Supplementary Material for
"Evolution of a Synthetic Approach for CP-263,114"

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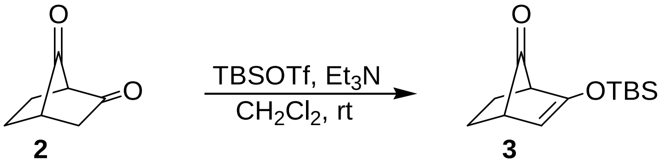
Materials and Methods

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).

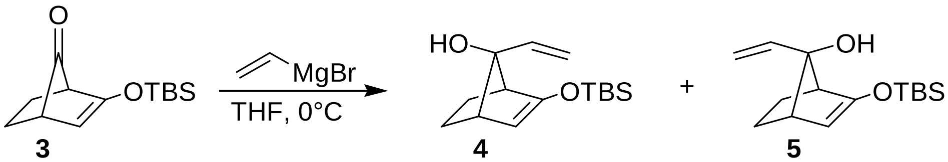
Preparation of Enol Ether 3:



Enol ether 3. To a mechanically stirred solution of diketone **2** (9.1 g, 73.3 mmol, 1 equiv) in CH_2Cl_2 (350 mL) was added TBSOTf (21.9 mL, 95.3 mmol, 1.3 equiv) followed by triethylamine (15.3 mL, 110.0 mmol, 1.5 equiv) 20 minutes later. The reaction mixture was stirred at room temperature for 1 h, quenched with saturated $NaHCO_3$ (350 mL), and extracted with CH_2Cl_2 (3 X 300 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Silica gel chromatography using 1% Et_3N/1% EtOAc/Hexane furnished pure enol ether **3** (15.16 g, 87% yield) as a yellow oil.

Enol ether 3. FTIR (thin film/NaCl) 2955 (s), 2932 (s), 2859 (s), 2858 (w), 1783 (s), 1603 (s), 1472 (m), 1463 (m), 1326 (s), 1277 (m), 1255 (m), 1225 (m), 1195 (m), 1139 (w), 932 (m), 841 (m), 784 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.17 (dd, *J*=4.2, 1.4 Hz, 1H), 2.82-2.80 (m, 1H), 2.60 (ddd, *J*=3.2, 3.2, 1.6 Hz, 1H), 1.97-1.87 (m, 2H), 1.42-1.29 (m, 2H), 0.91 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 156.5, 104.7, 49.4, 46.4, 26.7, 23.8, 20.7, 18.2, -4.3, -4.4; HRMS (EI) *m/z* 239.1464 [calc'd for $C_{13}H_{22}O_2Si$ (M+H) 239.1467].

Preparation of Alcohols 4 and 5:

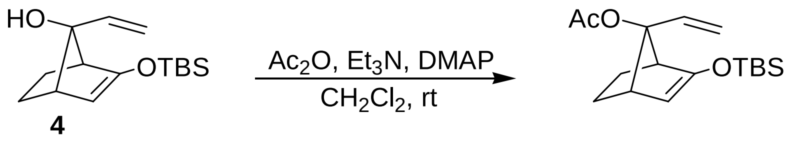


Alcohols 4 and 5. To a stirred solution of **3** (1874 mg, 7.86 mmol, 1 equiv) in THF (10 mL) at 0°C was added 1.0M vinylmagnesium bromide in THF (11.8 mL, 11.8 mmol, 1.5 equiv). After stirring for 1 h, the reaction mixture was treated with a solution of saturated $NaHCO_3$ (20 mL) and extracted with EtOAc (3 X 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give an oil. Silica gel chromatography using 1% Et_3N/4% EtOAc/Hexanes gave two analytically pure compounds**:** **5** (270 mg, 13% yield, eluted first) as a clear oil and **4** (835 mg, 40% yield, eluted second) also as a clear oil.

Alcohol 5. FTIR (thin film/NaCl) 3470 (w), 2957 (s), 2930 (s), 2884 (m), 2858 (m), 1613 (m), 1472 (w), 1464 (w), 1326 (m), 1254 (m), 1224 (m), 1197 (m), 929 (m), 857 (m), 838 (s), 781 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_33$) δ 5.97 (dd, *J*=16.8, 10.5 Hz, 1H), 5.44 (dd, *J*=17.2, 1.8 Hz, 1H), 5.22 (dd, *J*=10.8, 1.8 Hz, 1H), 4.74 (dd, *J*=3.5, 1.5 Hz, 1H), 2.95 (d, *J*=1.0 Hz, 1H), 2.58 (m, 1H), 2.42 (app t, *J*=2.0 Hz, 1H), 1.88-1.81 (m, 2H), 1.25-1.18 (m, 2H), 0.94 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 136.6, 116.8, 101.8, 89.6, 54.6, 50.3, 26.0, 25.8, 22.5, 18.3, -4.2, -4.6; HRMS (EI) *m/z* 266.1705 [calc'd for $C_{15}H_{26}O_2Si$ (M+) 266.1702].

Alcohol 4. FTIR (thin film/NaCl) 3414 (m), 3083 (w), 2957 (s), 2859 (s), 1618 (s), 1472 (w), 1463 (w), 1331 (m), 1256 (m), 1225 (m), 1201 (m), 1149 (w), 1120 (w), 1003 (w), 930 (m), 860 (m), 834 (m), 782 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (dd, *J*=17.6, 10.8 Hz, 1H), 5.33 (dd, *J*=18.0, 1.6 Hz, 1H), 5.13 (dd, *J*=10.8, 1.6 Hz, 1H), 4.63 (dd, *J*=3.6, 1.6 Hz, 1H), 2.42 (ddd, *J*=3.6, 3.2, 2.0 Hz, 1H), 2.25 (ddd, *J*= 3.2, 2.0, 1.2 Hz, 1H), 2.08-1.96 (m, 2H), 1.55 (s, 1H), 1.29-1.18 (m, 2H), 0.91 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 140.6, 115.1, 104.1, 88.8, 53.7, 49.4, 26.9, 25.9, 23.5, 18.2, -4.2, -4.3; HRMS (EI) *m/z* 266.1702 [calc'd for $C_{15}H_{26}O_2Si$ (M+) 266.1702].

Preparation of Acetate:

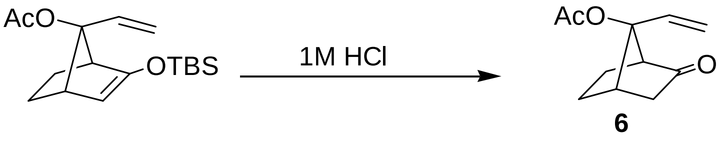


Acetate. To a stirred solution of **4** (1.01 g, 3.75 mmol, 1 equiv) in CH_2Cl_2 (10 mL) was added acetic anhydride (1.8 mL, 18.76 mmol, 5 equiv), triethylamine (2.6 mL, 18.76 mmol, 5 equiv) and dimethylaminopyridine (46 mg, 0.38 mmol, 0.1 equiv). The reaction mixture was stirred at room temperature for 2.5 h, quenched with saturated $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (3 X 30 mL). The combined organic layers were dried over Na_2SO_4 and evaporated. Silica gel chromatography using 1% Et_3N/5% EtOAc/Hexanes furnished **acetate** (1.03 g, 89% yield) as a clear oil.

Acetate. FTIR (thin film/NaCl) 3086 (w), 2955 (s), 2859 (m), 1742 (s), 1621 (s), 1472 (m), 1464 (m), 1366 (m), 1333 (m), 1242 (s), 1227 (s), 1173 (w), 1117 (w), 1019 (w), 989 (w), 932 (m), 858 (m), 838 (m), 784 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (dd, *J*=18.0, 10.8 Hz, 1H), 5.20 (dd, *J*=17.6, 1.2 Hz, 1H), 5.15 (dd, *J*=10.8, 1.2 Hz, 1H), 4.60 (dd, *J*=3.8, 1.4 Hz, 1H), 2.96 (ddd, *J*=3.6, 3.2, 2.0 Hz, 1H), 2.81 (ddd, *J*=3.6, 1.6, 1.6 Hz, 1H), 1.98 (s, 3H), 1.89-

1.74 (m, 2H), 1.31-1.19 (m, 2H), 0.90 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 158.1, 136.2, 116.6, 102.8, 93.6, 52.0, 47.7, 26.4, 25.8, 22.9, 21.8, 18.2, -4.3, -4.4; HRMS (EI) *m/z* 308.1814 [calc'd for $C_{17}H_{28}O_3Si$ (M+) 308.1808].

Preparation of Ketone 6:

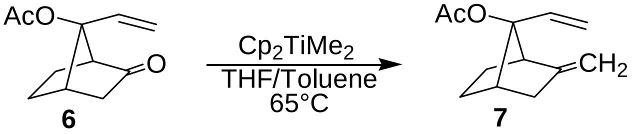


6

Ketone 6. To a stirred solution of **acetate** (2.4 g, 7.78 mmol, 1 equiv) in THF (40 mL) at room temperature was added 1.0N HCl (312 mg, 8.56 mmol, 1.1 equiv). After stirring for 5 minutes the reaction mixture was treated with a solution of saturated $NaHCO_3$ (50 mL) and extracted with Et_2O (3 X 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give an oil. Purification using silica gel chromatography yielded an analytically pure sample of **6** (1.46 g, 97% yield).

Ketone 6. FTIR (thin film/NaCl) 2961 (w), 2885 (w), 1753 (s), 1410 (w), 1369 (m), 1243 (s), 1223 (s), 1150 (w), 1126 (w), 1074 (w), 1044 (m), 1024 (m), 940 (w), 907 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dd, *J*=17.6, 10.8 Hz, 1H), 5.40 (dd, *J*=17.6, 0.8 Hz, 1H), 5.36 (dd, *J*=10.8, 1.2 Hz, 1H), 3.13 (d, *J*=4.8 Hz, 1H), 2.86 (app t, *J*=3.8 Hz, 1H), 2.31 (ddt, *J*=18.8, 4.8, 1.2 Hz, 1H), 2.04 (s, 3H), 2.09-2.01 (m, 2H), 1.93 (d, *J*=18.4 Hz, 1H), 1.59-1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.6, 169.7, 133.5, 120.9, 89.8, 55.5, 43.9, 42.1, 26.6, 22.2, 21.6; HRMS (EI) *m/z* 194.0948 [calc'd for $C_{11}H_{14}O_3$ (M+) 194.0943].

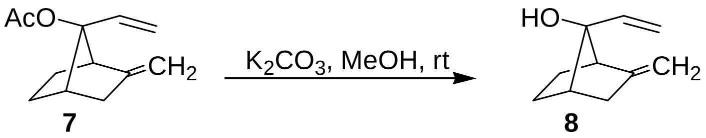
Preparation of Diene 7:



Diene 7. Enone **6** (130 mg, 0.67 mmol, 1 equiv) was treated with 0.6M solution of Petasis reagent in toluene (3 mL) in the dark, and heated at 65°C for 5h. The crude reaction mixture was filtered, concentrated, and subjected to silica gel chromatography using 5% EtOAc/Hexane as the eluent yielding an analytically pure sample of **7** (84 mg, 65% yield) as a clear oil.

Diene 7. FTIR (thin film/NaCl) 3072 (w), 2969 (m), 2875 (w), 1740 (s), 1665 (w), 1433 (w), 1367 (m), 1247 (s), 1224 (s), 1155 (w), 1023 (m), 932 (w), 882 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (dd, *J*=18.0, 10.8 Hz, 1H), 5.33 (dd, *J*=17.2, 1.6 Hz, 1H), 5.22 (dd, *J*=10.8, 1.2 Hz, 1H), 4.93 (app t, *J*=2.0 Hz, 1H), 4.67 (br s, 1H), 3.06 (d, *J*=2.4 Hz, 1H), 2.48 (t, *J*=4.0 Hz, 1H), 2.30 (dddd, *J*=16.4, 4.8, 2.8, 2.0 Hz, 1H), 2.02 (s, 3H), 1.96-1.86 (m, 3H), 1.42-1.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 151.2, 134.9, 117.6, 105.9, 91.2, 51.4, 44.1, 35.3, 27.9, 27.8, 21.7; HRMS (EI) *m/z* 192.1152 [calc'd for $C_{12}H_{16}O_2$ (M+) 192.1150].

