SUPPORTING INFORMATION

Synthesis of an alkene-containing copolylactide and its facile modification by the addition of thiols

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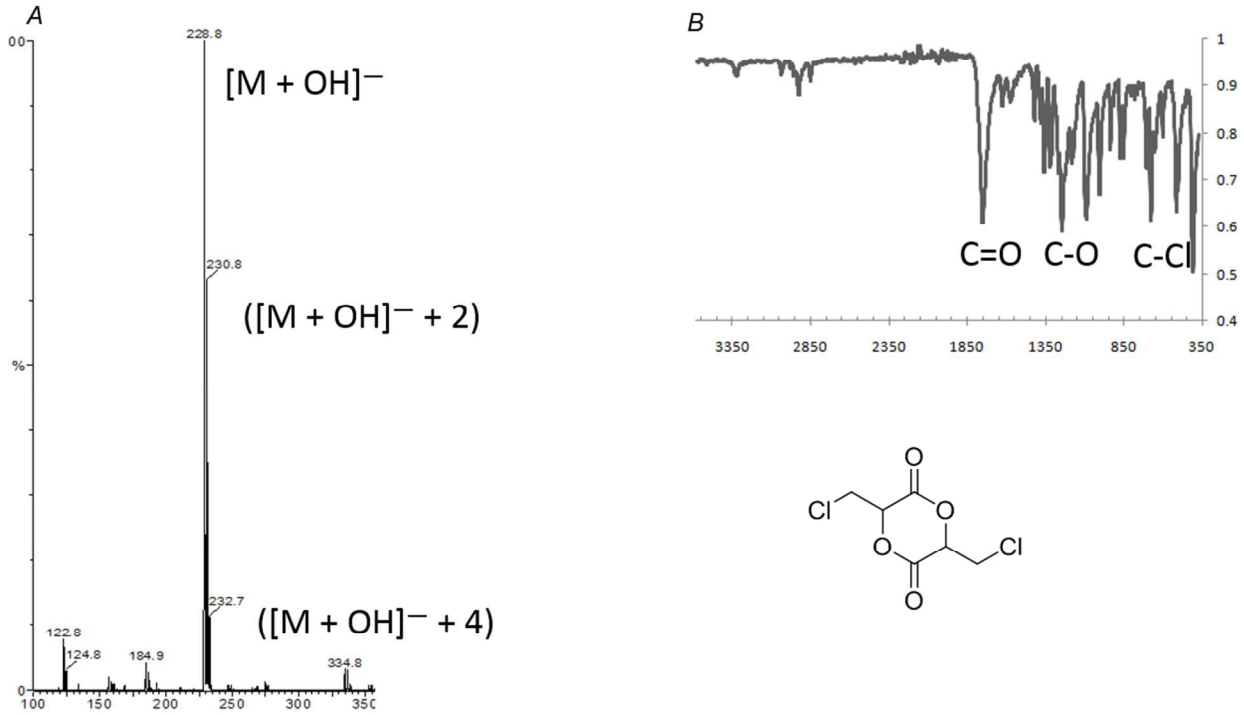


Figure S-1. 3-chlorolactide monomer: A, mass spectrum; B, IR spectrum.

