Supporting Information

for

"Stereospecific Anionically-Promoted Transannular Hydride Shifts in Medium-Ring Hydroxy Ketones. Probe of their Reversibility and the Potential for Regiocontrol"

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(21 pages)

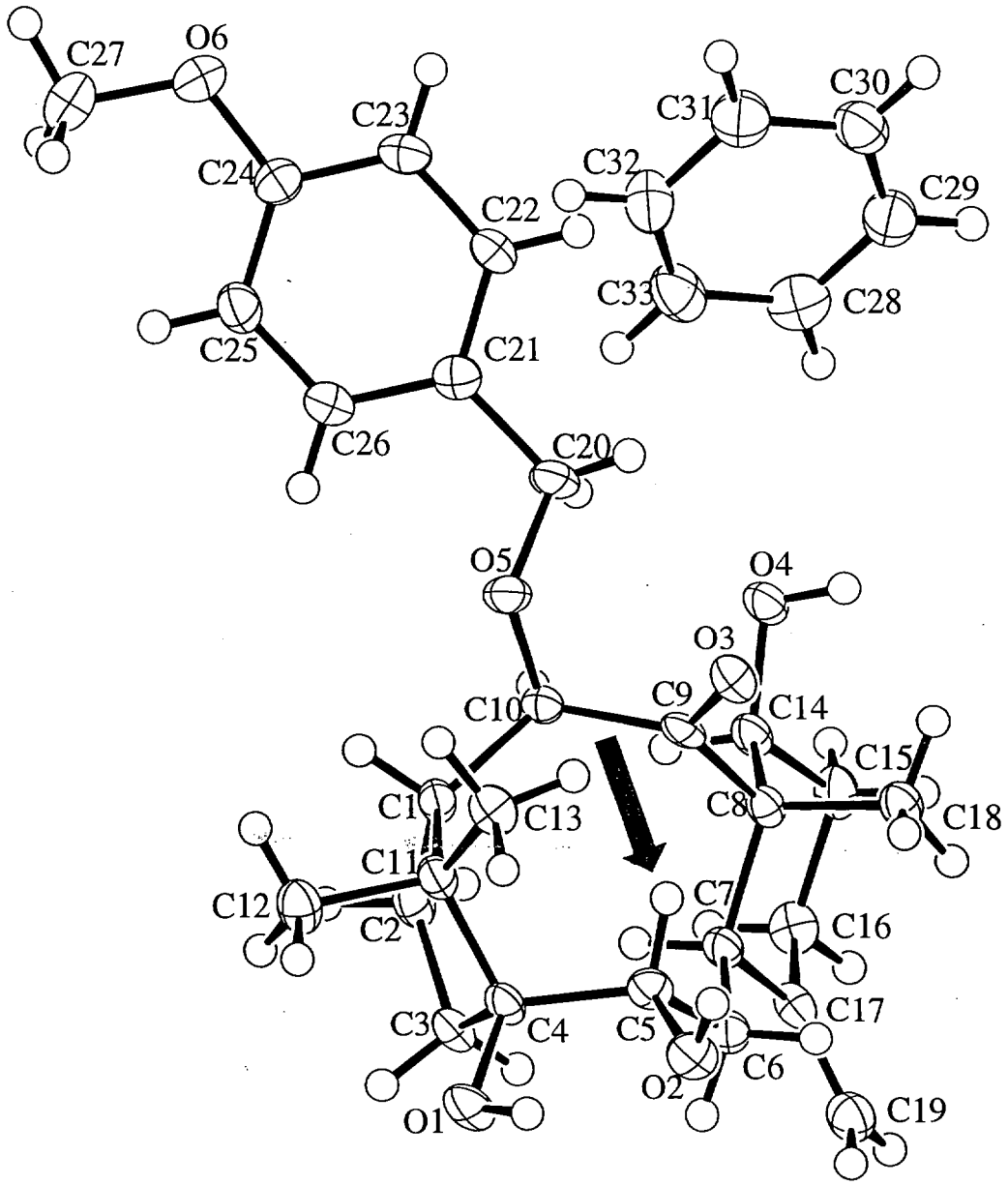
Conversion of 6 to 7. To a solution of **6** (36 mg, 0.08 mmol) in dry benzene (20 mL) was added potassium *tert*-butoxide (5 mg, 0.4 equiv). The suspension was stirred at room temperature for 30 min, quenched with pH 8 NH_4Cl/NH_4OH solution, and stirred for 10 min prior to filtration. The aqueous layer was removed by pipette and the organic phase was dried and evaporated to give pure **7** as a colorless glass (32 mg, 89%); crystallization from methanol afforded colorless crystals, mp 158-160 °C, suited for X-ray crystallography; IR (film, cm^{-1}) 3406, 1681, 1514; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 4.97 (s, 1 H), 4.89 (s, 1 H), 4.67 (d, J =10.7 Hz, 1 H), 4.63 (s, 1 H), 4.43 (d, J = 10.9 Hz, 1 H), 4.39 (s, 1 H), 4.03 (dd, J = 11.1, 4.5 Hz, 1 H), 3.80 (s, 3 H), 3.75 (dd, J = 9.5, 1.8 Hz, 1 H), 3.54 (d, J = 9.1 Hz, 1 H), 3.08 (s, 1 H), 2.93-2.86 (m, 1 H), 2.77-2.60 (m, 3 H), 2.58-2.45 (m, 1 H), 2.41-2.34 (m, 1 H), 2.24-1.99 (m, 3 H), 1.88-1.82 (m, 1 H), 1.80-1.65 (m, 1 H), 1.60-1.46 (m, 1 H), 1.14 (s, 3 H), 1.05 (s, 3 H), 1.04 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.2, 159.8, 146.8, 129.8 (2C), 129.1, 114.3 (2C), 110.1, 87.7, 83.0, 77.6, 73.6, 55.5, 50.3, 48.9, 44.7, 44.2, 39.7, 34.4, 31.4, 31.0, 30.4, 25.8, 19.3, 12.5; EI MS *m/z* for $C_{27}H_{38}O_6$ (M^+-H) calcd 457.2590, obsd 457.2545; $[\alpha]^{22}_D$ -37.6 (*c* 1.54, $CHCl_3$).