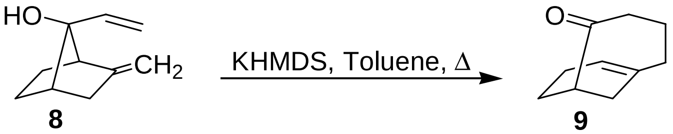
Preparation of Alcohol 8:



Alcohol 8. To a stirred solution of **7** (88 mg, 0.46 mmol, 1 equiv) in MeOH (3 mL) was added K_2CO_3 (138 mg, 1 mmol, 2.2 equiv). The reaction mixture was stirred at room temperature for 6 h, the solvent was evaporated, and the crude reaction mixture diluted with $NaHCO_3$ (5 mL, CH_2Cl_2 (5 mL) and extracted with CH_2Cl_2 (3 X 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to yield pure **8** (62 mg, 91% yield).

Alcohol 8. FTIR (thin film/NaCl) 3379 (s), 3071 (m), 2957 (s), 2870 (m), 1663 (m), 1464 (w), 1417 (w), 1309 (w), 1289 (w), 1262 (m), 1159 (m), 1102 (w), 1082 (w), 1011 (m), 994 (m), 923 (m), 874 (m), 855 (w), 782 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.20 (dd, *J*=17.6, 10.8 Hz, 1H), 5.43 (dd, *J*=17.6, 1.6 Hz, 1H), 5.18 (dd, *J*=10.8, 1.6 Hz, 1H), 4.88 (app t, *J*=2.4 Hz, 1H), 4.64 (app t, *J*=1.2 Hz, 1H), 2.40-2.33 (m, 2H), 2.25-2.04 (m, 2H), 2.00-1.93 (m, 2H), 1.44-1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 139.4, 115.3, 105.0, 85.1, 53.8, 45.6, 36.6, 28.4, 28.3; HRMS (EI) *m/z* 150.1046 [calc'd for $C_{10}H_{14}O$ (M+) 150.1045].

Preparation of Bridgehead olefin 9:

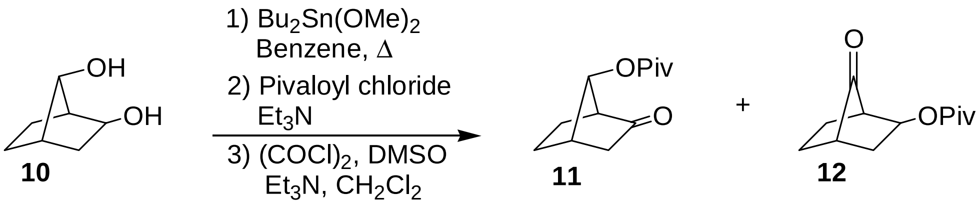


8 **9**

Bridgehead olefin 9. To a stirred solution of **8** (6 mg, 0.04 mmol, 1 equiv) in toluene (0.4 mL) was added KHMDS (16 mg, 0.08 mmol, 2 equiv). The mixture was heated to reflux for 2h, and then quenched by the addition of *p*-toluenesulfonic acid (30 mg). The solution was transferred onto a silica gel column where it was eluted with 5%-15% Et_2O/Pentane furnishing pure **9** (6 mg, 99% yield) as a clear oil.

Bridgehead olefin 9. FTIR (thin film/NaCl) 3025 (w), 2960 (s), 2933 (s), 2854 (m), 1740 (w), 1702 (s), 1453 (m), 1441 (m), 1260 (m), 1234 (w), 1102 (m), 1019 (s), 800 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.56 (m, 1H), 2.89 (ddd, *J*=10.8, 9.2, 2.8 Hz, 1H), 2.64-2.61 (m, 1H), 2.54 (dddd, *J*=11.2, 2.8, 1.2, 1.2 Hz, 1H), 2.37 (ddd, *J*=9.6, 5.6, 1.2 Hz, 1H), 2.30 (ddd, *J*=9.2, 4.8, 2.0 Hz, 1H), 2.20 (ddd, *J*=9.6, 5.6, 4.8 Hz, 1H), 2.12-2.01 (m, 4H), 1.86-1.79 (m, 2H), 1.54-1.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.9, 145.1, 123.9, 47.3, 42.1, 36.0, 32.6, 32.0, 24.5, 21.4; HRMS (EI) *m/z* 150.1039 [calc'd for $C_{10}H_{14}O$ (M+) 150.1045].

Preparation of Ketones 11 and 12:

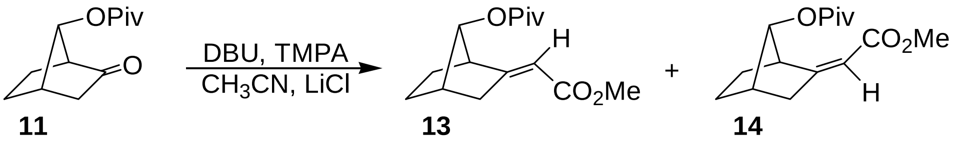


Ketones 11 and 12. To a stirred solution of 2,7-*exo*-*syn* norbornadiol **10** (1025 mg, 8.00 mmol, 1 equiv) in C_6H_6 (100 mL) was added dibutyltindimethoxide (2020 µl, 8.8 mmol, 1.1 equiv) via syringe. The reaction mixture was stirred at reflux using a Dean-Stark apparatus for 2 h and then cooled to room temperature. The volume was reduced to 15 mL on a rotary evaporator. To this mixture was added pivaloyl chloride (1084 µL, 8.8 mmol, 1.1 equiv) followed by triethylamine (58 µL, 0.05 mmol, 0.4 equiv) and the mixture was stirred for a further 2 h and the solvents were removed *in vacuo*. The crude reaction mixture was purified using silica gel chromatography employing a 0 to 5% EtOAc:Hexanes gradient, which furnished a 8:1 mixture of pivaloate alcohols (1450 mg, 86% yield). This mixture was carried on on to the next step. To a stirred solution of oxalyl chloride (1.43 mL, 16.42 mmol, 2.5 equiv) in CH_2Cl_2 at –78 ºC was added dimethylsulfoxide (2.80 mL, 39.40 mmol, 6.0 equiv). The solution was stirred for 20 minutes and then a solution of pivaloyl alcohols (1392 mg, 6.57 mmol, 1 equiv) in 10 mL CH_2Cl_2 was added dropwise to the mixture. Stirring was continued for another 20 minutes at –78 ºC after which triethylamine (10 mL, 65.67 mmol, 10 equiv) was added slowly and the mixture was allowed to warm to room temperature. The reaction was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 X 15 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to a yellow oil. Silica gel chromatography using 0 to 20% EtOAc:Hexanes gradient furnished analytically pure samples of **11** (1120 mg, 80% yield) as a white solid and **12** (140 mg, 10% yield) as a yellow oil.

Ketone 11. m.p. 45-46 °C; FTIR (thin film/NaCl) 2973 (s), 2874 (m), 1746 (s), 1725 (s), 1462 (w), 1297 (m), 1283 (m), 1261 (m), 1158 (s), 1086 (m), 1056 (m), 1038 (m), 1015 (m), 803 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (dd, *J*= 3.6, 2.0 Hz, 1H), 2.69 (m, 1H), 2.62 (d, *J*=2.8 Hz, 1H), 2.41 (dd, *J*=18, 4.8 Hz, 1H), 1.95 (m, 2H), 1.92 (d, *J*=2.0 Hz, 1H), 1.53 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 178.3, 80.00, 52.1, 41.3, 39.0, 38.0, 27.2, 27.1, 24.9, 20.7; HRMS (EI) *m/z* 210.1259 [calc'd for $C_{12}H_{18}O_3$ (M+) 210.1256].

Ketone 12. FTIR (thin film/NaCl) 2972 (m), 2878 (s), 1845 (w), 1782 (s), 1727 (s), 1481 (w), 1297 (w), 1281 (m), 1152 (s), 1065 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.81 (dd, *J*=8.4, 1.2 Hz, 1H), 2.1 (dd, *J*=14, 8.4 Hz, 1H), 2.01-1.97 (m, 2H), 1.93-1.89 (m, 1H), 1.86-1.80 (m, 2H), 1.57-1.44 (m, 2H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 178.0, 71.4, 43.3, 38.7, 37.8, 35.1, 27.0, 23.0, 18.6; HRMS (EI) *m/z* 210.1257 [calc'd for $C_{12}H_{18}O_3$ (M+) 210.1256].

Preparation of Enoates 13 and 14:



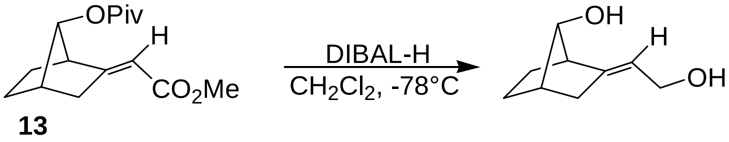
Enoates 13 and 14. To a stirred solution of lithium chloride (2.1 g, 50 mmol, 2 equiv) in CH_3CN (50 mL) was added trimethyl phosphonoacetate (8.1 mL, 50 mmol, 2 equiv) followed

DBU (7.2 mL, 48 mmol, 1.9 equiv). After 20 minutes the resultant yellow solution of **11** (5.28 g, 25 mmol, 1 equiv) in 10 mL CH_3CN. Stirring was continued overnight at room temperature. Solvent was evaporated, and the crude reaction mixture was filtered through a plug of silica using 10% EtOAc/Hexanes as the eluent yielding a 2.4:1 mixture (6.59 g, 99% yield) of **13** and **14**. Analytically pure samples were prepared using a chromatotron employing 3% CH_2Cl_2/Hexanes as the eluent.

Enoate 13. m.p. 39-40 °C; FTIR (thin film/NaCl) 2972 (m), 2876 (w), 1728 (s), 1717 (s), 1667 (m), 1435 (w), 1359 (w), 1297 (m), 1282 (m), 1204 (s), 1146 (s), 1091 (w), 1041 (w), 1025 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (t, *J*=2.4 Hz, 1H), 4.73 (dd, *J*=3.4, 1.4 Hz, 1H), 3.69 (s, 3H), 2.91-2.84 (m, 1H), 2.83 (d, *J*=4.4 Hz, 1H), 2.55 (t, *J*=1.6 Hz, 1H), 2.51 (t, *J*=1.8 Hz, 1H), 2.42 (t, *J*=4 Hz, 1H), 1.93-1.87 (m, 1H), 1.79-1.73 (m, 1H), 1.32 (app dd, *J*=19.2, 11.2 Hz, 2H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 168.3, 167.4, 110.7, 80.8, 51.1, 49.2, 39.0, 38.9, 36.5, 27.2, 25.4, 25.0; HRMS (EI) *m/z* 266.1514 [calc'd for $C_{15}H_{22}O_4$ (M+) 266.1518].

Enoate 14. FTIR (thin film/NaCl) 2972 (m), 2876 (w), 1727 (s), 1665 (m), 1461 (w), 1434 (w), 1397 (w), 1363 (m), 1283 (m), 1213 (m), 1185 (m), 1150 (m), 1136 (m), 1041 (w), 1024 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, *J*=0.8 Hz, 1H), 4.83 (d, *J*=1.6 Hz, 1H), 3.91 (d, *J*=4.8 Hz, 1H), 3.67 (s, 3H), 2.62 (dd, *J*=17.2, 1.6 Hz, 1H), 2.36 (t, *J*=4.2 Hz, 1H), 2.12 (d, *J*=17.2 Hz, 1H), 1.96-1.90 (m, 1H), 1.81-1.74 (m, 1H), 1.36-1.24 (m, 2H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 167.1, 167.0, 111.9, 81.4, 51.1, 45.2, 38.9, 38.0, 37.3, 27.2, 27.1, 25.1, 24.9; HRMS (EI) *m/z* 266.1514 [calc'd for $C_{15}H_{22}O_4$ (M+) 266.1518].

