ELECTROTELLURATION: A New Approach to Tri- and Tetra-substituted Alkenes

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SUPPORTING INFORMATION

A. General remarks

All needles and syringes are oven-dried and cooled down to room temperature in the desiccator prior used. All reactions are carried out under a nitrogen (or argon) atmosphere to avoid air oxidation of the tellurolate anion to ditelluride. Unless indicated otherwise, all starting materials are used as received. *n*-Butyl lithium, *t*-butyl lithium, phenyl lithium, and both phenylmagnesium bromide and vinylmagnesium bromide

(Aldrich) came as a 2.5M solution in hexanes, 1.7M solution in pentane, 1.8M solution in cyclohexane-ether, 1.0M solution in THF respectively and titrated prior to use.¹ Tetrahydrofuran was dried over 4 Å molecular sieves and distilled over Na/Benzophenone. Benzaldehyde (Fisher) was distilled *via* a Kugelrohr (room temperature, 0.4 torr) and used immediately. Butyraldehyde (Aldrich) was distilled *via* a short-path distillation and stored in a dark glass bottle. Silica gel, 40 Microns, was purchased from Scientific Absorbents Incorporated. TLC monitoring is best using Hex:EtAc solvent system. The vinylic tellurides are detected using UV, iodine, and vanillin solution (27 mL H₂O, 6 mL concentrated H₂SO₄, 27 mL MeOH and 1.2 g vanillin).

Infrared spectra (IR) were recorded on a Perkin-Elmer 1600 series FT-IR Spectrophotometer with internal calibration. Spectra were recorded either from neat oil between sodium chloride salt plates, or from a potassium bromide pellet. IR data are reported in wavenumber (cm⁻¹).

Proton nuclear magnetic resonance spectra (¹H NMR) were obtained either on a 300, 400, or 500 MHz Varian FT NMR spectrometers. Spectra were recorded in deuteriochloroform (CDCl₃) with residual proteo form as an internal reference or tetramethylsilane (TMS) as the external reference. Data are reported as followed: chemical shift (δ) in ppm (multiplicity, integrated intensity, and coupling constant (J) in Hertz (Hz)). Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet), and br (broad).

Two-dimensional correlated off resonance spectroscopy (COSY) and difference nuclear Overhauser effect (NOE) experiments were performed on the 400 and 500 MHz Varian FT NMR spectrometers using automated programs.

Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either on the 75, 100 or 125 MHz Varian FT NMR spectrometers. Spectra were recorded in deuteriochloroform with 77.0 ppm resonance of deuteriochloroform as the internal reference.

High resolution mass spectra (HRMS) were determined on a VG 70-250S instrument by the University of Michigan, Department of Chemistry Instrument Services Branch. Sample introduction was *via* direct probe, and ionization was accomplished by electron impact (EI) at 70 eV, by chemical ionization (CI) with methane or ammonia, or by fast atom bombardment (FAB) with sodium. Masses were reported in units of mass over charge (m/z) to four decimal places in conjunction with the relative intensity normalized to 100.

B. Deuteration experiments

To a solution of phenyl acetylene (0.11 mL, 1 mmol, 1 equiv) and dibutylditelluride (185 mg, 0.5 mmol, 0.5 equiv) in ethanol (2 mL) was added NaBH_4 (95 mg, 2.5 mmol, 2.5 equiv) at room temperature under a nitrogen atmosphere. Sizzling occurred immediately upon addition of sodium borohydride and the red solution became light yellow within 5 minutes. TLC indicated that hydrotelluration of the diyne had not taken place. After the sizzling subsided, the reaction was refluxed for one hour. The reaction was cooled down to room temperature, diluted with ethyl acetate, washed with brine and dried over MgSO_4 . Solvents were removed and the resulting oil was subjected

to column chromatography (Hex) on silica gel (92% yield). A yield of 92% was obtained when phenyl acetylene (1 equiv) dibutylditelluride (0.5 equiv), sodium deuteroborohydride (2.5 equiv) and ethanol were used.

(Z)-(2-Butyltellanyl-vinyl)-benzene (5): isolated by column chromatography using hexanes on silica gel; 92% yield, a yellow oil; TLC (Hex) $R_f = 0.21$; ^1H NMR (500 MHz, CDCl_3 and TMS) δ 7.45 (d, 1H, $J = 10.7$ Hz), 7.41 (d, 2H, $J = 7.5$ Hz), 7.33-7.27 (m, 3H), 7.05 (d, 1H, $J = 10.7$ Hz), 2.77 (t, 2H, $J = 7.3$ Hz), 1.86 (quint, 2H, $J = 7.3$ Hz), 1.44 (sext, 2H, $J = 7.3$ Hz), 0.97 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 139.216, 137.0, 128.6, 127.8, 127.5, 105.6, 34.2, 25.2, 13.7, 9.3; IR (neat) cm^{-1} 3055, 3020, 2957, 2926, 2870, 1598, 1491, 1462, 1443, 1330, 1185, 1167, 770, 698; HRMS (EI, 70 eV) for $\text{C}_{12}\text{H}_{16}\text{Te}$ [M^+] calcd. 290.0314, found 290.0316; m/z (rel int) 104 (100), 232 (11.1), 290 (30.6).

(Z)-(2-Butyltellanyl-1-deuterio-vinyl)-benzene (4) and (Z)-(2-Butyltellanyl-1,2-dideuterio-vinyl)-benzene (3): isolated by column chromatography using hexanes on silica gel; 93% yield, a yellow oil; TLC (Hex) $R_f = 0.26$; ^1H NMR (500 MHz, CDCl_3 and TMS) δ 7.40-7.36 (m, 2H), 7.30-7.24 (m, 3H), 7.01 (s, monodeuteration product), 2.76 (t, 2H, $J = 7.3$ Hz), 1.84 (quint, 2H, $J = 7.3$ Hz), 1.44 (sext, 2H, $J = 7.3$ Hz), 0.95 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 139.1, 136.9, 128.6, 127.8, 127.5, 105.4, 34.2, 25.2, 13.7, 9.2; IR (neat) cm^{-1} 3054, 3021, 2957, 2926, 2870, 1598, 1577,

1558, 1489, 1441, 1036, 1020, 773, 694; HRMS (EI, 70 eV) for $C_{12}H_{14}D_2Te$ [M^+] calcd. 292.0440, found 292.0441; m/z (rel int) 106 (100), 234 (13.0), 292 (28.1).

General procedure for H-D exchange reaction

In a NMR tube equipped with a small magnetic stir bar was added the alkyne (ca. 30 mg, 1 equiv), $EtOH-d_6$ (0.6 mL) and $NaBH_4$ (1 equiv). The reaction was stirred at rt and the disappearance of the alkynyl hydrogen was monitored after one hour and twelve hours. The ratio of the non-deuterated alkyne and deuterated alkyne was determined from the integration.

Deuterioethynyl-benzene (2): 1H NMR (500 MHz, $EtOH-d_6$, after 12 hours) δ 7.65-7.63 (m, 32H), 7.56-7.50 (m, 50H), 3.31 (alkynyl hydrogen, s, 1H).

1-Deuterio-hex-1-yne (6): 1H NMR (400 MHz, $EtOH-d_6$, after 12 hours) δ 2.19 (t, 21H, $J = 6.6$ Hz), 1.76-1.63 (m, 44H), 2.11 (alkynyl hydrogen, t, 1H, $J = 2.6$ Hz), 1.16 (t, 34H, $J = 7.3$ Hz).

1-Deuterioethynyl-cyclohexene (7): 1H NMR (400 MHz, $EtOH-d_6$, after 12 hours) δ 6.34 (m, 13H), 2.91 (alkynyl hydrogen, s, 1H), 2.38-2.30 (m, 64H), 1.91-1.80 (m, 63H).

tert-Butyl-(5-deuterio-3-methyl-pent-2-en-4-ynyloxy)-dimethyl-silane (8): 1H NMR (400 MHz, $EtOH-d_6$, after 12 hours) δ 6.13-6.09 (m, 17H), 4.46 (dd, 41H, $J = 6.2, 1.1$ Hz), 3.30 (alkynyl hydrogen, s, 1H), 1.95 (m, 56H), 1.14 (s, 189H), 0.28 (s, 135H).

C. A sample procedure for the electrotelluration reaction

A 50-mL, three-necked, round-bottomed flask was equipped with a magnetic stir bar, two rubber septa for transferring liquid materials, venting and monitoring purposes, and a glass adapter for a nitrogen inlet. This reaction flask was flame-dried twice under a positive nitrogen stream and cooled down to room temperature. Elemental tellurium

(Aldrich, 255 mg, 2.00 mmol, 1 equiv) was weighed and transferred quickly to the reaction flask followed by freshly distilled THF (Fisher, 5 mL). *n*-Butyl lithium (Aldrich, 0.8 mL of a 2.5 M solution in hexanes, 2 mmol, 1 equiv) was added dropwise to a vigorously stirred Te/THF mixture at room temperature under a nitrogen atmosphere. After stirring for 30 minutes, the Te powder was completely consumed and the deep red lithium *n*-butyl tellurolate solution was cooled down to $-20\text{ }^{\circ}\text{C}$. In a separate flame dried flask, a mixture of freshly distilled benzaldehyde (Fisher, 0.20 mL, 2 mmol, 1 equiv) and methyl propiolate (Aldrich, 0.15 mL, 2 mmol, 1 equiv) in 2 mL of THF was prepared, and stored under nitrogen. The mixture of electrophile and alkyne was cannulated (or syringed dropwise) to the lithium *n*-butyl tellurolate solution. The trapping experiment usually completed in less than 30 minutes according to TLC. After the reaction was complete, the reaction mixture was quenched with 8 mL of a saturated ammonium chloride solution at $-10\text{ }^{\circ}\text{C}$ and warmed to room temperature. The product was extracted several times with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Column chromatography (90:10 Hex:EtAc) of the crude orange oil on silica gel afforded a light yellow oil (0.397 g, 1.06 mmol, 71%).