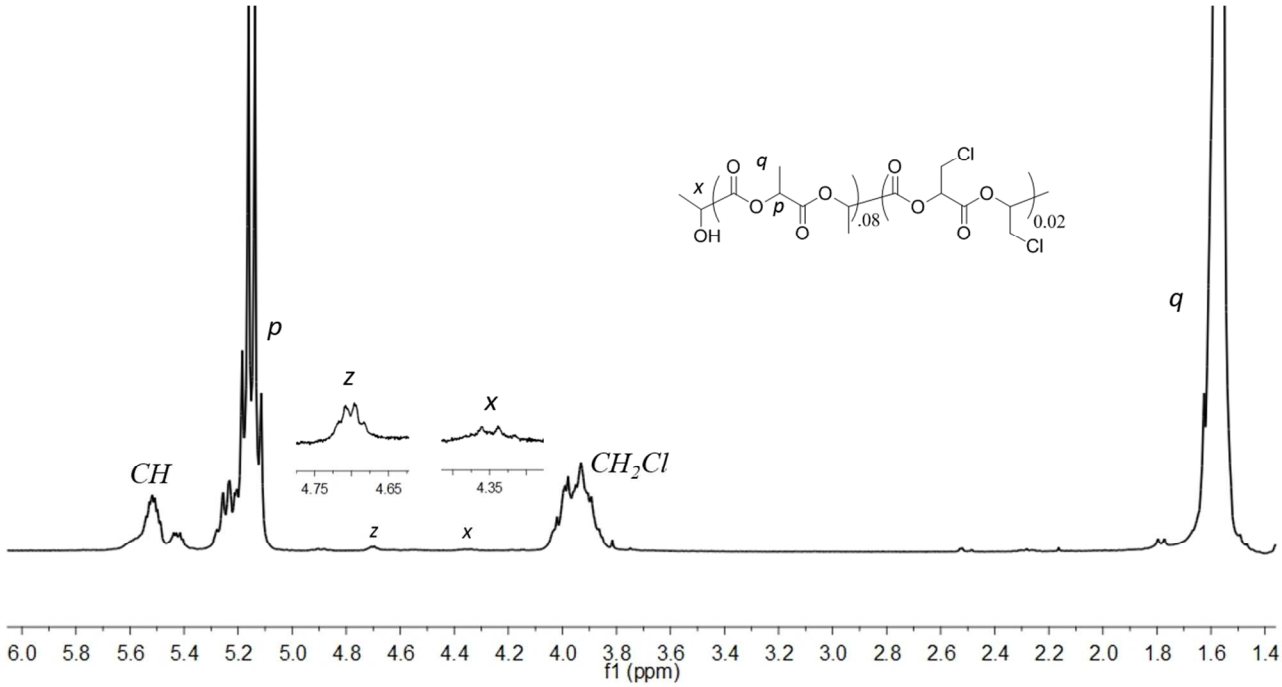


Figure S-2.[1]H NMR spectrum (300 MHz, $CDCl_3$) of 20 % chloro-PL. Signal labelled z is associated with the methine hydrogen of the chlorolactide unit at the hydroxyl terminus of the copolymer.

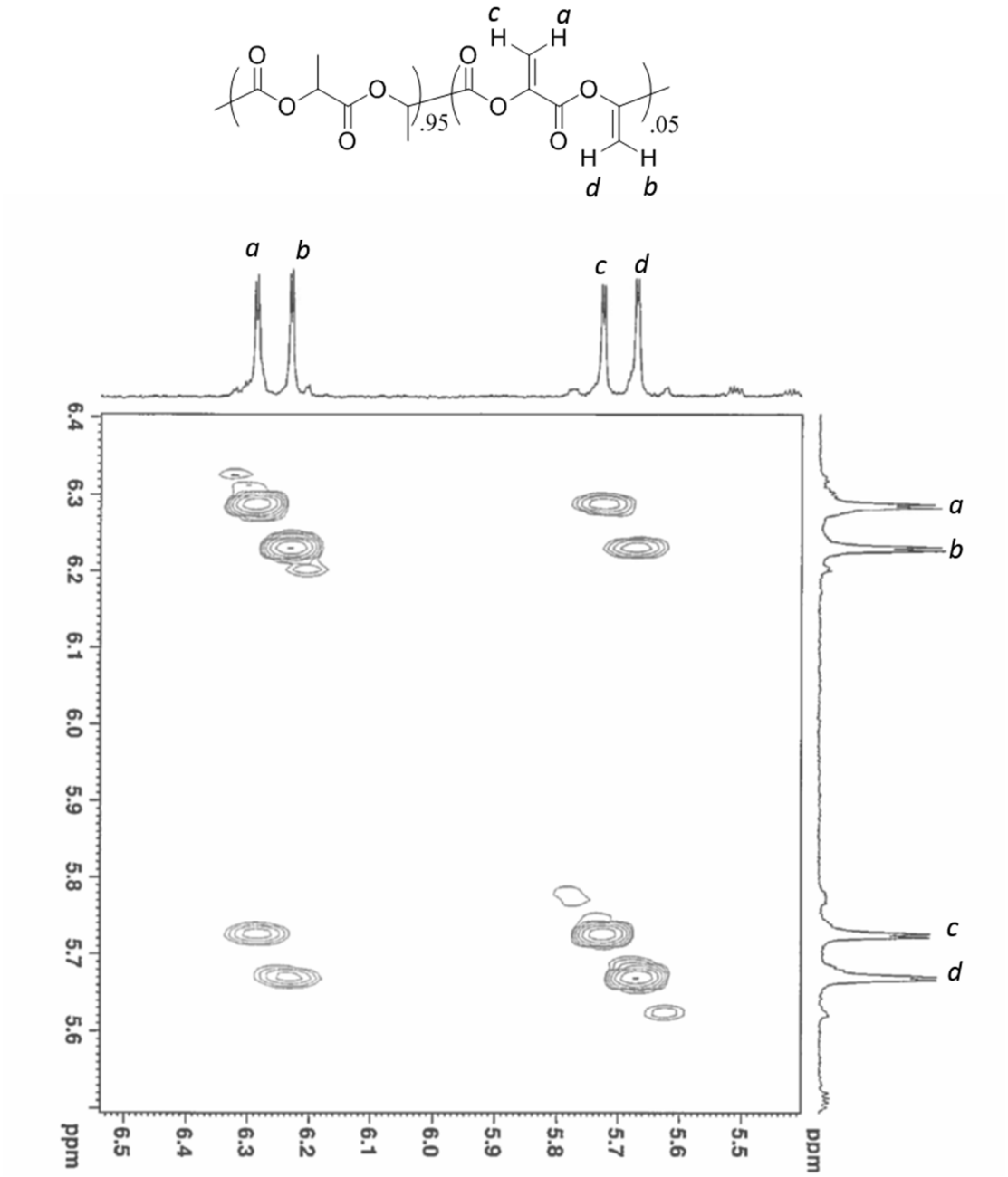


Figure S-3. ene-PL COSY NMR spectrum (500 MHz, $CDCl_3$).

