Total Synthesis of (±)-Phomactin B2 via an Intramolecular Cyclohexadienone Annulation of a Chromium Carbene Complex.

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Supporting information

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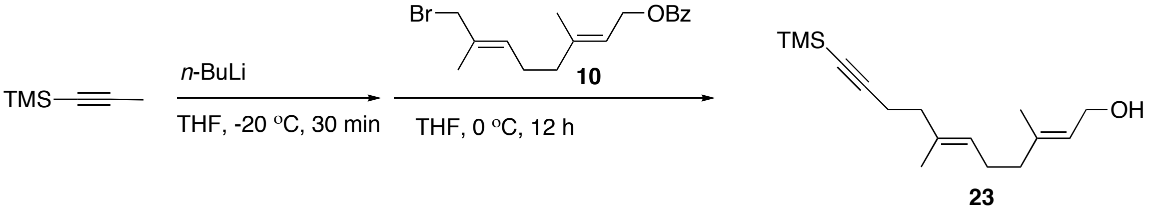
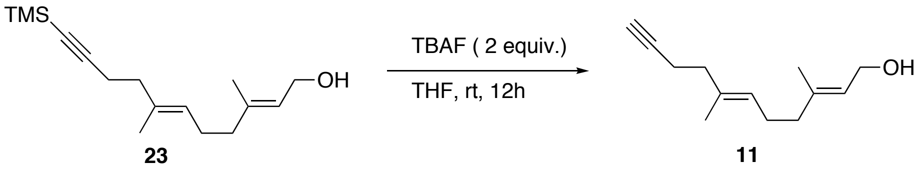
Preparation of (2*E*,6*E*)-3, 7-dimethyl-11-(trimethylsilyl)undeca-2,6-dien-10-yn-1-ol **23.**



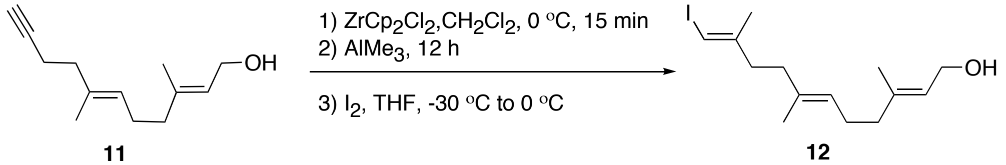
To a solution of TMS propyne (26 mL, 175 mmol) in THF (100 mL) at –20 °C was added *n*-BuLi (2.5 M, 70.0 mL, 175 mmol) dropwise. After 30 minutes, the bromide **10** (14.73 g, 43.7 mmol) in THF (50 mL) was transferred by cannulated to the above solution and the temperature was raised to 0 °C slowly. The reaction mixture was stirred for 12 hours at 0 °C and then quenched with H_2O. The aqueous layer was separated and extracted with Et_2O (2 * 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (3 * 30 mL), brine (30 mL) and dried over $MgSO_4$. Concentration followed by flash chromatography on silica gel with a 4:1 mixture of hexanes/EtOAc as eluent provided the title compound **23** which was not further purified but taken on directly in the next step. A sample can be further purified for characterization. ^{1}HNMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 1.58 (s, 3H), 1.66 (s, 3H), 2.02-2.28 (m, 8H), 4.12-4.14 (d, 2H, *J* = 6.6 Hz), 5.14 (t, 1H, *J* = 6.6 Hz), 5.39 (t, 1H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.09, 15.80, 16.22, 19.17, 26.18, 38.52, 39.37, 59.36, 84.55, 107.18, 123.33, 125.04, 133.75, 139.61; IR (neat) 3360br, 2925, 2176, 1250, 1003, 814s, 760 cm^{-1}; MS (EI) *m/z* (% rel intensity): 264 M$^+$ (0.03), 249 (1.30), 159 (31), 149 (30), 135 (21), 119 (21), 105 (21), 96 (47), 83 (32), 81 (32), 75 (49), 73 (100), 59 (68). Anal calcd for $C_{16}H_{28}OSi$: C. 72.66; H, 10.67. Found: C, 72.83; H, 10.39. Colorless oil; R_f = 0.35 (3:1 hexanes/EtOAc).

Preparation of (2*E*,6*E*)-3,7-dimethylundeca-2,6-dien-10-yn-1-ol 11.



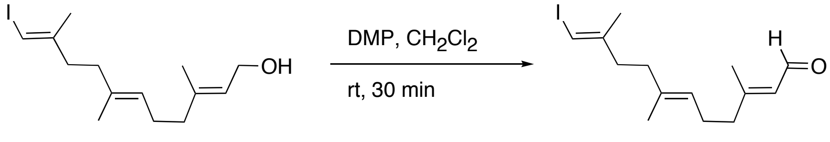
The trimethylsilyl protected acetylene **23** prepared by the previous procedure was treated with TBAF (1.0 M in THF, 100 mL) at room temperature for 12 hours followed by quenching with saturated aqueous $NaHCO_3$. The aqueous layer was separated and extracted with Et_2O (2 * 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (3 * 30 mL), brine (30 mL) and dried over $MgSO_4$. Concentration followed by Flash chromatography on silica gel with a 4:1 mixture of hexanes/EtOAC as eluent provided the desired product **11** as a colorless oil (6.09 g, 0.0317 mmol, 71% 2 steps). ^{1}HNMR ($CDCl_3$, 300 MHz) δ 1.59 (s, 3H), 1.65 (s, 3H), 1.93 (t, 1H, *J* = 2.4 Hz), 2.00-2.29 (m, 8H), 4.12-4.14 (d, 2H, *J* = 6.9 Hz), 5.16 (t, 1H, *J* = 6.3 Hz), 5.40 (t, 1H, *J* = 6.6 Hz); ^{13}CNMR ($CDCl_3$, 75 MHz) δ 15.79, 16.25, 17.56, 26.19, 38.21, 39.34, 59.39, 68.36, 84.37, 123.50, 125.13, 133.55, 139.53; IR (neat) 3350br, 3304, 2922, 2857, 2118, 1725, 1668, 1445, 1383 cm^{-1}; MS (EI) *m/z* (% rel intensity): 191 (M-1)$^+$ (0.02), 177 (1), 173 (0.23), 161 (3), 159 (6), 105 (43), 91 (100), 79 (76). Anal calcd for $C_{13}H_{20}O$: C. 81.20; H, 10.48. Found: C, 81.36; H, 10.38. Colorless oil; R_f = 0.29 (3:1 hexanes/EtOAc).

Preparation of (2*E*,6*E*,10*E*)-11-iodo-3,7,10-trimethylundeca-2,6,10-trien-1-ol 12.



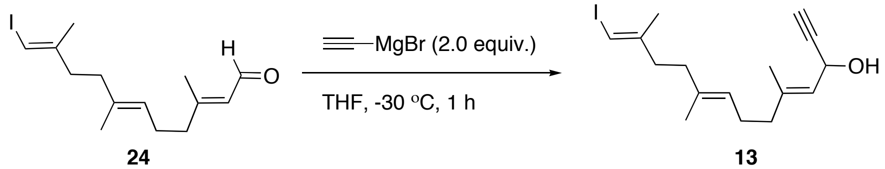
To a solution of zirconocene dichloride (1.25 g, 4.28 mmol) in CH_2Cl_2 (34 mL) at room temperature under an argon atmosphere, was added dropwise a solution of trimethylaluminum in pentane (2 M in pentane, 25.7 mL, 51.4 mmol). After 15 minutes, the solution was cooled to 0 °C, and a solution of alkyne **11** (3.25 g, 17.1 mmol) dissolved in CH_2Cl_2 (34 mL) was added to the above lemon yellow solution. The reaction mixture was stirred at 0 °C for 12 hours and then cooled to –30 °C. Iodine (8.69 g, 34.2 mmol) was added as a solution in 20 mL of THF. The resulting brown slurry was raised to 0 °C and poured slowly with stirring into an iced saturated aqueous $NaHCO_3$. The aqueous layer was extracted with Et_2O (3 * 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. Concentration followed by flash chromatography on silica gel with 4:1 hexanes/EtOAC as eluent provided the desired product **12** as a colorless oil (3.69 g, 11 mmol, 65%). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 3 H), 1.66 (s, 3 H), 1.80 (s, 3 H), 1.97-2.10 (m, 6 H), 2.27 (t, 2H, *J* = 6.6 Hz), 4.13 (d, 2H, *J* = 6.9 Hz), 5.08 (t, 1H, *J* =6.9 Hz), 5.39 (t, 1H, *J* = 6.9 Hz), 5.83 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.82, 26.26, 23.85, 26.17, 37.84, 38.21, 39.41, 59.39, 74.66, 123.41, 124.70, 134.21, 139.60, 147.82; IR (neat) 3312br, 2919, 2858, 1441 cm^{-1}; MS (EI) *m/z* (% rel intensity): 239 (3), 207 $(M-127)^+$ (2), 189 (11), 181 (44), 121 (80), 107 (98), 93 (100), 53 (73). Anal calcd for $C_{14}H_{23}OI$: C. 50.31; H, 6.94. Found: C, 50.64; H, 6.90. Colorless oil; R_f = 0.30 (3:1 hexanes/EtOAc).

Preparation of (2*E*,6*E*,10*E*)-11-iodo-3,7,10-trimethylundeca-2,6,10-trienal 24.



To a solution of allylic alcohol **12** (0.80 g, 2.4 mmol) in CH_2Cl_2 (10 mL) was added freshly prepared DMP[1] (1.10 g, 2.6 mmol) as powder. The reaction mixture was stirred at room temperature for 30 minutes before quenching with 10% aqueous NaOH (10 mL). The stirring was continued for another 5 minutes, and then Et_2O (3 * 10 mL) was added to extract the product from the reaction mixture. The combined organic layer was dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash chromatography on a silica gel column (9:1 hexanes/EtOAc as eluent) provided the desired aldehyde **24** as a colorless oil (0.784 g, 2.36 mmol, 98%). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3H), 1.80 (s, 3H), 2.15 (s, 3H), 2.05-2.29 (m, 8H), 5.02-5.08 (m, 1H), 5.83-5.86 (m, 1H), 5.83 (s, 1H), 9.97 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.89, 17.61, 23.83, 25.57, 37.77, 38.13, 40.50, 74.79, 123.45, 127.46, 135.43, 147.63, 163.47, 191.22. IR (neat) 2939m, 2853m, 2772w, 1684s, 1437m, 1194m, 1122m, 827w, 667w cm^{-1}; MS (EI) *m/z* (% rel intensity): 332 M^+ (3), 205 (22), 187 (34), 181 (77), 177 (33), 161 (17), 159 (16), 149 (16), 145 (24), 135 (16), 133 (24), 125 (20), 121 (100), 107 (76), 105 (28), 95 (67), 93 (73), 84 (30), 81 (100), 67 (63), 55 (85), 53 (86). Anal calcd for $C_{14}H_{21}OI$: C. 50.61; H, 6.37. Found: C, 50.28; H, 6.64. Colorless oil; R_f = 0.6 (3:1 hexanes/EtOAc).

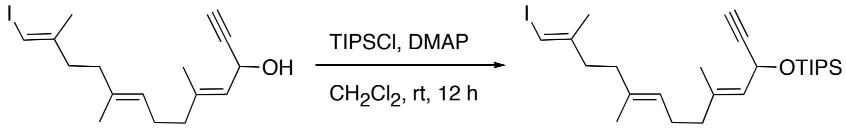
Preparation of (4*E*,8*E*,12*E*)-13-iodo-5,9,12-trimethyltrideca-4,8,12-trien-1-yn-3-ol 13.



24 **13**

To a solution of aldehyde **24** (0.16 g, 0.48 mmol) in THF (2 mL) at –30 °C under an argon atmosphere was added ethynyl magnesium bromide (0.5 M solution in THF, 1.92 mL, 0.96 mmol) dropwise. The reaction mixture was stirred at –30 °C for 1 hour and quenched with saturated aqueous NH_4Cl (8 mL). The aqueous layer was extracted with Et_2O (3 * 5 mL). The combined organic layer was washed with brine (15 mL) and dried over $MgSO_4$. Flash chromatography on a silica gel column using 15% EtOAC in hexanes as eluent provided the desired propargylic alcohol **13** as a colorless oil (0.16 g, 0.45 mmol, 93%). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.57 (s, 3H), 1.70 (s, 3H), 1.80 (s, 3H), 2.01-2.10 (m, 6H), 2.27 (t, 2H, *J* = 7.2 Hz), 2.47 (d, 1H, *J* = 2.1 Hz), 5.07-5.12 (m, 2H), 5.37 (d, 1H, *J* = 8.4 Hz), 5.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.87, 16.59, 23.86, 25.94, 37.82, 38.22, 39.13, 58.89, 72.49, 74.69, 84.44, 124.09, 124.36, 134.46, 140.77, 147.81; IR (neat) 3400 (broad), 3299, 2919, 2853, 2120 (weak), 1956, 1667 cm^{-1}. HRMS (CI) calcd for $C_{16}H_{22}I$ $(M-H_2O+H)^+$ *m/z* 341.0766, meas 341.0771. Colorless oil; R_f = 0.43 (3:1 hexanes/EtOAc).

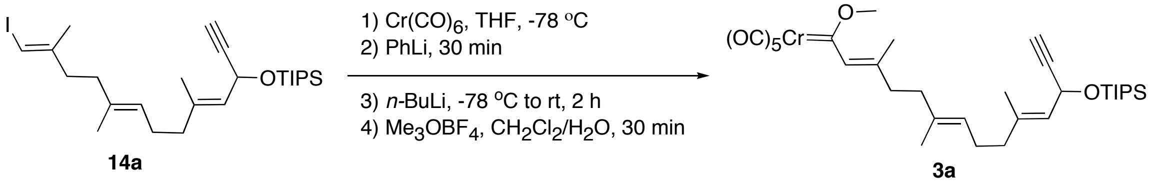
Preparation of ((4*E*,8*E*,2*E*)-13-iodo-5,9,12-trimethyltrideca-4,8,12-trien-1-yn-3-yloxy) tri*iso*propylsilane 14a.



13 **14a**

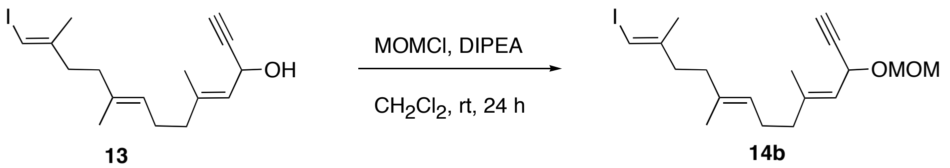
To a solution of propargyl alcohol **13** (1.0 g, 2.8 mmol) in CH_2Cl_2 (10 mL) was added DMAP (0.68 g, 5.6 mmol) and TIPSCl (1.2 mL, 5.6 mmol). The reaction mixture was stirred at room temperature for 12 hours and quenched with H_2O (10 mL). Diethyl ether (3 * 20 mL) was added to extract the product from the aqueous layer. The combined organic layer was washed with saturated aqueous NH_4Cl (50 mL), brine (50 mL), and then dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (19:1 hexanes/EtOAc as eluent) provided the desired product **14a** as a colorless oil (1.43 g, 2.8 mmol, 100%). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.03-1.13 (m, 21H), 1.57 (s, 3H), 1.65 (s, 3H), 1.80 (s, 3H), 1.98-2.08 (m, 6H), 2.58 (t, 2H, *J* = 2.7Hz), 2.41 (d, 1H, *J* = 2.1Hz), 5.07-5.12 (m, 2H), 5.32-5.34 (d, 1H, *J* = 7.8 Hz), 5.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.19, 15.89, 16.68, 17.90, 23.88, 25.98, 37.90, 38.29, 39.08, 59.94, 71.43, 74.61, 85.08, 124.54, 126.19, 134.25, 136.56, 147.91; IR (neat) 3308, 2942, 2889, 1462 cm^{-1}; MS (EI) *m/z* (% rel intensity) 514 M$^+$ (0.04), 471 (1.4), 131 (81), 103 (100), 75 (83). Anal calcd for $C_{25}H_{43}OISi$: C. 58.35; H, 8.42. Found: C, 58.60; H, 8.77. Colorless oil; R_f = 0.20 (hexanes).

Preparation of carbene complex 3a



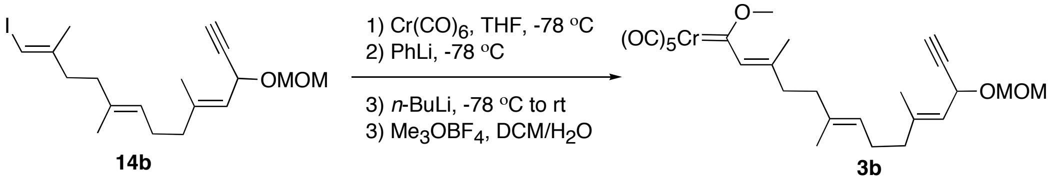
To a solution of vinyl iodine **14a** (375 mg, 0.73 mmol) in THF (15 mL) at room temperature was added $Cr(CO)_6$ (177 mg, 0.80 mmol) as a powder. The reaction mixture was cooled to –78 °C, and PhLi (0.456 mL, 0.73 mmol, 1.6 M solution) was added dropwise. The mixture was stirred for 30 minutes at –78 °C, and then *n*-BuLi (0.34 mL, 0.73 mmol, 2.27 M) was added dropwise. The solution was stirred for another 30 minutes, and then warmed up to room temperature and stirred for 1.5 hours. The solvent of the reaction was then removed *in vacuo*, and the residue was dissolved in 1:1 H_2O/CH_2Cl_2 (15 mL). Upon addition of Me_3OBF_4 (210 mg, 1.47 mmol), the solution turned red immediately. After stirring 30 minutes at room temperature, saturated aqueous $NaHCO_3$ and Et_2O was added to quench the alkylation. The aqueous layer was extracted with Et_2O until the color of the aqueous layer was pale. The combined organic layer was washed with brine, and then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using 2% EtOAC in hexanes as eluent to give carbene complex **3a** (233 mg, 0.37 mmol, 51%) as a red oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.03-1.10 (m, 21), 1.60 (s, 3 H), 1.65 (s, 3H), 1.82 (s, 3H), 2.00-2.15 (m, 8H), 2.40 (d, 1 H, *J* = 2.1Hz), 4.69 (s, 3H), 5.01-5.12 (m, 2H), 5.32 (d, 1 H, *J* = 7.8Hz), 7.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.10, 15.87, 16.57, 17.85, 17.91, 20.61, 25.86, 37.80, 38.96, 39.74, 59.86, 66.13, 71.43, 84.97, 124.66, 126.15, 133.94, 136.40, 140.95, 142.79, 216.75, 223.94, 339.37; IR (neat) 2946w, 2868w, 2058s, 1935vs, 1250w, 1061w, 667s, 650m cm^{-1}. Anal calcd for $C_{32}H_{46}CrO_7Si$: C. 61.71; H, 7.44. Found: C, 62.05; H, 7.76. Red oil; R_f = 0.63 (3:1 hexanes/EtOAc).

Preparation of MOM protected vinyl iodine 14b.



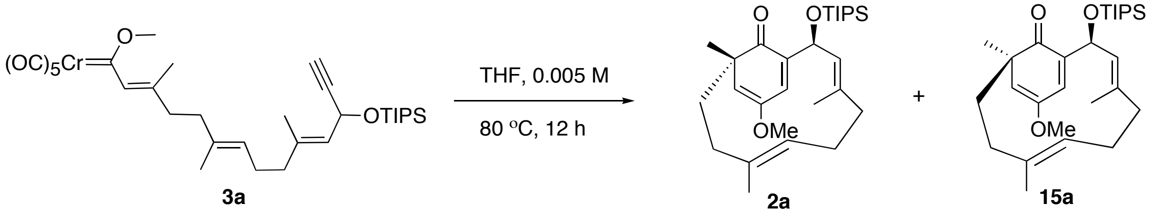
To a solution of **13** (562 mg, 1.57 mmol) in 10 mL of CH_2Cl_2 at room temperature was added DIPEA (0.820 mL, 4.71 mmol) and MOMCl (0.238 mL, 3.14 mmol). The resulting solution was stirred for 1 day, and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with Et_2O (2 * 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by chromatography on silica gel using 9:1 hexanes/EtOAC as eluent to give an 80% yield of MOM ether **14b** (504 mg, 1.25 mmol). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.57 (s, 3H), 1.71 (d, 3H, *J* = 1.3 Hz), 1.80 (d, 3H, *J* = 1.1 Hz), 2.02-2.14 (m, 6H), 2.25-2.27 (m, 2H), 2.43 (d, 1H, *J* = 2.1 Hz), 3.38 (s, 3H), 4.60 (d, 1H, *J* = 6.9 Hz), 4.82 (d, 1H, *J* = 6.9 Hz), 5.02-5.09 (m, 2H), 5.29 (dq, 1H, *J* = 8.9, 1.2 Hz), 5.83-5.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.88, 16.57, 23.85, 25.94, 37.84, 38.24, 39.20, 55.61, 61.46, 73.13, 74.66, 82.18, 93.13, 121.63, 124.36, 134.44, 141.56, 147.82; IR (neat) 3295, 2926, 1449, 1150, 1094, 1028, 924, 629 cm^{-1}; HRMS (CI) calcd for $(C_{18}H_{27}O_2I+H)^+$ *m/z* 403.1134, meas 403.1124. Colorless oil; R_f = 0.34 (9:1 hexanes/EtOAc).

Preparation of carbene complex 3b.



To a solution of vinyl iodine **14b** (49.1 mg, 0.122 mmol) in THF (5 mL) at room temperature was added Cr(CO)$_6$ (30 mg, 0.136 mmol) as a powder. The solution was cooled to –78 °C, and PhLi (0.076 mL, 0.122 mmol, 1.6 M in THF) was added dropwise. After stirring for 30 minutes at –78 °C, *n*-BuLi (0.047 mL, 0.122 mmol, 2.6 M in hexanes) was added dropwise. The solution was stirred for another 30 minutes, and then warmed up to room temperature and stirred for 1.5 hours. The solvent of the reaction was removed *in vacuo*, and the residue was dissolved in 1:1 mixture of H_2O/CH_2Cl_2. Upon addition of Me_3OBF_4 (36 mg, 0.249 mmol), the solution turned red immediately. After stirring 30 minutes at room temperature, saturated aqueous $NaHCO_3$ (10 mL) and Et_2O (10 mL) was added to quench the alkylation reaction. The aqueous layer was extracted with Et_2O until the color of the aqueous layer was pale. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using 9:1 hexanes/EtOAC as eluent to give carbene complex **3b** as a red oil (26.6 mg, 0.052 mmol, 43%). This carbene complex was unstable and subjected to thermolysis right after isolation. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.60 (s, 3H), 1.71 (d, 3H, *J* = 1.1 Hz), 1.82 (s, 3H), 2.03-2.21 (m, 8H), 2.44 (d, 1H, *J* = 2.2 Hz), 3.38 (s, 3H), 4.60 (d, 1H, *J* = 6.9 Hz), 4.70 (s, 3H), 4.83 (d, 1H, *J* = 6.9 Hz), 5.05 (dd, 1H, *J* = 8.9, 2.2 Hz), 5.10-5.13 (m, 1H), 5.28-5.30 (m, 1H), 7.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.60, 16.55, 20.60, 25.98, 37.88, 39.18, 39.75, 55.64, 61.54, 66.18, 73.14, 82.22, 93.20, 115.23, 121.77, 124.57, 134.27, 141.02, 141.47, 216.82, 223.97 (The carbene carbon was not located); IR (neat) 3308, 2919, 2058, 1931, 665 cm^{-1}. Red oil; R_f = 0.19 (9:1 hexanes/EtOAc).

Thermolysis of carbene complex 3a.

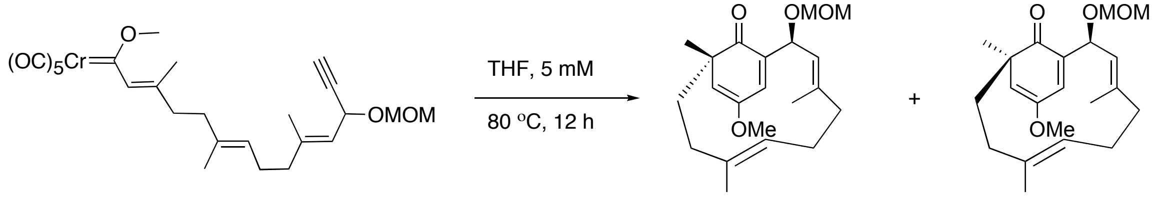


The carbene complex **3a** (212 mg, 0.341 mmol) was dissolved in THF (17 mL) and transferred to a Schlenk flask equipped with a threaded Teflon high vacuum stopcock. The reaction mixture was deoxygenated by the freeze-pump-thaw procedure with 3 cycles. Then the flask was back filled with an argon atmosphere at room temperature, sealed and heated to 80 °C. After the reaction was completed (indicated by the fading of the red color of **3a**), the solvent was removed *in vacuo*. The residue was taken up in 1:1 mixed solvent of Et_2O and CH_2Cl_2, and stirred in air for 12 hours. Then the solvent was removed and the residue was taken up in pure Et_2O. The insoluble material was removed by filtration through silica gel in a pipette-sized column using Et_2O as the eluent. Concentration of the filtrate provided the crude product mixture, which was further purified by flash column chromatography on silica gel (45:1:1 hexanes/Et_2O/CH_2Cl_2 as the eluent) to give a 37% yield of major isomer (57.7 mg, 0.126 mmol) and a 19% yield of minor isomer (29.7 mg, 0.065 mmol). The 2:1 ratio of diastereomers **2a** and **15a** was also verified on the crude reaction mixture by ^{1}H NMR based on the integral of the following vinyl peaks: δ 6.99 for **2a** and 6.42 for **15a**. This reaction was carried out several times at 80 °C with concentrations in the range of 0.005 to 0.02 M with ratios of **2a**:**15a** ranging from 2:1 to 3:1 and combined yields of 47-65%. This reaction was carried out three times at 60 °C with concentrations in the range of 0.005 to 0.02 M with ratios of **2a**:**15a** ranging from 3:1 to 4:1 and combined yields of 60-66%. This reaction was carried out once at 100 °C at 0.005 and gave a ratio of **2a**:**15a** of 2:1 and a combined yield of 63%.

Major isomer 2a ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.98-1.06 (m, 21H), 1.10 (s, 3H), 1.34-1.42 (m, 2H), 1.52 (s, 3H), 1.64 (s, 3H), 1.67-2.09 (m, 4H), 2.26-2.39 (m, 2H), 3.63 (s, 3H), 4.48 (d, 1H, *J* = 11.4 Hz), 4.67 (d, 1H, *J* = 8.1 Hz), 4.90 (d, 1H, *J* = 3.3 Hz), 5.42 (dd, 1H, *J* = 9.0, 0.9 Hz), 6.99 (dd, 1H, *J* = 3.3, 0.9 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.13, 15.28, 15.67, 17.91, 17.96, 25.53, 29.85, 36.24, 37.96, 46.70, 54.71, 64.93, 65.83, 110.40, 124.70, 129.97, 134.18, 134.38, 134.86, 141.82, 151.12, 202.25; IR (neat) 2944, 2867, 1647 cm^{-1}; MS(EI) *m/z* (% rel intensity) 458 M$^+$ (10), 430 (7), 415 (18), 347 (19), 324 (52), 279 (66), 241 (80), 189 (41), 131 (30), 115 (34), 103 (48), 81 (100), 75 (100). HRMS calcd for $C_{28}H_{46}O_3Si$ *m/z* 458.3216, meas 458.3218. Light yellow oil; R$_f$ = 0.65 (10:1:1 hexanes/Et$_2$O/CH$_2$Cl$_2$).

Minor isomer 15a ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.99-1.03 (m, 21H), 1.12 (s, 3H), 1.35-1.56 (m, 2H), 1.43 (s, 3H), 1.45 (s, 3H), 1.85-2.13 (m, 5H), 2.30 (t, 1H, *J* = 11.4 Hz), 3.60 (s, 3H), 4.59 (t, 1H, *J* = 8 Hz), 4.86 (d, 1H, *J* = 8.1 Hz), 4.93 (d, 1H, *J* = 2.7 Hz), 5.72 (d, 1H, *J* = 8.1 Hz), 6.42 (d, 1H, *J* = 3.0 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.19, 15.45, 15.50, 17.99, 25.29, 28.30, 36.01, 38.11, 39.43, 50.14, 54.80, 72.73, 111.05, 123.03, 130.67, 132.29, 134.92, 137.11, 138.35, 149.65, 201.08; IR (neat) 2940, 2864, 1651 cm^{-1}; MS (EI) *m/z* (% rel intensity) 458 M$^+$ (2), 415 (33), 347 (15), 279 (100), 241(11), 189 (13), 131 (30), 103 (38), 81 (67), 75 (68); HRMS calcd for $C_{28}H_{46}O_3Si$ *m/z* 458.3216, meas 458.3216. Light yellow solid, m.p. 84-86 °C; R$_f$ = 0.60 (10:1:1 hexanes/Et$_2$O/CH$_2$Cl$_2$).

Thermolysis of carbene complex 3b.



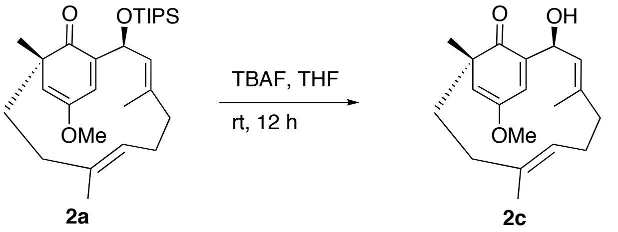
3b **2b** **15b**

The carbene complex **3b** (26.6 mg, 0.052 mmol) was dissolved in THF (10.4 mL) and transferred to a Schlenk flask equipped with a threaded Teflon high vacuum stopcock. The reaction mixture was deoxygenated by the freeze-pump-thaw procedure with 3 cycles. Then the flask was back filled with an argon atmosphere at room temperature, sealed and heated to 80 °C. After the reaction was completed (indicated by the fading of the red color of **3b**), the solvent was removed *in vacuo*. The residue was taken up in a 1:1 mixture of Et$_2$O and CH$_2$Cl$_2$, and stirred in air for 12 hours. Then the solvent was removed again and the residue was taken up in pure Et$_2$O. The insoluble material was removed by filtration through silica gel in a pipette-sized column using Et$_2$O as the eluent. Concentration of the filtrate provided the crude product mixture, which was further purified by flash column chromatography on silica gel (15:1:1 hexanes/Et$_2$O/CH$_2$Cl$_2$ as the eluent) to give a 1:1 ratio of **2b** (2.2 mg, 0.0064 mmol, 12%) and **15b** (2.5 mg, 0.0072 mmol, 14%). The ratio of diastereomers **2b** and **15b** was determined on the crude reaction mixture by ^{1}H NMR based on the integral of the following vinyl peaks: δ 6.92 for **2b** and 6.58 for **15b**.

Isomer 2b ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14 (s, 3H), 1.39-1.42 (m, 1H), 1.52 (s, 3H), 1.69 (s, 3H), 1.71-1.76 (m, 1H), 1.87-1.89 (m, 1H), 1.93-2.02 (m, 2H), 2.08-2.12 (m, 1H), 2.24-2.36 (m, 2H), 3.34 (s, 3H), 3.63 (s, 3H), 4.50 (d, 1H, *J* = 11.3 Hz), 4.55 (d, 1H, *J* = 6.4 Hz), 4.57 (d, 1H, *J* = 7.8 Hz), 4.71 (d, 1H, *J* = 6.4 Hz), 4.90 (d, 1H, *J* = 3.2 Hz), 5.37 (4.57 (d, 1H, *J* = 9.8 Hz), 6.92 (dd, 1H, *J* = 3.1 Hz, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.37, 15.71, 25.41, 29.59, 35.93, 38.16, 39.33, 49.56, 54.77, 55.49, 67.56, 93.66, 110.64, 124.55, 126.48, 134.60, 135.07, 138.80, 138.90, 150.80, 202.12; IR (neat) 2919, 1647, 1383, 1036 cm-1; mass spectrum *m/z* (% rel intensity) 346 M$^+$ (1), 318 (5), 284 (14), 253 (12), 241 (10), 212 (17), 203 (22), 189 (81), 175 (16), 164 (14), 151 (19), 91 (24), 81 (23), 67 (16), 45 (100). HRMS (FAB) calcd for $(C_{21}H_{30}O_4+H)^+$ *m/z* 347.2221; meas 347.2222. Light yellow solid, m.p. 77-79 °C; R_f = 0.28 (9:1 hexanes/Et_2O).

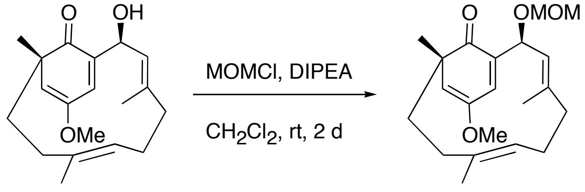
Isomer 15b ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17 (s, 3H), 1.30-1.37 (m, 1H), 1.45 (s, 3H), 1.48 (s, 3H), 1.84-1.89 (m, 1H), 1.92-2.06 (m, 3H), 2.10-2.15 (m, 2H), 2.25 (ddd, 1H, *J* = 13.9, 11.9, 2.1 Hz), 3.30 (s, 3H), 3.60 (s, 3H), 4.58 (d, 1H, *J* = 6.8 Hz), 4.59-4.62 (m, 1H), 4.65 (d, 1H, *J* = 6.8 Hz), 4.77 (d, 1H, *J* = 8.6 Hz), 4.98 (d, 1H, *J* = 3.0 Hz), 5.64 (d, 1H, *J* = 8.3 Hz), 6.58 (d, 1H, *J* = 3.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.58, 15.65, 25.07, 27.32, 35.16, 38.18, 39.44, 50.29, 54.79, 55.33, 75.07, 93.81, 111.96, 123.52, 126.42, 135.55, 136.01, 136.48, 137.65, 149.53, 201.88; IR (neat) 2917, 2849, 1649, 1390, 1042 cm^{-1}; mass spectrum *m/z* (% rel intensity) 346 M$^+$ (0.5), 318 (12), 241 (12), 189 (38), 91 (22), 81 (30), 45 (100). HRMS (CI) calcd for $(C_{21}H_{30}O_4+H)^+$ *m/z* 347.2222, meas 347.2213. Yellow oil; R_f = 0.20 (9:1 hexanes/Et_2O).

Preparation of alcohol 2c.



To a solution of **2a** (72 mg, 0.157 mmol) in 2.0 mL of THF at room temperature was added TBAF (0.31 mL, 1.0 M in THF). The reaction mixture was stirred overnight and then quenched with 5 mL of water. The aqueous layer was extracted with Et_2O (3 * 5 mL). The combined organic layer was washed with brine (5 mL), and then dried over $MgSO_4$, concentrated and chromatographed on silica gel using 9:1 hexanes/EtOAc as eluent to afford a 83% yield of the alcohol **2c** (39.5 mg, 0.131 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.13 (s, 3H), 1.38-1.42 (m, 2H), 1.52 (s, 3H), 1.57 (br s, 1H), 1.69 (s, 3H), 1.70-1.75 (m, 1H), 1.86-1.89 (m, 1H), 1.92-1.98 (m, 2H), 2.25-2.36 (m, 2H), 3.63 (s, 3H), 4.49 (d, 1H, *J* = 11.3 Hz), 4.67 (d, 1H, *J* = 9.3 Hz), 4.90 (d, 1H, *J* = 3.2 Hz), 5.46 (d, 1H, *J* = 9.3 Hz), 6.99 (d, 1H, *J* = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.32, 15.79, 25.42, 29.62, 35.95, 38.10, 39.21, 49.64, 54.77, 64.44, 110.65, 124.51, 128.33, 134.51, 134.58, 137.36, 140.51, 150.86, 202.29; IR (neat) 3443br m, 2917m, 1645s, 1597m, 1383s, 1129m, 1043m, 733m cm^{-1}; mass spectrum *m/z* (% rel intensity) 302 M$^+$ (4), 274 (16), 205 (18), 203 (21), 191 (17), 189 (73), 175 (26), 168 (42), 165 (17), 150 (18), 121 (16), 105 (15), 91 (26), 86 (62), 84 (100), 77 (24), 67 (18), 55 (25). HRMS (FAB) calcd for $(C_{19}H_{26}O_3+H)^+$ *m/z* 303.1959, meas 303.1960. Light yellow needle, m.p. 130-132 °C; R_f = 0.45 (3:1 hexanes/EtOAc).

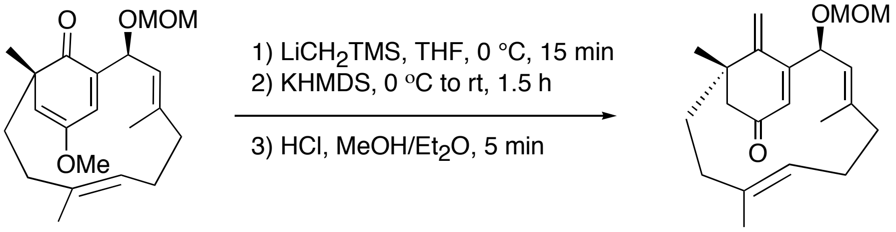
Preparation of MOM ether 362 from alcohol 2b.



2c **2b**

To a solution of **2c** (166 mg, 0.55 mmol) in 10 mL of CH_2Cl_2 at room temperature was added DIPEA (0.287 mL, 1.65 mmol) and MOMCl (0.083 mL, 1.10 mmol). The resulting solution was stirred for 2 days, and then quenched with saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with Et_2O (2 * 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel with 9:1 hexanes/EtOAc as eluent to give an 88% yield of MOM ether **2b** (167 mg, 0.0484 mmol). The spectral data for this compound matched that for a product obtained from the thermolysis of compound **2b** (vide supra).

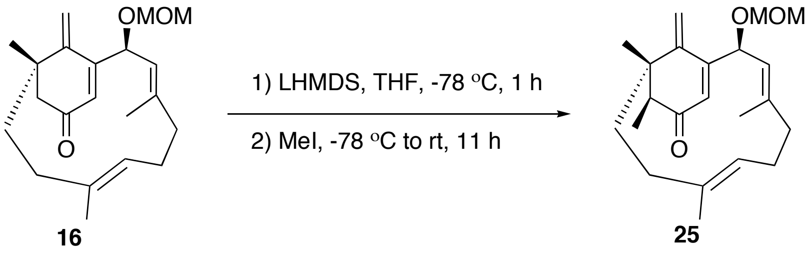
Preparation of dienone 16.



2b **16**

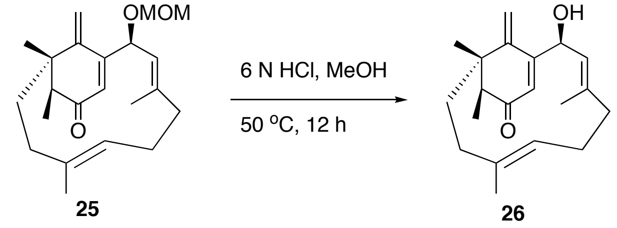
Trimethylsilylmethyllithium (1.0 M in THF, 0.12 mL) was added dropwise to a solution of compound **2b** (20.7 mg, 0.0598 mmol) in 0.3 mL of THF at 0 °C. The solution was stirred for 15 minutes at 0 °C, and then KHMDS (0.24 mL, 0.12 mmol, 0.5 M in toluene) was added. The reaction mixture was stirred for 1.5 hours at room temperature before quenching with H_2O (5 mL). The aqueous phase was separated and extracted with Et_2O (3 * 10 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give an unstable enol ether intermediate. The crude enol ether was dissolved in 1 mL of MeOH, and then treated with 1 mL of 1% aqueous HCl and stirred at room temperature for 5 minutes. The mixture was diluted with Et_2O (5 mL) and neutralized with saturated aqueous $NaHCO_3$ (10 mL). The aqueous phase was separated and then extracted with Et_2O (2 * 10 mL). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel with a 9:1 hexanes/Et_2O as eluent to give ketone **16** (14.6 mg, 0.0442 mmol, 74%). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.18 (s, 3H), 1.35-1.41 (m, 1H), 1.44 (s, 3H), 1.67 (d, 3H, *J* = 1.2 Hz), 1.69-1.80 (m, 2H), 2.02-2.13 (m, 5H), 2.23 (d, 1H, *J* = 16.0 Hz), 2.46 (d, 1H, *J* = 16.0 Hz), 3.35 (s, 3H), 4.53 (d, 1H, *J* = 6.8 Hz), 4.63-4.67 (m, 2H), 4.69 (d, 1H, *J* = 6.8 Hz), 5.27 (dd, 1H, *J* = 9.8, 1.1 Hz), 5.30 (d, 1H, *J* = 1.5 Hz), 5.42 (s, 1H), 6.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.33, 16.74, 24.34, 24.84, 34.23, 35.59, 38.43, 42.81, 54.21, 55.46, 68.86, 93.23, 114.90, 122.99, 124.46, 124.63, 135.80, 140.37, 146.42, 157.38, 199.45; IR (neat) 2923, 1671, 1583, 1150, 1036, 916 cm^{-1}; mass spectrum *m/z* (% rel intensity) 330 M^+ (0.8), 285 (2), 269 (3), 247 (3), 105 (15), 91 (24), 81 (15), 66 (18), 45 (100). HRMS (FAB) calcd for $(C_{21}H_{30}O_3+H)^+$ *m/z* 331.2271, meas 331.2273. Light yellow oil; R_f = 0.40 (3:1 hexanes/EtOAc).

Methylation of dienone 16.



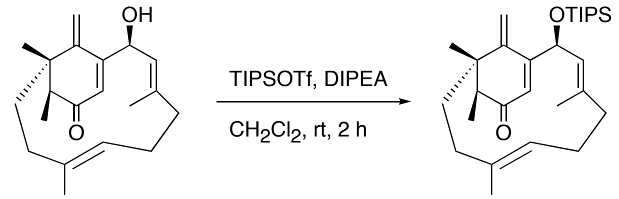
A solution of ketone **16** (9.7 mg, 0.0292 mmol) in 0.50 mL of THF was added to a solution of LHMDS (1.0 M in THF, 0.050 mL, 0.050 mmol) in THF at –78 °C. After stirring for 1 hour, iodomethane (4 μL, 0.07 mmol) was added. The cooling bath was removed immediately and the reaction mixture was allowed to warm to room temperature. After stirring for 11 hours, 2 mL of saturated aqueous NH_4Cl was added to the flask. The aqueous layer was extracted with Et_2O (2 * 10 mL). The combined organic layer was washed with brine (10 mL), and then dried over $MgSO_4$. The residue was purified by flash column chromatography on silica gel with 9:1 hexanes/Et_2O as eluent to give ketone **25** (9.0 mg, 0.0261 mmol, 96%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.96 (d, 3H, *J* = 7.3 Hz), 1.09 (s, 3H), 1.35-1.41 (m, 1H), 1.53 (s, 3H), 1.67 (d, 3H, *J* = 1.2 Hz), 1.69-1.74 (m, 1H), 1.78-1.83 (m, 1H), 2.01-2.16 (m, 6H), 3.35 (s, 3H), 4.53 (d, 1H, *J* = 6.5 Hz), 4.64-4.66 (m, 2H), 4.68 (d, 1H, *J* = 6.5 Hz), 5.26-5.28 (m, 2H), 5.51 (s, 1H), 6.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.95, 16.48, 16.58, 21.07, 24.33, 34.50, 36.41, 38.21, 45.65, 55.48, 55.51, 68.82, 93.34, 116.94, 120.98, 124.56, 124.80, 135.84, 140.14, 144.69, 156.08, 204.60; IR (neat) 2934, 1671s, 1587, 1150, 1036, 916 cm^{-1}; mass spectrum *m/z* (% rel intensity) 344 M$^+$ (1), 329 (0.4), 135 (13), 119 (15), 107 (16), 95 (12), 91 (15), 81 (22), 79 (17), 55 (24), 45 (100); HRMS (FAB) calcd for $(C_{22}H_{32}O_3+H)^+$ *m/z* 345.2430, meas 345.2430. Colorless oil; R_f = 0.38 (3:1 hexanes/EtOAc).

Cleavage of MOM group in 25.



To a solution of MOM ether **25** (25 mg, 0.0727 mmol) in 3.7 mL of MeOH at room temperature was added 6 N HCl (0.024 mL). The reaction mixture was heated at 50 °C for 12 hours, and then cooled to room temperature. The mixture was diluted with Et_2O (5 mL) and neutralized with saturated aqueous $NaHCO_3$ (10 mL). The aqueous phase was separated and then extracted with Et_2O (2 * 10 mL). The combined organic layer was washed with brine (10 mL), and then dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel with 7:3 hexanes/Et_2O as eluent to give alcohol **26** (20.2 mg, 0.0672 mmol, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (d, 3H, *J* = 7.2 Hz), 1.08 (s, 3H), 1.35-1.41 (m, 1H), 1.43 (s, 3H), 1.67 (d, 3H, *J* = 1.4 Hz), 1.71-1.72 (m, 1H), 1.78-1.83 (m, 1H), 2.02-2.14 (m, 6H), 4.64 (t, 1H, *J* = 6.5 Hz), 4.76 (dd, 1H, *J* = 9.5, 1.0 Hz), 5.24 (d, 1H, *J* = 1.6 Hz), 5.35 (d, 1H, *J* = 9.6 Hz), 5.47 (s, 1H), 6.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.89, 16.59, 16.37, 21.00, 24.29, 34.48, 36.43, 38.07, 45.72, 55.60, 66.50, 116.75, 120.28, 124.87, 126.74, 135.86, 128.98, 144.45, 157.73, 204.63; IR (neat) 3405 brs, 2932, 1653, 1385 cm^{-1}; mass spectrum *m/z* (% rel intensity) 300 M$^+$ (11), 189 (22), 187 (18), 176 (20), 173 (23), 169 (15), 161 (25), 159 (26), 148 (20), 145 (21), 141 (23), 135 (61), 128 (26), 121 (29) 105 (35), 91 (63), 81 (98), 77 (71), 67 (52), 55 (80), 53 (42), 41 (100); HRMS (FAB) calcd for $(C_{20}H_{28}O_2+H)^+$ *m/z* 301.2168, meas 301.2166. Colorless oil; R_f = 0.11 (3:1 hexanes/EtOAc).

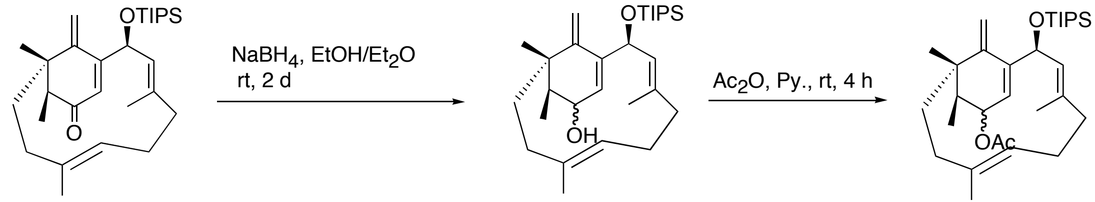
Preparation of TIPS ether 27.



26 **27**

To a solution of allylic alcohol **26** (10.4 mg, 0.0347 mmol) in CH_2Cl_2 (1.7 mL) was added DIEPA (0.024 mL, 0.139 mmol) followed by the addition of tri*iso*propylsilyl triflate (0.019 mL, 0.069 mmol). The reaction mixture was stirred at room temperature for 2 hours and quenched with H_2O (10 mL). Diethyl ether (3 * 10 mL) was added to extract the product from the aqueous layer. The combined organic layer was washed with brine (15 mL), and then dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash chromatography on silica gel (9:1 hexanes/EtOAc as eluent) provided the desired product **27** (15.4 mg, 0.0337 mmol, 97%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (d, 3H, *J* = 7.2 Hz), 1.00-1.07 (m, 21H), 1.08 (s, 3H), 1.35-1.40 (m, 1H), 1.44 (s, 3H), 1.59 (d, 3H, *J* = 2.4 Hz), 1.67-1.71 (m, 1H), 1.76-1.81 (m, 1H), 2.03-2.10 (m, 6H), 4.67-4.69 (m, 1H), 4.81 (d, 1H, *J* = 8.8 Hz), 5.24 (d, 1H, *J* = 1.5 Hz), 5.30 (dd, 1H, *J* = 9.0, 1.1 Hz), 5.45 (s, 1H), 6.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.15, 13.74, 16.40, 16.76, 17.87, 17.98, 20.99, 24.39, 34.34, 36.85, 38.60, 45.70, 55.87, 67.00, 116.42, 121.10, 124.50, 127.67, 135.75, 136.75, 144.67, 158.72, 205.07; IR (neat) 2944, 2857, 1671, 1462, 1109, 1096, 884 cm^{-1}; mass spectrum *m/z* (% rel intensity) 456 M$^+$ (7), 413 (42), 171 (17), 157 (16), 143 (18), 141 (18), 131 (51), 128 (42), 119 (30), 103 (86), 95 (36), 91 (28), 81 (45), 79 (38), 76 (58), 75 (100), 73 (29), 61 (81), 59 (58), 55 (40), 43 (37); HRMS (FAB) calcd for $(C_{29}H_{48}O_2Si+H)^+$ *m/z* 457.3489, meas 457.3484. White solid; R_f = 0.29 (9:1 hexanes/EtOAc).

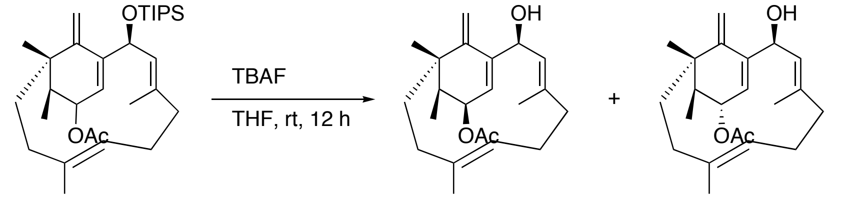
Reduction and acetylation of dienone 27.



27 **17** **28**

To a solution of dienone **27** (71.2 mg, 0.156 mmol) in 3.0 mL of 1:1 mixture of $EtOH/Et_2O$ was added $NaBH_4$ (53 mg, 1.56 mmol) at room temperature. The reaction mixture was stirred at room temperature until all of the ketone was consumed (monitored by TLC, ~ 2 days). The reaction was quenched with H_2O, and the aqueous layer was extracted with Et_2O (3 * 20 mL). The combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4. After filtration and concentration to give 61.7 mg alcohol **17** (0.147 mg, 94%). The residue was dissolved in 4 mL of pyridine, and then 1.0 mL of acetic anhydride was added. The mixture was stirred at room temperature for 4 hours and then was evaporated to dryness. The residue was purified by column chromatography on silica gel using 9:1 hexanes/EtOAc as eluent to give inseparable acetate **28** as a 2:1 Inseparable mixture of isomers (65.5 mg, 0.131 mmol, 84%) as a colorless oil.

Preparation of Alcohols 19 and 19.



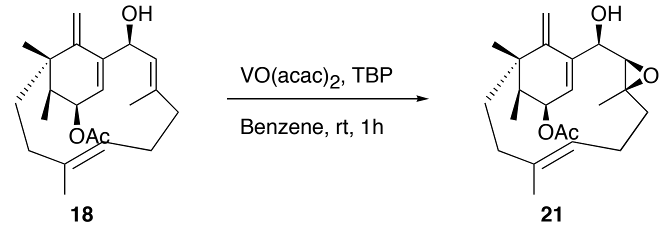
28 **18** **19**

To a solution of the above mixture of acetated **28** (65.5 mg, 0.131 mmol) in 6.5 mL of dry THF at room temperature was added TBAF (0.26 mL, 0.26 mmol, 1.0 M in THF) dropwise. The mixture was stirred overnight and then quenched with H_2O (15 mL). The aqueous layer was extracted with Et_2O (3 * 20 mL). The combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography on silica gel using 4:1 hexanes/EtOAc as eluent provided a ratio of 1:2 allylic alcohols **19** (10.1 mg) and **18** (20.0 mg) and 5.4 mg of mixture of the two products (0.103 mmol, 79% overall yield) as a colorless oil.

Major isomer 18 ^1H NMR ($CDCl_3$, 500 MHz) δ 0.71 (d, 3H, J = 6.8 Hz), 1.04 (s, 3H), 1.48 (s, 3H), 1.49-1.51 (m, 1H), 1.64 (s, 3H, J = 1.2 Hz), 1.71-1.76 (m, 1H), 1.84-1.89 (m, 2H), 2.06 (s, 3H), 2.01-2.10 (m, 5H), 4.65-4.68 (m, 1H), 4.75 (d, 1H, J = 9.5 Hz), 4.89 (s, 1H), 5.07 (s, 1H), 5.21-5.23 (m, 1H), 5.73 (d, 1H, J = 5.6 Hz), 5.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.31, 16.35, 17.03, 21.31, 21.62, 24.43, 33.71, 35.57, 38.40, 43.49, 44.92, 66.37, 72.19, 110.72, 118.91, 124.86, 128.96, 136.04, 136.84, 141.96, 144.49, 170.79; IR (neat) 3445, 2936, 1734, 1719, 1242, 1022 cm^{-1}; mass spectrum *m/z* (% rel intensity) 344 M$^+$ (1), 302 (1), 203 (16), 187 (19), 185 (17), 173 (34), 171 (25), 161 (16), 159 (30), 157 (19), 147 (34), 145 (31), 137 (25), 135 (36), 133 (36), 121 (45), 119 (67), 115 (23), 107 (44), 105 (61), 95 (36), 93 (49), 91 (69), 84 (43), 81 (100), 79 (43), 77 (33), 67 (32), 556 (32), 55 (27); HRMS (CI) calcd for $(C_{22}H_{31}O_2)^+$ (M-H_2O+H) *m/z* 327.2324, meas 327.2313. Colorless oil; R_f = 0.31 (3:1 hexanes/EtOAc).

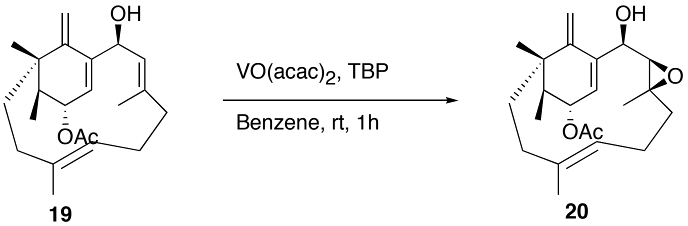
Minor isomer 19 ^1H NMR ($CDCl_3$, 500 MHz) δ 0.83 (d, 3H, J = 6.8 Hz), 0.97 (s, 3H), 1.48 (s, 3H), 1.49 (d, 1H, J = 2.4 Hz), 1.65 (d, 3H, J = 1.5 Hz), 1.73-1.75 (m, 1H), 1.81-1.85 (m, 2H), 2.01-2.06 (m, 4H), 2.08 (s, 3H), 2.11-2.15 (m, 1H), 4.68-4.70 (m, 1H), 4.78 (d, 1H, J = 9.6 Hz), 4.99 (d, 1H, J = 1.5 Hz), 5.04 (s, 1H), 5.11-5.14 (m, 1H), 5.23 (d, 1H, J = 9.3 Hz), 5.92-5.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.92, 15.91, 16.42, 21.42, 24.04, 24.91, 34.68, 34.81, 38.64, 40.61, 41.03, 66.41, 73.35, 110.39, 119.46, 124.89, 128.94, 135.40, 136.79, 141.93, 145.82, 170.78; IR (neat) 3438br, 2922, 1732, 1242,1022 cm^{-1}; mass spectrum *m/z* (% rel intensity) 344 M$^+$ (1), 266 (17), 251 (16), 209 (17), 195 (20), 185 (32), 183 (22), 173 (52), 171 (64), 159 (39), 157 (64), 147 (29), 143 (38), 134 (32), 128 (67), 119 (49), 105 (43), 95 (32), 93 (32), 91 (50), 81 (91), 77 (55), 69 (29), 67 (37), 60 (22), 55 (51), 53 (28), 45 (34), 43 (100); HRMS (CI) calcd for $(C_{22}H_{31}O_2)^+$ (M-H_2O+H) *m/z* 327.2324, meas 327.2325. Colorless oil; R_f = 0.29 (3:1 hexanes/EtOAc).

Epoxidation of allylic alcohol 18.



A solution of *tert*-butyl hydroperoxide (75% W/W) in H_2O (1.8 μL from a new bottle) was added to a stirred solution of vanadyl acetylacetonate (1.0 mg, 0.0038 mmol) and the allylic alcohol **18** (5.0 mg, 0.0145 mmol) in 0.72 mL of benzene at room temperature. After 15 minutes, another 0.9 μL of *tert*-butyl hydroperoxide was added to the solution. The light green solution turned yellow brown, and was stirred at room temperature for 60 minutes before quenching with 2 mL of saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with Et_2O (3 * 10 mL). The combined organic layer was washed with brine (15 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography on silica gel using 2:1 hexanes/EtOAc as eluent provided epoxy alcohol **21** (4.6 mg, 0.0128 mmol, 88%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.72 (d, 3H, *J* = 7.0 Hz), 1.03 (d, 3H, *J* = 0.5 Hz), 1.04-1.12 (m, 1H), 1.26 (s, 3H), 1.52 (s, 3H), 1,55-1.59 (m, 1H), 1.65-1.69 (m, 1H), 1.78-1.82 (m, 1H), 1.95-2.04 (m, 3H), 2.05 (s, 3H), 2.06-2.09 (m, 2H), 2.64 (s, 1H), 3.11 (d, 1H, *J* = 1.5 Hz), 4.79 (t, 1H, *J* = 6.8 Hz), 4.99 (s, 1H), 5.13-5.14 (m, 1H), 5.26 (s, 1H), 5.78-5.79 (m, 1H), 5.82-5.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.05, 14.82, 16.51, 21.25, 22.52, 23.43, 32.65, 34.25, 39.04, 43.04, 45.32, 62.59, 64.37, 65.02, 71.69, 111.29, 121.26, 121.57, 135.56, 137.14, 144.18,170.74; IR (neat) 3497br, 2924, 1738, 1373, 1242, 1024 cm^{-1}; mass spectrum *m/z* (% rel intensity) 318 (M-42)$^+$ (3), 167 (39), 162 (23), 150 (89), 149 (94), 135 (43), 124 (47), 121 (100), 119 (48), 105 (87), 91 (72), 81 (95); HRMS (CI) calcd for $(C_{22}H_{31}O_3)^+$ (M-H_2O+H) *m/z* 343.2273, meas 343.2281. Colorless oil; R_f = 0.30 (3:1 hexanes/EtOAc).

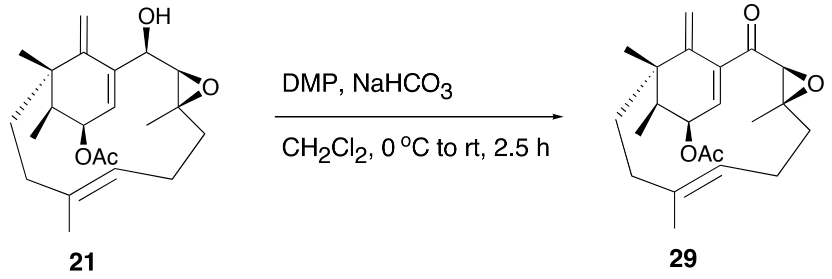
Epoxidation of allylic alcohol 19.



A solution of *tert*-butyl hydroperoxide (75% W/W) in H_2O (2.2 μL from a new bottle) was added to a stirred solution of vanadyl acetylacetonate (1.1 mg, 0.0041 mmol) and the allylic alcohol **19** (6.0 mg, 0.0174 mmol) in 0.87 mL of benzene at room temperature. After 15 minutes, another 1.1 μL of *tert*-butyl hydroperoxide was added to the solution. The light green solution turned yellow brown, and was stirred at room temperature for 60 minutes before quenching with 2 mL of saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with Et_2O (3 * 10 mL). The combined organic layer was washed with brine (15 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography on silica gel using 2:1 hexanes/ EtOAc as eluent provided epoxy alcohol **20** (7.6 mg, 0.0211 mmol, 93%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500

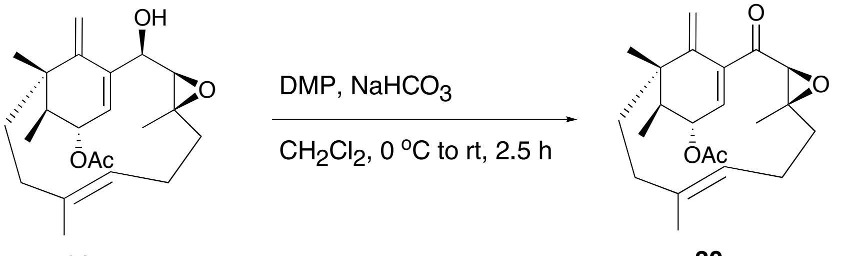
MHz) δ 0.84 (d, 3H, *J* = 7.3 Hz), 0.99 (s, 3H), 1.31 (s, 3H), 1.33-1.42 (m, 2H), 1.52 (s, 3H), 1.68-1.73 (m, 2H), 1.98-2.02 (m, 1H), 2.03 (s, 3H), 2.05-2.13 (m, 3H), 2.63 (s, 1H), 3.08 (d, 1H, *J* = 4.4 Hz), 4.83-4.85 (m, 1H), 5.06-5.08 (m, 2H), 5.16-5.17 (m, 1H), 5.33 (s, 1H), 5.96-5.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.63, 15.14, 16.21, 21.42, 23.02, 23.42, 33.98, 35.13, 39.09,41.95, 42.92, 62.68, 64.23, 65.31, 73.25, 112.02, 118.92, 121.18, 136.37, 137.06, 144.61, 170.45; IR (neat) 3495br, 2924, 1730, 1385, 1240 cm^{-1}; colorless oil; R_f = 0.25 (3:1 hexanes/EtOAc).

Oxidation of epoxy alcohol 21.



Freshly prepared DMP[1] (0.047 mmol, 20 mg) was added to a mixture of $NaHCO_3$ (0.189 mmol, 16 mg) and the epoxy alcohol **21** (8.5 mg, 0.0236 mmol) in 1 mL of dry CH_2Cl_2 at 0 °C. The mixture was stirred at 0 °C for 30 minutes, and then allowed to warm to room temperature over 2.5 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with Et_2O (3 * 10 mL). The combined organic layer was washed with brine (15 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography on silica gel using 3:1 hexanes/EtOAc containing 1% Et_3N as eluent provided epoxy ketone **29** (7.5 mg, 0.021 mmol, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.72 (d, 3H, *J* = 7.0 Hz), 1.079 (s, 3H), 1.082 (s, 3H), 1.15-1.23 (m, 2H), 1.47-1.53 (m, 1H), 1.55 (s, 3H), 1.86-1.94 (m, 2H), 1.96-2.02 (m, 1H), 2.07 (s, 3H), 2.07-2.21 (m, 3H), 4.04 (s, 1H), 4.98 (t, 1H, *J* = 6.8 Hz), 5.20 (s, 1H), 5.31 (s, 1H), 5.83 (dd, 1H, *J* = 5.9, 2.3 Hz), 5.86-5.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.16, 14.25, 16.82, 21.04, 22.22, 23.71, 32.30, 32.71, 38.23, 42.40, 45.85, 63.48, 65.18, 70.30, 116.76, 121.43, 129.92, 136.75, 142.80, 143.26, 170.50, 198.01. ^{1}H NMR (CD_3OD, 500 MHz) δ 0.70 (d, 3H, *J* = 7.0 Hz), 1.03 (d, 3H), 1.09 (s, 3H), 1.12-1.23 (m, 2H), 1.55 (s, 3H), 1.48-1.63 (m, 1H), 1.89-2.18 (m, 6H), 2.04 (s, 3H), 4.10 (s, 1H), 5.02 (t, 1H, *J* = 6.3 Hz), 5.26 (s, 1H), 5.34 (s, 1H), 5.77-5.78 (m, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 9.46, 14.57, 16.74, 20.91, 22.58, 24.61, 33.52, 33.80, 39.01, 43.47, 46.98, 64.69, 66.66, 71.76, 117.86, 122.91, 131.23, 137.91, 144.14, 144.42, 172.04, 199.92. IR (neat) 2926, 1740, 1696, 1385, 1238, 1215, 1024 cm^{-1}; mass spectrum *m/z* (% rel intensity) 358 M^+ (0.05), 316 (2), 288 (1), 283 (2), 255 (2), 149 (17), 147 (26), 121 (24), 109 (22), 105 (21), 93 (17), 91 (29), 81 (24), 79 (20), 55 (23), 43 (100); HRMS (FAB) calcd for $(C_{22}H_{31}O_4)^+$ *m/z* 359.2223, meas 359.2222. Colorless oil; R_f = 0.21 (3:1 hexanes/EtOAc).

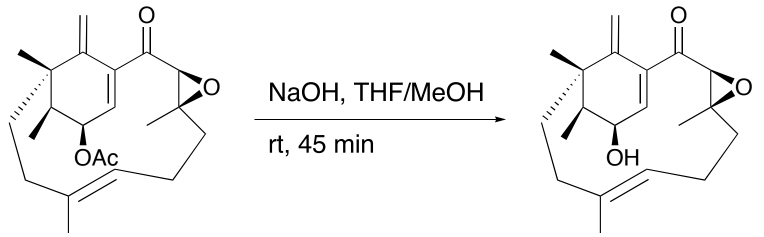
Oxidation of epoxy alcohol 20



20 **30**

Freshly prepared DMP[1] (0.032 mmol, 13.4 mg) was added to a mixture of $NaHCO_3$ (10.6vmg, 0.126 mmol) and the epoxy alcohol **20** (5.7 mg, 0.0158 mmol) in 1 mL of dry CH_2Cl_2 at 0 °C. The mixture was stirred at 0 °C for 30 minutes and then allowed to warm to room temperature over 2.5 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL). The aqueous layer was extracted with Et_2O (3 * 10 mL). The combined organic layer was washed with brine (15 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography on silica gel using 3:1 hexanes/EtOAc containing 1% Et_3N as eluent provided epoxy ketone **30** (5.0 mg, 0.014 mmol, 88%). The following spectral match those reported for the natural product.[2] The data for natural and synthetic **30** are presented in Table 1. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.81 (d, 3H, *J* = 7.3 Hz), 1.05 (s, 3H), 1.14 (s, 3H), 1.30-1.35 (m, 1H), 1.48-1.52 (m, 1H), 1.55 (s, 3H), 1.69-1.72 (m, 1H), 1.80 (br, 1H), 1.85-1.89 (m, 1H), 2.06-2.19 (m, 4H), 2.27-2.31 (m, 1H), 4.04 (s, 1H), 4.06 (s, 1H), 5.00 (t, 1H, *J* = 6.4 Hz), 5.26 (s, 1H), 5.27 (d, 1H, *J* = 1.5 Hz), 6.06 (d, 1H, *J* =3.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.45, 14.95, 16.48, 23.00, 23.65, 33.55, 34.15, 37.61, 41.35, 45.44, 63.54, 64.68, 71.57, 116.74, 122.23, 131.92, 136.67, 141.47, 144.73, 199.61. ^{1}H NMR (CD_3OD, 500 MHz) δ 0.76 (d, 3H, *J* = 7.3 Hz), 1.02 (s, 3H), 1.05 (s, 3H), 1.26-1.32 (m, 1H), 1.46-1.50 (m, 1H), 1.52 (s, 3H), 1.64-1.67 (m, 1H), 1.85-1.89 (m, 1H), 1.98-2.15 (m, 4H), 2.10-2.30 (m, 1H), 3.92 (t, 1H, *J* = 3.0 Hz), 4.06 (s, 1H), 5.01 (tq, 1H, *J* = 6.8 1.2 Hz), 5.19 (s, 1H), 5.27 (d, 1H, *J* = 1.6 Hz), 5.93 (d, 1H, *J* = 4.0 Hz); ^{13}C NMR (CD_3OD, 125 MHz) δ 14.62, 15.35, 16.53, 23.70, 24.51, 34.66, 35.34, 38.34, 42.45, 45.90, 64.75, 66.14, 71.98, 117.04, 123.66, 134.28, 137.93, 142.42, 146.62, 201.82. IR (neat) 3477, 2919, 1688, 1381, 1217, 1009 cm^{-1}; mass spectrum *m/z* (% rel intensity) 316 M$^+$ (0.4), 301 (2), 273 (3), 189 (16), 175 (17), 165 (71), 164 (28), 163 (24), 161 (20), 159 (17), 149 (55), 147 (34), 145 (20), 137 (20), 135 (45), 133 (35), 121 (56), 119 (38), 109 (43), 107 (41), 105 (49), 93 (53), 91 (81), 81 (56), 77 (48), 69 (26), 67 (48), 55 (74), 53 (48), 43 (100). HRMS (CI) calcd for $(C_{20}H_{28}O_3+Na)^+$ *m/z* 339.1936, meas 339.1945. Colorless oil; R_f = 0.31 (1:1 hexanes/EtOAc).

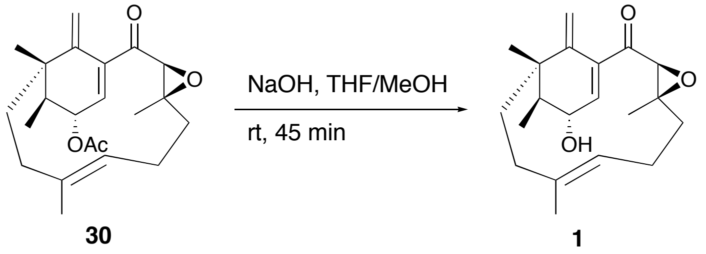
Cleavage of Acetate 29.



29 **22**

A solution of acetate **29** (7.5 mg, 0.0208 mmol) in 1.0 mL of 1:4 mixture of THF/MeOH containing 8.3 mg of NaOH (0.21 mmol) was stirred at room temperature for 45 minutes. The reaction was then quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with Et_2O (3 * 10 mL). The combined organic layer was washed with brine (15 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography on silica gel with 1:1 hexanes/EtOAc containing 1% Et_3N as eluent provided the C13-epimer of phomactin B2 **22** (5.9 mg, 0.0186 mmol, 90%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.74 (d, 3H, J = 6.9 Hz), 1.09 (s, 3H), 1.10 (s, 1H), 1.13-1.23 (m, 2H), 1.39-1.45 (m, 2H), 1.54 (s, 3H), 1.57 (br, 1H), 1.85-1.95 (m, 3H), 2.08-2.18 (m, 4H), 4.03 (s, 1H), 4.77 (s, 1H), 4.97-5.00 (m, 1H), 5.17 (s, 1H), 5.28 (s, 1H), 5.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 8.15, 14.25, 16.77, 22.50, 23.74, 32.11, 32.64, 38.25, 44.98, 45.79, 63.34, 65.25, 67.72, 116.31, 121.34, 133.54, 136.79, 142.16, 143.67, 198.35. ^1H NMR (CD_3OD, 500 MHz) δ 0.70 (d, 3H, J = 6.8 Hz), 1.02 (s, 3H), 1.08 (s, 3H), 1.14-1.20 (m, 1H), 1.35 (s, 1H), 1.39-1.45 (m, 1H), 1.54 (s, 3H), 1.77-1.79 (m, 1H), 1.98-1.98 (m, 1H), 2.06-2.17 (m, 4H), 4.12 (s, 1H), 4.70 (dd, 1H, J = 5.8, 2.2 Hz), 5.01 (t, 1H, J = 6.8 Hz), 5.20 (s, 1H), 5.27 (s, 1H), 5.87 (t, 1H, J = 0.7 Hz); ^{13}C NMR (CD_3OD, 125 MHz) δ 8.84, 14.54, 16.70, 22.83, 24.66, 33.62, 33.84, 39.15, 46.55, 46.97, 64.59, 66.80, 67.87, 116.79, 122.88, 136.14, 138.08, 142.87, 145.32, 200.40; IR (neat) 3483, 2973, 2924, 1689, 1251, 1039, 887 cm^{-1}; mass spectrum m/z (% rel intensity) 316 M^+ (1), 301 (2), 189 (18), 175 (19), 165 (56), 164 (33), 163 (26), 161 (22), 149 (84), 147 (27), 145 (15), 137 (20), 135 (66), 121 (60), 109 (40), 107 (44), 105 (40), 93 (46), 91 (73), 81 (60), 69 (33), 67 (37), 55 (30), 43 (100). HRMS (FAB) calcd for $(C_{20}H_{28}O_3+H)^+$ m/z 317.2116, meas 317.2117. Colorless oil; R_f = 0.31 (1:1 hexanes/EtOAc).

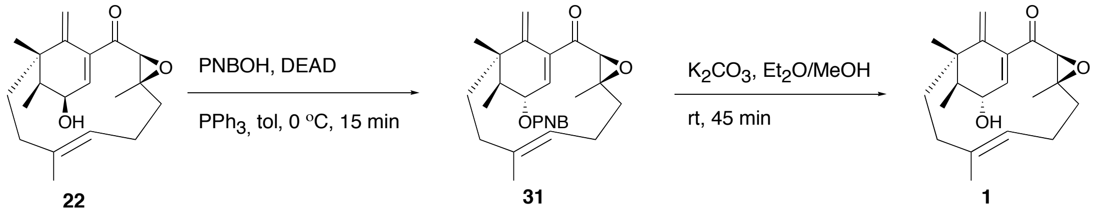
Cleavage of Acetate 30 and the Synthesis of Phomactin B2.



A solution of acetate **30** (6.5 mg, 0.018 mmol) in 1.0 mL of 1:4 mixture of THF/MeOH containing NaOH (8.4 mg, 0.21 mmol) was stirred at room temperature for 45 minutes. The reaction was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O (3 * 5 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography using 1:1 hexanes/EtOAc containing 1% Et_3N as eluent provided 5.4 mg of phomactin B2 **1** (0.017 mmol, 94%) as a colorless oil. The following spectral match those reported for the natural product.[2] The data for natural and synthetic Phomactin B2 are presented in Table 1. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.81 (d, 3H, J = 7.3 Hz), 1.05 (s, 3H), 1.14 (s, 3H), 1.30-1.35 (m, 1H), 1.48-1.52 (m, 1H), 1.55 (s, 3H), 1.69-1.72 (m, 1H), 1.80 (br, 1H), 1.85-1.89 (m, 1H), 2.06-2.19 (m, 4H), 2.27-2.31 (m, 1H), 4.04 (s, 1H), 4.06 (s, 1H), 5.00 (t, 1H, J = 6.4 Hz), 5.26 (s, 1H), 5.27 (d, 1H, J = 1.5 Hz), 6.06 (d, 1H, J =3.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.45, 14.95, 16.48, 23.00, 23.65, 33.55, 34.15, 37.61, 41.35, 45.44, 63.54, 64.68, 71.57, 116.74, 122.23, 131.92, 136.67, 141.47, 144.73, 199.61. ^1H NMR (CD_3OD, 500 MHz) δ 0.76 (d, 3H, J = 7.3 Hz), 1.02 (s, 3H), 1.05 (s, 3H), 1.26-1.32 (m, 1H), 1.46-1.50 (m, 1H), 1.52 (s, 3H), 1.64-1.67 (m, 1H), 1.85-1.89 (m, 1H), 1.98-2.15 (m, 4H), 2.10-2.30 (m, 1H), 3.92 (t, 1H, J = 3.0 Hz), 4.06 (s, 1H), 5.01 (tq, 1H, J = 6.8 1.2 Hz), 5.19 (s, 1H), 5.27 (d, 1H, J = 1.6 Hz), 5.93 (d, 1H, J = 4.0 Hz); ^{13}C NMR (CD_3OD, 125 MHz) δ 14.62, 15.35, 16.53, 23.70, 24.51, 34.66, 35.34, 38.34, 42.45, 45.90, 64.75, 66.14, 71.98, 117.04, 123.66, 134.28, 137.93, 142.42, 146.62, 201.82. IR (neat) 3477, 2919, 1688, 1381, 1217, 1009 cm^{-1}; mass spectrum m/z (% rel intensity) 316 M^+ (0.4), 301 (2), 273 (3), 189 (16), 175 (17), 165 (71), 164

(28), 163 (24), 161 (20), 159 (17), 149 (55), 147 (34), 145 (20), 137 (20), 135 (45), 133 (35), 121 (56), 119 (38), 109 (43), 107 (41), 105 (49), 93 (53), 91 (81), 81 (56), 77 (48), 69 (26), 67 (48), 55 (74), 53 (48), 43 (100). HRMS (CI) calcd for $(C_{20}H_{28}O_3+Na)^+$ *m/z* 339.1936, meas 339.1945. Colorless oil; R_f = 0.31 (1:1 hexanes/EtOAc).

Mitsunobu Inversion of Alcohol 22.



To a solution of *para*-nitrobenzoic acid (6.2 mg, 0.037 mmol), C13-epimer **22** (5.9 mg, 0.0187 mmol) and PPh_3 (9.8 mg, 0.037 mmol) in 0.9 mL of toluene at 0 °C was added DEAD (5.9 μL, 0.037mmol) dropwise. The reaction mixture was stirred at 0 °C for 15 minutes, and then quenched with saturated aqueous $NaHCO_3$ (5 mL). The aqueous layer was extracted with Et_2O (3 * 5 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography using 3:1 hexanes/EtOAc as eluent provided ester **31** (7.0 mg, 0.015 mmol, 81%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.92 (d, 3H, *J* = 7.3 Hz), 1.11 (s, 3H), 1.12 (s, 3H), 1.21-1.25 (m, 1H), 1.37-1.44 (m, 1H), 1.59 (s, 3H), 1.86-1.92 (m, 2H), 2.15-2.22 (m, 4H), 2.38-2.41 (m, 1H), 4.07 (s, 1H), 5.04-5.05 (m, 1H), 5.36 (d, 1H, *J* = 4.7 Hz), 5.38 (s, 1H), 5.43 (s, 1H), 6.11(d, 1H, *J* = 4.6 Hz), 8.16 (d, 2H, *J* = 9.0 Hz), 8.29 (d, 2H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.41, 14.61, 16.41, 22.01, 23.88, 33.31, 33.94, 38.19, 41.58, 43.83, 63.83, 64.80, 74.49, 118.73, 122.14, 123.72, 126.83, 130.62, 135.45, 136.50, 143.26, 143.86, 150.65, 163.66, 198.61; IR (neat) 2926, 1722, 1690, 15530, 1271, 1101, 720 cm^{-1}. HRMS (CI) calcd for $(C_{27}H_{31}NO_6+H)^+$ *m/z* 466.2243, meas 466.2237. Colorless oil; R_f = 0.41 (33% EtOAc in hexanes).

Cleavage of PNB ester 31.

To a solution of PNB-ester **31** (5.0 mg, 0.0108 mmol) in 0.5 mL of MeOH/Et_2O (2:1) at room temperature was added K_2CO_3 (7.4 mg, 0.054 mmol) as a powder. The reaction mixture was stirred at room temperature until all of the starting material was consumed, and then quenched with saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with Et_2O (3 * 5 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Filtration and concentration followed by flash chromatography using 1:1 hexanes/EtOAc as eluent provided phomactin B2 **1** (2.9 mg, 0.0092 mmol, 85%) as a colorless oil.

Table 1. ^{13}C NMR Chemical Shifts of Phomactin B2 (1) and Compound 30 (CD_3OD)

Phomactin B2 (**1**)		Compound **30**	
Natural (ppm)	Synthetic (ppm)	Natural (ppm)	Synthetic (ppm)
14.7	14.62	14.8	14.74
15.4	15.35	14.8	14.77
16.6	16.53	16.4	16.38
23.8	23.70	21.1	21.06
24.5	24.51	22.7	22.63
34.7	34.66	24.7	24.69
35.3	35.34	34.5	34.54
38.4	38.34	35.1	35.06
42.4	42.45	38.9	38.93
45.9	45.90	42.7	42.93
64.7	64.75	44.5	44.56
66.1	66.14	64.9	64.93
72.0	71.98	66.3	66.33
117.0	117.04	74.4	74.43
123.7	123.66	119.0	118.99
134.3	134.28	123.4	123.39
137.9	137.93	129.2	129.22
142.4	142.42	137.9	137.91
146.6	146.62	144.6	144.63
201.8	201.82	145.0	145.06
		171.8	171.83
		200.7	200.84

References:

1) Dess, D. B.; Martin, J. C. *J. Org. Chem*. **1983**, *48*, 4155.

2) Sugano, M.; Sato, A.; Iijima, Y.; Furuya, K.; Haruyama, H.; Yoda, K.; Hata, T.; *J. Org. Chem*. **1994**, *59*, 564.

APPENDIX A

Crystal Structure of the Major Alcohol 2c.

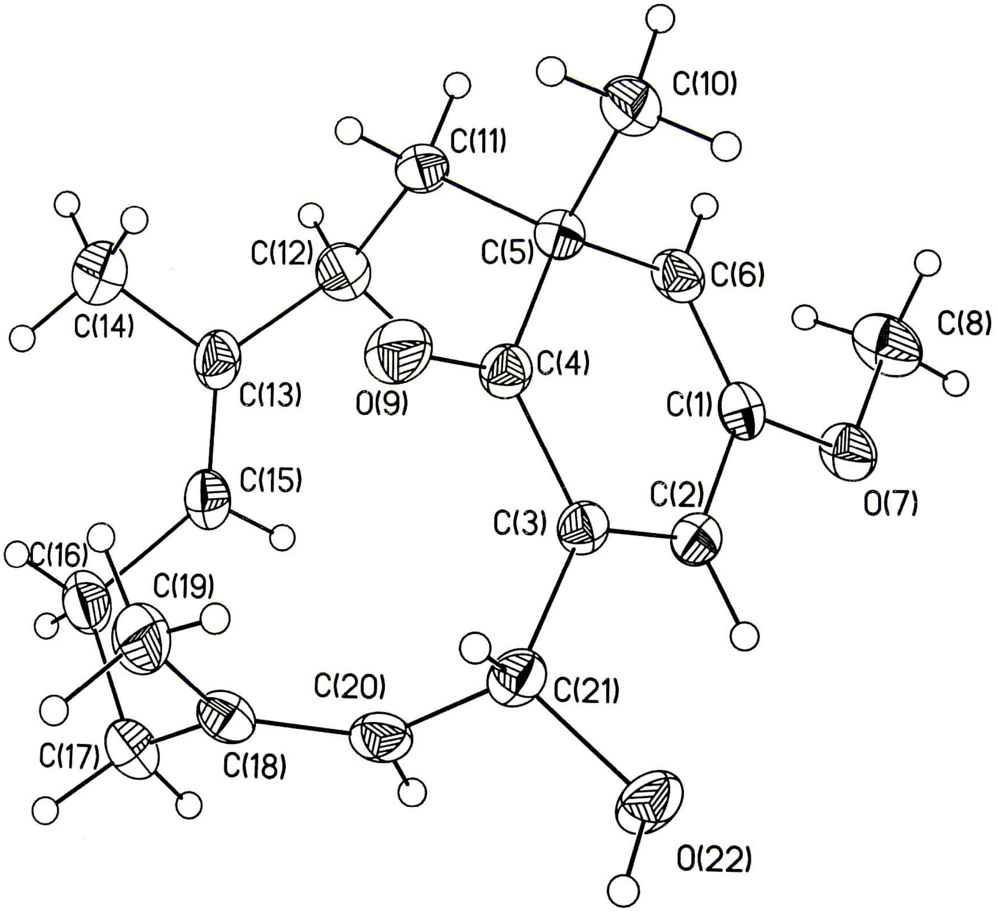


Figure 1. ORTEP for the Major Alcohol 2c.

Table 1. Crystal data and structure refinement for **2c**.

Identification code	p-1
Empirical formula	C19 H26 O3
Formula weight	302.40
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.4091(13) A
	b = 14.590(3) A
	c = 18.406(4) A
	alpha = 90.37(3) deg.
	beta = 94.69(3) deg.
	gamma = 100.75(3) deg.
Volume	1684.9(6) A^3
Z	4
Density (calculated)	1.192 Mg/m^3
Absorption coefficient	0.079 mm^-1
F(000)	656
Crystal size	1.4 x 1.2 x 0.5 mm
Theta range for data collection	1.78 to 28.31 deg.
Index ranges	-8<=h<=8, -19<=k<=19, -24<=l<=23
Reflections collected / unique	20386 / 7977 [R(int) = 0.0315]
Completeness to theta = 28.31	94.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7977 / 0 / 405
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1508
R indices (all data)	R1 = 0.0620, wR2 = 0.1559
Largest diff. peak and hole	0.556 and -0.311 e.A^-3

Table 2. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (A^2 x 10^3), and occupancies for **2c**.

	x	y	z	U(eq)	Occ.
C(1)	2902(2)	4041(1)	294(1)	22(1)	1
C(2)	2480(2)	4148(1)	-485(1)	22(1)	1
C(3)	3210(2)	3642(1)	-983(1)	20(1)	1
C(4)	4546(2)	2961(1)	-746(1)	21(1)	1
C(5)	5065(2)	2839(1)	69(1)	22(1)	1
C(6)	4041(2)	3420(1)	557(1)	24(1)	1
O(7)	1991(2)	4634(1)	691(1)	28(1)	1
C(8)	2241(3)	4553(1)	1462(1)	37(1)	1
O(9)	5300(2)	2517(1)	-1191(1)	32(1)	1
C(10)	7507(2)	3150(1)	206(1)	30(1)	1
C(11)	4479(2)	1793(1)	255(1)	26(1)	1
C(12)	2113(2)	1329(1)	124(1)	29(1)	1

C(13)	1398(2)	889(1)	-625(1)	26(1)	1
C(14)	2684(3)	194(1)	-862(1)	42(1)	1
C(15)	-329(2)	1069(1)	-1006(1)	26(1)	1
C(16)	-1290(2)	666(1)	-1740(1)	32(1)	1
C(17)	-1575(2)	1439(1)	-2286(1)	32(1)	1
C(18)	484(2)	2139(1)	-2301(1)	27(1)	1
C(19)	2306(2)	1781(1)	-2597(1)	33(1)	1
C(20)	641(2)	2977(1)	-1981(1)	25(1)	1
C(21)	2620(2)	3700(1)	-1793(1)	23(1)	1
O(22)	2234(2)	4620(1)	-1936(1)	31(1)	1
C(1A)	2206(2)	6079(1)	-5577(1)	22(1)	1
C(2A)	2426(2)	5816(1)	-4817(1)	22(1)	1
C(3A)	1598(2)	6227(1)	-4287(1)	20(1)	1
C(4A)	396(2)	6980(1)	-4461(1)	22(1)	1
C(5A)	100(2)	7267(1)	-5256(1)	24(1)	1
C(6A)	1199(2)	6770(1)	-5784(1)	25(1)	1
O(7A)	3147(2)	5539(1)	-6014(1)	28(1)	1
C(8A)	3201(2)	5785(1)	-6763(1)	36(1)	1
O(9A)	-420(2)	7349(1)	-3989(1)	33(1)	1
C(10A)	-2329(2)	7017(1)	-5471(1)	33(1)	1
C(11A)	787(2)	8338(1)	-5312(1)	30(1)	1
C(12A)	3135(2)	8752(1)	-5082(1)	32(1)	1
C(13A)	3691(2)	9002(1)	-4280(1)	31(1)	1
C(14A)	2366(3)	9635(1)	-3967(1)	51(1)	1
C(15A)	5329(2)	8724(1)	-3909(1)	30(1)	1
C(16A)	6145(3)	8942(1)	-3123(1)	37(1)	1
C(17A)	6284(2)	8051(1)	-2686(1)	37(1)	1
C(18A)	4179(2)	7376(1)	-2768(1)	30(1)	1
C(19A)	2357(3)	7676(1)	-2420(1)	41(1)	1
C(20A)	3987(2)	6623(1)	-3198(1)	26(1)	1
C(21A)	1969(2)	5994(1)	-3491(1)	24(1)	1
O(22A)	2262(2)	5041(1)	-3418(1)	29(1)	1

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Bond lengths [A] and angles [deg] for **2c**.

C(1)-C(6)	1.3345(19)
C(1)-O(7)	1.3687(15)
C(1)-C(2)	1.4529(17)
C(2)-C(3)	1.3392(17)
C(3)-C(4)	1.4734(17)
C(3)-C(21)	1.5159(17)
C(4)-O(9)	1.2238(16)
C(4)-C(5)	1.5282(17)
C(5)-C(6)	1.5006(18)
C(5)-C(10)	1.5455(19)
C(5)-C(11)	1.5495(18)
O(7)-C(8)	1.4232(17)
C(11)-C(12)	1.540(2)
C(12)-C(13)	1.516(2)
C(13)-C(15)	1.331(2)

C(13)-C(14)	1.503(2)
C(15)-C(16)	1.506(2)
C(16)-C(17)	1.541(2)
C(17)-C(18)	1.513(2)
C(18)-C(20)	1.3361(19)
C(18)-C(19)	1.505(2)
C(20)-C(21)	1.5047(19)
C(21)-O(22)	1.4330(15)
C(1A)-C(6A)	1.3346(19)
C(1A)-O(7A)	1.3708(15)
C(1A)-C(2A)	1.4566(17)
C(2A)-C(3A)	1.3376(18)
C(3A)-C(4A)	1.4788(18)
C(3A)-C(21A)	1.5154(17)
C(4A)-O(9A)	1.2214(16)
C(4A)-C(5A)	1.5310(18)
C(5A)-C(6A)	1.5025(18)
C(5A)-C(11A)	1.5489(19)
C(5A)-C(10A)	1.5490(19)
O(7A)-C(8A)	1.4290(17)
C(11A)-C(12A)	1.537(2)
C(12A)-C(13A)	1.515(2)
C(13A)-C(15A)	1.334(2)
C(13A)-C(14A)	1.507(2)
C(15A)-C(16A)	1.508(2)
C(16A)-C(17A)	1.546(2)
C(17A)-C(18A)	1.510(2)
C(18A)-C(20A)	1.331(2)
C(18A)-C(19A)	1.508(2)
C(20A)-C(21A)	1.497(2)
C(21A)-O(22A)	1.4433(16)

C(6)-C(1)-O(7)	126.72(12)
C(6)-C(1)-C(2)	121.43(12)
O(7)-C(1)-C(2)	111.86(11)
C(3)-C(2)-C(1)	122.67(12)
C(2)-C(3)-C(4)	119.88(12)
C(2)-C(3)-C(21)	122.48(11)
C(4)-C(3)-C(21)	117.56(11)
O(9)-C(4)-C(3)	121.04(12)
O(9)-C(4)-C(5)	119.71(11)
C(3)-C(4)-C(5)	119.21(11)
C(6)-C(5)-C(4)	114.53(10)
C(6)-C(5)-C(10)	107.88(11)
C(4)-C(5)-C(10)	105.75(11)
C(6)-C(5)-C(11)	110.48(11)
C(4)-C(5)-C(11)	109.62(11)
C(10)-C(5)-C(11)	108.30(11)
C(1)-C(6)-C(5)	122.13(12)
C(1)-O(7)-C(8)	116.01(11)
C(12)-C(11)-C(5)	116.78(11)
C(13)-C(12)-C(11)	116.34(12)
C(15)-C(13)-C(14)	123.96(13)

C(15)-C(13)-C(12)	121.13(13)
C(14)-C(13)-C(12)	114.75(13)
C(13)-C(15)-C(16)	127.74(13)
C(15)-C(16)-C(17)	111.56(12)
C(18)-C(17)-C(16)	110.33(12)
C(20)-C(18)-C(19)	124.69(14)
C(20)-C(18)-C(17)	119.02(13)
C(19)-C(18)-C(17)	115.82(12)
C(18)-C(20)-C(21)	128.09(13)
O(22)-C(21)-C(20)	111.08(11)
O(22)-C(21)-C(3)	108.04(10)
C(20)-C(21)-C(3)	107.27(10)
C(6A)-C(1A)-O(7A)	127.23(12)
C(6A)-C(1A)-C(2A)	121.45(12)
O(7A)-C(1A)-C(2A)	111.32(11)
C(3A)-C(2A)-C(1A)	122.70(12)
C(2A)-C(3A)-C(4A)	120.12(12)
C(2A)-C(3A)-C(21A)	122.23(11)
C(4A)-C(3A)-C(21A)	117.52(11)
O(9A)-C(4A)-C(3A)	121.22(12)
O(9A)-C(4A)-C(5A)	120.03(11)
C(3A)-C(4A)-C(5A)	118.70(11)
C(6A)-C(5A)-C(4A)	114.91(11)
C(6A)-C(5A)-C(11A)	110.60(11)
C(4A)-C(5A)-C(11A)	109.88(11)
C(6A)-C(5A)-C(10A)	107.96(11)
C(4A)-C(5A)-C(10A)	105.52(11)
C(11A)-C(5A)-C(10A)	107.59(11)
C(1A)-C(6A)-C(5A)	121.93(12)
C(1A)-O(7A)-C(8A)	116.56(11)
C(12A)-C(11A)-C(5A)	116.67(12)
C(13A)-C(12A)-C(11A)	116.52(13)
C(15A)-C(13A)-C(14A)	123.93(14)
C(15A)-C(13A)-C(12A)	121.15(13)
C(14A)-C(13A)-C(12A)	114.77(14)
C(13A)-C(15A)-C(16A)	127.86(14)
C(15A)-C(16A)-C(17A)	112.29(12)
C(18A)-C(17A)-C(16A)	110.57(13)
C(20A)-C(18A)-C(19A)	124.46(14)
C(20A)-C(18A)-C(17A)	119.01(13)
C(19A)-C(18A)-C(17A)	116.12(13)
C(18A)-C(20A)-C(21A)	127.40(13)
O(22A)-C(21A)-C(20A)	108.20(11)
O(22A)-C(21A)-C(3A)	110.72(10)
C(20A)-C(21A)-C(3A)	106.78(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **2c**.

	U11	U22	U33	U23	U13	U12
C(1)	22(1)	21(1)	20(1)	-4(1)	3(1)	1(1)
C(2)	24(1)	19(1)	21(1)	1(1)	1(1)	4(1)
C(3)	22(1)	17(1)	18(1)	3(1)	3(1)	2(1)
C(4)	22(1)	19(1)	22(1)	1(1)	2(1)	3(1)
C(5)	25(1)	21(1)	21(1)	0(1)	-2(1)	5(1)
C(6)	28(1)	26(1)	17(1)	-1(1)	-1(1)	3(1)
O(7)	31(1)	33(1)	21(1)	-8(1)	2(1)	11(1)
C(8)	41(1)	54(1)	19(1)	-9(1)	2(1)	13(1)
O(9)	38(1)	36(1)	26(1)	-2(1)	4(1)	18(1)
C(10)	25(1)	30(1)	34(1)	-4(1)	-3(1)	4(1)
C(11)	34(1)	21(1)	24(1)	4(1)	-6(1)	6(1)
C(12)	36(1)	24(1)	23(1)	6(1)	1(1)	0(1)
C(13)	32(1)	18(1)	28(1)	1(1)	3(1)	0(1)
C(14)	45(1)	34(1)	48(1)	-10(1)	-8(1)	16(1)
C(15)	31(1)	21(1)	25(1)	-2(1)	3(1)	1(1)
C(16)	35(1)	28(1)	31(1)	-6(1)	-2(1)	1(1)
C(17)	34(1)	34(1)	27(1)	-7(1)	-7(1)	6(1)
C(18)	35(1)	31(1)	15(1)	1(1)	-2(1)	9(1)
C(19)	43(1)	33(1)	23(1)	-5(1)	4(1)	11(1)
C(20)	30(1)	29(1)	16(1)	4(1)	0(1)	10(1)
C(21)	33(1)	22(1)	17(1)	4(1)	6(1)	8(1)
O(22)	50(1)	23(1)	21(1)	7(1)	6(1)	12(1)
C(1A)	21(1)	23(1)	18(1)	-4(1)	2(1)	1(1)
C(2A)	24(1)	20(1)	21(1)	2(1)	1(1)	3(1)
C(3A)	21(1)	20(1)	18(1)	3(1)	1(1)	1(1)
C(4A)	22(1)	22(1)	22(1)	0(1)	1(1)	3(1)
C(5A)	27(1)	23(1)	22(1)	0(1)	-2(1)	6(1)
C(6A)	28(1)	27(1)	17(1)	2(1)	0(1)	2(1)
O(7A)	32(1)	35(1)	20(1)	-4(1)	6(1)	9(1)
C(8A)	33(1)	56(1)	18(1)	-3(1)	5(1)	10(1)
O(9A)	38(1)	38(1)	27(1)	-3(1)	5(1)	17(1)
C(10A)	28(1)	36(1)	35(1)	-3(1)	-5(1)	8(1)
C(11A)	38(1)	23(1)	30(1)	4(1)	-5(1)	8(1)
C(12A)	38(1)	23(1)	32(1)	5(1)	2(1)	2(1)
C(13A)	35(1)	19(1)	36(1)	-4(1)	3(1)	1(1)
C(14A)	56(1)	42(1)	60(1)	-19(1)	-6(1)	23(1)
C(15A)	33(1)	24(1)	31(1)	-6(1)	3(1)	0(1)
C(16A)	38(1)	34(1)	36(1)	-12(1)	-2(1)	-1(1)
C(17A)	37(1)	44(1)	25(1)	-10(1)	-6(1)	3(1)
C(18A)	34(1)	38(1)	17(1)	0(1)	-2(1)	5(1)
C(19A)	42(1)	53(1)	26(1)	-14(1)	4(1)	6(1)
C(20A)	29(1)	32(1)	18(1)	4(1)	1(1)	7(1)
C(21A)	31(1)	24(1)	16(1)	4(1)	4(1)	6(1)
O(22A)	39(1)	24(1)	22(1)	7(1)	1(1)	5(1)

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

Table 5. Hydrogen coordinates (x 10^4), isotropic displacement parameters (A^2 x 10^3), and occupancies for **2c**.

	x	y	z	U(eq)	Occ.
H(2A)	1669	4585	-645	26	1
H(6A)	4205	3345	1058	29	1
H(8A)	1554	4998	1689	56	1
H(8B)	3731	4673	1625	56	1
H(8C)	1607	3934	1594	56	1
H(10A)	7901	3798	93	45	1
H(10B)	8201	2784	-98	45	1
H(10C)	7937	3062	709	45	1
H(11A)	5299	1450	-29	32	1
H(11B)	4930	1727	765	32	1
H(12A)	1807	851	484	34	1
H(12B)	1257	1796	209	34	1
H(14A)	2129	-52	-1339	63	1
H(14B)	2600	-305	-523	63	1
H(14C)	4144	497	-877	63	1
H(15A)	-1025	1494	-794	32	1
H(16A)	-2666	275	-1686	38	1
H(16B)	-376	278	-1930	38	1
H(17A)	-1995	1163	-2770	39	1
H(17B)	-2694	1753	-2147	39	1
H(19A)	3531	2275	-2584	49	1
H(19B)	1909	1562	-3091	49	1
H(19C)	2642	1277	-2305	49	1
H(20A)	-631	3133	-1860	30	1
H(21A)	3782	3573	-2070	28	1
H(22A)	2290(30)	4731(14)	-2432(11)	47(5)	1
H(2AA)	3173	5342	-4695	26	1
H(6AA)	1177	6948	-6268	30	1
H(8AA)	3887	5362	-7016	53	1
H(8AB)	3982	6410	-6797	53	1
H(8AC)	1773	5748	-6979	53	1
H(10D)	-2804	6356	-5439	49	1
H(10E)	-2625	7206	-5961	49	1
H(10F)	-3065	7335	-5145	49	1
H(11C)	480	8505	-5813	36	1
H(11D)	-92	8633	-5015	36	1
H(12C)	3994	8307	-5218	38	1
H(12D)	3543	9310	-5359	38	1
H(14D)	2820	9760	-3461	77	1
H(14E)	893	9337	-4017	77	1
H(14F)	2543	10211	-4225	77	1
H(15B)	6056	8350	-4166	36	1
H(16C)	5205	9287	-2898	44	1
H(16D)	7548	9335	-3105	44	1
H(17C)	7390	7755	-2859	44	1
H(17D)	6661	8218	-2175	44	1

H(19D)	1101	7201	-2504	61	1
H(19E)	2093	8249	-2628	61	1
H(19F)	2719	7768	-1904	61	1
H(20B)	5250	6469	-3331	31	1
H(21B)	774	6100	-3222	28	1
H(22B)	1120(40)	4629(17)	-3697(14)	77(7)	1

APPENDIX B

Crystal Structure of the Minor TIPS Ether 15a.

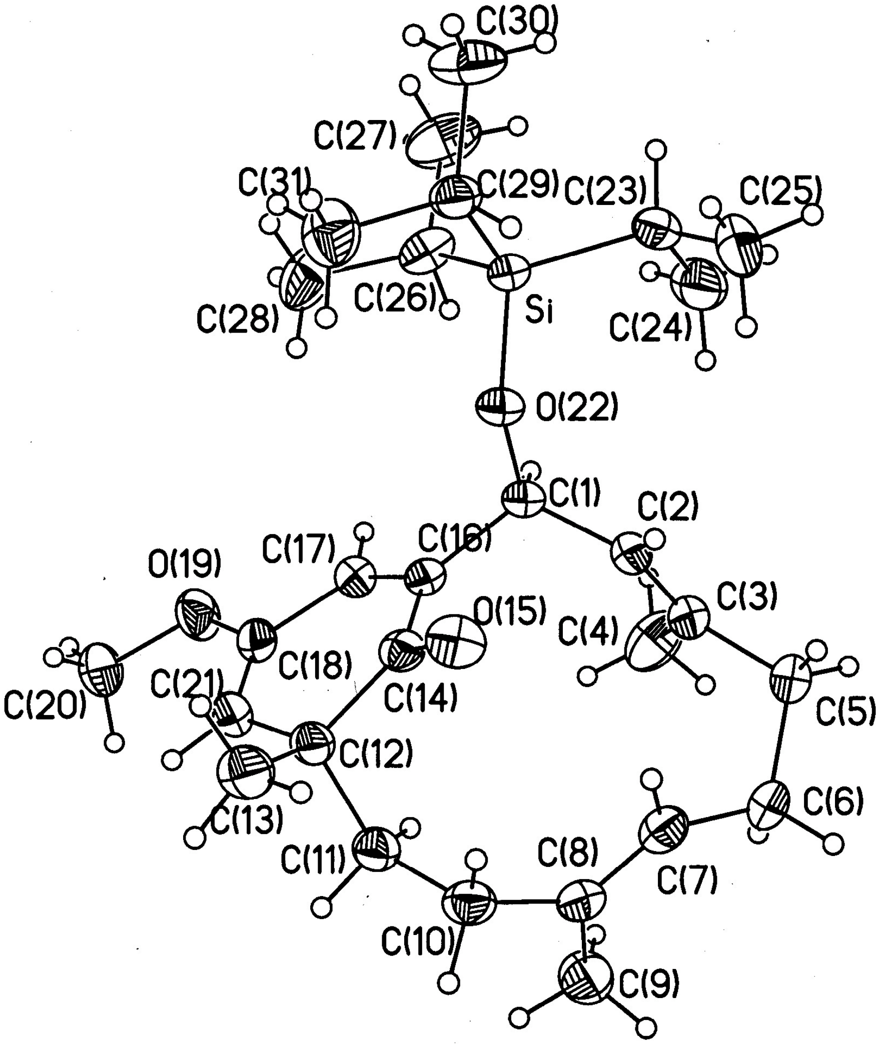


Figure 2. ORTEP for the Minor TIPS Ether 15a.

Table 1. Crystal data and structure refinement for **15a**.

Identification code	wulff07
Empirical formula	C28 H46 O3 Si
Formula weight	458.74
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 12.384(3) A
	b = 12.584(3) A
	c = 18.686(4) A
	alpha = 90 deg.
	beta = 107.07(3) deg.
	gamma = 90 deg.
Volume	2783.9(10) A^3
Z	4
Density (calculated)	1.095 Mg/m^3
Absorption coefficient	0.109 mm^-1
F(000)	1008
Crystal size	0.8 x 0.3 x 0.1 mm
Theta range for data collection	1.72 to 28.24 deg.
Index ranges	-16<=h<=16, -16<=k<=16, -24<=l<=24
Reflections collected / unique	27573 / 6693 [R(int) = 0.0463]
Completeness to theta = 28.24	97.1%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6693 / 0 / 317
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1429
R indices (all data)	R1 = 0.0857, wR2 = 0.1602
Largest diff. peak and hole	0.345 and -0.351 e.A^-3

Table 2. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (A^2 x 10^3), and occupancies for **15a**.

	x	y	z	U(eq)	Occ.
Si	1981(1)	9034(1)	1936(1)	28(1)	1
C(1)	4273(1)	9484(2)	2520(1)	27(1)	1
C(2)	4837(1)	9026(2)	3284(1)	29(1)	1
C(3)	5507(2)	9549(2)	3864(1)	32(1)	1
C(4)	5789(2)	10709(2)	3843(1)	51(1)	1
C(5)	6125(2)	8964(2)	4574(1)	39(1)	1
C(6)	7405(2)	8874(2)	4661(1)	41(1)	1

C(7)	7595(2)	8443(2)	3953(1)	36(1)	1
C(8)	8322(2)	8777(2)	3605(1)	34(1)	1
C(9)	9217(2)	9617(2)	3909(1)	51(1)	1
C(10)	8271(2)	8358(2)	2835(1)	36(1)	1
C(11)	7820(2)	9206(2)	2225(1)	34(1)	1
C(12)	6722(2)	8916(2)	1585(1)	30(1)	1
C(13)	6927(2)	7924(2)	1158(1)	43(1)	1
C(14)	5792(1)	8694(1)	1956(1)	28(1)	1
O(15)	5678(1)	7814(1)	2196(1)	38(1)	1
C(16)	5067(1)	9603(1)	2038(1)	26(1)	1
C(17)	5074(2)	10496(2)	1645(1)	29(1)	1
C(18)	5738(2)	10602(2)	1119(1)	31(1)	1
O(19)	5482(1)	11522(1)	706(1)	42(1)	1
C(20)	6079(2)	11684(2)	164(1)	46(1)	1
C(21)	6476(2)	9859(2)	1069(1)	33(1)	1
O(22)	3350(1)	8811(1)	2122(1)	31(1)	1
C(23)	1526(2)	9052(2)	2816(1)	40(1)	1
C(24)	2007(2)	10015(2)	3324(1)	61(1)	1
C(25)	1805(2)	8012(2)	3252(1)	63(1)	1
C(26)	1633(2)	10364(2)	1451(1)	40(1)	1
C(27)	416(2)	10749(2)	1361(2)	63(1)	1
C(28)	1913(2)	10440(2)	703(1)	54(1)	1
C(29)	1358(2)	7828(2)	1365(1)	34(1)	1
C(30)	65(2)	7742(2)	1183(2)	55(1)	1
C(31)	1736(2)	7668(2)	658(1)	51(1)	1

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Bond lengths [A] and angles [deg] for **15a**.

Si-O(22)	1.6528(13)
Si-C(29)	1.885(2)
Si-C(23)	1.888(2)
Si-C(26)	1.892(2)
C(1)-O(22)	1.442(2)
C(1)-C(2)	1.507(2)
C(1)-C(16)	1.523(2)
C(2)-C(3)	1.329(3)
C(3)-C(4)	1.504(3)
C(3)-C(5)	1.514(2)
C(5)-C(6)	1.549(3)
C(6)-C(7)	1.511(3)
C(7)-C(8)	1.325(3)
C(8)-C(9)	1.516(3)
C(8)-C(10)	1.517(3)
C(10)-C(11)	1.540(3)
C(11)-C(12)	1.569(2)

C(12)-C(21)	1.502(3)
C(12)-C(14)	1.535(2)
C(12)-C(13)	1.541(3)
C(14)-O(15)	1.219(2)
C(14)-C(16)	1.490(3)
C(16)-C(17)	1.344(3)
C(17)-C(18)	1.461(2)
C(18)-C(21)	1.330(3)
C(18)-O(19)	1.375(2)
O(19)-C(20)	1.433(2)
C(23)-C(25)	1.526(3)
C(23)-C(24)	1.546(3)
C(26)-C(28)	1.538(3)
C(26)-C(27)	1.546(3)
C(29)-C(31)	1.538(3)
C(29)-C(30)	1.540(3)

O(22)-Si-C(29)	101.90(8)
O(22)-Si-C(23)	111.66(8)
C(29)-Si-C(23)	109.03(9)
O(22)-Si-C(26)	109.01(8)
C(29)-Si-C(26)	116.28(9)
C(23)-Si-C(26)	108.85(10)
O(22)-C(1)-C(2)	109.96(14)
O(22)-C(1)-C(16)	107.66(14)
C(2)-C(1)-C(16)	113.46(14)
C(3)-C(2)-C(1)	125.94(18)
C(2)-C(3)-C(4)	123.62(18)
C(2)-C(3)-C(5)	120.47(18)
C(4)-C(3)-C(5)	115.67(17)
C(3)-C(5)-C(6)	111.51(15)
C(7)-C(6)-C(5)	110.56(16)
C(8)-C(7)-C(6)	128.2(2)
C(7)-C(8)-C(9)	124.41(19)
C(7)-C(8)-C(10)	120.68(18)
C(9)-C(8)-C(10)	114.86(17)
C(8)-C(10)-C(11)	111.44(16)
C(10)-C(11)-C(12)	116.62(16)
C(21)-C(12)-C(14)	113.29(15)
C(21)-C(12)-C(13)	109.96(16)
C(14)-C(12)-C(13)	110.27(16)
C(21)-C(12)-C(11)	105.83(15)
C(14)-C(12)-C(11)	107.11(14)
C(13)-C(12)-C(11)	110.24(15)
O(15)-C(14)-C(16)	121.48(16)
O(15)-C(14)-C(12)	120.96(16)
C(16)-C(14)-C(12)	117.52(15)
C(17)-C(16)-C(14)	119.01(16)
C(17)-C(16)-C(1)	120.98(16)
C(14)-C(16)-C(1)	119.87(15)
C(16)-C(17)-C(18)	122.65(17)
C(21)-C(18)-O(19)	127.05(17)
C(21)-C(18)-C(17)	121.13(17)
O(19)-C(18)-C(17)	111.82(16)
C(18)-O(19)-C(20)	115.73(16)
C(18)-C(21)-C(12)	121.69(17)

C(1)-O(22)-Si	128.19(12)
C(25)-C(23)-C(24)	111.1(2)
C(25)-C(23)-Si	112.07(16)
C(24)-C(23)-Si	112.58(15)
C(28)-C(26)-C(27)	110.78(19)
C(28)-C(26)-Si	114.26(15)
C(27)-C(26)-Si	114.01(16)
C(31)-C(29)-C(30)	111.08(18)
C(31)-C(29)-Si	114.54(14)
C(30)-C(29)-Si	114.04(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **15a**.

	U11	U22	U33	U23	U13	U12
Si	20(1)	36(1)	25(1)	-1(1)	4(1)	-2(1)
C(1)	20(1)	31(1)	28(1)	-1(1)	6(1)	-2(1)
C(2)	26(1)	34(1)	28(1)	5(1)	10(1)	-1(1)
C(3)	29(1)	41(1)	27(1)	2(1)	10(1)	3(1)
C(4)	60(1)	38(1)	43(1)	-7(1)	-2(1)	0(1)
C(5)	36(1)	56(1)	26(1)	6(1)	9(1)	2(1)
C(6)	35(1)	58(1)	26(1)	10(1)	4(1)	2(1)
C(7)	31(1)	39(1)	32(1)	5(1)	3(1)	4(1)
C(8)	25(1)	41(1)	32(1)	2(1)	4(1)	5(1)
C(9)	40(1)	71(2)	42(1)	-12(1)	10(1)	-14(1)
C(10)	28(1)	40(1)	39(1)	-3(1)	8(1)	5(1)
C(11)	27(1)	42(1)	33(1)	-4(1)	9(1)	-4(1)
C(12)	27(1)	35(1)	28(1)	-7(1)	9(1)	1(1)
C(13)	40(1)	47(1)	42(1)	-15(1)	12(1)	6(1)
C(14)	25(1)	28(1)	27(1)	-6(1)	5(1)	-4(1)
O(15)	38(1)	27(1)	50(1)	-2(1)	14(1)	-2(1)
C(16)	21(1)	31(1)	24(1)	-2(1)	4(1)	-2(1)
C(17)	28(1)	32(1)	28(1)	1(1)	9(1)	1(1)
C(18)	30(1)	38(1)	26(1)	3(1)	8(1)	-4(1)
O(19)	45(1)	44(1)	40(1)	15(1)	20(1)	4(1)
C(20)	49(1)	55(1)	38(1)	13(1)	20(1)	-3(1)
C(21)	31(1)	44(1)	27(1)	-2(1)	13(1)	-2(1)
O(22)	21(1)	36(1)	34(1)	-1(1)	6(1)	-5(1)
C(23)	26(1)	61(1)	35(1)	-5(1)	11(1)	-3(1)
C(24)	45(1)	98(2)	43(1)	-28(1)	19(1)	-16(1)
C(25)	55(1)	99(2)	44(1)	22(1)	26(1)	6(1)
C(26)	36(1)	35(1)	40(1)	-2(1)	-2(1)	0(1)
C(27)	47(1)	49(2)	77(2)	1(1)	-5(1)	14(1)
C(28)	71(2)	44(1)	39(1)	10(1)	1(1)	-4(1)
C(29)	26(1)	39(1)	35(1)	-4(1)	6(1)	-3(1)
C(30)	29(1)	56(2)	72(2)	-19(1)	4(1)	-9(1)

C(31)	64(2)	47(1)	46(1)	-10(1)	20(1)	-4(1)

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

Table 5. Hydrogen coordinates (x 10^4), isotropic displacement parameters (A^2 x 10^3), and occupancies for **15a**.

	x	y	z	U(eq)	Occ.
H(1)	3971	10186	2583	32	1
H(2)	4694(17)	8256(19)	3306(11)	43(6)	1
H(4A)	6276	10922	4323	76	1
H(4B)	5106	11120	3725	76	1
H(4C)	6164	10826	3468	76	1
H(5A)	5808	8257	4563	47	1
H(5B)	6019	9337	5002	47	1
H(6A)	7754	9569	4770	49	1
H(6B)	7758	8406	5077	49	1
H(7)	7045(18)	7888(18)	3693(12)	43(6)	1
H(9A)	9640	9730	3560	77	1
H(9B)	9717	9383	4379	77	1
H(9C)	8861	10269	3980	77	1
H(10A)	7784	7739	2724	43	1
H(10B)	9021	8140	2831	43	1
H(11A)	8412	9367	1998	41	1
H(11B)	7674	9850	2467	41	1
H(13A)	7079	7324	1489	65	1
H(13B)	7562	8047	972	65	1
H(13C)	6268	7785	745	65	1
H(17)	4594(18)	11098(16)	1651(11)	40(6)	1
H(20A)	5847	12344	-91	69	1
H(20B)	5914	11111	-191	69	1
H(20C)	6876	11704	412	69	1
H(21)	6943(17)	9916(17)	768(11)	38(5)	1
H(23)	721(17)	9097(15)	2662(11)	34(5)	1
H(24A)	1817	10659	3038	91	1
H(24B)	2813	9953	3513	91	1
H(24C)	1689	10033	3734	91	1
H(25A)	1492	7428	2927	95	1
H(25B)	1487	8022	3663	95	1
H(25C)	2609	7932	3440	95	1
H(26)	2214(19)	10865(17)	1758(13)	48(6)	1
H(27A)	258	10695	1833	94	1

H(27B)	-108	10316	997	94	1
H(27C)	341	11476	1198	94	1
H(28A)	2671	10198	770	82	1
H(28B)	1844	11165	536	82	1
H(28C)	1397	10005	336	82	1
H(29)	1717(18)	7205(18)	1709(12)	45(6)	1
H(30A)	-148	7843	1632	82	1
H(30B)	-176	7052	979	82	1
H(30C)	-286	8278	824	82	1
H(31A)	2544	7718	787	77	1
H(31B)	1401	8205	297	77	1
H(31C)	1499	6979	450	77	1