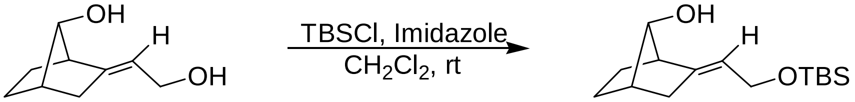
Preparation of Diol:



Diol. To a stirred solution of **13** (1220 mg, 4.58 mmol, 1 equiv) in CH_2Cl_2 (60 mL) at –78°C was added neat diisobutylaluminum hydride (4.9 mL, 27.49 mmol, 6 equiv). After 20 minutes the mixture was diluted with CH_2Cl_2 (100 mL) and 20% solution of sodium-/potassium-tartrate (Rochelle's salt) (100 mL). The resulting mixture was vigorously stirred until homogeneous (1.5 h). The mixture was poured into a separatory funnel and extracted with CH_2Cl_2 (5 X 50 mL). The combined organic layers were dried over Na_2SO_4 and evaporated. Silica gel chromatography furnished **diol** (570 mg, 95% yield) as a white solid.

Diol. m.p. 73-74 °C; FTIR (thin film/NaCl) 3330 (s), 2958 (s), 2915 (s), 2871 (s), 1467 (w), 1346 (w), 1161 (m), 1069 (s), 994 (s), 96. (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.59-5.53 (m, 1H), 4.16 (dd, *J*=11.2, 8.0 Hz, 1H), 4.14 (dd, *J*=11.2, 8.0 Hz, 1H), 3.98 (br s, 1H), 2.57-2.45 (m, 4H), 2.16 (br s, 1H), 1.94 (d, *J*=16.0 Hz, 1H), 1.78-1.61 (m, 2H), 1.31-1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 119.8, 79.4, 60.3, 50.0, 41.0, 31.6, 26.3, 26.2; HRMS (CI) *m/z* 153.0918 [calc'd for $C_9H_{14}O_2$ (M-H) 153.0916].

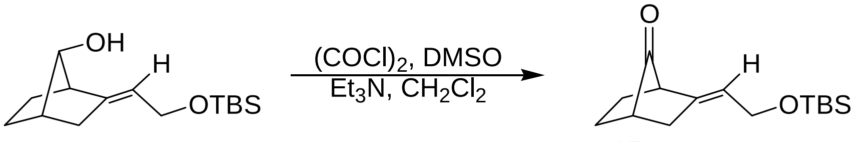
Preparation of TBS-ether:



TBS-ether. To a stirred solution of **diol** (706 mg, 4.58 mmol, 1 equiv) in CH_2Cl_2 (50 mL) was added TBSCl (760 mg, 5.04 mmol, 1.1 equiv) and imidazole (343 mg, 5.04 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 12 h. D-Sorbitol was then added and stirring was continued for 30 minutes, at which point the reaction mixture was gravity filtered and the solid was washed with CH_2Cl_2 (3 X 50 mL). Evaporation of CH_2Cl_2 yielded pure **TBS-ether** as a clear oil (1.09 g, 89% yield).

TBS-ether. FTIR (thin film/NaCl) 3387 (m), 2957 (s), 2857 (s), 1682 (m), 1667 (m), 1471 (m), 1254 (s), 1161 (m), 1088 (s), 1042 (s), 835 (s), 776 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (m, 1H), 4.17 (app t, *J*=5.2 Hz, 2H), 3.96 (d, *J*=1.2 Hz, 1H), 2.48 (d, *J*=16.4 Hz, 1H), 2.42 (d, *J*= 3.6 Hz, 1H), 2.15 (br s, 1H), 1.90 (d, *J*=16.0 Hz, 1H), 1.75-1.61 (m, 2H), 1.33-1.19 (m, 2H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 121.2, 79.6, 61.4, 50.1, 41.1, 31.8, 26.5, 26.2, 26.1, 18.6, -4.9; HRMS (CI) *m/z* 267.1781 [calc'd for $C_{15}H_{28}O_2Si$ (M-H) 267.1780].

Preparation of Ketone 15:

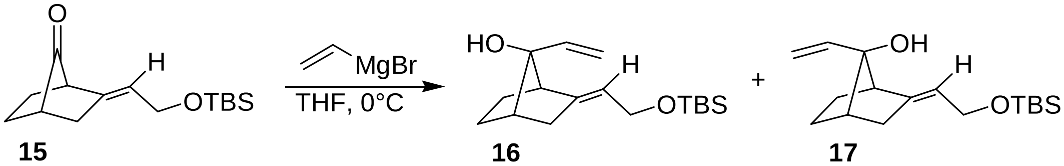


15

Ketone 15. To a stirred solution of oxalyl chloride (520 μL, 5.98 mmol, 1.5 equiv) in CH_2Cl_2 (30 mL) at –78 ºC was added dimethylsulfoxide (850 μL, 11.96 mmol, 3.0 equiv). The resulting mixture was stirred for 5 minutes. A solution of **TBS-ether** (1070 mg, 3.99 mmol, 1 equiv) dissolved in 10 mL CH_2Cl_2 was added dropwise to the mixture and stirring was continued for another 10 minutes at –78 ºC. Triethylamine (2.9 mL, 19.94 mmol, 5 equiv) was added slowly and then after allowing the mixture to warm to room temperature, it was diluted with water (10 mL) and CH_2Cl_2 (150 mL). The organic layer was washed with water (2 X 100mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to provide a yellow oil. Silica gel chromatography furnished an analytically pure sample of **15** (956 mg, 90% yield).

Ketone 15. FTIR (thin film/NaCl) 2952 (s), 2929 (s), 2856 (s), 1775 (s), 1682 (w), 1463 (m), 1254 (m), 1088 (m), 1041 (m), 1006 (w), 835 (s), 776 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.50 (dq, *J*=6.4, 2.4 Hz, 1H), 4.15 (dq, *J*=6.4, 1.4 Hz, 2H), 2.63 (dt, *J*=16.4, 2.0 Hz, 1H), 2.45 (d, *J*=4.0 Hz, 1H), 2.31 (app d, *J*=16.0 Hz, 1H), 2.14 (t, *J*=4.4 Hz, 1H), 2.07-1.97 (m, 2H), 1.73-1.56 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 136.9, 121.8, 59.8, 48.4, 40.4, 33.5, 29.9, 26.2, 24.5, 23.7, 18.6, -4.9; HRMS (CI) *m/z* 267.1778 [calc'd for $C_{15}H_{26}O_2Si$ (M+H) 267.1780].

Preparation of Dienes 16 and 17:



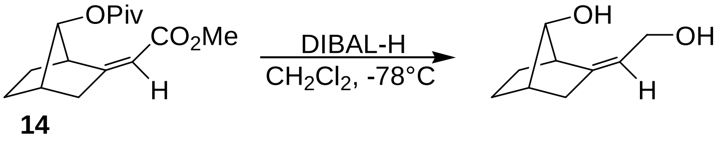
Dienes 16 and 17. To a stirred solution of **15** (400 mg, 1.5 mmol, 1 equiv) in THF (20 mL) at 0°C was added 1.0M vinylmagnesium bromide in THF (4.5 mL, 4.5 mmol, 3 equiv). After stirring for 10 minutes the reaction mixture was treated with a solution of saturated ammonium chloride (10 mL) and extracted with EtOAc (3 X 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give an oil. Silica gel chromatography employing a 50% CH_2Cl_2/Hexanes-100% CH_2Cl_2 gradient gave two analytically pure compounds: **16** (219 mg, 50% yield, eluted first) as a clear oil and **17** (67 mg, 15% yield, eluted second) also as a clear oil.

Diene 16. FTIR (thin film/NaCl) 3414 (m), 2955 (s), 2857 (s), 1471 (m), 1255 (s), 1087 (s), 1006 (m), 923 (w), 834 (s), 776 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.16 (dd, *J*=17.4, 10.6 Hz, 1H), 5.42 (dd, *J*=17.6, 1.6 Hz, 1H), 5.40-5.37 (m, 1H), 5.16 (dd, *J*=10.6, 1.6 Hz, 1H), 4.08 (app d, *J*=6.4 Hz, 2H), 2.35 (d, *J*=4.4 Hz, 1H), 2.32-2.28 (m, 1H), 2.19-2.04 (m, 2H), 2.01 (app t, *J*=4.2 Hz, 1H), 1.89 (br d, *J*=16.0 Hz, 1H), 1.54 (br s, 1H), 1.45-1.29 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 139.4, 120.0, 115.3, 85.0, 60.7, 53.4, 45.1, 34.1, 28.3, 28.1, 26.2, 18.6, -4.8; HRMS (EI) *m/z* 293.1935 [calc'd for $C_{17}H_{30}O_2Si$ (M-H) 293.1937].

Diene 17. FTIR (thin film/NaCl) 3420 (m), 2955 (s), 2928 (m), 2856 (m), 1471 (m), 1254 (m), 1175 (w), 1087 (m), 1041 (m), 924 (w), 834 (s), 814 (w), 775 (m) cm^{-1}; ^1H NMR (500

MHz, $CDCl_3$) δ 6.22 (dd, *J*=17.5, 10.5 Hz, 1H), 5.46 (dd, *J*=17.5, 2.0 Hz, 1H), 5.46-5.45 (m, 1H), 5.24 (dd, *J*=11.0, 1.5 Hz, 1H), 4.18 (app t, *J*=7.0 Hz, 2H), 2.66 (dt, *J*=17.5, 1.5 Hz, 1H), 2.34 (d, *J*=3.5 Hz, 1H), 2.07 (t, *J*=4.5 Hz, 1H), 1.95 (d, *J*=16.0 Hz, 1H), 1.89-1.83 (m, 1H), 1.81-1.75 (m, 1H), 1.60 (s, 1H), 1.43-1.38 (m, 1H), 1.34-1.29 (m, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 138.1, 120.5, 116.0, 85.1, 61.1, 53.6, 44.6, 34.1, 27.1, 26.2, 18.6, -4.8, -4.9; HRMS (EI) *m/z* 293.1940 [calc'd for $C_{17}H_{30}O_2Si$ (M-H) 293.1937].

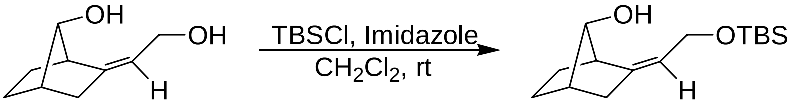
Preparation of Diol:



Diol. Prepared in the same manner as the diol above, giving a white solid (88% yield).

Diol. m.p. 81-82 °C; FTIR (thin film/NaCl) 3327 (s), 2960 (s), 2916 (s), 2872 (s), 1680 (w), 1447 (w), 1347 (w), 1304 (w), 1164 (m), 1130 (m), 1071 (s), 989 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (t, *J*=7.4 Hz, 1H), 4.16 (dd, *J*=12.0, 8.4 Hz, 1H), 4.07 (dd, *J*=12.0, 8.0 Hz, 1H), 4.04 (s, 1H), 2.83 (d, *J*=4.0 Hz, 1H), 2.60 (app d, *J*=15.6 Hz, 1H), 2.12 (app t, *J*=4.0 Hz, 1H), 2.01 (br s, 2H), 1.97 (br s, 1H), 1.79-1.64 (m, 2H), 1.31-1.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 79.9, 120.5, 60.5, 45.0, 40.7, 34.9, 26.3, 26.2; HRMS (CI) *m/z* 153.0916 [calc'd for $C_9H_{14}O_2$ (M-H) 153.0916].

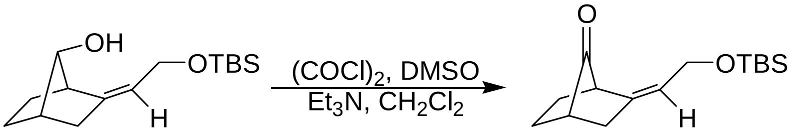
Preparation of TBS-ether:



TBS-ether. Prepared in the same manner as TBS-ether **above**, furnishing a clear oil (97% yield).

