Supplementary Material for "An Expeditious Approach Toward the Total Synthesis of CP-263,114"

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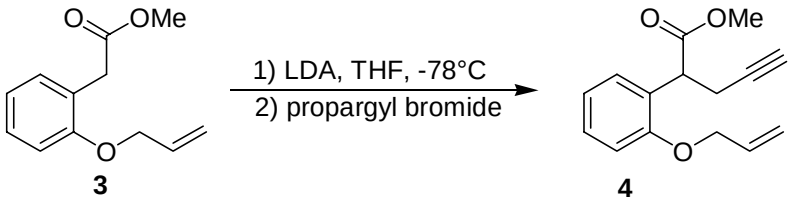
Organic Letters.

Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under a nitrogen atmosphere using freshly distilled solvents. All commercially-obtained reagents were used as received. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plated (0.25 mm). Silica gel (Particle size 0.032-0.063 mm) was used for flash chromatography. High-pressure liquid chromatography (HPLC) was performed with either a rainin Microsob 80-199-C5 or 80-120-C5 column. ^{1}H and ^{13}C NMR chemical shifts are reported as δ values relative to internal tetramethylsilane. Melting points are uncorrected. High-resolution mass spectra were acquired at The University if Illinois Mass Spectrometry Center. Single crystal X-ray analysis was performed by Dr. Susan Degala (Yale University).

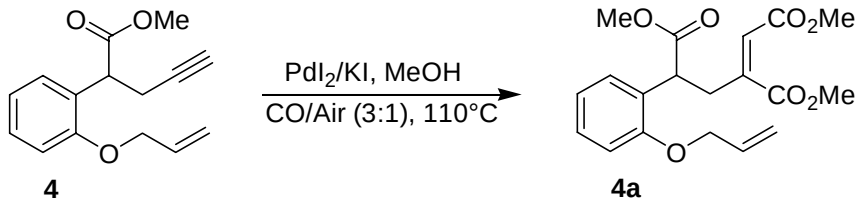
Preparation of Alkyne 4:



Alkyne 4. To a stirred solution of diisopropylamine (2180 ml, 15.52 mmol, 1.6 equiv) in THF (70 ml) at –78 °C was added BuLi (2.4M in hexanes: 5.5 ml, 13.10 mmol, 1.35 equiv). After stirring the reaction mixture for 45 minutes, **3** (2000 mg, 9.70 mmol, 1 equiv) dissolved in THF (30 ml) was added dropwise at –78 °C and stirred for additional 40 minutes. At this point propargyl bromide (80% wt in toluene: 2.2 ml, 19.40 mmol, 2 equiv) was added, the reaction mixture warmed to –50 °C and kept at that temperature for 1 h. The reaction mixture was quenched by the addition of saturated ammonium chloride (50 ml) and extracted with EtOAc (3 X 50 ml). The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and passed through a silica plug furnishing **4** (2300 mg, 97% yield) as a clear oil

Alkyne 4. FTIR (thin film/NaCl) 3291 (m), 2951 (w), 1736 (s), 1600 (w), 1588 (w), 1493 (m), 1453 (m), 1434 (m), 1343 (w), 1244 (s), 1227 (s), 1167 (m), 1117 (w), 1019 (w), 997 (w), 929 (w), 753 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 6.94 (dt, *J*=7.5, 1.5 Hz, 1H), 6.87 (dd, *J*=8.5, 1.5 Hz, 1H), 6.06-5.98 (m, 1H), 5.41 (dq, *J*=17.0, 2.0 Hz, 1H), 5.27 (dq, *J*=17.0, 2.0 Hz, 1H), 4.59-4.51 (m, 2H), 4.14 (t, *J*=7.5 Hz, 1H), 3.67 (s, 3H), 2.94 (ddd, *J*=17.5, 7.0, 2.0 Hz, 1H), 2.69 (ddd, *J*=17.5, 7.0, 2.0 Hz, 1H), 1.93 (t, *J*=2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 155.9, 133.1, 129.5, 128.8, 126.8, 120.9, 117.3, 112.1, 82.2, 69.7, 69.0, 52.2, 45.2, 21.6; HRMS (EI) *m/z* 244.1102 [calc'd for $C_{15}H_{16}O_3$ (M+) 244.1099].

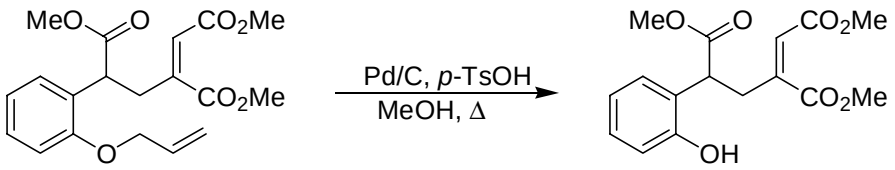
Preparation of Maleate 4a:



Maleate 4a. To alkyne **4** (5280 mg, 21.61 mmol, 1 equiv) dissolved in MeOH (100 ml) was added potassium iodide (72 mg, 0.43 mmol, 0.02 equiv) and PdI_2 (16 mg, 0.04 mmol, 0.002 equiv). This mixture was transferred to a stainless steel autoclave (300 ml). The autoclave was pressurized with CO (450 psi) and air (600 psi). The reaction mixture was stirred and heated at 110 °C for 24 h. The autoclave was cooled to room temperature, the mixture diluted with CH_2Cl_2 (150 ml) and filtered through a Celite cake with a thin charcoal layer on top, followed by a short silica plug, giving **4a** (5.34 g, 66% yield) as a clear oil.

Maleate 4a. FTIR (thin film/NaCl) 3005 (w), 2952 (m), 1735 (s), 1650 (w), 1600 (w), 1493 (m), 1452 (m), 1435 (w), 1371 (w), 1265 (m), 1200 (m), 1168 (m), 1115 (w), 1021 (w), 997 (w), 755 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (ddd, *J*=8.0, 7.5, 2.0 Hz, 1H), 7.17 (dd, *J*=8.0, 1.5 Hz, 1H), 6.91 (dt, *J*=7.5, 1.5 Hz, 1H), 6.86 (d, *J*=8.0 Hz, 1H), 6.06-5.99 (m, 1H), 5.74 (t, *J*=1.0 Hz, 1H), 5.40 (dq, *J*=17.5, 1.5 Hz, 1H), 5.28 (dq, *J*=17.5, 1.5 Hz, 1H), 4.59-4.51 (m, 2H), 4.22 (t, *J*=2.5 Hz, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 3.65 (s, 3H), 3.15 (ddd, *J*=14.5, 7.5, 1.0 Hz, 1H), 2.73 (ddd, *J*=14.5, 7.5, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 168.7, 165.5, 155.8, 146.6, 133.2, 129.2, 128.9, 126.7, 122.5, 121.2, 117.5, 112.2, 69.1, 52.5, 52.3, 52.0, 43.7, 36.7; HRMS (EI) *m/z* 362.1367 [calc'd for $C_{19}H_{22}O_7$ (M+) 362.1366].

Preparation of Phenol 5:

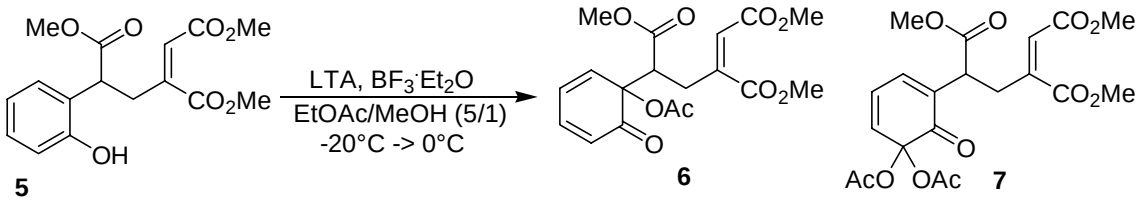


4a **5**

Phenol 5. To a stirred solution of **4a** (5650 mg, 15.6 mmol, 1 equiv) in MeOH (150 ml) was added Pd/C (3000 mg) and *p*-TsOH (1000 mg, 5.26 mmol, 0.34 equiv). The reaction mixture was refluxed for 24 h, concentrated *in vacuo*, diluted with CH_2Cl_2 (50 ml) and brine (50 ml) and extracted with CH_2Cl_2 (5 X 50 ml). The combined organic layers were combined, concentrated, and passed through a short silica plug furninshing **5** (4554 mg, 91% yield).

Phenol 5. FTIR (thin film/NaCl) 3425 (m), 3003 (w), 2953 (m), 2847 (w), 1729 (s), 1650 (m), 1597 (m), 1505 (m), 1457 (m), 1437 (m), 1372 (m), 1273 (s), 1206 (s), 1170 (s), 1119 (w), 1100 (w), 1024 (w), 971 (w), 835 (w), 757 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (dt, *J*=8.0, 1.5 Hz, 1H), 7.09-7.07 (m, 2H), 6.88-6.85 (m, 2H), 5.79 (t, *J*=1.0 Hz, 1H), 4.10 (t, *J*=7.5 Hz, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 3.15 (ddd, *J*=14.0, 7.5, 1.5 Hz, 1H), 2.82 (ddd, *J*=14.0, 7.5, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 168.9, 165.4, 154.4, 145.3, 129.5, 129.4, 123.5, 123.3, 121.2, 117.7, 52.9, 52.1, 45.5, 36.1; HRMS (EI) *m/z* 322.1044 [calc'd for $C_{16}H_{18}O_7$ (M+) 322.1053].

Preparation of Acetates 6 and 7:



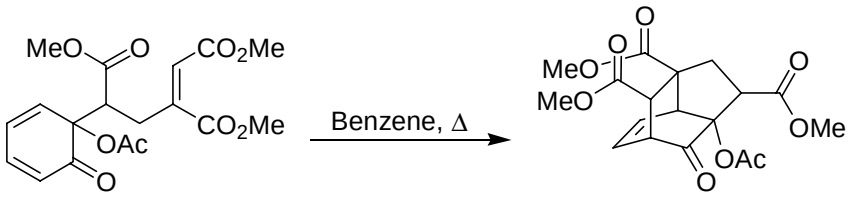
Acetates 6 and 7. Lead(IV) tetraacetate (834 mg, 1.88 mmol, 1.5 equiv) was dissolved in a dry mixture og EtOAc (2 ml) and MeOH (0.5 ml) and cooled to –20 °C. Next MeOH (0.5 ml) was added followed by $BF_3{\cdot}OEt_2$ (0.4 ml, 3.13 mmol, 2.5 equiv) dissolved in a mixture of EtOAc (2 ml) and MeOH (0.4 ml) and **5** (415 mg, 1.25 mmol, 1 equiv) dissolved in a mixture of EtOAc (0.8 ml) and MeOH (0.2 ml). The reaction mixture was warmed to 0 °C and stirred for 1 h at which point ethylene glycol (0.1 ml) was added followed by careful addition of saturated $NaHCO_3$ (5 ml). The crude reaction mixture was filtered through a Celite cake and washed thoroughly with EtOAc. The mixture was poured into a separatory funnel, phases separated and the aqueous phase extracted with EtOAc (3 X 20 ml). The combined organic layers were dried over $MgSO_4$ and concentrated yielding a crude 3:1 mixture of **7**:**6**. This mixture was purified using silica gel chromatography furnishing **7** (328 mg, 60% yield) as a clear oil and **6** (95 mg, 20% yield) as a clear oil.