(Z)-3-Butyltellanyl-2-(hydroxy-phenyl-methyl)-acrylic acid methyl ester (9): isolated by column chromatography using 90:10 Hex:EtAc on silica gel; 71% yield, a yellow oil; TLC (80:20 Hex:EtAc) $R_f = 0.44$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 8.41 (d, 1H, $J = 0.8\text{ Hz}$), 7.27-7.36 (m, 5H), 5.64 (dd, 1H, $J = 5.2, 0.8\text{ Hz}$), 3.74 (s, 3H), 2.57 (d, 1H, 5.2

Hz), 2.55 (t, 2H, $J = 7.7$ Hz), 1.78 (m, 2H), 1.38 (sext, 2H, $J = 7.4, 7.1$ Hz), 0.91 ppm (t, 3H, $J = 7.1$ Hz); D₂O shake yields the following changes in ¹H NMR (300 MHz, CDCl₃ and TMS) δ 5.63 ppm (d, 1H, $J = 0.8$ Hz) and the doublet at 2.57 ppm disappears; ¹³C NMR (100 MHz, CDCl₃ and TMS) δ : 167.6, 141.8, 135.9, 133.3, 128.4, 127.7, 126.5, 74.8, 52.0, 33.8, 24.9, 13.4, 10.0; IR (neat) cm⁻¹ 3449 (br), 3025, 2955, 1685, 1558, 1440, 1287, 1201, 1016, 820, 758, 697; HRMS (EI, 70 eV) for C₁₅H₂₀O₃Te [M⁺] calcd. 378.0474, found 378.0478; m/z (rel int) 378 (52.6), 321 (95.6), 159 (100), 142 (93.9), 105 (95.7), 77 (89.8), 57 (61.4).

(Z)-2-Butyltellanylmethylene-3-hydroxy-hexanoic acid methyl ester (10): isolated by column chromatography using 95:05 Hex:EtAc on silica gel; 46% yield, a yellow oil; TLC (80:20 Hex:EtAc) $R_f = 0.58$; ¹H NMR (300 MHz, CDCl₃ and TMS) δ 8.35 (d, 1H, $J = 0.5$ Hz), 4.52 (m, 1H), 3.83 (s, 3H), 2.57 (t, 2H, $J = 7.7$ Hz), 2.16 (d, 1H, $J = 6$ Hz), 1.87-1.76 (m, 2H), 1.67-1.59 (m, 2H), 1.49-1.36 (m, 4H), 0.94 (t, 3H, $J = 7.4$ Hz), 0.93 (t, 3H, $J = 7.4$ Hz); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 167.9, 137.1, 131.7, 73.0, 52.0, 38.9, 34.0, 25.0, 19.1, 13.9, 13.5, 9.9; IR (neat) cm⁻¹ 3437 (br), 2952, 2924, 2868, 1680, 1560, 1433, 1286, 1202, 998, 850, 730; HRMS (EI, 70 eV) for C₁₂H₂₂O₃Te [M⁺] calcd. 344.0631, found 344.0638; m/z (rel int) 344 (81.7), 301 (43.4), 287 (100), 269 (68.3), 213 (18.7), 185 (11.7), 125 (30.0).

(*E/Z*)-3-Butyltellanyl-2-(hydroxy-diphenyl-methyl)-acrylic acid methyl ester (11):

isolated by column chromatography using gradient hexanes, then 95:05 Hex:EtAc on silica gel to isolate the (*E*)- and (*Z*)-isomers.

(*Z*)-3-Butyltellanyl-2-(hydroxy-diphenyl-methyl)-acrylic acid methyl ester: 30%

yield, a light yellow viscous oil; TLC (90:10 Hex:EtAc) $R_f = 0.52$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.59 (s, 1H), 7.30-7.24 (m, 10H), 4.63 (s, 1H), 3.65 (s, 3H), 2.26 (t, 2H, $J = 7.4$ Hz), 1.56 (sext, 2H, $J = 7.4$ Hz), 1.22 (quint, 2H, $J = 7.4$ Hz), 0.80 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 167.8, 145.1, 139.0, 136.5, 127.8, 127.2, 127.1, 82.7, 51.8, 33.4, 24.5, 13.2, 9.9; NOE (400 MHz, CDCl_3 and TMS) the vinylic and methoxy hydrogens enhanced 0.3 and 1.6% respectively when the hydroxy hydrogen was irradiated.

(*E*)-3-Butyltellanyl-2-(hydroxy-diphenyl-methyl)-acrylic acid methyl ester: 13%

yield, a yellow oil; TLC (90:10 Hex:EtAc) $R_f = 0.44$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.33 (m, 10H), 5.98 (s, 1H), 3.69 (s, 3H), 3.34 (s, 1H), 2.48 (t, 2H, $J = 7.4$ Hz), 1.34 (m, 2H), 1.15 (quint, 2H, $J = 7.4$ Hz), 0.74 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 167.1, 144.2, 128.1, 127.7, 127.5, 125.4, 85.7, 51.6, 32.6, 24.7, 13.2, 10.7 (only 12 carbons are accounted); NOE (400 MHz, CDCl_3 and TMS) the hydrogen alpha to the tellurium atom enhanced 1.3% when the hydroxy hydrogen was irradiated.

(*E/Z*)-2-(Hydroxy-phenyl-methyl)-3-phenyltellanyl-acrylic acid methyl ester (12):

isolated by column chromatography using gradient 95:05, 90:10 Hex:EtAc on silica gel; attempt to purified the title compound by Kugelrohr distillation resulted in isomerization

from the *Z*-olefin to its more stable *E*-olefin; 84% combined yield (*Z*:*E* ratio is 13:1), a viscous yellow oil; TLC (90:10 Hex:EtAc) R_f = 0.24. TLC (85:15 Hex:EtAc) showed two isomers with R_f = 0.33 (*Z*) and R_f = 0.41 (*E*).

(*Z*)-2-(Hydroxy-phenyl-methyl)-3-phenyltellanyl-acrylic acid methyl ester (12A): ^1H NMR (300 MHz, CDCl_3 and TMS) δ 8.49 (d, 1H, J = 1.1 Hz), 7.73-7.71 (m, 2H), 7.27-7.25 (m, 4H), 7.23-7.18 (m, 4H), 5.56 (dd, 1H, J = 5.1, 1.1 Hz), 3.68 (s, 3H), 2.43 ppm (d, 1H, J = 5.1 Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 167.8, 141.8, 137.9, 137.1, 135.3, 129.4, 128.4, 128.2, 127.8, 126.5, 120.4, 74.8, 52.3; NOE (400 MHz, CDCl_3 and TMS) the carbinol and hydroxy hydrogens enhanced 1.3 and 0.6% respectively when the vinyl hydrogen was irradiated; IR (neat) cm^{-1} 3416 (br), 3064, 3030, 2950, 1675, 1560, 1434, 1288, 1203, 1019, 910, 828, 733, 697; HRMS (EI, 70 eV) for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Te}$ [M^+] calcd. 398.0161, found 398.0159; m/z (rel int) 398 (49.4), 207 (22.6), 159 (54.0), 105 (100), 77 (80.9), 51 (23.7).

(*E*)-2-(Hydroxy-phenyl-methyl)-3-phenyltellanyl-acrylic acid methyl ester (12B): ^1H NMR (300 MHz, CDCl_3 and TMS) δ 8.70 (d, 1H, J = 0.8 Hz), 7.85-7.82 (m, 2H), 7.55-7.52 (m, 2H), 7.39-7.27 (m, 6H), 5.75 (distorted d, 1H, J = 4.1 Hz), 3.63 (s, 3H), 2.76 (d, 1H, J = 4.4 Hz); NOE (400 MHz, CDCl_3 and TMS) none of the ^1H NMR peak enhanced when the vinyl hydrogen was irradiated.

(*E*)-3-Butyltellanyl-2-trimethylsilanyl-acrylic acid methyl ester (13): isolated by column chromatography using hexanes on silica gel; 45% yield, a light yellow oil; TLC (95:05 Hex:EtAc) R_f = 0.79; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 8.84 (s, 1H), 3.81

(s, 3H), 2.59 (t, 2H, $J = 7.7$ Hz), 1.82 (quint, 2H, $J = 7.7$ Hz), 1.44 (s, 2H, $J = 7.3$ Hz), 0.94 (t, 3H, $J = 7.3$ Hz), 0.17 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 171.4, 147.4, 138.4, 51.8, 33.9, 25.0, 13.5, 10.0, -1.0; IR (neat) cm^{-1} 2952, 2924, 2860, 1729, 1673, 1504, 1272, 1202, 1033, 977, 843; HRMS (EI, 70 eV) for $\text{C}_{11}\text{H}_{22}\text{O}_2\text{SiTe}$ [M^+] calcd. 344.0451, found 344.0463; m/z (rel int) 344 (34.1), 287 (100), 89 (53.0).

(Z)-2-Benzenesulfonyl-3-butyltellanyl-1-phenyl-but-2-en-1-ol (14): isolated by column chromatography using 90:10 Hex:EtAc on silica gel; 69% yield, a viscous yellow oil; TLC (90:10 Hex:EtAc) $R_f = 0.13$; ^1H NMR (400 MHz, CDCl_3 and TMS) δ 7.90 (d, 2H, $J = 7.7$ Hz), 7.57 (t, 1H, $J = 7.3$ Hz), 7.43 (t, 2H, $J = 7.7$ Hz), 7.20 (distorted br s, 4H), 5.96 (s, 1H), 3.24 (br s, 1H), 2.67 (t, 2H, $J = 7.7$ Hz), 2.31 (s, 3H), 1.69 (quint, 2H, $J = 8.1, 7.3$ Hz), 1.39 (sext, 2H, $J = 7.3, 7.7$ Hz), 0.92 (t, 1H, $J = 7.3$ Hz); D_2O addition yields the following change in ^1H NMR (300 MHz, CDCl_3 and TMS) the singlet at 3.24 ppm disappears; ^{13}C NMR (100 MHz, CDCl_3 and TMS, only 14 carbons are accounted for) δ 142.8, 140.7, 133.3, 128.9, 128.3, 127.4, 127.1, 125.5, 71.2, 32.6, 25.4, 25.2, 13.5, 9.4; ^{13}C NMR (100 MHz, CD_3CN , all 16 carbons are accounted for) δ 144.1, 143.6, 142.1, 141.6, 134.8, 130.4, 129.2, 128.4, 127.9, 126.5, 71.0, 33.9, 26.3, 25.9, 13.9, 9.6; IR (neat) cm^{-1} 3495 (br), 3061, 2956, 2921, 2865, 1590, 1549, 1443, 1290, 1143, 1079, 1017, 953, 841, 736; HRMS (EI, 70 eV) for [M^+] calcd. 474.0508, found 474.0503; m/z (rel int) 474 (9.7), 417 (2.5), 372 (5.6), 314 (3.8), 287 (23.4), 258 (5.5), 209 (7.2), 181 (11.6), 145 (100).