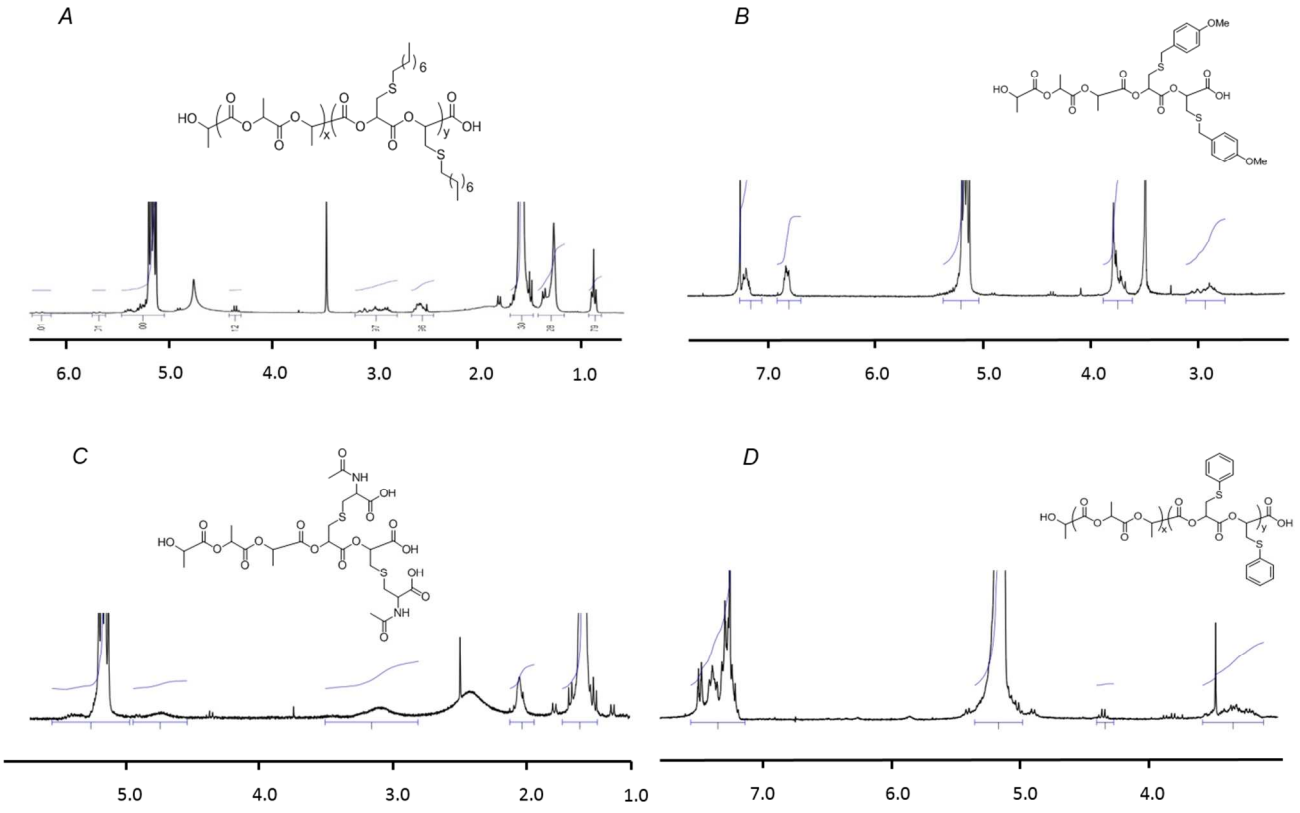


Figure S-4. Nucleophilic conjugate addition of thiol onto ene-PL. A, octylthial-PL; B, 4-(methoxy)-benzylthia-PL, C, *N*-acetylcysteine-PL; D, thiophenyl-PL.

