Supplementary Material for
Progress Towards the Total Synthesis of Ingenol:
Construction of the Complete Carbocyclic Skeleton

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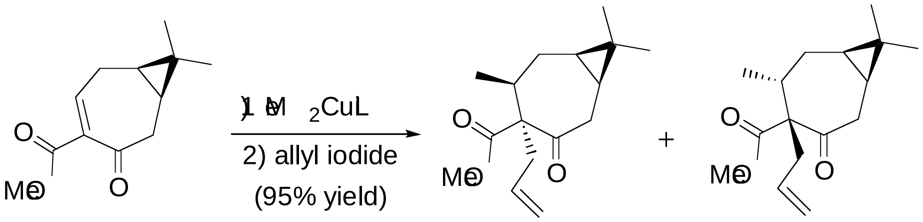
Materials and Methods

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 _ 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 3-component adducts 6a and 6b.



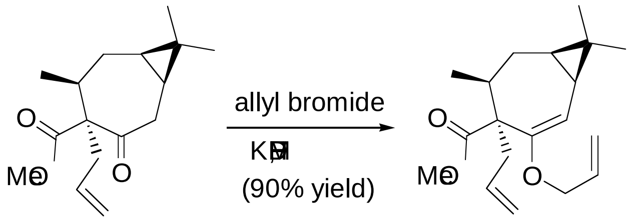
5 **6a** (1 : 1.2) **6b**

A solution of lithium dimethylcuprate in anhydrous ether (12 mL) was prepared from CuI (481 mg, 2.5 mmol, 2.0 equiv) and 1.4 M MeLi solution in ether (3.6 mL, 5.0 mmol, 4.0 equiv). After stirring at 0°C for 15 minutes, an ether (6 mL) solution of **5** (265 mg, 1.3 mmol, 1.0 equiv) was slowly added into the reaction flask. The mixture was allowed to stir at 0°C under N_2 for 40 minutes. A mixture of THF (4 mL) and HMPA (5 mL) was injected into the reaction solution, followed by rapid addition of allyl iodide (3 mL, large excess). The reaction was kept stirring at 0°C for one more hour. The reaction mixture was poured into 10% NH_4OH solution, and the product was extracted with ether. The extraction was washed with water and brine. After drying with $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by flash chromatography (40:1 Hexanes:EtOAc eluent).

First to elute was **6a** (285 mg, 43% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 6.35 (dddd, *J* = 17, 11, 9, 5.0 Hz, 1H), 5.17-5.24 (m, 2H), 3.32 (s, 3H), 3.26 (ddt, *J* = 14, 5, 2 Hz, 1H), 2.70 (dd, *J* = 12, 6 Hz, 1H), 2.65 (dd, *J* = 14, 9 Hz, 1H), 2.61 (t, *J* = 11.5 Hz, 1H), 2.12 (dt, *J* = 15.5, 11 Hz, 1H), 1.96 (ddtd 11, *J* = 7.5, 7, 1.5 Hz, 1H), 1.72 (ddd, *J* = 15, 6, 1.5 Hz, 1H), 1.32 (d, *J* = 7 Hz, 3H), 1.07 (s, 3H), 0.99 (s, 3H), 0.72 (ddd, *J* = 11, 9, 6 Hz, 1H), 0.57 (ddd, *J* = 11, 9, 6 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 204.6, 172.3, 136.4, 118.1, 67.2, 51.9, 39.3, 39.2, 38.8, 30.6, 28.7, 27.8, 22.8, 22.0, 18.8, 15.7; **IR** (thin film/NaCl) 3075 (w), 2979 (m), 2948 (m), 1743 (m), 1711 (s), 1637 (w), 1459 (m), 1434 (m), 1377 (w), 1278 (w), 1232 (m), 1212 (s), 1170 (w), 1133 (w), 1119 (w), 1004 (w), 915 (w), 753 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 264.1723 [calc'd for $C_{16}H_{24}O_3$ (M+): 264.1725].

Second to elute was **6b** (342 mg, 52% yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.64 (ddt, *J* = 17, 10, 7.5 Hz, 1H), 5.03 (m, 2H), 3.67 (s, 3H), 2.67 (dd, *J* = 15, 8 Hz, 2H), 2.56 (dd, *J* = 14, 7.5 Hz, 1H), 2.24 (dd, *J* = 15, 9 Hz, 1H), 2.04 (td, *J* = 7, 5 Hz, 1H), 1.82 (dt, *J* = 15, 6.5 Hz, 1H), 1.42 (ddd, *J* = 15, 8.5, 5 Hz, 1H), 1.16 (d, *J* = 7 Hz, 3H), 1.05 (s, 3H), 0.99 (s, 3H), 0.80 (td, *J* = 9, 6.5 Hz, 1H), 0.63 (q, *J* = 9 Hz, 1H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 208.0, 171.9, 133.0, 118.3, 65.6, 51.4, 39.7, 37.6, 36.4, 28.5, 28.4, 22.9, 20.5, 20.2, 16.8, 15.0; **IR** (thin film/NaCl) 3076 (w), 2947 (m), 1738 (s), 1703 (s), 1639 (w), 1457 (m), 1434 (m), 1379 (w), 1268 (w), 1210 (s), 1148 (w), 1130 (w), 1078 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 264.1725 [calc'd for $C_{16}H_{24}O_3$ (M+): 264.1725].

Preparation of enol ether 7.

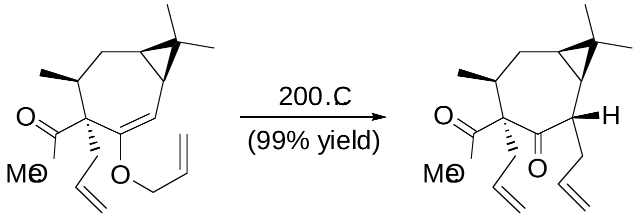


6a **7**

To a sealed 50 ml round bottom flask containing KH powder (23 mg, 0.57 mmol, 1.5 equiv) was added a solution of **6a** (102 mg, 0.38 mmol, 1.0 equiv) in DMF (10 mL). After stirring the mixture for 5 minutes, allyl bromide (100 *u*L, 1.0 mmol, 3.0 equiv) was injected into the reaction. The reaction was allowed to stir at room temperature for half an hour. Several drops of methanol were added into the reaction to quench excess KH. The crude product was diluted with ether and washed with NH_4Cl and brine. After drying with $MgSO_4$, the solvent was evaporated under reduced pressure. The yellow residue was purified by flash chromatography (50:1 Hexanes:EtOAc eluent). Enol ether **7** was collected as a light yellow oil (104 mg, 90% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 6.15 (dtd, *J* = 17, 9, 5 Hz, 1H), 5.82 (ddt, *J* = 17, 11, 4.5 Hz, 1H), 5.37 (dq, *J* = 17, 2 Hz, 1H), 5.29 (m, 1H), 5.26 (m, 1H), 5.13 (qd, *J* = 11, 2 Hz, 1H), 4.90 (d, *J* = 2.5 Hz, 1H), 4.06 (m, 2H), 3.51 (s, 3H), 2.92 (dd, *J* = 14, 9 Hz, 1H), 3.36 (dtd, *J* = 15, 3.5, 1.5

Hz, 1H), 2.40 (ddd, *J* = 14, 9, 7 Hz, 1H), 2.30 (dt, *J* = 14, 5 Hz, 1H), 1.55 (dd, *J* = 14, 7 Hz, 1H), 1.30 (s, 3H), 1.18 (s, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.96-1.08 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 174.3, 155.6, 136.2, 134.6, 118.0, 116.0, 101.4, 68.8, 62.1, 51.6, 39.7, 35.6, 31.2, 28.6, 28.4, 22.3, 20.7, 19.1, 16.6; **IR** (thin film/NaCl) 3075 (w), 2976 (m), 2947 (m), 1663 (w), 1646 (w), 1456 (w), 1433 (w), 1375 (w), 1295 (w), 1220 (s), 1185 (m), 1172 (m), 1138 (m), 1079 (w), 996 (w), 915 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 304.2037 [calc'd for $C_{19}H_{28}O_3$ (M+): 304.2038].

Preparation of diene 8 via Claisen rearrangement.



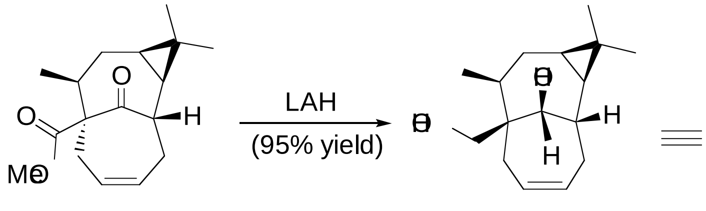
7 **8**

In a 2 dram Fisher brand vial, enol ether **7** (104 mg, 0.34 mmol, 1.0 equiv) was dissolved in xylene (2 mL). The vial was stoppered and sealed with Teflon tape and heated in a 200¡C sand bath for 1 hour. The vial was removed from the sand bath and allowed to cool to room temperature. The yellow solution was purified by flash chromatography (40:1 Hexanes:EtOAc eluent). Diene **8** was collected as a light yellow oil (103 mg, 99% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 6.41 (dddd, *J* = 17, 10.5, 9, 5.5 Hz, 1H), 5.89 (dddd, *J* = 17, 12.5, 7.5, 7.0 Hz, 1H), 5.04-5.24 (m, 4H), 3.35 (s, 3H), 3.23 (ddt, *J* = 14, 5.5, 1.5 Hz, 1H), 2.83 (dt, *J* = 13, 7 Hz, 1H), 2.65 (dd, *J* = 14, 9 Hz, 1H), 2.59 (dt, *J* = 10.5, 7 Hz, 1H), 2.48-2.54 (m, 1H), 2.15 (dt, *J* = 15.5, 11.5 Hz, 1H), 1.94 (dtd, *J* = 15, 7, 1.5 Hz, 1H), 1.75 (ddd, *J* = 15, 5.5, 1.5 Hz, 1H), 1.39 (d, *J* = 7 Hz, 3H), 1.08 (s, 3H), 1.01 (s, 3H), 0.56 (ddd, *J* = 12, 9, 6 Hz, 1H), 0.39 (dd, *J* = 10, 9 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 206.0, 172.1, 137.4, 136.5, 118.1, 116.5, 66.9, 51.7, 48.4, 39.7, 39.4, 36.9, 30.7, 29.3, 29.0, 27.5, 22.0, 18.7, 16.0; **IR** (thin film/NaCl) 3075 (w), 2978 (m), 2948 (m), 1744 (w), 1910 (s), 1639 (w), 1457 (w), 1434 (w), 1376 (w), 1216 (s), 1211 (w), 1029 (w), 913 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 304.2045 [calc'd for $C_{19}H_{28}O_3$(M+): 304.2038].

Preparation of RCM product 9.

To a solution of diene **8** (136 mg, 0.45 mmol, 1.0 equiv) in CH_2Cl_2 (60 mL) was added Grubbs s catalyst (**4**) (37 mg, 0.05 mmol, 10 mol%). The reaction was heated to reflux for 24 hours. The crude solution was concentrated, and the residue was purified by flash chromatography (20:1 Hexanes:EtOAc eluent). The RCM product **9** was collected as a light pink oil (105 mg, 85% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 5.80-5.91 (m, 2H), 2.58 (s, 3H), 3.21 (m, 1H), 3.13 (dd, *J* = 15.5, 7 Hz, 1H), 2.55 (dd, *J* = 16, 5.5 Hz, 1H), 2.39 (dqd, *J* = 17, 7, 2.5 Hz, 1H), 2.21-2.27 (m, 1H), 2.18 (dt, *J* = 16, 6 Hz, 1H), 1.78 (dt, *J* = 15.5, 10.5 Hz, 1H), 1.71 (ddd, *J* = 15.5, 7.5, 2 Hz, 1H), 1.07 (s, 3H), 1.06 (s, 3H), 1.01 (s, 3H), 0.58 (ddd, *J* = 11, 9, 7.5 Hz, 1H), 0.40 (dd, *J* = 9, 1.5 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 211.1, 173.2, 131.5, 130.0, 71.7, 54.4, 51.9, 37.2, 34.2, 33.5, 30.8, 29.9, 29.2, 27.2, 21.3, 18.3, 16.3; **IR** (thin film/NaCl) 3026 (w), 2949 (m), 1739 (s), 1682 (s), 1455 (m), 1376 (w), 1237 (m), 1181 (m), 1147 (w), 1046 (w), 998 (w), 808 (w), 779 (w), 686 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 276.1722 [calc'd for $C_{17}H_{24}O_3$ (M+): 276.1725].

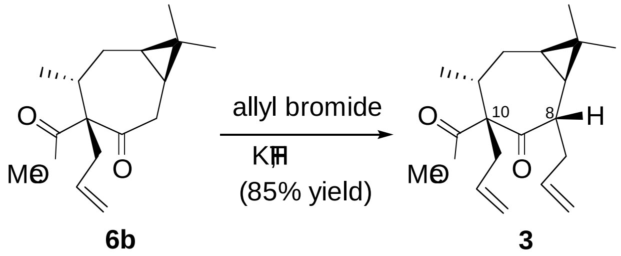
Preparation of diol 10.



