Synthesis of Oxepanes and Fused Bis-oxepanes via Biomimetic, *Endo*-regioselective Tandem Oxacyclizations of Polyepoxides

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SUPPORTING INFORMATION

(34 pages)

Representative experimental procedure for the tandem oxacyclization of diepoxide-*tert*-butylcarbonate **7** to fused oxepane-cyclic carbonate **14**

Charaterization data for compounds **3 – 8**, **10 – 15**, **20 – 23**

Thermal ellipsoid figures and X-ray crystallographic tables for compounds **11**, **14**, **22**

Representative Procedure for *Endo*-selective Polyepoxide Oxacyclization: Diepoxide-tert-butylcarbonate **7** (85 mg, 0.3 mmol) was added to a 50 mL oven-dried round-bottom flask containing a magnetic stir bar, and anhydrous CH_2Cl_2 (5 mL) was added under inert atmosphere. The solution was stirred and cooled to –40°C, and precooled BF_3-OEt_2 in CH_2Cl_2 (1.0 mL of a 0.30 M solution freshly prepared from redistilled BF_3-OEt_2 and anhydrous CH_2Cl_2) was added dropwise. The reaction mixture was stirred for 20 minutes while maintaining temperature between –40°C and –50°C, and was then quenched with H_2O (0.2 mL). The reaction mixture was allowed to warm to rt, washed with CH_2Cl_2 (3 x 15 mL), and the combined organic layers were dried over $MgSO_4$. After removal of volatiles by rotary evaporation, the crude product was dissolved in anhydrous CH_2Cl_2 (10 mL), and sequentially treated with 4-(dimethylamino)pyridine (1 mg), triethylamine (0.42 mL, 3 mmol), and acetic anhydride (0.11 mL, 1.2 mmol). The reaction mixture was stirred for 1 h at rt, then washed with water (2 x 1.5 mL) and brine (1.5 mL), the organic layer was dried over $MgSO_4$, and then concentrated to give the crude acetylated product. Purification by silica gel flash chromatography (hexanes : EtOAc, gradient elution 9 : 1 to 4 : 1) provided fused oxepane-cyclic carbonate product **14** (48 mg, 60%). m.p. 119-121°C; $[\alpha]^{23}_D$ = -13.28 ($CHCl_3$, c = 1.02); IR 3133, 2361, 2339, 1756, 1629, 1401, 1245, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, *J* = 6.8 Hz, 1H), 4.19 (dd, *J* = 9.6, 6.0 Hz, 1H), 4.12-4.00 (m, 2H), 2.16 (s, 1H), 2.08-1.92 (m, 2H), 1.84-1.74 (m, 2H), 1.46 (d, *J* = 0.8 Hz, 3H), 1.21 (s, 3H), 1.18 (m, 3H); ^{13}C NMR (100 MHz) δ 169.90, 148.08, 83.43, 79.34, 77.03, 66.87, 65.07, 34.08, 28.16, 22.34, 22.06, 21.15, 19.05; Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.26; H, 7.40.

(*R, R, R*)-Diepoxide-ketone (3): IR (neat) 2964, 2928, 1717, 1379, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69-2.63 (m, 1H), 2.61-2.56 (m, 1H), 2.55-2.49 (m, 2H), 2.07 (s, 1H), 1.85-1.74 (m, 1H), 1.70-1.42 (m, 5H), 1.19 (s, 3H), 1.18 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.62, 63.73, 62.16, 60.69, 58.38, 40.15, 35.15, 29.96, 24.81, 24.52, 22.72, 18.64, 16.66; Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.71; H, 9.82.

(*R, R, R*)-Diepoxide-acetate (4): IR (neat) 2964, 2930, 1744, 1378, 1235, 1037 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (AB q, *J* = 12.0, 4.5 Hz, 1H), 4.04 (AB q, *J* = 12.0, 6.9 Hz, 1H), 3.01 (dd, *J* = 6.9, 4.5 Hz, 1H), 2.70 (m, 1H), 2.09 (s, 3H), 1.90-1.76 (m, 1H), 1.72-1.49 (m, 3H), 1.33 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.06, 63.83, 63.45, 60.33, 59.49, 58.68, 34.97, 25.00, 24.54, 20.99, 18.86, 17.20; Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.16; H, 8.86.

(*S, S, R*)-Diepoxide-acetate (5): IR (neat) 2964, 2930, 1744, 1458, 1378, 1236, 1037 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (AB q, *J* = 12.0, 4.2 Hz, 1H), 3.92 (AB q, *J* = 12.3, 6.9 Hz, 1H), 2.89 (dd, *J* = 6.9, 4.2 Hz), 2.58 (m, 1H), 1.97 (s, 3H), 1.63-1.42 (m, 4H), 1.20 (s, 3H), 1.18 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.67, 63.62, 63.21, 60.10, 59.70, 58.16, 35.15, 24.73, 24.49, 20.71, 18.61, 16.66.

(*R, R,*)-Diepoxide-acetate (6): IR (neat) 2963, 2931, 1744, 1377, 1238, 1040 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.19 (d, *J* = 16 Hz, 1H), 3.98 (d, *J* = 16 Hz, 1H), 2.74-2.62 (m, 3H), 2.03 (s, 3H), 1.98-1.44 (m, 4H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.60, 65.93, 63.69, 58.55, 56.80, 50.45, 28.57, 24.83, 23.91, 20.80, 18.71; Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.51; H, 8.54.

(*R, R, R*)-Diepoxide-*tert*-butylcarbonate (7): IR (neat) 2977, 2932, 1744, 1459, 1373, 1279, 1257, 1164, 1095 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17-4.06 (m, 2H), 2.99 (t, *J* = 5.4 Hz, 1H), 2.66 (t, *J* = 6.0 Hz, 1H), 1.80-1.72 (m, 1H), 1.69-1.50 (m, 3H), 1.43 (s, 9H), 1.27 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.35, 82.66, 66.83, 65.55, 65.48, 63.86, 63.71, 60.21, 59.70, 59.16, 58.88, 58.56, 34.82, 27.80, 24.89, 24.45, 18.73, 17.03; Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 63.00; H, 9.19.

(*R, R*)-Diepoxide-*tert*-butylcarbonate (8): IR (neat) 2979, 2933, 1744, 1278, 1256, 1161 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (s, 2H), 2.82-2.76 (m, 1H), 2.75-2.69 (m, 2H), 1.72-1.54 (m, 2H), 1.48 (s, 9H), 1.31 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.40, 82.82, 68.51, 63.79, 58.73, 56.88, 50.72, 28.57, 27.92, 25.00, 23.96, 18.86; Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.47; H, 8.93.

Oxepanol-ketone (10): IR (neat) 3527(br), 2976, 2876, 1733, 1719, 1373, 1241, 1056, 1027 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.83 (dd, *J* = 10.8, 2.1Hz, 1H), 3.82-3.72 (m, 1H), 2.58-2.34 (m, 2H), 2.13 (s, 3H), 1.25 (s, 3H), 1.21 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.50, 171.37, 85.83, 83.97, 76.67, 70.81, 39.86, 34.93, 30.32, 28.04, 26.24, 24.79, 23.84, 22.61, 21.44. HRMS Calcd. for $C_{15}H_{26}O_5Li$ $[(M+Li)]^+$ 293.1940, found 293.1947.

Oxepanol-diacetate (11): m.p. 96-98 °C; $[\alpha]^{23}_D$ = +11.2 ($CHCl_3$, c = 1.17); IR (KBr) 3524(br), 2992, 2952, 1735, 1720, 1398, 1246 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (d, *J* = 7.2 Hz, 1H), 4.39 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.99 (dd, *J* = 11.4, 9.2 Hz, 1H), 3.82 (dd, *J* = 9.2, 3.2 Hz, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 1.94-1.72 (m, 4H), 1.58-1.48 (m, 1H), 1.24 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.32, 170.24, 78.40, 75.39, 73.60, 65.00, 60.49, 38.04, 28.81, 23.25, 21.49, 21.15, 14.24; Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.28; H, 8.44.

Oxepanol-diacetate (12): $[\alpha]^{23}_{D}$ = -27.4 ($CHCl_3$, c = 1.02); IR (neat) 3418(br), 2976, 2941, 1739, 1463, 1439, 1372, 1242, 1086, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.76 (d, *J* = 9.2 Hz, 1H), 4.42 (dd, *J* = 11.0, 2.6 Hz, 1H), 3.98 (dd, *J* = 11.2, 8.8 Hz, 1H), 3.65 (dd, *J* = 9.0, 2.6 Hz, 1H), 2.053 (s, 3H), 2.048 (s, 3H), 1.88-1.76 (m, 2H), 1.70-1.60 (m, 1H), 1.56-1.48 (m, 1H), 1.20 (s, 3H), 1.19 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.66, 170.96, 79.96, 76.56, 73.95, 65.28, 43.17, 26.58, 24.93, 23.81, 22.14, 21.80, 21.57; Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.40; H, 8.43.

Oxepanol-diacetate (13): IR (neat) 3463(br), 2936, 1738, 1372, 1243, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.79 (d, *J* = 8.8 Hz, 1H), 4.05 (s, 2H), 3.51 (dd, *J* = 7.2, 1.2 Hz, 2H), 2.89 (s, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.78-1.70 (m, 1H), 1.68-1.54 (m, 1H), 1.202 (s, 3H), 1.197 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.30, 170.45, 78.79, 77.16, 7.48, 68.38, 66.47, 33.40, 26.08, 24.04, 22.56, 21.41, 21.11; Anal. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.87; H, 8.16.