(Z)-3-Benzenesulfonyl-2-butyrtellanyl-hept-2-en-4-ol (15): isolated by column chromatography using gradient 95:05, then 90:10 Hex:EtAc on silica gel gave three products: (A) the proton trapped product confirmed by ^1H NMR ($R_f = 0.28$, 21% yield); (B) $R_f = 0.22$ (8% yield) and (C) the desired butyraldehyde trapped ($R_f = 0.17$, 60% yield).

(Z)-2-Butyrtellurium-3-phenylsulfone-4-hydroxy-2-heptene (15C): 60% yield, a viscous yellow oil; $R_f = 0.17$ (90:10 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 8.08-8.05 (m, 2H), 7.62-7.58 (m, 1H), 7.52-7.48 (m, 2H), 4.76 (dd, 1H, $J = 9.5, 4.4$ Hz), 2.80-2.60 (m, 2H), 2.48 (s, 3H), 1.96-1.86 (m, 1H), 1.70-1.62 (quint, 2H, $J = 7.7$ Hz), 1.58-1.21 (m, 6H), 0.91 (t, 3H, $J = 7.3$ Hz), 0.85 (t, 3H, $J = 7.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 141.4, 141.0, 138.6, 133.2, 128.7, 127.4, 71.4, 39.1, 32.7, 25.1, 24.7, 19.4, 13.6, 13.4, 9.1; NOE (400 MHz, CDCl_3 and TMS) the carbinol hydrogens and the hydrogens alpha to the tellurium enhanced 1.3% and 1.2% respectively when the methyl hydrogens were irradiated; IR (neat) cm^{-1} 3513 (br), 3064, 2958, 2929, 2871; overtone or combination bands: 1965, 1899, 1812, 1772, 1717, 1683; 1551, 1463, 1446, 1286, 1149, 1129, 1078, 912, 732, 721, 687; HRMS (EI, 70 eV) for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{STe}$ [M^+] calcd. 440.0665, found 440.0658; m/z (rel int) 439 (49.0), 382 (42.9), 253 (25.7), 207 (34.4), 125 (76.7), 93 (65.2), 57 (100).

3-Benzenesulfonyl-2-butyltellanyl-hept-1-en-4-ol (15B): 8% yield, a viscous yellow oil; $R_f = 0.22$ (90:10 Hex:EtAc) ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.91-7.88 (m, 2H), 7.68-7.63 (m, 1H), 7.57-7.28 (m, 2H), 5.90 (s, 1H), 5.51 (s, 1H), 4.61-4.54 (distorted tt, 1H, $J = 8.5, 2.2$), 3.97 (distorted s, 1H), 3.70 (d, 1H, $J = 9.0$ Hz), 2.75-2.59 (m, 2H), 1.74-1.29 (m, 8H), 0.97-0.88 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 137.4, 134.0, 130.9, 129.3, 128.8, 116.1, 80.3, 70.1, 36.2, 32.8, 25.1, 18.1, 13.8, 13.3, 9.4; APT (100 MHz, CDCl_3 and TMS) showed 137.4 (quaternary), 134.0 (methine), 130.9 (quaternary), 129.3 (methine), 128.8 (methine), 116.1 (quaternary), 80.3 (methine), 70.1 (methine), 36.2 (methylene), 32.8 (methylene), 25.1 (methylene), 18.1 (methylene), 13.8 (methyl), 13.3 (methyl), 9.4 (methylene). APT confirmed the proposed structure; COSY (400 MHz, CDCl_3 and TMS) showed carbinol proton at 4.61-4.54 (distorted tt, 1H, $J = 8.5, 2.2$), OH at 3.97 (distorted s, 1H), proton next to the sulfone at 3.70 (d, 1H, $J = 9.0$ Hz); HRMS (EI, 70 eV) for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{STe}$ [M^+] calcd. 440.0665, found 440.0661; m/z (rel int) 440 (35.9), 369 (11.6), 315 (21.0), 181 (86.6), 141 (53.1), 111 (57.3), 71 (100).

(Z)-2-Benzenesulfinyl-3-butyltellanyl-1-phenyl-but-2-en-1-ol (16): isolated by column chromatography using 80:20 Hex:EtAc on silica gel to afford a mixture of diastereomers (namely **A** and **B**) in 65% combined yield having Z-configuration exclusively according to NOE experiment.

Diastereomer 16A: a viscous yellow oil; TLC (80:20 Hex:EtAc) $R_f = 0.32$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.67-7.64 (m, 2H), 7.43-7.40 (m, 3H), 7.33-7.31 (m, 2H),

7.22-7.18 (m, 2H), 7.15-7.13 (m, 2H), 5.75 (d, 1H, $J = 4.4$ Hz), 2.93-2.79 (m, 2H), 2.69-2.68 (d, 1H, $J = 5.1$ Hz), 2.33 (s, 3H), 1.83-1.75 (m, 2H), 1.47-1.38 (sext, 2H, $J = 7.3$ Hz), $J = 0.94$ (t, 3H, $J = 7.3$ Hz); NOE (400 MHz, CDCl_3 and TMS) the carbinol hydrogen, the hydroxy hydrogen and the hydrogens alpha to the tellurium atom enhanced 0.69, 0.15 and 10.9% respectively when the methyl hydrogens were irradiated; ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 147.5, 142.6, 141.6, 133.6, 130.5, 129.1, 127.9, 126.6, 125.5, 124.0, 68.7, 33.7, 25.1, 24.7, 13.4, 8.8; HRMS (EI, 70 eV) for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{STe}$ $[\text{M}^+]$ calcd. 458.0559, found 458.0558; m/z (rel int) 458(24.4), 401(30.4), 236(20.9), 128(100).

Diastereomer 16B: a viscous yellow oil; TLC (80:20 Hex:EtAc) $R_f = 0.44$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.80-7.76 (m, 2H), 7.51-7.47 (m, 3H), 7.15-7.11 (m, 3H), 6.92-6.89 (m, 2H), 5.68 (distorted s, 1H), 3.77 (br s, 1H), 2.94-2.74 (m, 2H), 2.08 (s, 3H), 1.84-1.73 (m, 2H), 1.42 (quint, 2H, $J = 7.4$ Hz), 0.9 (t, 3H, $J = 7.4$ Hz); NOE (400 MHz, CDCl_3 and TMS) the carbinol hydrogen, the hydroxy hydrogen and the hydrogens alpha to the tellurium atom enhanced 0.43, 0.14 and 12.9% respectively when the methyl hydrogens were irradiated the methyl hydrogens are being irradiated; ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 148.1, 142.7, 141.8, 133.0, 130.9, 129.3, 128.0, 126.6, 125.4, 124.3, 68.5, 33.7, 25.2, 25.1, 13.3, 9.0; IR (neat) cm^{-1} 3388 (br), 3060, 2958, 2928, 2245, 1574, 1443, 1033, 1020, 909, 733; HRMS (EI, 70 eV) for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{STe}$ $[\text{M}^+]$ calcd. 458.0559, found 458.0564; m/z (rel int) 105(41.6), 370(8.5), 401(10.4), 458(6.7).

(Z)-3-Benzenesulfinyl-2-butyltellanyl-hept-2-en-4-ol (17): isolated by column chromatography using gradient 90:10, then 85:15 Hex:EtAc on silica gel to afford a

mixture of diastereomers in equal amount (namely **A** and **B**) in 67% combined yield with exclusive Z-configuration according to NOE experiment. **A** and **B** diastereomers are separated by employing CH₂Cl₂ to flush out **A** completely and 95:05 CH₂Cl₂:MeOH to obtain diastereomer **B**.

Diastereomer 17A: a light yellow solid (mp = 72-79 °C, did not recrystallized); TLC (CH₂Cl₂) R_f = 0.20; ¹H NMR (300 MHz, CDCl₃ and TMS) δ 7.75-7.72 (m, 2H), 7.50-7.45 (m, 3H), 4.65-4.61 (m, 1H), 3.20 (br s, 1H), 2.99-2.81 (m, 2H), 2.48 (s, 3H), 1.87-1.77 (m, 2H), 1.66-1.56 (m, 1H), 1.51-1.28 (m, 4H), 1.15-1.13 (m, 1H), 0.96 (t, 3H, J = 7.1 Hz), 0.74 (t, 3H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃ and TMS) δ 145.9, 142.3, 130.6, 130.2, 128.8, 124.0, 70.8, 39.1, 33.6, 25.1, 24.4, 19.2, 13.7, 13.4, 8.7; NOE (400 MHz, CDCl₃ and TMS) the carbinol hydrogen, and the hydrogens alpha to the tellurium atom enhanced 1.2, 1.1% respectively when the methyl hydrogens were irradiated; IR (KBr) cm⁻¹ 3379 (br), 3063, 2957, 2924, 2869, 1581, 1442, 1379, 1302, 1143, 1050, 1021, 746, 694, 686; HRMS (EI, 70 eV) for C₁₇H₂₆O₂STe [M⁺] calcd. 424.0716, found 424.0717; m/z (rel int) 424 (17.0), 367 (38.2), 295 (12.7), 256 (10.2), 238 (30.8), 218 (26.5), 125 (41.7), 109 (34.9) 77 (46.5), 57 (100).