9 **10**

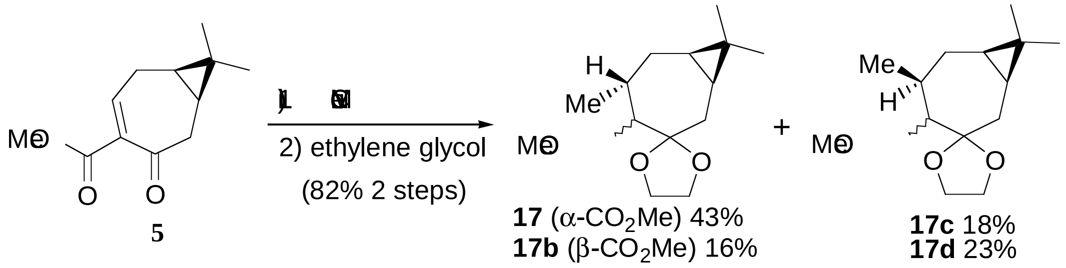
To a solution of **9** (60 mg, 0.22 mmol, 1.0 equiv) in ether (10 mL) was added lithium aluminum hydride (12 mg, 0.44 mmol, 2.0 equiv). The mixture was allowed to stir at room temperature for 1 hour. Saturated Na_2SO_4 aqueous solution (0.5 mL) was carefully added into the solution to quench excess LAH. The mixture was kept stirring until the precipitates turned white. After adding $MgSO_4$ to dry the solution, the product was filtered. The solvent was removed under reduced pressure. Diol **10** was collected as colorless crystals (50 mg, 95% yield): m.p. 146.5-148.7¡C; **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 5.53 (m, 2H), 4.04 (s, 1H), 3.64 (d, *J* = 4.0 Hz, 2H), 3.14-3.20 (m, 1H), 2.74 (s broad, 1H), 2.47-2.54 (m, 1H), 2.29 (s broad, 1H), 2.24-2.28 (m, 1H), 2.15 (m, 1H), 2.01 (dt, *J* = 14, 12 Hz, 1H), 1.74 (ddd, *J* = 14, 6, 4.5 Hz, 1H), 1.66 (m, 1H), 1.60 (dd, *J* = 16, 8 Hz, 1H), 1.12 (d, *J* = 7 Hz, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 0.85 (ddd, *J* = 12, 9, 6 Hz, 1H), 0.55 (dd, *J* = 9.5, 4 Hz, 1H); **^{13}C NMR** (400 MHz, CD_2Cl_2) δ 129.2, 125.3, 80.0, 71.5, 48.4, 41.0, 40.6, 39.0, 34.6, 31.0, 30.7, 28.9, 27.5, 20.8, 19.9, 15.9; **IR** (thin film/NaCl) 3428 (m), 3329 (s broad), 3011 (w), 2984 (m), 2949 (m), 2891 (s), 2860 (s), 1478 (w), 1452 (w), 1441 (w), 1373 (w), 1090 (w), 1048 (s), 1015 (m), 895 (w), 846 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 250.1934 [calc'd for $C_{16}H_{26}O_2$(M+): 250.1933].

Preparation of diene 3.



To a solution of **6b** (125 mg, 0.47 mmol, 1.0 equiv) in dry THF (25 mL) was added KH powder (55 mg, 1.4 mmol, 3.0 equiv). The flask was then sealed under N_2. Allyl bromide (150 *u*L, 1.5 mmol, 3.0 equiv) was injected into the solution. The reaction was allowed to reflux vigorously for 12 hours. The solution was cooled to room temperature, and carefully quenched with methanol (0.5 mL). The crude product was diluted with ether and washed with saturated NH_4Cl and brine. After drying with $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by flash chromatography (40:1 Hexanes:EtOAc eluent). Diene **3** was collected as a light yellow oil (121 mg, 85% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 5.90 (dddd, *J* = 17, 10, 7.5, 7 Hz, 1H), 5.81 (ddt, *J* = 17, 10, 7.5 Hz, 1H), 5.07-5.21 (m, 4H), 3.52 (s, 3H), 2.89 (ddt, *J* = 14, 7.5, 1.5 Hz, 1H), 2.80 (ddt, *J* = 14, 8, 1.5 Hz, 1H), 2.69-2.76 (m, 1H), 2.57 (m, 1H), 2.43 (ddd, *J* = 10, 9, 5.5 Hz, 1H), 2.25 (m, 1H), 1.94 (ddd, *J* = 17, 10, 8 Hz, 1H), 1.60 (ddd, *J* = 17, 5.5, 4 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.03 (s, 3H), 0.95 (s, 3H), 0.78 (ddd, *J* = 9.5, 8.5, 5.5 Hz, 1H), 0.36 (t, *J* = 9.5 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 206.9, 172.2, 137.2, 133.5, 119.5, 117.0, 67.7, 51.9, 45.9, 40.3, 36.5, 35.0, 29.3, 29.1, 28.9, 23.6, 20.0, 17.2, 16.2; **IR** (thin film/NaCl) 3077 (w), 2978 (m), 2948 (m), 2865 (m), 1735 (s), 1705 (s), 1640 (w), 1435 (m), 1379 (w), 1262 (m), 1213 (s), 1155 (w), 995 (m), 915 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 304.2044 [calc'd for $C_{19}H_{28}O_3$ (M+): 304.2038].

Preparation of ketal 17.



In a flame-dried 100 mL round bottom flask, CuCN (600 mg, 6.6 mmol, 1.4 equiv) was stirred with anhydrous ether (30 mL). The solution was chilled to —78¡C before adding MeLi (1.4 M, 4.7 mL, 6.6 mmol, 1.4 equiv). After the mixture was stirred for 30 minutes, a solution of **5** (998 mg, 4.7 mmol, 1.0 equiv) in ether (30 mL) was slowly added to the cuprate solution. The reaction was allowed to stir at —78¡C for 2 hours. After the reaction was warmed to room temperature, it was diluted with ether and washed with 10% NH_4OH solution, water and brine. After drying with $MgSO_4$, The solvent was evaporated under reduced pressure. The crude product was then dissolved in benzene (50 mL), followed by addition of ethylene glycol (1.3 ml, 23.5 mmol, 5.0 equiv) and catalytic PTSA (5 mg). The mixture was heated under Dean-Stark conditions for 12 hours. The crude solution was then washed with saturated $NaHCO_3$ solution and brine. After drying with $MgSO_4$, the solvent was removed. The residue was purified by flash chromatography (15:1:1 Hexanes:EtOAc:CH_2Cl_2 eluent).

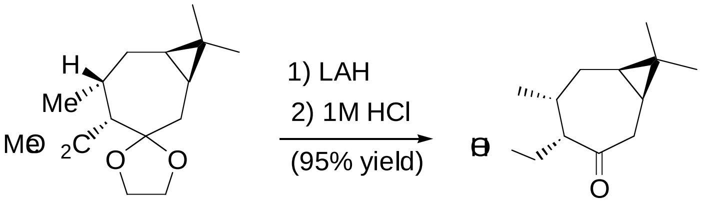
First to elute was **17c** (186 mg, 15% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 3.58-3.74 (m, 4H), 3.50 (s, 3H), 3.11 (s, 1H), 2.94 (dd, *J* = 14, 12 Hz, 1H), 2.48 (m, 1H), 2.35 (td, *J* = 11, 7.5 Hz, 1H), 2.12 (ddd, *J* = 15, 6, 2 Hz, 1H), 1.61 (dd, *J* = 15, 6 Hz, 1H), 1.41 (s, 3H), 1.19 (s, 3H), 1.08 (d, *J* = 7 Hz, 3H), 0.99 (m, 1H), 0.85 (ddd, *J* = 10.5, 9, 6.5 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 172.7, 111.5, 65.1, 64.7, 59.6, 51.2, 33.4, 31.2, 29.3, 28.1, 28.0, 22.5, 22.1, 20.8, 16.3; **IR** (thin film/NaCl) 2953 (m), 2932 (m), 2874 (m), 1732 (s), 1461 (w), 1368 (w), 1333 (w), 1308 (w), 1214 (m), 1148 (m), 1096 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 268.1672 [calc'd for $C_{15}H_{24}O_4$ (M+): 268.1675].

Ketal **17b** was eluted the second to deliver a colorless oil (165 mg, 13% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 3.54-3.70 (m, 4H), 3.52 (s, 3H), 3.12 (dd, *J* = 3, 1.5 Hz, 1H), 2.82 (dd, *J* = 15, 11 Hz, 1H), 2.22-2.32 (m, 2H), 2.13 (ddd, *J* = 15, 6.5, 2 Hz, 1H), 1.78 (dt, *J* = 15, 6 Hz, 1H), 1.45 (d, *J* = 7 Hz, 3H), 1.35 (s, 3H), 1.17 (s, 3H), 0.88 (ddd, *J* = 10.5, 9, 6.5 Hz, 1H), 0.83 (ddt, *J* = 9.5, 5.5, 5.5 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 174.0, 112.7, 65.2, 64.5, 58.5, 51.6, 33.8, 32.4, 29.6, 26.3, 24.1, 21.6, 21.0, 20.0, 16.3; **IR** (thin film/NaCl) 2986 (m), 2951 (m), 2930 (m), 2875 (m), 1736 (s), 1459 (w), 1434 (w), 1378 (w), 1331 (w), 1306 (m), 1194 (m), 1173 (m), 1153 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 268.1675 [calc'd for $C_{15}H_{24}O_4$(M+): 268.1675].

Ketal **17** was eluted the third to furnish a white solid (444 mg, 35% yield): m.p. 92.6-94.7¡C; **^{1}H NMR** (500 MHz, C_6D_6) δ 4.31 (q, *J* = 7.0 Hz, 1H), 3.86 (td, *J* = 7, 5 Hz, 1H), 3.77 (td, *J* = 7, 5 Hz, 1H), 3.59 (q, *J* = 7 Hz, 1H), 3.54 (s, 3H), 3.05 (d, *J* = 3.5 Hz, 1H), 2.40 (m, 1H), 2.06 (ddd, *J* = 14, 4, 2.5 Hz, 1H), 1.91 (dt, *J* = 14.5, 6 Hz, 1H), 1.63 (d, *J* = 7 Hz, 3H), 1.35-1.42 (m, 1H), 1.18-1.26 (m, 1H), 1.14 (s, 3H), 1.02 (s, 3H), 0.79-0.89 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 172.2, 112.8, 66.9, 64.3, 60.6, 51.1, 36.4, 34.1, 31.4, 29.6, 24.3, 21.8, 20.1, 16.0, 15.2; **IR** (thin film/NaCl) 2952 (s), 2932 (s), 2875 (s), 1739 (s), 1455 (m), 1434 (m), 1379 (m), 1352 (w), 1310 (w), 1271 (w), 1195 (m), 1179 (m), 1131 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 268.1675 [calc'd for $C_{15}H_{24}O_4$ (M+): 268.1675].

The last to elute was **17d** (237 mg, 19% yield), which furnished a white solid: m.p. 53.2-54.0¡C; **^{1}H NMR** (500 MHz, C_6D_6) δ 4.02 (m, 1H), 3.72 (m, 2H), 3.57-3.62 (m, 1H), 3.58 (s, 3H), 2.58-2.69 (m, 2H), 2.09 (dd, *J* = 14, 6 Hz, 1H), 1.73 (dd, *J* = 15, 6 Hz, 1H), 1.46 (dd, *J* = 14.5 Hz, 1H), 1.13 (s, 3H), 1.04 (d, *J* = 7 Hz, 3H), 1.02 (s, 3H), 0.97 (m, 1H), 0.89 (ddd, *J* = 11, 9, 6.5 Hz, 1H), 0.81 (ddd, *J* = 11, 9, 6.5 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 173.0, 111.7, 66.2, 65.1, 64.8, 51.3, 35.9, 34.5, 33.4, 29.5, 27.5, 22.72, 22.68, 20.2, 16.1; **IR** (thin film/NaCl) 2953 (m), 1740 (s), 1460 (w), 1434 (w), 1353 (w), 1271 (w), 1208 (w), 1168 (w), 1140 (m), 1044 (m), 984 (w), 948 (w), 801 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 268.1674 [calc'd for $C_{15}H_{24}O_4$(M+): 268.1675].

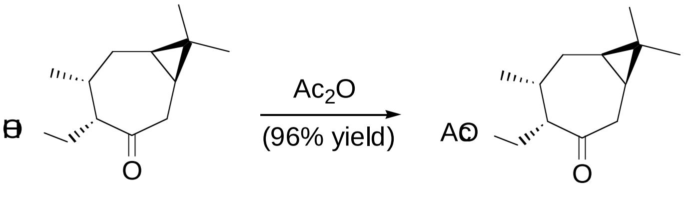
Preparation of alcohol 18.