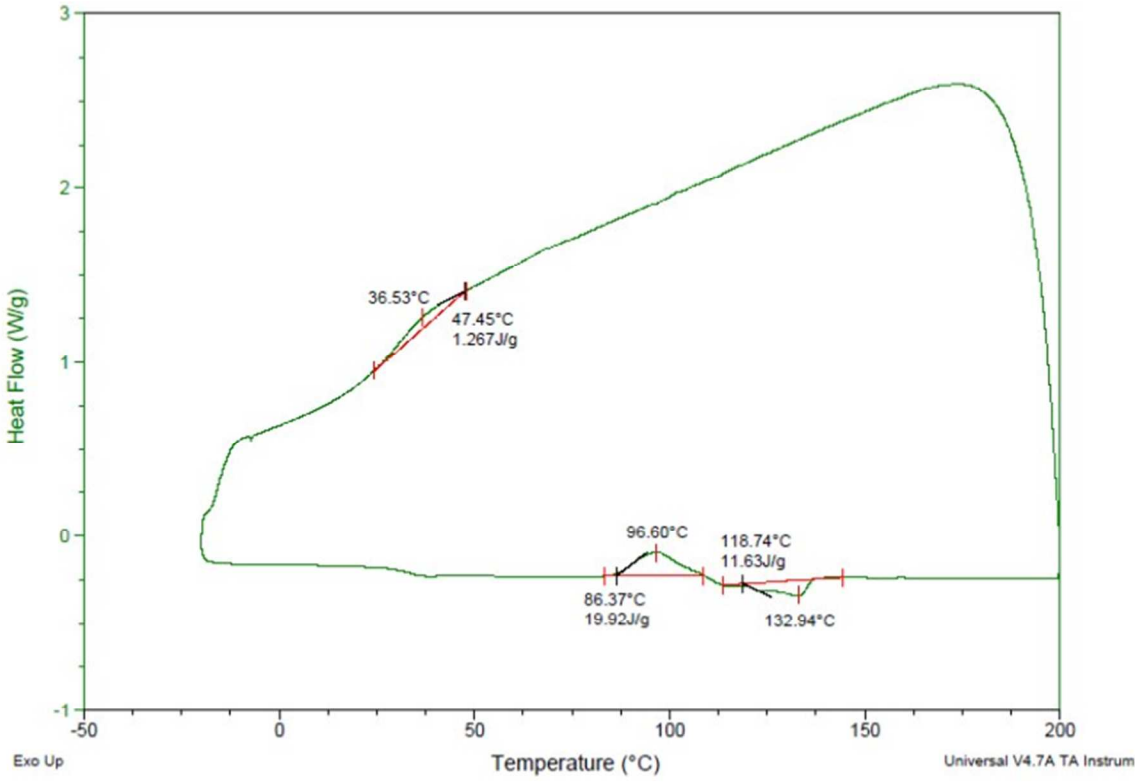


Figure S-5. DSC thermogram (5°C/min, -20 °C to 200 °C) of 3-chloro-PL.

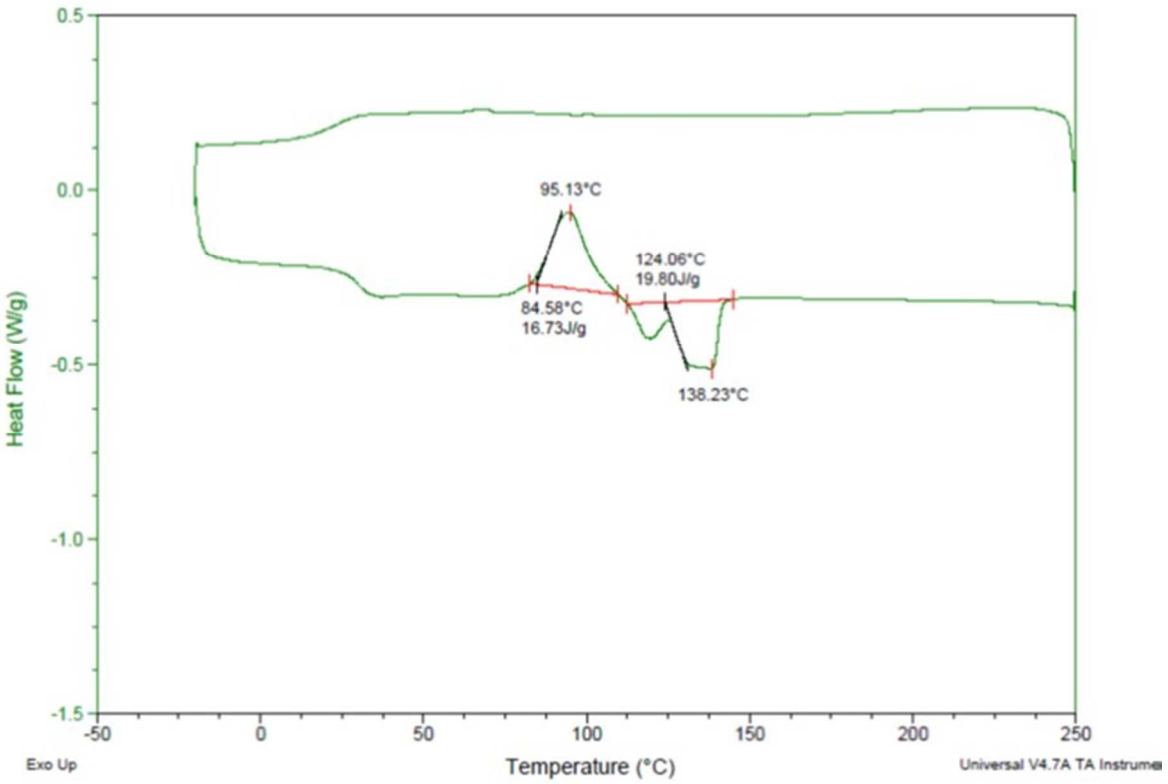


Figure S-6. DSC thermogram of ene-PL showing the second thermal cycle. 10 °C/min, -20 °C to 250 °C.

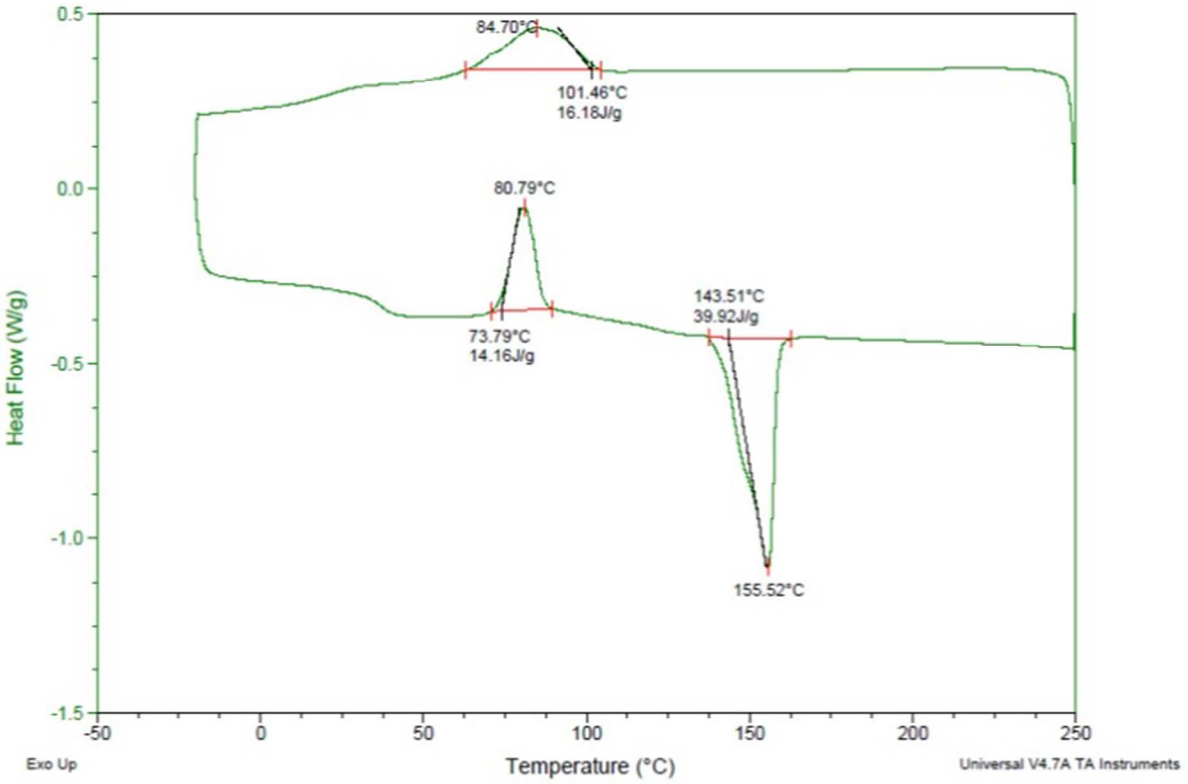
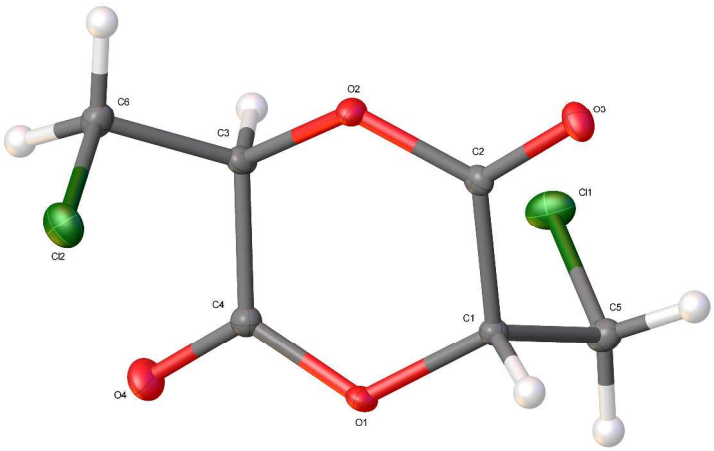


Figure S-7. DSC thermogram of MBT-PL showing the second thermal cycle. 10 °C/min, -20 °C to 250 °C.

