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Supporting Information to the paper:

Microwave-Assisted Group-Transfer Cyclisation of Organotellurium Compounds

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Experimental Section

General: All NMR experiments were conducted on a 400 MHz spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) in CDCl_3 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl_3 . J values are given in Hz using the following abbreviations: s (singlet), br s (broad singlet), t (triplet), q (quartet) and m (multiplet). Infrared spectra were recorded on a FTIR spectrometer. M^+ ions are given for ^{80}Se and ^{130}Te . Except for the microwave-assisted reactions, all experiments were carried out in a dry Ar-atmosphere. The stereochemistry of the products was determined by gNOESY-experiments.

β -Hydroxyalkyl phenyl chalcogenides and β -allyloxyalkyl phenyl chalcogenides were prepared as described in (compounds **1c**, **1g**, **2c**, **5**, **6**), or, in analogy with (compounds **1a-b**, **1d-f**, **2a-b**, **2d-f**) literature.¹ For yields see Table 1.

Spectroscopic data for 2-hydroxycyclohexyl phenyl telluride (**1b**),² 2-hydroxy-1-phenylethyl phenyl selenide,³ *cis*-3-[[4-(trifluoromethyl)-phenyltelluro]methyl]octahydrobenzofuran (**3c**),¹ 3-[(phenyltelluro)methyl]cyclopentanol (**4**)¹ and 3-methyl-4-phenyltetrahydrofuran (**8**)¹ were in good agreement with the literature.

***trans*-2-Hydroxycyclohexyl 4-methoxyphenyl telluride (1a):** ^1H NMR (CDCl_3) δ 1.16-1.35 (several peaks, 3H), 1.41-1.56 (several peaks, 2H), 1.76 (m, 1H), 2.13 (m, 1H), 2.26 (m, 1H), 2.64 (d, $J = 2.3$, 1H), 2.98 (dd, $J = 3.9$, 10.2, 12.4, 1H), 3.35 (ddt, $J = 2.2$, 4.5, 10.2, 1H), 3.80 (s, 3H), 6.77 (m, 2H), 7.72 (m, 2H). ^{13}C NMR (CDCl_3) δ 24.8, 27.8, 34.1,

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35.0, 39.4, 55.1, 73.3, 98.5, 115.1, 143.0, 160.1. IR (neat): ν 3367, 2930, 2853, 1586, 1488, 1246 cm^{-1} . HRMS: calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Te}$, 336.0369, found 336.0320.

2-Hydroxy-3-phenylpropyl phenyl telluride (1d): ^1H NMR (CDCl_3) δ 2.20 (d, J = 4.1, 1H), 2.87 (dd, J = 7.4, 13.5, 1H), 2.94 (dd, J = 5.3, 13.5, 1H), 3.05 (dd, J = 7.6, 12.2, 1H), 3.18 (dd, J = 4.5, 12.2, 1H), 4.02 (m, 1H), 7.16-7.35 (several peaks, 8H), 7.74 (m, 2H). ^{13}C NMR (CDCl_3) δ 18.7, 44.2, 72.3, 111.4, 126.6, 127.8, 128.6, 129.3, 129.4, 137.9, 138.4. IR (neat): ν 3401, 3062, 3025, 2926, 1574, 1434, 1078, 1018 cm^{-1} . HRMS: calcd for $\text{C}_{15}\text{H}_{16}\text{OTe}$, 342.0263, found 342.0223.

2-Hydroxy-3-phenylpropyl 4-(trifluoromethyl)phenyl telluride (1e): ^1H NMR (CDCl_3) δ 2.24 (br s, 1H), 2.89 (dd, J = 7.3, 13.5, 1H), 2.95 (dd, J = 5.5, 13.5, 1H), 3.12 (dd, J = 7.6, 12.3, 1H), 3.23 (dd, J = 4.4, 12.3, 1H), 4.07 (m, 1H), 7.17-7.38 (several peaks, 5H), 7.43 (m, 2H), 7.79 (m, 2H). ^{13}C NMR (CDCl_3) δ 18.6, 44.5, 72.4, 117.3, 124.0 (q, J = 272.3), 125.7 (q, J = 3.8), 126.8, 128.7, 129.3, 129.7 (q, J = 32.7), 137.5, 137.6. IR (neat): ν 3401, 3028, 2920, 1599, 1394, 1326, 1125, 1074, 1012 cm^{-1} . HRMS: calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{OTe}$, 410.0137, found 410.0109.