Conversion of 9 to 8. To a solution of **9** (5.0 mg, 8.7 μmol) dissolved in MeOH (5 mL) and THF (0.5 mL) was added aqueous NaOH solution (2 mL, 0.02 N). The reaction mixture was stirred at 20 °C for 3 h. Saturated NH_4Cl solution (10 mL) was added and stirring was maintained for another 2 min prior to extraction with EtOAc (2 x 10 mL). The combined organic extracts were dried, filtered, and concentrated, followed by flash chromatography of the residue on silica gel with 2:1 hexanes/EtOAc as elutant to afford **8** (4.6 mg, 92%) as a white solid, mp 145-146 °C; IR (KBr, cm^{-1}) 3440, 1697, 1513; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.6 Hz, 2 H); 6.90 (d, J = 8.6 Hz, 2 H), 5.05 (s, 1 H), 4.98 (s,

1 H), 4.54-4.52 (m, 1 H), 4.51 (d, J = 11 Hz, 1 H), 4.41 (d, J = 3.1 Hz, 1 H), 4.17 (d, J = 11 Hz, 1 H), 3.84 (s, 5 H), 2.96 (d, J = 12.3 Hz, 1 H), 2.72 (br s, 1 H), 2.70-2.62 (m, 1 H), 2.61-2.59 (m, 1 H), 2.50-2.49 (m, 1 H), 2.32-2.29 (m, 1 H), 2.22-2.11 (m, 2 H), 2.10-2.01 (m, 2 H), 1.90-1.85 (m, 1 H), 1.65-1.60 (m, 2 H), 1.11 (s, 6 H), 1.01 (s, 3 H), 0.87 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 158.7, 145.7, 131.2, 128.4, 113.5, 110.1, 87.1, 85.4, 77.0, 72.2, 71.9, 60.5, 56.4, 55.2, 48.4, 37.0, 34.3, 32.5, 32.3, 31.1, 31.0, 26.2, 25.7, 18.5, 17.2, 9.89, -2.20, -2.97; ES MS *m/z* for $C_{33}H_{52}O_6Si$ + Na (M^++Na) calcd 595.3431 obsd 595.3426; $[\alpha]^{20}_D$ -30.8 (*c* 0.83, $CHCl_3$).

ORTEP Drawing for **6**•C_6H_6

The molecular structure is drawn with 50% probability displacement ellipsoids for the non-H atoms. The H atoms are drawn with circles of arbitrary radii.


C27
O6
C23
C24
C22
C31
C30
C32
C29
C33
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C20
O5
O4
O3
C10
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C14
C15
C1
C13
C8
C18
C11
C12
C2
C7
C16
C3
C4
C5
C17
O2
C6
O1
C19

6•C_6H_6

The data collection crystal was a clear, colorless, thin plate. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated an orthorhombic crystal system. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. A quadrant of data was measured using the ω scan method with a frame width of 1.0° and a redundancy of 2. (By definition, a redundancy of 2 implies that 90% of the reflections in the quadrant have been measured at least twice.) Data integration was done with Denzo[1], and scaling and merging of the data was done with Scalepack[1]. Merging the data and averaging the symmetry equivalent reflections, including the Friedel pairs, resulted in an Rint value of 0.043. The space group was determined to be $P2_12_12_1$ by the teXsan package[2].

The structure was solved by the direct methods procedure in SHELXS-86[3]. Along with the molecule of interest, there is a benzene solvent molecule present in the asymmetric unit. The correct enantiomer was chosen based on the known absolute configuration for a portion of the molecule. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93[4].

The hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(attached atom), except for the three hydroxyl H atoms, which were refined isotropically. For a methyl group, the torsion angle which defines its orientation was allowed to refine, and these hydrogen atoms were assigned U(H) = 1.5 * Ueq(attached carbon atom). The final refinement cycle was based on all the 2845 intensities and 368 variables and resulted in agreement factors of R1(F) = 0.045 and wR2(F^2) = 0.083. For the subset of data with $I > 2\sigma(I)$, the R1(F) value is 0.037 for 2556 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.18 and -0.17 e/$\AA^3$. Neutral atom scattering factors were used and include terms for anomalous dispersion[5].

All of the hydroxyl H atoms are involved in either intramolecular or intermolecular hydrogen bonds.

References

(1) DENZO: Otwinowski, Z. & Minor, W., Methods in Enzymology, Vol 276: Macromolecular Crystallography, part A, 307-326, (1997), Carter, Jr., C. W. & Sweet, R. M., Eds., Academic Press.

(2) teXsan: Crystal Structure Analysis Package, version 1.7-2, Molecular Structure Corporation, The Woodlands, TX (1995).

(3) SHELXS-86: Sheldrick, G. M., Acta Cryst., (1990), A46, 467-473.

(4) SHELXL-93: Sheldrick, G. M., Universitat Gottingen, Germany, 1993.

(5) International Tables for Crystallography (1992). Volume C. Dordrecht: Kluwer Academic Publishers.