Acetate 6. FTIR (thin film/NaCl) 2953 (w), 1736 (s), 1677 (m), 1652 (w), 1436 (m), 1372 (m), 1270 (m), 1232 (s), 1202 (m), 1171 (m), 1021 (m), 761 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (ddd, *J*=9.5, 6.0, 2.0 Hz, 1H), 6.45 (ddd, *J*=10.0, 6.0, 1.0 Hz, 1H), 6.37 (ddd, *J*=10.0, 1.5, 0.5 Hz, 1H), 6.24 (d, *J*=10.0 Hz, 1H), 5.87 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.70

(s, 3H), 3.17 (dd, *J*=12.5, 3.5 Hz, 1H), 2.66 (ddd, *J*=14.5, 11.5, 1.0 Hz, 1H), 2.53 (ddd, *J*=14.5, 3.0, 1.5 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 170.5, 168.9, 167.6, 165.3, 143.7, 140.0, 137.7, 128.0, 125.6, 124.1, 78.7, 52.7, 52.6, 52.4, 52.2, 29.9, 20.5; HRMS (EI) *m/z* 380.1111 [calc'd for $C_{18}H_{20}O_9$ (M+) 380.1107].

Acetate 7. FTIR (thin film/NaCl) 3002 (w), 2954 (m), 2846 (w), 1738 (s), 1691 (m), 1650 (m), 1436 (m), 1403 (m), 1372 (m), 1268 (m), 1225 (s), 1202 (m), 1170 (m), 1126 (w), 1013 (s), 975 (w), 919 (w), 755 (w), 733 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (dt, *J*=6.5, 0.5 Hz, 1H), 6.44 (dd, *J*=10.0, 6.5 Hz, 1H), 6.19 (dd, *J*=9.5, 1.0 Hz, 1H), 5.95 (t, *J*=1.0 Hz, 1H), 3.87-3.80 (m, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.01 (ddd, *J*=14.0, 7.5, 1.5 Hz, 1H), 2.59 (ddd, *J*=14.0, 7.5, 1.5 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 168.0, 167.9, 165.5, 146.1, 135.8, 135.2, 130.3, 128.1, 123.1, 92.6, 52.6, 52.5, 52.0, 42.8, 35.6, 20.5; HRMS (EI) *m/z* 438.1152 [calc'd for $C_{20}H_{22}O_{11}$ (M+) 438.1162].

Preparation of Diels-Alder Adduct 8:

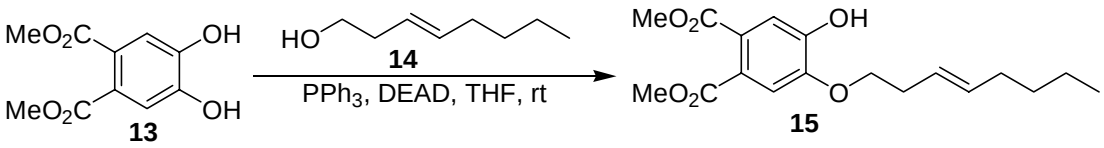


6 **8**

Diels-Alder adduct 8. A benzene solution (15 ml) **6** (44 mg, 0.116 mmol, 1 equiv) was refluxed overnight for 12 h. The reaction mixture was cooled to room temperature, concentrated *in vacuo*, and passed through a small silica plug furnishing pure **8** (42 mg, 95% yield).

Diels-Alder adduct 8. FTIR (thin film/NaCl) 2954 (w), 1741 (s), 1435 (m), 1368 (m), 1262 (m), 1218 (s), 1175 (m), 1125 (w), 1087 (w), 1062 (w), 1015 (w), 915 (w), 728 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 (ddd, *J*=8.0, 6.5, 1.0 Hz, 1H), 6.29 (ddd, *J*=8.0, 6.5, 1.0 Hz, 1H), 389 (dd, *J*=6.5, 1.5 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.64 (s, 3H), 3.64-3.63 (m, 1H), 3.16 (dd, *J*=9.0, 6.5 Hz, 1H), 2.96 (d, *J*=3.0 Hz, 1H), 2.70 (dd, *J*=14.0, 7.0 Hz, 1H), 2.22 (dd, *J*=14.0, 9.0 Hz, 1H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 172.5, 172.2, 170.4, 168.6, 131.1, 126.7, 81.3, 54.5, 52.7, 52.6, 52.6, 52.5, 51.2, 48.7, 46.3, 38.6, 21.0; HRMS (EI) *m/z* 380.1052 [calc'd for $C_{18}H_{20}O_9$ (M+) 380.1107].

Preparation of Phenol 15:

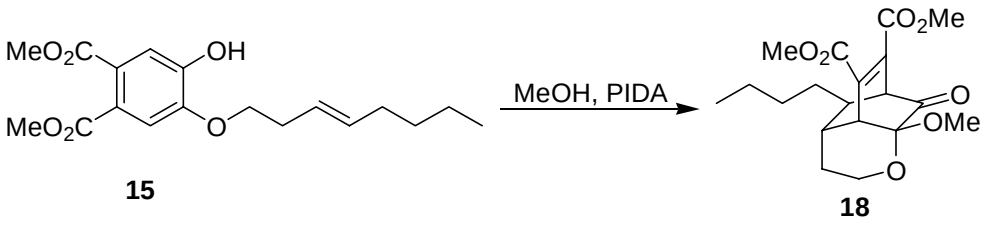


Phenol 15. To a stirred mixture of PPh_3 (3014 mg, 11.5 mmol, 1.3 equiv) in THF (80 ml) at room temperature (reaction vessel wrapped with aluminum foil) was added DEAD (2000 mg, 11.5 mmol, 1.3 equiv) and stirring continued for 10 min at which point **14** (1132 mg, 8.85 mmol, 1.0 equiv) was added. After stirring for 10 min **13** (6000 mg, 26.55 mmol, 3.0 equiv) dissolved in THF (20 ml) was added quickly and stirred for another 12 h. The reaction mixture was concentrated *in vacuo*, and purified via silica gel chromatography using 10-25% EtOAc/Hexanes as the eluent furnishing **15** (2150 mg, 72% yield) as a clear oil.

Phenol 15. FTIR (thin film/NaCl) 3419 (m), 2954 (m), 2928 (m), 2857 (m), 1724 (s), 1613 (m), 1580 (m), 1517 (m), 1436 (m), 1366 (m), 1303 (s), 1262 (m), 1200 (m), 1054 (w),

1012 (w), 972 (m), 783 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.19 (s, 1H), 6.11 (s, 1H), 5.56 (m, 1H), 5.41 (m, 1H), 4.08 (t, *J*=7.2 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.48 (dq, *J*=6.8, 1.2 Hz, 2H), 1.99 (dd, *J*=13.2, 6.8 Hz, 2H), 1.34-1.25 (m, 4H), 0.87 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 167.7, 148.3, 147.4, 134.4, 126.6, 124.6, 124.0, 115.2, 112.5, 69.1, 52.7, 52.6, 32.4, 31.6, 22.3, 14.0; HRMS (EI) *m/z* 336.1581 [calc'd for $C_{18}H_{24}O_6$ (M+) 336.1573].

Preparation of Methyl Acetal 18:



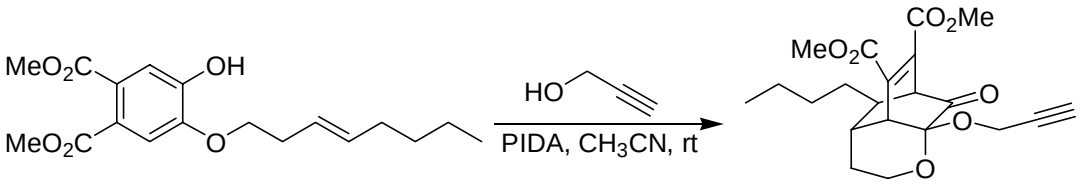
15 **18**

Methyl Acetal 18. To a stirred solution of **15** (47 mg, 0.14 mmol, 1 equiv) in MeOH (1.5 ml) was added PIDA (54 mg, 0.17 mmol, 1.2 equiv). Upon addition of PIDA, the reaction mixture went immediately from being colorless to clear yellow and upon stirring at room temperature for 2 h it went clear again. The reaction mixture was concentrated *in vacuo* and passed through a silica plug furnishing analytically pure **18** (36 mg, 70% yield) as a clear oil.

Methyl Acetal 18. FTIR (thin film/NaCl) 2953 (m), 2930 (m), 2858 (w), 1736 (s), 1723 (s), 1642 (w), 1436 (m), 1357 (w), 1278 (s), 1247 (m), 1178 (w), 1148 (w), 1083 (s), 1033 (w), 767 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.95 (dd, *J*=12.0, 6.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.59 (dt, *J*=12.8, 3.0 Hz, 1H), 3.53 (d, *J*=2.5 Hz, 1H), 3.40 (s, 3H), 3.17 (d, *J*=3.0 Hz, 1H), 1.99-1.90 (m, 3H), 1.56-1.52 (m, 1H), 1.43-1.41 (m, 1H), 1.29-1.25 (m, 5H), 0.87 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 165.5, 138.8, 133.8, 91.9, 61.6, 55.0, 52.8, 51.5,

45.8, 41.2, 35.9, 34.7, 29.4, 29.3, 22.6, 14.1; HRMS (CI) *m/z* 367.1760 [calc'd for $C_{19}H_{26}O_7$ (M+H) 367.1757].