2-Hydroxy-3-phenoxypropyl phenyl telluride (1f): ^1H NMR (CDCl_3) δ 2.91 (br s, 1H), 3.22 (d, J = 6.2, 2H), 4.02 (dd, J = 6.2, 9.4, 1H), 4.07 (dd, J = 4.1, 9.4, 1H), 4.21 (dq, J = 4.1, 6.2, 1H), 6.88 (m, 2H), 6.99 (tt, J = 1.3, 7.4, 1H), 7.22 (tm, J = 7.4, 2H), 7.26-7.33 (several peaks, 3H), 7.79 (m, 2H). ^{13}C NMR (CDCl_3) δ 13.7, 70.1, 71.5, 111.4, 114.5,

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121.2, 127.8, 129.3, 129.4, 138.7, 158.3. IR (neat): ν 3400, 3064, 2928, 1599, 1496, 1244 cm^{-1} . HRMS: calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Te}$, 358.0213, found 358.0182.

***trans*-2-Allyloxycyclohexyl 4-methoxyphenyl telluride (2a):** ^1H NMR (CDCl_3) δ 1.08-1.34 (several peaks, 3H), 1.44-1.60 (several peaks, 2H), 1.69-1.91 (several peaks, 2H), 2.12 (m, 1H), 3.38 (m, 1H), 3.51 (m, 1H), 3.80 (s, 3H), 3.94 (ddm, $J = 5.6, 12.6$, 1H), 4.13 (ddm, $J = 5.6, 12.6$, 1H), 5.17 (dm, $J = 10.4$, 1H), 5.29 (dm, $J = 17.2$, 1H), 5.94 (m, 1H), 6.74 (m, 2H), 7.73 (m, 2H). ^{13}C NMR (CDCl_3) δ 24.1, 27.5, 31.7, 32.3, 33.7, 55.1, 69.7, 82.7, 100.4, 114.8, 116.7, 135.1, 143.1, 159.8. IR (neat): ν 3077, 2931, 2854, 1586, 1488, 1245 cm^{-1} . HRMS: calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2\text{Te}$, 376.0682, found 376.0651.

***trans*-2-Allyloxycyclohexyl phenyl telluride (2b):** ^1H NMR (CDCl_3) δ 1.14-1.37 (several peaks, 3H), 1.47-1.64 (several peaks, 2H), 1.80 (m, 1H), 1.94 (m, 1H), 2.14 (m, 1H), 3.44 (m, 1H), 3.61 (m, 1H), 3.96 (ddm, $J = 5.6, 12.6$, 1H), 4.14 (ddm, $J = 5.6, 12.6$, 1H), 5.18 (dm, $J = 10.4$, 1H), 5.31 (dm, $J = 17.2$, 1H), 5.95 (m, 1H), 7.21 (m, 2H), 7.32 (m, 1H), 7.85 (m, 2H). ^{13}C NMR (CDCl_3) δ 23.8, 27.3, 31.9, 32.0, 33.6, 69.5, 82.4, 111.1, 116.5, 127.6, 128.7, 134.9, 140.7. IR (neat): ν 3065, 2931, 2854, 1434, 1093 cm^{-1} . HRMS: calcd for $\text{C}_{15}\text{H}_{20}\text{OTe}$, 346.0576, found 346.0547.