Diastereomer 17B: a light yellow solid (mp 78-82°C); TLC (CH₂Cl₂) R_f = 0.09; ¹H NMR (400 MHz, CDCl₃ and TMS) δ 7.71-7.69 (m, 2H), 7.50-7.44 (m, 3H), 4.59-4.56 (m, 1H), 3.61 (d, 1H, J = 5.5 Hz), 2.97-2.80 (m, 2H), 2.50 (s, 3H), 1.84-1.72 (m, 3H), 1.49-1.28 (m, 3H), 1.54-0.99 (m, 1H), 0.95 (t, 3H, J = 7.3 Hz), 0.85-0.75 (m, 1H) 0.68 (t, 3H, J = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 148.4, 142.6, 130.4, 129.0, 129.0 (overlapped), 124.4, 68.7, 39.8, 33.7, 25.0, 24.8, 19.2, 13.6, 13.3, 8.4; NOE (400 MHz, CDCl₃ and TMS) the carbinol hydrogen, the hydroxy hydrogen and the hydrogens

alpha to the tellurium atom enhanced 0.8, 0.3 and 1.4% respectively when the methyl hydrogens were irradiated; IR (KBr) cm^{-1} 3420, 3299, 2954, 2925, 2866, 1581, 1443, 1376, 1304, 1137, 1065, 1043, 1020, 747, 690; HRMS (EI, 70 eV) for $\text{C}_{17}\text{H}_{26}\text{O}_2\text{STe}$ [M^+] calcd. 424.0716, found 424.0703; m/z (rel int) 424 (39.0), 367 (68.0), 256 (16.5), 239 (46.6), 185 (18.4), 148 (29.1), 125 (55.3), 95 (32.8), 77 (59.0), 55 (100).

(Z)-2-Phenyltellanyl-3-(toluene-4-sulfinyl)-hept-2-en-4-ol (18): Two diastereomers were obtained. Diastereomer **A** was insoluble in 80:20 Hex:EtAc at room temperature and thus was partially removed from the crude mixture. The mother liquor was concentrated down and subjected to column chromatography (gradient hexane, then 98:02 Hex:Acetone). Unfortunately, the two isomers were not completely separated. A second attempt at column chromatography was performed using CH_2Cl_2 to removed diastereomer **A** ($R_f = 0.33$, CH_2Cl_2) and then 90:10 CH_2Cl_2 :MeOH to flush out diastereomer **B** ($R_f = 0.32$, CH_2Cl_2). Combined yield of diastereomer **A** (55%) and **B** (23%) is 78%.

Diastereomer 18A: an off-white solid, a small portion was recrystallized and had a melting point of 136 °C (average of two trials, recrystallized from CHCl_3 and Et_2O), 55% yield; TLC (CH_2Cl_2) $R_f = 0.33$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.96-7.93 (m, 2H), 7.83-7.80 (m, 2H), 7.57-7.49 (m, 3H), 7.48-7.42 (m 1H), 7.35-7.26 (m, 2H), 4.72-4.65 (dt, 1H, $J = 8.5, 5.2$ Hz), 2.86 (d, 1H, $J = 5.2$ Hz), 2.15 (s, 3H), 1.64-1.55 (m, 1H), 1.46-1.31 (m, 2H), 1.17-1.09 (m, 1H), 0.74 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 144.5, 142.4, 141.7, 134.7, 130.7, 129.5, 129.3, 129.2, 124.5, 114.7,

71.6, 39.1, 25.1, 19.2, 13.7; NOE (400 MHz, CDCl₃ and TMS) the carbinol hydrogen enhanced 1.1% when the methyl hydrogens were irradiated; IR (KBr) cm⁻¹ 3309, 3066, 2949, 2926, 2869, 1587, 1573 (sh) 1467, 1442, 1308, 1140, 1067, 1018, 996, 738, 694, 683; HRMS (EI, 70 eV) for C₁₉H₂₂O₂STe [M⁺] calcd. 444.0403, found 444.0392; *m/z* (rel int) 444 (28.3), 351 (12.8), 284 (8.4), 207 (88.8), 125 (52.2), 91 (83.6), 77 (100), 49 (81.8).

Diastereomer 18B: a yellow oil/foamy solid, 23% yield; TLC (100% CH₂Cl₂) R_f = 0.33; ¹H NMR (400 MHz, CDCl₃ and TMS) δ 7.93-7.91 (m, 2H), 7.76-7.73 (m, 2H), 7.51-7.48 (m, 3H), 7.47-7.40 (m, 1H), 7.31-7.27 (m, 2H), 4.59-4.56 (m, 1H), 3.71 (d, 1H, J = 4.8 Hz), 2.22 (s, 3H), 1.74-1.65 (m, 1H), 1.34-1.25 (m, 1H), 1.23-1.04 (m, 1H), 0.79-0.71 (m, 1H), 0.65 (t, 3H, J = 7.7 Hz); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 146.8, 142.1, 141.4, 133.2, 130.6, 129.4, 129.1, 129.0, 124.3, 114.3, 68.4, 39.5, 25.3, 19.2, 13.3; NOE (400 MHz, CDCl₃ and TMS) the carbinol hydrogen enhanced 0.7% when the methyl hydrogens were irradiated; IR (neat) cm⁻¹ 3400, 3054, 2957, 2870, 1573, 1474, 1443, 1434, 1137, 1017, 735, 693; HRMS (EI, 70 eV) for C₁₉H₂₂O₂STe [M⁺] calcd. 444.0403, found 444.0393; *m/z* (rel int) 444 (51.9), 410 (12.2), 351 (18.0), 284 (12.1), 207 (100), 186 (31.4), 148 (25.8), 125 (81.0).

(Z)-3-Butyltellanyl-1-phenyl-2-p-tolylsulfanyl-prop-2-en-1-ol (19): isolated by column chromatography using 95:5, then 90:10 Hex:EtAc on silica gel, 56% yield (A minor product from 1,2-addition of acetylenic sulfide to benzaldehyde was also isolated in 8% yield); TLC (90:10 Hex:EtAc) R_f = 0.38; ¹H NMR (300 MHz, CDCl₃ and TMS) δ 7.56

(d, 1H, $J = 1.1$ Hz), 7.32-7.30 (m, 5H), 7.25-7.19 (d of m, 2H), 7.09-7.06 (d of m, 2H), 5.15 (distorted d, 1H, $J = 3$ Hz), 2.69 (t, 2H, $J = 7.4$ Hz), 2.34 (distorted broad t, 1H, $J = 1.9$ Hz), 2.31 (s, 3H), 1.84-1.74 (m, 2H), 1.44-1.31 (sext, 2H, $J = 7.4$ Hz), 0.91 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 142.2, 141.1, 137.0, 129.92, 129.88, 129.8, 128.4, 127.9, 126.8, 118.3, 77.4, 34.2, 25.0, 21.1, 13.4, 6.9; NOE (400 MHz, CDCl_3 and TMS) the carbinol hydrogen, the hydroxy hydrogen and the hydrogens alpha to the tellurium atom enhanced 1.2, 0.9 and 2.2% respectively when the vinylic hydrogen was irradiated; IR (neat) cm^{-1} 3419 (br), 3061, 3028, 2956, 2924, 2869, 1600, 1559, 1491, 1453, 1179, 1057, 992, 806, 689; HRMS (EI, 70 eV) for $\text{C}_{20}\text{H}_{24}\text{OSTe} [\text{M}^+]$ calcd. 442.06102, found 442.0598; m/z (rel int) 84 (96.4), 131 (100), 205 (57.1), 254 (14.6), 442 (43.1).

1-Phenyl-3-*p*-tolylsulfanyl-prop-2-yn-1-ol (19B): a light yellow oil, 8% yield; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.58-7.54 (m, 2H), 7.42-7.28 (m, 5H), 7.15-7.11 (m, 2H), 5.66 (d, 1H, $J = 5.8$ Hz), 2.32 (s and overlapped broad singlet, 4H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 140.2, 136.9, 130.0, 128.7, 128.48, 128.45, 126.8, 126.6, 97.6, 74.8, 65.5, 21.0.

1-Butyltellanyl-propan-2-ol: a product from ring opening of propylene oxide by lithium *n*-butyl tellurolate in THF at -20 °C; it is isolated by column chromatography using 95:5 Hex:EtAc on silica gel, 63% yield; TLC (95:5 Hex:EtAc) $R_f = 0.25$; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 3.85-3.81 (br m, 1H), 2.91 (dd, 1H, $J = 4.6, 12.4$ Hz), 2.73-2.61 (m,

3H), 2.21 (exchanged with D₂O, distorted d, 1H, $J = 4.1$ Hz), 1.72 (quint, 2H, $J = 7.7$ Hz), 1.40 (overlapped sext, 2H, $J = 7.7$ Hz), 1.30 (overlapped d, 3H, $J = 6.3$ Hz), 0.92 (t, 3H, $J = 7.4$ Hz); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 67.3, 34.3, 25.0, 23.6, 16.3, 13.4, 3.5.

D. Intramolecular electrotelluration condition screening

To a suspension of Te (127 mg, 1 mmol, 1 equiv) in THF (20 mL, 0.05 M high dilution) was added *n*-BuLi (0.32 mL of 3.13 M solution in hexanes, 1 mmol, 1 equiv) dropwise at rt giving a red/purple solution. After stirring for 30 min at rt, all elemental tellurium had reacted. A solution of aldehyde (1 mL of 1 M solution in THF, 1 mmol, 1 equiv) was added slowly. Aldehyde starting material ($R_f = 0.47$ in 65:35 Hex:EtAc) disappeared after 5 min and a new lower R_f spot ($R_f = 0.39$ 65:35 Hex:EtAc) appeared. After stirring for an additional 10 min, the reaction was quenched slowly with NH₄Cl under nitrogen. The product was extracted with ethyl acetate, washed with brine and dried over MgSO₄. ¹H NMR at this stage showed a complex mixture of products. We decided to purify the product by flash column chromatography on silica gel using 80:20 Hex:EtAc to isolate the $R_f = 0.39$ spot. The purification proceeded smoothly; however, ¹H NMR was still complex. We believe that the product was formed but probably oxidized during the purification. To further confirm our hypothesis, we run a GC-MS of a NMR sample and indeed obtained a single peak on GC with a m/z of 372. This mass corresponded to the tellurone compound (C₁₂H₂₀O₅Te), an oxidation product of the vinylic telluride, instead of the expected vinylic telluride compound (C₁₂H₂₀O₃Te, $m/z = 340$). In addition, running a TLC of the isolated sample in the ¹H NMR tube revealed diphenylditelluride, the vinylic telluride and two lower spots (possibly telluroxide and

tellurone). In conclusion, we believe that the product was formed in the intramolecular electrotelluration but it is oxidized to tellurone during the workup. From our experience, vinylic phenyl telluride does not oxidize as quickly as vinyl butyl telluride because the lone pair of the tellurium atom can localize within the phenyl ring preventing its oxidation. Therefore, we run the same reaction with phenyltellurolate anion to test this idea. Indeed, we obtain the product and it does not oxidize during work up and purification.