Empirical formula	C27 H38 O6 with benzene
Formula weight	536.68
Temperature	150 K
Wavelength	0.71073 A
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 9.4567(2) A b = 12.0433(3) A c = 24.8317(5) A
Volume	2828.1(1) A^3
Z	4
Density (calculated)	1.260 Mg/m^3
Absorption coefficient	0.085 mm^-1
F(000)	1160
Crystal size	0.04 x 0.31 x 0.31 mm
Theta range for data collection	2.30 to 25.02 deg.
Index ranges	0<=h<=11, 0<=k<=14, 0<=l<=29
Reflections collected	24075
Independent reflections	2845 [R(int) = 0.043]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2845 / 0 / 368
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.037, wR2 = 0.079
R indices (all data)	R1 = 0.045, wR2 = 0.083
Largest diff. peak and hole	0.18 and -0.17 e/A^3

Bond lengths [A] and angles [deg] for **6**•C_6H_6

O(1)-C(4)	1.438(3)
O(1)-H(1O1)	0.87(3)
O(2)-C(5)	1.453(3)
O(2)-H(1O2)	0.86(3)
O(3)-C(9)	1.211(3)
O(4)-C(14)	1.434(3)
O(4)-H(1O4)	0.90(3)
O(5)-C(10)	1.416(3)
O(5)-C(20)	1.431(3)
O(6)-C(24)	1.374(3)
O(6)-C(27)	1.410(3)
C(1)-C(2)	1.542(3)
C(1)-C(11)	1.551(3)
C(1)-C(10)	1.567(3)
C(2)-C(3)	1.536(3)
C(3)-C(4)	1.535(3)
C(4)-C(11)	1.565(3)
C(4)-C(5)	1.576(3)
C(5)-C(6)	1.514(3)
C(6)-C(7)	1.543(3)
C(7)-C(17)	1.528(3)
C(7)-C(8)	1.578(3)
C(8)-C(18)	1.524(3)
C(8)-C(9)	1.559(3)
C(8)-C(14)	1.564(3)
C(9)-C(10)	1.558(3)
C(11)-C(13)	1.528(3)
C(11)-C(12)	1.543(3)
C(14)-C(15)	1.513(3)
C(15)-C(16)	1.526(4)
C(16)-C(17)	1.505(3)
C(17)-C(19)	1.320(3)
C(20)-C(21)	1.505(3)
C(21)-C(26)	1.387(3)
C(21)-C(22)	1.389(3)
C(22)-C(23)	1.388(3)
C(23)-C(24)	1.382(4)
C(24)-C(25)	1.385(4)
C(25)-C(26)	1.390(3)
C(28)-C(29)	1.386(4)
C(28)-C(33)	1.387(4)
C(29)-C(30)	1.375(4)
C(30)-C(31)	1.378(4)
C(31)-C(32)	1.385(4)
C(32)-C(33)	1.377(4)

C(4)-O(1)-H(1O1)	106(2)
C(5)-O(2)-H(1O2)	110(2)
C(14)-O(4)-H(1O4)	108(2)
C(10)-O(5)-C(20)	115.2(2)
C(24)-O(6)-C(27)	117.5(2)
C(2)-C(1)-C(11)	104.0(2)
C(2)-C(1)-C(10)	114.6(2)
C(11)-C(1)-C(10)	122.1(2)
C(3)-C(2)-C(1)	106.9(2)
C(4)-C(3)-C(2)	107.1(2)
O(1)-C(4)-C(3)	106.6(2)
O(1)-C(4)-C(11)	112.6(2)
C(3)-C(4)-C(11)	103.2(2)
O(1)-C(4)-C(5)	108.1(2)
C(3)-C(4)-C(5)	116.3(2)
C(11)-C(4)-C(5)	110.0(2)

Donor-H....Acceptor	D - H	H...A	D...A	D - H...A
O(1)-H(101)...O(2)	0.88(4)	1.89(3)	2.511(3)	126(3)
O(2)-H(102)...O(4)'	0.85(3)	2.14(3)	2.970(2)	162(3)
O(4)-H(104)...O(1)'	0.89(3)	2.10(3)	2.927(3)	155(3)

Symmetry code for O(4)' is: -x,-1/2+y,3/2-z
Symmetry code for O(1)' is: 1+x,y,z

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **6**•C_6H_6

	x	y	z	U(eq)
O(1)	-5255(2)	8669(2)	7327(1)	28(1)
O(2)	-3482(2)	7215(1)	7064(1)	27(1)
O(3)	365(2)	8265(1)	7807(1)	26(1)
O(4)	2398(2)	10253(2)	7341(1)	25(1)
O(5)	-342(2)	9845(1)	8483(1)	26(1)
O(6)	1748(2)	12065(2)	10658(1)	37(1)
C(1)	-2351(2)	10262(2)	7960(1)	22(1)
C(2)	-2905(3)	11012(2)	7503(1)	25(1)
C(3)	-3885(3)	10293(2)	7155(1)	24(1)
C(4)	-3855(2)	9116(2)	7391(1)	21(1)
C(5)	-2776(3)	8279(2)	7127(1)	22(1)
C(6)	-2142(3)	8603(2)	6590(1)	24(1)
C(7)	-1024(2)	9535(2)	6607(1)	21(1)
C(8)	295(2)	9268(2)	6975(1)	20(1)
C(9)	-49(2)	9097(2)	7583(1)	20(1)
C(10)	-723(2)	10023(2)	7939(1)	21(1)
C(11)	-3460(2)	9317(2)	7995(1)	22(1)
C(12)	-4768(3)	9776(2)	8292(1)	29(1)
C(13)	-3006(3)	8278(2)	8304(1)	27(1)
C(14)	1288(2)	10306(2)	6948(1)	23(1)
C(15)	1810(3)	10517(2)	6381(1)	26(1)
C(16)	537(3)	10789(2)	6027(1)	27(1)
C(17)	-552(3)	9879(2)	6043(1)	24(1)
C(18)	1043(3)	8229(2)	6771(1)	24(1)
C(19)	-1088(3)	9463(2)	5595(1)	30(1)
C(20)	1111(3)	10055(2)	8609(1)	30(1)
C(21)	1213(3)	10581(2)	9157(1)	23(1)
C(22)	2436(3)	10450(2)	9460(1)	26(1)
C(23)	2581(3)	10963(2)	9958(1)	28(1)
C(24)	1494(3)	11607(2)	10160(1)	26(1)
C(25)	262(3)	11744(2)	9867(1)	28(1)
C(26)	136(3)	11233(2)	9367(1)	27(1)
C(27)	643(3)	12672(3)	10900(1)	47(1)
C(28)	3198(3)	7165(2)	9099(1)	39(1)
C(29)	4317(3)	6469(2)	9227(1)	37(1)
C(30)	4483(3)	6075(2)	9742(1)	37(1)
C(31)	3538(3)	6382(2)	10138(1)	42(1)
C(32)	2418(3)	7079(2)	10016(1)	42(1)
C(33)	2251(3)	7469(2)	9499(1)	39(1)