Crystal Data and Experimental



Experimental. Single colourless prism-shaped crystals of (**PK001**) were recrystallised from DCM by slow evaporation. A suitable crystal (0.93×0.34×0.32 mm) was selected and mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was cooled to T = 100(2) K during the data collection. The structure was solved with **ShelXT** (Sheldrick, 2015) using direct and dual-space solution methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version of **ShelXL-97** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_6H_6Cl_2O_4$, M_r = 213.01, monoclinic, $P2_1$ (No. 4), a = 5.2416(11) Å, b = 9.3607(19) Å, c = 8.1773(16) Å, β = 94.886(2)°, $\alpha = \gamma = 90°$, V = 399.76(14) Å^3, T = 100(2) K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.780, 6970 reflections measured, 2428 unique (R_{int} = 0.0252) which were used in all calculations. The final wR_2 was 0.0521 (all data) and R_1 was 0.0207 (I > 2(I)).

Compound	**PK001**
Formula	$C_6H_6Cl_2O_4$
$D_{calc.}$/ g cm^{-3}	1.770
μ/mm^{-1}	0.780
Formula Weight	213.01
Colour	colourless
Shape	prism
Max Size/mm	0.93
Mid Size/mm	0.34
Min Size/mm	0.32
T/K	100(2)
Crystal System	monoclinic
Flack Parameter	0.06(2)
Hooft Parameter	0.08(2)
Space Group	$P2_1$
a/Å	5.2416(11)
b/Å	9.3607(19)
c/Å	8.1773(16)
α/°	90
β/°	94.886(2)
γ/°	90
V/Å^3	399.76(14)
Z	2
Z'	1
Θ_{min}/°	2.500
Θ_{max}/°	30.513
Measured Refl.	6970
Independent Refl.	2428
Reflections Used	2391
R_{int}	0.0252
Parameters	130
Restraints	31
Largest Peak	0.303
Deepest Hole	-0.209
GooF	1.064
wR_2 (all data)	0.0521
wR_2	0.0518
R_1 (all data)	0.0211
R_1	0.0207

Structure Quality Indicators

Reflections:	d min 0.70	I/σ 31.6	Rint 2.52%	complete 99%
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.2	GooF 1.064

A colourless prism-shaped crystal with dimensions 0.93×0.34×0.32 mm was mounted on a loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at T = 100(2) K.

Data were measured using ϕ and ω scans scans of 2° per frame for 20 s using MoK_{α} radiation (sealed tube, 45 kV, 35 mA). The total number of runs and images was based on the strategy calculation from the program **APEX2** (Bruker, 2014). The maximum resolution achieved was Θ = 30.5°.

Unit cell indexing was performed by using the **APEX2** (Bruker, 2014) software and refined using **SAINT** (Bruker, V8.34A, 2013) on 6759 reflections, 97% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.34A, 2013) and SADABS-2014/5 (Bruker, 2014). wR_2(int) was 0.1458 before and 0.0488 after correction. The Ratio of minimum to maximum transmission is 0.7612. The λ/2 correction factor is 0.0015. The final completeness is 100.00% out to 30.513° in Θ. The absorption coefficient (μ) of this material is 0.780 mm^{-1} and the minimum and maximum transmissions are 0.5679 and 0.7461.

The structure was solved with **ShelXT** (Sheldrick, 2015) in the space group $P2_1$ (# 4) using direct and dual-space solution methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The structure was refined by Least Squares using version of **ShelXL-97** (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were refined freely

The Flack parameter was refined to 0.06(2). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.08(2). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted.