E. General procedure for intramolecular electrotelluration with phenyl tellurolate anion

PhTeLi procedure: to a suspension of Te (384 mg, 3 mmol, 1 equiv) in THF (60 mL, 0.05 M high dilution) was added PhLi (1.49 mL of 2.02 M solution in cyclohexane-ether, 3 mmol, 1 equiv) dropwise at rt giving a red/purple solution. After stirring for 30 min at rt, all elemental tellurium had reacted. A solution of the ω -keto alkynyl ester (**23b**, 3 mL of 1M solution in THF, 3 mmol, 1 equiv) was added slowly. Aldehyde starting material (R_f = 0.47 in 65:35 Hex:EtAc) disappeared after 5 min and a new lower R_f spot (R_f = 0.39 65:35 Hex:EtAc) appeared. After stirring for an additional 10 min, the reaction was quenched slowly with NH_4Cl under a nitrogen atmosphere. The product was extracted with ethyl acetate, washed with brine and dried over MgSO_4 , and concentrated. Column chromatography (70:30 Hex:EtAc) affords a yellow oil. Yield 80%.

PhTeMgBr procedure: to a suspension of Te (256 mg, 2 mmol, 1 equiv) in THF (10 mL) at room temperature was added PhMgBr (1.48 mL of 1.35M solution, 2 mmol, 1 equiv). The reaction was refluxed for 20 minutes and cooled down to room temperature. 30 mL of THF was added and a solution of the ω -keto alkynyl ester (**23b**, 2 mL of 1M solution

in THF, 2 mmol, 1 equiv) was added dropwise. After 10 minutes, the reaction was quenched slowly with NH_4Cl under a nitrogen atmosphere. The product was extracted with ethyl acetate, washed with brine and dried over MgSO_4 , and concentrated. Column chromatography (70:30 Hex:EtAc) affords a yellow oil. Yield 51%.

6-Hydroxy-2-phenyltellanyl-cyclohex-1-enecarboxylic acid methyl ester (31):

isolated by column chromatography using 70:30 Hex:EtAc on silica gel; a yellow oil; R_f = 0.22 (70:30 Hex:EtAc); 80% yield (PhTeLi); 51% yield (PhTeMgBr , 1 equiv); 79% yield (PhTeMgBr , 2 equiv); ^1H NMR (400 MHz, CDCl_3 and TMS) δ 7.83 (d, 2H, J = 7.0 Hz), 7.36 (t, 1H, J = 7.3 Hz), 7.24 (t, 2H, J = 7.3 Hz), 4.57 (distorted t, 1H, J = 3.7 Hz), 3.84 (s, 3H), 2.51 (s, 1H), 2.28-2.01 (dt, 1H, J = 19.4, 4.0 Hz), 2.00-1.85 (m, 2H), 1.72-1.54 (m, 2H), 1.48-1.42 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 168.9, 153.2, 141.5, 129.1, 128.8, 128.7, 118.6, 64.7, 52.4, 36.5, 29.6, 19.2; IR (neat) cm^{-1} 3423, 3063, 2991, 2946, 2869, 1669, 1260, 1433, 1271, 1253, 1140, 1058, 735, 696; HRMS (EI, 70 eV) for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{Te}$ [M^+] calcd. 362.0162, found 362.0145; m/z (rel int) 49 (62.6), 84 (90.9), 123 (100), 285 (24.4), 362 (70.6).

2-tert-Butyltellanyl-6-hydroxy-cyclohex-1-enecarboxylic acid methyl ester (33):

$\text{C}_{12}\text{H}_{20}\text{O}_3\text{Te}$; FW = 340; R_f = 0.33 (70:30 Hex:EtAc). Column chromatography (80:20 Hex:EtAc) affords a yellow; unstable oil, 31% yield. ^1H NMR (400 MHz, CDCl_3 and

TMS) δ 4.62 (s, 1H), 3.92 (s, 3H), 2.57 (br s, 1H), 2.39-2.33 (m, 1H), 2.05-2.00 (m, 1H), 1.70-1.50 (m, 13H).

6-Hydroxy-2-vinyltellanyl-cyclohex-1-enecarboxylic acid methyl ester (32):

vinylTeMgBr was prepared in a similar manner as PhTeMgBr;² isolated by column chromatography using 80:20 Hex:EtAc on silica gel; a yellow and stench oil, 74% yield; R_f = 0.27 (70:30 Hex:EtAc); ^1H NMR (500 MHz, CDCl_3 and TMS) δ 7.31 (dd, 1H, J = 18.3, 10.5 Hz), 6.46 (dt, 1H, J = 10.5, 1.2 Hz), 6.08 (dt, 1H, J = 18.3, 1.2 Hz), 4.61 (distorted t, 1H), 3.85 (s, 3H), 2.76 (dt, 1H, J = 2.9 Hz), 2.55 (br s, 1H), 2.46- 2.39 (m, 1H), 2.00-1.90 (m, 1H), 1.90-1.82 (m, 1H), 1.72-1.65 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 169.1, 152.2, 133.5, 129.4, 115.2, 64.8, 52.5, 36.3, 29.9, 19.4; IR (neat) cm^{-1} 3420 (br), 3054, 2978, 2946, 2869, 1670, 1561, 1436, 1271, 1059; HRMS (EI, 70 eV) for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{Te}$ [M^+] calcd. 312.0005, found 311.9993; m/z (rel int) 84 (48.5), 312 (17.6).

5-Hydroxy-2-phenyltellanyl-cyclopent-1-enecarboxylic acid methyl ester (29): isolate

by column chromatography using 80:20 Hex:EtAc on silica gel; a yellow oil, 72% yield (PhTeLi); R_f = 0.25 (70:30 Hex:EtAc); ^1H NMR (400 MHz, CDCl_3 and TMS) δ 7.93-7.91 (m, 2H), 7.44-7.40 (m, 1H), 7.29 (t, 2H, J = 7.6 Hz), 5.06 (distorted br s, 1H), 3.87 (s, 3H), 2.54-2.47 (m, 2H), 2.34-2.19 (m, 2H), 1.88-1.82 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 166.6, 153.3, 141.4, 135.3, 129.4, 129.2, 114.8, 76.2, 52.1, 39.0,

33.7; IR (neat) cm^{-1} 3419 (br), 3051, 2949, 1674, 1571, 1435, 1295, 1198, 1159, 1139, 1063, 1037, 736, 695; HRMS (EI, 70 eV) for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Te}$ [M^+] calcd. 348.0005, found 348.0011; m/z (rel int) 84 (53.4), 348 (4.6).

2-*tert*-Butyltellanyl-5-hydroxy-cyclopent-1-enecarboxylic acid methyl ester (30):

isolated by column chromatography using 80:20 Hex:EtAc on silica gel; a yellow oil; unstable, 51% yield (*t*-BuTeLi); R_f = 0.19 (80:20 Hex:EtAc); ^1H NMR (400 MHz, CDCl_3 and TMS) δ 5.11 (distorted s, 1H), 3.83 (s, 3H), 3.00-2.92 (m, 1H), 2.73-2.65 (m, 1H), 2.45 (br s, 1H), 2.40-2.31 (m, 1H), 1.92-1.85 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 166.5, 142.4, 136.2, 76.7, 52.2, 44.2, 36.4, 33.5, 24.8; IR (neat) cm^{-1} 3420 (br), 2948, 1717, 1673, 1575, 1436, 1294, 1139.

7-Hydroxy-2-phenyltellanyl-cyclooct-1-enecarboxylic acid methyl ester (34): isolated

by column chromatography using 80:20 Hex:EtAc on silica gel; a yellow oil, 41% yield (PhTeLi); 30% yield (PhTeMgBr, 1 equiv), R_f = 0.26 (80:20 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.89-7.87 (m, 2H), 7.38-7.34 (m, 1H), 7.24 (distorted t, 2H, J = 7.3 Hz), 4.92 (td, 1H, J = 11.0, 5.1 Hz), 3.86 (s, 3H), 3.28 (distorted m, 1H), 2.68-2.34 (m, 2H), 1.88-1.74 (m, 2H), 1.66-1.52 (m, 2H), 1.30-0.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ : 168.3, 156.0, 141.8, 130.1, 129.4, 129.1, 120.3, 71.0, 52.5, 38.5, 35.6, 31.1, 27.0, 24.7; IR (neat) cm^{-1} 3583 (br), 3064, 2924, 2855, 1734, 1717, 1669, 1541, 1271, 1204, 1161, 1050, 735, 696; HRMS (EI, 70 eV) for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{Te}$ [M^+] calcd.

376.0318, found 376.0321; m/z (rel int) 77 (33.1), 137 (100), 207 (8.1), 299 (6.9), 376 (42.9).

8-Hydroxy-2-phenyltellanyl-cyclooct-1-enecarboxylic acid methyl ester (35): isolated by column chromatography using 80:20 Hex:EtAc on silica gel; a sticky yellow solid, 48% yield (PhTeLi); R_f = 0.23 (80:20 Hex:EtAc); ^1H NMR (400 MHz, CDCl_3 and TMS) δ 7.89-7.87 (m, 2H), 7.38-7.34 (m, 1H), 7.26-7.22 (m, 2H), 4.95-4.88 (m, 1H), 3.86 (s, 3H), 3.30-3.27 (m, 1H), 2.68-2.24 (m, 2H), 1.88-1.74 (m, 2H), 1.66-1.52 (m, 2H), 1.30-0.96 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 168.3, 156.0, 141.8, 130.1, 129.4, 129.1, 120.3, 71.0, 52.5, 38.5, 35.6, 31.1, 27.0, 24.7; IR (neat) cm^{-1} 3500, (br), 3064, 2942, 2855, 1734, 1717, 1669, 1541, 1433, 1271, 1240, 1050, 735; HRMS (EI, 70 eV) for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Te}$ [M^+] calcd. 390.0475, found 390.0460; m/z (rel int) 151 (64.4), 390 (100).

