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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 CDCl₃ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl₃ 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 (¹³C NMR) were obtained at 100 MHz. Spectra were recorded in CDCl₃ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl₃. 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 Sonogashira Coupling Reaction 3a-r: To a Schlenk tube under argon atmosphere containing PdCl₂(PPh₃)₂ (1 mol%, 0.0035g) and Et₃N (2 mL), was added the appropriate 3-iodo-2-(methylthio)benzofuran 1a-c (0.5 mmol). To the resulting solution was added CuI (2 mol%, 0.0019g). The reaction was stirred for 15 minutes at room temperature. After this time, the appropriate terminal alkyne (1.25 mmol) dissolved in 1mL of Et₃N was then added dropwise, and the reaction mixture was stirred at room temperature. After this, the mixture was diluted with dichloromethane (20mL), and washed with brine (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 eluent.

2-(methylthio)-3-(phenylethynyl)benzofuran (3a): Yield: 0.130 g (99%). ¹H NMR: CDCl₃, 400 MHz, δ(ppm): 7.63-7.56 (m, 3H), 7.43-7.32 (m, 4H), 7.28-7.26 (m, 2H), 2.67 (s, 3H). ¹³C NMR: CDCl₃, 100 MHz, δ(ppm): 154.9, 131.5, 128.9, 128.3, 124.7, 123.4, 123.2, 119.6, 110.8, 104.8, 97.1, 79.0, 16.1. MS (EI, 70 eV) m/z (relative intensity): 264 (3), 261 (100), 246 (56), 218 (20), 202 (22), 149 (14).

3-((4-methoxyphenyl)ethynyl)-2-(methylthio)benzofuran (3c): Yield: 0.139 g (95%). ¹H NMR: CDCl₃, 400 MHz, δ(ppm): 7.63-7.61 (m, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.42-7.40 (m, 1H), 7.30-7.25 (m, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H), 2.66 (s, 3H). ¹³C NMR:

CDCl₃, 100 MHz, δ(ppm): 159.7, 155.0, 154.4, 132.9, 129.0, 124.7, 123.3, 119.7, 115.3, 113.9, 110.7, 105.3, 55.3, 16.2. MS (EI, 70 eV) m/z (relative intensity): 292 (20), 290 (100), 276 (23), 261 (5), 216 (2), 163 (3).

3-((2-methoxyphenyl)ethynyl)-2-(methylthio)benzofuran (3d): Yield: 0.124 g (85%). ¹H NMR: CDCl₃, 400 MHz, δ(ppm): 7.66-7.64 (m, 1H), 7.53 (dd, J = 5.8 Hz and J = 1.7 Hz, 1H), 7.41-7.39 (m, 1H), 7.31-7.24 (m, 3H), 6.96-6.86 (m, 2H), 3.91 (s, 3H), 2.69 (s, 3H).

³C NMR: CDCl₃, 100 MHz, δ(ppm): 159.8, 154.7, 134.0, 133.1, 129.7, 124.6, 123.3, 120.4, 119.7, 112.4, 110.6, 105.2, 93.5, 82.9, 81.0, 55.7, 16.1. MS (EI, 70 eV) m/z (relative intensity): 293 (6), 290 (100), 275 (48), 261 (45), 244 (19), 215 (23), 186 (16).

2-methyl-4-(2-(methylthio)benzofuran-3-yl)but-3-yn-2-ol (3e): Yield: 0.114 g (93%). ¹H NMR: (CDCl₃, 400 MHz) δ(ppm): 7.52-7.49 (m, 1H), 7.38-7.36 (m, 1H), 7.25-7.20 (m, 2H), 2.76 (s, 1H), 2.60 (s, 3H), 1.68 (s, 6H). ³C NMR: (CDCl₃, 100 MHz), δ(ppm): 154.8, 154.7, 128.8, 124.5, 123.2, 119.3, 110.6, 104.1, 101.8, 71.8, 65.7, 31.5, 15.9. MS (EI, 70 eV) m/z (relative intensity): 246 (2), 243 (89), 228 (55), 186 (17), 143 (28), 42 (100). HRMS Calcd. for C₁₄H₁₄O₂S: 246.0715. Found: 246.0717.