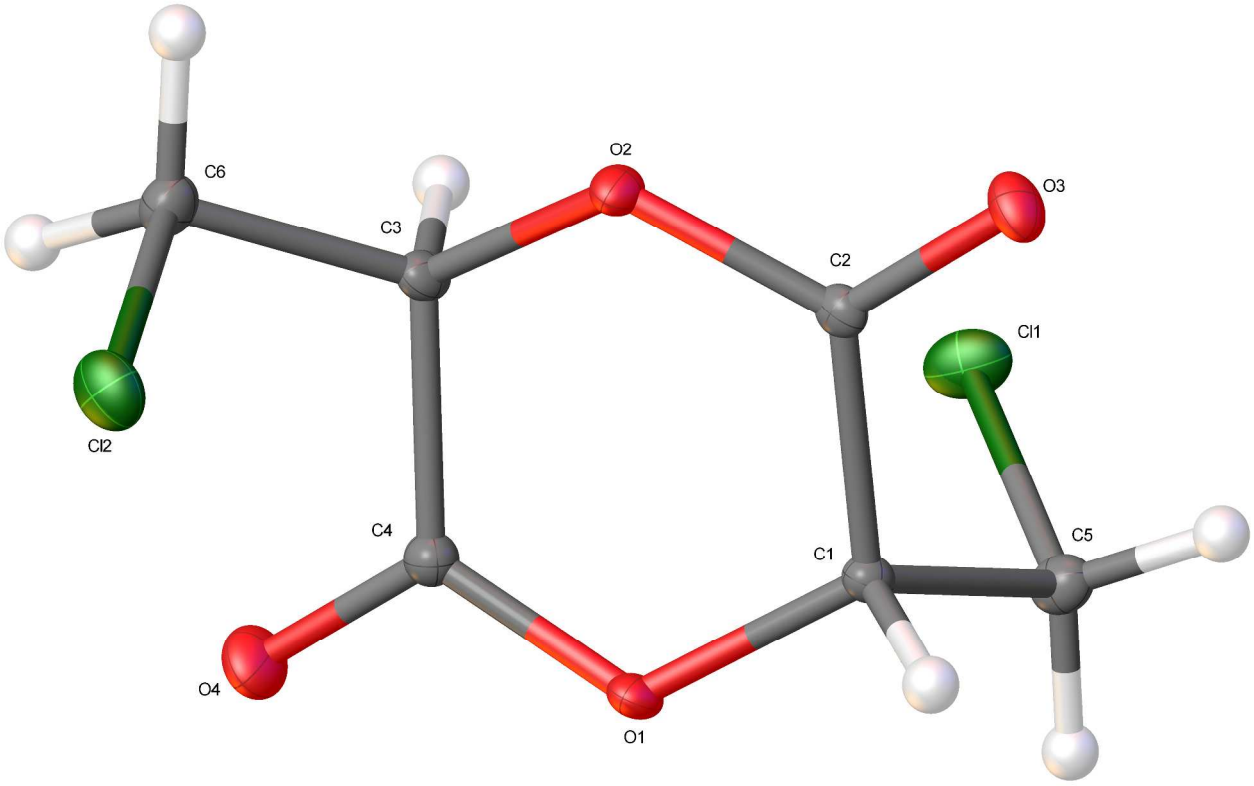


Figure S-8. Plot of the molecular structure.

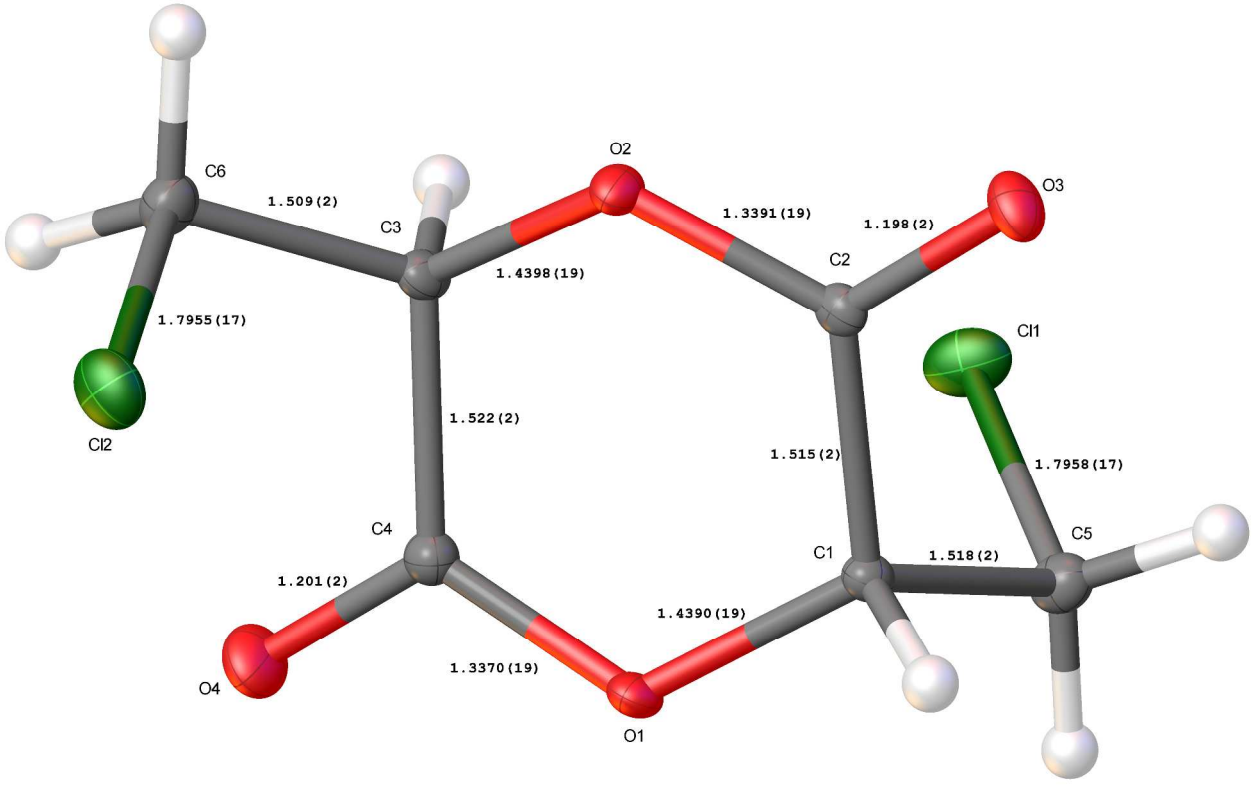


Figure S-9. Plot of the molecular structure with bond distances.