TBS-ether. FTIR (thin film/NaCl) 3372 (m), 2956 (s), 2929 (s), 2856 (m), 1679 (w), 1471 (m), 1254 (m), 1084 (s), 1040 (m), 836 (s), 776 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.45 (app t, *J*=7.0 Hz, 1H), 4.19-4.15 (m, 2H), 3.99 (d, *J*=1.2 Hz, 1H), 2.74 (d, *J*=3.6 Hz, 1H), 2.56 (dt, *J*=16.0, 2.0 Hz, 1H), 2.09 (app t, *J*=4.2 Hz, 1H), 1.96 (d, *J*=16.0 Hz, 1H), 1.72-1.62 (m, 2H), 1.30-1.22 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 121.6, 79.8, 61.4, 45.1, 40.5, 34.9, 26.2, 26.2, 26.1, 18.6, -4.9; HRMS (CI) *m/z* 267.1775 [calc'd for $C_{15}H_{28}O_2Si$ (M-H) 267.1780].

Preparation of Ketone:

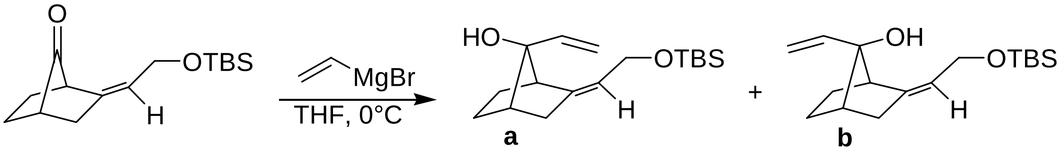


Ketone. Prepared in the same manner as ketone above, furnishing a clear oil (92% yield).

Ketone. FTIR (thin film/NaCl) 2953 (s), 2929 (s), 2856 (s), 1776 (s), 1471 (w), 1254 (m), 1109 (m), 1082 (m), 1049 (m), 835 (s), 776 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.39

(app t, *J*=6.6 Hz, 1H), 4.15 (app dt, *J*=6.8, 1.6 Hz, 2H), 2.72 (app d, *J*=4.0 Hz, 1H), 2.70-2.64 (m, 1H), 2.31 (dd, *J*=16.4, 1.6 Hz, 1H), 2.12 (t, *J*=4.4 Hz, 1H), 2.06-1.95 (m, 2H), 1.70-1.57 (m, 2H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 136.9, 122.9, 60.9, 44.5, 40.1, 35.7, 26.1, 24.3, 23.6, 18.6, -4.9, -5.0; HRMS (CI) *m/z* 267.1772 [calc'd for $C_{15}H_{26}O_2Si$ (M+H) 267.1780].

Preparation of Dienes:

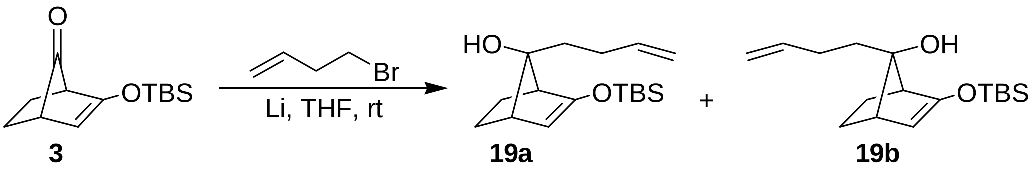


Dienes. Prepared in the same manner as Dienes above, yielding two analytically pure compounds**:** **a** (219 mg, 59% yield, eluted first) as a clear oil and **b** (77 mg, 21% yield, eluted second) also as a clear oil .

Diene a. FTIR (thin film/NaCl) 3362 (m), 2955 (s), 2930 (s), 2856 (m), 1471 (w), 1463 (w), 1255 (m), 1085 (s), 1048 (m), 1005 (m), 922 (w), 834 (s), 813 (w), 775 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dd, *J*=17.2, 10.8 Hz, 1H), 5.41 (dd, *J*=17.2, 1.6 Hz, 1H), 5.24 (app t, *J*=6.8 Hz, 1H), 5.16 (dd, *J*=10.8, 1.6 Hz, 1H), 4.16-4.13 (m, 2H), 2.63 (d, *J*=4.0 Hz, 1H), 2.39 (dt, *J*=16.8, 1.6 Hz, 1H), 2.15-2.07 (m, 2H), 1.97-1.92 (m, 2H), 1.54 (s, 1H), 1.37-1.35 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.4, 120.5, 115.3, 85.5, 61.3, 48.8, 44.6, 36.8, 28.3, 27.7, 26.2, 18.6, -4.9; HRMS (EI) *m/z* 293.1942 [calc'd for $C_{17}H_{30}O_2Si$ (M-H) 293.1937].

Diene b. FTIR (thin film/NaCl) 3409 (m), 2955 (s), 2927 (s), 2855 (m), 1471 (m), 1254 (m), 1084 (m), 1054 (m), 834 (s), 776 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (dd, *J*=17.0, 11.0 Hz, 1H), 5.48 (dd, *J*=17.5, 1.5 Hz, 1H), 5.43 (app t, *J*=7.0 Hz, 1H), 5.25 (dd, *J*=10.5, 1.5 Hz, 1H), 4.18 (ddd, *J*=5.0, 3.0, 1.0 Hz, 2H), 2.74 (d, *J*=16.0 Hz, 1H), 2.64 (d, *J*=4.0 Hz, 1H), 2.03-2.00 (m, 2H), 1.88-1.78 (m, 2H), 1.41-1.32 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 138.1, 121.1, 116.1, 85.4, 61.4, 48.9, 43,9 37.0, 29.9, 27.1, 26.7, 26.2, 18.7, -4.8, -4.9; HRMS (CI) *m/z* 293.1937 [calc'd for $C_{17}H_{30}O_2Si$ (M-H) 293.1937].

Preparation of Alcohols 19a and 19b:

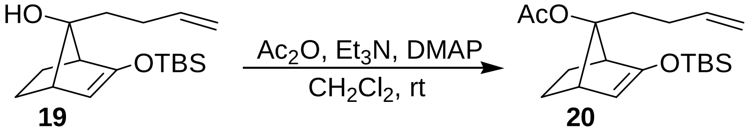


Alcohols 19a and 19b. To a suspension of lithium metal (110 mg, 15.87 mmol, 3 equiv) in THF (9 mL) was added a solution 4-bromo-1-butene (752 µL, 7.41 mmol, 1.4 equiv) and **3** (1260 mg, 5.29 mmol, 1.0 equiv) in THF (1 mL). Upon addition the reaction mixture turned dark and the lithium metal began dissolving. After stirring for 12 h at room temperature, saturated $NaHCO_3$ (20 mL) was added, and the mixture extracted with EtOAc (3 X 30 mL).The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give an oil (as a 1:1 mixture of **19a** and **19b**). Silica gel chromatography furnished two analytically pure compounds. **19a** (535 mg, 44% yield, eluted first) as a clear oil and **19b** (545 mg, 45% yield, eluted second) also as a clear oil .

Alcohol 19b. FTIR (thin film/NaCl) 3563 (m), 3076 (m), 2959 (s), 2930 (s), 2884 (m), 2859 (m), 1641 (w), 1610 (s), 1472 (m), 1381 (m), 1325 (s), 1254 (m), 1221 (m), 1197 (m), 1163 (w), 1101 (w), 932 (m), 909 (m), 888 (w), 860 (s), 838 (s), 784 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88-5.80 (m, 1H), 5.01 (app dq, *J*=16.5, 6.0 Hz, 1H), 4.93-4.90 (m, 1H), 4.69 (dd, *J*=3.5, 1.0 Hz, 1H), 2.87 (s, 1H), 2.48 (app q, *J*=3.5 Hz, 1H), 2.30 (m, 1H), 2.14 (dq, *J*=7.8, 1.0 Hz, 2H), 1.84-1.73 (m, 2H), 1.58-1.49 (m, 2H), 1.11-1.10 (m, 2H), 0.92 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 139.4, 114.3, 102.1, 90.3, 53.4, 48.7, 31.3, 28.3, 26.0, 25.8, 22.6, 18.2, -4.2, -4.6; HRMS (CI) *m/z* 295.2093 [calc'd for $C_{17}H_{30}O_2Si$ (M+H) 295.2093].

Alcohol 19a. FTIR (thin film/NaCl) 3434 (m), 3077 (w), 2957 (s), 2932 (s), 2899 (m), 2859 (s), 1641 (w), 1616 (s), 1472 (m), 1463 (m), 1362 (m), 1330 (s), 1256 (s), 1225 (m), 1200 (m), 1130 (m), 1006 (m), 932 (m), 859 (s), 836 (s), 781 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90-5.80 (m, 1H), 5.03 (app dq, *J*=16.8, 1.6 Hz, 1H), 4.96-4.92 (m, 1H), 4.62 (dd, *J*=3.2, 1.2 Hz, 1H), 2.4 (m, 1H), 2.21 (app t, *J*=1.6 Hz, 1H), 2.17-2.08 (m, 2H), 1.99-1.82 (m, 4H), 1.48 (s, 1H), 1.26-1.12 (m, 2H), 0.92 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 139.5, 114.6, 104.2, 89.8, 52.5, 47.6, 32.2, 30.5, 26.5, 25.9, 23.1, 18.3, -4.2, -4.4; HRMS (CI) *m/z* 295.2091 [calc'd for $C_{17}H_{30}O_2Si$ (M+H) 295.2093].

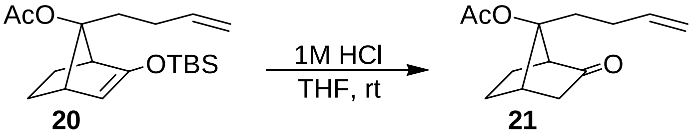
Preparation of Acetate 20:



Acetate 20. Prepared in the same manner as acetate **6**, giving a yellow oil (95% yield).

Acetate 20. FTIR (thin film/NaCl) 3078 (w), 2955 (s), 2932 (s), 2859 (m), 1770 (m), 1738 (s), 1640 (w), 1620 (s), 1472 (m), 1464 (m), 1367 (m), 1331 (m), 1246 (m), 1229 (m), 1171 (w), 1113 (w), 1018 (m), 912 (m), 857 (m), 838 (s), 783 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.80-5.73 (m, 1H), 4.97 (dq, *J*=16.8, 2.0 Hz, 1H), 4.92-4.89 (m, 1H), 4.59 (dd, *J*=3.5, 2.0 Hz, 1H), 2.87 (ddd, *J*=3.5, 3.5, 2.0 Hz, 1H), 2.80-2.79 (m, 1H), 2.14 (t, J=7.5 Hz, 2H), 2.06-1.97 (m, 2H), 1.97 (s, 3H), 1.82-1.78 (m, 1H), 1.71-1.66 (m, 1H), 1.24-1.12 (m, 2H), 0.91 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 158.5, 138.9, 114.4, 102.4, 96.4, 51.1, 46.0, 30.2, 27.3, 26.3, 25.9, 22.8, 21.9, 18.2, -4.3, -4.4; HRMS (CI) *m/z* 337.2209 [calc'd for $C_{19}H_{32}O_3Si$ (M+H) 337.2199].

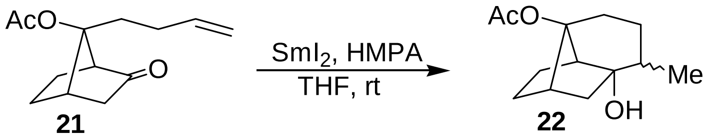
Preparation of Ketone 21:



Ketone 21: Prepared in the same manner as ketone **6**, giving a clear oil (98% yield).

Ketone 21. FTIR (thin film/NaCl) 2957 (m), 2884 (w), 1752 (s), 1738 (s), 1642 (w), 1452 (w), 1415 (w), 1246 (m), 1223 (m), 1205 (w), 1137 (w), 1073 (w), 1044 (w), 1020 (w), 914 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.81-5.71 (m, 1H), 5.01 (dq, *J*=17.2, 1.6 Hz, 1H), 4.98-4.94 (m, 1H), 2.99 (d, *J*=4.8 Hz, 1H), 2.86 (t, *J*=5.0 Hz, 1H), 2.33 (ddd, *J*=18.4, 4.8, 2.0 Hz, 1H), 2.14-1.87 (m, 6H), 2.06 (s, 3H), 1.59-1.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 170.0, 137.7, 115.4, 91.5, 56.6, 43.6, 40.8, 29.2, 28.9, 26.9, 22.4, 21.6; HRMS (CI) *m/z* 223.1341 [calc'd for $C_{13}H_{18}O_3$ (M+H) 223.1334].

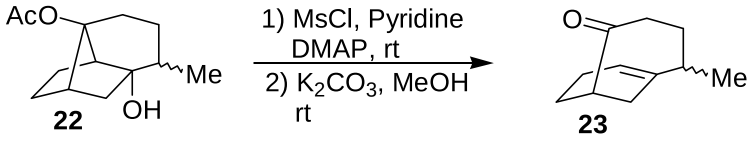
Preparation of Alcohol 22:



Alcohol 22. To a stirred suspension of samarium metal filings (433 mg, 2.88 mmol, 4 equiv) in THF (13 mL) was added diiodoethane (609 mg, 2.16 mmol, 3 equiv). After stirring the reaction mixture for 2 h at room temperature it turned deep blue at which point HMPA (1252 μL, 7.2 mmol, 10 equiv) was added (and the deep blue suspension changed to dark deep purple). After stirring for 10 minutes, a solution of *t*-butyl alcohol (207 μl, 2.16 mmol, 3 equiv) and **21** (160 mg, 0.72 mmol, 1 equiv) in THF (14 mL) was added dropwise. After stirring for 1 h the reaction mixture was treated with a solution of saturated $NaHCO_3$ (20 mL) and extracted with Et_2O (3 X 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give an oil. Silica gel chromatography yielded a 1:1 mixture of **22** (96 mg, 59% yield).

Alcohol 22. FTIR (thin film/NaCl) 3446 (m), 2953 (s), 2876 (m), 1734 (s), 1715 (s), 1456 (w), 1369 (m), 1326 (w), 1254 (s), 1237 (s), 1171 (w), 1096 (w), 1082 (m), 1039 (m), 992 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48-2.44 (m, 2H), 2.30 (dd, *J*=13.5, 7.0 Hz, 1H), 2.25 (d, *J*=3.5 Hz, 1H), 2.19-2.14 (m, 1H), 2.06-2.00 (m, 5H), 1.99 (s, 3H), 1.98 (s, 3H), 2.00-1.87 (m, 3H), 1.78-1.65 (m, 7H), 1.46-1.41 (m, 2H), 1.37-1.25 (m, 4H), 1.13 (d, *J*=13.0 Hz, 1H), 1.03 (d, *J*=7.0 Hz, 3H), 0.85 (d, *J*=6.5 Hz, 3H), 0.82 (d, *J*=13.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.3, 92.7, 92.5, 79.1, 78.8, 54.4, 46.3, 42.7, 42.5, 42.0, 39.7, 39.3, 35.5, 31.2, 30.7, 29.0, 28.3, 26.8, 25.6, 22.0, 21.9, 19.1, 18.8, 14.6, 14.2; HRMS (CI) *m/z* 223.1334 [calc'd for $C_{13}H_{20}O_3$ (M-H) 223.1334].

Preparation of Olefin 23:

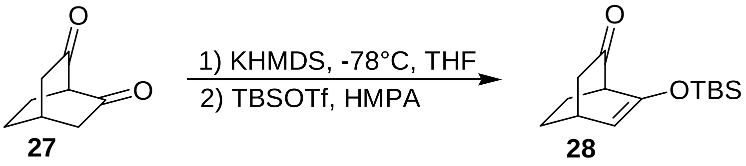


Olefin 23. To a stirred solution of **22** (96 mg, 0.43 mmol, 1 equiv) in pyridine (4 mL) was added methanesulfonyl chloride (330 μl, 4.28 mmol, 10 equiv) and DMAP (52 mg, 0.43 mmol, 1 equiv). The reaction mixture was stirred overnight at room temperature, diluted with 20% EtOAc/Hexanes (30 mL), and washed consecutively with saturated copper sulfate (3 X 15 mL) and 1N HCl (2 X 10 mL). The organic layer was dried with $MgSO_4$ and concentrated to yield mesylate (103 mg, 80% yield), which was carried on to the next step. The mesylate (54 mg, 0.18 mmol, 1 equiv) was dissolved in MeOH (2 mL) and stirred with K_2CO_3 (124 mg, 0.90 mmol, 5 equiv) for 3 h at room temperature. The reaction mixture was filtered, evaporated, diluted with water (5 mL), and extracted with 10 % EtOAc/Hexane (2 X 10 mL) before drying over Na_2SO_4. Silica gel chromatography gave an analytically pure 1:1 diastereomeric mixture of **23** (28 mg, 95% yield).

Olefin 23. FTIR (thin film/NaCl) 2956 (m), 2930 (m), 2873 (m), 1702 (s), 1453 (m), 1379 (w), 1035 (w), 887 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67-5.65 (m, 1H), 5.57-5.56 (m, 1H), 2.98-2.93 (m, 1H), 2.71-2.47 (m, 8H), 2.28-2.19 (m, 3H), 2.16-2.08 (m, 3H), 1.97-1.71

(m, 7H), 1.65-1.60 (m, 2H), 1.15 (d, *J*=7.0 Hz, 3H), 1.05 (d, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.1, 216.7, 149.2, 146.6, 124.9, 119.6, 47.3, 47.2, 41.9, 41.5, 40.5, 39.4, 39.1, 36.3, 33.2, 25.7, 24.8, 24.2, 21.9, 21.1, 17.7, 17.1; HRMS (CI) *m/z* 165.1278 [calc'd for $C_{11}H_{14}O$ (M+H) 165.1279].

Preparation of Enol Ether 28:

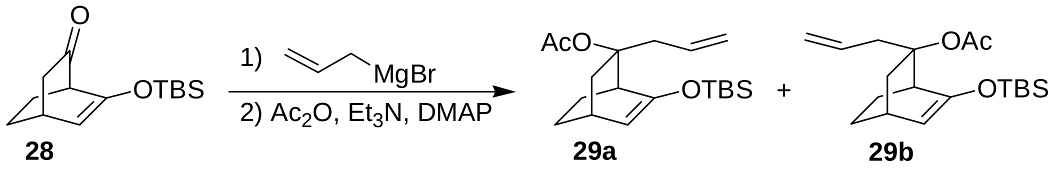


Enol Ether 28. To a stirred solution of KHMDS (1173 mg, 5.88 mmol, 1.2 equiv) in THF (40 mL) at –78°C was added ketone **27** (677 mg, 4.90 mmol, 1 equiv). Stirring was continued for 1 h, at which point HMPA (852 µL, 4.90 mmol, 1 equiv) was added. The reaction mixture stirred for additional 10 minutes before adding TBSOTf (1125 µL, 4.90 mmol, 1 equiv). Stirring was continued for 3 h at –78°C before the reaction was quenched with saturated Na_2CO_3 (20 mL) and extracted with EtOAc (3 X 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. The resulting crude oil was purified using silica gel chromatography with 1% Et_3N /Hexanes as the eluent, yielding **28** (1111 mg, 90% yield).

Enol Ether 28. FTIR (thin film/NaCl) 2954 (s), 2859 (m), 1729 (s), 1638 (s), 1472 (m), 1464 (m), 1406 (w), 1362 (w), 1340 (m), 1301 (m), 1250 (m), 1227 (m), 1193 (m), 1170 (m), 1142 (w), 1091 (m), 915 (m), 896 (m), 868 (w), 839 (m), 782 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (dd, *J*=7.2, 2.4 Hz, 1H), 2.95 (q, *J*=2.4 Hz, 1H), 2.92-2.88 (m, 1H), 2.04 (t, *J*=2.8 Hz, 1H), 2.00 (d, *J*=2.8 Hz, 1H), 1.87-1.73 (m, 2H), 1.69-1.62 (m, 1H), 1.57-1.49 (m, 1H), 0.90

(s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 151.8, 108.2, 54.7, 41.9, 31.1, 25.8, 25.6, 22.8, 18.2, -4.4; HRMS (CI) *m/z* 253.1618 [calc'd for $C_{14}H_{24}O_2Si$ (M+H) 253.1624].

Preparation of Acetates 29a and 29b:



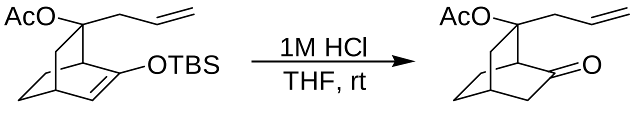
Acetates 29a and 29b. The allylation of **28** was done in a manner analogous to the preparation of **4**, and the resulting alcohols were acetylated in the same manner as **6**, to furnish a 3:1 separable mixture of **29a** and **29b** (82% yield over two steps).

Acetates 29a. FTIR (thin film/NaCl) 3076 (w), 2954 (s), 2859 (m), 1736 (s), 1641 (s), 1472 (s), 1464 (s), 1439 (s), 1363 (m), 1353 (m), 1237 (s), 1222 (s), 1198 (m), 1135 (w), 1112 (m), 1017 (m), 988 (w), 913 (m), 890 (w), 840 (s), 794 (m), 779 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80-5.70 (m, 1H), 5.07-5.02 (m, 2H), 4.98 (dd, *J*=7.2, 2.4 Hz, 1H), 2.80 (q, *J*=2.4 Hz, 1H), 2.74 (ddt, *J*=14.8, 7.2, 0.8 Hz, 1H), 2.56 (ddt, *J*=14.8, 7.2, 0.8 Hz, 1H), 2.53-2.50 (m, 1H), 1.98 (s, 3H), 1.87 (td, *J*=5.2, 2.8 Hz, 1H), 1.72 (dd, *J*=13.6, 2.8 Hz, 1H), 1.61 (dt, *J*=14.0, 2.8 Hz, 1H), 1.50-1.45 (m, 1H), 1.33-1.25 (m, 2H), 0.92 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.9, 133.4, 118.2, 104.6, 86.4, 44.0, 42.3, 41.7, 30.4, 25.9, 25.8, 22.3, 19.7, 18.2, -4.4, -4.5; HRMS (CI) *m/z* 337.2195 [calc'd for $C_{19}H_{32}O_3Si$ (M+H) 337.2199].

Acetates 29b. FTIR (thin film/NaCl) 3076 (m), 2954 (s), 2859 (s), 1735 (s), 1641 (s), 1472 (m), 1464 (m), 1363 (s), 1279 (m), 1238 (s), 1238 (s), 1198 (s), 1135 (m), 1112 (m), 1055 (w), 1017 (s), 988 (m), 913 (s), 890 (m), 840 (s), 794 (m), 780 (m) cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 5.78-5.68 (m, 1H), 5.06-5.00 (m, 2H), 4.97 (dd, *J*=7.2, 2.0 Hz, 1H), 2.79 (app q, *J*=2.4 Hz, 1H), 2.73 (ddt, *J*=13.6, 7.2, 0.8 Hz, 1H), 2.55 (ddt, *J*=13.6, 7.2, 0.8 Hz, 1H), 2.51-2.47 (m, 1H), 1.96 (s, 3H), 1.88-1.83 (m, 1H), 1.71 (dd, *J*=14.0, 2.8 Hz, 1H), 1.60 (dd, *J*=14.0, 2.8 Hz, 1H), 1.49-1.44 (m, 1H), 1.32-1.20 (m, 2H), 0.90 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.9, 133.4, 118.2, 104.5, 86.4, 44.0, 42.3, 41.7 30.4, 25.8, 25.7, 22.2, 19.6, 18.1 -4.4, -4.5; HRMS (CI) *m/z* 335.2041 [calc'd for $C_{19}H_{32}O_3Si$ (M-H) 335.2043].