F. Preparation of starting materials

1. Preparation of acetylenic sulfide, sulfoxide and sulfone

Prop-1-ynylsulfanyl-benzene: a colorless liquid.³

(Prop-1-yne-1-sulfinyl)-benzene: a yellow liquid; stores in the desiccator. Prepare by oxidation of prop-1-ynylsulfanyl-benzene with one equiv of mCPBA in CH_2Cl_2 at 0 °C for 24 hours.⁴

(Prop-1-yne-1-sulfonyl)-benzene: a white solid; stores in the desiccator. Oxidation of prop-1-ynylsulfanyl-benzene with two equiv of mCPBA affords the title compound.⁵

1-Ethynylsulfanyl-4-methyl-benzene:⁶

The literature did not provide the experimental details for either the first or second step. The first step is straightforward but because of a minor modification in the second step, the actual experimental procedure will be provided here. In the second step, three equiv of LDA is employed to avoid the formation the olefinic compound (*via* ¹H-NMR) when two equiv of LDA is used. As thioethyne is formed, its acetylenic proton is acidic enough to consume the LDA base. Brandsma described in a similar procedure using three equiv of sodamide in liquid ammonia to make alkylthioethyne from 1,2-dibromoalkyl.⁷ These observations prompt us to use three equiv of LDA and as expected, the olefinic product is not detected.

In a flamed-dried, 500-mL, three-necked, round-bottom flask equipped with a stir bar and an addition funnel, was added 150 mL of freshly distilled diethyl ether. After cooling the reaction vessel down to -78 °C, three equiv of diisopropyl amine (15.68 mL, 111.9 mmol) were syringed into the cold ether dropwise and allowed to stir at -78 °C for 10 minutes. Butyl lithium (111.9 mmol) was added dropwise *via* an addition funnel. The 1,1-diethoxy-2-(4-methylphenylthio)ethane in 5 mL of ether was cannulated into the LDA solution at -78 °C. A milky solution was observed as the cold bath was removed

and the temperature was brought up to 0 °C. TLC (Hex) showed that the reaction was complete in 15 minutes. The reaction mixture was diluted with 100 mL of ether, quenched with 30 mL of saturated NH₄Cl, and neutralized with 1M HCl. The organic layer was extracted, dried with MgSO₄, and solvent removed afforded the title compound that was used without further purification. To dry further, the product is azeotropically distilled with benzene three times prior the trapping experiment.

1-Ethynylsulfanyl-4-methyl-benzene: C₉H₈S; FW = 148; TLC (hexanes) R_f = 0.61; a light yellow liquid but turns orange/red quickly, 92% yield; ¹H NMR (300 MHz, CDCl₃ and TMS) δ 7.33 (m, 2H), 7.13 (m, 2H), 3.19 (s, 1H), 2.33 (s, 3H).

2. General procedure for the alkyne synthesis

To avoid the formation of allyl alcohol, a reduction product of propargyl alcohol, lithioamide must be generated in the present of Fe(NO₃)₃. A 3-L, three-necked, RBF was equipped with a combination of ammonia and a nitrogen gas inlet, a stir bar and a cold (-78 °C) finger in which its vent was connected to a drying tube leading to the air. One liter of ammonia gas was condensed rapidly to the flask and then catalytic Fe(NO₃)₃. Li wire (2.78 g, 400 mmol, 2 equiv) was cut into small pieces and added to the ammonia solution slowly at -78 °C. During the addition, a brilliant blue solution was formed but soon disappeared. At the end of the Li addition, the solution should be colorless indicative of the complete formation of lithioamide. More Fe(NO₃)₃ was added if the blue solution still persisted. Freshly distilled propargyl alcohol (11.6 mL, 200 mmol, 1 equiv) was syringed slowly to the lithioamide solution at -78°C. Subsequently, distilled butyl bromide (21.5 mL, 200 mmol, 1 equiv) was added dropwise over 45 min at -78 °C. The white

suspension was stirred for an additional 1.5 hr at this temperature and the cold bath was removed. Ammonia was allowed to evaporated overnight under a nitrogen stream through a KOH drying tube. To the solid residue was added 100 mL of ice water. The product was extracted repeatedly with ether. The combine organic layers were dried over MgSO_4 and concentrated. The crude product was pure enough for the next step. Yield 85 %.

Hept-2-yn-1-ol: $\text{C}_7\text{H}_{12}\text{O}$; FW = 112; colorless oil, 83% yield, bp 98-99 °C at 20 mmHg.

Oct-2-yn-1-ol: $\text{C}_8\text{H}_{14}\text{O}$; FW = 126; colorless oil, 85% yield; ^1H NMR (300 MHz, CDCl_3 and TMS) δ 4.21 (t, 2H, $J = 2.2$ Hz), 2.16 (td, 2H, $J = 7.0, 2.2$ Hz), 1.54 (br s, 1H), 1.47 (quint, 2H, $J = 7.0$ Hz), 1.34-1.24 (m, 4H), 0.87 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 86.9, 78.4, 51.6, 31.2, 28.5, 22.4, 18.9, 14.1.

3. General procedure for the zipper reaction

KH (17.9 g of 37 wt% dispersion in mineral oil, 157 mmol, 3 equiv) was washed with HPLC-grade hexanes (3x100 mL) under nitrogen at rt. 1,3-diaminopropane (55 mL) was added slowly at rt. After the reaction had been subsided, the temperature was raised to 70 °C forming a brown solution. After 30 min, the reaction was allowed to reach rt. The internal acetylene (6.6 g, 52 mmol, 1 equiv) was added dropwise at rt. After stirring for three hours, the reaction mixture was repeatedly extracted with ether (5x50 mL). The ether layers were combined and washed with water, dilute HCl, brine and dried over MgSO_4 . The MgSO_4 was filtered off and the solvents were removed under reduced pressure yielding pure product (68%).

Oct-7-yn-1-ol (20d): $C_8H_{14}O$; FW = 126; a colorless oil, 68% yield; 1H NMR (300 MHz, $CDCl_3$ and TMS) δ 3.61 (t, 2H, J = 6.6 Hz), 2.16 (td, 2H, J = 6.9, 2.7 Hz), 1.92 (t, 1H, J = 2.7 Hz), 1.75 (br s, 1H), 1.74-1.29 (m, 8H).

Hept-6-yn-1-ol (20c): $C_7H_{12}O$; FW = 112; a colorless oil, 59% yield; 1H NMR (300 MHz, $CDCl_3$ and TMS) δ 3.66 (t, 2H, J = 6.3 Hz), 2.20 (td, 2H, J = 6.6, 2.5 Hz), 1.94 (t, 1H, J = 2.7 Hz), 1.67-1.42 (m, 6H), 1.37 (br s, 1H).

4. General procedure for alcohol protection with DHP

To a cold (0 °C) mixture of 5-hexyn-1-ol (**20b**, 19.1 g, 195 mmol, 1 equiv), and 3,4-dihydro-2*H*-pyran (19.6 mL, 215 mmol, 1.1 equiv) in dry methylene chloride (50 mL) was added CSA (50 mg, catalytic). The reaction mixture was warmed up to rt and stirred for 4 hours. The reaction was quenched with saturated aqueous $NaHCO_3$, partitioned with CH_2Cl_2 and the organic phase was separated. The combined organic layers were dried over $MgSO_4$, concentrated to give pure 1-hex-5-ynyloxy-tetrahydro-pyran (98% yield).

1-Hex-5-ynyloxy-tetrahydro-pyran (21b):⁸ $C_{11}H_{18}O_2$; FW = 182, 98% yield; R_f = 0.51 (90:10 Hex:EtAc); 1H NMR (300 MHz, $CDCl_3$ and TMS) δ 4.68-4.51 (m, 1H), 4.04-3.70 (m, 2H), 3.68-3.27 (m, 2H), 2.37-2.12 (m, 2H), 1.93 (t, 1H, J = 3 Hz), 1.89-1.39 (m, 10H).

2-Penty-4-ynoxy-tetrahydro-pyran (21a):⁹ C₁₀H₁₆O₂; FW = 168; 97 % yield; ¹H and ¹³C NMR matched with the literature.

2-Hept-6-ynoxy-tetrahydro-pyran (21c): C₁₂H₂₀O₂; FW = 196, 97% yield; R_f = 0.45 (90:10 Hex:EtAc); ¹H NMR (300 MHz, CDCl₃ and TMS) δ 4.57-4.55 (m, 1H), 3.89-3.81 (m, 1H), 3.77-3.69 (m, 1H), 3.52-3.41 (m, 1H), 3.39-3.34 (m, 1H), 2.21-2.14 (m, 2H), 1.92 (t, 1H, J = 2.7 Hz), 1.85-1.41 (m, 12H); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 99.0, 84.7, 68.4, 67.5, 62.5, 30.9, 29.4, 28.5, 25.7, 25.6, 19.8, 18.5.

2-Oct-7-ynoxy-tetrahydro-pyran (21d): C₁₃H₂₁O₂; FW = 209, bp 60-65 °C (0.2 mmHg), 99% yield; R_f = 0.55 (90:10 Hex:EtAc); ¹H NMR (300 MHz, CDCl₃ and TMS) δ 4.52-4.50 (m, 1H), 3.83-3.78 (m, 1H), 3.70-3.65 (m, 1H), 3.47-3.41 (m, 1H), 3.35-3.30 (m, 1H), 2.15-2.11 (m, 2H), 1.88 (t, 1H, J = 2.6 Hz), 1.78-1.29 (m, 14H); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 99.0, 84.8, 68.3, 67.7, 62.5, 30.9, 29.8, 28.7, 28.6, 25.9, 25.7, 19.9, 18.5.