Preparation of Propargyl Acetal 19:



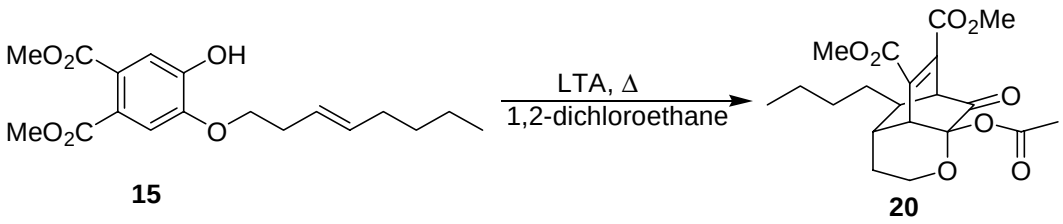
15 **19**

Propargyl Acetal 19. To a stirred solution of **15** (82 mg, 0.24 mmol, 1 equiv) and propargyl alcohol (285 µl, 4.88 mmol, 20 equiv) in CH_3CN (2 ml) was added PIDA (86 mg, 0.27 mmol, 1.1 equiv). Upon addition of PIDA, the reaction mixture went immediately from being colorless to yellow and upon stirring at room temperature overnight it became clear again. The reaction mixture was concentrated *in vacuo* and passed through a silica plug employing 4% Et_3N/18% EtOAc/Hexanes as the eluent yielding **19** (90 mg, 95% yield) as an oil.

Propargyl Acetal 19. FTIR (thin film/NaCl) 3280 (m), 2955 (s), 2930 (s), 2873 (m), 2858 (m), 1722 (s), 1642 (m), 1436 (m), 1358 (m), 1279 (s), 1247 (s), 1173 (m), 1145 (m), 1083 (s), 1032 (m), 1008 (m), 959 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.54 (dd, *J*=15.5, 2.5 Hz, 1H), 4.32 (dd, *J*=16.0, 2.5 Hz, 1H), 3.97 (dd, *J*=12.5, 5.5 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.58 (dt, *J*=13.0, 3.0 Hz, 1H), 3.55 (d, *J*=2.5 Hz, 1H), 3.20 (d, *J*=3.5 Hz, 1H), 2.36 (t, *J*=2.5 Hz, 1H), 2.05-1.97 (m, 1H), 1.94-1.88 (m, 2H), 1.59-1.53 (m, 2H), 1.41 (app t, *J*=7.0 Hz, 1H), 1.31-1.22 (m, 4H), 0.87 (t, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 165.5, 165.4, 138.7,

133.5, 91.6, 80.0, 74.1, 61.6, 54.9, 52.8, 52.2, 46.2, 41.2, 35.7, 29.3, 22.6, 14.1; HRMS (CI) *m/z* 391.1759 [calc'd for $C_{21}H_{26}O_7$ (M+H) 391.1757].

Preparation of Acetate 20:

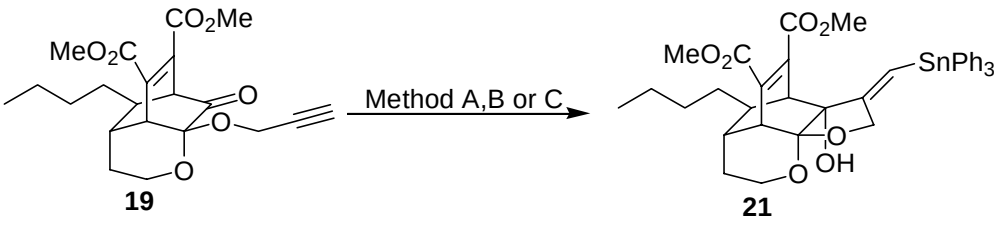


15 **20**

Acetate 20. To a stirred solution of **15** (157 mg, 0.47 mmol, 1 equiv) in CH_2ClCH_2Cl (8 ml) at reflux was added LTA (230 mg, 0.51 mmol, 1.1 equiv) dissolved in CH_2ClCH_2Cl (3 ml) via syringe pump dropwise over 5 min. The reaction mixture was stirred at reflux for a further 30 min before being cooled and solution filtered through a Celite cake and washed with CH_2Cl_2. Concentration *in vacuo* gave mostly pure **20** as an oil. Purification using silica gel chromatography furnished pure **20** (166 mg, 90% yield) as a clear oil.

Acetate 20. FTIR (thin film/NaCl) 2954 (m), 2928 (m), 2858 (w), 1742 (s), 1723 (s), 1642 (w), 1436 (m), 1366 (w), 1277 (s), 1250 (m), 1219 (w), 1087 (s), 1029 (w), 959 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.09-4.06 (m, 1H), 3.87 (d, *J*=3.5 Hz, 1H), 3.84-3.80 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.71 (dt, *J*=12.5, 3.5 Hz, 1H), 2.12-2.06 (m, 1H), 2.04 (s, 3H), 2.00 (t, *J*=3.5 Hz, 1H), 1.94-1.91 (m, 1H), 1.60 (q, *J*=3.0 Hz, 1H), 1.58 (br s, 1H), 1.43-1.39 (m, 1H), 1.31-1.25 (m, 4H), 0.88 (t, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 168.8, 166.5, 164.0, 140.8, 131.5, 92.1, 62.5, 53.1, 52.9, 44.7, 40.7, 36.0, 34.7, 29.2, 29.0, 22.6, 21.5, 14.2; HRMS (CI) *m/z* 395.1703 [calc'd for $C_{20}H_{26}O_8$ (M+H) 395.1706].

Preparation of Vinylstannane 21:



19 **21**

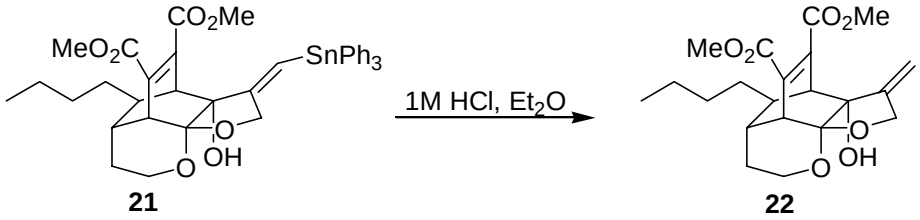
Vinylstannane 21. **Method A**: To a stirred, degassed solution of alkyne **19** (140 mg, 0.36 mmol, 1 equiv) in toluene (22 ml) was added Ph_3SnH (550 μl, 2.16 mmol, 6 equiv) and Et_3B (1.0M solution in hexanes: 1076 μl, 1.08 mmol, 3 equiv), in 6 portions over a 24 h period at room temperature. The crude reaction mixture was put directly onto a silica gel column and purified using 15-20% EtOAc/Hexanes as the eluent furnishing **21** (240 mg, 90% yield) as a white solid.

Method B: A mixture of alkyne **19** (654 mg, 1.68 mmol, 1 equiv), AIBN (276 mg, 1.68 mmol, 1 equiv) and Ph_3SnH (882 mg, 2.51 mmol, 1.5 equiv) in toluene (24 ml) was degassed with argon for 30 min. The reaction mixture was photolyzed whith argon bubbling for 1 h. The crude reaction mixture was put directly onto a silica gel column and purified using 15-20% EtOAc/Hexanes as the eluent furnishing **21** (875 mg, 70% yield) as a white solid.

Method C: A mixture of alkyne **19** (75 mg, 0.19 mmol, 1 equiv), AIBN (32 mg, 0.19 mmol, 1 equiv) and Ph_3SnH (101 mg, 0.29 mmol, 1.5 equiv) in benzene (4 ml) was heated at reflux overnight. The crude reaction mixture was put directly onto a silica gel column and purified using 15-20% EtOAc/Hexanes as the eluent furnishing **21** (42 mg, 29% yield) as a white solid.

Vinylstannane 21. m.p. 164-167 °C; FTIR (thin film/NaCl) 3416 (m), 3064 (w), 3046 (w), 2952 (m), 2926 (m), 2855 (w), 1719 (s), 1641 (w), 1480 (w), 1457 (w), 1430 (w), 1359 (w), 1275 (s), 1130 (w), 1076 (m), 1054 (w), 997 (w), 910 (w), 730 (s), 699 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.32 (m, 15H), 6.58 (t, *J*=2.4 Hz, 1H), 4.46 (ddd, *J*=12.0, 10.8, 4.8 Hz, 1H), 4.37 (dd, *J*=14.0, 2.4 Hz, 1H), 4.03 (dd, *J*=14.0, 2.4 Hz, 1H), 3.96 (ddd, *J*=11.6, 6.0, 2.4 Hz, 1H), 3.79 (s, 3H), 3.50 (s, 3H), 3.46 (d, *J*=2.0 Hz, 1H), 2.90 (s, 1H), 2.89 (d, *J*=2.0 Hz, 1H), 2.15-2.12 (m, 1H), 2.00-1.91 (m, 1H), 1.70 (br s, 1H), 1.63-1.58 (m, 1H), 1.31-1.26 (m, 5H), 1.18-1.14 (m, 1H), 0.89 (t, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.1, 164.5, 141.4, 137.5, 137.2, 137.0, 136.9, 135.6, 129.4, 129.1, 128.9, 128.6, 118.3, 106.3, 81.1, 72.3, 62.6, 52.6, 52.3, 48.1, 47.4, 37.6, 35.7, 29.8, 29.2, 22.8, 14.3; HRMS (EI) *m/z* 742.1969 [calc'd for $C_{39}H_{42}O_7Sn$ (M+H) 742.0112].

Preparation of Alcohol 22:

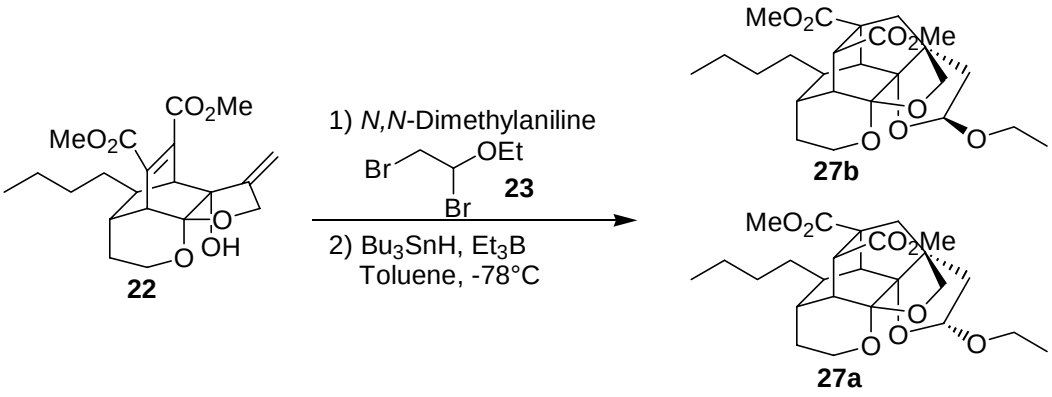


Alcohol 22. To solid **21** (333 mg, 0.45 mmol, 1 equiv) was added 1M HCl in Et_2O (9 ml) and stirred for 9 h at room temperature. The reaction mixture was quenched by the addition of saturated $NaHCO_3$ (20 ml), and extracted with CH_2Cl_2 (4 X 15 ml) and EtOAc (2 X 20 ml). The combined organic layers were dried over Na_2SO_4 and filtered through a Celite plug and washed thoroughly with CH_2Cl_2. The filtrate was concentrated *in vacuo* and purified using silica

gel chromatography employing CH_2Cl_2-50% EtOAc/Hexanes as the gradient yielding **22** (159 mg, 90% yield) as a clear oil.