Oxepane-spirocarbonate (15): m.p. 74-76 °C; $[\alpha]^{23}_{D}$ = -6.1 ($CHCl_3$, c = 0.71); IR (neat) 2980, 2940, 1805, 1736, 1373, 1244, 1058 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.91 (d, *J* = 7.6 Hz, 1H), 4.47 (d, *J* = 8.8 Hz, 1H), 4.17 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.93 (dd, *J* = 12.4, 0.8 Hz, 1H), 3.54 (dd, *J* = 12.4, 2.0 Hz, 1H), 2.12 (s, 3H), 2.18-1.98 (m, 2H), 1.89-1.80 (m, 1H), 1.74-1.63 (m, 1H), 1.19 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.06, 154.38, 82.95, 78.18, 77.41, 72.84, 66.50, 31.43, 27.73, 21.67, 21.64, 21.15; Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.81; H, 7.02. Found: C, 55.84; H, 7.00.

(*R, R, R, R, R*)-Triepoxide-*tert*-butylcarbonate (20): IR (neat) 2971, 2932, 1743, 1460, 1279, 1164, 861 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (AB q, *J* = 11.6, 5.2 Hz, 1H), 4.11 (AB q, *J* = 12.0, 6.0 Hz, 1H), 3.01 (t, *J* = 5.6 Hz, 1H), 2.74-2.66 (m, 2H), 1.82-1.70 (m, 2H), 1.70-1.54

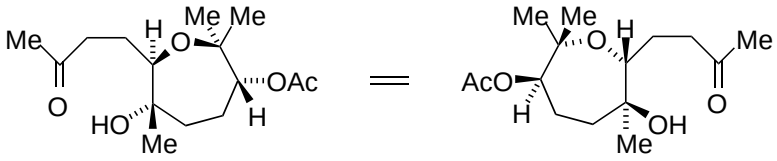
(m, 6H), 1.47 (s, 9H), 1.31 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.43, 82.81, 65.56, 63.97, 62.64, 60.58, 60.26, 59.21, 58.61, 35.32, 34.82, 27.88, 25.01, 24.74, 24.32, 18.82, 17.12, 16.77.

(*R, R, R, R*)-Triepoxide-*tert*-butylcarbonate (21): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (s, 2H), 2.78-2.62 (m, 4H), 1.95-1.72 (m, 3H), 1.68-1.51 (m, 5H), 1.46 (s, 9H), 1.28 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.34, 82.76, 68.45, 63.96, 62.64, 60.62, 58.61, 56.78, 50.69, 35.30, 28.50, 27.87, 24.99, 24.72, 23.73, 18.81, 16.79.

Fused bisoxepane-cyclic carbonate *p*-bromobenzoate ester (22): m.p. 203-205°C; $[\alpha]^{23}_{D}$ = -10.2 ($CHCl_3$, c = 0.98); IR (KBr) 3130, 2985, 2359, 1750, 1724, 1271, 1100 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 9.2 Hz, 2H), 5.17 (d, *J* = 6.8 Hz, 1H), 4.22-4.12 (m, 2H), 4.08-4.02 (m, 1H), 3.63 (dd, *J* = 11.2, 2.4 Hz, 1H), 2.25 (dq, *J* = 16.0, 2.8 Hz, 1H), 2.12-1.96 (m, 3H), 1.94-1.70 (m, 2H), 1.62-1.50 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.72, 148.82, 132.18, 130.95, 129.06, 128.64, 83.10, 80.60, 79.20, 78.66, 78.13, 66.90, 63.74, 38.14, 36.12, 28.53, 28.16, 23.18, 22.62, 21.91, 16.43.

Fused bisoxepane-cyclic carbonate *p*-bromobenzoate ester (23): IR (neat) 2977, 2936, 1801, 1718, 1590, 1274, 1100, 1066 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 5.18 (d, *J* = 6.8 Hz, 1H), 4.21 (d, *J* = 8.4 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 3.70-3.62 (m, 2H), 2.17 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.10-2.02 (m, 2H), 1.92-1.73 (m, 3H), 1.66-1.60 (m, 1H), 1.55-1.50 (m, 1H), 1.30 (s, 3H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.92, 154.32, 132.24, 131.02, 129.18, 128.66, 85.47, 81.11, 79.69, 78.23, 78.13, 73.81, 66.63, 34.91, 34.62, 28.70, 27.64, 23.43, 22.17, 17.05. HRMS Calcd. for $C_{22}H_{27}O_7Br$ $[M]^+$ 491.1080, found 491.1098.

Crystal Structure Analysis of Compound 11:



A suitable crystal of compound **11** was mounted on a glass fiber using epoxy cement. Diffraction intensity data were measured at room temperature (omega scans) using graphite monochromated CuK_{α} radiation (1.54178 Å) on a Siemens P4/RA diffractometer. Three representative reflections were monitored after every 97 reflections as a check on instrument and crystal stability; no appreciable decay was observed. Lorentz, polarization, and an absorption correction, based on a series of psi scans, were applied to the data (XSCANS). The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10). Hydrogen atoms were placed at their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij}'s related to the atom's ridden upon. The C-H distances were fixed at 0.93 Å, 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. The weighting scheme used during refinement was $1/\sigma^2$, based on counting statistics. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography.* Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software. Additional details of data collection and structure refinement are given in Table 1.

The Flack parameter was –3.8(14) and approximately 4 for the inverted structure, therefore crystallographic determination of the absolute configuration of the molecule is uncertain.

Thermal ellipsoid figure for compound **11**.

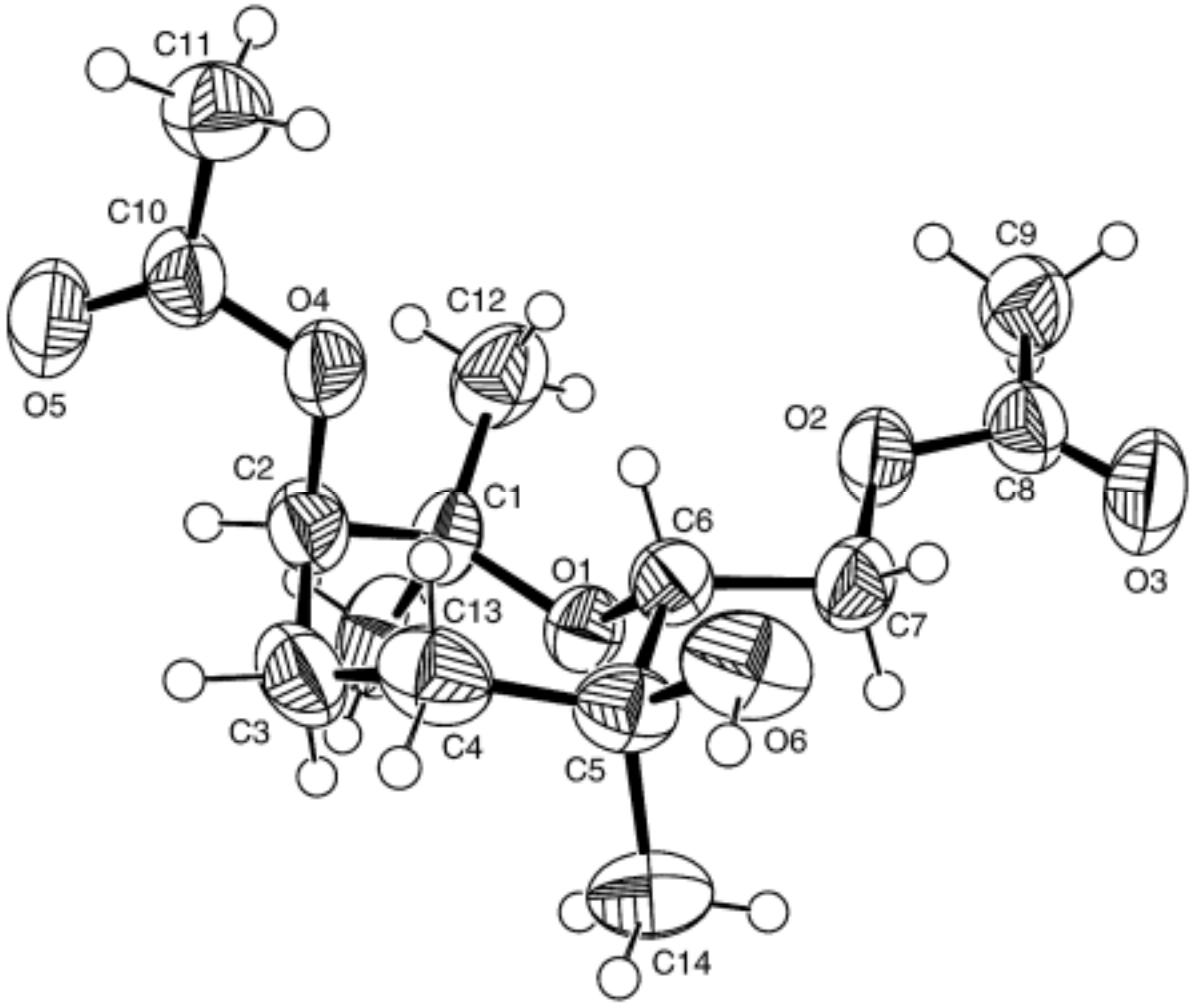


Table 1. Crystal data and structure refinement for compound **11**.