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

Anisotropic displacement parameters (A^2 x 10^3) for **6**•C_6H_6
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	16(1)	23(1)	46(1)	-2(1)	-3(1)	-5(1)
O(2)	25(1)	18(1)	38(1)	-2(1)	-4(1)	-5(1)
O(3)	22(1)	24(1)	31(1)	2(1)	0(1)	3(1)
O(4)	16(1)	25(1)	35(1)	-4(1)	-3(1)	0(1)
O(5)	19(1)	38(1)	21(1)	-2(1)	-2(1)	-3(1)
O(6)	35(1)	46(1)	30(1)	-12(1)	-7(1)	1(1)
C(1)	18(1)	20(1)	27(1)	-4(1)	2(1)	1(1)
C(2)	21(1)	18(1)	36(1)	-2(1)	2(1)	1(1)
C(3)	16(1)	22(1)	33(1)	2(1)	0(1)	2(1)
C(4)	12(1)	21(1)	31(1)	-2(1)	0(1)	-1(1)
C(5)	19(1)	18(1)	28(1)	-1(1)	-3(1)	-4(1)
C(6)	20(1)	23(1)	29(1)	-5(1)	1(1)	-2(1)
C(7)	16(1)	21(1)	26(1)	-3(1)	0(1)	-1(1)
C(8)	16(1)	19(1)	25(1)	0(1)	1(1)	0(1)
C(9)	12(1)	18(1)	30(1)	1(1)	-4(1)	-2(1)
C(10)	17(1)	22(1)	24(1)	-2(1)	-2(1)	-1(1)
C(11)	18(1)	20(1)	28(1)	-1(1)	0(1)	2(1)
C(12)	23(1)	30(1)	34(1)	-1(1)	6(1)	0(1)
C(13)	24(1)	26(1)	32(1)	4(1)	2(1)	0(1)
C(14)	17(1)	19(1)	33(1)	-3(1)	-1(1)	0(1)
C(15)	23(1)	22(1)	32(1)	0(1)	8(1)	-3(1)
C(16)	29(1)	26(1)	27(1)	5(1)	4(1)	-2(1)
C(17)	19(1)	25(1)	27(1)	4(1)	1(1)	5(1)
C(18)	23(1)	20(1)	29(1)	0(1)	1(1)	1(1)
C(19)	25(1)	36(2)	28(1)	2(1)	2(1)	3(1)
C(20)	16(1)	46(2)	29(1)	-5(1)	-4(1)	-1(1)
C(21)	21(1)	25(1)	24(1)	3(1)	0(1)	-5(1)
C(22)	16(1)	32(1)	31(1)	-1(1)	-1(1)	1(1)
C(23)	21(1)	34(1)	30(1)	-1(1)	-7(1)	-3(1)
C(24)	29(1)	25(1)	26(1)	-2(1)	-1(1)	-3(1)
C(25)	25(1)	25(1)	34(1)	-1(1)	1(1)	4(1)
C(26)	23(1)	29(1)	29(1)	2(1)	-4(1)	1(1)
C(27)	50(2)	54(2)	37(2)	-19(2)	-2(2)	8(2)
C(28)	41(2)	40(2)	37(2)	3(1)	-1(1)	-8(1)
C(29)	30(2)	38(2)	42(2)	-7(1)	2(1)	-6(1)
C(30)	29(2)	35(2)	47(2)	-3(1)	-3(1)	0(1)
C(31)	44(2)	44(2)	37(2)	2(1)	-2(2)	5(2)
C(32)	40(2)	41(2)	45(2)	-7(2)	5(2)	7(2)
C(33)	34(2)	28(2)	55(2)	-1(1)	-5(2)	4(1)