Alcohol 22. FTIR (thin film/NaCl) 3433 (m), 2954 (s), 2927 (s), 2858 (m), 2253 (w), 1721 (s), 1642 (m), 1435 (m), 1360 (m), 1278 (s), 1216 (m), 1195 (m), 1134 (m), 1086 (m), 1054 (m), 1019 (m), 961 (w), 909 (m), 809 (w), 799 (w), 770 (w), 732 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.28 (t, *J*=2.5 Hz, 1H), 5.00 (t, *J*=2.5 Hz, 1H), 4.54 (dt, *J*=13.5, 2.5 Hz, 1H), 4.46 (ddd, *J*=12.0, 11.0, 4.5 Hz, 1H), 4.15 (dt, *J*=13.5, 2.5 Hz, 1H), 3.99-3.95 (m, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.31 (d, *J*=2.0 Hz, 1H), 2.92 (d, *J*=3.0 Hz, 1H), 2.91 (s, 1H), 2.11-2.09 (m, 1H), 1.67-1.59 (m, 2H), 1.32-1.23 (m, 5H), 1.13-1.08 (m, 1H), 0.86 (s, 3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 165.5, 152.3, 140.4, 136.1, 108.0, 106.2, 80.3, 70.8, 62.5, 52.5, 52.5, 48.3, 46.8, 37.4, 36.4, 35.6, 29.7, 22.8, 14.2; HRMS (EI) *m/z* 392.1828 [calc'd for $C_{21}H_{28}O_7$ (M+) 392.1835].

Preparation of Acetals 27a and 27b:



Acetlas 27a and 27b. To a stirred solution of **22** (800 mg, 2.04 mmol, 1 equiv) in CH_2Cl_2 (15 ml) was added dibromoacetal **23** (4730 mg, 20.41 mmol, 10 equiv) and *N*,*N*-dimethylaniline (5.2 ml, 40.82 mmol, 20 equiv). The reaction was stirred at room temperature

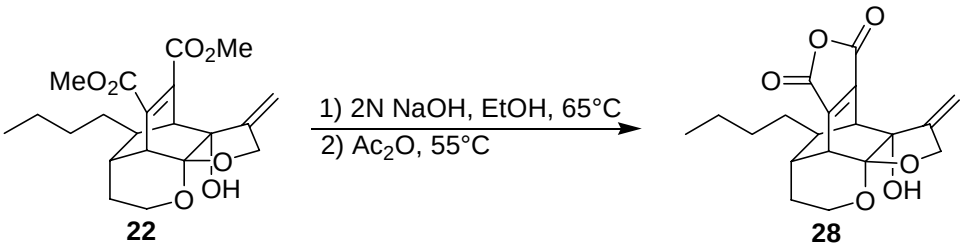
for 5 h, at which point it was quenched with water (20 ml) and diluted with EtOAc (150 ml). The organic layer was washed consecutively with 2M HCl (3 X 100 ml), $NaHCO_3$ (50 ml), and brine (50 ml) and then dried over Na_2SO_4. The solution was concentrated *in vacuo* to yield almost pure bromoacetal **27** (1050 mg, 95% yield) that was carried directly to the next step without further purification. To a stirred solution of the bromoacetal and Bu_3SnH (1370 μl, 5.1 mmol, 2.5 equiv) in toluene (55 ml) at –78 °C was added Et_3B (1.0M solution of hexanes: 6.1 ml, 6.12 mmol, 3 equiv). The reaction mixture was stirred under an atmosphere of nitrogen using a balloon for 3 h at room temperature. The crude reaction mixture was poured onto a silica gel column and eluted with 10-30% EtOAc/Hexanes furnishing **27b** (420 mg, 44% yield, eluted first) as a clear oil and **27a** (400 mg, 42 % yield, eluted second) as a white solid.

Acetal 27b. FTIR (thin film/NaCl) 2954 (m), 2924 (m), 1730 (s), 1457 (w), 1436 (w), 1252 (w), 1226 (m), 1123 (m), 1094 (s), 1022 (w), 1001 (w), 983 (w), 951 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.46 (d, *J*=5.5 Hz, 1H), 4.45 (d, *J*=8.0 Hz, 1H), 4.24 (ddd, *J*=13.5, 12.0, 3.5 Hz, 1H), 3.87-3.83 (m, 1H), 3.79 (dd, *J*=12.0, 6.0 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.63 (d, *J*=8.0 Hz, 1H), 3.63-3.42 (m, 1H), 3.16 (s, 1H), 2.98 (d, *J*=14.0 Hz, 1H), 2.52 (d, *J*=3.0 Hz, 2H), 1.30 (d, *J*=14.0 Hz, 1H), 2.18 (d, *J*=13.0 Hz, 1H), 2.07 (dd, *J*=13.5, 5.5 Hz, 1H), 1.99-1.91 (m, 1H), 1.78 (t, *J*=3.0 Hz, 1H), 1.71-1.57 (m, 3H), 1.38-1.12 (m, 2H), 1.19 (t, *J*=7.0 Hz, 3H), 0.96-0.85 (m, 1H), 0.92 (t, *J*=7.0 Hz, 2H), 0.87 (t, *J*=6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 172.4, 110.2, 108.0, 103.3, 77.1, 63.1, 61.6, 58.0, 54.5, 53.7, 52.7, 51.7, 44.8, 43.5, 42.8, 42.7, 39.7, 35.3, 33.6, 32.1, 30.2, 28.5, 27.0, 23.0, 17.5, 15.2, 14.2, 13.8; HRMS (EI) *m/z* 464.2410 [calc'd for $C_{25}H_{36}O_8$ (M+) 464.2410].

Acetal 27a. m.p. 138-139 °C; FTIR (thin film/NaCl) 2954 (s), 2928 (s), 2871 (s), 1736 (s), 1726 (s), 1461 (m), 1433 (m), 1376 (w), 1275 (m), 1227 (s), 1170 (m), 1121 (m), 1093 (s),

1060 (m), 1024 (m), 992 (m), 970 (m), 907 (w), 731 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (dd, *J*=6.0, 4.0 Hz, 1H), 4.22 (dt, *J*=6.8, 3.6 Hz, 1H), 3.88-3.70 (m, 4H), 3.72 (s, 3H), 3.65 (s, 3H), 3.59-3.51 (m, 1H), 3.19 (s, 1H), 3.01 (d, *J*=3.2 Hz, 1H), 2.88 (d, *J*=14.4 Hz, 1H), 2.56 (dd, *J*=2.8, 0.8 Hz, 1H), 2.52 (d, *J*=14.4 Hz, 1H), 2.44 (dd, *J*=14.0, 6.0 Hz, 1H), 2.00-1.93 (m, 1H), 1.93 (dd, *J*=14.0, 3.6 Hz, 1H), 1.78 (t, *J*=3.6 Hz, 1H), 1.71-1.70 (m, 1H), 1.33 (dt, *J*=13.2, 2.8 Hz, 1H), 1.26-1.24 (m, 9H), 0.87 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 172.3, 110.8, 107.8, 101.9, 77.1, 64.3, 62.4, 58.6, 53.0, 52.7, 52.4, 51.8, 44.9, 43.7, 42.3, 41.8, 39.9, 35.1, 33.8, 31.8, 30.2, 22.8, 15.5, 14.2; HRMS (EI) *m/z* 464.2410 [calc'd for $C_{25}H_{36}O_8$ (M+) 464.2410].

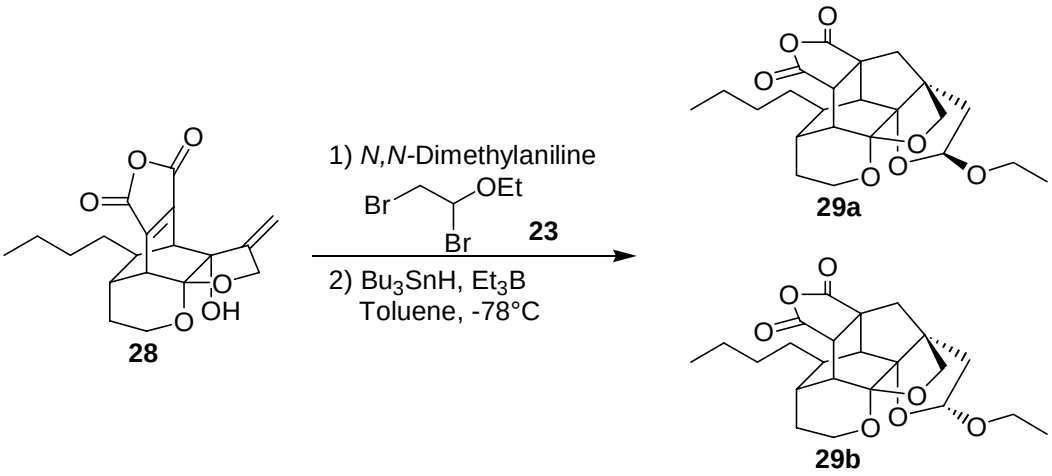
Preparation of Anhydride 28:



Anhydride 28. To a stirred solution of **22** (157 mg, 0.4 mmol, 1 equiv) was added 2N NaOH (1.6 ml, 3.2 mmol, 8 equiv) in EtOH (1.6 ml) and heated at 65 °C for 3h. The reaction mixture was then cooled, quenced by the addition of 1N HCl (3.5 ml), and extracted with EtOAc (5 X 15 ml). The combined organic layers were dried over Na_2SO_4, evaporated and the resulting solid dissolved in Ac_2O (3 ml) and heated at 65°C for 3 h. After cooling, the Ac_2O was evaporated and azeotroped with toluene, furnishing a mostly pure solid that was passed through a small silica plug to obtain analytically pure **28** (125 mg, 90% yield).