Identification code	xw289fr2	
Empirical formula	$C_{14}H_{24}O_6$	
Formula weight	288.33	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.7703(3) Å	α= 90°.
	b = 15.9227(12) Å	β= 99.446(4)°.
	c = 7.3866(5) Å	γ = 90°.
Volume	785.49(9) $Å^3$	
Z	2	
Density (calculated)	1.219 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	312	
Crystal size	0.74 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.56 to 22.67°.	
Index ranges	$-6 \le h \le 6$, $-17 \le k \le 17$, $-8 \le l \le 8$	
Reflections collected	2261	
Independent reflections	1993 [R(int) = 0.0281]	
Completeness to theta = 22.67°	97.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.5033 and 0.4587	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1993 / 1 / 191	
Goodness-of-fit on F^2	1.168	
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0907	
R indices (all data)	R1 = 0.0358, wR2 = 0.1129	
Absolute structure parameter	-3.8(14)	
Extinction coefficient	0.128(11)	
Largest diff. peak and hole	0.130 and -0.112 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10137(3)	1821(1)	5014(2)	48(1)
O(2)	6914(3)	951(1)	6051(3)	60(1)
O(3)	6062(4)	-313(2)	6876(4)	90(1)
O(4)	8026(3)	3069(1)	1789(3)	60(1)
O(5)	8680(4)	4319(2)	722(4)	94(1)
O(6)	8852(4)	337(2)	1310(4)	74(1)
C(1)	9846(5)	2710(2)	4834(4)	52(1)
C(2)	10019(4)	3030(2)	2901(4)	57(1)
C(3)	11341(5)	2494(2)	1873(5)	69(1)
C(4)	10422(5)	1676(2)	1022(4)	65(1)
C(5)	10113(4)	959(2)	2326(4)	54(1)
C(6)	8905(4)	1280(2)	3776(4)	47(1)
C(7)	8205(5)	584(2)	4884(5)	59(1)
C(8)	5950(5)	434(2)	6995(4)	59(1)
C(9)	4713(6)	892(2)	8150(5)	72(1)
C(10)	7576(4)	3737(2)	735(4)	55(1)
C(11)	5539(5)	3685(2)	-351(4)	66(1)
C(12)	7885(6)	2959(2)	5440(5)	75(1)
C(13)	11626(6)	3071(2)	6163(5)	80(1)
C(14)	12102(5)	583(2)	3199(5)	71(1)

Table 3. Bond lengths [Å] and angles [°] for compound **11**.

O(1)-C(6)	1.423(4)	C(2)-C(3)-C(4)	116.6(3)
O(1)-C(1)	1.433(3)	C(5)-C(4)-C(3)	117.6(2)
O(2)-C(8)	1.318(4)	O(6)-C(5)-C(14)	111.1(3)
O(2)-C(7)	1.447(4)	O(6)-C(5)-C(4)	108.4(3)
O(3)-C(8)	1.197(4)	C(14)-C(5)-C(4)	111.0(3)
O(4)-C(10)	1.323(4)	O(6)-C(5)-C(6)	104.7(2)
O(4)-C(2)	1.461(4)	C(14)-C(5)-C(6)	111.8(3)
O(5)-C(10)	1.191(4)	C(4)-C(5)-C(6)	109.5(2)
O(6)-C(5)	1.436(4)	O(1)-C(6)-C(7)	107.5(2)
C(1)-C(12)	1.522(5)	O(1)-C(6)-C(5)	109.0(2)
C(1)-C(13)	1.536(5)	C(7)-C(6)-C(5)	112.8(2)
C(1)-C(2)	1.538(4)	O(2)-C(7)-C(6)	107.6(2)
C(2)-C(3)	1.526(5)	O(3)-C(8)-O(2)	122.6(3)
C(3)-C(4)	1.532(5)	O(3)-C(8)-C(9)	125.4(3)
C(4)-C(5)	1.530(5)	O(2)-C(8)-C(9)	111.9(3)
C(5)-C(14)	1.517(5)	O(5)-C(10)-O(4)	123.0(3)
C(5)-C(6)	1.538(4)	O(5)-C(10)-C(11)	124.7(3)
C(6)-C(7)	1.499(4)	O(4)-C(10)-C(11)	112.2(3)
C(8)-C(9)	1.482(5)		
C(10)-C(11)	1.480(4)		
C(6)-O(1)-C(1)	118.8(2)		
C(8)-O(2)-C(7)	117.6(2)		
C(10)-O(4)-C(2)	117.9(2)		
O(1)-C(1)-C(12)	110.1(2)		
O(1)-C(1)-C(13)	103.2(3)		
C(12)-C(1)-C(13)	110.2(3)		
O(1)-C(1)-C(2)	112.5(2)		
C(12)-C(1)-C(2)	113.0(3)	Symmetry transformations used to generate	
C(13)-C(1)-C(2)	107.3(3)	equivalent atoms:	
O(4)-C(2)-C(3)	107.9(2)		
O(4)-C(2)-C(1)	109.4(2)		
C(3)-C(2)-C(1)	114.6(3)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	55(1)	43(1)	46(1)	-1(1)	9(1)	-1(1)
O(2)	71(2)	41(1)	76(1)	1(1)	34(1)	-3(1)
O(3)	116(2)	53(2)	112(2)	13(1)	54(2)	-6(2)
O(4)	55(1)	51(1)	69(1)	13(1)	-1(1)	-12(1)
O(5)	77(2)	85(2)	113(2)	51(2)	-7(1)	-23(2)
O(6)	68(2)	78(2)	76(2)	-35(1)	11(1)	1(1)
C(1)	67(2)	35(2)	55(2)	2(1)	10(1)	-6(1)
C(2)	49(2)	60(2)	60(2)	11(2)	3(1)	-12(2)
C(3)	54(2)	90(3)	65(2)	22(2)	15(2)	-12(2)
C(4)	60(2)	90(2)	50(2)	-3(2)	21(1)	6(2)
C(5)	51(2)	56(2)	56(2)	-13(1)	10(1)	4(1)
C(6)	49(2)	42(1)	52(2)	-7(1)	12(1)	-1(1)
C(7)	68(2)	39(2)	76(2)	1(1)	27(2)	2(1)
C(8)	58(2)	62(2)	60(2)	10(2)	14(1)	-6(2)
C(9)	81(2)	70(2)	72(2)	12(2)	30(2)	3(2)
C(10)	58(2)	59(2)	51(2)	8(1)	14(1)	-7(2)
C(11)	60(2)	75(2)	62(2)	2(2)	8(2)	5(2)
C(12)	97(3)	56(2)	77(2)	0(2)	32(2)	16(2)
C(13)	106(3)	61(2)	65(2)	-1(2)	-11(2)	-21(2)
C(14)	61(2)	80(2)	72(2)	-12(2)	12(2)	22(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **11**.

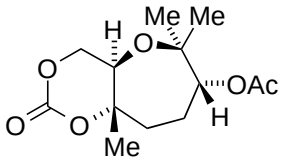
	x	y	z	U(eq)
H(2A)	10572	3600	3015	69
H(3A)	12551	2354	2716	83
H(3B)	11734	2833	901	83
H(4A)	9132	1810	298	78
H(4B)	11270	1470	180	78
H(6A)	7741	1595	3164	56
H(7A)	7476	167	4080	71
H(7B)	9341	312	5625	71
H(9A)	3467	602	8132	108
H(9B)	4454	1450	7679	108
H(9C)	5415	921	9388	108
H(11A)	5469	4026	-1432	99
H(11B)	4582	3883	375	99
H(11C)	5243	3112	-702	99
H(12A)	7878	2763	6668	112
H(12B)	6786	2711	4628	112
H(12C)	7753	3559	5406	112
H(13A)	11665	2824	7354	120
H(13B)	11478	3668	6248	120
H(13C)	12848	2945	5717	120
H(14A)	11866	116	3959	106
H(14B)	12880	1001	3935	106
H(14C)	12817	394	2256	106
H(1)	9560(70)	140(30)	630(60)	95(15)

Table 6. Torsion angles [°] for compound **11**.