17 **18**

To a solution of **17** (1.2 g, 4.5 mmol, 1.0 equiv) in anhydrous ether (100 mL) was added lithium aluminum hydride (342 mg, 9.0 mmol, 2.0 equiv). The mixture was allowed to stir under N_2 for two hours. Saturated Na_2SO_4 solution was carefully added into the solution to quench excess LAH. The mixture was kept stirring until the precipitates turned white. After adding $MgSO_4$ to dry the solution, the product was filtered. The solvent was removed under reduced pressure. The crude oil was dissolved in acetone (20 mL), followed by addition of 1 M HCl (1.0 mL). The solution was allowed to stir at room temperature for 30 minutes. Saturated sodium bicarbonate solution (5 mL) was added to neutralize the acid. Organic solvent was removed under reduced pressure. The aqueous phase was extracted with ether, and the extraction was washed with brine. After drying with $MgSO_4$, the solution was concentrated under reduced pressure. The crude product was purified by flash chromatography (3:1 Hexane:EtOAc eluent). Alcohol **18** was collected as a colorless oil (0.84 g, 95% 2 steps): **^{1}H NMR** (500 MHz, C_6D_6) δ 4.23 (t, J = 10 Hz, 1H), 3.58 (m, 1H), 2.55 (dd, J = 11.5, 6.5 Hz, 1H), 2.48 (dt, J = 8, 4.5 Hz, 1H), 2.19 (s broad, 1H), 2.00 (m, 1H), 1.83 (m, 2H), 1.13 (ddd, J = 15, 11, 1.5 Hz, 1H), 1.00 (s, 3H), 0.94 (s, 3H), 0.88 (d, J = 7.0 Hz, 3H), 0.51-0.61 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 209.6, 62.54, 62.50, 41.2, 32.9, 30.9, 29.1, 24.2, 21.2, 20.8, 15.6, 14.0; **IR** (thin film/NaCl) 3430 (m broad), 2935 (s), 2877 (s), 1698 (s), 1455 (m), 1382 (m), 1289 (w), 1202 (w), 1155 (w), 1117 (w), 1025 (m), 984 (w), 940 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 196.1457 [calc'd for $C_{12}H_{20}O_2$ (M+): 196.1463].

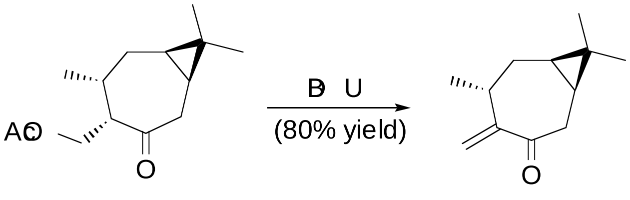
Preparation of acetal 19.



18 **19**

To a solution of alcohol **18** (450 mg, 2.3 mmol, 1.0 equiv) in pyridine (10 mL) was sequentially added acetic anhydride (1.1 mL, 12 mmol, 5.0 equiv) and catalytic DMAP (2 mg). The mixture was allowed to stir at room temperature for half an hour. Pyridine was removed from the reaction under reduced pressure. The yellow colored residue was purified by flash chromatography (20:1 Hexanes:EtOAc eluent). A colorless oil **19** was collected (526 mg, 96% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 4.82 (dd, *J* = 11, 8 Hz, 1H), 4.29 (dd, *J* = 11, 6 Hz, 1H), 2.62 (ddd, *J* = 7.5, 6, 4.5 Hz, 1H), 2.51 (m, 1H), 2.05 (m, 1H), 1.83 (s, 3H), 1.80 (m, 2H), 1.10 (ddd, *J* = 15, 11, 1.5 Hz, 1H), 0.99 (s, 3H), 0.92 (s, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.54 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 206.1, 170.7, 63.9, 58.6, 40.8, 32.8, 30.6, 29.1, 24.0, 21.2, 21.1, 21.0, 15.6, 13.4; **IR** (thin film/NaCl) 2937 (m), 1742 (s), 1703 (s), 1456 (m), 1368 (m), 1240 (s), 1203 (m), 1152 (w), 1031 (m), 983 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 238.1563 [calc'd for $C_{14}H_{22}O_3$ (M+): 238.1569].

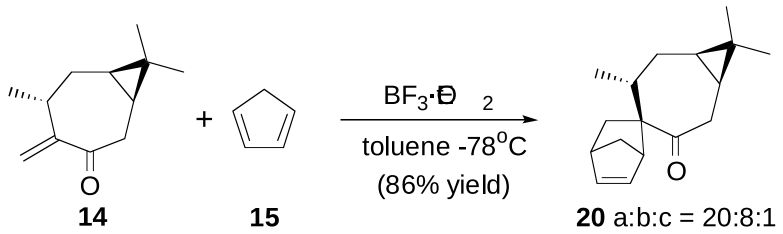
Preparation of *exo*-olefin 14.



19 **14**

To a solution of **19** (500 mg, 2.1 mmol 1.0 equiv) in benzene (150 mL), was added DBU (947 *u*L, 6.3 mmol, 3.0 equiv). The mixture was heated to reflux for 10 hours. After cooling to room temperature, the crude product was washed with saturated NH_4Cl solution, brine, and then dried over anhydrous $MgSO_4$. Concentration under reduced pressure afforded a yellow oil, which was purified by flash chromatography (60:1 Hexanes:Et_2O eluent). A colorless oil was collected as *exo*-olefin **14** (332 mg, 88% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 6.07 (dd, *J* = 2.0, 0.5 Hz, 1H), 5.06 (dd, *J* = 2.0, 1.0 Hz, 1H), 2.69 (dd, *J* = 13, 7.0 Hz, 1H), 2.33 (h, *J* = 7.0 Hz, 1H), 2.18 (dd, *J* = 13, 11 Hz, 1H), 1.63 (m, 2H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.97 (s, 3H), 0.86 (s, 3H), 0.66 (ddd, *J* = 11, 9.0, 7.0 Hz, 1H), 0.57 (td, *J* = 9.0, 7.0 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 201.8, 155.0, 118.3, 38.3, 36.3, 32.5, 31.0, 29.0, 22.7, 20.5, 19.3, 15.3; **IR** (thin film/NaCl) 2959 (s), 1697 (s), 1608 (m), 1457 (m), 1377 (w), 1266 (m), 1138 (w), 940 (w), 770 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 178.1359 [calc'd for $C_{17}H_{24}O$ (M+): 178.1358].

Preparation of Diels-Alder product 20a.



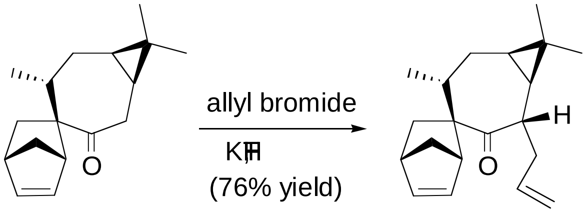
In a flame-dried 100 mL round bottom flask, *exo*-olefin **14** (400 mg, 2.25 mmol, 1.0 equiv) was dissolved in toluene (25 mL). After the solution was chilled to —78¡C in a dry ice bath, boron trifluoride diethyl etherate (556 *u*L, 4.50 mmol, 2.0 equiv) was added into the flask. The mixture was allowed to stir at —78¡C for 15 minutes before adding newly cracked cyclopentadiene monomer (**15**) (1.85 mL, 22.5 mmol, 10 equiv). The reaction mixture was allowed to stir at -78¡C under N_2 for one hour. Water (2 mL) was injected into the flask to quench the reaction. The reaction was allowed to warm to room temperature slowly. The reaction mixture was diluted with ether, and the crude product was washed with 1 M NaOH, water and brine. After drying with $MgSO_4$, the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (150:1 hexanes: Et_2O eluent).

First to elute was product **20b** to furnish a light yellow solid (130 mg, 24% yield): m.p. 63.5-66.2¡C; **^{1}H NMR** (500 MHz, C_6D_6) δ 6.22 (dd, *J* = 5.8, 3.0 Hz, 1H), 5.97 (dd, *J* = 5.0, 3.0 Hz, 1H), 3.18 (dd, *J* = 12, 4 Hz, 1H), 2.94 (d, *J* = 1.5 Hz, 1H), 2.72 (s, 1H), 2.62 (dd, *J* = 12, 7.0 Hz, 1H), 2.48 (dd, *J* = 7.0, 5.0 Hz, 1H), 1.79 (dt, *J* = 15, 6.0 Hz, 1H), 1.55 (m, 1H), 1.46 (m, 2H), 1.20 (d, *J* = 8.0 Hz, 1H), 1.08 (s, 3H), 1.06 (s, 3H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.77 (dd, *J* = 12, 2.5 Hz, 1H), 0.70 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 208.9, 141.3, 133.4, 67.9, 50.1, 48.4, 42.8, 40.4, 36.7, 33.5, 29.2, 27.1, 24.9, 21.9, 21.2, 16.2, 15.9; **IR** (thin film/NaCl) 3058 (w), 2944 (s), 2875 (m), 1693 (s), 1457 (m), 1380 (m), 1301 (w), 1240 (w), 1206 (w), 1191 (w), 1148 (w), 982 (w), 778 (w), 721 (m), 644 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 244.1826 [calc'd for $C_{17}H_{24}O$ (M+): 244.1827].

Product **20c** was eluted the second to furnish a colorless oil (16 mg, 3.0% yield): **^{1}H NMR** (500 MHz, C_6D_6) δ 6.70 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.10 (dd, *J* = 5.5, 3.0 Hz, 1H), 3.40 (q, *J* = 1.5 Hz, 1H), 2.70 (s, 1H), 2.35 (dd, *J* = 11.8, 6.8 Hz, 1H), 2.10 (t, *J* = 11 Hz, 1H), 1.80 (m, 2H), 1.50 (m, 3H), 1.40 (m, 1H), 1.32 (d, *J* = 12 Hz, 1H), 1.12 (d, *J* = 6.5 Hz, 3H), 1.04 (s, 3H), 1.02 (s, 3H), 0.75 (ddd, *J* = 11, 10.5, 6.5 Hz, 1H), 0.66 (m, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 209.2, 140.8, 136.4, 68.3, 46.9, 46.3, 42.8, 41.6, 38.6, 37.7, 29.2, 28.0, 23.6, 22.5, 21.8, 15.8, 14.9; **IR** (thin film/NaCl) 3058 (w), 2959 (s), 2875 (s), 1694 (s), 1455 (m), 1379 (w), 1332 (w), 1253 (w), 1148 (w), 781 (w), 717 (m), 646 (m), 589 (m) cm^{-1}; **HRMS** (EI) *m/z* found: 244.1825 [calc'd for $C_{17}H_{24}O$ (M+): 244.1827].

Third to elute was product **20a** (326 mg, 59% yield): m.p. 62.1-64.2¡C; **^{1}H NMR** (500 MHz, C_6D_6) δ 6.19 (dd, *J* = 5.5, 3.0 Hz, 1H), 5.93 (dd, *J* = 5.5, 3.0 Hz, 1H), 2.82 (s, 1H), 2.72 (s, 1H), 2.66 (dd, *J* = 12, 3.0 Hz, 1H), 2.49 (dd, *J* = 12, 7.0 Hz, 1H), 2.18 (t, *J* = 11 Hz, 1H), 1.80 (m, 1H), 1.76 (m, 2H), 1.59 (dd, *J* = 14, 11 Hz, 1H), 1.48 (m, 1H), 1.44 (d, *J* = 8.5 Hz, 1H), 1.36 (dd, *J* = 12, 4.0 Hz, 1H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.08 (s, 3H), 1.06 (s, 3H), 0.70 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 206.8, 140.5, 133.9, 67.2, 48.9, 48.2, 43.8, 40.4, 38.1, 35.9, 29.2, 27.4, 24.2, 21.59, 21.56, 16.5, 16.1; **IR** (thin film/NaCl) 3056 (w), 2971 (s), 2877 (m), 1700 (s), 1457 (w), 1380 (w), 1336 (w), 1277 (w), 779 (w), 710 (m), 647 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 244.1827 [calc'd for $C_{17}H_{24}O$ (M+): 244.1827].

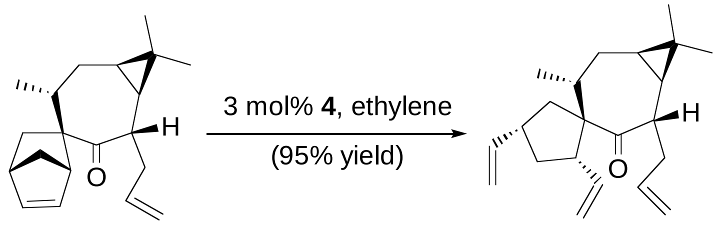
Preparation of 13.



20a **13**

To a 25ml round bottom flask containing a solution of **20a** (25 mg, 0.10 mmol, 1.0 equiv) in THF (10 mL) was sequentially added KH powder (20 mg, 0.50 mmol, 5.0 equiv) and allyl bromide (100 *u*L, 1.0 mmol, 10 equiv). The reaction was allowed to reflux vigorously for 12 hours. After the solution was cooled to room temperature, methanol (0.5 mL) was carefully added to quench excess KH. The crude product was diluted with ether. The solution was then washed with saturated NH_4Cl and brine. After drying with $MgSO_4$, the crude product was concentrated. The residue was purified by flash chromatography. Compound **13** was collected as a white solid (22 mg, 76% yield): m.p. 61.2-62.9¡C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.15 (dd, *J* = 6, 3 Hz, 1H), 5.94 (dd, *J* = 6, 3 Hz, 1H), 5.75 (ddt, *J* = 17, 10, 7.5 Hz, 1H), 5.00-5.09 (m, 2H), 2.99 (s, 1H), 2.78 (s, 1H), 2.37 (m, 1H), 2.26 (td, *J* = 10, 4 Hz, 1H), 2.18 (m, 2H), 1.90 (m, 2H), 1.63 (m, 1H), 1.57 (d, *J* = 8.5 Hz, 1H), 1.42-1.46 (m, 1H), 1.40 (dd, *J* = 12, 4 Hz, 1H), 1.060 (s, 3H), 1.058 (s, 3H), 0.94 (d, *J* = 7 Hz, 3H), 0.70 (ddd, *J* = 11, 9, 6 Hz, 1H), 0.15 (t, *J* = 9 Hz, 1H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 210.2, 139.9, 136.7, 133.1, 115.9, 66.4, 47.9, 47.4, 46.6, 42.8, 40.1, 36.1, 35.6, 28.8, 27.1, 26.7, 23.3, 21.0, 16.0, 15.6; **IR** (thin film/NaCl) 3063 (w), 2975 (s), 2878 (m), 1699 (s), 1640 (w), 1445 (w), 1381 (w), 1261 (w), 1088 (w), 994 (w), 909 (m), 864 (w), 712 (m), 680 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 284.2140 [calc'd for $C_{20}H_{28}O$ (M+): 284.2140].

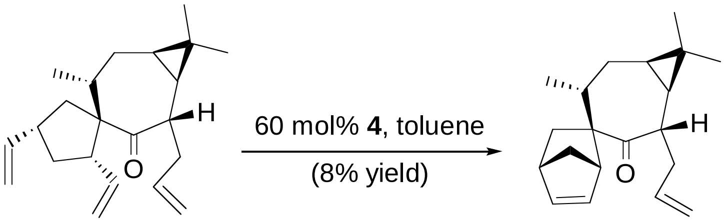
Preparation of triene 12 via ROM.



13 **12**

To a solution of **13** (56 mg, 0.20 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was added catalyst **4** (5.0 mg, 0.006 mmol, 3 mol%). The reaction was allowed to stir under ethylene gas for 6 hours. Concentration under reduced pressure with concomitant adsorption onto silica gel was followed by flash chromatography (40:1 Hexanes:Et_2O eluent). A light pink oil was collected as triene **12** (59 mg, 95% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 17, 10, 7.5 Hz, 1H), 5.69 (ddt, *J* = 17, 10, 7 Hz, 1H), 5.59 (dt, *J* = 17, 10 Hz, 1H), 4.94-5.03 (m, 5H), 4.90 (dt, *J* = 10, 1.5 Hz, 1H), 2.75 (m, 1H), 2.54 (m, 1H), 2.20-2.37 (m, 3H), 2.16 (t, *J* = 9 Hz, 1H), 2.01 (dd, *J* = 14, 7 Hz, 1H), 1.95 (ddd, *J* = 14, 7, 2 Hz, 1H), 1.83 (m, 2H), 1.63 (ddd, *J* = 15, 10, 2 Hz, 1H), 1.36 (ddd, *J* = 13, 8, 4 Hz, 1H), 1.03 (s, 3H), 1.00 (s, 3H), 0.94 (d, *J* = 7 Hz, 3H), 0.69 (td, *J* = 9, 7 Hz, 1H), 0.15 (t, *J* = 9.5 Hz, 1H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 212.1, 143.2, 140.9, 136.7, 115.6, 115.1, 112.7, 68.1, 50.1, 47.1, 39.8, 38.0, 35.9, 35.6, 34.9, 28.7, 27.4, 27.0, 22.7, 20.8, 15.9, 14.8; **IR** (thin film/NaCl) 3075 (m), 2977 (s), 2954 (s), 2864 (m), 1694 (s), 1640 (w), 1453 (m), 1419 (w), 1378 (w), 1264 (w), 1164 (w), 996 (m), 909 (s) cm^{-1}; **HRMS** (EI) *m/z* found: 312.2444 [calc'd for $C_{22}H_{32}O$ (M+): 312.2453].

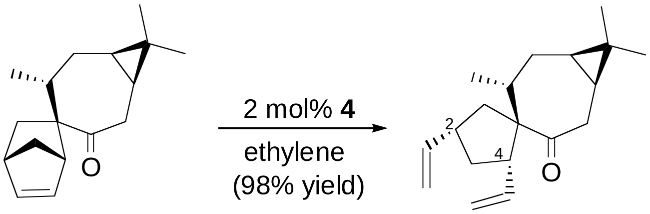
Reversion to 13 via RCM.



12 **13**

A solution of **12** (40 mg, 0.06 mmol, 1.0 equiv) in toluene (40 mL) was heated to reflux for 3 hours. During this time, three portions of catalyst **4** (20 mg, 0.0024 mmol, 20 mol%) was added to the reaction every 60 minutes. Toluene was removed under reduced pressure. The crude product was purified by flash chromatography (30:1 Hexanes:Et_2O eluent). A light pink solid was collected as compound **22** (2.6 mg, 8% yield). (Experimental data identical to the alkylation product)

Preparation of diene 22.

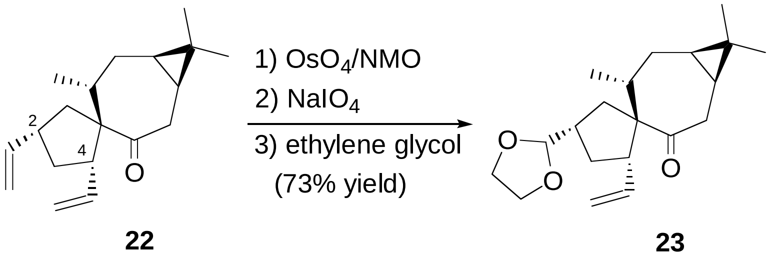


20a **22**

To a solution of **20a** (250 mg, 1.0 mmol, 1.0 equiv) in dichloromethane (150 mL) was added **4** (16 mg, 0.020 mmol, 2.0 mol%). The solution was allowed to stir at room temperature under ethylene gas for 12 hours. Concentration under reduced pressure with concomitant adsorption onto silica gel was followed by flash chromatography (40:1 Hexanes:Et_2O eluent). Diene **22** was collected to furnish a white solid (266 mg, 98% yield): m.p.64.5-65.5¡C; **^{1}H NMR** (500 MHz, C_6D_6) δ 5.94 (ddd, *J* = 17, 10, 7.5 Hz, 1H), 5.69 (dt, *J* = 17, 10 Hz, 1H), 5.16 (ddd, *J* = 17, 2, 1

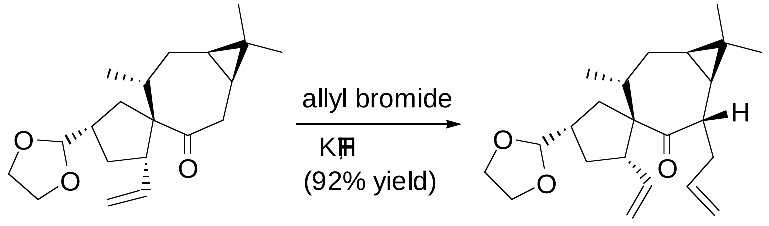
Hz, 1H), 5.06 (ddd, *J* = 10, 2, 1 Hz, 1H), 4.96 (ddd, *J* = 17, 2, 0.5 Hz, 1H), 4.91 (dd, *J* = 10, 2 Hz, 1H), 2.48-2.61 (m, 3H), 2.32 (dd, *J* = 12, 11 Hz, 1H), 2.20-2.27 (m, 2H), 2.16 (ddd, *J* = 13, 9, 8 Hz, 1H), 1.69-1.81 (m, 2H), 1.59 (ddd, *J* = 14.5, 9.5, 1.5 Hz, 1H), 1.50 (ddd, *J* = 14, 7.5, 4 Hz, 1H), 1.07 (s, 3H), 1.03 (s, 3H), 0.96 (d, *J* = 7 Hz, 3H), 0.70 (ddd, *J* = 10.5, 9, 6.5 Hz, 1H), 0.65 (td, *J* = 9, 6 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 209.1, 144.2, 141.9, 115.4, 113.5, 69.2, 50.9, 40.9, 39.6, 38.8, 36.9, 35.5, 29.1, 27.3, 23.5, 21.7, 21.4, 15.8, 15.5; **IR** (thin film/NaCl) 3076 (w), 2975 (m), 2944 (m), 1696 (s), 1639 (w), 1457 (w), 1420 (w), 1378 (w), 1297 (w), 1272 (w), 1203 (w), 996 (m), 911 (m), 643 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 272.2140 [calc'd for $C_{19}H_{28}O$ (M+): 272.2140].

Preparation of acetal 23.



To a solution of diene **22** (794 mg, 3.0 mmol, 1.0 equiv) in THF/H_2O (4:1, 25 mL) was added 2.5 wt. % OsO_4 solution in 2-methyl-2-propanol (940 *u*L, 0.08 mmol, 2.5 mol%) and NMO (386 mg, 3.3 mmol, 1.1 equiv). The mixture was allowed to stir at room temperature for 8 hours. The crude solution was diluted with ether. After washing with $NaHCO_3$ and brine, the solution was filtered through a silica gel pad. After drying with $MgSO_4$, the solvent was evaporated under reduced pressure. The residue was then dissolved in a solvent mixture of CH_3OH/THF (4:1, 30 mL), followed by addition of an aqueous solution of 0.5 M $NaIO_4$ (18 mL, 9.0 mmol, 3.0 equiv). The mixture was allowed to stir at room temperature for 1 hour. The reaction was diluted with water (20 mL), and the crude product was extracted with ether. After drying with $MgSO_4$, the solvent was rotavapored and the resultant colorless oil was then dissolved in benzene (30 mL). To this solution was added ethylene glycol (0.85 mL, 15 mmol, 5.0 equiv) and catalytic PPTS (5 mg). The reaction was heated to reflux for 4 hours under Dean-Stark conditions. After the solution was cooled to room temperature, the crude product was diluted with ether. The crude solution was washed with $NaHCO_3$ and brine, and then dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (10:1 Hexanes:EtOAc eluent). A colorless oil was collected as acetal **23** (696 mg, 73% yield over 3 steps): **^{1}H NMR** (500 MHz, C_6D_6) δ 5.91 (dt, *J* = 17, 10 Hz, 1H), 4.98 (dd, *J* = 17, 2 Hz, 1H), 4.94 (dd, *J* = 10, 2 Hz, 1H), 4.89 (d, *J* = 5 Hz, 1H), 3.68 (m, 2H), 3.52 (m, 2H), 2.62 (td, *J* = 9, 2.5 Hz, 1H), 2.57 (dd, *J* = 12, 6.5 Hz, 1H), 2.34-2.48 (m, 3H), 2.29 (dd, *J* = 12, 11 Hz, 1H), 2.22 (m, 1H), 1.72-1.82 (m, 2H), 1.70 (dt, *J* = 15, 6 Hz, 1H), 1.57 (ddd, *J* = 15, 10, 1 Hz, 1H), 1.06 (s, 3H), 1.02 (s, 3H), 0.98 (d, *J* = 7 Hz, 3H), 0.67 (m, 2H); **^{13}C NMR** (400 MHz, C_6D_6) δ 209.0, 141.9, 115.2, 107.9, 69.5, 65.7, 65.6, 50.3, 40.2, 39.7, 35.2, 33.0, 31.8, 29.1, 26.9, 23.7, 21.6, 15.9, 15.3; **IR** (thin film/NaCl) 3073 (w), 2953 (m), 1696 (s), 1457 (w), 1380 (w), 1272 (w), 1156 (m), 1096 (m), 1077 (m), 995 (w), 940 (w), 913 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 318.2191 [calc'd for $C_{20}H_{30}O_3$ (M+): 318.2195].

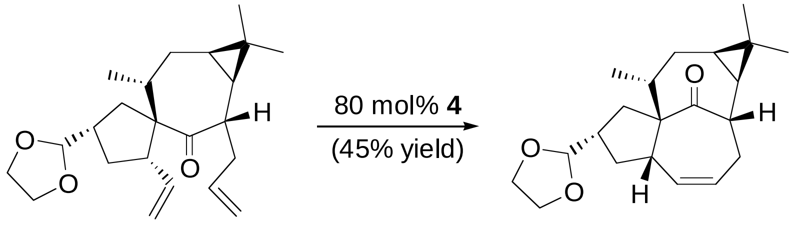
Preparation of RCM precursor 24.



23 **24**

To a solution of acetal **23** (580 mg, 1.8 mmol, 1.0 equiv) in dry THF (40 mL) was sequentially added KH powder (365 mg, 9.1 mmol, 5.0 equiv) and allyl bromide (2.0 ml, 18.2 mmol, 10 equiv). The reaction was heated to reflux vigorously for 10 hours. After cooling to room temperature, methanol was carefully added into the reaction to quench excess KH. The crude product was extracted with ether, and the solution was washed with NH_4Cl and brine. After drying with $MgSO_4$, the solvent was removed, and the yellow residue was purified by silica gel chromatography (30:1 Hexanes:EtOAc eluent). Diene **24** was collected to furnish a white solid (592 mg, 92% yield): m.p. 64.1-65.1°C; **^{1}H NMR** (500 MHz, C_6D_6) δ 5.63 (ddd, *J* = 17, 10, 7.5 Hz, 1H), 5.62 (ddd, *J* = 17, 10.5, 10 Hz, 1H), 4.91 (dd, *J* = 17, 2 Hz, 1H), 4.85 (dd, *J* = 10, 2 Hz, 1H), 4.70 (dd, *J* = 17, 2.5 Hz, 1H), 4.67 (dd, *J* = 10, 2.5 Hz, 1H), 4.62 (d, *J* = 3 Hz, 1H), 3.41 (m, 2H), 3.24 (m, 2H), 2.51 (ddd, *J* = 13, 10, 8 Hz, 1H), 2.38 (m, 1H), 2.25 (ddd, *J* = 12.5, 7.5, 4 Hz, 1H), 2.11 (m, 4H), 1.95 (m, 1H), 1.40-1.50 (m, 3H), 1.28 (dd, *J* = 14, 11 Hz, 1H), 0.81 (s, 3H), 0.80 (s, 3H), 0.71 (d, *J* = 6.5 Hz, 3H), 0.41 (td, *J* = 10, 6 Hz, 1H), 0.00 (dd, *J* = 10, 9 Hz, 1H); **^{13}C NMR** (400 MHz, C_6D_6) δ 210.6, 142.1, 137.9, 116.2, 115.2, 107.8, 69.3, 65.7, 65.6, 50.1, 48.1, 39.9, 37.0, 35.2, 33.0, 32.1, 29.3, 27.9, 27.1, 23.6, 21.6, 16.8, 15.2; **IR** (thin film/NaCl) 3073 (w), 2975 (s), 2880 (s), 1694 (s), 1639 (w), 1454 (m), 1415 (w), 1379 (w), 1156 (m), 1094 (m), 1034 (m), 996 (m), 911 (m), 752 (w), 651 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 358.2503 [calc'd for $C_{23}H_{34}O_3$ (M+): 358.2508].

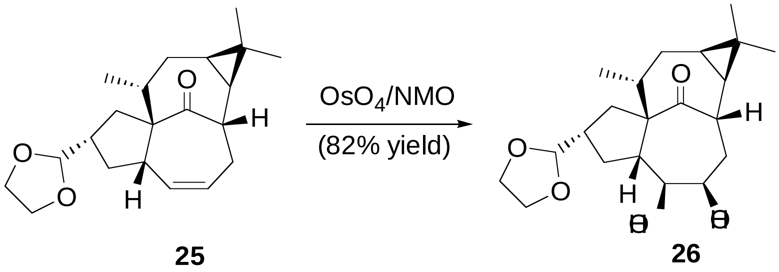
Preparation of 25 using RCM.



24 **25**

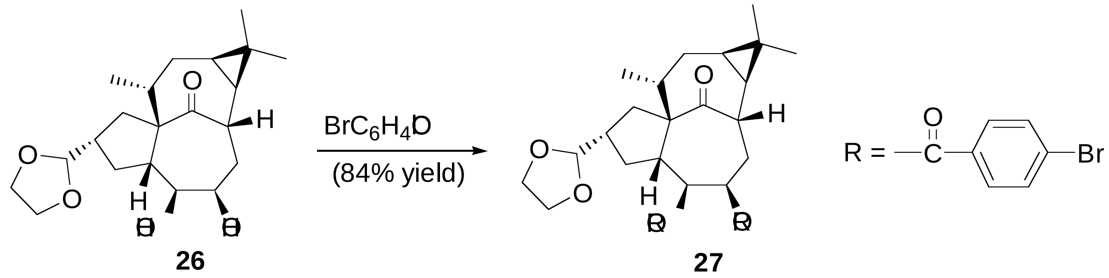
A solution of **24** (50 mg, 0.14 mmol, 1.0 equiv) in dry toluene (50 mL) was heated to reflux for 3 hours. During this time, four portions of catalyst **4** (23 mg, 0.028 mmol, 20 mol%) were added to the solution every 45 minutes. After cooling to room temperature, $Pb(OAc)_4$ (101 mg, 0.28 mmol, 2.0 equiv), and the mixture was allowed to stir for 24 hours. The crude solution was poured on a short silica gel column (15:1 Hexanes:Et_2O eluent), and the product was collected as a pink oil. The RCM product was further purified by HPLC (20:1 Hexanes:Et_2O eluent). The purified product was a colorless oil **25** (21 mg, 45% yield): **^{1}H NMR** (500 MHz, 80°C, C_6D_6) δ 5.50 (m, 2H), 4.82 (d, *J* = 5 Hz, 1H), 3.70 (m, 2H), 3.55 (m, 2H), 3.29 (td, *J* = 13, 3.5 Hz, 1H), 3.06 (d, J = 3.5 Hz, 1H), 2.66 (m, 1H), 2.10-2.45 (m, 5H), 1.90 (m, 1H), 1.76 (dd, J = 7.5, 4.5 Hz, 2H), 1.70 (ddd, J = 12.5, 7, 4.5 Hz, 1H), 1.13 (s, 3H), 1.05 (d, J = 7 Hz, 3H), 1.04 (s, 3H), 0.91 (dd, J = 12, 9 Hz, 1H), 0.70 (q, J = 8 Hz, 1H); ^{13}**C NMR** (400 MHz, 80°C, C_6D_6) δ 210.5, 138.4, 131.2, 108.0, 72.4, 66.7, 46.3, 46.1, 43.3, 37.5, 35.9, 32.6, 31.2, 30.3, 29.8, 29.3, 25.1, 24.7, 23.5, 16.3, 15.7; IR (thin film/NaCl) 2999 (m), 2948 (m), 2876 (m), 1721 (s), 1457 (w), 1380 (w), 1160 (w), 1103 (w), 1036 (w), 960 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 330.2187 [calc'd for $C_{21}H_{30}O_3$ (M+ 330.2195].

Preparation of diol 26.



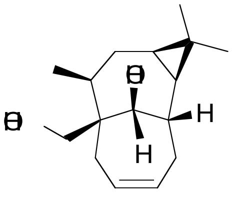
To a solution of RCM product **25** (66 mg, 0.20 mg, 1.0 equiv) in THF/H_2O (4:1 15 mL) was added 2.5 wt. % OsO_4 solution in 2-methyl-2-propanol (50 *u*L, 0.004 mmol, 2 mol%) and NMO (117 mg, 1.0 mmol, 5.0 equiv). The mixture was allowed to stir at room temperature for 12 hours. The crude product was extracted with ether. The solution was washed with brine. After drying over $MgSO_4$, solvent was removed under reduced pressure. The residue was purified with flash chromatography (2:1 Hexanes:EtOAc eluent). After evaporation of solvent, diol **26** was collected as a colorless oil (60 mg, 82% yield): ^{1}**H NMR** (500 MHz, 80¡C, C_6D_6) δ 4.82 (d, J = 4 Hz, 1H), 4.00 (s broad, 1H), 3.70 (m, 2H), 3.55 (m, 2H), 3.34 (d, J = 8 Hz, 1H), 3.25 (td, J = 14, 2 Hz, 1H), 2.66 (q, J = 7 Hz, 1H), 2.43 (m, 1H), 2.35 (broad, 1H), 2.20 (m, 2H), 2.14 (td, J = 6.5, 2.5 Hz, 1H), 2.08 (dd, J = 14, 7 Hz, 1H), 1.97 (t, J = 7.5 Hz, 2H), 1.87 (ddd, J = 13, 7.5, 2.5 Hz, 1H), 1.78 (m, 2H), 1.50 (broad, 1H), 1.32 (s, 3H), 1.06 (s, 3H), 1.03 (d, J = 7 Hz, 3H), 0.90 (dd, J = 11.5, 8.5 Hz, 1H), 0.67 (q, J = 8.5 Hz, 1H); ^{13}**C NMR** (400 MHz, 80¡C, C_6D_6) δ 212.4, 107.9, 77.4, 75.2, 68.8, 65.8, 65.6, 47.9, 42.4, 42.2, 37.6, 34.0, 30.9, 29.6, 28.1, 27.9, 25.8, 25.2, 23.7, 17.0, 15.4; **IR** (thin film/NaCl) 3454 (m broad), 2926 (s), 2883 (s), 1713 (s), 1453 (w), 1220 (w), 1159 (w), 1034 (m), 940 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 364.2248 [calc'd for $C_{21}H_{32}O_5$ (M+): 364.2250].

Preparation of dibenzoate 27.

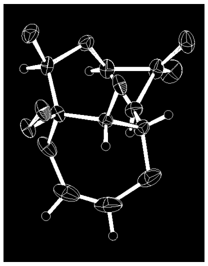


To a solution of diol **26** (30 mg, 0.08 mmol, 1.0 equiv) in dichloromethane (10 mL) was sequentially added *para*-bromobenzoic chloride (88 mg, 0.40 mmol, 5.0 equiv) and DMAP (25 mg, 0.20 mmol, 2.5 equiv). The flask was then sealed under N_2. Triethyl amine (110 *u*L, 0.80 mmol, 10 equiv) was injected into the reaction. The reaction was allowed to stir at room temperature for 8 hours. Concentration under reduced pressure with concomitant adsorption onto silica gel was followed by flash chromatography (4:1 Hexanes:EtOAc eluent). A crystalline solid was collected as diester **27 (**51 mg, 84% yield): m.p. 183.6-184.8¡C; **^{1}H NMR** (500 MHz, 80¡C, C_6D_6) δ 7.88 (dd, *J* = 8.5, 7 Hz, 4H), 7.34 (m, 4H), 5.88 (t, *J* = 4.5 Hz, 1H), 5.69 (s broad, 1H), 4.77 (d, *J* = 5.5 Hz, 1H), 3.67 (m, 2H), 3.59 (t, *J* = 10 Hz, 1H), 3.51 (m, 2H), 2.89 (d, *J* = 6 Hz, 1H), 2.70 (t, *J* = 13 Hz, 1H), 2.56 (dt, *J* = 13, 5 Hz, 1H), 2.37 (m, 1H), 2.31 (m, 1H), 2.21 (dt, *J* = 14, *J* = 7 Hz, 1H), 1.85-2.00 (m, 4H), 1.75 (ddd, *J* = 16, 9, 7 Hz, 1H), 1.50 (broad, 1H), 1.23 (s, 3H), 1.02 (s, 3H), 0.96 (d, *J* = 7 Hz, 3H), 0.65 (ddd, *J* = 8.5, 6.5, 4.5 Hz, 1H); **^{13}C NMR** (400 MHz, 80¡C, C_6D_6) δ 210.4, 165.4, 165.2, 132.6, 131.9, 131.8, 130.4, 130.3, 107.6, 79.3, 74.8, 68.1, 65.7, 50.1, 43.3, 41.5, 41.3, 39.6, 32.1, 31.4, 31.0, 29.4, 27.1, 26.5, 25.4, 22.9, 17.1, 15.8; **IR** (thin film/NaCl) 2955 (w), 2883 (w), 1723 (s), 1590 (m), 1484 (w), 1398 (w), 1272 (s), 1173 (w), 1113 (m), 1100 (m), 1012 (m), 923 (w), 847 (w), 754 (m), 737 (w), 682 (w) cm^{-1}; **HRMS** (EI) *m/z* found: 730.0952 [calc'd for $C_{35}H_{38}$ Br_2O_7 (M+): 730.0964].

X-RAY CRYSTALLOGRAPHY REPORT FOR DIOL 10



10



Data Collection

A colorless plate crystal of $C_{32}H_{52}O_4$ having approximate dimensions of 0.05 x 0.12 x 0.19 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in _, 10s exposure, de-zingered) data frames, corresponded to a primitive monoclinic cell with dimensions: a = 9.7381(2) , b = 13.3319(4) , _ = 101.424(2)°, c = 11.5709(3) , and V = 1472.46(6) ^{3}. For Z = 2 and F.W. = 500.76, the calculated density is 1.13 g/cm^3. Based on the systematic absences of: 0k0: k = 2n+1; packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1$ (#4). There are two independent, but essentially identical, molecules per asymmetric unit.

The data were collected at a temperature of -90 ± 1°C to a maximum 2_ value of 50.0°. Three omega scans consisting of 55, 54 and 55 data frames, respectively, were collected with a scan width of 2° and a detector-to-crystal distance, Dx, of 33mm. Each frame was exposed twice (for the purpose of de-zingering) for 180s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, Processing of X-Ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

Of the 4748 reflections which were collected, 2708 were unique (R$_{int}$ = 0.016). No decay correction was applied. The linear absorption coefficient, _, for Mo-K_ radiation is 0.7 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms (OH group hydrogens) were refined isotropically, the rest were included in fixed positions. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 2171 observed reflections (I > 3.00_(I)) and 340 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R = _ ||Fo| - |Fc|| / _ |Fo| = 0.041

R$_W$ = [(_ w (|Fo| - |Fc|)^2 / _ w Fo^2)]$^{1/2}$ = 0.043

The standard deviation of an observation of unit weight[4] was 1.99. The weighting scheme was based on counting statistics and included a factor (p = 0.010) to downweight the intense reflections. Plots of _ w (|Fo| - |Fc|)^2 versus |Fo|, reflection order in data collection, sin _/_, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.15 and -0.16 e$^-$/ ^{3}, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for _f’ and _f" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G.; *J. Appl. Cryst.*, 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $Sw(|F_o|-|F_c|)^2$

where $w = 4F_o^2/^2(F_o^2)$

and $s^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[S w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where N_o = number of observations and N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr*., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{32}H_{52}O_4$
Formula Weight	500.76
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.05 X 0.12 X 0.19 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.7381(2)
	b = 13.3319(4)
	c = 11.5709(3)
	_ = 101.424(2)^{o}
	V = 1472.46(6) ^{3}
Space Group	$P2_1$ (#4)
Z value	2
Dcalc	1.129 g/cm^{3}
F000	552.00
(MoK)	0.72 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoK_ (_ = 0.71069)
	graphite monochromated

Take-off Angle	2.8^{o}
Crystal to Detector Distance	33 mm
Temperature	-90.0^{o}C
Scan Type	_
Scan Rate	180s/frame
Scan Width	2.0^{o}/frame
2_max	50.0^{o}
No. of Reflections Measured	Total: 4748
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	_ w (|Fo| - |Fc|)^{2}
Least Squares Weights	1/_^{2}(Fo)
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00_(I))	2171
No. Variables	340
Reflection/Parameter Ratio	6.39
Residuals: R; Rw	0.041; 0.043
Goodness of Fit Indicator	1.99
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.15 e^{-}/ ^{3}
Minimum peak in Final Diff. Map	-0.16 e^{-}/ ^{3}

Table 1. Atomic coordinates and B_{iso}/B_{eq}

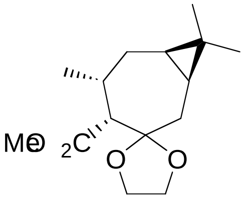
atom	**˚˚˚x**	**˚˚˚y**	**˚˚˚z**	**˚Beq**
O(1)	˚0.8727(2)	˚0.7035	-0.0938(2)	˚3.03(5)
O(2)	˚0.6094(2)	˚0.7626(3)	-0.0948(2)	˚3.52(5)
O(3)	˚0.6482(2)	˚0.2768(2)	˚0.2293(2)	˚3.37(5)
O(4)	˚0.9070(2)	˚0.2409(3)	˚0.1965(2)	˚3.83(5)
C(1)	˚0.8100(3)	˚0.6123(3)	-0.0612(2)	˚2.58(6)
C(2)	˚0.9193(3)	˚0.5272(3)	-0.0414(3)	˚3.22(7)
C(3)	˚0.8480(4)	˚0.4334(4)	-0.1027(4)	˚5.9(1)
C(4)	˚0.7099(5)	˚0.4051(4)	-0.0701(5)	˚6.8(1)
C(5)	˚0.6423(4)	˚0.4468(4)	˚0.0031(5)	˚6.4(1)
C(6)	˚0.6866(3)	˚0.5307(4)	˚0.0869(3)	˚4.61(9)
C(7)	˚0.7279(2)	˚0.6329(3)	˚0.0370(2)	˚2.74(7)
C(8)	˚0.5871(3)	˚0.6803(3)	-0.0209(3)	˚3.43(7)
C(9)	˚0.8098(3)	˚0.6980(3)	˚0.1400(3)	˚3.55(7)
C(10)	˚0.7822(4)	˚0.8108(4)	˚0.1310(3)	˚5.01(9)
C(11)	˚0.9694(3)	˚0.6817(3)	˚0.1636(3)	˚3.31(7)
C(12)	˚1.0170(3)	˚0.5754(3)	˚0.1845(2)	˚3.11(7)
C(13)	˚0.9925(3)	˚0.5014(3)	˚0.0839(3)	˚3.20(7)
C(14)	˚1.1409(3)	˚0.5336(3)	˚0.1406(3)	˚3.03(7)
C(15)	˚1.2247(3)	˚0.5985(3)	˚0.0729(3)	˚4.04(8)
C(16)	˚1.2305(3)	˚0.4584(3)	˚0.2187(3)	˚4.48(8)
C(17)	˚0.7344(3)	˚0.3145(3)	˚0.3356(2)	˚2.57(6)
C(18)	˚0.6395(3)	˚0.3603(3)	˚0.4150(3)	˚3.09(7)
C(19)	˚0.7038(4)	˚0.4617(4)	˚0.4584(4)	˚5.5(1)
C(20)	˚0.8556(5)	˚0.4573(4)	˚0.5173(4)	˚6.5(1)
C(21)	˚0.9425(4)	˚0.3811(5)	˚0.5379(3)	˚5.9(1)

C(22)	˚0.9152(3)	˚0.2713(4)	˚0.5162(3)	˚4.25(8)
C(23)	˚0.8434(2)	˚0.2372(3)	˚0.3905(2)	˚2.67(6)
C(24)	˚0.9619(2)	˚0.2403(3)	˚0.3199(2)	˚3.42(7)
C(25)	˚0.7846(3)	˚0.1290(3)	˚0.3974(3)	˚3.24(7)
C(26)	˚0.7867(3)	˚0.0608(3)	˚0.2915(3)	˚4.59(9)
C(27)	˚0.6343(3)	˚0.1264(3)	˚0.4215(3)	˚3.41(8)
C(28)	˚0.6094(3)	˚0.1871(3)	˚0.5249(3)	˚3.30(7)
C(29)	˚0.6125(3)	˚0.3003(3)	˚0.5192(3)	˚3.29(7)
C(30)	˚0.4765(3)	˚0.2459(3)	˚0.5234(3)	˚3.58(7)
C(31)	˚0.3605(3)	˚0.2440(4)	˚0.4178(3)	˚4.83(9)
C(32)	˚0.4241(4)	˚0.2516(4)	˚0.6385(3)	˚5.7(1)
H(1)	˚0.7421	˚0.5933	-0.1284	˚3.0971
H(2)	˚0.9906	˚0.5456	-0.0827	˚3.8645
H(3)	˚0.8315	˚0.4446	-0.1853	˚7.1147
H(4)	˚0.9105	˚0.3785	-0.0832	˚7.1147
H(5)	˚0.6658	˚0.3477	-0.1097	˚8.1492
H(6)	˚0.5519	˚0.4200	˚0.0032	˚7.6580
H(7)	˚0.6112	˚0.5438	˚0.1258	˚5.5324
H(8)	˚0.7655	˚0.5081	˚0.1427	˚5.5324
H(9)	˚0.5408	˚0.7040	˚0.0388	˚4.1220
H(10)	˚0.5305	˚0.6312	-0.0672	˚4.1220
H(11)	˚0.7797	˚0.6763	˚0.2092	˚4.2635
H(12)	˚0.6880	˚0.8238	˚0.1370	˚6.0125
H(13)	˚0.8438	˚0.8442	˚0.1931	˚6.0125
H(14)	˚0.7978	˚0.8346	˚0.0573	˚6.0125
H(15)	˚1.0031	˚0.7059	˚0.0972	˚3.9746
H(16)	˚1.0096	˚0.7197	˚0.2313	˚3.9746
H(17)	˚1.0046	˚0.5484	˚0.2577	˚3.7370
H(18)	˚0.9699	˚0.4362	˚0.1074	˚3.8398

H(19)	˚1.2601	˚0.5584	˚0.0176	˚4.8438
H(20)	˚1.3005	˚0.6282	˚0.1262	˚4.8438
H(21)	˚1.1662	˚0.6496	˚0.0325	˚4.8438
H(22)	˚1.2964	˚0.4928	˚0.2768	˚5.3774
H(23)	˚1.1728	˚0.4172	˚0.2562	˚5.3774
H(24)	˚1.2789	˚0.4178	˚0.1723	˚5.3774
H(25)	˚0.533(3)	˚0.775(3)	-0.141(3)	˚5.1(9)
H(26)	˚0.806(3)	˚0.743(3)	-0.119(3)	˚4.7(9)
H(27)	˚0.7855	˚0.3690	˚0.3123	˚3.0803
H(28)	˚0.5511	˚0.3736	˚0.3659	˚3.7028
H(29)	˚0.6950	˚0.5054	˚0.3925	˚6.6400
H(30)	˚0.6525	˚0.4882	˚0.5133	˚6.6400
H(31)	˚0.8955	˚0.5202	˚0.5441	˚7.8454
H(32)	˚1.0366	˚0.3980	˚0.5716	˚7.1244
H(33)	˚1.0031	˚0.2381	˚0.5350	˚5.1058
H(34)	˚0.8575	˚0.2498	˚0.5687	˚5.1058
H(35)	˚1.0198	˚0.1829	˚0.3391	˚4.1072
H(36)	˚1.0160	˚0.2993	˚0.3405	˚4.1072
H(37)	˚0.8427	˚0.0977	˚0.4632	˚3.8892
H(38)	˚0.7280	˚0.0883	˚0.2235	˚5.5052
H(39)	˚0.7535	-0.0039	˚0.3067	˚5.5052
H(40)	˚0.8798	˚0.0556	˚0.2786	˚5.5052
H(41)	˚0.5728	˚0.1507	˚0.3531	˚4.0865
H(42)	˚0.6120	˚0.0585	˚0.4348	˚4.0865
H(43)	˚0.6504	˚0.1599	˚0.5996	˚3.9596
H(44)	˚0.6535	˚0.3299	˚0.5926	˚3.9475
H(45)	˚0.3983	˚0.2493	˚0.3484	˚5.7996
H(46)	˚0.2990	˚0.2987	˚0.4214	˚5.7996
H(47)	˚0.3102	˚0.1828	˚0.4164	˚5.7996

H(48)	˚0.3674	˚0.1947	˚0.6452	˚6.8856
H(49)	˚0.5018	˚0.2526	˚0.7028	˚6.8856
H(50)	˚0.3704	˚0.3109	˚0.6395	˚6.8856
H(51)	˚0.705(3)	˚0.256(3)	˚0.186(3)	˚5.2(9)
H(52)	˚0.981(3)	˚0.231(3)	˚0.161(3)	˚4.1(7)

X-RAY CRYSTALLOGRAPHY REPORT FOR ACETAL 17



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Data Collection

A colorless plate crystal of $C_{15}H_{24}O_4$ having approximate dimensions of 0.05 x 0.20 x 0.24 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in _, 10s exposure, de-zingered) data frames, corresponded to a primitive orthorhombic cell with dimensions: a = 5.8792(2) , b = 7.0770(3) , c = 34.695(1) , and V = 1443.56(8) ^{3}. For Z = 4 and F.W. = 268.35, the calculated density is 1.24 g/cm^{3}. The systematic absences of: h00: h = 2n+1, 0k0: k = 2n+1, 00l: l = 2n+1; uniquely determine the space group to be: $P2_12_12_1$ (#19).

The data were collected at a temperature of -90 ± 1°C to a maximum 2_ value of 55.0°. Three omega scans consisting of 133, 172 and 172 data frames, respectively, were collected with a scan width of 0.8° and a detector-to-crystal distance, Dx, of 45mm. Each frame was exposed twice (for the purpose of de-zingering) for 48s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, Processing of X-Ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

Of the 3333 reflections which were collected, 1994 were unique (R_{int} = 0.046). No decay correction was applied. The linear absorption coefficient, _, for Mo-K_ radiation is 0.9 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 1188 observed reflections (I > 3.00_(I)) and 172 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R = _ ||Fo| - |Fc|| / _ |Fo| = 0.052

R_W = [(_ w (|Fo| - |Fc|)^2 / _ w Fo^2)]$^{1/2}$ = 0.055

The standard deviation of an observation of unit weight[4] was 2.38. The weighting scheme was based on counting statistics and included a factor (p = 0.010) to downweight the intense reflections. Plots of _ w (|Fo| - |Fc|)^2 versus |Fo|, reflection order in data collection, sin _/_, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.24 and -0.25 e$^-$/ ^{3}, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for _f’ and _f" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G.; *J. Appl. Cryst.*, 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $Sw(|F_o|-|F_c|)^2$

where $w = 4F_o^2/{}^2(F_o^2)$

and $s^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[S w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where N_o = number of observations and N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr*., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{15}H_{24}O_4$
Formula Weight	268.35
Crystal Color, Habit	colorless, plates
Crystal Dimensions	0.05 X 0.20 X 0.24 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 5.8792(2) b = 7.0770(3) c = 34.695(1) V = 1443.56(8) ^{3}
Space Group	$P2_12_12_1$ (#19)
Z value	4
Dcalc	1.235 g/cm^{3}
F000	584.00
(MoK)	0.88 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoK_ (_ = 0.71069) graphite monochromated
Take-off Angle	2.8^{o}

Crystal to Detector Distance	45 mm
Temperature	-90.0^{o}C
Scan Rate	48s/frame
Scan Width	0.8^{o}/frame
2_max	55.0^{o}
No. of Reflections Measured	Total: 3333
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	_ w $(\vert Fo \vert - \vert Fc \vert)^2$
Least Squares Weights	1/_ ^{2}(Fo)
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00_(I))	1188
No. Variables	172
Reflection/Parameter Ratio	6.91
Residuals: R; Rw	0.052; 0.055
Goodness of Fit Indicator	2.38
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.24 e^-/ ^{3}
Minimum peak in Final Diff. Map	-0.25 e^-/ ^{3}

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	**°°°x**	**°°°y**	**°°°z**	**˚Beq**
O(1)	-0.2389(4)	˚0.3153(4)	˚0.30847(6)	˚2.64(6)
O(2)	˚0.0588(4)	˚0.2579(4)	˚0.34940(6)	˚2.73(6)
O(3)	-0.1105(5)	-0.1129(5)	˚0.30737(8)	˚4.06(8)
O(4)	-0.4884(5)	-0.1143(4)	˚0.31139(7)	˚3.53(7)
C(1)	-0.1803(7)	˚0.2690(6)	˚0.34778(10)	˚2.39(10)
C(2)	-0.2662(7)	˚0.4256(5)	˚0.37406(9)	˚2.61(10)
C(3)	-0.1656(7)	˚0.4216(6)	˚0.41410(10)	˚2.27(9)
C(4)	-0.1968(6)	˚0.2540(6)	˚0.44089(10)	˚2.50(9)
C(5)	-0.3312(8)	˚0.0812(6)	˚0.4293(1)	˚3.2(1)
C(6)	-0.2409(8)	-0.0256(6)	˚0.3944(1)	˚3.0(1)
C(7)	-0.3001(7)	˚0.0763(6)	˚0.35590(10)	˚2.59(9)
C(8)	-0.0354(8)	˚0.3767(7)	˚0.2904(1)	˚3.7(1)
C(9)	˚0.1476(8)	˚0.309(1)	˚0.3136(1)	˚7.1(2)
C(10)	-0.3009(7)	˚0.4429(6)	˚0.45099(10)	˚2.59(10)
C(11)	-0.1923(7)	˚0.5503(6)	˚0.4835(1)	˚3.28(10)
C(12)	-0.5556(7)	˚0.4692(7)	˚0.4494(1)	˚3.9(1)
C(13)	˚0.0099(8)	-0.0777(6)	˚0.3987(1)	˚3.3(1)
C(14)	-0.2833(8)	-0.0548(7)	˚0.3226(1)	˚2.9(1)
C(15)	-0.4967(7)	-0.2452(6)	˚0.2802(1)	˚4.0(1)
H(1)	-0.2298	˚0.5437	˚0.3626	˚3.1314
H(2)	-0.4267	˚0.4140	˚0.3762	˚3.1314
H(3)	-0.0181	˚0.4761	˚0.4155	˚2.7192
H(4)	-0.0648	˚0.2253	˚0.4555	˚2.9956
H(5)	-0.3326	-0.0033	˚0.4506	˚3.8970
H(6)	-0.4822	˚0.1203	˚0.4237	˚3.8970

H(7)	-0.3213	-0.1420	˚0.3938	˚3.5754
H(8)	-0.4572	˚0.1060	˚0.3579	˚3.1086
H(9)	-0.0250	˚0.3255	˚0.2651	˚4.4920
H(10)	-0.0319	˚0.5107	˚0.2890	˚4.4920
H(11)	˚0.2579	˚0.4061	˚0.3168	˚8.5283
H(12)	˚0.2162	˚0.2027	˚0.3017	˚8.5283
H(13)	-0.0315	˚0.5442	˚0.4810	˚3.9361
H(14)	-0.2368	˚0.4961	˚0.5073	˚3.9361
H(15)	-0.2399	˚0.6785	˚0.4826	˚3.9361
H(16)	-0.6228	˚0.4163	˚0.4718	˚4.6729
H(17)	-0.5900	˚0.6002	˚0.4481	˚4.6729
H(18)	-0.6142	˚0.4077	˚0.4271	˚4.6729
H(19)	˚0.0575	-0.1488	˚0.3769	˚3.9954
H(20)	˚0.0300	-0.1510	˚0.4214	˚3.9954
H(21)	˚0.0983	˚0.0344	˚0.4005	˚3.9954
H(22)	-0.4978	-0.1782	˚0.2565	˚4.8259
H(23)	-0.6308	-0.3195	˚0.2822	˚4.8259
H(24)	-0.3671	-0.3253	˚0.2812	˚4.8259

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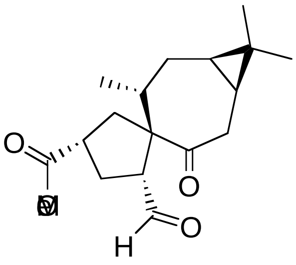

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Data Collection

A colorless plate crystal of $C_{18}H_{26}O_4$ having approximate dimensions of 0.07 x 0.17 x 0.19 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1^{o} in _, 10s exposure, de-zingered) data frames, corresponded to a primitive orthorhombic cell with dimensions: a = 6.0539(2) , b = 12.3425(3) , c = 23.046(1) , and V = 1722.03(9) ^{3}. For Z = 4 and F.W. = 306.40, the calculated density is 1.18 g/cm^{3}. The systematic absences of: h00: h = 2n+1, 0k0: k = 2n+1, 00l: l = 2n+1; uniquely determine the space group to be: $P2_12_12_1$ (#19). In this acentric space group, both enantiomers refine identically.

The data were collected at a temperature of $-90 \pm 1^{o}C$ to a maximum 2_ value of 50.1^{o}. Three omega scans consisting of 82, 77, and 77 data frames, respectively, were collected with a scan width of 1.4^{o} and a detector-to-crystal distance, Dx, of 35mm. Each frame was exposed twice (for the purpose of de-zingering) for 84s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, Processing of X-Ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, vol. 276:

Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

Of the 3072 reflections which were collected, 1814 were unique (R_{int} = 0.025). No decay correction was applied. The linear absorption coefficient, _, for Mo-K_ radiation is 0.8 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[3] was based on 1422 observed reflections (I > 3.00_(I)) and 303 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \_\ ||Fo| - |Fc|| / \_\ |Fo| = 0.036$$

$$R_W = [(\ \_\ w\ (|Fo| - |Fc|)^2 / \_\ w\ Fo^2)]^{1/2} = 0.036$$

The standard deviation of an observation of unit weight[4] was 1.88. The weighting scheme was based on counting statistics and included a factor (p = 0.020) to downweight the intense reflections. Plots of _ w $(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin _/_ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.19 and -0.19 $e^{-}/\ ^{3}$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for _f' and _f" were those of Creagh and

McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G.; *J. Appl. Cryst.,* 27, 435-436 (1994).

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $Sw(|F_o|-|F_c|)^2$

where $w = 4F_o^2/^2(F_o^2)$

and $s^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

p = p-factor

(4) Standard deviation of an observation of unit weight:

$[Sw(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where N_o = number of observations and N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
(6) Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr*., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{18}H_{26}O_4$
Formula Weight	306.40
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.07 X 0.17 X 0.19 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 6.0539(2)
	b = 12.3425(3)
	c = 23.046(1)
	V = 1722.03(9) ^{3}
Space Group	$P2_12_12_1$ (#19)
Z value	4
Dcalc	1.182 g/cm^{3}
F000	664.00
(MoK)	0.82 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoK_ (_ = 0.71069)
	graphite monochromated
Take-off Angle	2.8^{o}

Crystal to Detector Distance	35 mm
Temperature	-90.0$^{\mathrm{o}}$C
Scan Rate	84s/frame
Scan Width	1.4$^{\mathrm{o}}$/frame
2_max	50.1$^{\mathrm{o}}$
No. of Reflections Measured	Total: 3072
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

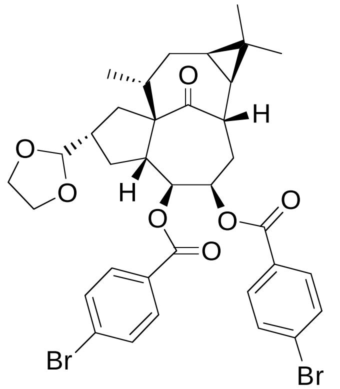
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	_ w (|Fo| - |Fc|)^{2}
Least Squares Weights	1/_ ^{2}(Fo)
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00_(I))	1422
No. Variables	303
Reflection/Parameter Ratio	4.69
Residuals: R; Rw	0.036; 0.036
Goodness of Fit Indicator	1.88
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.19 e^{-}/ ^{3}
Minimum peak in Final Diff. Map	-0.19 e^{-}/ ^{3}

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	**˚˚˚x**	**˚˚˚y**	**˚˚˚z**	**˚Beq**
O(1)	-0.0465(3)	-0.0325(1)	˚0.29639(7)	˚3.31(4)
O(2)	˚0.3870(3)	˚0.0385(1)	˚0.22267(8)	˚3.83(4)
O(3)	˚0.3276(4)	-0.2450(2)	˚0.08171(8)	˚6.48(7)
O(4)	-0.0163(3)	-0.2703(2)	˚0.11030(7)	˚3.93(5)
C(1)	˚0.2376(4)	-0.1603(2)	˚0.2739(1)	˚2.25(5)
C(2)	˚0.2414(4)	-0.2585(2)	˚0.3175(1)	˚2.57(5)
C(3)	˚0.3728(5)	-0.2385(2)	˚0.3737(1)	˚2.94(6)
C(4)	˚0.2532(5)	-0.1720(2)	˚0.4192(1)	˚2.92(6)
C(5)	˚0.2106(5)	-0.0531(2)	˚0.4080(1)	˚2.81(6)
C(6)	˚0.2814(5)	-0.0058(2)	˚0.3506(1)	˚2.60(6)
C(7)	˚0.1454(4)	-0.0608(2)	˚0.3045(1)	˚2.46(6)
C(8)	˚0.0112(6)	-0.3022(3)	˚0.3309(1)	˚3.81(7)
C(9)	˚0.3642(5)	-0.0858(2)	˚0.4563(1)	˚3.48(6)
C(10)	˚0.2734(7)	-0.0731(3)	˚0.5174(1)	˚4.60(9)
C(11)	˚0.6091(5)	-0.0652(3)	˚0.4520(2)	˚4.41(9)
C(12)	˚0.4717(4)	-0.1461(2)	˚0.2477(1)	˚2.33(5)
C(13)	˚0.4873(5)	-0.2330(2)	˚0.1993(1)	˚2.75(6)
C(14)	˚0.2479(4)	-0.2638(2)	˚0.18382(10)	˚2.40(5)
C(15)	˚0.1024(5)	-0.1865(2)	˚0.2193(1)	˚2.66(6)
C(16)	˚0.5131(5)	-0.0367(2)	˚0.2214(1)	˚3.02(6)
C(17)	˚0.1980(5)	-0.2583(2)	˚0.1200(1)	˚2.92(6)
C(18)	-0.0904(7)	-0.2672(4)	˚0.0506(1)	˚4.48(9)
H(1)	˚0.317(4)	-0.312(2)	˚0.296(1)	˚3.0(6)
H(2)	˚0.404(5)	-0.314(2)	˚0.389(1)	˚4.4(6)
H(3)	˚0.522(5)	-0.209(2)	˚0.3644(10)	˚2.6(5)

H(4)	˚0.136(5)	-0.208(2)	˚0.438(1)	˚3.4(6)
H(5)	˚0.071(4)	-0.026(2)	˚0.4189(9)	˚1.3(4)
H(6)	˚0.254(5)	˚0.076(2)	˚0.349(1)	˚3.9(5)
H(7)	˚0.436(4)	-0.016(2)	˚0.3452(9)	˚1.9(5)
H(8)	-0.081(4)	-0.246(2)	˚0.349(1)	˚3.1(6)
H(9)	-0.057(5)	-0.338(2)	˚0.295(1)	˚4.2(6)
H(10)	˚0.026(5)	-0.363(2)	˚0.360(1)	˚3.9(6)
H(11)	˚0.301(5)	˚0.002(2)	˚0.532(1)	˚4.6(7)
H(12)	˚0.102(7)	-0.088(2)	˚0.517(1)	˚5.7(8)
H(13)	˚0.340(5)	-0.126(2)	˚0.543(1)	˚5.2(7)
H(14)	˚0.675(5)	-0.079(2)	˚0.412(1)	˚4.7(7)
H(15)	˚0.681(7)	-0.116(3)	˚0.479(2)	˚7.0(10)
H(16)	˚0.646(5)	˚0.005(2)	˚0.466(1)	˚5.0(7)
H(17)	˚0.589(4)	-0.152(2)	˚0.2750(10)	˚1.9(5)
H(18)	˚0.560(5)	-0.211(2)	˚0.164(1)	˚3.8(6)
H(19)	˚0.571(4)	-0.297(2)	˚0.211(1)	˚3.4(6)
H(20)	˚0.222(4)	-0.341(2)	˚0.1955(9)	˚2.7(5)
H(21)	-0.041(5)	-0.219(2)	˚0.227(1)	˚2.8(5)
H(22)	˚0.088(4)	-0.117(2)	˚0.195(1)	˚3.2(5)
H(23)	˚0.657(5)	-0.031(2)	˚0.201(1)	˚3.6(6)
H(24)	-0.048(6)	-0.200(3)	˚0.036(1)	˚5.4(8)
H(25)	-0.016(7)	-0.326(3)	˚0.028(2)	˚7.2(9)
H(26)	-0.249(6)	-0.265(2)	˚0.052(1)	˚5.4(8)

X-RAY CRYSTALLOGRAPHY REPORT FOR DIESRER 27



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Data Collection

A colorless needle crystal of $C_{35}H_{38}O_7Br_2$ having approximate dimensions of 0.05 x 0.05 x 0.16 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in _, 10s exposure, de-zingered) data frames, corresponded to a primitive orthorhombic cell with dimensions: a = 7.0834(3) , b = 12.7467(4) , c = 36.377(1) , and V = 3284.4(2) ^{3}. For Z = 4 and F.W. = 730.49, the calculated density is 1.48 g/cm^{3}. The systematic absences of: h00: h = 2n+1, 0k0: k = 2n+1, 00l: l = 2n+1; uniquely determine the space group to be: $P2_12_12_1$ (#19).

The data were collected at a temperature of -90 ± 1°C to a maximum 2_ value of 50.1°. Two omega scans consisting of 163 and 163 data frames, respectively, were collected with a scan width of 0.9° and a detector-to-crystal distance, Dx, of 50mm. Each frame was exposed twice (for the purpose of de-zingering) for 81s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, Processing of X-Ray

Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction

Of the 5842 reflections which were collected, 3378 were unique (R_{int} = 0.112). No decay correction was applied. The linear absorption coefficient, _, for Mo-K_ radiation is 25.2 cm^{-1} and a SORTAV absorption correction was applied [SORTAV: Blessing, R.H.; *Acta Cryst.*, A51, 33-37 (1995). Blessing, R.H.; *J. Appl. Cryst.*, 30, 421-426 (1997)]. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 6.99826e-08).

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogen atoms, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement[3] was based on 1514 observed reflections (I > 3.00_(I)) and 397 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R = _ ||Fo| - |Fc|| / _ |Fo| = 0.040

R_w = [(_ w (|Fo| - |Fc|)^2 / _ w Fo^2)]$^{1/2}$ = 0.034

The standard deviation of an observation of unit weight[4] was 1.34. Refinement of the Flack parameter supports the assigned stereochemistry. In addition the other enantiomer yielded

R/Rw values equal to 5.7 and 5.3 per cent, respectively, upon least squares refinement. The weighting scheme was based on counting statistics and included a factor (p = 0.020) to downweight the intense reflections. Plots of _ w $(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin _/_ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.38 $e^{-}/^{3}$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for _f' and _f" were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G. (1994). J. Appl. Cryst., in preparation.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

Function minimized $Sw(|Fo|-|Fc|)^2$

where $w = 4Fo^2/^2(Fo^2)$

and $s^2(Fo^2) = [S^2(C+R^2B) + (pFo^2)^2]/Lp^2$

S = Scan rate

C = Total integrated peak count
R = Ratio of scan time to background counting time
B = Total background count
Lp = Lorentz-polarization factor
p = p-factor

(4) Standard deviation of an observation of unit weight:

$$[S w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$$

where N_o = number of observations
N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

EXPEREMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{35}H_{38}O_7Br_2$
Formula Weight	730.49
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.05 X 0.05 X 0.16 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 7.0834(3)
	b = 12.7467(4)
	c = 36.377(1)
	V = 3284.4(2) ^{3}
Space Group	$P2_12_12_1$ (#19)
Z value	4
Dcalc	1.477 g/cm^{3}
F000	1496.00
(MoK)	25.23 cm^{-1}

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoK_ (_ = 0.71069)
	graphite monochromated
Take-off Angle	2.8°
Crystal to Detector Distance	50 mm

Temperature	-90.0^{o}C
Scan Rate	81s/frame
Scan Width	0.9^{o}/frame
2_max	50.1^{o}
No. of Reflections Measured	Total: 5842
	Unique: 3378 (R$_{int}$ = 0.112)
Corrections	Lorentz-polarization
	Secondary Extinction
	(coefficient: 6.99826e-08)
	Absorption: SORTAV

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	_ w (|Fo| - |Fc|)^{2}
Least Squares Weights	1/_ ^{2}(Fo)
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00_(I))	1514
No. Variables	397
Reflection/Parameter Ratio	3.81
Residuals: R; Rw	0.040; 0.034
Goodness of Fit Indicator	1.34
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.34 e^{-}/ ^{3}
Minimum peak in Final Diff. Map	-0.38 e^{-}/ ^{3}

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

atom	**˚˚˚x**	**˚˚˚y**	**˚˚˚z**	**˚Beq**
Br(1)	-0.4058(2)	-0.09229(8)	˚0.59808(3)	˚4.37(3)
Br(2)	˚0.5498(3)	˚0.03313(10)	˚0.49628(3)	˚8.26(5)
O(1)	˚0.0951(9)	˚0.3186(4)	˚0.6682(1)	˚2.0(1)
O(2)	˚0.339(1)	˚0.2107(5)	˚0.6535(2)	˚3.7(2)
O(3)	˚0.2547(9)	˚0.4174(5)	˚0.6115(2)	˚2.4(2)
O(4)	˚0.568(1)	˚0.4444(5)	˚0.6178(2)	˚3.5(2)
O(5)	˚0.375(1)	˚0.6719(5)	˚0.5804(2)	˚3.6(2)
O(6)	˚0.1633(9)	˚0.7095(5)	˚0.5361(2)	˚3.3(2)
O(7)	˚0.1976(10)	˚0.6703(5)	˚0.7125(2)	˚3.0(2)
C(1)	˚0.194(1)	˚0.4397(7)	˚0.7154(2)	˚2.1(2)
C(2)	˚0.233(1)	˚0.4022(7)	˚0.6763(2)	˚2.1(2)
C(3)	˚0.214(1)	˚0.4815(7)	˚0.6438(2)	˚1.9(3)
C(4)	˚0.020(1)	˚0.5342(7)	˚0.6361(2)	˚1.9(2)
C(5)	-0.006(1)	˚0.6371(7)	˚0.6609(2)	˚1.6(2)
C(6)	˚0.084(2)	˚0.6141(7)	˚0.6976(2)	˚1.8(3)
C(7)	˚0.023(1)	˚0.5107(7)	˚0.7141(2)	˚1.5(2)
C(8)	˚0.172(2)	˚0.2295(8)	˚0.6551(3)	˚2.4(3)
C(9)	˚0.026(2)	˚0.1538(8)	˚0.6420(3)	˚2.2(3)
C(10)	-0.162(2)	˚0.1634(8)	˚0.6508(3)	˚2.9(3)
C(11)	-0.292(1)	˚0.0895(9)	˚0.6373(3)	˚3.3(3)
C(12)	-0.227(2)	˚0.0095(8)	˚0.6158(2)	˚2.5(3)
C(13)	-0.042(2)	-0.0006(7)	˚0.6062(3)	˚2.8(3)
C(14)	˚0.082(2)	˚0.0705(8)	˚0.6204(3)	˚3.3(3)
C(15)	˚0.439(2)	˚0.3999(8)	˚0.6034(3)	˚2.4(3)
C(16)	˚0.463(2)	˚0.3162(8)	˚0.5752(2)	˚2.5(3)
C(17)	˚0.309(2)	˚0.2644(8)	˚0.5610(3)	˚3.9(3)
C(18)	˚0.333(2)	˚0.180(1)	˚0.5379(3)	˚5.0(4)

C(19)	˚0.511(3)	˚0.1499(9)	˚0.5277(3)	˚4.9(4)
C(20)	˚0.667(2)	˚0.199(1)	˚0.5412(3)	˚6.4(5)
C(21)	˚0.644(2)	˚0.2863(9)	˚0.5651(3)	˚4.0(4)
C(22)	˚0.002(1)	˚0.5785(6)	˚0.5970(2)	˚2.2(2)
C(23)	˚0.053(1)	˚0.6966(6)	˚0.5983(2)	˚1.9(2)
C(24)	˚0.099(2)	˚0.7189(6)	˚0.6389(2)	˚2.0(2)
C(25)	˚0.211(2)	˚0.7281(8)	˚0.5728(3)	˚2.8(3)
C(26)	˚0.468(2)	˚0.6527(8)	˚0.5460(3)	˚4.8(3)
C(27)	˚0.343(2)	˚0.7065(8)	˚0.5178(2)	˚4.0(3)
C(28)	-0.218(2)	˚0.6633(7)	˚0.6693(2)	˚2.4(3)
C(29)	-0.337(1)	˚0.5869(7)	˚0.6923(2)	˚1.8(2)
C(30)	-0.294(1)	˚0.5786(7)	˚0.7336(2)	˚2.0(2)
C(31)	-0.103(2)	˚0.5366(7)	˚0.7465(2)	˚2.3(2)
C(32)	-0.233(1)	˚0.7739(6)	˚0.6865(2)	˚3.5(3)
C(33)	-0.280(2)	˚0.4734(7)	˚0.7533(2)	˚2.3(3)
C(34)	-0.350(1)	˚0.4731(7)	˚0.7927(2)	˚3.5(3)
C(35)	-0.313(1)	˚0.3690(8)	˚0.7343(2)	˚3.0(3)
H(1)	˚0.2998	˚0.4773	˚0.7246	˚2.4670
H(2)	˚0.1691	˚0.3813	˚0.7309	˚2.4670
H(3)	˚0.3562	˚0.3727	˚0.6756	˚2.5762
H(4)	˚0.3077	˚0.5342	˚0.6462	˚2.3383
H(5)	-0.0790	˚0.4859	˚0.6408	˚2.2444
H(6)	-0.0581	˚0.4800	˚0.6963	˚1.7760
H(7)	-0.2040	˚0.2197	˚0.6658	˚3.5054
H(8)	-0.4221	˚0.0951	˚0.6430	˚3.9384
H(9)	-0.0004	-0.0550	˚0.5902	˚3.3720
H(10)	˚0.2122	˚0.0624	˚0.6152	˚4.0002
H(11)	˚0.1850	˚0.2868	˚0.5670	˚4.7119
H(12)	˚0.2272	˚0.1424	˚0.5290	˚5.9753
H(13)	˚0.7897	˚0.1760	˚0.5347	˚7.6458
H(14)	˚0.7510	˚0.3236	˚0.5740	˚4.8455

H(15)	-0.1234	˚0.5699	˚0.5885	˚2.6213
H(16)	˚0.0867	˚0.5428	˚0.5810	˚2.6213
H(17)	-0.0564	˚0.7356	˚0.5918	˚2.2817
H(18)	˚0.2306	˚0.7132	˚0.6431	˚2.4223
H(19)	˚0.0572	˚0.7872	˚0.6455	˚2.4223
H(20)	˚0.2356	˚0.8008	˚0.5759	˚3.3312
H(21)	˚0.4754	˚0.5795	˚0.5413	˚5.7604
H(22)	˚0.5908	˚0.6821	˚0.5460	˚5.7604
H(23)	˚0.3871	˚0.7751	˚0.5125	˚4.8360
H(24)	˚0.3361	˚0.6669	˚0.4957	˚4.8360
H(25)	-0.2786	˚0.6678	˚0.6461	˚2.8602
H(26)	-0.3205	˚0.5189	˚0.6821	˚2.1550
H(27)	-0.4649	˚0.6076	˚0.6899	˚2.1550
H(28)	-0.3435	˚0.6342	˚0.7481	˚2.4168
H(29)	-0.0456	˚0.5698	˚0.7671	˚2.8144
H(30)	-0.2227	˚0.8254	˚0.6678	˚4.1554
H(31)	-0.3517	˚0.7808	˚0.6985	˚4.1554
H(32)	-0.1346	˚0.7833	˚0.7039	˚4.1554
H(33)	-0.4233	˚0.5343	˚0.7970	˚4.1477
H(34)	-0.2452	˚0.4723	˚0.8090	˚4.1477
H(35)	-0.4254	˚0.4126	˚0.7968	˚4.1477
H(36)	-0.2561	˚0.3145	˚0.7482	˚3.6318
H(37)	-0.2578	˚0.3708	˚0.7104	˚3.6318
H(38)	-0.4444	˚0.3566	˚0.7322	˚3.6318