Preparation of Ketone 30:

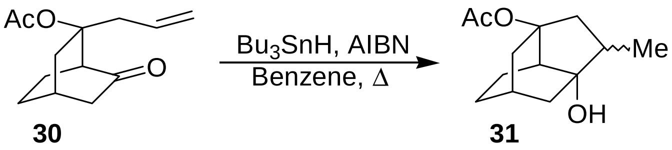


29a **30**

Ketone 30. Prepared in the same manner as ketone **21**, giving a clear oil (91% yield).

Ketone 30. FTIR (thin film/NaCl) 2941 (m), 2874 (w), 1728 (s), 1641 (w), 1368 (w), 1325 (m), 1285 (w), 1239 (s), 1213 (m), 1115 (m), 1017 (m), 983 (w), 924 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73-5.62 (m, 1H), 5.11-5.02 (m, 2H), 2.95 (t, *J*=2.8 Hz, 1H), 2.67 (ddt, *J*=14.4, 7.2, 1.2 Hz, 1H), 2.52 (ddt, *J*=14.4, 7.2, 1.2 Hz, 1H), 2.26-2.22 (m, 1H), 2.20 (t, *J*=2.8 Hz, 1H), 2.16 (t, *J*=2.8 Hz, 1H), 2.11 (t, *J*=2.8 Hz, 1H), 2.07 (t, *J*=2.8 Hz, 1H), 2.00 (s, 3H), 1.85 (dt, *J*=15.2, 2.6 Hz, 1H), 1.73-1.67 (m, 1H), 1.64-1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 170.2, 131.6, 119.4, 82.0, 51.2, 43.5, 43.4, 40.7, 27.6, 23.5, 22.1, 17.9; HRMS (CI) *m/z* 223.1329 [calc'd for $C_{13}H_{18}O_3$ (M+H) 223.1334].

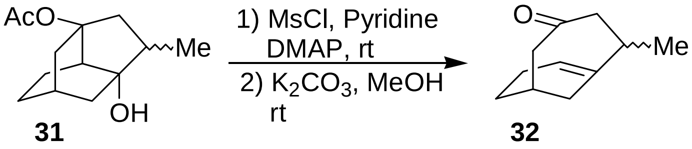
Preparation of Alcohol 31:



Alcohol 31. To a stirred solution of **30** (484 mg, 2.18 mmol, 1 equiv) in benzene (40 mL) was added tributyltin hydride (1.75 mL, 6.54 mmol, 3 equiv) and AIBN (179 mg, 1.09 mmol, 0.5 equiv). The reaction mixture was refluxed for 10 h, cooled to room temperature, and poured onto a silica gel column. Silica gel chromatography using 12-14% EtOAcHexanes as the eluent afforded alcohol **31** as a 9:1 mixture of diastereomers (356 mg, 73% yield).

Alcohol 31. FTIR (thin film/NaCl) 3450 (m), 2939 (s), 2866 (m), 1735 (s), 1715 (s), 1453 (w), 1369 (m), 1336 (w), 1280 (m), 1252 (s), 1296 (s), 1129 (w), 1044 (m), 1024 (m), 987 (m), 899 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.54 (dd, *J*=13.5, 8.5 Hz, 1H), 2.28 (ddd, *J*=14.0, 11.5, 2.0 Hz, 2H), 2.12-2.06 (m, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.95-1.89 (m, 3H), 1.84 (t, *J*=3.0 Hz, 1H), 1.77-1.61 (m, 10H), 1.49-1.44 (m, 6H), 1.19-1.16 (m, 2H), 1.02 (d, *J*=7.5 Hz, 3H), 0.94 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 83.8, 83.2, 77.7, 76.8, 48.3, 46.4, 45.8, 45.4, 43.9, 43.1, 42.8, 42.0, 41.0, 35.8, 26.8, 26.3, 26.1, 25.8, 21.9, 21.8, 18.5, 13.3, 13.1, 13.0; HRMS (CI) *m/z* 223.1339 [calc'd for $C_{13}H_{20}O_3$ (M-H) 223.1334].

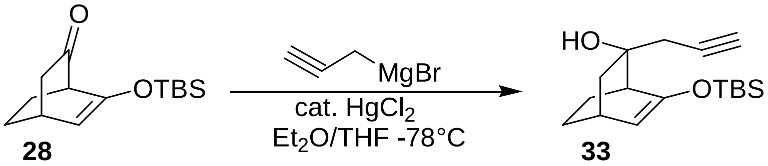
Preparation of Olefin 32:



Olefin 32. Prepared in the same manner as **23**, furnishing **32** as a diastereomeric mixture of olefins (82% yield over two steps).

Olefin 32. FTIR (thin film/NaCl) 3032 (w), 2931 (s), 2866 (m), 1700 (s), 1470 (w), 1454 (m), 1377 (w), 1331 (w), 1275 (m), 1164 (w), 1140 (m), 1082 (w), 1049 (w), 1008 (w), 820 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71-5.68 (m, 1H), 5.63-5.60 (m, 1H), 3.01 (dd, *J*=11.0, 8.5 Hz, 1H), 2.64 (br t, *J*=7.0 Hz, 1H), 2.58-2.47 (m, 7H), 2.41 (d, *J*=13.0 Hz, 1H), 2.25 (d, *J*=13.0 Hz, 1H), 2.17-1.94 (m, 8H), 1.84-1.71 (m, 2H), 1.15 (d, *J*=7.0 Hz, 3H), 1.12 (d, *J*=6.5 Hz, 3H), 1.05-0.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 211.6, 144.1, 143.7, 126.5, 122.1, 54.7, 53.5, 50.8, 50.3, 36.0, 33.5, 33.4, 30.8, 30.3, 29.0, 28.7, 27.7, 23.2, 22.5, 19.9, 17.2; HRMS (EI) *m/z* 164.1206 [calc'd for $C_{11}H_{16}O$ (M+) 164.1201].

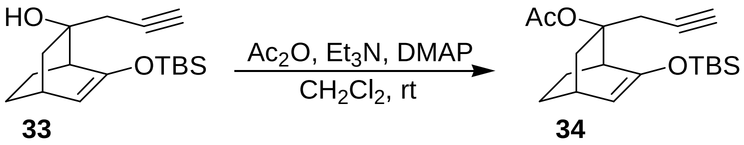
Preparation of Alkyne 33:



Alkyne 33. To a strirred suspension of magnesium metal (1237 mg, 50.92 mmol, 3.4 equiv) and $HgCl_2$ (407 mg, 1.5 mmol, 0.1 equiv) in Et_2O (40 mL) was added propargyl bromide (80 wt % in toluene) (7.4 mL, 49.42 mmol, 3.3 equiv) in Et_2O dropwise. The mixture was heated until all the magnesium had dissolved, and then cooled to –78 °C before cannulating it quickly into a precooled solution (-78 °C) of **28** dissolved in THF (40 mL). The reaction mixture was stirred for 30 minutes and then quenched with saturated $NaHCO_3$ (60 mL) followed by extraction with EtOAc (3 X 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to yield a yellow oil. Silica gel chromatography using 1% Et_3N/1% EtOAc/Hexanes as the eluent gave analytically pure **33** (3940 mg, 90% yield).

Alkyne 33. FTIR (thin film/NaCl) 3561 (m), 3451 (m), 3310 (s), 3059 (w), 2937 (s), 2859 (s), 1639 (s), 1472 (m), 1464 (m), 1353 (m), 1325 (m), 1252 (m), 1240 (m), 1194 (m), 1111 (m), 1050 (m), 1001 (w), 916 (m), 998 (m), 837 (s), 793 (m), 779 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.93 (dd, *J*=7.2, 2.0 Hz, 1H), 2.52-2.49 (m, 1H), 2.42-2.30 (m, 3H), 2.13-2.08 (m, 1H), 2.03 (br s, 1H), 2.02 (t, *J*=2.8 Hz, 1H), 1.58 (dt, *J*=10.0, 2.4 Hz, 1H), 1.43 (dd, *J*=2.8, 0.8 Hz, 2H), 1.34-1.26 (m, 2H), 0.92 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 103.6, 81.1, 75.2, 71.0, 46.6, 42.6, 33.5, 30.8, 25.9, 25.8, 19.6, 18.1, -4.4, -4.5; HRMS (CI) *m/z* 292.1851 [calc'd for $C_{17}H_{28}O_2Si$ (M+) 292.1859].

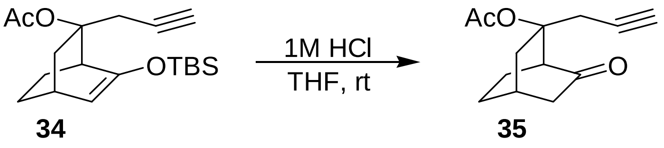
Preparation of Acetate 34:



Acetate 34. Prepared in the same manner as acetate **20**, furnishing **34** as a clear oil (89% yield).

Acetate 34. FTIR (thin film/NaCl) 3312 (w), 2953 (s), 2859 (m), 1737 (s), 1642 (s), 1472 (w), 1464 (w), 1362 (m), 1354 (m), 1234 (s), 1199 (w), 1182 (w), 1029 (m), 913 (m), 840 (s), 794 (w), 780 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (dd, *J*=7.0, 2.0 Hz, 1H), 2.98-2.94 (m, 2H), 2.72 (dd, *J*=17.0, 2.0 Hz, 1H), 2.54-2.50 (m, 1H), 2.06 (s, 3H), 1.91 (t, *J*=3.0 Hz, 2H), 1.74 (dd, *J*=14.5, 2.5 Hz, 1H), 1.63-1.59 (m, 1H), 1.51-1.46 (m, 1H), 1.37-1.27 (m, 2H), 0.92 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 154.7, 104.5, 84.4, 80.5, 69.7, 44.1, 41.3, 30.3, 28.5, 25.8, 25.7, 22.2, 19.5, 18.1, -4.4, -4.5; HRMS (CI) *m/z* 335.2044 [calc'd for $C_{19}H_{30}O_3Si$ (M+H) 335.2042].

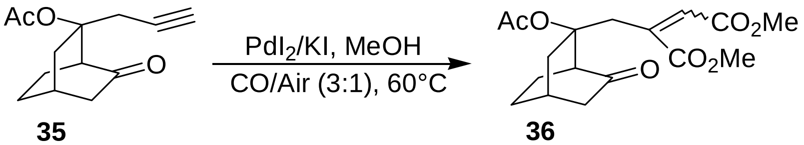
Preparation of Ketone 35:



Ketone 35. Prepared in the same manner as ketone **21**, furnishing **35** (96% yield, waxy solid).

Ketone 35. m.p. 100-102 °C; FTIR (thin film/NaCl) 3283 (m), 2942 (m), 2874 (w), 1727 (s), 1426 (w), 1368 (w), 1237 (m), 1213 (m), 1110 (w), 1062 (w), 1038 (m), 1017 (w) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.08 (t, *J*=2.0 Hz, 1H), 2.92 (dd, *J*=17.5, 3.0 Hz, 1H), 2.73 (dd, *J*=17.5, 3.0 Hz, 1H), 2.29-2.27 (m, 1H), 2.25-2.12 (m, 1H), 2.09 (s, 3H), 1.98 (t, *J*=2.0 Hz, 1H), 1.92 (dt, *J*=15.0, 2.0 Hz, 1H), 1.76-1.63 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.5, 170.4, 80.3, 78.7, 71.3, 51.2, 43.3, 40.3, 29.6, 27.5, 23.2, 22.1, 18.0; HRMS (CI) *m/z* 221.1177 [calc'd for $C_{13}H_{16}O_3$ (M+H) 221.1178].

Preparation of Enoate 36:

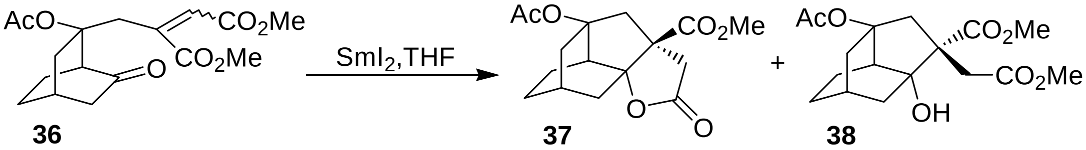


35 **36**

Enoate 36. To a solution of ketone **35** (150 mg, 0.68 mmol, 1 equiv) in MeOH (7 mL) was added potassium iodide (23 mg, 0.14 mmol, 0.2 equiv) and PdI$_2$ (5 mg, 0.014 mmol, 0.02 equiv). This mixture was transferred to a stainless steel autoclave (25 mL). The autoclave was pressurized with CO (370 psi) and air (560 psi). The reaction mixture was stirred and heated at 60 °C for 20 h. The autoclave was cooled to room temperature, the mixture diluted with CH$_2$Cl$_2$ (20 mL) and filtered through a Celite cake with a thin charcoal layer on top. A second filtration through a short silica plug, gave pure mixture of maleates **36** (197 mg, 89% yield).