C(6)-O(1)-C(1)-C(12)	71.1(3)
C(6)-O(1)-C(1)-C(13)	-171.2(3)
C(6)-O(1)-C(1)-C(2)	-55.8(3)
C(10)-O(4)-C(2)-C(3)	-97.5(3)
C(10)-O(4)-C(2)-C(1)	137.2(3)
O(1)-C(1)-C(2)-O(4)	94.5(3)
C(12)-C(1)-C(2)-O(4)	-31.0(4)
C(13)-C(1)-C(2)-O(4)	-152.7(3)
O(1)-C(1)-C(2)-C(3)	-26.8(4)
C(12)-C(1)-C(2)-C(3)	-152.3(3)
C(13)-C(1)-C(2)-C(3)	86.0(3)
O(4)-C(2)-C(3)-C(4)	-44.5(3)
C(1)-C(2)-C(3)-C(4)	77.6(3)
C(2)-C(3)-C(4)-C(5)	-71.2(4)
C(3)-C(4)-C(5)-O(6)	167.3(3)
C(3)-C(4)-C(5)-C(14)	-70.4(4)
C(3)-C(4)-C(5)-C(6)	53.6(4)
C(1)-O(1)-C(6)-C(7)	-134.4(2)
C(1)-O(1)-C(6)-C(5)	103.1(3)
O(6)-C(5)-C(6)-O(1)	172.3(2)
C(14)-C(5)-C(6)-O(1)	52.0(3)
C(4)-C(5)-C(6)-O(1)	-71.5(3)
O(6)-C(5)-C(6)-C(7)	53.0(3)
C(14)-C(5)-C(6)-C(7)	-67.3(3)
C(4)-C(5)-C(6)-C(7)	169.2(3)
C(8)-O(2)-C(7)-C(6)	172.5(3)
O(1)-C(6)-C(7)-O(2)	66.0(3)
C(5)-C(6)-C(7)-O(2)	-173.9(3)
C(7)-O(2)-C(8)-O(3)	-2.3(5)
C(7)-O(2)-C(8)-C(9)	179.1(3)
C(2)-O(4)-C(10)-O(5)	-3.7(5)
C(2)-O(4)-C(10)-C(11)	178.5(3)

Symmetry transformations used to generate equivalent atoms:

Crystal Structure Analysis of Compound 14:



A suitable crystal of compound **14** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 100 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK_α radiation (0.071073 Å). A hemisphere of data were measured using a series of combinations of phi and omega scans with 10 second frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all handled using SMART software. Frame integration and final cell refinements were carried out using SAINT software. The final cell parameters were determined from least-squares refinement on 8192 reflections. The SADABS program was used to carry out absorption corrections. The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10). Hydrogen atoms were placed at their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij}'s related to the atom's ridden upon. The C-H distances were fixed at 0.93 Å, 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. The weighting scheme used during refinement was $1/\sigma^2$, based on counting statistics. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software. Additional details of data collection and structure refinement are given in Table 1.

The structure was solved and successfully refined in space group $P2_12_12_1$ and the Flack parameter was 0.1(9) which indicates that the reported molecular configuration is most likely the absolute configuration, but there is a large uncertainty in the statistics as well. The final difference Fourier revealed the presence of some water molecules present in the crystal lattice, approximately 1.6 water molecules per unit cell. These water molecules were disordered throughout the lattice, but contributed greatly to the crystalline structure since they were strongly hydrogen bonded to the carbonyl and ring oxygens of neighboring molecules and weakly bonded to hydrogens attached to carbons, as well.

Thermal ellipsoid figure for compound **14.**

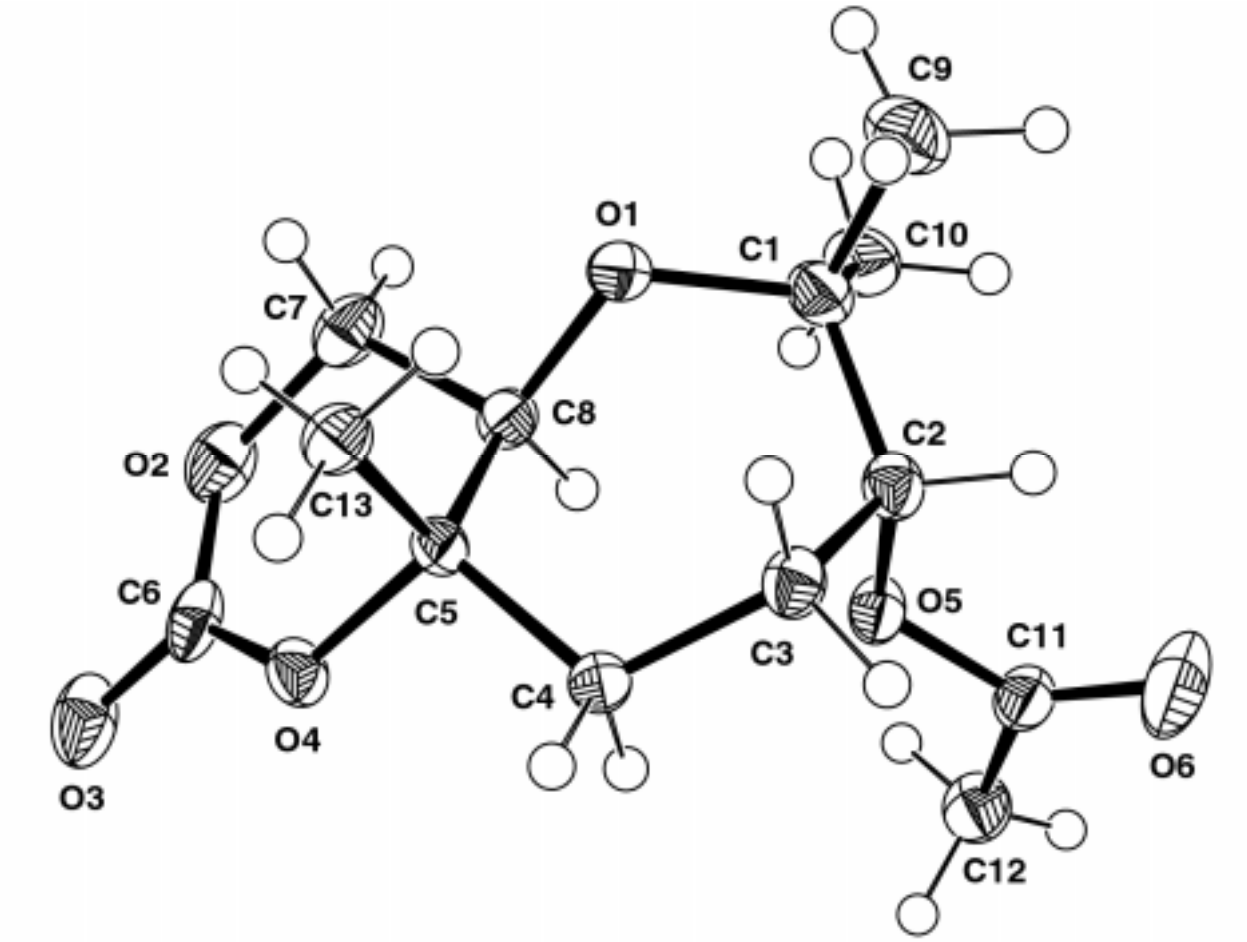


Table 1. Crystal data and structure refinement for compound **14**.

Identification code	xw2101f2	
Empirical formula	C13 H20.80 O6.40	
Formula weight	279.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.0614(8) Å	α= 90°.
	b = 10.6645(11) Å	β= 90°.
	c = 16.1512(16) Å	γ = 90°.
Volume	1388.5(2) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.107 mm^{-1}	
F(000)	600	
Crystal size	.46 x .25 x .19 mm^3	
Theta range for data collection	2.52 to 28.81°.	
Index ranges	-10<=h<=8, -14<=k<=14, -20<=l<=17	
Reflections collected	9043	
Independent reflections	3332 [R(int) = 0.0228]	
Completeness to theta = 28.81°	94.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3332 / 0 / 181	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0919	
R indices (all data)	R1 = 0.0419, wR2 = 0.0929	
Absolute structure parameter	0.1(9)	
Largest diff. peak and hole	0.297 and -0.259 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4016(1)	10409(1)	2571(1)	24(1)
C(1)	4839(2)	9992(2)	3321(1)	26(1)
O(2)	1567(2)	9021(1)	925(1)	33(1)
C(2)	3606(2)	9578(1)	3992(1)	23(1)
O(3)	-1034(2)	8447(1)	901(1)	39(1)
C(3)	1960(2)	10275(1)	4021(1)	22(1)
O(4)	-199(1)	9423(1)	2019(1)	23(1)
C(4)	649(2)	9850(1)	3395(1)	20(1)
O(5)	3252(1)	8242(1)	3897(1)	23(1)
C(5)	1059(2)	10133(1)	2496(1)	18(1)
O(6)	3958(2)	7844(1)	5213(1)	52(1)
C(6)	66(2)	8953(1)	1267(1)	27(1)
C(7)	2933(2)	9660(1)	1323(1)	28(1)
C(8)	2752(2)	9629(1)	2249(1)	20(1)
C(9)	5726(2)	11168(2)	3611(1)	38(1)
C(10)	6072(2)	8959(2)	3107(1)	33(1)
C(11)	3457(2)	7489(1)	4553(1)	25(1)
C(12)	2977(2)	6173(2)	4346(1)	29(1)
C(13)	813(2)	11514(1)	2292(1)	23(1)
O(1S)	5870(5)	8428(3)	156(2)	47(1)

Table 3. Bond lengths [Å] and angles [°] for compound **14**.