2-Allyloxy-3-phenylpropyl phenyl telluride (2d): ^1H NMR (CDCl_3) δ 2.95 (dd, $J = 6.4, 13.6$, 1H), 3.03 (dd, $J = 6.1, 13.6$, 1H), 3.12 (dd, $J = 5.9, 12.0$, 1H), 3.15 (dd, $J = 5.7, 12.0$, 1H), 3.83 (dddd, $J = 5.7, 5.9, 6.1, 6.4$, 1H), 3.97 (dddd, $J = 1.3, 1.5, 5.6, 12.6$, 1H), 4.04 (dddd, $J = 1.3, 1.5, 5.6, 12.6$, 1H), 5.17 (dm, $J = 10.3$, 1H), 5.24 (dm, $J = 17.1$, 1H),

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5.87 (m, 1H), 7.17-7.35 (several peaks, 8H), 7.74 (m, 2H). ^{13}C NMR (CDCl_3) δ 14.5, 41.6, 70.4, 80.2, 112.0, 116.8, 126.2, 127.4, 128.2, 129.0, 129.4, 134.7, 138.1, 138.1. IR (neat): ν 3064, 2931, 2855, 1434, 1080 cm^{-1} . HRMS: calcd for $\text{C}_{18}\text{H}_{20}\text{OTe}$, 382.0576, found 382.0581.

2-Allyloxy-3-phenylpropyl 4-(trifluoromethyl)phenyl telluride (2e): ^1H NMR (CDCl_3) δ 2.86 (dd, $J = 7.1, 13.6$, 1H), 3.04 (dd, $J = 5.7, 13.6$, 1H), 3.09 (dd, $J = 6.3, 12.0$, 1H), 3.16 (dd, $J = 5.1, 12.0$, 1H), 3.82 (m, 1H), 4.00 (dm, $J = 5.6$, 2H), 5.15 (tdd, $J = 1.3, 1.8, 10.3$, 1H), 5.21 (qd, $J = 1.7, 17.2$, 1H), 5.84 (tdd, $J = 5.6, 10.3, 17.2$, 1H), 7.18 (m, 2H), 7.22-7.31 (several peaks, 3H), 7.37 (m, 2H), 7.71 (m, 2H). ^{13}C NMR (CDCl_3) δ 15.1, 41.8, 70.6, 80.1, 117.1, 118.0, 124.4 (q, $J = 271.9$), 125.5 (q, $J = 3.8$), 126.5, 128.5, 129.4 (q, $J = 32.5$), 129.5, 134.5, 137.3, 137.9. IR (neat): ν 3028, 2921, 1326, 1125, 1074 cm^{-1} . HRMS: calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{OTe}$, 450.0450, found 450.0455.

2-Allyloxy-3-phenoxypropyl phenyl telluride (2f): ^1H NMR (CDCl_3) δ 3.28 (dd, $J = 5.9, 12.2$, 1H), 3.34 (dd, $J = 6.2, 12.2$, 1H), 4.04 (m, 1H), 4.13 (dd, $J = 5.1, 9.7$, 1H), 4.18 (dd, $J = 5.2, 9.7$, 1H), 4.18 (m, 2H), 5.23 (tdd, $J = 1.2, 1.8, 10.4$, 1H), 5.32 (qd, $J = 1.6, 17.2$, 1H), 5.96 (m, 1H), 6.94 (m, 2H), 7.01 (m, 1H), 7.22 (m, 2H), 7.28-7.37 (several peaks, 3H), 7.80 (m, 2H). ^{13}C NMR (CDCl_3) δ 11.3, 70.0, 71.0, 77.3, 112.0, 114.4, 117.2, 120.9, 127.5, 129.1, 129.3, 134.5, 128.2, 158.4. IR (neat): ν 3065, 2926, 2867, 1495, 1244, 1079 cm^{-1} . HRMS: calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Te}$, 398.0526, found 398.0472.

General procedure for group-transfer cyclisation.

The organochalcogen compound (0.5 mmol) was suspended in 2 mL of solvent and heated in the microwave oven (for solvent, temperature and reaction time see Tables 2 and 3, eqn 2 and Scheme 1). The reaction mixture was extracted with Et₂O, washed with water and dried over MgSO₄. The crude product was then purified by flash chromatography (pentane + 3-10 % EtOAc). For yields, *endo/exo* and *cis/trans*-ratios see Tables 2 and 3, eqn 2 and Scheme 1.