5. General procedure for acylation of alkyne

Brandsma's procedure employed an inverse addition order for this esterification which was very reliable and high yielding.¹⁰ To a cold (-78 °C) solution of 1-hex-5-ynoxy-tetrahydro-pyran (**21b**, 35.5 g, 195 mmol, 1 equiv) in THF (200 mL) was added *n*-BuLi (62.3 mL of 3.13M solution, 195 mmol, 1 equiv) dropwise over a period of 30 minutes. After stirring for two hours at -78 °C, this solution was syringed in portions to a cold (-35 °C) mixture of methyl chloroformate (45.2 mL, 585 mmol, 3 equiv) in THF (50

mL) over a period of 30 minutes while keeping the temperature between -35 and -25 °C. Stirring at this temperature was continued for another 30 minutes and the cooling bath was removed. After stirring for another hour at rt, the reaction mixture was poured onto a saturated aqueous NH₄Cl solution. The product was extracted with ether (3 times), washed with brine and dried over MgSO₄. Solvents were removed under vacuum to afford the acetylenic ester product (98%). Physical characterization matched with the literature.⁸

7-(Tetrahydro-pyran-2-yloxy)-hept-2-ynoic acid methyl ester (22b): C₁₃H₂₀O₄; FW = 240; bp 148-152 °C (0.4 mmHg). Column chromatography (90:10 Hex:EtAc) affords a colorless oil, 98% yield; R_f = 0.33 (90:10 Hex:EtAc); ¹H NMR (300 MHz, CDCl₃ and TMS) δ 4.66-4.48 (m, 1H), 3.74 (s, 3H), 4.01-3.20 (m, 4H), 2.54-2.24 (m, 2H), 1.96-1.37 (m, 10H); IR (neat) cm⁻¹: 2950, 2240, 1710, 1260.

6-(Tetrahydro-pyran-2-yloxy)-hex-2-ynoic acid methyl ester (22a): isolated by column chromatography using 90:10 Hex:EtAc on silica gel; a colorless oil, 99% yield; R_f = 0.25 (90:10 Hex:EtAc); ¹H NMR (300 MHz, CDCl₃ and TMS) δ 4.56 (t, 1H, J = 3.0 Hz), 3.85-3.75 (m, 2H), 3.72 (s, 3H), 3.51-3.40 (m, 2H), 2.44 (t, 2H, J = 6.9 Hz), 1.88-1.45 (8H); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 154.4, 99.0, 89.4, 73.2, 65.7, 62.4, 52.7, 30.8, 28.0, 25.6, 19.6, 15.8; IR (neat) cm⁻¹ 2946, 2871, 2237, 1716, 1436, 1354, 1256, 1136, 1121, 1076, 1034, 989; HRMS (CI with NH₃) for C₁₂H₁₈O₄ [M+H]⁺ calcd 227.1283, found 227.1288; from CI with NH₃ m/z (rel int) 85 (89.0), 102 (100), 160

(72.8), 244 (14.3); from EI 70 eV m/z (rel. int) 85 (100), 111 (50.4), 167 (28.4), 227 (12.2).

8-(Tetrahydro-pyran-2-yloxy)-oct-2-ynoic acid methyl ester (22c): $C_{14}H_{22}O_4$; FW = 234. Column chromatography (90:10 Hex:EtAc) affords a colorless oil, 97% yield; R_f = 0.22 (90:10 Hex:EtAc); 1H NMR (300 MHz, $CDCl_3$ and TMS) δ 4.54 (distorted t, 1H, J = 2.7 Hz), 3.86-3.80 (m, 1H), 3.79-3.67 (overlapped m, 1H), 3.72 (overlapped s, 3H), 3.50-3.39 (m, 1H), 3.37-3.32 (m, 1H), 2.32 (t, 2H, J = 6.9 Hz), 1.81-1.41 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$ and TMS) δ 154.4, 99.0, 89.8, 73.1, 67.4, 62.5, 52.7, 30.9, 29.3, 27.5, 25.7, 25.6, 19.8, 18.8.

9-(Tetrahydro-pyran-2-yloxy)-non-2-ynoic acid methyl ester (22d): $C_{15}H_{22}O_4$; FW = 266. Column chromatography (90:10 Hex:EtAc) affords a colorless oil, 96% yield; R_f = 0.26 (90:10 Hex:EtAc); 1H NMR (300 MHz, $CDCl_3$ and TMS) δ 4.52 (distorted t, 1H, J = 2.7 Hz), 3.85-3.74 (m, 1H), 3.72-3.64 (m, 4H), 3.48-3.41 (m, 1H), 3.37-3.29 (m, 1H), 2.29 (t, 2H, J = 6.9 Hz), 1.85-1.29 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$ and TMS) δ 154.4, 99.0, 89.9, 73.0, 67.5, 62.5, 52.7, 30.9, 29.7, 28.8, 27.6, 25.8, 25.6, 19.8, 18.7.

6. General procedure for THP deprotection

A mixture containing a THP-protected alkyne (**22b**, 35.1 g, 146 mmol, 1 equiv), *p*-TsOH (1.11 g, catalytic) and MeOH (650 mL) was stirred overnight at rt. The reaction was quenched with saturated aqueous $NaHCO_3$ until it is neutral. Methanol was partially removed under a reduced pressure. The product was extracted several times with ether

and then CH_2Cl_2 until TLC indicated that no more product was in the aqueous layer. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated. Column chromatography (70:30 Hex:EtAc) of the crude oil afforded a colorless oil (95% yield). Physical characterization of the product matched with the literature.⁸

7-Hydroxy-hept-2-ynoic acid methyl ester (23b): $\text{C}_8\text{H}_{12}\text{O}_3$; FW = 156. Column chromatography (70:30 Hex:EtAc) affords a colorless oil, 95% yield; R_f = 0.40 (50:50 Hex:EtAc). ^1H NMR (300 MHz, CDCl_3 and TMS) δ 3.69 (s, 3H), 3.61-3.59 (m, 2H), 2.46 (s, 1H), 2.33-2.32 (m, 2H), 1.43-1.59 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 154.2, 89.4, 72.9, 61.7, 52.5, 31.4, 23.7, 18.2.

6-Hydroxy-hex-2-ynoic acid methyl ester (23a): isolated by column chromatography using 70:30 Hex:EtAc on silica gel; a colorless oil, 99% yield; R_f = 0.38 (80:20 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 3.70 (overlapped s, 3H), 3.68 (overlapped t, 2H, J = 5.9 Hz), 2.41 (t, 2H, J = 7.0 Hz), 1.93 (br s, 1H), 1.76 (distorted quint, 2H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 154.4, 89.4, 73.2, 61.1, 52.8, 30.3, 15.3; IR (neat) cm^{-1} 3407 (br), 2954, 2882, 2236, 1715, 1436, 1259, 1080, 943, 921, 817, 752; HRMS (CI with NH_3) for $\text{C}_7\text{H}_{10}\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd 147.0708, found 143.0714; from CI with NH_3 , m/z (rel int) 111 (66.4), 143 (82.6), 160 (100); from EI 70 eV, m/z (rel int) 53 (29.8), 69 (40.6), 75 (36.2), 84 (27.5), 93 (32.6), 111 (100).

8-Hydroxy-oct-2-ynoic acid methyl ester (23c): isolated by column chromatography using 70:30 Hex:EtAc on silica gel; a colorless oil, 99% yield; $R_f = 0.31$ (50:50 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 3.71 (s, 3H), 3.59 (t, 2H, $J = 6.3$ Hz), 2.31 (t, 2H, $J = 6.9$ Hz), 2.01 (br s, 1H), 1.60-1.43 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 154.5, 89.8, 73.1, 62.6, 52.8, 32.2, 27.4, 25.2, 18.8; IR (neat) cm^{-1} 3400 (br), 2942, 2865, 2237, 1716, 1436, 1258, 1075, 753; HRMS (CI with NH_3) for $\text{C}_9\text{H}_{14}\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd. 171.1021, found 171.1015; from CI with NH_3 , m/z (rel int) 121 (12.9), 171 (80.9), 188 (100); from EI 70 eV with DCI probe, m/z (rel int) 41 (63.5), 55 (69.0), 67 (61.3), 79 (100), 93 (65.1), 111 (77.8), 139 (58.4).

9-Hydroxy-non-2-ynoic acid methyl ester (23d): isolated by column chromatography using 70:30 Hex:EtAc on silica gel; a colorless oil, 99% yield; $R_f = 0.42$ (50:50 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 3.69 (s, 3H), 3.57 (t, 2H, $J = 6.6$ Hz), 2.27 (t, 2H, $J = 7.3$ Hz), 1.66 (s, 1H), 1.54-1.47 (m, 4H), 1.39-1.28 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 154.5, 90.0, 73.1, 62.9, 52.8, 32.6, 28.7, 27.6, 25.3, 18.7; IR (neat) cm^{-1} 3392 (br), 2937, 2862, 2236, 1716, 1436, 1258, 1076, 753; HRMS (CI with NH_3) for $\text{C}_{10}\text{H}_{16}\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd. 185.1178, found 185.1175; m/z (rel int) 107 (43.8), 153 (29.1), 185 (100).

7. General procedure for Swern oxidation

A solution of $(\text{COCl})_2$ (3.49 mL, 40 mmol, 2 equiv) and CH_2Cl_2 (150 mL) was cooled to -78°C . To this mixture was added DMSO (3.41 mL, 48 mmol, 2.4 equiv) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred for 15 minutes. The alcohol (**23b**, 3.12 g, 20 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added at -78°C giving a white

suspension and was stirred for another 15 minutes. Dry Et₃N (13.9 mL, 100 mmol, 5 equiv) was added slowly and then the reaction was stirred for another 15 minutes and the cold bath was removed. After 20 minutes, the reaction was poured onto 100 mL of H₂O. The product was extracted with CH₂Cl₂, washed with brine and dried over MgSO₄. Column chromatography (70:30 Hex:EtAc) of the crude oil gave the aldehyde (99% yield).

7-Oxo-hept-2-ynoic acid methyl ester (24b): C₈H₁₀O₃; FW = 154. Column chromatography (70:30 Hex:EtAc) affords a colorless oil, 99% yield; R_f = 0.34 (70:30 Hex:EtAc). ¹H NMR (300 MHz, CDCl₃ and TMS) δ 9.70 (s, 1H), 3.66 (s, 3H), 2.54 (t, 2H, J = 7.3 Hz), 2.33 (t, 2H, J = 7.0 Hz), 1.81 (quint, 2H, J = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 201.0, 153.8, 88.0, 73.5, 52.5, 42.2, 19.8, 17.8.