3-methyl-1-(2-(methylthio)benzofuran-3-yl)pent-1-yn-3-ol (3f): Yield: 0.104 g (80%). ¹H NMR: (CDCl₃, 200 MHz) δ(ppm): 7.54-7.49 (m, 1H), 7.42-7.37 (m, 1H), 7.29-7.20 (m, 2H), 2.62 (s, 3H), 2.33 (s, 1H), 1.83 (quartet, J = 7.6 Hz, 2H), 1.63 (s, 3H), 1.17 (t, J = 7.4 Hz, 3H). ³C NMR: (CDCl₃, 50 MHz), δ(ppm): 154.9, 154.8, 128.9, 124.6, 123.3, 119.4, 110.7, 104.2, 100.7, 73.1, 69.4, 36.6, 29.4, 15.9, 9.1. MS (EI, 70 eV) m/z (relative intensity): 259 (7), 242 (3), 228 (78), 115 (7), 114 (21), 43 (100).

3-(2-(methylthio)benzofuran-3-yl)prop-2-yn-1-ol (3g): Yield: 0.095 g (88%). ¹H NMR: (CDCl₃, 200 MHz) δ(ppm): 7.54-7.52 (m, 1H), 7.40-7.38 (m, 1H), 4.60 (s, 2H), 2.62 (s, 3H), 2.23 (s, 1H). ³C NMR: (CDCl₃, 50 MHz), δ(ppm): 155.3, 154.9, 128.8, 124.7, 123.4, 119.5, 110.7, 104.1, 95.2, 75.4, 51.7, 16.1. MS (EI, 70 eV) m/z (relative intensity): 215 (100), 200 (2), 169 (73), 146 (13), 114 (59).

1-((2-(methylthio)benzofuran-3-yl)ethynyl)cyclohexanol (3h): Yield: 0.122 g (86%). ¹H NMR: (CDCl₃, 400 MHz) δ(ppm): 7.53-7.50 (m, 1H), 7.40-7.38 (m, 1H), 2.62 (s, 3H), 2.33 (s, 1H), 2.10-2.0 (m, 2H), 1.70-1.59 (m, 7H), 1.34-1.25 (m, 1H). ³C NMR: (CDCl₃, 100 MHz), δ(ppm): 154.9, 153.8, 125.8, 124.6, 123.3, 119.5, 110.7, 104.3, 100.8, 74.1, 69.4, 40.1, 25.2, 23.5, 16.0. MS (EI, 70 eV) m/z (relative intensity): 282 (100), 267 (13), 236 (61), 185 (34), 163 (12), 143 (26).

2-(methylthio)-3-(3-(p-tolyloxy)prop-1-ynyl)benzofuran (3k): Yield: 0.129 g (84%). ¹H NMR: (CDCl₃, 400 MHz) δ(ppm): 7.47-7.45 (m, 1H), 7.38-7.36 (m, 1H), 7.26-7.20 (m, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 4.96 (s, 2H), 2.58 (s, 3H), 2.29 (s, 3H). ³C NMR: (CDCl₃, 100 MHz), δ(ppm): 155.8, 155.6, 154.8, 130.7, 129.9, 129.8, 124.7, 123.4, 119.6, 115.0, 114.7, 110.7, 103.8, 92.1, 56.9, 20.5, 16.0. MS (EI, 70 eV) m/z (relative intensity): 304 (16), 230 (14), 198 (100), 166 (16).
3-(hex-1-ynyl)-2-(methylthio)benzofuran (3l): Yield: 0.108 g (89%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.54-7.51 (m, 1H), 7.40-7.36 (m, 1H), 7.27-7.21 (m, 2H), 2.60 (s, 3H), 2.52 (t, J = 6.8 Hz, 2H), 1.64 (quint, J = 7.0 Hz, 2H), 1.53 (sext, J = 7.0 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 154.9, 153.6, 129.3, 124.5, 123.1, 119.6, 110.7, 105.9, 98.4, 69.9, 30.8, 21.9, 19.5, 16.3, 13.6. MS (EI, 70 eV) m/z (relative intensity): 241 (100), 226 (32), 198 (38), 185 (15), 166 (25), 126 (19), 113 (36).