Anhydride 28. m.p. 149-150 °C; FTIR (thin film/NaCl) 3422 (m), 2958 (m), 2928 (m), 2858 (m), 1844 (m), 1775 (s), 1660 (w), 1467 (w), 1320 (w), 1260 (w), 1193 (w), 1145 (w), 1119 (w), 1090 (m), 1074 (m), 1052 (m), 1006 (m), 911 (m), 878 (m), 758 (w), 740 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27 (t, *J*=1.5 Hz, 1H), 5.00 (t, *J*=1.5 Hz, 1H), 4.54-4.47 (m, 2H), 4.08 (ddd, *J*=12.0, 7.0, 3.0 Hz, 1H), 3.99 (dt, *J*=12.5, 1.5 Hz, 1H), 3.51 (d, *J*=2.0 Hz, 1H), 3.21 (d, *J*=3.0 Hz, 1H), 3.13 (br s, 1H), 2.34-2.31 (m, 1H), 2.06-2.01 (m, 1H), 1.75-1.68 (m, 2H), 1.30-1.23 (m, 5H), 1.06-1.02 (m, 1H), 0.87 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 161.4, 150.9, 150.2, 148.6, 108.6, 106.4, 81.1, 70.4, 63.0, 44.5, 41.6, 38.1, 37.7, 36.0, 29.5, 18.7, 22.7, 14.1; HRMS (EI) *m/z* 346.1409 [calc'd for $C_{19}H_{22}O_6$ (M+) 346.1416].

Preparation of Anhydrides 29a and 29b:

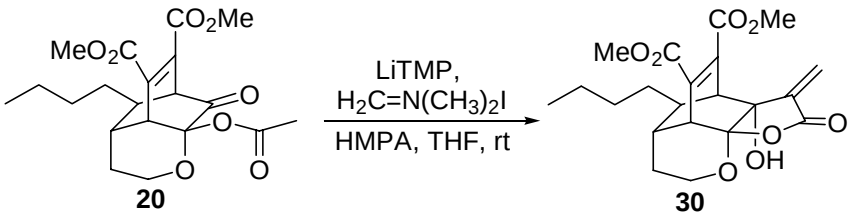


Anhydrides 29a and 29b. These were prepared in the same manner as **27a** and **27b**, giving **29a** (45% yield, eluted first) as a white solid and **29b** (45% yield, eluted second) also as a white solid.

Anhydride 29a. FTIR (thin film/NaCl) 2957 (m), 2930 (m), 2872 (w), 1842 (w), 1780 (s), 1482 (w), 1453 (w), 1377 (w), 1233 (m), 14190 (m), 1129 (m), 1004 (s), 963 (w), 938 (s), 916 (m), 730 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (d, *J*=5.5 Hz, 1H), 4.63 (d, *J*=8.5 Hz, 1H), 4.27 (ddd, *J*=18.0, 8.0, 3.0 Hz, 1H), 3.89-3.81 (m, 3H), 3.45-3.39 (m, 1H), 3.25 (d, *J*=4.5 Hz, 1H), 2.54 (d, *J*=13.5 Hz, 1H), 2.45 (d, *J*=2.5 Hz, 1H), 2.24 (dd, *J*=4.5, 3.0 Hz, 1H), 2.28 (d, *J*=14.0 Hz, 1H), 2.09 (dd, *J*=13.5, 2.5 Hz, 1H), 1.98-1.91 (m, 1H), 1.87-1.80 (m, 3H), 1.38-1.18 (m, 10H), 0.83 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 171.2, 110.5, 107.7, 103.2, 78.2, 63.5, 61.6, 58.5, 53.2, 52.1, 47.5, 47.2, 42.6, 41.0, 34.6, 32.6, 31.3, 30.4, 22.7, 15.2, 14.1; HRMS (EI) *m/z* 418.1983 [calc'd for $C_{23}H_{30}O_7$ (M+) 418.1992].

Anhydride 29b. FTIR (thin film/NaCl) 2957 (m), 2918 (m), 2873 (w), 1850 (w), 1779 (s), 1231 (m), 1168 (w), 1120 (m), 1094 (m), 1068 (m), 1021 (w), 988 (m), 962 (m), 937 (m), 921 (m), 731 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 (dd, *J*=6.0, 3.0 Hz, 1H), 4.25 (ddd, *J*=13.5, 12.0, 4.0 Hz, 1H), 3.94-3.88 (m, 3H), 3.84-3.78 (m, 1H), 3.57-3.51 (m, 1H), 3.21 (d, *J*=4.5 Hz, 1H), 3.01 (d, *J*=2.5 Hz, 1H), 2.73 (d, *J*=13.5 Hz, 1H), 2.50 (dd, *J*=6.5, 4.0 Hz, 1H), 2.34 (dd, *J*=5.0, 3.0 Hz, 1H), 1.99-1.92 (m, 2H), 1.89-1.82 (m, 3H), 1.40-1.22 (m, 10H), 0.88 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 171.1, 111.1, 107.3, 102.0, 78.0, 64.5, 62.4, 59.0, 51.3, 51.0, 47.2, 46.8, 43.9, 40.2, 34.5, 32.6, 31.1, 30.3, 22.6, 15.4, 14.1; HRMS (EI) *m/z* 418.2000 [calc'd for $C_{23}H_{30}O_7$ (M+) 418.1992].

Preparation of Lactone 30:

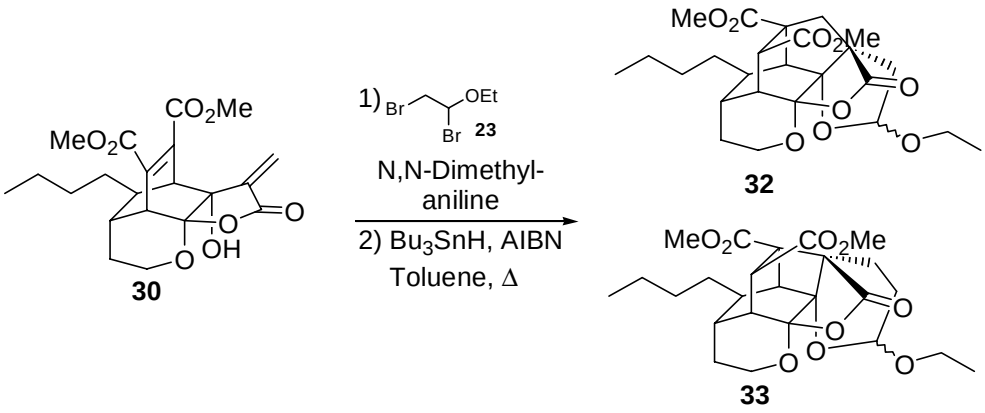


Lactone 30: To a stirred solution of TMP (979 mL, 5.80 mmol, 3.4 equiv) in THF (24mL) was added n-BuLi (2.13 mL of 2.5M in hexane solution, 5.32 mmol, 3.1 equiv), after 10 min at –10 °C the solution was cooled to –45 °C and a solution of **20** (670 mg, 1.70 mmol, 1 equiv) in THF (4 mL) was added, followed 2 min later by the addition of Eschenmosher salt (1.96 g, 10.6 mmol, 6.2 equiv). The reaction mixture was warmed and stirred at room temperature overnight. The reaction was quenched by the addition of 1N HCL, and the resulting solution was diluted with EtOAc, washed with saturated $NaHCO_3$ and brine before being dried over $MgSO_4$ and evaporated *in vacuo*. The reaction mixture was purified using silica gel chromatography, employing 25% EtOAc/Hexanes as the eluent, to give **30** (275 mg, 40% yield) as a clear oil.

Lactone 30. FTIR (thin film/NaCl) 3446 (s), 2926 (s), 2856 (s), 1780 (s), 1726 (s), 1644 (m), 1437 (s), 1280 (s), 1219 (m), 1147 (m), 910 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (s, 1H), 6.03 (s, 1H), 4.51 (ddd, *J*=11.5, 11.0, 5.0 Hz, 1H), 4.16 (ddd, *J*=11.5, 6.5, 3.5 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.38 (d, *J*=2.0 Hz, 1H), 3.18 (d, *J*=3.0 Hz, 1H), 2.92 (s, 1H), 2.24-2.22 (m, 1H), 2.13-2.06 (m, 1H), 1.85-1.81 (m, 1H), 1.76 (ddt, *J*=13.5, 4.5, 3.5 Hz, 1H), 1.36-1.24 (m, 5H), 1.19-1.14 (m, 1H), 0.89 (t, *J*=10.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.5,

165.0, 140.3, 138.3, 137.3, 127.5, 103.5, 76.2, 64.1, 52.6, 52.5, 48.5, 44.9, 37.1, 36.4, 35.3, 29.4, 28.9, 22.5, 14.0; HRMS (FAB) *m/z* 407.1706 [calc'd for $C_{21}H_{26}O_8$ (M+H) 407.1706].

Preparation of Acetals 32, 33a and 33b:



Acetals 32, 33a and 33b: To a stirred solution of **30** (187 mg, 0.46 mmol, 1 equiv) in CH_2Cl_2 (6 mL) was added dibromoacetal **23** (2670 mg, 11.00 mmol, 24 equiv) and *N,N*-dimethylaniline (1.67 g, 13.80 mmol, 30 equiv). The reaction was stirred at room temperature for 14 h, at which point it was quenched with water (10 ml) and diluted with EtOAc (50 ml). The organic layer was washed consecutively with 1M HCl (3 X 50 ml), $NaHCO_3$ (30 ml), and brine (50 ml) and then dried over $MgSO_4$. The solution was filtered and concentrated *in vacuo* to yield the corresponding bromoacetal (91 mg, 35% yield, 67% based on recovered starting material) along with unreacted **30** (89 mg, 48%). To a stirred solution of the bromoacetal (516 mg, 0.93 mmol, 1 equiv) in benzene (20 ml) was added Bu_3SnH (484 µl, 1.8 mmol, 1.94 equiv) and AIBN (153 mg, 0.93 mmol, 1 equiv). The reaction mixture was stirred at reflux for 2h, at which point the crude reaction mixture was poured onto a silica gel column to yield **32** (280 mg,

63% yield, eluted first) as a mixture of acetal diastereomers and **33a/33b** (120 mg, 27 % yield, eluted second) both as clear oils.