***cis*-3-[[4-Methoxyphenyl]telluro]methyl]octahydrobenzofuran (3a):** ¹H NMR (CDCl₃) *exo*-3a δ 1.05-1.96 (several peaks, 9H), 2.23 (m, 1H), 2.77 (dd, *J* = 8.4, 11.7, 1H), 2.96 (dd, *J* = 7.2, 11.7, 1H), 3.44 (dd, *J* = 5.0, 9.0, 1H), 3.80 (s, 3H), 3.95 (m, 1H), 4.13 (dd, *J* = 7.6, 9.0, 1H), 6.76 (m, 2H), 7.68 (m, 2H). ¹H NMR (CDCl₃) *endo*-3a δ 1.05-1.96 (several peaks, 9H), 2.65 (m, 1H), 2.74 (dd, *J* = 7.6, 11.4, 1H), 2.84 (dd, *J* = 8.3, 11.4, 1H), 3.48 (dd, *J* = 8.0, 9.8, 1H), 3.80 (s, 3H), 3.95 (m, 1H), 3.98 (t, *J* = 8.5, 1H), 6.76 (m, 2H), 7.69 (m, 2H). ¹³C NMR (CDCl₃) *exo+endo* δ 5.7, 13.4, 20.4, 21.0, 21.6, 23.6, 24.3, 27.4, 28.3, 28.6, 41.6, 45.5, 45.7, 45.8, 55.1, 72.0, 73.9, 76.3, 78.3, 100.0, 115.2, 141.2, 141.3, 159.8. IR (neat): ν 2928, 2855, 1245, 1028 cm⁻¹. HRMS: calcd for C₁₆H₂₂O₂Te, 376.0682, found 376.0612.

***cis*-3-[(Phenyltelluro)methyl]octahydrobenzofuran (3b):** ¹H NMR (CDCl₃) *exo*-3b δ 1.04-2.01 (several peaks, 9H), 2.29 (m, 1H), 2.86 (m, 1H), 3.06 (dd, *J* = 7.2, 11.7, 1H), 3.48 (dd, *J* = 5.1, 9.0, 1H), 3.98 (m, 1H), 4.17 (dd, *J* = 7.8, 9.0, 1H), 7.22 (m, 2H), 7.30 (m, 1H), 7.75 (m, 2H). ¹H NMR (CDCl₃) *endo*-3b δ 1.04-2.01 (several peaks, 9H), 2.71

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(m, 1H), 2.86 (dd, $J = 8.4, 11.5$, 1H), 2.93 (dd, $J = 8.4, 11.5$, 1H), 3.53 (dd, $J = 8.2, 10.0$, 1H), 3.98 (m, 1H), 4.01 (t, $J = 8.8$, 1H), 7.22 (m, 2H), 7.30 (m, 1H), 7.75 (m, 2H). ^{13}C NMR (CDCl_3) *exo+endo* δ 5.4, 13.1, 20.3, 20.9, 21.5, 23.5, 24.2, 27.3, 28.2, 28.5, 41.5, 45.4, 45.7, 45.8, 72.0, 73.9, 76.2, 78.3, 111.2, 127.7, 127.7, 129.2, 138.6, 138.6. IR (neat): ν 3065, 2927, 2855, 1019 cm^{-1} . HRMS: calcd for $\text{C}_{15}\text{H}_{20}\text{OTe}$, 346.0576, found 346.0565.