O(1)-C(8)	1.4142(17)	C(12)-H(12A)	0.8400
O(1)-C(1)	1.4504(17)	C(12)-H(12B)	0.9815
C(1)-C(9)	1.518(2)	C(12)-H(12C)	0.9814
C(1)-C(10)	1.524(2)	C(13)-H(13A)	0.8400
C(1)-C(2)	1.535(2)	C(13)-H(13B)	0.9803
O(2)-C(6)	1.332(2)	C(13)-H(13C)	0.9802
O(2)-C(7)	1.4451(19)	O(1S)-H(2S)	1.0317
C(2)-O(5)	1.4615(16)	O(1S)-H(1S)	1.0128
C(2)-C(3)	1.522(2)		
C(2)-H(2A)	1.0000	C(8)-O(1)-C(1)	117.14(10)
O(3)-C(6)	1.1950(19)	O(1)-C(1)-C(9)	102.76(12)
C(3)-C(4)	1.5305(19)	O(1)-C(1)-C(10)	109.29(12)
C(3)-H(3A)	0.9900	C(9)-C(1)-C(10)	111.07(13)
C(3)-H(3B)	0.9900	O(1)-C(1)-C(2)	112.43(11)
O(4)-C(6)	1.3314(18)	C(9)-C(1)-C(2)	108.92(13)
O(4)-C(5)	1.4806(16)	C(10)-C(1)-C(2)	112.01(12)
C(4)-C(5)	1.5194(19)	C(6)-O(2)-C(7)	122.21(11)
C(4)-H(4A)	0.9900	O(5)-C(2)-C(3)	108.01(11)
C(4)-H(4B)	0.9900	O(5)-C(2)-C(1)	109.43(12)
O(5)-C(11)	1.3397(17)	C(3)-C(2)-C(1)	116.46(12)
C(5)-C(8)	1.5200(19)	O(5)-C(2)-H(2A)	107.5
C(5)-C(13)	1.5226(19)	C(3)-C(2)-H(2A)	107.5
O(6)-C(11)	1.2019(18)	C(1)-C(2)-H(2A)	107.5
C(7)-C(8)	1.503(2)	C(2)-C(3)-C(4)	115.90(11)
C(7)-H(7A)	0.9900	C(2)-C(3)-H(3A)	108.3
C(7)-H(7B)	0.9900	C(4)-C(3)-H(3A)	108.3
C(8)-H(8A)	1.0000	C(2)-C(3)-H(3B)	108.3
C(9)-H(9A)	0.8400	C(4)-C(3)-H(3B)	108.3
C(9)-H(9B)	0.9803	H(3A)-C(3)-H(3B)	107.4
C(9)-H(9C)	0.9803	C(6)-O(4)-C(5)	123.84(12)
C(10)-H(10A)	0.8400	C(5)-C(4)-C(3)	114.97(11)
C(10)-H(10B)	0.9806	C(5)-C(4)-H(4A)	108.5
C(10)-H(10C)	0.9806	C(3)-C(4)-H(4A)	108.5
C(11)-C(12)	1.493(2)	C(5)-C(4)-H(4B)	108.5

C(3)-C(4)-H(4B)	108.5
H(4A)-C(4)-H(4B)	107.5
C(11)-O(5)-C(2)	118.54(11)
O(4)-C(5)-C(4)	104.27(10)
O(4)-C(5)-C(8)	107.33(10)
C(4)-C(5)-C(8)	112.06(11)
O(4)-C(5)-C(13)	107.05(11)
C(4)-C(5)-C(13)	111.73(12)
C(8)-C(5)-C(13)	113.71(11)
O(3)-C(6)-O(2)	119.54(14)
O(3)-C(6)-O(4)	120.21(16)
O(2)-C(6)-O(4)	120.23(14)
O(2)-C(7)-C(8)	111.00(12)
O(2)-C(7)-H(7A)	109.4
C(8)-C(7)-H(7A)	109.4
O(2)-C(7)-H(7B)	109.4
C(8)-C(7)-H(7B)	109.4
H(7A)-C(7)-H(7B)	108.0
O(1)-C(8)-C(7)	106.45(11)
O(1)-C(8)-C(5)	110.05(10)
C(7)-C(8)-C(5)	109.89(11)
O(1)-C(8)-H(8A)	110.1
C(7)-C(8)-H(8A)	110.1
C(5)-C(8)-H(8A)	110.1
C(1)-C(9)-H(9A)	109.5
C(1)-C(9)-H(9B)	108.7
H(9A)-C(9)-H(9B)	110.7
C(1)-C(9)-H(9C)	109.7
H(9A)-C(9)-H(9C)	108.8
H(9B)-C(9)-H(9C)	109.4
C(1)-C(10)-H(10A)	109.5
C(1)-C(10)-H(10B)	109.7
H(10A)-C(10)-H(10B)	110.2
C(1)-C(10)-H(10C)	109.2
H(10A)-C(10)-H(10C)	108.8
H(10B)-C(10)-H(10C)	109.4
O(6)-C(11)-O(5)	123.67(14)
O(6)-C(11)-C(12)	125.55(14)
O(5)-C(11)-C(12)	110.78(12)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	110.2
H(12A)-C(12)-H(12B)	106.9
C(11)-C(12)-H(12C)	109.7
H(12A)-C(12)-H(12C)	111.2
H(12B)-C(12)-H(12C)	109.3
C(5)-C(13)-H(13A)	109.5
C(5)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.9
C(5)-C(13)-H(13C)	109.4
H(13A)-C(13)-H(13C)	109.2
H(13B)-C(13)-H(13C)	109.5
H(2S)-O(1S)-H(1S)	99.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	27(1)	26(1)	6(1)	-1(1)	-3(1)
C(1)	20(1)	27(1)	30(1)	3(1)	-4(1)	-2(1)
O(2)	45(1)	37(1)	18(1)	-4(1)	1(1)	1(1)
C(2)	26(1)	19(1)	22(1)	0(1)	-4(1)	-2(1)
O(3)	59(1)	28(1)	29(1)	0(1)	-18(1)	-9(1)
C(3)	25(1)	24(1)	18(1)	-1(1)	-1(1)	0(1)
O(4)	24(1)	24(1)	22(1)	-3(1)	-5(1)	-3(1)
C(4)	18(1)	23(1)	18(1)	0(1)	1(1)	0(1)
O(5)	29(1)	19(1)	20(1)	1(1)	-5(1)	-1(1)
C(5)	18(1)	18(1)	18(1)	-1(1)	-2(1)	-3(1)
O(6)	94(1)	37(1)	23(1)	6(1)	-15(1)	-18(1)
C(6)	45(1)	17(1)	20(1)	3(1)	-9(1)	1(1)
C(7)	32(1)	29(1)	22(1)	2(1)	6(1)	5(1)
C(8)	21(1)	21(1)	20(1)	2(1)	1(1)	1(1)
C(9)	33(1)	30(1)	50(1)	6(1)	-11(1)	-8(1)
C(10)	21(1)	36(1)	42(1)	6(1)	0(1)	3(1)
C(11)	26(1)	27(1)	21(1)	3(1)	0(1)	1(1)
C(12)	33(1)	24(1)	32(1)	4(1)	-3(1)	0(1)
C(13)	25(1)	20(1)	23(1)	1(1)	1(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **14**.

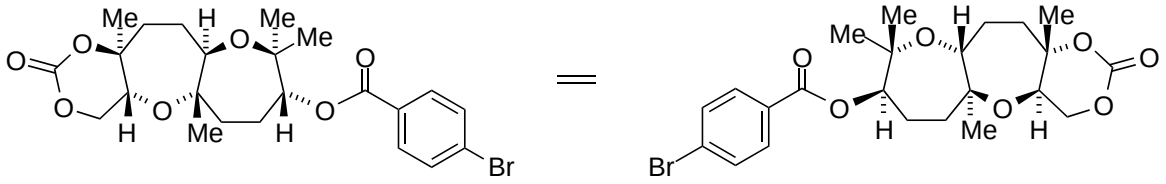
	x	y	z	U(eq)
H(2A)	4159	9695	4541	27
H(3A)	2180	11178	3930	27
H(3B)	1490	10185	4584	27
H(4A)	490	8934	3455	24
H(4B)	-416	10260	3534	24
H(7A)	2970	10541	1133	33
H(7B)	3989	9252	1164	33
H(8A)	2893	8752	2457	25
H(9A)	6297	11460	3221	56
H(9B)	6432	10951	4085	56
H(9C)	4910	11799	3781	56
H(10A)	6781	9238	2773	49
H(10B)	5484	8245	2862	49
H(10C)	6641	8688	3613	49
H(12A)	3406	5680	4690	44
H(12B)	3411	5942	3799	44
H(12C)	1763	6098	4343	44
H(13A)	996	11633	1786	34
H(13B)	1578	12021	2625	34
H(13C)	-332	11756	2419	34
H(2S)	5341	7580	-2	70
H(1S)	7012	8125	325	70

Table 6. Torsion angles [°] for compound **14**.

C(8)-O(1)-C(1)-C(9)	-164.98(13)	C(13)-C(5)-C(8)-C(7)	-65.28(15)
C(8)-O(1)-C(1)-C(10)	77.00(15)	C(2)-O(5)-C(11)-O(6)	-1.9(2)
C(8)-O(1)-C(1)-C(2)	-48.03(16)	C(2)-O(5)-C(11)-C(12)	177.89(13)
O(1)-C(1)-C(2)-O(5)	89.65(14)		
C(9)-C(1)-C(2)-O(5)	-157.13(12)		
C(10)-C(1)-C(2)-O(5)	-33.88(16)		
O(1)-C(1)-C(2)-C(3)	-33.15(17)		
C(9)-C(1)-C(2)-C(3)	80.06(15)		
C(10)-C(1)-C(2)-C(3)	-156.68(13)		
O(5)-C(2)-C(3)-C(4)	-42.75(16)		
C(1)-C(2)-C(3)-C(4)	80.80(15)		
C(2)-C(3)-C(4)-C(5)	-67.95(16)		
C(3)-C(2)-O(5)-C(11)	-105.89(14)		
C(1)-C(2)-O(5)-C(11)	126.41(14)		
C(6)-O(4)-C(5)-C(4)	-149.68(12)		
C(6)-O(4)-C(5)-C(8)	-30.64(16)		
C(6)-O(4)-C(5)-C(13)	91.79(15)		
C(3)-C(4)-C(5)-O(4)	169.22(11)		
C(3)-C(4)-C(5)-C(8)	53.45(15)		
C(3)-C(4)-C(5)-C(13)	-75.49(15)		
C(7)-O(2)-C(6)-O(3)	177.71(13)		
C(7)-O(2)-C(6)-O(4)	-3.7(2)		
C(5)-O(4)-C(6)-O(3)	-176.08(13)		
C(5)-O(4)-C(6)-O(2)	5.3(2)		
C(6)-O(2)-C(7)-C(8)	28.73(19)		
C(1)-O(1)-C(8)-C(7)	-141.09(12)		
C(1)-O(1)-C(8)-C(5)	99.87(13)		
O(2)-C(7)-C(8)-O(1)	-172.60(11)		
O(2)-C(7)-C(8)-C(5)	-53.46(15)		
O(4)-C(5)-C(8)-O(1)	169.83(10)		
C(4)-C(5)-C(8)-O(1)	-76.27(13)		
C(13)-C(5)-C(8)-O(1)	51.63(15)		
O(4)-C(5)-C(8)-C(7)	52.92(14)		
C(4)-C(5)-C(8)-C(7)	166.82(12)		