3-(3,3-dimethylbut-1-ynyl)-2-(methylthio)benzofuran (3m): Yield: 0.091 g (75%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.52-7.50 (m, 1H), 7.39-7.34 (m, 1H), 7.26-7.21 (m, 2H), 2.62 (s, 3H), 1.37 (s, 9H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 154.8, 153.6, 129.3, 124.5, 123.0, 119.5, 110.6, 106.7, 105.6, 68.3, 31.0, 28.4, 16.1. MS (EI, 70 eV) m/z (relative intensity): 244 (2), 241 (100), 226 (89), 211 (26), 179 (20), 151 (20).

3-(cyclohexenylethynyl)-2-(methylthio)benzofuran (3n): Yield: 0.060 g (45%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.56-7.52 (m, 1H), 7.41-7.37 (m, 1H), 7.28-7.21 (m, 2H), 6.27 (m, 1H), 2.62 (s, 3H), 2.30-2.26 (m, 2H), 2.19-2.14 (m, 2H), 1.73-1.60 (m, 4H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 154.9, 154.0, 135.2, 129.0, 124.6, 123.2, 120.7, 119.6, 110.7, 105.5, 99.0, 76.1, 29.2, 25.7, 22.3, 21.5, 16.2. MS (EI, 70 eV) m/z (relative intensity): 266 (34), 265 (100), 250 (13), 237 (14), 217 (14), 163 (11), 150 (10).

5-methyl-2-(methylthio)-3-(phenylethynyl)benzofuran (3o): Yield: 0.104 g (75%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.59-7.57 (m, 2H), 7.40-7.27 (m, 5H), 7.09-7.06 (m, 1H), 2.65 (s, 3H), 2.45 (s, 3H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 154.8, 153.5, 133.0, 131.4, 128.9, 128.3, 128.2, 125.9, 119.4, 110.3, 96.9, 79.2, 21.2, 16.1. MS (EI, 70 eV) m/z (relative intensity): 274 (100), 260 (70), 231 (16), 216 (16), 199 (11), 137 (10).

5-fluoro-2-(methylthio)-3-(phenylethynyl)benzofuran (3p): Yield: 0.101 g (72%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.57-7.55 (m, 2H), 7.35-7.33 (m, 3H), 7.32-7.25 (m, 2H), 6.97 (td, J = 6.4 Hz and J = 3.0 Hz, 1H), 2.67 (s, 3H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 160.8, 158.4, 156.9, 151.1, 131.4, 128.5, 128.3, 122.9, 122.1 (d, J = 26.3 Hz), 111.4 (d, J = 9.5 Hz), 105.3 (d, J = 25.6 Hz), 97.4, 78.3, 15.7. MS (EI, 70 eV) m/z (relative intensity): 280 (26), 278 (100), 264 (84), 236 (28), 220 (39), 191 (23), 139 (9).