2-Benzyl-4-[(phenyltelluro)methyl]tetrahydrofuran (3d): ^1H NMR (CDCl_3) *trans*-**3d** δ 1.73 (ddd, $J = 5.7, 7.0, 12.6$, 1H), 1.86 (ddd, $J = 6.9, 8.4, 12.6$, 1H), 2.57 (m, 1H), 2.73 (dd, $J = 6.5, 13.6$, 1H), 2.86-3.01 (several peaks, 3H), 3.43 (dd, $J = 6.7, 8.7$, 1H), 4.07 (dd, $J = 6.8, 8.7$, 1H), 4.25 (m, 1H), 7.18-7.26 (several peaks, 5H), 7.27-7.34 (several peaks, 3H), 7.74 (m, 2H). ^1H NMR (CDCl_3) *cis*-**3d** δ 1.32 (td, $J = 9.1, 12.3$, 1H), 2.17 (ddd, $J = 5.8, 7.3, 12.3$, 1H), 2.57 (m, 1H), 2.79 (dd, $J = 6.5, 13.6$, 1H), 2.86-3.01 (several peaks, 3H), 3.55 (dd, $J = 7.0, 8.6$, 1H), 3.92 (dd, $J = 7.4, 8.6$, 1H), 4.12 (dtd, $J = 5.9, 6.3, 9.3$, 1H), 7.18-7.26 (several peaks, 5H), 7.27-7.34 (several peaks, 3H), 7.74 (m, 2H). ^{13}C NMR (CDCl_3) *trans+cis* δ 12.1, 12.3, 39.3, 40.5, 41.3, 42.1, 74.3, 74.6, 79.5, 80.8, 111.2, 126.2, 127.8, 128.3, 129.2, 129.2, 138.5, 138.7. IR (neat): ν 3063, 2927, 2857, 1062, 1018 cm^{-1} . HRMS: calcd for $\text{C}_{18}\text{H}_{20}\text{OTe}$, 382.0576, found 382.0541.

2-Benzyl-4-[[4-(trifluoromethyl)phenyltelluro]methyl]tetrahydrofuran (3e): ^1H NMR (CDCl_3) *trans*-**3e** δ 1.74 (ddd, $J = 5.6, 7.1, 12.7$, 1H), 1.89 (ddd, $J = 6.9, 8.3, 12.7$, 1H), 2.59 (m, 1H), 2.75 (dd, $J = 6.4, 13.6$, 1H), 2.91 (dd, $J = 6.5, 13.6$, 1H), 2.96 (dd, $J = 7.6, 11.8$, 1H), 3.04 (dd, $J = 7.3, 11.8$, 1H), 3.45 (dd, $J = 6.5, 8.8$, 1H), 4.08 (dd, $J = 6.6$,

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8.8, 1H), 4.28 (m, 1H), 7.19-7.27 (several peaks, 3H), 7.27-7.34 (several peaks, 2H), 7.45 (m, 2H), 7.79 (m, 2H). ^1H NMR (CDCl_3) *cis*-**3e** δ 1.33 (ddd, $J = 8.7, 9.3, 12.3$, 1H), 2.18 (ddd, $J = 5.9, 7.5, 12.3$, 1H), 2.59 (m, 1H), 2.81 (dd, $J = 6.4, 13.6$, 1H), 2.97 (dd, $J = 6.7, 13.6$, 1H), 2.98 (dd, $J = 7.1, 11.8$, 1H), 3.01 (dd, $J = 7.5, 11.8$, 1H), 3.58 (dd, $J = 6.7, 8.6$, 1H), 3.93 (dd, $J = 7.3, 8.6$, 1H), 4.14 (dtd, $J = 5.9, 6.3, 9.2$, 1H), 7.19-7.27 (several peaks, 3H), 7.27-7.34 (several peaks, 2H), 7.45 (m, 2H), 7.80 (m, 2H). ^{13}C NMR (CDCl_3) *trans*+*cis* δ 12.6, 12.9, 39.3, 40.4, 40.4, 41.2, 41.9, 42.0, 74.2, 74.5, 79.5, 80.8, 116.8, 116.9, 124.0 (q, $J = 272.0$), 125.7 (q, $J = 3.6$), 126.3, 128.3, 129.2, 129.8 (q, $J = 32.7$), 137.8, 138.4, 138.4. IR (neat): ν 3028, 2929, 2858, 1598, 1326, 1166, 1124, 1074, 1012 cm^{-1} . HRMS: calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{OTe}$, 450.0450, found 450.0467.