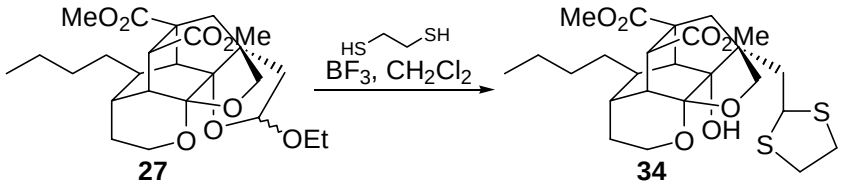
Acetal 32. FTIR (thin film/NaCl) 2926 (s), 2856 (s), 1788 (s), 1731 (s), 1436 (s), 1230 (s), 1110 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (dd, *J*=5.5, 2.0 Hz, 0.5H), 5.38 (d, *J*=4.0 Hz, 0.5H), 4.22 (m, 1H), 4.01 (dd, *J*=12.0, 6.0 Hz, 0.5H), 3.95 (dd, *J*=12.0, 6.0 Hz, 0.5H), 3.80 (m, 1H), 3,75 (s, 1.5H), 3.73 (s, 1.5H), 3.70 (s, 1.5H), 3.69 (1.5H), 3.55 (dq, *J*=10.0, 6.5 Hz, 0.5H), 3.48 (s, 0.5H), 3.44 (s, 0.5H), 3.36 (dq, *J*=9.0, 7.0 Hz, 0.5H), 3.23 (d, *J*=14.0 Hz, 0.5H), 3.17 (d, *J*=14.0 Hz, 0.5H), 3.02 (d, *J*=2.5 Hz, 0.5H), 2.74 (dd, *J*=14.0, 6.0 Hz, 0.5H), 2.68 (d, *J*=2.0 Hz, 0.5H), 2.66 (d, *J*=2.0 Hz, 0.5H), 2.63 (d, *J*=13.0 Hz, 0.5H), 2.61 (s, 0.5H), 2.60 (d, *J*=13.0 Hz, 0.5H), 2.36 (d, *J*=14.5 Hz, 0.5H), 2.18 (dd, *J*=14.5, 2.5 Hz, 0.5H), 2.08-1.98 (m, 1.5H), 1.89-1.79 (m, 2H), 1.41 (m, 1H), 1.32-1.15 (m, 6H), 1.14 (t, *J*=7.0 Hz, 3H), 0.89 (t, *J*=6.5 Hz, 1.5H), 0.88 (t, *J*=7.0 Hz, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 176.0, 174.2, 170.73, 170.71, 110.3, 108.9, 106.8, 106.2, 97.8, 97.3, 63.9, 62.7, 62.0, 59.1, 58.9, 55.0, 53.5, 53.3, 52.81, 52.80, 56.6, 52.24, 52.20, 44.1, 43.9, 43.8, 43.0, 42.5, 42.0, 41.6, 41.4, 39.5, 34.8, 34.7, 33.2, 33.1, 31.3, 31.1, 29.84, 29.80, 22.63, 22.59, 15.1, 14.5, 13.9; HRMS (FAB) *m/z* 479.2282 [calc'd for $C_{25}H_{34}O_9$ (M+H) 479.2281].

β-Acetals 33a. FTIR (thin film/NaCl) 2955 (s), 2860 (s), 1784 (s), 1747 (s), 1437 (s), 1206 (m), 1176 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (dd, *J*=6.0, 1.5 Hz, 1H), 4.14-4.03 (m, 2H), 3.96 (dq, *J*=9.5, 7.0 Hz, 1H), 3.73 (s, 3H), 3.48 (dq, *J*=9.0, 7.0 Hz, 1H), 3.17 (d, *J*=3.0 Hz, 1H), 3.16 (d, *J*=5.0 Hz, 1H), 2.54 (dd, *J*=5.0, 3.5 Hz, 1H), 2.36 (dt, *J*=14.0, 5.5 Hz, 1H), 1.99 (m, 1H), 1.82-1.70 (m, 3H), 1.67-1.20 (m, 9H), 1.21 (t, *J*=7.0 Hz, 3H), 0.91 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 170.7, 170.3, 106.5, 97.1, 75.5, 63.7, 63.6, 54.0, 52.4,

52.3, 47.9, 43.4, 42.7, 41.8, 34.9, 33.6, 33.0, 31.7, 30.0, 26.8, 22.6, 17.7, 14.8, 14.1; HRMS (FAB) *m/z* 479.2281 [calc'd for $C_{25}H_{34}O_9$ (M+H) 479.2281].

α-Acetals 33b. FTIR (thin film/NaCl) 2955 (s), 2860 (s), 1783 (s), 1748 (s), 1437 (m), 1206 (m), 1178 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.99 (dd, *J*=2.8, 1.6 Hz, 1H), 4.18-4.05 (m, 2H), 3.82 (dq, *J*=9.6, 6.8 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.63 (d, *J*=2.4 Hz, 1H), 3.54 (dq, *J*=9.6, 6.8 Hz, 1H), 3.14 (d, *J*=4.8 Hz, 1H), 2.54 (dd, *J*=5.2, 3.6 Hz, 1H), 2.09-1.94 (m, 3H), 1.82-1.70 (m, 3H), 1.62-1.17 (m, 8H), 1.26 (t, *J*=7.2 Hz, 3H), 0.91 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.6, 170.1, 107.3, 96.6, 73.5, 63.3, 62.9, 55.5, 52.4, 52.3, 47.4, 43.8, 43.2, 42.4, 35.4, 33.6, 33.4, 31.5, 30.1, 26.1, 22.6, 15.0, 14.1, 13.9; HRMS (FAB) *m/z* 479.2281 [calc'd for $C_{25}H_{34}O_9$ (M+H) 479.2281].

Preparation of Dithiolane 34:

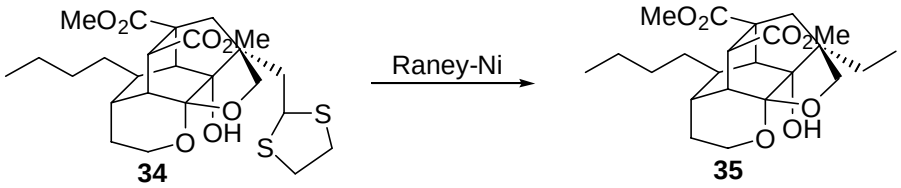


Dithiolane 34. To a solution of **27** (1050 mg, 2.26 mmol, 1 equiv) and ethanedithiol (285 μL, 3.39 mmol, 1.5 equiv) in CH_2Cl_2 (23 mL) was added BF_3Et2O (345 μl, 2.71mmol, 1.2 equiv) in one portion. The reaction was allowed to stir overnight, at which point the mixture was poured into saturated $NaHCO_3$ solution. The phases were seperated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine and then dride over Na_2SO_4. Solides were removed by filtration and the solvent was removed by rotary

evaporation. The crude mixture was purified by flash chromatography to furnish **34** (1100 mg, 95% yield) as a clear oil.

Dithiolane 34. FTIR (thin film/NaCl) 3427 (w), 2924 (m), 2858 (w), 1730 (s), 1436 (w), 1230 (m), 1169 (m), 1091 (m), 1024 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (dd, *J*=9.5, 5.5 Hz, 1H), 4.22 (dd, *J*=11.5, 9.6 Hz, 1H), 4.01 (ddd, *J*=11.4, 6.1, 4.4 Hz, 1H), 3.82 (d, *J*=8.5 Hz, 1H), 3.74 (d, *J*=5.5 Hz, 1H), 3.73 (s, 3H), 3.35-3.15 (m, 5H), 2.91 (s, 1H), 2,71 (d, *J*=2.5 Hz, 1H), 2.62 (d, *J*=15.0 Hz, 1H), 2.57 (d, *J*=2.0 Hz, 1H), 2.35 (d, *J*=15.0 Hz, 1H), 2.2-2.1 (m, 2H), 2.07-2.0 (m, 2H), 1.80-1.74 (m, 1H), 1.71-1.65 (m, 1H), 1.54 (m, 1H), 1.46-1.40 (m, 1H), 1.30-1.16 (m, 7H), 0.90-0.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 172.2, 107.6, 87.9, 63.5, 53.0, 52.6, 52.2, 52.0, 50.4, 48.9, 45.8, 44.4, 41.7, 39.3, 39.2, 39.1, 38.6, 35.6, 34.4, 32.3, 30.4, 23.1, 14.5, 14.4; HRMS (FAB) *m/z* 513.1983 [calc'd for $C_{25}H_{36}O_7S_2$ (M+H) 513.1981].

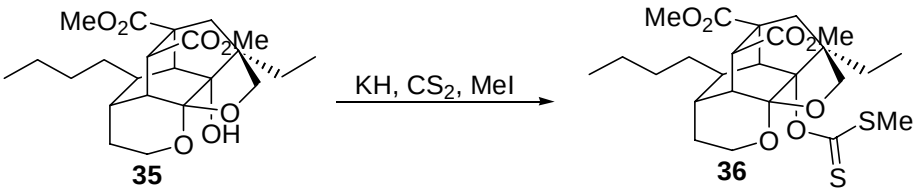
Preparation of Diester 35:



Diester 35. A suspension of Raney-Nickel (25g, 50% in water, 12.5wt equiv, washed with water until pH 7.—7.5) in ethanol (100 mL) was added to **34** (1.14 g, 2.23 mmol, 1 equiv). The mechanically stirred mixture was refluxed for 2h, at which point the solids were removed by filtration over a Celite cake, and washed thoroughly with EtOAc. Solvent was removed in vacuo to provide a crude oil that was purified using silica gel chromatography to yield **35** (893 mg, 95% yield) as a clear oil.

Diester 35. FTIR (thin film/NaCl) 3462 (w), 2853 (m), 2930 (m), 2862 (w), 1730 (s), 1651 (w), 1540 (w), 1510 (w), 1459 (w), 1438 (w), 1368 (w), 1227 (m), 1121 (m), 1090 (m), 1059 (m), 868 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.25 (ddd, *J*=10.4, 10.4, 5.3 Hz, 1H), 3.97 (ddd, *J*=11.5, 6.5, 4.0 Hz, 1H), 3.71 (s, 3H), 3.67 (d, *J*=8.5 Hz, 1H), 3.66 (s, 3H), 3.57 (d, *J*=8.5 Hz, 1H), 3.26 (s, 1H), 2.65 (d, *J*=3.0 Hz, 1H), 2.58 (d, *J*=3.0 Hz, 1H), 2.54 (d, *J*=15.0 Hz, 1H), 2.30 (d, *J*=15 Hz, 1H), 2.01 (dddd, *J*=13.5, 10.2, 5.8, 6.5 Hz, 1H), 1.76-1.74 (m, 1H), 1.65-1.71 (m, 1H), 1.59 (ddd, *J*=15.0, 13.0, 7.5 Hz, 1H), 1.48-1.39 (m, 2H), 1.30-1.16 (m, 7H), 0.88 (t, *J*=7.5 Hz, 3H), 0.85 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 171.9, 108.1, 86.9, 76.5, 63.0, 52.6, 52.5, 52.0, 51.6, 48.3, 45.6, 41.2, 39.2, 38.5, 35.1, 35.0, 31.9, 30.8, 27.2, 22.7, 14.0, 9.0; HRMS (FAB) *m/z* 423.2383 [calc'd for $C_{23}H_{34}O_7$ (M+H) 423.2382].