Enoate 36. FTIR (thin film/NaCl) 2951 (m), 2875 (w), 2847 (w), 1776 (m), 1729 (s), 1645 (m), 1436 (m), 1368 (m), 1247 (m), 1212 (s), 1173 (m), 1115 (m), 1062 (w), 1036 (m), 1017 (m), 969 (w), 941 (w), 801 (w), 734 (m) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.76 (s, 1H), 5.89 (s, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.42 (s, 3H), 3.39 (s, 3H), 3.15 (s, 1H), 3.02-2.92 (m, 2H), 2.95 (d, *J*=9.0 Hz, 1H), 2.80 (d, *J*=15.0 Hz, 1H), 2.28-2.21 (m, 6H), 2.16 (t, *J*=2.5 Hz, 1H), 2.14-2.08 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 2.02-1.97 (m, 2H), 1.82-1.80 (m, 2H), 1.72-1.61 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 213.6, 170.6, 170.5, 168.9, 168.7, 165.0, 145.2, 144.1, 133.4, 124.9, 119.0, 81.3, 80.7, 52.6, 52.5, 52.2, 52.1, 52.0, 51.9, 51.8, 51.0, 50.9, 43.3, 43.2, 43.1, 43.0, 40.9, 40.8, 40.7, 38.7, 34.2, 27.5, 23.4, 23.1, 22.3, 22.2, 22.1, 17.7; HRMS (CI) *m/z* 339.1434 [calc'd for $C_{17}H_{22}O_7$ (M+H) 339.1444].

Preparation of Acetates 37 and 38:



Acetates 37 and 38. To a stirred suspension of samarium metal filings (95 mg, 0.63 mmol, 4 equiv) in THF (6 mL) was added diiodoethane (135 mg, 0.47 mmol, 3 equiv). After stirring the reaction mixture for 2 h at room temperature. The resultant deep blue solution was cooled to 0 °C and a solution of MeOH (40 μl, 0.95 mmol, 5 equiv) and **36** (51 mg, 0.16 mmol, 1 equiv) dissolved in THF (7 mL) was added dropwise. After stirring for 30 minutes the reaction mixture was treated with K_2CO_3/Rochelle’s salt solution and extracted with 20% Et_2O/Hexanes (3 X 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a solid as a 1:7 mixture of **37:38**. Silica gel chromatography furnished pure **37** (5 mg, 8% yield, eluted first) as a clear oil and **38** (37 mg, 70% yield, eluted second) as a white solid.

Acetate 37. FTIR (thin film/NaCl) 2951 (m), 2872 (w), 1788 (s), 1734 (s), 1437 (w), 1370 (w), 1312 (w), 1249 (m), 1231 (m), 1197 (m), 1170 (m), 1066 (m), 1026 (m), 906 (w), 737 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.38 (d, *J*=13.5 Hz, 1H), 3.20 (d, *J*=13.0 Hz, 1H), 2.70 (d, *J*=13.0 Hz, 1H), 2.27 (dt, *J*=15.0, 3.0 Hz, 1H), 2.18 (t, *J*=3.0 Hz, 1H), 2.04 (s, 3H), 1.92 (dd, *J*=13.5, 2.0 Hz, 1H), 1.89-1.81 (m, 3H), 1.76-1.72 (m, 1H), 1.61-1.56 (m, 3H), 1.46-1.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 173.1, 170.3, 91.4, 82.3, 55.6, 52.9, 46.0, 45.2, 43.7, 41.2, 34.6, 25.9, 25.1, 21.8, 13.1; HRMS (CI) *m/z* 309.1337 [calc'd for $C_{16}H_{20}O_6$ (M+H) 309.1338].

Acetate 38. m.p. 128-130 °C; FTIR (thin film/NaCl) 3479 (m), 2950 (m), 2868 (w), 1732 (s), 1436 (m), 1369 (m), 1250 (m), 1206 (m), 1023 (w), 915 (w), 731 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.07 (s, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.80 (dd, *J*=15.0, 2.0 Hz, 1H), 2.78-2.69 (m, 2H), 2.43 (t, *J*=3.0, 1 Hz, 1H), 2.11 (ddd, *J*=7.0, 4.5, 2.5 Hz, 1H), 2.03 (s, 3H), 2.04-1.99 (m, 2H), 1.83-1.67 (m, 4H), 1.53-1.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.2, 171.0, 82.0, 78.7, 54.8, 52.9, 52.2, 48.8, 44.2, 43.6, 39.2, 39.1, 26.3, 25.7, 21.9, 13.2; HRMS (CI) *m/z* 341.1600 [calc'd for $C_{17}H_{24}O_7$ (M+) 341.1600].

X-ray Structure Report for Isotwistane 31.

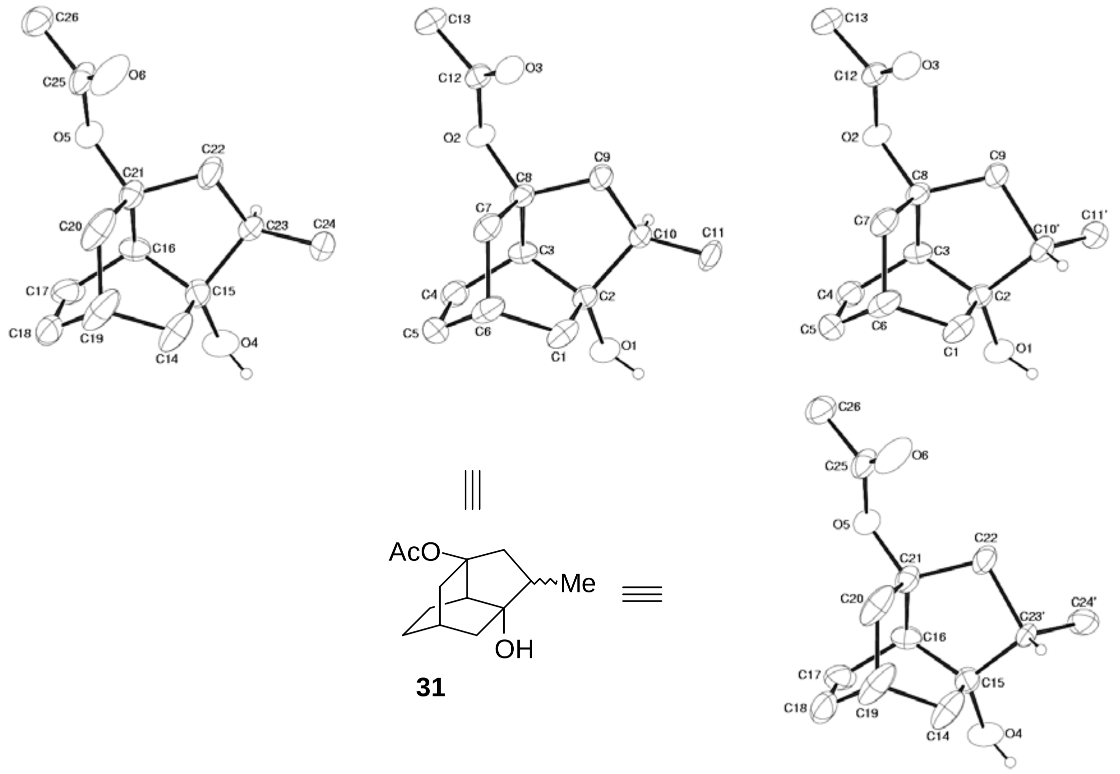


Figure 1 ORTEP plot of Isotwistane **31** (shown are the four contributing structures in the asymmetric unit)

Crystal Data

Empirical Formula	$C_{13}H_{20}O_3$
Formula weight	224.29
Crystal Color, Habit	Colorless, plate
Crystal Dimensions	0.45 x 0.45 x 0.20
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.6682(9)Å b = 11.9896(10)Å c = 9.6426(11)Å β = 91.397(6)° V = 1178.2(2)$Å^3$

Space group	P$\bar{1}$ (#2)
Z value	4
D_{calc}	1.264 g/cm^3
F(000)	488
μ(MoKα)	0.88 cm^{-1}

Intensity Measurements.

Diffractometer	Rigaku R-AXIS Iic
Radiation	MoKα (λ = 0.71069 Å) Graphite monochromated
Crystal to Detector Distance	82 mm
Temperature	-100°C
Scan Rate	150s/frame
2θmax	50.68°
No. of Reflections Measured	Total = 8066
Corrections	Lorentz-polarization

Structure Solution and Refinement.

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Funtion Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	1/[σ^2(Fo^2)+0.0670P^2+ 1.1718P]
p-factor	P = (Fo^2 + 2Fc^2)/3
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I.)	3870
No. Variables	332
Reflection/Parameter Ratio	11.66

Residuals: R; Rw	0.182 ; 0.186
Goodness of Fit Indicator	1.133
Max Shift/Error in Final Cycle	0.009
Maximum peak in Final Diff. Map	0.25 e/Å^3
Minimum peak in Fianl Diff. Map	-0.36 e/Å^3

Atomic Coordinates and Biso/Beq.

Table 1 Atomic Coordinates and Biso/Beq for Isotwistane 31

atom	x	y	z	Beq
C(1)	0.7692(3)	0.7193(3)	1.2142(3)	0.0539(9)
C(10)	0.7798(7)	0.5597(5)	0.9899(9)	0.044(2)
C(10')	0.8223(13)	0.5770(10)	1.053(2)	0.040(3)
C(11)	0.8436(8)	0.4870(7)	1.0698(11)	0.082(3)
C(11')	0.7702(14)	0.4551(9)	0.972(2)	0.059(4)
C(12)	0.9299(3)	0.8436(3)	0.7506(3)	0.0419(7)
C(13)	0.9107(3)	0.8898(3)	0.6179(3)	0.0535(8)
C(14)	0.6745(4)	0.3019(3)	0.3100(5)	0.0734(12)
C(15)	0.6422(3)	0.3781(3)	0.4353(4)	0.0518(9)
C(16)	0.5798(3)	0.2990(3)	0.5393(3)	0.0457(7)
C(17)	0.4638(3)	0.2033(4)	0.4753(4)	0.0733(13)
C(18)	0.5009(6)	0.1315(4)	0.3490(4)	0.111(2)
C(19)	0.6441(6)	0.1745(4)	0.3325(4)	0.096(2)
C(2)	0.7036(3)	0.6331(2)	1.0833(3)	0.0424(7)
C(20)	0.7174(5)	0.1658(3)	0.4667(4)	0.0767(13)
C(21)	0.6964(3)	0.2573(3)	0.5830(3)	0.0446(7)
C(22)	0.8061(4)	0.3714(3)	0.6106(5)	0.0788(14)
C(23)	0.7455(5)	0.4615(4)	0.5511(7)	0.042(2)
C(23')	0.7929(9)	0.4389(7)	0.4723(11)	0.038(3)
C(24)	0.8443(8)	0.5503(8)	0.4892(10)	0.058(2)
C(24')	0.808(2)	0.563(2)	0.550(2)	0.062(4)
C(25)	0.7610(3)	0.1733(3)	0.7752(4)	0.0568(9)
C(26)	0.7197(3)	0.1257(3)	0.9059(4)	0.0613(9)
C(3)	0.6784(3)	0.7042(3)	0.9717(3)	0.0406(7)
C(4)	0.6010(3)	0.7900(3)	1.0208(4)	0.0574(9)
C(5)	0.6659(4)	0.8710(3)	1.1515(4)	0.0680(11)
C(6)	0.7936(4)	0.8452(3)	1.1859(3)	0.0588(10)
C(7)	0.8783(3)	0.8594(3)	1.0583(3)	0.0472(8)
C(8)	0.8188(3)	0.7584(2)	0.9403(3)	0.0372(6)
C(9)	0.8820(3)	0.6560(3)	0.9322(4)	0.0558(9)
H(1)	0.6016(5)	0.521(3)	1.180(3)	0.082