2-Phenoxymethyl-4-[(phenyltelluro)methyl]tetrahydrofuran (3f): ^1H NMR (CDCl_3) *trans*-**3f** δ 1.88 (ddd, $J = 6.4, 7.8, 12.8$, 1H), 2.08 (ddd, $J = 6.1, 8.1, 12.8$, 1H), 2.68 (m, 1H), 2.97 (dd, $J = 7.5, 11.9$, 1H), 3.03 (dd, $J = 7.4, 11.9$, 1H), 3.54 (dd, $J = 6.7, 8.7$, 1H), 3.93 (dd, $J = 4.7, 9.8$, 1H), 3.96 (dd, $J = 5.5, 9.8$, 1H), 4.12 (dd, $J = 6.6, 8.7$, 1H), 4.44 (tdd, $J = 5.2, 5.5, 7.7$, 1H), 6.89-7.00 (several peaks, 3H), 7.21-7.35 (several peaks, 5H), 7.78 (m, 2H). ^1H NMR (CDCl_3) *cis*-**3f** δ 1.55 (td, $J = 8.2, 12.4$, 1H), 2.33 (ddd, $J = 6.9, 7.4, 12.4$, 1H), 2.68 (m, 1H), 3.01 (dd, $J = 7.3, 11.8$, 1H), 3.06 (dd, $J = 7.6, 11.8$, 1H), 3.62 (dd, $J = 7.3, 8.7$, 1H), 3.99-4.04 (several peaks, 3H), 4.34 (tdd, $J = 5.0, 6.7, 8.8$, 1H), 6.89-7.00 (several peaks, 3H), 7.21-7.35 (several peaks, 5H), 7.78 (m, 2H). ^{13}C NMR (CDCl_3) *trans*+*cis* δ 11.4, 11.5, 36.6, 37.1, 40.6, 41.3, 70.2, 70.2, 74.6, 74.9, 76.8, 77.9, 111.2, 114.5, 114.5, 120.8, 127.8, 129.3, 129.3, 138.7, 158.7. IR (neat): ν 3064, 2925,

2866, 1575, 1496, 1173, 1018 cm^{-1} . HRMS: calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Te}$, 398.0526, found 398.0509.

3-Phenyl-4-[(phenylseleno)methyl]tetrahydrofuran (7): ^1H NMR (CDCl_3) *trans*-7 δ 2.66 (m, 1H), 2.90 (dd, $J = 9.0, 12.0$, 1H), 3.14 (m, 1H), 3.14 (dd, $J = 5.2, 12.0$, 1H), 3.70 (dd, $J = 7.7, 8.9$, 1H), 3.82 (dd, $J = 8.3, 8.7$, 1H), 4.23 (m, 1H), 4.25 (m, 1H), 7.18-7.30 (several peaks, 6H), 7.33 (m, 2H), 7.40 (m, 2H). ^{13}C NMR (CDCl_3) *trans*-7 δ 29.8, 48.3, 52.3, 74.1, 75.4, 126.8, 127.0, 127.6, 128.7, 129.0, 129.9, 132.6, 140.7. ^1H NMR (CDCl_3) *cis*-7 δ 2.43 (dd, $J = 9.3, 12.2$, 1H), 2.61 (dd, $J = 6.1, 12.2$, 1H), 2.83 (m, 1H), 3.51 (m, 1H), 3.72 (t, $J = 8.4$, 1H), 4.13 (dd, $J = 7.6, 8.6$, 1H), 4.17 (dd, $J = 4.0, 8.8$, 1H), 4.20 (dd, $J = 6.1, 8.8$, 1H), 7.23-7.30 (several peaks, 6H), 7.35 (m, 2H), 7.41 (m, 2H). ^{13}C NMR (CDCl_3) *cis*-7 δ 27.0, 44.2, 48.5, 72.2, 73.9, 126.8, 127.0, 128.5, 128.5, 129.0, 127.7, 132.8, 139.5. IR (neat):v 3028, 2929, 2859, 1478, 1053 cm^{-1} . HRMS: calcd for $\text{C}_{17}\text{H}_{18}\text{OSe}$, 318.0523, found 318.0493.

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