Symmetry transformations used to generate equivalent atoms:

Crystal Structure Analysis of Compound 22:



A suitable crystal of compound **22** was coated with Paratone N oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 100 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated MoK_{α} radiation (0.071073 Å). A hemisphere of data were measured using a series of combinations of phi and omega scans with 10 second frame exposures and 0.3° frame widths. Data collection, indexing and initial cell refinements were all handled using SMART software. Frame integration and final cell refinements were carried out using SAINT software. The final cell parameters were determined from least-squares refinement on 8192 reflections. The SADABS program was used to carry out absorption corrections. The structure was solved using Direct methods and difference Fourier techniques (SHELXTL, V5.10). Hydrogen atoms were placed at their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij}'s related to the atom's ridden upon. The C-H distances were fixed at 0.93 Å, 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*. Structure solution, refinement, graphics and generation of publication materials were performed by using SHELXTL, V5.10 software. Additional details of data collection and structure refinement are given in Table 1.

The compound crystallized in the chiral space group, $P2_1$ and it was possible to determine that the molecular conformation determined is the absolute configuration of the molecule, since the Flack parameter was –0.0009(5), and should be 0.00 for the correct structure. In addition, there was one dichloromethane solvent molecule per molecule of compound **22** incorporated, uniformly into the crystal lattice.

Thermal ellipsoid figure for compound **22** (for clarity, hydrogen atoms are shown only at chiral carbon centers).

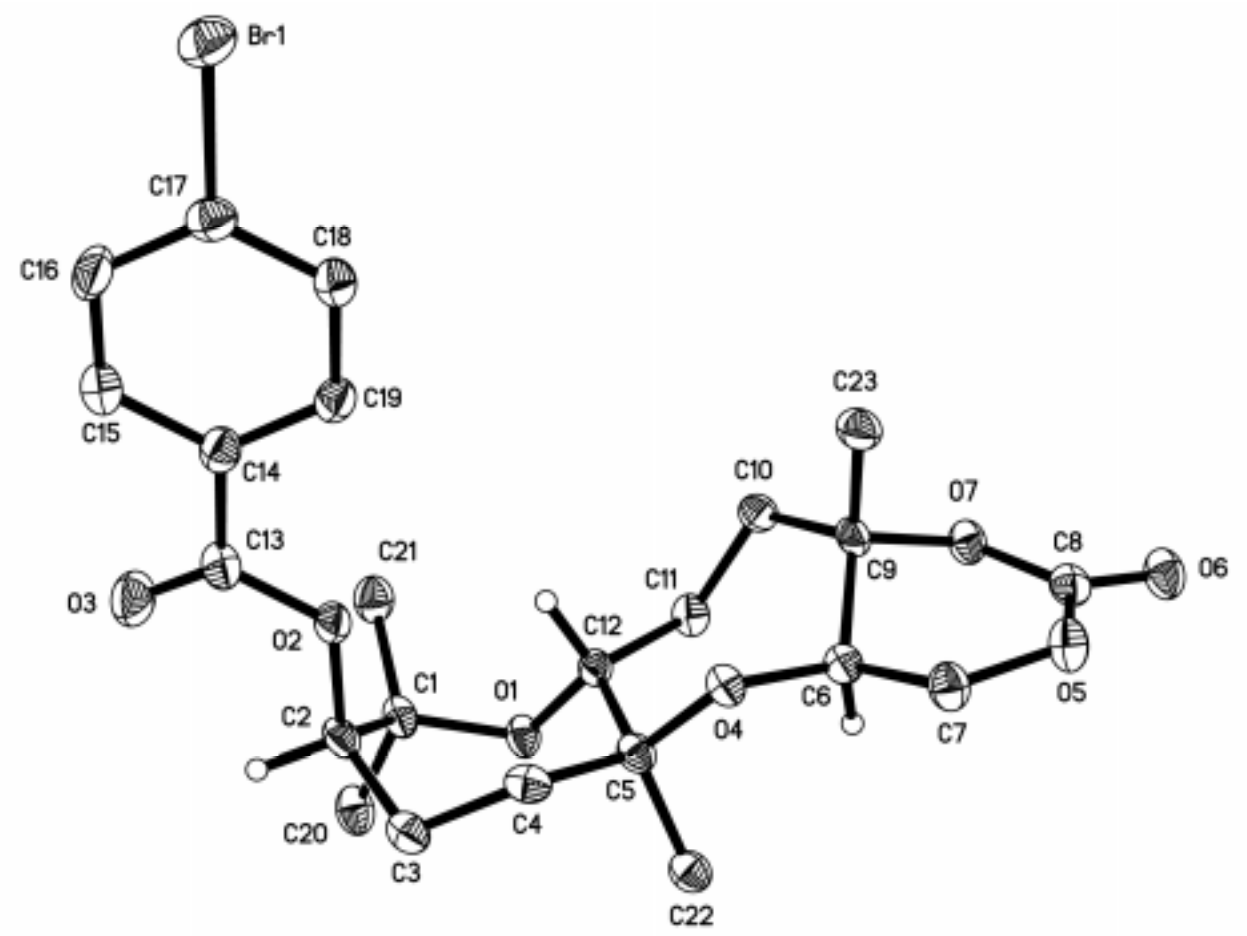


Table 1. Crystal data and structure refinement for compound **22**.

Identification code	xw2123	
Empirical formula	C24 H31 Br Cl2 O7	
Formula weight	582.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.3128(7) Å	α= 90°.
	b = 10.7363(7) Å	β= 94.1510(10)°.
	c = 11.5382(8) Å	γ = 90°.
Volume	1274.17(15) $Å^3$	
Z	2	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	1.865 mm^{-1}	
F(000)	600	
Crystal size	0.30 x 0.18 x 0.18 mm^3	
Theta range for data collection	1.77 to 30.53°.	
Index ranges	-11<=h<=14, -13<=k<=15, -16<=l<=16	
Reflections collected	11284	
Independent reflections	6775 [R(int) = 0.0425]	
Completeness to theta = 30.53°	99.7 %	
Absorption correction	SADABS2	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6775 / 1 / 311	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0567	
R indices (all data)	R1 = 0.0448, wR2 = 0.0575	
Absolute structure parameter	-0.009(5)	
Largest diff. peak and hole	1.262 and -0.665 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **22**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	580(1)	15208(1)	10221(1)	30(1)
O(1)	2104(2)	7318(2)	6700(1)	20(1)
O(2)	2939(1)	10108(2)	7627(1)	22(1)
O(3)	4652(2)	10419(2)	8928(2)	36(1)
O(4)	-236(2)	9361(2)	5084(2)	18(1)
O(5)	-3452(2)	8668(2)	3704(2)	26(1)
O(6)	-4852(2)	7246(2)	4181(2)	28(1)
O(7)	-3234(2)	7659(2)	5488(2)	22(1)
C(1)	3156(2)	7801(2)	7455(2)	22(1)
C(2)	3603(2)	9092(2)	7061(2)	20(1)
C(3)	3387(2)	9327(2)	5761(2)	20(1)
C(4)	1995(2)	9685(2)	5315(2)	20(1)
C(5)	968(2)	8664(2)	5328(2)	18(1)
C(6)	-1380(2)	8640(2)	4846(2)	18(1)
C(7)	-2169(2)	9234(2)	3857(2)	23(1)
C(8)	-3885(2)	7831(2)	4451(2)	22(1)
C(9)	-2191(2)	8540(2)	5887(2)	19(1)
C(10)	-1461(2)	7930(2)	6937(2)	21(1)
C(11)	-205(2)	7217(2)	6753(2)	20(1)
C(12)	955(2)	8063(2)	6539(2)	17(1)
C(13)	3594(3)	10717(2)	8500(2)	24(1)
C(14)	2843(3)	11818(2)	8885(2)	22(1)
C(15)	3470(3)	12655(3)	9647(2)	28(1)
C(16)	2809(3)	13688(3)	10031(2)	28(1)
C(17)	1523(3)	13834(2)	9665(2)	22(1)
C(18)	866(3)	13014(2)	8911(2)	22(1)
C(19)	1548(2)	12000(2)	8507(2)	22(1)
C(20)	4262(2)	6883(2)	7308(2)	26(1)
C(21)	2792(3)	7800(3)	8715(2)	27(1)
C(22)	1175(2)	7718(2)	4378(2)	22(1)
C(23)	-2801(2)	9743(2)	6245(2)	24(1)
C(1S)	3634(3)	8768(3)	2122(3)	38(1)
Cl(1)	2917(1)	7345(1)	1720(1)	37(1)
Cl(2)	2630(1)	10024(1)	1689(1)	56(1)

Table 3. Bond lengths [Å] and angles [°] for compound **22**.