H(10)	0.7222(7)	0.5093(5)	0.9124(9)	0.058
H(10')	0.8819(13)	0.5834(10)	1.134(2)	0.053
H(11a)	0.8874(8)	0.4428(7)	1.0060(11)	0.124
H(11a´)	0.8409(14)	0.4209(9)	0.950(2)	0.088
H(11b)	0.7786(8)	0.4347(7)	1.1133(11)	0.124
H(11b´)	0.7245(14)	0.4589(9)	0.886(2)	0.088
H(11c)	0.9052(8)	0.5374(7)	1.1407(11)	0.124
H(11c´)	0.7119(14)	0.4082(9)	1.028(2)	0.088
H(13a)	0.900(2)	0.9674(8)	0.6405(3)	0.080
H(13b)	0.8347(13)	0.8403(12)	0.5646(12)	0.080
H(13c)	0.9851(10)	0.891(2)	0.5635(12)	0.080
H(14a)	0.7659(4)	0.3289(3)	0.2943(5)	0.098
H(14b)	0.6248(4)	0.3078(3)	0.2271(5)	0.098
H(16)	0.5544(3)	0.3461(3)	0.6203(3)	0.061
H(17a)	0.3954(3)	0.2371(4)	0.4474(4)	0.098
H(17b)	0.4311(3)	0.1536(4)	0.5442(4)	0.098
H(18a)	0.4801(6)	0.0500(4)	0.3609(4)	0.147
H(18b)	0.4524(6)	0.1379(4)	0.2654(4)	0.147
H(19)	0.6695(6)	0.1269(4)	0.2520(4)	0.128
H(1a)	0.7141(3)	0.7087(3)	1.2923(3)	0.072
H(1b)	0.8510(3)	0.7038(3)	1.2396(3)	0.072
H(20a)	0.6857(5)	0.0886(3)	0.4919(4)	0.102
H(20b)	0.8093(5)	0.1785(3)	0.4522(4)	0.102
H(22a)	0.8824(4)	0.3624(3)	0.5619(5)	0.105
H(22b)	0.8301(4)	0.3950(3)	0.7102(5)	0.105
H(23)	0.7018(5)	0.5001(4)	0.6243(7)	0.056
H(23')	0.8516(9)	0.4300(7)	0.3972(11)	0.050
H(24a)	0.8030(8)	0.6043(8)	0.4548(10)	0.086
H(24a´)	0.898(2)	0.600(2)	0.574(2)	0.093
H(24b)	0.8818(8)	0.5116(8)	0.4131(10)	0.086
H(24b´)	0.762(2)	0.559(2)	0.635(2)	0.093
H(24c)	0.9112(8)	0.5918(8)	0.5601(10)	0.086
H(24c´)	0.773(2)	0.607(2)	0.491(2)	0.093
H(26a)	0.728(2)	0.0472(9)	0.8983(12)	0.092
H(26b)	0.6308(8)	0.126(2)	0.919(2)	0.092
H(26c)	0.773(2)	0.1733(14)	0.9849(5)	0.092
H(3)	0.6332(3)	0.6511(3)	0.8883(3)	0.054
H(4)	0.585(3)	0.472(4)	0.321(3)	0.107
H(4a)	0.5146(3)	0.7479(3)	1.0402(4)	0.076
H(4b)	0.5926(3)	0.8352(3)	0.9471(4)	0.076
H(5a)	0.6104(4)	0.8600(3)	1.2292(4)	0.090
H(5b)	0.6809(4)	0.9514(3)	1.1363(4)	0.090
H(6)	0.8383(4)	0.8994(3)	1.2687(3)	0.078
H(7a)	0.8808(3)	0.9333(3)	1.0272(3)	0.063

H(7b)	0.9663(3)	0.8583(3)	1.0843(3)	0.063
H(9a)	0.9630(3)	0.6780(3)	0.9895(4)	0.074
H(9b)	0.8987(3)	0.6297(3)	0.8360(4)	0.074
O(1)	0.5851(2)	0.5576(2)	1.1195(3)	0.0546(6)
O(2)	0.8156(2)	0.8009(2)	0.8059(2)	0.0421(5)
O(3)	1.0336(2)	0.8454(2)	0.8039(2)	0.0531(6)
O(4)	0.5586(3)	0.4450(2)	0.3913(3)	0.0713(8)
O(5)	0.6678(2)	0.2097(2)	0.7141(2)	0.0459(5)
O(6)	0.8660(3)	0.1786(3)	0.7300(4)	0.0903(11)

$$B_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$$

X-ray Structure Report for Alkyne 35.

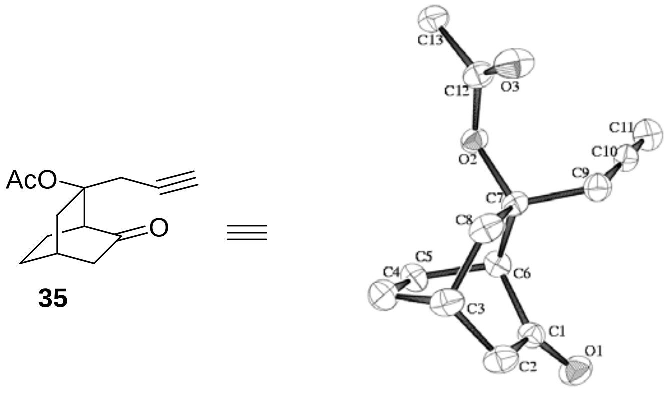


Figure 2 ORTEP plot of Alkyne 35.

Crystal Data

Empirical Formula	$C_{26}H_{32}O_{6}$
Formula weight	440.54
Crystal Color, Habit	colorless, cut-plate
Crystal Dimensions	0.10 X 0.17 X 0.21 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 14.484(1)Å b = 12.0275(4) Å c = 14.8735(5) Å β = 117.326(2)^{o} V = 2301.9(2) Å^{3}
Space group	P2_{1}/a (#14)
Z value	4
D_{calc}	1.271 g/cm^{3}
F(000)	944.00
μ(MoKα)	0.89 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°C
Scan Rate	60s/frame
Scan Width	1°/frame
$2\theta_{max}$	61.0°
No. of Reflections Measured	Total: 6841
Corrections	Lorentz-polarization

Structure Solution and Refinement.

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\ w\ (\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/^{2}\sigma(Fo) = 4Fo^{2}/\sigma^{2}(Fo^{2})$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>5.00\sigma(I)$)	3119
No. Variables	289
Reflection/Parameter Ratio	10.79
Residuals: R; Rw	0.056 ; 0.066
Goodness of Fit Indicator	2.89
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.33 e^{-}/Å^{3}
Minimum peak in Final Diff. Map	-0.30 e^{-}/Å^{3}

Atomic coordinates and B_{iso}/B_{eq}.

Table 2. Atomic coordinates and B_{iso}/B_{eq} for Alkyne 35.

atom	x	y	z	Beq
O(1)	0.9323(1)	0.6896(1)	0.2947(1)	3.54(5)
O(2)	0.7041(1)	0.6671(1)	0.4328(1)	2.38(4)
O(3)	0.5674(1)	0.5490(2)	0.3740(1)	4.10(5)
O(4)	0.6440(1)	0.3009(1)	0.2053(1)	3.51(4)
O(5)	0.2859(1)	0.3056(1)	0.0664(1)	2.31(4)
O(6)	0.2064(1)	0.4262(2)	0.1254(1)	3.97(5)
C(1)	0.8498(2)	0.7204(2)	0.2882(2)	2.51(6)
C(2)	0.7629(2)	0.7665(2)	0.1920(2)	3.33(6)
C(3)	0.6720(2)	0.7970(2)	0.2117(2)	3.23(6)
C(4)	0.7055(2)	0.8864(2)	0.2934(2)	3.80(7)
C(5)	0.8013(2)	0.8450(2)	0.3886(2)	3.06(6)
C(6)	0.8235(2)	0.7228(2)	0.3751(2)	2.30(5)
C(7)	0.7263(2)	0.6504(2)	0.3469(2)	2.29(5)
C(8)	0.6368(2)	0.6937(2)	0.2471(2)	3.21(6)
C(9)	0.7509(2)	0.5277(2)	0.3401(2)	2.90(6)
C(10)	0.8289(2)	0.4802(2)	0.4351(2)	2.90(6)
C(11)	0.8921(2)	0.4442(2)	0.5122(2)	3.71(7)
C(12)	0.6249(2)	0.6129(2)	0.4374(2)	2.76(6)
C(13)	0.6191(2)	0.6424(2)	0.5319(2)	3.15(6)
C(14)	0.5690(2)	0.2606(2)	0.2099(2)	2.60(6)
C(15)	0.5750(2)	0.2087(2)	0.3041(2)	3.61(7)
C(16)	0.4655(2)	0.1809(2)	0.2866(2)	3.32(6)
C(17)	0.4202(2)	0.0932(2)	0.2034(2)	3.78(7)
C(18)	0.4288(2)	0.1331(2)	0.1094(2)	2.73(6)
C(19)	0.4612(2)	0.2562(2)	0.1220(2)	2.26(5)
C(20)	0.3894(2)	0.3271(2)	0.1498(2)	2.32(5)
C(21)	0.3989(2)	0.2853(2)	0.2519(2)	3.15(6)
C(22)	0.4162(2)	0.4507(2)	0.1531(2)	2.97(6)
C(23)	0.3909(2)	0.4994(2)	0.0545(2)	3.06(6)
C(24)	0.3700(2)	0.5391(2)	-0.0247(3)	4.08(8)
C(25)	0.2028(2)	0.3616(2)	0.0620(2)	2.63(6)
C(26)	0.1076(2)	0.3343(2)	-0.0320(2)	3.18(6)
H(1)	0.7865	0.8308	0.1715	3.9985
H(2)	0.7416	0.7120	0.1401	3.9985
H(3)	0.6163	0.8242	0.1511	3.8746
H(4)	0.7225	0.9526	0.2696	4.5563
H(5)	0.6503	0.9009	0.3096	4.5563
H(6)	0.8598	0.8892	0.3991	3.6679

H(7)	0.7885	0.8514	0.4455	3.6679
H(8)	0.8802	0.6957	0.4350	2.7576
H(9)	0.5789	0.7120	0.2579	3.8508
H(10)	0.6175	0.6376	0.1967	3.8508
H(11)	0.6885	0.4863	0.3188	3.4838
H(12)	0.7755	0.5210	0.2911	3.4838
H(13)	0.9433	0.4150	0.5746	4.4509
H(14)	0.6258	0.7207	0.5416	3.7860
H(15)	0.6737	0.6064	0.5879	3.7860
H(16)	0.5541	0.6191	0.5266	3.7860
H(17)	0.6154	0.1427	0.3194	4.3354
H(18)	0.6062	0.2594	0.3589	4.3354
H(19)	0.4672	0.1535	0.3472	3.9838
H(20)	0.4575	0.0256	0.2269	4.5365
H(21)	0.3492	0.0813	0.1862	4.5365
H(22)	0.4795	0.0898	0.1014	3.2720
H(23)	0.3635	0.1248	0.0512	3.2720
H(24)	0.4615	0.2836	0.0622	2.7104
H(25)	0.3315	0.2690	0.2443	3.7847
H(26)	0.4298	0.3418	0.3014	3.7847
H(27)	0.3789	0.4901	0.1814	3.5662
H(28)	0.4887	0.4592	0.1954	3.5662
H(29)	0.3532	0.5711	-0.0887	4.8920
H(30)	0.0484	0.3616	-0.0272	3.8123
H(31)	0.1111	0.3679	-0.0882	3.8123
H(32)	0.1021	0.2559	-0.0409	3.8123

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