Preparation of Xanthate 36:

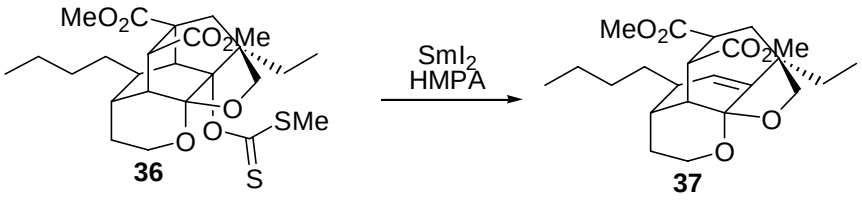


Xanthate 36. To a suspension of KH (30% in mineral oil, 350 mg, 2.6 mmol, 4 equiv) in THF (4 mL) at 0 °C was added **35** (273 mg, 0.65 mmol, 1 equiv) in THF (5 mL). The mixture was stirred for 30 min, at which point CS_2 (390 μl, 6.5mmol, 10 equiv) was added. The mixture was stirred for an additional 30 min, at which point CH_3I (405 μl, 6.5 mmol, 10 equiv) was added. The reaction mixture was allowed to warm to room temperature and was reacted for 3h before being quenched with MeOH (3 mL) and evaporated *in vacuo*. The residue was dissolved

in EtOAc, washed with water (3 X 30 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4, evaporated and purified using silica gel chromatography, employing a gradient 7%-15% EtOAc/Hexanes to furnish **36** (216 mg, 65% yield) as a clear oil.

Xanthate 36. FTIR (thin film/NaCl) 2955 (m), 2926 (m), 2864 (w), 1731 (s), 1438 (w), 1231 (s), 1148 (m), 1093 (s), 1036 (s), 730 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.94 (s, 1H), 3.92-3.82 (m, 3H), 3.58 (s, 3H), 3.61 (s, 3H), 3.59 (d, *J*=8.5 Hz, 1H), 3.21 (s, 1H), 2.75 (d, *J*=14.0 Hz, 1H), 2.56 (d, *J*=1.5 Hz, 1H), 2.53 (s, 3H), 2.41 (d, *J*=14.0 Hz, 1H), 2.07-1.98 (m, 2H), 1.80-1.75 (m, 2H), 1.68-1.54 (m, 3H), 1.39-1.36 (m, 2H), 1.28-1.18 (m, 3H), 0.89-0.79 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.6, 176.3, 172.0, 109.0, 103.2, 77.2, 76.4, 62.1, 55.8, 52.8, 51.7, 48.3, 48.2, 44.9, 41.2, 39.3, 35.0, 33.1, 31.1, 29.7, 28.2, 22.8, 19.7, 14.0, 9.3; HRMS (FAB) *m/z* 513.1983 [calc'd for $C_{25}H_{36}O_7S_2$ (M+H) 513.1980].

Preparation of Olefin 37:



Olefin 37. To a solution of SmI_2 (25mL of 0.1M in THF) was added HMPA (3 mL). After 15 minutes, **36** (38 mg, 0.074 mmol, 1 equiv) dissolved in THF (1 mL) was added over 1 min. The reaction was allowed to stir at room temperature for 30 min, at which point it was quenched with a saturated ammonium chloride (20 mL) solution and diluted with EtOAc (100 mL). The organic layer was separated and washed with water (8 X 20 mL) and brine (1 X 20

mL), then dried over Na_2SO_4 and concentrated *in vacuo*. Purification using silica gel chromatography furnished **37** (18 mg, 60% yield).

Olefin 37. FTIR (thin film/NaCl) 2952 (m), 2926 (m), 2859 (m), 1731 (s), 1435 (w), 1378 (w), 1235 (m), 1202 (m), 1030 (w), 1035 (w), 1008 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.42 (d, *J*=1.5 Hz, 1H), 3.85 (ddd, *J*=11.0, 5.8, 3.5 Hz, 1H), 3.81 (s, 2H), 3.74-3.65 (m, 2H), 3.70 (s, 3H), 3.62 (s, 3H), 3.54 (ddd, *J*=5.4, 2.8, 2.6 Hz, 1H), 2.74 (dd, *J*=7.5, 1.7 Hz, 1H), 2.71 (s, 1H), 2,27 (s, 1H), 2,16 (dd, *J*=7.7, 2.7 Hz, 1H), 2.11-2.06 (m, 1H), 2.05-1.97 (m, 1H), 1.72-1.62 (m, 2H), 1.60-1.48 (m, 1H), 1.40-1.22 (m, 6H), 1.07 (dd, *J*=13.8, 6.3 Hz, 1H), 0.97-0.85 (m, 6H); HRMS (EI) *m/z* 406.2360 [calc'd for $C_{23}H_{34}O_6$ (M+) 406.2355].

X-ray Structure Report for Vinylstannane 21.

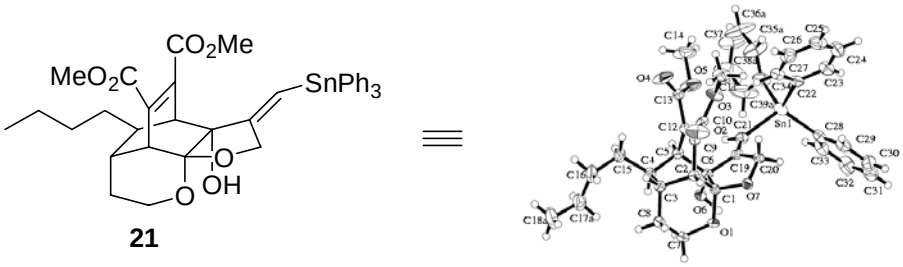


Figure 1 ORTEP plot of Vinylstannane **21**.

Crystal Data

Empirical Formula	$C_{39}H_{42}O_7Sn$
Formula Weight	741.45
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.24 X 0.30 X 0.32 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.1207(5)Å b = 17.656(1) Å c = 20.181(1) Å β = 104.705(3)° V = 3488.0(3) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
Dcalc	1.412 g/cm^3
F000	1528.00
μ(MoKα)	7.81 cm^{-1}

Intensity Measurements.

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated

Take-off Angle	2.8°
Crystal to Detector Distance	35 mm
Temperature	-90.0°C
Scan Rate	16s/frame
Scan Width	1.6°/frame
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 6809
Corrections	Lorentz-polarization

Structure Solution and Refinement.

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2$(Fo)
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4550
No. Variables	487
Reflection/Parameter Ratio	9.34
Residuals: R; Rw	0.045 ; 0.046
Goodness of Fit Indicator	2.09
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.87 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.69 $e^-/Å^3$

Atomic Coordinates and Biso/Beq.

Table 1 Atomic Coordinates and Biso/Beq for Vinylstannane 21.

atom	x	y	z	Beq
C(1)	0.2216(4)	0.4868(2)	1.0725(2)	2.19(9)
C(10)	0.5843(4)	0.4931(2)	1.1610(2)	2.60(9)
C(11)	0.8033(5)	0.5387(3)	1.1626(3)	4.7(1)
C(12)	0.3947(4)	0.5764(2)	1.1804(2)	2.19(8)
C(13)	0.4846(5)	0.6383(2)	1.2188(2)	2.47(9)
C(14)	0.5162(7)	0.7699(2)	1.2319(3)	7.0(2)

C(15)	0.2569(5)	0.5257(2)	1.2906(2)	3.2(1)
C(16)	0.2225(6)	0.4632(3)	1.3349(2)	4.8(1)
C(17a)	0.083(1)	0.4416(5)	1.3346(5)	4.7(3)
C(17b)	0.271(2)	0.4835(6)	1.4115(4)	6.8(4)
C(18a)	0.068(2)	0.3761(6)	1.3810(5)	7.4(4)
C(18b1)	0.245(3)	0.4209(9)	1.4528(8)	6.8(6)
C(18b2)	0.402(3)	0.454(2)	1.435(1)	7.0(9)
C(19)	0.2281(4)	0.6203(2)	1.0482(2)	2.34(9)
C(2)	0.3318(4)	0.4544(2)	1.1313(2)	2.06(8)
C(20)	0.3038(4)	0.5755(2)	1.0063(2)	2.46(9)
C(21)	0.2062(4)	0.6941(2)	1.0464(2)	2.81(9)
C(22)	0.4850(5)	0.7595(2)	0.9842(2)	3.2(1)
C(23)	0.5366(6)	0.7924(2)	0.9330(2)	4.0(1)
C(24)	0.6702(6)	0.7839(2)	0.9308(2)	4.6(1)
C(25)	0.7590(6)	0.7408(3)	0.9799(3)	4.6(1)
C(26)	0.7100(6)	0.7071(2)	1.0308(3)	4.5(1)
C(27)	0.5764(6)	0.7161(2)	1.0334(2)	3.9(1)
C(28)	0.1564(5)	0.7795(2)	0.8841(2)	3.3(1)
C(29)	0.1968(5)	0.7391(2)	0.8334(2)	3.7(1)
C(3)	0.2645(4)	0.4361(2)	1.1900(2)	2.34(8)
C(30)	0.1192(6)	0.7391(2)	0.7657(2)	4.5(1)
C(31)	-0.0018(6)	0.7795(3)	0.7490(3)	5.0(1)
C(32)	-0.0445(6)	0.8183(3)	0.7992(3)	4.8(1)
C(33)	0.0328(5)	0.8187(2)	0.8662(2)	4.1(1)
C(34)	0.2635(6)	0.8790(2)	1.0430(3)	4.5(1)
C(35a)	0.371(1)	0.9176(5)	1.0799(6)	6.3(3)
C(35b)	0.293(2)	0.8754(9)	1.1096(7)	6.3(5)
C(36a)	0.362(2)	0.9799(10)	1.1214(9)	9.1(5)
C(36b)	0.296(3)	0.944(1)	1.143(1)	8.0(7)
C(37)	0.250(1)	1.0060(4)	1.1230(4)	9.5(3)
C(38a)	0.134(2)	0.961(1)	1.105(1)	15.9(8)
C(38b)	0.207(2)	1.0116(7)	1.0469(6)	9.1(5)
C(39a)	0.145(2)	0.8967(7)	1.0635(8)	11.1(5)
C(39b)	0.201(2)	0.9453(7)	1.0065(6)	8.9(5)
C(4)	0.2066(4)	0.5106(2)	1.2135(2)	2.42(9)
C(5)	0.2439(4)	0.5774(2)	1.1711(2)	2.27(8)
C(6)	0.1737(4)	0.5654(2)	1.0944(2)	2.11(8)
C(7)	0.0523(4)	0.4014(2)	1.1015(2)	2.72(9)
C(8)	0.1572(4)	0.3749(2)	1.1644(2)	2.80(9)
C(9)	0.4415(4)	0.5128(2)	1.1569(2)	2.08(8)
H(1)	0.3699	0.4100	1.1171	2.4780
H(10)	0.8208	0.5388	1.1185	5.5969
H(11)	0.8555	0.5773	1.1899	5.5969
H(12)	0.5093	0.7705	1.2779	8.4554
H(13)	0.6094	0.7653	1.2313	8.4554

H(14)	0.4800	0.8156	1.2098	8.4554
H(15)	0.3534	0.5315	1.3017	3.8136
H(16)	0.2164	0.5714	1.3007	3.8136
H(17)	0.2641	0.4186	1.3231	5.7852
H(18)	0.2654	0.4769	1.3808	5.7852
H(19)	0.0400	0.4846	1.3482	5.6234
H(2)	0.3323	0.4163	1.2275	2.8037
H(20)	0.0371	0.4281	1.2890	5.6234
H(21)	-0.0258	0.3665	1.3767	8.8296
H(22)	0.1100	0.3322	1.3681	8.8296
H(23)	0.1116	0.3887	1.4272	8.8296
H(24)	0.3995	0.5823	1.0235	2.9518
H(25)	0.2769	0.5910	0.9597	2.9518
H(26)	0.1514	0.7124	1.0749	3.3762
H(27)	0.4771	0.8217	0.8985	4.7771
H(28)	0.7018	0.8077	0.8954	5.4625
H(29)	0.8516	0.7345	0.9787	5.5626
H(3)	0.1098	0.5065	1.2025	2.9065
H(30)	0.7698	0.6771	1.0646	5.4361
H(31)	0.5457	0.6926	1.0692	4.6704
H(32)	0.2793	0.7109	0.8453	4.4492
H(33)	0.1489	0.7117	0.7316	5.4155
H(34)	-0.0555	0.7806	0.7029	5.9928
H(35)	-0.1286	0.8452	0.7874	5.8115
H(36)	0.0017	0.8456	0.9001	4.9014
H(37)	0.4590	0.9016	1.0777	7.5241
H(38)	0.4436	1.0022	1.1485	10.9142
H(39)	0.2432	1.0571	1.1364	11.3684
H(4)	0.2163	0.6242	1.1864	2.7222
H(40)	0.0541	0.9714	1.1196	19.0758
H(41)	0.0681	0.8645	1.0490	13.3531
H(42)	-0.0238	0.5649	1.0378	4.7494
H(5)	-0.0032	0.4390	1.1147	3.2650
H(6)	-0.0028	0.3595	1.0820	3.2650
H(7)	0.2007	0.3307	1.1534	3.3570
H(8)	0.1128	0.3634	1.1994	3.3570
H(9)	0.8279	0.4909	1.1838	5.5969
O(1)	0.1130(3)	0.4334(1)	1.0500(1)	2.45(6)
O(2)	0.6279(3)	0.4298(2)	1.1677(2)	5.52(10)
O(3)	0.6606(3)	0.5522(2)	1.1558(2)	3.94(8)
O(4)	0.5776(4)	0.6300(1)	1.2660(2)	5.63(9)
O(5)	0.4392(4)	0.7056(1)	1.1959(2)	5.72(9)
O(6)	0.0324(3)	0.5725(1)	1.0872(1)	2.41(6)
O(7)	0.2678(3)	0.4977(1)	1.0126(1)	2.52(6)
Sn(1)	0.27871(3)	0.77715(1)	0.98755(1)	3.223(8)

$Beq = 8/3\ \pi^2(U11(aa^*)^2 + U22(bb^*)^2 + U33(cc^*)^2 + 2U12(aa^*bb^*)\cos\gamma + 2U13(aa^*cc^*)\cos\beta + 2U23(bb^*cc^*)\cos\alpha)$

X-ray Structure Report for Diester 27a.

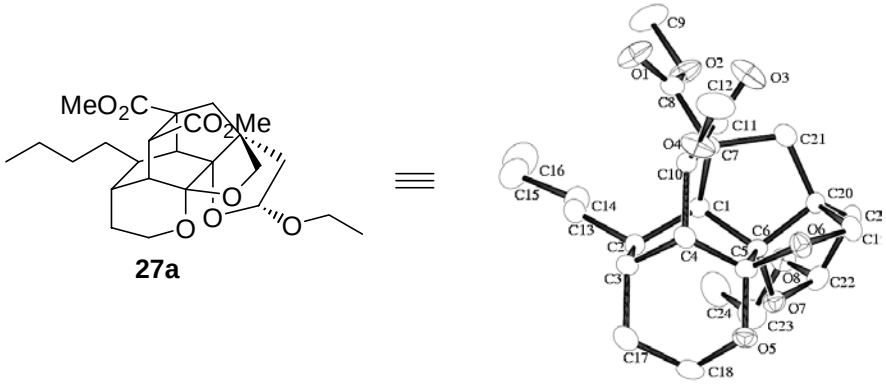


Figure 2 ORTEP plot of Diester **27a**.

Crystal Data

Empirical Formula	$C_{25}H_{36}O_8$
Formula Weight	464.55
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.17 X 0.21 X 0.28 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 14.539(1)Å
	b = 8.7759(4) Å
	c = 19.117(1) Å
	β = 90.135(3)^o
	V = 2439.2(2) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4

D_{calc}	1.265 g/cm^3
F_{000}	1000.00
μ(MoKα)	0.93 cm^{-1}

Intensity Measurements.

Diffractometer	Nonius KappaCCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8^o
Crystal to Detector Distance	35 mm
Temperature	-90.0^{o}C
Scan Rate	19s/frame
Scan Width	1.9^o/frame
2θmax	54.9^o
No. of Reflections Measured	Total: 5932
Corrections	Lorentz-polarization

Structure Solution and Refinement.

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	1/σ^2(Fo)
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>5.00σ(I))	1975
No. Variables	298
Reflection/Parameter Ratio	6.63
Residuals: R; Rw	0.042 ; 0.049
Goodness of Fit Indicator	2.04
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.32 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.25 e$^-$/Å^3

Atomic Coordinates and Biso/Beq.

Table 2 Atomic Coordinates and Biso/Beq for Diester 27a.

atom	x	y	z	Beq
O(1)	0.0629(2)	0.4151(3)	-0.0612(1)	3.82(7)
O(2)	0.0485(2)	0.1761(2)	-0.0247(1)	3.35(7)
O(3)	0.2214(2)	0.4000(3)	-0.1812(1)	4.00(7)
O(4)	0.3145(2)	0.5813(3)	-0.1411(1)	3.18(6)
O(5)	0.4761(2)	0.2890(2)	0.0270(1)	2.34(6)
O(6)	0.4214(2)	0.2452(2)	-0.0827(1)	2.46(6)
O(7)	0.3716(1)	0.0431(2)	0.0578(1)	2.10(6)
O(8)	0.2601(2)	-0.1391(2)	0.0869(1)	2.44(6)
C(1)	0.2356(2)	0.2087(3)	0.0310(2)	1.77(8)
C(2)	0.2471(2)	0.3277(3)	0.0892(2)	1.94(8)
C(3)	0.3132(2)	0.4555(3)	0.0647(2)	2.03(8)
C(4)	0.3405(2)	0.4257(3)	-0.0119(2)	1.98(8)
C(5)	0.3937(2)	0.2771(4)	-0.0128(2)	2.05(9)
C(6)	0.3295(2)	0.1438(3)	0.0092(2)	1.65(8)
C(7)	0.2007(2)	0.2651(3)	-0.0412(2)	1.81(8)
C(8)	0.0978(2)	0.2966(4)	-0.0445(2)	2.24(9)
C(9)	-0.0500(3)	0.1992(4)	-0.0228(2)	4.5(1)
C(10)	0.2528(2)	0.4156(3)	-0.0570(2)	1.86(8)
C(11)	0.2609(3)	0.4576(4)	-0.1330(2)	2.31(10)
C(12)	0.3171(3)	0.6460(4)	-0.2108(2)	4.0(1)
C(13)	0.1569(2)	0.3866(4)	0.1199(2)	2.43(9)
C(14)	0.0976(2)	0.2653(4)	0.1544(2)	2.88(9)
C(15)	0.0131(3)	0.3258(4)	0.1923(2)	3.8(1)
C(16)	-0.0453(3)	0.1994(5)	0.2225(2)	5.4(1)
C(17)	0.4015(3)	0.4680(4)	0.1075(2)	2.51(9)
C(18)	0.4611(2)	0.3286(4)	0.0995(2)	2.53(9)
C(19)	0.4017(2)	0.0875(4)	-0.0976(2)	2.58(9)
C(20)	0.3134(2)	0.0543(3)	-0.0578(2)	1.88(8)
H(8)	0.2139	0.4923	-0.0382	2.2333
H(9)	0.3412	0.5730	-0.2425	4.8238
H(10)	0.3553	0.7340	-0.2107	4.8238
H(11)	0.2567	0.6736	-0.2248	4.8238
H(12)	0.1712	0.4618	0.1539	2.9177
H(13)	0.1222	0.4316	0.0831	2.9177
H(14)	0.0775	0.1965	0.1192	3.4597
H(15)	0.1346	0.2123	0.1875	3.4597
H(16)	0.0327	0.3905	0.2293	4.5682
H(17)	-0.0230	0.3826	0.1601	4.5682
H(18)	-0.0958	0.2423	0.2470	6.5219

H(19)	-0.0675	0.1366	0.1857	6.5219
H(20)	-0.0092	0.1399	0.2537	6.5219
H(21)	0.4350	0.5548	0.0923	3.0109
H(22)	0.3859	0.4796	0.1555	3.0109
H(23)	0.4321	0.2453	0.1222	3.0366
H(24)	0.5190	0.3478	0.1209	3.0366
H(25)	0.3929	0.0725	-0.1464	3.0924
H(26)	0.4502	0.0239	-0.0815	3.0924
H(27)	0.1778	0.0540	-0.0896	2.7629
H(28)	0.2381	0.1600	-0.1355	2.7629
H(29)	0.3843	-0.1796	0.0528	2.9957
H(30)	0.3263	-0.2206	0.1686	4.3339
H(31)	0.3067	-0.0472	0.1739	4.3339
H(32)	0.1447	-0.1262	0.1784	5.1106
H(33)	0.2016	-0.1393	0.2469	5.1106
H(34)	0.1845	-0.2826	0.2011	5.1106
H(35)	0.2459	-0.1489	-0.0357	2.9146
H(36)	0.3471	-0.1761	-0.0581	2.9146

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$