Br(1)-C(17)	1.904(2)	C(10)-H(10A)	0.9900
O(1)-C(12)	1.430(3)	C(10)-H(10B)	0.9900
O(1)-C(1)	1.438(3)	C(11)-C(12)	1.536(3)
O(2)-C(13)	1.342(3)	C(11)-H(11A)	0.9900
O(2)-C(2)	1.467(3)	C(11)-H(11B)	0.9900
O(3)-C(13)	1.208(3)	C(12)-H(12)	1.0000
O(4)-C(6)	1.421(3)	C(13)-C(14)	1.498(4)
O(4)-C(5)	1.460(3)	C(14)-C(15)	1.384(3)
O(5)-C(8)	1.343(3)	C(14)-C(19)	1.388(3)
O(5)-C(7)	1.455(3)	C(15)-C(16)	1.391(4)
O(6)-C(8)	1.201(3)	C(15)-H(15)	0.9500
O(7)-C(8)	1.342(3)	C(16)-C(17)	1.371(3)
O(7)-C(9)	1.481(3)	C(16)-H(16)	0.9500
C(1)-C(20)	1.526(3)	C(17)-C(18)	1.380(3)
C(1)-C(21)	1.528(3)	C(18)-C(19)	1.395(3)
C(1)-C(2)	1.539(3)	C(18)-H(18)	0.9500
C(2)-C(3)	1.522(3)	C(19)-H(19)	0.9500
C(2)-H(2)	1.0000	C(20)-H(20A)	0.9800
C(3)-C(4)	1.538(3)	C(20)-H(20B)	0.9800
C(3)-H(3A)	0.9900	C(20)-H(20C)	0.9800
C(3)-H(3B)	0.9900	C(21)-H(21A)	0.9800
C(4)-C(5)	1.525(3)	C(21)-H(21B)	0.9800
C(4)-H(4A)	0.9900	C(21)-H(21C)	0.9800
C(4)-H(4B)	0.9900	C(22)-H(22A)	0.9800
C(5)-C(22)	1.521(3)	C(22)-H(22B)	0.9800
C(5)-C(12)	1.540(3)	C(22)-H(22C)	0.9800
C(6)-C(7)	1.495(3)	C(23)-H(23A)	0.9800
C(6)-C(9)	1.517(3)	C(23)-H(23B)	0.9800
C(6)-H(6)	1.0000	C(23)-H(23C)	0.9800
C(7)-H(7A)	0.9900	C(1S)-Cl(1)	1.745(3)
C(7)-H(7B)	0.9900	C(1S)-Cl(2)	1.750(3)
C(9)-C(23)	1.508(3)	C(1S)-H(24A)	0.9900
C(9)-C(10)	1.527(3)	C(1S)-H(24B)	0.9900
C(10)-C(11)	1.533(3)		

C(12)-O(1)-C(1)	117.34(17)	O(4)-C(6)-C(9)	112.49(19)
C(13)-O(2)-C(2)	118.09(19)	C(7)-C(6)-C(9)	109.5(2)
C(6)-O(4)-C(5)	116.18(18)	O(4)-C(6)-H(6)	108.8
C(8)-O(5)-C(7)	122.87(19)	C(7)-C(6)-H(6)	108.8
C(8)-O(7)-C(9)	119.65(19)	C(9)-C(6)-H(6)	108.8
O(1)-C(1)-C(20)	103.7(2)	O(5)-C(7)-C(6)	110.8(2)
O(1)-C(1)-C(21)	110.4(2)	O(5)-C(7)-H(7A)	109.5
C(20)-C(1)-C(21)	110.0(2)	C(6)-C(7)-H(7A)	109.5
O(1)-C(1)-C(2)	112.0(2)	O(5)-C(7)-H(7B)	109.5
C(20)-C(1)-C(2)	107.8(2)	C(6)-C(7)-H(7B)	109.5
C(21)-C(1)-C(2)	112.4(2)	H(7A)-C(7)-H(7B)	108.1
O(2)-C(2)-C(3)	106.0(2)	O(6)-C(8)-O(7)	120.8(2)
O(2)-C(2)-C(1)	112.2(2)	O(6)-C(8)-O(5)	119.5(2)
C(3)-C(2)-C(1)	114.5(2)	O(7)-C(8)-O(5)	119.8(2)
O(2)-C(2)-H(2)	108.0	O(7)-C(9)-C(23)	108.89(18)
C(3)-C(2)-H(2)	108.0	O(7)-C(9)-C(6)	103.24(18)
C(1)-C(2)-H(2)	108.0	C(23)-C(9)-C(6)	114.9(2)
C(2)-C(3)-C(4)	116.0(2)	O(7)-C(9)-C(10)	106.2(2)
C(2)-C(3)-H(3A)	108.3	C(23)-C(9)-C(10)	110.0(2)
C(4)-C(3)-H(3A)	108.3	C(6)-C(9)-C(10)	113.0(2)
C(2)-C(3)-H(3B)	108.3	C(9)-C(10)-C(11)	118.4(2)
C(4)-C(3)-H(3B)	108.3	C(9)-C(10)-H(10A)	107.7
H(3A)-C(3)-H(3B)	107.4	C(11)-C(10)-H(10A)	107.7
C(5)-C(4)-C(3)	116.68(19)	C(9)-C(10)-H(10B)	107.7
C(5)-C(4)-H(4A)	108.1	C(11)-C(10)-H(10B)	107.7
C(3)-C(4)-H(4A)	108.1	H(10A)-C(10)-H(10B)	107.1
C(5)-C(4)-H(4B)	108.1	C(10)-C(11)-C(12)	113.8(2)
C(3)-C(4)-H(4B)	108.1	C(10)-C(11)-H(11A)	108.8
H(4A)-C(4)-H(4B)	107.3	C(12)-C(11)-H(11A)	108.8
O(4)-C(5)-C(22)	111.4(2)	C(10)-C(11)-H(11B)	108.8
O(4)-C(5)-C(4)	102.19(18)	C(12)-C(11)-H(11B)	108.8
C(22)-C(5)-C(4)	109.83(19)	H(11A)-C(11)-H(11B)	107.7
O(4)-C(5)-C(12)	109.03(18)	O(1)-C(12)-C(11)	107.24(18)
C(22)-C(5)-C(12)	112.7(2)	O(1)-C(12)-C(5)	106.86(19)
C(4)-C(5)-C(12)	111.24(19)	C(11)-C(12)-C(5)	116.9(2)
O(4)-C(6)-C(7)	108.32(19)	O(1)-C(12)-H(12)	108.5