6-Oxo-hex-2-ynoic acid methyl ester (24a): R_f = 0.16 (80:20 Hex:EtAc), 97% yield; ¹H NMR (400 MHz, CDCl₃ and TMS) δ 9.79 (d, 1H, J = 0.7 Hz), 3.66 (s, 3H), 2.71 (distorted t, 2H, J = 6.6 Hz), 2.56 (t, 2H, J = 7.0 Hz); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 199.0, 154.0, 87.4, 73.4, 52.8, 41.4, 11.8; IR (neat) cm⁻¹ 3007, 2957, 2912, 2843, 2736, 2241, 1714, 1436, 1259, 1082, 850, 753; HRMS (CI with NH₃) for C₇H₈O₃ [M+H]⁺ calcd. 141.0552, found 141.0557; m/z (rel int) 109 (53.2), 158 (100).

8-Oxo-oct-2-ynoic acid methyl ester (24c): isolated by column chromatography using 80:20 Hex:EtAc on silica gel; a colorless oil, 96% yield; $R_f = 0.29$ (90:10 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 9.74 (s, 1H), 3.73 (s, 3H), 2.46 (td, 2H, $J = 6.9, 1.1$ Hz), 2.35 (t, 2H, $J = 6.9$ Hz), 1.78-1.71 (m, 2H), 1.68-1.57 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 202.0, 154.3, 89.0, 73.5, 52.8, 43.3, 27.0, 21.3, 18.7; IR (neat) cm^{-1} 2953, 2870, 2833, 2728, 2237, 1716, 1436, 1258, 1074, 753; HRMS (EI, 70 eV) for $\text{C}_9\text{H}_{12}\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd. 169.0865, found 169.0867; m/z (rel int) 68 (66.3), 79 (31.1), 111 (84.1), 125 (100), 137 (89.5), 169 (12.2).

9-Oxo-non-2-ynoic acid methyl ester (24d): isolated by column chromatography using 80:20 Hex:EtAc on silica gel; a colorless oil, 95% yield; $R_f = 0.39$ (70:30 Hex:EtAc); ^1H NMR (300 MHz, CDCl_3 and TMS) δ 9.74 (t, 1H, $J = 1.6$ Hz), 3.72 (s, 3H), 2.46 (td, 2H, $J = 7.1, 1.6$ Hz), 2.32 (t, 2H, $J = 6.9$ Hz), 1.73-1.53 (m, 4H), 1.47-1.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 202.5, 154.4, 89.4, 73.2, 52.7, 43.8, 28.4, 27.4, 21.6, 18.6; IR (neat) cm^{-1} 3414 (overtone), 2945, 2865, 2726, 2236, 1714, 1435, 1257, 1077, 753; HRMS (CI with NH_3) for $\text{C}_{10}\text{H}_{14}\text{O}_3$ $[\text{M}+\text{H}]^+$ calcd. 183.1021, found 183.1029; from CI with NH_3 , m/z (rel int) 183 (50.5), 200 (100); from EI 70 eV, m/z 41 (67.1), 79 (100), 111 (89.9), 139 (83.2), 151 (50.7), 183 (7.6).

7. Attempts to prepare alkynyl sulfoxide for intramolecular electrotelluration

(*R*_S)-2-[6-(Toluene-4-sulfinyl)-hex-5-ynyloxy]-tetrahydro-pyran (**25**): was made from (1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-*p*-toluenesulfinate¹¹ and 1-hex-5-ynyloxy-tetrahydro-pyran (**21b**) in 43% yield.¹² Besides obtaining the desired product (**25**), we also isolated another product (**25A**) in 6% yield which came from the Michael addition of the alkyne starting material (**21b**) to the desired product (**25**). Physical characterization of **25**: ¹H NMR (300 MHz, CDCl₃ and TMS) δ 7.65 (d, 2H, *J* = 8.2 Hz), 7.29 (d, 2H, *J* = 8.2 Hz), 4.49 (distorted t, 1H, *J* = 3.2 Hz), 3.81-3.47 (m, 2H), 3.45-3.29 (m, 2H), 2.42 (distorted t, 2H), 2.36 (s, 3H), 1.80-1.40 (m, 10H). HRMS (DCI with NH₃): [M+H]⁺ predicted 321.1524, observed 321.1529.

(7*Z*,*R*_S)-2-[11-(Tetrahydro-pyran-2-yloxy)-7-(toluene-4-sulfinylmethylene)-undec-5-ynyloxy]-tetrahydro-pyran (**25A**): ¹H NMR (300 MHz, CDCl₃ and TMS) δ 7.56 (d, 2H, *J* = 8.3 Hz), 7.31 (d, 2H, *J* = 8.3 Hz), 6.29 (s, 1H), 4.59-4.54 (m, 2H), 3.88-3.69 (m, 4H), 3.52-3.35 (m, 4H), 2.50 (t, 2H, *J* = 6.8 Hz), 2.41 (m, 3H), 2.24 (t, 2H, *J* = 7.6 Hz), 1.80-1.51 (m, 20H); HRMS (FAB⁺ in NBA w/Na⁺): [M+Na]⁺ predicted 525.2651, observed 525.2652. The alkene stereochemistry cannot be confirmed by NOE experiment because of overlapping peaks. Upon THP deprotection of compound **25A**, we obtained the diol **25B** which had a simpler ¹H NMR spectra that facilitated the confirmation of the alkene geometry by NOE experiment.

(7Z,*R_S*)-7-(Toluene-4-sulfinylmethylene)-undec-5-yne-1,11-diol (25B): ^1H NMR (500 MHz, CDCl_3 and TMS) δ : 7.55 (d, 2H, $J = 8.3$ Hz), 7.32 (d, 2H, $J = 8.3$ Hz), 7.27 (s, 1H), 3.69 (t, 2H, $J = 6.1$ Hz), 3.62 (t, 2H, $J = 6.3$ Hz), 2.51 (propargylic methylene, t, 2H, $J = 6.6$ Hz), 2.41 (s, 3H), 2.31 (br s, 1H), 2.25 (allylic methylene, t, 2H, $J = 7.3$ Hz), 2.05 (br s, 1H), 1.78-1.62 (m, 6H), 1.57-1.51 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 and TMS) δ 141.5, 141.4, 140.1, 136.0, 130.2, 124.1, 101.9, 77.4, 62.5, 62.3, 37.7, 32.0, 31.9, 24.8, 24.2, 21.6, 19.7; NOE (400 MHz, CDCl_3 and TMS) the allylic hydrogens enhanced 2.4% when the vinyl hydrogen was irradiated; IR (neat) cm^{-1} 3382 (br), 3023, 2937, 2866, 2219, 1581, 1493, 1455, 1332, 1079, 1025, 808, 732; HRMS (CI with NH_3): $[\text{M}+\text{H}]^+$ calcd. 335.1681, found 335.1680; from CI with NH_3 , m/z (rel int) 197 (37.2), 319 (55.2), 335 (100); from EI 70 eV, m/z (rel int) 91 (100), 124 (40.7), 149 (33.2).

(*R_S*)-6-(Toluene-4-sulfinyl)-hex-5-yn-1-ol (26): $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$; FW = 236; 89% yield; R_f = 0.29 (30:70 Hex:EtAc). ^1H NMR (300 MHz, CDCl_3 and TMS) δ 7.64 (d, 2H, $J = 8.1$ Hz), 7.29 (d, 2H, $J = 8.1$ Hz), 3.57 (distorted q, 2H, $J = 5.9$ Hz), 2.41 (t, 2H, $J = 6.6$ Hz), 2.36 (s, 3H), 2.15 (br s, 1H), 1.63-1.56 (m, 4H).

(2*E*,*R_S*)-2-(Toluene-4-sulfinylmethylene)-tetrahydropyran (27): $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$; FW = 236; R_f = 0.16 (30:70 Hex:EtAc); beside the set of peaks belonged to the starting material acetylenic sulfoxide (26) and the pyran (28), these peaks belonged to the pyran 27: ^1H NMR (400 MHz, CDCl_3 and TMS) δ 7.48 (d, 2H, $J = 8.1$ Hz), 7.22 (d, 2H, $J = 8.1$ Hz),

5.27 (s, 1H), 4.10-4.05 (m, 2H), 2.33 (s, 3H), 2.28-2.23 (m, 2H), 1.79-1.71 (m, 4H); NOE (400 MHz, CDCl₃ and TMS) irradiation of the alkene hydrogen did not show any no peak enhancement.

(2Z,R_S)-2-(Toluene-4-sulfinylmethylene)-tetrahydropyran (28): C₁₃H₁₆O₂S; FW = 236; R_f = 0.47 (30:70 Hex:EtAc); ¹H NMR (500 MHz, CDCl₃ and TMS) δ 7.51 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.3 Hz), 4.66 (t, 1H, J = 3.7 Hz), 3.97-3.94 (m, 2H), 3.48 (d, 1H, J = 12.9 Hz), 3.28 (d, 1H, J = 12.7 Hz), 2.39 (s, 3H), 2.02-1.96 (m, 2H), 1.79-1.76 (m, 2H); ¹³C NMR (100 MHz, CDCl₃ and TMS) δ 144.9, 141.6, 141.2, 129.8, 124.4, 103.5, 66.6, 64.1, 22.0, 21.5, 20.5; NOE (400 MHz, CDCl₃ and TMS) allylic hydrogens enhanced 0.6% when the vinylic hydrogen was irradiated; IR (neat) cm⁻¹ 3047, 2928, 2876, 2848, 2233, 1672, 1596, 1494, 1388, 1350, 1300, 1246, 1163, 1085, 1060, 1046, 933, 809, 730; HRMS (CI with NH₃) for C₁₃H₁₆O₂S [M+H]⁺ calcd. 237.0949, found 237.0958; from CI with NH₃, m/z (rel int) 99 (47.8), 221 (100), 237 (76.6); from EI 70 eV, m/z (rel int) 97 (100), 140 (24.7) 237 (1.8).

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