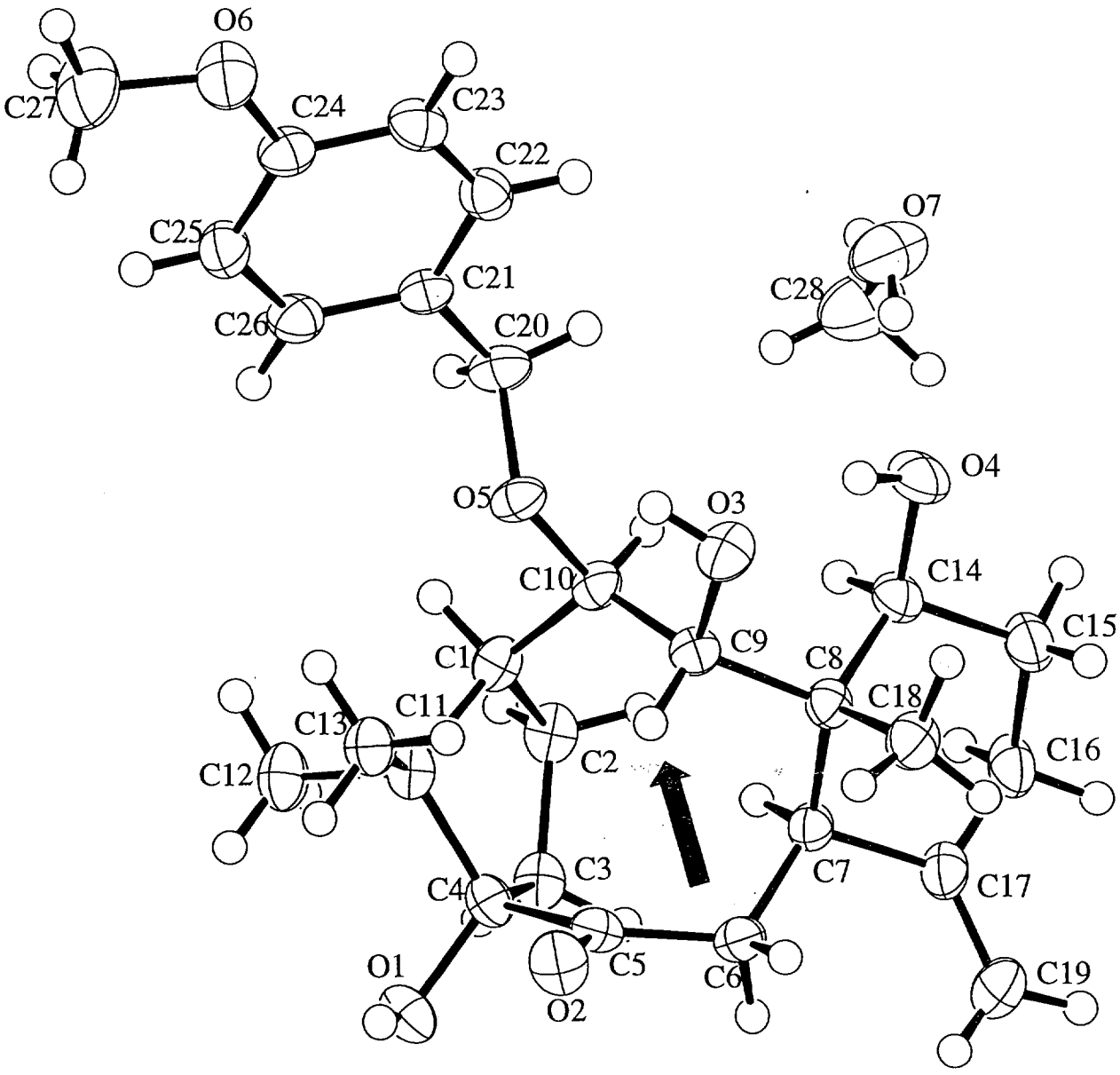
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6**•C_6H_6

	x	y	z	U(eq)
H(1O1)	-5141(32)	7951(27)	7294(11)	42(9) *
H(1O2)	-3155(34)	6747(27)	7293(12)	48(10)*
H(1O4)	2934(34)	9657(27)	7268(12)	47(9) *
H(1)	-2488(2)	10697(2)	8290(1)	26
H(2A)	-3420(3)	11638(2)	7651(1)	30
H(2B)	-2123(3)	11292(2)	7290(1)	30
H(3A)	-4840(3)	10587(2)	7161(1)	28
H(3B)	-3557(3)	10285(2)	6784(1)	28
H(5)	-1995(3)	8174(2)	7382(1)	26
H(6A)	-2902(3)	8835(2)	6353(1)	29
H(6B)	-1711(3)	7949(2)	6431(1)	29
H(7)	-1489(2)	10184(2)	6766(1)	25
H(10)	-271(2)	10721(2)	7831(1)	25
H(12A)	-5104(11)	10428(8)	8109(4)	43
H(12B)	-4516(5)	9964(13)	8655(2)	43
H(12C)	-5499(7)	9223(5)	8296(6)	43
H(13A)	-3689(10)	7700(5)	8249(5)	41
H(13B)	-2945(17)	8447(4)	8681(1)	41
H(13C)	-2100(9)	8036(8)	8176(5)	41
H(14)	704(2)	10947(2)	7045(1)	27
H(15A)	2291(3)	9864(2)	6244(1)	31
H(15B)	2472(3)	11132(2)	6379(1)	31
H(16A)	112(3)	11477(2)	6149(1)	33
H(16B)	851(3)	10896(2)	5659(1)	33
H(18A)	1152(15)	8274(6)	6387(1)	36
H(18B)	491(9)	7586(2)	6860(6)	36
H(18C)	1957(7)	8173(7)	6937(5)	36
H(19A)	-794(3)	9732(2)	5263(1)	36
H(19B)	-1761(3)	8900(2)	5613(1)	36
H(20A)	1517(3)	10547(2)	8341(1)	36
H(20B)	1638(3)	9364(2)	8605(1)	36
H(22)	3168(3)	10013(2)	9328(1)	32
H(23)	3410(3)	10874(2)	10154(1)	34
H(25)	-473(3)	12174(2)	10002(1)	34
H(26)	-690(3)	11330(2)	9169(1)	33
H(27A)	926(9)	12901(15)	11254(4)	70
H(27B)	-185(8)	12214(6)	10925(8)	70
H(27C)	436(15)	13316(10)	10686(5)	70
H(28)	3084(3)	7425(2)	8749(1)	47
H(29)	4960(3)	6267(2)	8961(1)	44
H(30)	5231(3)	5603(2)	9824(1)	44
H(31)	3653(3)	6120(2)	10488(1)	50
H(32)	1780(3)	7283(2)	10283(1)	50
H(33)	1499(3)	7938(2)	9417(1)	47

*Refined isotropically

ORTEP Drawing for **7**•CH_3OH

The molecular structure is drawn with 50% probability displacement ellipsoids for the non-H atoms. The H atoms are drawn with circles of arbitrary radii.


O6
C27
C24
C23
C22
C25
C21
C26
C20
O7
C28
O5
O3
O4
C10
C14
C15
C1
C9
C8
C18
C11
C13
C2
C16
C12
C3
C7
C17
C4
O1
C5
C6
O2
C19

7•CH_3OH

The data collection crystal was cut from a cluster of colorless, intergrown crystals. Examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. All work was done at 173 K using an Oxford Cryosystems Cryostream Cooler. A quadrant of data was measured using the ω scan method with a frame width of 1.0° and a redundancy of 2. (By definition a redundancy of 2 implies that 90% of the data have been measured at least twice.) Data integration was done with Denzo[1], and scaling and merging of the data was done with Scalepack[1]. Merging the data and averaging the symmetry equivalent reflections, including the Friedel pairs, resulted in an Rint value of 0.029. The space group was determined to be $P2_1$ by the teXsan package[2].

The structure was solved by the direct methods procedure in SHELXS-86[3]. Along with the molecule of interest, there is a methanol solvent molecule present in the asymmetric unit. The correct enantiomer was chosen based on the known absolute configuration for a portion of the molecule. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93[4].

The hydrogen atoms were included in the model at calculated positions using a riding model with U(H) = 1.2 * Ueq(attached atom), except for the four hydroxyl H atoms (three on the molecule of interest and one on the methanol molecule) which were refined isotropically. For a methyl group, the torsion angle which defines its orientation was allowed to refine, and these hydrogen atoms were assigned U(H) = 1.5 * Ueq(attached carbon atom). The final refinement cycle was based on all the 2429 intensities and 337 variables and resulted in agreement factors of R1(F) = 0.039 and wR2(F^2) = 0.082. For the subset of data with $I > 2\sigma(I)$, the R1(F) value is 0.034 for 2216 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.14 and -0.16 e/$\AA^3$. Neutral atom scattering factors were used and include terms for anomalous dispersion[5].

All of the hydroxyl H atoms are involved in either intramolecular or intermolecular hydrogen bonds.

References

(1) DENZO: Otwinowski, Z. & Minor, W., Methods in Enzymology, Vol 276: Macromolecular Crystallography, part A, 307-326, (1997), Carter, Jr., C. W. & Sweet, R. M., Eds., Academic Press.

(2) teXsan: Crystal Structure Analysis Package, version 1.7-2, Molecular Structure Corporation, The Woodlands, TX (1995).

(3) SHELXS-86: Sheldrick, G. M., Acta Cryst., (1990), A46, 467-473.

(4) SHELXL-93: Sheldrick, G. M., Universitat Gottingen, Germany, 1993.

(5) International Tables for Crystallography (1992). Volume C. Dordrecht: Kluwer Academic Publishers.

Empirical formula	C27 H38 O6 and methanol
Formula weight	490.62
Temperature	173 K
Wavelength	0.71073 A
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 7.0561(1) A b = 18.3476(4) A c = 10.7886(2) A beta = 107.401(1) deg.
Volume	1332.80(4) A^3
Z	2
Density (calculated)	1.223 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	532
Crystal size	0.23 x 0.23 x 0.31 mm
Theta range for data collection	2.27 to 25.02 deg.
Index ranges	0<=h<=8, 0<=k<=21, -12<=l<=12
Reflections collected	15760
Independent reflections	2429 [R(int) = 0.029]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2429 / 1 / 337
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.034, wR2 = 0.078
R indices (all data)	R1 = 0.039, wR2 = 0.082
Largest diff. peak and hole	0.14 and -0.16 e/A^3

Bond lengths [A] and angles [deg] for **7**•CH_3OH

O(1)-C(4)	1.434(3)
O(1)-H(101)	0.91(4)
O(2)-C(5)	1.219(3)
O(3)-C(9)	1.448(3)
O(3)-H(103)	0.86(4)
O(4)-C(14)	1.439(3)
O(4)-H(104)	0.91(4)
O(5)-C(20)	1.437(3)
O(5)-C(10)	1.449(3)
O(6)-C(24)	1.377(3)
O(6)-C(27)	1.418(4)
O(7)-C(28)	1.424(4)
O(7)-H(107)	0.87(5)
C(1)-C(2)	1.551(3)
C(1)-C(10)	1.552(3)
C(1)-C(11)	1.554(3)
C(2)-C(3)	1.543(4)
C(3)-C(4)	1.531(3)
C(4)-C(5)	1.550(3)
C(4)-C(11)	1.570(4)
C(5)-C(6)	1.510(3)
C(6)-C(7)	1.524(3)
C(7)-C(17)	1.528(3)
C(7)-C(8)	1.563(3)
C(8)-C(18)	1.539(3)
C(8)-C(14)	1.547(3)
C(8)-C(9)	1.554(3)
C(9)-C(10)	1.571(3)
C(11)-C(13)	1.526(3)
C(11)-C(12)	1.545(3)
C(14)-C(15)	1.514(3)
C(15)-C(16)	1.530(4)
C(16)-C(17)	1.500(4)
C(17)-C(19)	1.329(4)
C(20)-C(21)	1.498(3)
C(21)-C(26)	1.387(3)
C(21)-C(22)	1.393(3)
C(22)-C(23)	1.372(4)
C(23)-C(24)	1.391(4)
C(24)-C(25)	1.382(3)
C(25)-C(26)	1.392(4)

C(4)-O(1)-H(101)	106(2)
C(9)-O(3)-H(103)	103(2)
C(14)-O(4)-H(104)	106(2)
C(20)-O(5)-C(10)	114.7(2)
C(24)-O(6)-C(27)	117.5(2)
C(28)-O(7)-H(107)	112(3)
C(2)-C(1)-C(10)	117.3(2)
C(2)-C(1)-C(11)	103.2(2)
C(10)-C(1)-C(11)	119.9(2)
C(3)-C(2)-C(1)	107.3(2)
C(4)-C(3)-C(2)	106.8(2)
O(1)-C(4)-C(3)	108.6(2)
O(1)-C(4)-C(5)	104.0(2)
C(3)-C(4)-C(5)	115.6(2)
O(1)-C(4)-C(11)	112.5(2)
C(3)-C(4)-C(11)	102.9(2)
C(5)-C(4)-C(11)	113.4(2)
O(2)-C(5)-C(6)	119.1(2)
O(2)-C(5)-C(4)	116.9(2)
C(6)-C(5)-C(4)	123.4(2)