C(11)-C(12)-H(12)	108.5	H(20A)-C(20)-H(20C)	109.5
C(5)-C(12)-H(12)	108.5	H(20B)-C(20)-H(20C)	109.5
O(3)-C(13)-O(2)	124.6(2)	C(1)-C(21)-H(21A)	109.5
O(3)-C(13)-C(14)	124.0(3)	C(1)-C(21)-H(21B)	109.5
O(2)-C(13)-C(14)	111.4(2)	H(21A)-C(21)-H(21B)	109.5
C(15)-C(14)-C(19)	120.2(3)	C(1)-C(21)-H(21C)	109.5
C(15)-C(14)-C(13)	118.2(2)	H(21A)-C(21)-H(21C)	109.5
C(19)-C(14)-C(13)	121.6(2)	H(21B)-C(21)-H(21C)	109.5
C(14)-C(15)-C(16)	120.2(3)	C(5)-C(22)-H(22A)	109.5
C(14)-C(15)-H(15)	119.9	C(5)-C(22)-H(22B)	109.5
C(16)-C(15)-H(15)	119.9	H(22A)-C(22)-H(22B)	109.5
C(17)-C(16)-C(15)	118.6(3)	C(5)-C(22)-H(22C)	109.5
C(17)-C(16)-H(16)	120.7	H(22A)-C(22)-H(22C)	109.5
C(15)-C(16)-H(16)	120.7	H(22B)-C(22)-H(22C)	109.5
C(16)-C(17)-C(18)	122.8(2)	C(9)-C(23)-H(23A)	109.5
C(16)-C(17)-Br(1)	119.4(2)	C(9)-C(23)-H(23B)	109.5
C(18)-C(17)-Br(1)	117.8(2)	H(23A)-C(23)-H(23B)	109.5
C(17)-C(18)-C(19)	118.1(2)	C(9)-C(23)-H(23C)	109.5
C(17)-C(18)-H(18)	120.9	H(23A)-C(23)-H(23C)	109.5
C(19)-C(18)-H(18)	120.9	H(23B)-C(23)-H(23C)	109.5
C(14)-C(19)-C(18)	120.1(2)	Cl(1)-C(1S)-Cl(2)	111.58(16)
C(14)-C(19)-H(19)	119.9	Cl(1)-C(1S)-H(24A)	109.3
C(18)-C(19)-H(19)	119.9	Cl(2)-C(1S)-H(24A)	109.3
C(1)-C(20)-H(20A)	109.5	Cl(1)-C(1S)-H(24B)	109.3
C(1)-C(20)-H(20B)	109.5	Cl(2)-C(1S)-H(24B)	109.3
H(20A)-C(20)-H(20B)	109.5	H(24A)-C(1S)-H(24B)	108.0
C(1)-C(20)-H(20C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **22**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	35(1)	24(1)	32(1)	-7(1)	3(1)	2(1)
O(1)	16(1)	18(1)	25(1)	-1(1)	-2(1)	1(1)
O(2)	17(1)	22(1)	28(1)	-8(1)	1(1)	-1(1)
O(3)	26(1)	40(1)	40(1)	-10(1)	-9(1)	5(1)
O(4)	16(1)	15(1)	23(1)	2(1)	1(1)	0(1)
O(5)	22(1)	26(1)	29(1)	4(1)	-6(1)	-1(1)
O(6)	22(1)	23(1)	38(1)	-5(1)	-3(1)	-1(1)
O(7)	18(1)	19(1)	27(1)	0(1)	0(1)	-3(1)
C(1)	15(1)	22(1)	27(1)	0(1)	-1(1)	0(1)
C(2)	13(1)	18(1)	29(2)	-3(1)	3(1)	2(1)
C(3)	19(1)	14(1)	28(1)	0(1)	6(1)	-1(1)
C(4)	22(1)	15(1)	22(1)	1(1)	7(1)	1(1)
C(5)	16(1)	15(1)	23(1)	0(1)	2(1)	1(1)
C(6)	18(1)	13(1)	23(1)	-1(1)	1(1)	0(1)
C(7)	20(1)	22(1)	25(1)	3(1)	0(1)	-3(1)
C(8)	20(1)	17(1)	29(2)	-4(1)	0(1)	5(1)
C(9)	13(1)	21(1)	25(1)	-4(1)	2(1)	-4(1)
C(10)	19(1)	24(1)	20(1)	1(1)	5(1)	-5(1)
C(11)	20(1)	18(1)	22(1)	4(1)	0(1)	-2(1)
C(12)	16(1)	15(1)	21(1)	-3(1)	1(1)	-2(1)
C(13)	19(1)	25(1)	28(2)	0(1)	0(1)	-3(1)
C(14)	23(1)	23(1)	20(1)	2(1)	1(1)	-5(1)
C(15)	21(1)	33(2)	30(2)	-3(1)	-2(1)	-3(1)
C(16)	30(2)	27(2)	27(2)	-7(1)	-2(1)	-9(1)
C(17)	27(2)	18(1)	23(1)	0(1)	8(1)	-2(1)
C(18)	20(1)	24(2)	22(1)	2(1)	-1(1)	-1(1)
C(19)	23(1)	20(1)	21(1)	-2(1)	0(1)	-3(1)
C(20)	21(1)	21(1)	36(2)	2(1)	-3(1)	1(1)
C(21)	25(2)	30(2)	25(2)	4(1)	-2(1)	-3(1)
C(22)	20(1)	20(1)	25(1)	1(1)	3(1)	1(1)
C(23)	21(1)	22(1)	30(2)	-5(1)	5(1)	-2(1)
C(1S)	33(2)	33(2)	46(2)	-1(2)	-8(1)	-1(1)
Cl(1)	56(1)	25(1)	30(1)	1(1)	7(1)	2(1)
Cl(2)	61(1)	28(1)	74(1)	0(1)	-19(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **22**.

	x	y	z	U(eq)
H(2)	4556	9168	7281	24
H(3A)	3636	8566	5346	24
H(3B)	3980	10002	5550	24
H(4A)	1712	10389	5790	23
H(4B)	2018	9989	4507	23
H(6)	-1125	7784	4608	21
H(7A)	-2260	10136	4011	27
H(7B)	-1717	9137	3135	27
H(10A)	-2067	7346	7285	25
H(10B)	-1249	8590	7520	25
H(11A)	-363	6652	6079	24
H(11B)	22	6696	7446	24
H(12)	1002	8739	7136	21
H(15)	4354	12523	9909	34
H(16)	3240	14280	10535	34
H(18)	-27	13137	8675	27
H(19)	1126	11433	7972	26
H(20A)	3976	6040	7492	39
H(20B)	5013	7111	7834	39
H(20C)	4507	6909	6503	39
H(21A)	2008	8304	8780	40
H(21B)	3509	8151	9215	40
H(21C)	2625	6944	8958	40
H(22A)	658	6971	4504	32
H(22B)	2098	7494	4399	32
H(22C)	903	8080	3619	32
H(23A)	-3387	10056	5604	36
H(23B)	-2118	10360	6438	36
H(23C)	-3295	9596	6927	36
H(24A)	4473	8848	1763	45
H(24B)	3814	8790	2977	45

Table 6. Torsion angles [°] for compound **22**.

C(12)-O(1)-C(1)-C(20)	-172.89(19)
C(12)-O(1)-C(1)-C(21)	69.3(2)
C(12)-O(1)-C(1)-C(2)	-56.9(3)
C(13)-O(2)-C(2)-C(3)	-131.2(2)
C(13)-O(2)-C(2)-C(1)	103.1(2)
O(1)-C(1)-C(2)-O(2)	92.6(2)
C(20)-C(1)-C(2)-O(2)	-153.8(2)
C(21)-C(1)-C(2)-O(2)	-32.4(3)
O(1)-C(1)-C(2)-C(3)	-28.3(3)
C(20)-C(1)-C(2)-C(3)	85.3(3)
C(21)-C(1)-C(2)-C(3)	-153.3(2)
O(2)-C(2)-C(3)-C(4)	-44.9(3)
C(1)-C(2)-C(3)-C(4)	79.4(3)
C(2)-C(3)-C(4)-C(5)	-70.1(3)
C(6)-O(4)-C(5)-C(22)	52.7(3)
C(6)-O(4)-C(5)-C(4)	169.90(18)
C(6)-O(4)-C(5)-C(12)	-72.3(2)
C(3)-C(4)-C(5)-O(4)	169.3(2)
C(3)-C(4)-C(5)-C(22)	-72.4(3)
C(3)-C(4)-C(5)-C(12)	53.0(3)
C(5)-O(4)-C(6)-C(7)	-138.2(2)
C(5)-O(4)-C(6)-C(9)	100.6(2)
C(8)-O(5)-C(7)-C(6)	7.2(3)
O(4)-C(6)-C(7)-O(5)	-170.11(18)
C(9)-C(6)-C(7)-O(5)	-47.1(3)
C(9)-O(7)-C(8)-O(6)	-169.1(2)
C(9)-O(7)-C(8)-O(5)	10.9(3)
C(7)-O(5)-C(8)-O(6)	-167.6(2)
C(7)-O(5)-C(8)-O(7)	12.4(4)
C(8)-O(7)-C(9)-C(23)	74.1(3)
C(8)-O(7)-C(9)-C(6)	-48.5(3)
C(8)-O(7)-C(9)-C(10)	-167.6(2)
O(4)-C(6)-C(9)-O(7)	-174.29(18)
C(7)-C(6)-C(9)-O(7)	65.2(2)
O(4)-C(6)-C(9)-C(23)	67.3(3)
C(7)-C(6)-C(9)-C(23)	-53.2(3)

O(4)-C(6)-C(9)-C(10)	-60.0(3)
C(7)-C(6)-C(9)-C(10)	179.5(2)
O(7)-C(9)-C(10)-C(11)	97.3(2)
C(23)-C(9)-C(10)-C(11)	-145.0(2)
C(6)-C(9)-C(10)-C(11)	-15.1(3)
C(9)-C(10)-C(11)-C(12)	73.5(3)
C(1)-O(1)-C(12)-C(11)	-129.7(2)
C(1)-O(1)-C(12)-C(5)	104.2(2)
C(10)-C(11)-C(12)-O(1)	164.47(19)
C(10)-C(11)-C(12)-C(5)	-75.7(3)
O(4)-C(5)-C(12)-O(1)	175.76(18)
C(22)-C(5)-C(12)-O(1)	51.5(2)
C(4)-C(5)-C(12)-O(1)	-72.3(2)
O(4)-C(5)-C(12)-C(11)	55.7(3)
C(22)-C(5)-C(12)-C(11)	-68.5(3)
C(4)-C(5)-C(12)-C(11)	167.7(2)
C(2)-O(2)-C(13)-O(3)	-7.2(4)
C(2)-O(2)-C(13)-C(14)	173.2(2)
O(3)-C(13)-C(14)-C(15)	10.5(4)
O(2)-C(13)-C(14)-C(15)	-169.8(2)
O(3)-C(13)-C(14)-C(19)	-168.8(3)
O(2)-C(13)-C(14)-C(19)	10.9(3)
C(19)-C(14)-C(15)-C(16)	-0.5(4)
C(13)-C(14)-C(15)-C(16)	-179.8(2)
C(14)-C(15)-C(16)-C(17)	1.9(4)
C(15)-C(16)-C(17)-C(18)	-1.6(4)
C(15)-C(16)-C(17)-Br(1)	177.8(2)
C(16)-C(17)-C(18)-C(19)	-0.2(4)
Br(1)-C(17)-C(18)-C(19)	-179.53(18)
C(15)-C(14)-C(19)-C(18)	-1.3(4)
C(13)-C(14)-C(19)-C(18)	178.0(2)
C(17)-C(18)-C(19)-C(14)	1.6(4)

Symmetry transformations used to generate equivalent atoms: