allowed to stir at room temperature for the desired time showed in Table 3. The excess I₂ or ICl was removed by washing with saturated aq Na₂S₂O₃. The mixture was then extracted by CH₂Cl₂ (3x10 mL). The combined organic layers were dried over anhydrous Mg₂SO₄ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. **2,5-diphenyl-3-iodoselenophene (2a).** Yield: 0.189 g (93%). ¹H NMR

(CDCl₃, 200 MHz): δ 7.62-7.30 (m, 11H). C¹³ NMR (CDCl₃, 100 MHz): δ 151.27, 146.01, 136.33, 134.97, 134.59, 129.27, 129.01, 128.41, 128.34, 128.19, 126.00, 80.23. MS (relative intensity) *m/z*: 409 (12), 283 (100), 206 (55), 129 (25), 126 (31), 77 (16). HRMS calcd for C₁₆H₁₁ISE: 409.9070. Found: 409.9074

2,5-Bis-(*p*-methylphenyl)-3-iodoselenophene (2c). Yield: 0.205g (94%). H¹ NMR (CDCl₃, 200 MHz): δ 7.51-7.39 (m, 5H), 7.25-7.16 (m, 4H), 2.39-2.36 (m, 6H). C¹³ NMR (CDCl₃, 50 MHz): δ 151.07, 145.56, 138.29, 138.16, 133.97, 133.51, 132.30, 129.67, 129.55, 129.13, 125.87, 79.90, 21.32, 21.20. MS (relative intensity) *m/z*: 437 (100), 311 (58), 220 (25), 126 (12), 129 (77), 91 (53). HRMS calcd for C₁₈H₁₅ISE: 437.9383. Found: 437.9388.

2,5-bis-(*n*-butyl)-3-iodoselenophene (2d). Yield: 0.166g (90%). H¹ NMR (CDCl₃, 200 MHz): δ 6.77 (s, 1H), 2.83-2.70 (m, 4H), 1.69-1.29 (m, 8H), 0.98-0.89 (m, 6H). C¹³ NMR (CDCl₃, 50 MHz): δ 151.36, 146.90, 79.63, 34.83, 34.18, 33.98, 32.15, 22.17, 22.07, 13.89, 13.79. MS (relative intensity) *m/z*: 369 (23), 243 (100), 228 (39), 214 (40), 200 (31), 186 (44), 129 (56), 126 (67), 57 (13), 43 (11). HRMS calcd for C₁₂H₁₉ISE: 369.9696. Found: 369.9701.

2,5-bis-(*n*-octyl)-3-iodoselenophene (2e). Yield: 0.212g (88%). H¹ NMR (CDCl₃, 200 MHz): δ 6.77 (s, 1H), 2.81-2.69 (m, 4H), 1.66-1.53 (m, 4H), 1.43-1.41 (m, 20H), 0.91-0.85 (m, 6H). C¹³ NMR (CDCl₃, 50 MHz): δ 151.44, 146.96, 133.40, 79.61, 35.12, 32.49, 32.11, 31.85, 31.84, 29.33, 29.32, 29.18, 29.17, 29.05, 29.04, 29.01, 22.65, 22.64, 14.10, 14.09. MS (relative intensity) *m/z*: 481 (26), 355 (100), 340 (37), 326 (41), 312 (29), 298 (54), 284 (32), 270 (39), 259 (28), 256 (53), 229 (43), 126 (75), 96 (34), 57 (18), 43 (13). HRMS calcd for C₂₀H₃₅ISE: 482.0948. Found: 482.0953.

2,5-bis-[(α -hydroxy- α,α -dimethyl)methyl]-3-iodoselenophene (2f). Yield: 0.080g (43%). H¹ NMR (CDCl₃, 200 MHz): δ 7.00 (s, 1H), 2.33 (s, 2H), 1.73 (s, 6H), 1.61 (s, 6H). C¹³ NMR (CDCl₃, 100 MHz): δ 159.59, 155.95, 134.53, 74.30, 72.44, 71.90, 32.07, 29.68. MS (relative intensity) *m/z*: 373 (100), 356 (73), 338

(55), 211 (23), 157 (39), 126 (14), 45 (11). HRMS calcd for C₁₀H₁₅IO₂Se: 373.9282. Found: 373.9286.

2-(*n*-butyl)-3-iodo-5-phenylselenophene (2g). Yield: 0.175g (90%). ¹H NMR (CDCl₃, 200 MHz): δ 7.56-7.51 (m, 2H), 7.43-7.33 (m, 3H), 6.98 (s, 1H), 2.85 (t, *J* = 7.06 Hz, 2H), 1.56 (quint, *J* = 7.06 Hz, 2H), 1.42 (sex, *J* = 7.06 Hz, 2H), 0.95 (t, *J* = 7.06, 3H). ¹³C NMR (CDCl₃, 50 MHz): δ 154.32, 144.16, 136.74, 135.76, 129.30, 128.23, 127.97, 78.54, 34.20, 32.13, 22.11, 13.79. MS (relative intensity) *m/z*: 389 (23), 263 (100), 206 (39), 129 (64), 77 (29), 57 (54), 43 (19). HRMS calcd for C₁₄H₁₅ISE: 389.9383. Found: 389.9387.

2-Phenyl-3-iodo-5-(α-hydroxy-α,α-dimethyl)methyl-3-iodoselenophene (2h). Yield: 0.111g (57%). ¹H NMR (CDCl₃, 200 MHz): δ 7.55-7.50 (m, 2H), 7.41-7.36 (m, 3H), 7.08 (s, 1H), 2.29 (s, 1H), 1.65 (s, 6H). ¹³C NMR (CDCl₃, 50 MHz): δ 163.04, 145.42, 136.55, 132.93, 129.25, 128.33, 128.17, 78.54, 72.71. MS (relative intensity) *m/z*: 391 (13), 374 (100), 332 (71), 265 (54), 205 (38), 129 (41), 77 (29), 58 (12), 43 (16). HRMS calcd for C₁₃H₁₃IOSe: 391.9176. Found: 391.9179.

2-phenyl-3-iodoselenophene (2i). Yield: 0.136g (82%). ¹H NMR (CDCl₃, 400 MHz): δ 7.90 (d, *J* = 5.74 Hz, 1H), 7.57-7.54 (m, 2H), 7.43-7.35 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 147.00, 139.19, 136.35, 131.99, 129.41, 128.35, 128.27, 79.68. MS (relative intensity) *m/z*: 333 (21), 205 (100), 129 (72), 126 (47), 77 (21). HRMS calcd for C₁₀H₇ISE: 333.8757. Found: 333.8761.

2-(*n*-butyl)-3-iodoselenophene (2j). Yield: 0.127g (81%). ¹H NMR (CDCl₃, 400 MHz): δ 7.75 (d, *J* = 5.74 Hz, 1H), 7.18 (d, *J* = 5.74 Hz, 1H), 2.95 (t, *J* = 7.06 Hz, 2H), 1.81 (quint, *J* = 7.06 Hz, 2H), 1.57 (sex, *J* = 7.06 Hz, 2H), 1.08 (t, *J* = 7.06, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 149.63, 137.21, 129.11, 80.85, 34.59, 32.09, 22.19, 13.87. MS (relative intensity) *m/z*: 185 (100), 128 (78), 115 (25), 56 (32), 42 (12). HRMS calcd for C₈H₁₁ISE: 313.9071. Found: 313.9076.

General Procedure for the PhSeBr and PhSeCl cyclizations. To a solution of (*Z*)-selenoenyne **1c** (0.169g; 0.5 mmol) in 3 mL of CH₂Cl₂ was added gradually 1.1 equiv of PhSeBr or PhSeCl dissolved in 7 mL of CH₂Cl₂. The reaction mixture was

allowed to stir at room temperature for the desired time showed in Table 3. The reaction mixture was washed with 40 mL of water and extracted with CH₂Cl₂ (3x10 mL). The combined organic layers were dried over anhydrous Mg₂SO₄ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using hexane as the eluent. **2,5-diphenyl-3-(selenophenyl)-selenophene (2b)**. Yield: 0.175g (80%). ¹H NMR (CDCl₃, 400 MHz): δ 7.56-7.54 (m, 2H), 7.49-7.47 (m, 2H), 7.40-7.19 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 149.44, 135.90, 135.52, 132.43, 131.03, 129.32, 129.24, 128.95, 128.33, 128.24, 128.13, 127.94, 127.86, 126.67, 126.05, 122.164. MS (relative intensity) *m/z*: 439 (100), 284 (46), 207 (58), 156 (75), 129 (37), 77 (21). HRMS calcd for C₂₂H₁₆Se₂: 439.9582. Found: 439.9585.

2,5-Diphenylselenophene (4a)⁴ by reaction of 2a with *n*-BuLi in hexane. To a two-neck round-bottomed flask, under argon, containing a solution of **2a** (0.102g; 0.25 mmol) in hexane (2 mL) at – 78 °C was added *n*-BuLi (0.08 mL of a 2.5 M solution in hexane, 0.20 mmol) in one portion. The reaction mixture was stirred for 10 minutes, and then water (2 mL) was added. The reaction mixture was diluted with hexane (20 mL) and washed with brine (3x20 mL). The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel using hexane as the eluent. Yield: 0.055g (97%). ¹H NMR (CDCl₃, 400 MHz): δ 7.59-7.57 (m, 4H), 7.46 (s, 2H), 7.40-7.36 (m, 4H), 7.31-7.26 (m, 2H). ¹³C NMR (CDCl₃, 50 MHz): δ 149.83, 136.33, 128.92, 127.60, 126.21, 126.06. MS (relative intensity) *m/z*: 283 (100), 205 (79), 128 (51), 115 (13), 77 (32). HRMS calcd for C₁₆H₁₂Se: 284.0104. Found: 284.0110.

General procedure for the reactions of intermediate 2,5-diphenyl-3-lithioselenophene (3) with aldehydes. To a two-neck round-bottomed flask, under argon, containing a solution of **2a** (0.102g; 0.25 mmol) in hexane (2 mL) at – 78 °C was added *n*-BuLi (0.08 mL of a 2.5 M solution in hexane, 0.20 mmol) in one portion. The reaction mixture was stirred for 10 minutes, and then a solution of

(⁴) Prediger, P.; Moro, A. V.; Nogueira, C. W.; Savegnago, L.; Rocha, J. B. T.; Zeni, G. *J. Org. Chem.* **2006**, *71*, 3786.

appropriated aldehyde (0.3 mmol) in hexane (1 mL) at -78 °C was added. The reaction mixture was allowed to stir at room temperature for 3 hours. After this time, the mixture was diluted with ethyl acetate (20 mL) and washed with saturated aq NH₄Cl (20 mL) and water (3x20 mL). The organic phase was separated, dried over MgSO₄, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. **(2,5-Diphenyl-selenophen-3-yl)-phenyl-methanol (4b)**. Yield: 0.064g (82%). ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.25 (m, 16H), 5.88 (s, 1H), 2.28 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 149.47, 145.97, 143.28, 142.38, 136.02, 135.31, 129.49, 128.84, 128.66, 128.42, 128.03, 127.69, 127.36, 126.15, 126.07, 125.92, 70.64. MS (relative intensity) *m/z*: 371 (100), 294 (15), 281 (21), 205 (52), 128 (34), 115 (21), 91 (42), 77 (23). HRMS calcd for C₂₃H₁₈OSe: 390.0523. Found: 390.0528.

(2,5-Diphenyl-selenophen-3-yl)-*p*-tolyl-methanol (4c). Yield: 0.069g (86%). ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.46 (m, 5H), 7.41-7.21 (m, 8H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 2.33 (m, 4H). ¹³C NMR (CDCl₃, 50 MHz): δ 149.35, 145.68, 142.56, 140.49, 136.99, 136.07, 135.36, 129.47, 129.10, 128.80, 128.60, 127.95, 127.63, 126.12, 126.05, 125.82, 70.55, 21.06. MS (relative intensity) *m/z*: 385 (100), 281 (32), 205 (44), 128 (62), 115 (17), 104 (23), 91 (29), 77 (21). HRMS calcd for C₂₄H₂₀OSe: 404.0679. Found: 404.0682.

(2,5-Diphenyl-selenophen-3-yl)-*o*-tolyl-methanol (4d). Yield: 0.070g (87%). ¹H NMR (CDCl₃, 200 MHz): δ 7.54-7.12 (m, 15H), 5.86 (s, 1H), 2.32 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 143.07, 141.52, 141.13, 136.03, 135.45, 135.34, 134.41, 130.47, 130.31, 129.28, 128.81, 128.69, 127.64, 127.06, 126.39, 126.24, 126.04, 125.08, 70.68, 19.03. MS (relative intensity) *m/z*: 385 (100), 281 (39), 205 (41), 128 (77), 115 (19), 104 (29), 91 (32), 77 (35). HRMS calcd for C₂₄H₂₀OSe: 404.0679. Found: 404.0684.

(2,5-Diphenyl-selenophen-3-yl)-(*p*-methoxy-phenyl)-methanol (4e). Yield: 0.059g (70%). ¹H NMR (CDCl₃, 200 MHz): δ 7.54-7.25 (m, 13H), 6.91-6.85 (m, 2H), 5.83 (s, 1H), 3.79 (s, 3H), 2.27 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 158.85, 149.37, 145.56, 142.61, 136.05, 135.54, 135.33, 129.45, 128.84, 128.62, 127.96,

127.67, 127.50, 126.05, 125.96, 113.80, 70.38, 55.24. MS (relative intensity) m/z : 401 (100), 370 (19), 281 (45), 205 (32), 128 (82), 120 (54), 77 (28). HRMS calcd for $C_{24}H_{20}O_2Se$: 420.0628. Found: 420.0633.

(2,5-Diphenyl-selenophen-3-yl)-(o-methoxy-phenyl)-methanol (4f). Yield: 0.057g (68%). H^1 NMR ($CDCl_3$, 200 MHz): δ 7.60-7.23 (m, 13H), 6.98-6.86 (m, 2H), 6.09 (s, 1H), 3.77 (s, 3H), 3.19 (s, 1H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 156.74, 148.85, 145.70, 140.94, 136.26, 135.73, 131.64, 129.37, 128.81, 128.73, 128.47, 128.43, 127.68, 127.53, 126.62, 126.04, 120.82, 110.56, 67.58, 55.29. MS (relative intensity) m/z : 401 (100), 370 (17), 281 (38), 205 (40), 128 (77), 120 (47), 77 (31). HRMS calcd for $C_{24}H_{20}O_2Se$: 420.0628. Found: 420.0631.

(2,5-Diphenyl-selenophen-3-yl)-(p-chloro-phenyl)-methanol (4g). Yield: 0.063g (74%). H^1 NMR ($CDCl_3$, 200 MHz): δ 7.51-7.22 (m, 15H), 5.83 (s, 1H), 2.42 (s, 1H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 149.79, 146.16, 143.27, 141.95, 135.83, 135.11, 133.06, 129.40, 128.87, 128.72, 128.49, 128.14, 127.54, 127.24, 126.02, 125.55, 73.94. MS (relative intensity) m/z : 369 (100), 356 (21), 281 (35), 205 (49), 128 (72), 124 (38), 115 (23), 77 (39). HRMS calcd for $C_{23}H_{17}ClOSe$: 424.0133. Found: 424.0140.

(2,5-Diphenyl-selenophen-3-yl)-(o-chloro-phenyl)-methanol (4h). Yield: 0.054g (64%). H^1 NMR ($CDCl_3$, 200 MHz): δ 7.56-7.17 (m, 15H), 6.07 (s, 1H), 2.47 (s, 1H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 149.17, 147.30, 140.79, 140.02, 136.02, 135.46, 132.68, 129.68, 129.29, 128.83, 128.72, 128.61, 127.98, 127.67, 127.43, 127.03, 126.04, 125.96, 68.39. MS (relative intensity) m/z : 369 (100), 356 (34), 281 (42), 205 (27), 128 (79), 124 (30), 115 (12), 77 (28). HRMS calcd for $C_{23}H_{17}ClOSe$: 424.0133. Found: 424.0139.

(2,5-Diphenyl-selenophen-3-yl)-cyclohexyl-methanol (4i). Yield: 0.053g (67%). H^1 NMR ($CDCl_3$, 200 MHz): δ 7.59-7.55 (m, 3H), 7.46-7.25 (m, 8H), 4.34 (d, J = 8.82 Hz, 1H), 2.15 (s, 1H), 1.86-0.63 (m, 11H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 149.39, 145.86, 142.56, 136.19, 135.58, 129.69, 128.89, 128.49, 127.76, 127.64, 126.05, 124.85, 73.77, 44.62, 29.66, 26.29, 25.87. MS (relative intensity) m/z : 377

(100), 281 (72), 205 (61), 128 (64), 96 (45), 82 (23), 77 (34). HRMS calcd for $C_{23}H_{24}OSe$: 396.0992. Found: 396.0998.

1-(2,5-Diphenyl-selenophen-3-yl)-heptan-1-ol (4j). Yield: 0.049g (62%). H^1 NMR ($CDCl_3$, 200 MHz): δ 7.64-7.55 (m, 3H), 7.46-7.26 (m, 8H), 4.72 (t, J = 7.48 Hz, 1H), 1.96-1.70 (m, 3H), 1.42-1.23(m, 8H), 0.91-0.82 (m, 3H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 149.55, 145.08, 143.67, 136.20, 135.51, 129.56, 128.89, 128.55, 127.81, 127.67, 126.06, 124.82, 69.16, 38.23, 31.71, 29.08, 25.94, 22.57, 14.03. MS (relative intensity) m/z : 379 (100), 364 (53), 350 (23), 336 (45), 322 (41), 281 (52), 205 (73), 128 (72), 98 (88), 77 (35). HRMS calcd for $C_{23}H_{26}OSe$: 398.1149. Found: 398.1151.

1-(2,5-Diphenyl-selenophen-3-yl)-decan-1-ol (4k). Yield: 0.062g (71%). H^1 NMR ($CDCl_3$, 200 MHz): δ 7.63 (s, 1H), 7.58-7.54 (m, 2H), 7.45-7.24 (m, 8H), 4.74-4.67 (m, 1H), 2.01-1.69 (m, 3H), 1.40-1.20 (m, 14H), 0.87 (t, J = 6.76 Hz, 3H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 149.51, 145.03, 143.67, 136.17, 135.49, 129.54, 128.87, 128.53, 127.78, 127.64, 126.02, 124.82, 69.12, 38.19, 31.85, 29.49, 29.48, 29.39, 29.26, 25.95, 22.63, 14.08. MS (relative intensity) m/z : 421 (100), 406 (29), 392 (32), 378 (39), 364 (41), 350 (36), 336 (26), 281 (63), 205 (77), 128 (65), 140 (86), 77 (31). HRMS calcd for $C_{26}H_{32}OSe$: 440.1618. Found: 440.1616.

General procedure for the palladium-catalyzed coupling reaction of 2a with alkynes. To a Schlenk tube, under argon, containing a solution of 2,5-diphenyl-3-iodoselenophene **2a** (0.204g; 0.50 mmol) in DMF (2.5 mL) was added to $Pd(PPh_3)_2Cl_2$ (0.035g, 0.05 mmol). The resulting solution was stirred for 5 minutes at room temperature. After this time appropriate alkyne (1.5 mmol) dissolved in 1 mL of Et_3N was then added dropwise, and the reaction mixture was allowed to stir at room temperature for 12 hours. After this the mixture was diluted with dichloromethane (20 mL), and washed with brine (3x20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. **4-(2,5-Diphenyl-selenophen-3-yl)-2-methyl-but-3-yn-2-ol (5a).** Yield: 0.166g (91%). H^1 NMR ($CDCl_3$, 400 MHz): δ 7.83-7.81 (m, 2H), 7.54-7.50 (m, 3H),

7.42-7.29 (m, 6H), 2.11 (s, 1H), 1.60 (s, 6H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 151.79, 147.42, 135.50, 135.41, 129.59, 128.95, 128.45, 128.12, 128.05, 127.97, 125.99, 119.94, 94.66, 79.44, 65.67, 31.20. MS (relative intensity) m/z : 347 (100), 305 (77), 281 (61), 128 (50), 77 (21). HRMS calcd for $C_{21}H_{18}OSe$: 366.0523. Found: 366.0529.

2,5-diphenyl-3-(phenylethynyl)-selenophene (5b). Yield: 0.180g (94%). H^1 NMR ($CDCl_3$, 400 MHz): δ 7.92-7.89 (m, 2H), 7.61 (s, 1H), 7.58-7.56 (m, 2H), 7.49-7.29 (m, 11H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 151.76, 147.47, 135.71, 135.50, 131.41, 129.61, 129.00, 128.59, 128.36, 128.16, 128.15, 128.14, 128.00, 126.08, 123.37, 120.57, 90.34, 86.86. MS (relative intensity) m/z : 383 (100), 306 (56), 282 (77), 204 (38), 128 (51), 101 (19), 77 (28). HRMS calcd for $C_{24}H_{16}Se$: 384.0417. Found: 384.0411.

General procedure for the copper-catalyzed coupling reaction of 2a with alcohols. To a Schlenk tube, under argon, containing a mixture of CuI (0.095 g; 0.05 mmol) in dry toluene (1.5 mL) was added 1,10-phen (0.018g, 0.1 mmol). The resulting solution was stirred for 30 minutes at room temperature. After this 2,5-diphenyl-3-iodoselenophene **2a** (0.204g; 0.50 mmol) was added and the resulting solution was stirred for additional 15 minutes at room temperature. After this time, Cs_2CO_3 (0.325g; 1.0 mmol) and appropriate alcohol (1.5 mmol) was added. The mixture was then heated at 110 °C for 12 hours. After this the solution was cooled to room temperature diluted with dichloromethane (20 mL), and washed with saturated aq NH_4Cl (3x20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. **2,5-Diphenyl-3-Butoxy-selenophene (6a).** Yield: 0.119g (67%). H^1 NMR ($CDCl_3$, 400 MHz): δ 7.73-7.71 (m, 2H), 7.57-7.26 (m, 9H), 4.08 (t, J = 7.44Hz, 2H), 1.79 (quint, J = 7.44Hz, 2H), 1.49 (sex, J = 7.44Hz, 2H), 0.96 (t, J = 7.44Hz, 3H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 153.69, 144.76, 136.04, 135.07, 128.89, 128.47, 127.78, 127.53, 126.36, 126.02, 125.42, 118.10, 71.69, 31.83, 19.24, 13.83. MS (relative intensity) m/z : 355 (100), 341 (39), 327 (27), 313 (25), 283 (60), 206 (52), 129 (28),

77 (11), 73 (9), 57 (16), 43 (17). HRMS calcd for $C_{20}H_{20}OSe$: 356.0679. Found: 356.0682.

2,5-diphenyl-3-Octyloxy-selenophene (6b). Yield: 0.131g (64%). H^1 NMR ($CDCl_3$, 400 MHz): δ 7.73-7.71 (m, 2H), 7.55-7.53 (m, 2H), 7.45 (s, 1H), 7.38-7.27 (m, 6H), 4.07 (t, $J = 7.44$ Hz, 2H), 1.63-1.53 (m, 2H), 1.38-1.18 (m, 10H), 0.89-0.87 (m, 3H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 153.69, 144.74, 136.04, 135.07, 128.89, 128.46, 127.77, 127.55, 126.36, 126.01, 125.41, 118.11, 72.01, 31.76, 29.74, 29.26, 29.20, 26.00, 22.64, 14.09. MS (relative intensity) m/z : 411 (100), 397 (19), 383 (21), 369 (23), 355 (29), 341 (18), 327 (16), 283 (52), 206 (33), 129 (61), 77 (30), 57 (21), 43 (12). HRMS calcd for $C_{24}H_{28}OSe$: 412.1305. Found: 412.1309.

SELECTED SPECTRA













































