C(6)-C(7)-C(17)	112.1(2)
C(6)-C(7)-C(8)	114.1(2)
C(17)-C(7)-C(8)	109.5(2)
C(18)-C(8)-C(14)	111.3(2)
C(18)-C(8)-C(9)	107.6(2)
C(14)-C(8)-C(9)	110.0(2)
C(18)-C(8)-C(7)	109.8(2)
C(14)-C(8)-C(7)	107.3(2)
C(9)-C(8)-C(7)	111.0(2)
O(3)-C(9)-C(8)	105.3(2)
O(3)-C(9)-C(10)	106.8(2)
C(8)-C(9)-C(10)	119.8(2)
O(5)-C(10)-C(1)	106.0(2)
O(5)-C(10)-C(9)	103.4(2)
C(1)-C(10)-C(9)	124.1(2)
C(13)-C(11)-C(12)	106.6(2)
C(13)-C(11)-C(1)	116.3(2)
C(12)-C(11)-C(1)	106.8(2)
C(13)-C(11)-C(4)	115.9(2)
C(12)-C(11)-C(4)	107.2(2)
C(1)-C(11)-C(4)	103.4(2)
O(4)-C(14)-C(15)	107.4(2)
O(4)-C(14)-C(8)	112.7(2)
C(15)-C(14)-C(8)	113.3(2)
C(14)-C(15)-C(16)	109.8(2)
C(17)-C(16)-C(15)	110.4(2)
C(19)-C(17)-C(16)	122.1(2)
C(19)-C(17)-C(7)	124.5(2)
C(16)-C(17)-C(7)	113.4(2)
O(5)-C(20)-C(21)	107.1(2)
C(26)-C(21)-C(22)	117.8(2)
C(26)-C(21)-C(20)	120.4(2)
C(22)-C(21)-C(20)	121.7(2)
C(23)-C(22)-C(21)	121.4(2)
C(22)-C(23)-C(24)	119.9(2)
O(6)-C(24)-C(25)	124.3(2)
O(6)-C(24)-C(23)	115.4(2)
C(25)-C(24)-C(23)	120.3(2)
C(24)-C(25)-C(26)	118.9(2)
C(21)-C(26)-C(25)	121.8(2)

Donor-H....Acceptor	D - H	H...A	D...A	D - H...A
O(1)-H(101).. O(2)	0.91(4)	2.31(4)	2.688(3)	104(2)
O(1)-H(101).. O(7)'	0.91(4)	2.08(4)	2.951(3)	161(3)
O(3)-H(103).. O(5)	0.86(3)	1.85(3)	2.474(3)	127(3)
O(7)-H(107).. O(4)	0.87(5)	1.95(5)	2.806(3)	167(5)
O(4)-H(104).. O(3)	0.91(3)	1.83(3)	2.667(3)	152(3)

The primed atom is related to the corresponding unprimed atom by:
1-x, -1/2+y, 1-z

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **7**•CH_3OH

	x	y	z	U(eq)
O(1)	3168(3)	1567(1)	6848(2)	35(1)
O(2)	5367(3)	1442(1)	5210(2)	38(1)
O(3)	6833(2)	3537(1)	3435(2)	35(1)
O(4)	4027(3)	4246(1)	1625(2)	40(1)
O(5)	6735(2)	4016(1)	5558(2)	28(1)
O(6)	14839(3)	5551(1)	8138(2)	44(1)
O(7)	3193(4)	5713(1)	1980(2)	56(1)
C(1)	3843(3)	3480(1)	5913(2)	27(1)
C(2)	1562(3)	3362(1)	5479(2)	30(1)
C(3)	1193(3)	2540(1)	5609(2)	30(1)
C(4)	3232(3)	2170(1)	6015(2)	27(1)
C(5)	3886(4)	1823(1)	4899(2)	28(1)
C(6)	2633(4)	1843(1)	3493(2)	30(1)
C(7)	1909(3)	2562(1)	2807(2)	25(1)
C(8)	3587(3)	3037(1)	2544(2)	26(1)
C(9)	5243(3)	3206(1)	3830(2)	26(1)
C(10)	4797(3)	3729(1)	4860(2)	26(1)
C(11)	4650(3)	2794(1)	6748(2)	28(1)
C(12)	4249(4)	2906(2)	8066(2)	38(1)
C(13)	6870(4)	2646(1)	7051(2)	31(1)
C(14)	2619(3)	3754(1)	1906(2)	29(1)
C(15)	962(4)	3636(2)	654(2)	36(1)
C(16)	-646(4)	3151(2)	908(2)	37(1)
C(17)	240(4)	2451(2)	1539(2)	32(1)
C(18)	4554(4)	2620(2)	1652(2)	34(1)
C(19)	-394(4)	1805(2)	1023(3)	46(1)
C(20)	6796(4)	4792(1)	5747(3)	33(1)
C(21)	8918(3)	4994(1)	6396(2)	28(1)
C(22)	10053(4)	5357(1)	5733(2)	31(1)
C(23)	12000(4)	5536(1)	6333(2)	32(1)
C(24)	12884(3)	5344(1)	7624(2)	31(1)
C(25)	11814(4)	4971(2)	8304(2)	34(1)
C(26)	9835(4)	4801(1)	7680(2)	32(1)
C(27)	15732(4)	5451(2)	9491(3)	62(1)
C(28)	1409(5)	5680(2)	2338(4)	64(1)

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

Anisotropic displacement parameters (A^2 x 10^3) for 7•CH_3OH

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
O(1)	35(1)	38(1)	34(1)	10(1)	14(1)	1(1)
O(2)	40(1)	38(1)	38(1)	1(1)	13(1)	13(1)
O(3)	23(1)	45(1)	37(1)	-6(1)	12(1)	-7(1)
O(4)	36(1)	41(1)	42(1)	11(1)	10(1)	-10(1)
O(5)	22(1)	24(1)	35(1)	-4(1)	2(1)	-2(1)
O(6)	29(1)	62(1)	40(1)	2(1)	10(1)	-12(1)
O(7)	59(2)	47(1)	67(1)	-16(1)	27(1)	-15(1)
C(1)	24(1)	31(1)	27(1)	-6(1)	8(1)	4(1)
C(2)	23(1)	37(1)	31(1)	-2(1)	10(1)	6(1)
C(3)	21(1)	40(1)	29(1)	-1(1)	9(1)	0(1)
C(4)	25(1)	31(1)	25(1)	4(1)	10(1)	2(1)
C(5)	31(1)	23(1)	31(1)	2(1)	12(1)	-1(1)
C(6)	36(1)	26(1)	30(1)	-4(1)	11(1)	-7(1)
C(7)	26(1)	29(1)	22(1)	-2(1)	8(1)	-4(1)
C(8)	25(1)	29(1)	24(1)	-1(1)	9(1)	-2(1)
C(9)	20(1)	28(1)	29(1)	0(1)	9(1)	-2(1)
C(10)	19(1)	26(1)	28(1)	-2(1)	1(1)	1(1)
C(11)	23(1)	36(1)	25(1)	-1(1)	7(1)	4(1)
C(12)	35(1)	53(2)	27(1)	-3(1)	12(1)	2(1)
C(13)	26(1)	36(1)	30(1)	1(1)	6(1)	4(1)
C(14)	29(1)	33(1)	28(1)	4(1)	10(1)	-6(1)
C(15)	35(1)	44(2)	27(1)	7(1)	5(1)	-3(1)
C(16)	30(1)	52(2)	25(1)	6(1)	2(1)	-6(1)
C(17)	26(1)	44(2)	25(1)	0(1)	7(1)	-9(1)
C(18)	33(1)	41(2)	31(1)	-4(1)	14(1)	-6(1)
C(19)	48(2)	51(2)	34(1)	-5(1)	2(1)	-16(1)
C(20)	30(1)	23(1)	44(2)	-3(1)	9(1)	0(1)
C(21)	29(1)	21(1)	33(1)	-3(1)	10(1)	0(1)
C(22)	33(1)	28(1)	31(1)	2(1)	10(1)	3(1)
C(23)	33(1)	32(1)	38(1)	2(1)	19(1)	-3(1)
C(24)	26(1)	31(1)	37(1)	-2(1)	12(1)	-5(1)
C(25)	34(1)	41(1)	28(1)	1(1)	9(1)	-7(1)
C(26)	33(1)	31(1)	36(1)	-1(1)	16(1)	-8(1)
C(27)	36(2)	96(3)	45(2)	1(2)	0(1)	-23(2)
C(28)	54(2)	59(2)	81(2)	-16(2)	25(2)	-15(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **7**•CH_3OH

	x	y	z	U(eq)
H(1O1)	4394(55)	1361(20)	7068(34)	62(11)*
H(1O3)	7527(47)	3752(19)	4128(34)	50(10)*
H(1O4)	5233(52)	4113(18)	2162(32)	50(9) *
H(1O7)	3650(66)	5283(30)	1886(42)	94(16)*
H(1)	4075(3)	3884(1)	6535(2)	33
H(2A)	959(3)	3642(1)	6024(2)	36
H(2B)	988(3)	3517(1)	4585(2)	36
H(3A)	517(3)	2459(1)	6259(2)	36
H(3B)	378(3)	2345(1)	4787(2)	36
H(6A)	1466(4)	1547(1)	3424(2)	36
H(6B)	3383(4)	1597(1)	2995(2)	36
H(7)	1350(3)	2845(1)	3384(2)	30
H(9)	5728(3)	2742(1)	4259(2)	31
H(10)	4000(3)	4135(1)	4386(2)	31
H(12A)	2862(6)	3002(11)	7922(3)	57
H(12B)	5014(23)	3312(7)	8511(9)	57
H(12C)	4622(27)	2475(4)	8585(8)	57
H(13A)	7198(6)	2593(10)	6254(2)	47
H(13B)	7203(6)	2206(5)	7551(15)	47
H(13C)	7605(4)	3046(5)	7539(15)	47
H(14)	2049(3)	3999(1)	2519(2)	35
H(15A)	1489(4)	3407(2)	16(2)	43
H(15B)	393(4)	4102(2)	309(2)	43
H(16A)	-1276(4)	3405(2)	1469(2)	44
H(16B)	-1654(4)	3046(2)	94(2)	44
H(18A)	3542(4)	2381(8)	976(10)	51
H(18B)	5459(20)	2263(7)	2151(4)	51
H(18C)	5263(22)	2956(2)	1272(13)	51
H(19A)	-1419(4)	1777(2)	246(3)	56
H(19B)	187(4)	1381(2)	1438(3)	56
H(20A)	5975(4)	4931(1)	6286(3)	40
H(20B)	6305(4)	5040(1)	4918(3)	40
H(22)	9479(4)	5482(1)	4866(2)	37
H(23)	12728(4)	5784(1)	5877(2)	39
H(25)	12405(4)	4835(2)	9164(2)	41
H(26)	9107(4)	4552(1)	8135(2)	38
H(27A)	17051(15)	5650(13)	9739(5)	92
H(27B)	15794(33)	4940(2)	9690(5)	92
H(27C)	14957(21)	5696(11)	9959(3)	92
H(28A)	439(14)	5396(12)	1711(15)	95
H(28B)	908(21)	6164(2)	2367(25)	95
H(28C)	1678(10)	5458(13)	3179(12)	95

*Refined isotropically