4-(5-fluoro-2-(methylthio)benzofuran-3-yl)-2-methylbut-3-yn-2-ol (3q): Yield: 0.105 g (80%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.30 (dd, J = 5.0 Hz and J = 4.0 Hz, 1H), 7.15 (dd, J = 5.0 Hz and J = 3.0 Hz, 1H), 6.95 (td, J = 6.4 Hz and J = 3.0 Hz, 1H), 2.69 (s, 1H), 2.62 (s, 3H), 1.67 (s, 6H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 160.7, 158.3, 156.7, 150.7, 129.9, 112.0 (d, J = 26.3 Hz), 111.4 (d, J = 9.5 Hz), 105.1 (d, J = 25.6 Hz), 103.7 (d, J = 3.6 Hz), 102.2, 71.2, 65.7, 31.4, 15.6. MS (EI, 70 eV) m/z (relative intensity): 261 (79), 246 (59), 203 (13), 188 (18), 161 (22), 131 (16), 42 (100).

3-(phenylethynyl)-2-(phenylselanyl)benzofuran (3s): Yield: 0.093 g (50%). ¹H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.72-7.68 (m, 1H), 7.62-7.52 (m, 4H), 7.48-7.14 (m, 9H). ¹³C NMR: (CDCl₃, 100 MHz), δ (ppm): 156.5, 132.5, 131.7, 131.6, 131.5, 129.3, 128.5, 128.4, 128.3, 127.8, 125.5, 123.4, 120.2, 112.0, 111.3, 79.3. MS (EI, 70 eV) m/z (relative intensity): 372 (14), 294 (100), 265 (27), 189 (15).
3-(2-(phenylselanyl)benzofuran-3-yl)prop-2-yn-1-ol (3t):
Yield: 0.065 g (40%). 
$^1$H NMR: (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.61-7.59 (m, 1H), 7.54-7.52 (m, 2H), 7.42-7.40 (m, 1H), 7.29-7.24 (m, 5H), 4.53 (s, 2H), 2.05 (s, 1H). 
$^{13}$C NMR: (CDCl$_3$, 100 MHz), $\delta$ (ppm): 156.4, 148.1, 132.6, 129.4, 128.7, 128.5, 127.8, 125.5, 123.4, 120.1, 111.3, 111.0, 94.9, 75.8, 51.7. MS (EI, 70 eV) $m/z$ (relative intensity): 326 (100), 310 (95), 267 (67), 199 (78), 155 (25), 113 (64).

4-(2-(phenylselanyl)benzofuran-3-yl)but-3-yn-1-ol (3u):
Yield: 0.093 g (55%). 
$^1$H NMR: (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.61-7.58 (m, 1H), 7.52-7.50 (m, 2H), 7.43-7.41 (m, 1H), 7.27-7.22 (m, 5H), 3.80 (t, $J = 6.1$ Hz, 2H), 2.74 (t, $J = 6.1$ Hz, 2H), 2.07 (s, 1H). 
$^{13}$C NMR: (CDCl$_3$, 100 MHz), $\delta$ (ppm): 156.4, 147.4, 132.0, 129.3, 129.0, 128.9, 128.5, 127.7, 125.5, 123.3, 120.1, 112.2, 111.3, 94.2, 72.6, 61.0, 24.1. MS (EI, 70 eV) $m/z$ (relative intensity): 340 (18), 262 (100), 231 (96), 202 (72), 156 (9), 126 (23).

2-methyl-4-(2-(phenylselanyl)benzofuran-3-yl)but-3-yn-2-ol (3v):
Yield: 0.080 g (45%). 
$^1$H NMR: (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.56-7.53 (m, 3H), 7.41-7.34 (m, 1H), 7.28-7.22 (m, 5H), 2.05 (s, 1H), 1.61 (s, 6H). 
$^{13}$C NMR: (CDCl$_3$, 100 MHz), $\delta$ (ppm): 156.5, 148.1, 132.6, 129.3, 129.0, 128.6, 128.5, 125.4, 123.3, 120.0, 111.3, 101.8, 72.5, 65.8, 31.4. MS (EI, 70 eV) $m/z$ (relative intensity): 355 (23), 337 (4), 297 (17), 276 (31), 218 (100), 189 (34).

General Procedure for the Retro-Favorskii Reaction 4a:
Powered NaOH (0.120 g, 3 mmol) was added to a two-neck round bottomed flask equipped with a reflux condenser, containing a solution of 2-methyl-4-(2-(methylthio)benzofuran-3-yl)but-3-yn-2-ol 3e (0.246 g, 1.0 mmol) in 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 for 12 hours. After this, the mixture was diluted with dichloromethane (20mL), 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 eluent.

3-ethynyl-2-(methylthio)benzofuran (4a):
Yield: 0.133 g (71%). 
$^1$H NMR: (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.57-7.53 (m, 1H), 7.43-7.38 (m, 1H), 7.29-7.24 (m, 2H), 3.52 (s, 1H), 2.64 (s, 3H). 
$^{13}$C NMR: (CDCl$_3$, 100 MHz), $\delta$ (ppm): 156.2, 154.8, 128.9, 124.7, 123.5, 119.5, 110.8, 103.7, 85.0, 73.7, 16.0. MS (EI, 70 eV) $m/z$ (relative intensity): 188 (2), 185 (100), 171 (84), 143 (62), 127 (15), 100 (17).

General Procedure for the Preparation of (Z)-vinylic telluride 5a:
To a solution of the 3-ethynylbenzofuran 4a (0.188 g, 1 mmol) in THF (5 mL) and the dibutyl ditelluride (0.184 g, 0.5 mmol) in ethanol (10 mL) at room temperature under argon was added in small portions sodium borohydride (0.095 g, 2.5 mmol). Toward the end of the addition when the red color of the solution had disappeared, the mixture was refluxed for 12 h. After this, the mixture was diluted with ethyl acetate (20mL) 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 eluent.

(Z)-3-(2-(butyltellanyl)vinyl)-2-(methylthio)benzofuran (5a): Yield: 0.223 g (60%). ^1H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.50-7.47 (m, 1H), 7.42-7.39 (m, 1H), 7.34 (d, J = 10 Hz, 1H), 7.28 (d, J = 10 Hz, 1H), 7.27-7.19 (m, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.54 (s, 3H), 1.78 (quint, J = 7.4 Hz, 2H), 1.37 (sext, J = 7.3 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^13C NMR: (CDCl₃, 100 MHz), δ (ppm): 155.3, 146.9, 127.7, 127.5, 124.5, 122.6, 121.7, 119.9, 110.7, 110.3, 99.9, 33.9, 24.9, 17.2, 13.3, 8.1. MS (EI, 70 eV) m/z (relative intensity): 371 (42), 315 (25), 300 (22), 268 (21), 186 (43), 172 (100), 143 (30), 113 (23).

General Procedure for the Preparation of Diyne 5b: In a two-neck round bottomed flask under oxygen atmosphere containing CuCl (0.0049 g, 5 mol%), acetone and TMEDA (5 mol%) was added the 3-ethynyl-2-(methylthio)benzofuran 4a (0.188 g, 1 mmol) dropwise. The mixture was heated to 45 °C for 4 hours until the complete evaporation of acetone. After this, the mixture was diluted with dichloromethane (20mL), and washed with brine (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 eluent.

1,4-bis(2-(methylthio)benzofuran-3-yl)buta-1,3-diyne (5b): Yield: 0.280 g (75%). ^1H NMR: (CDCl₃, 400 MHz) δ (ppm): 7.62-7.59 (m, 1H), 7.43-7.39 (m, 1H), 7.30-7.26 (m, 2H), 2.69 (s, 3H). ^13C NMR: (CDCl₃, 100 MHz), δ (ppm): 158.2, 154.8, 128.8, 124.8, 123.7, 119.7, 110.8, 103.0, 81.5, 73.2, 15.9. MS (EI, 70 eV) m/z (relative intensity): 374 (2), 369 (100), 355 (43), 340 (11), 323 (15).
SELECTED SPECTRA