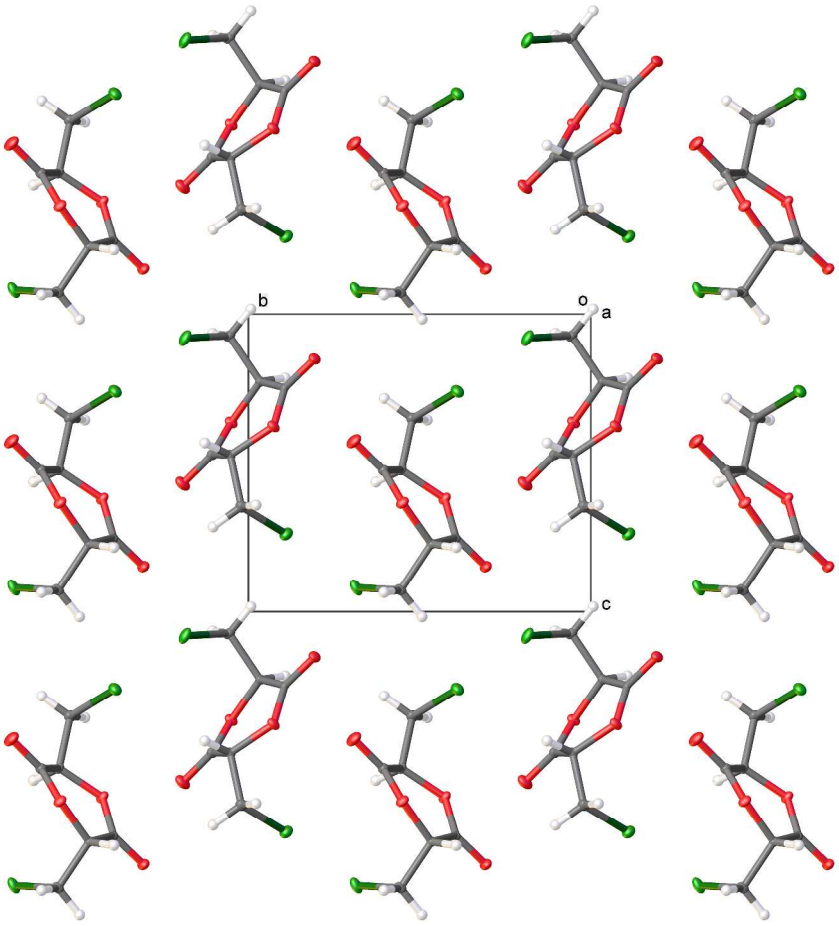


Figure S-10. Packing diagram viewed along the a-axis.

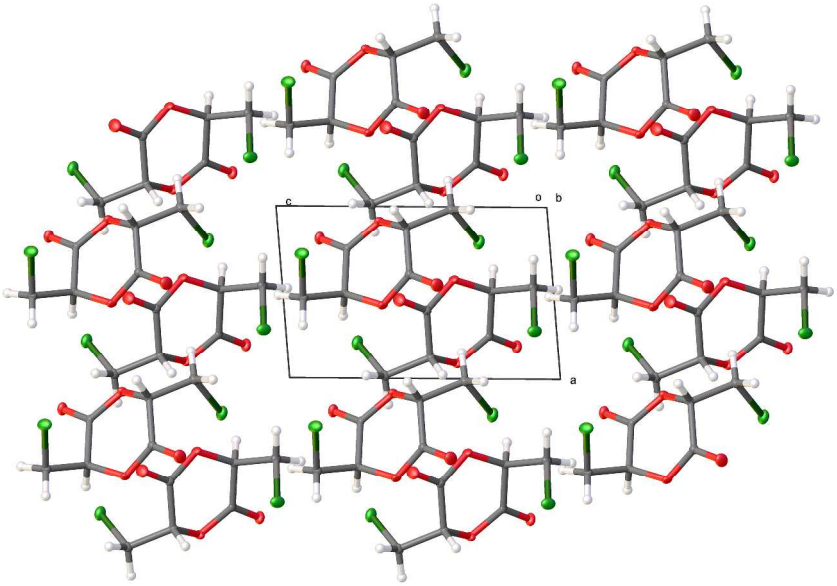


Figure S-11. Packing diagram viewed along the b-axis.

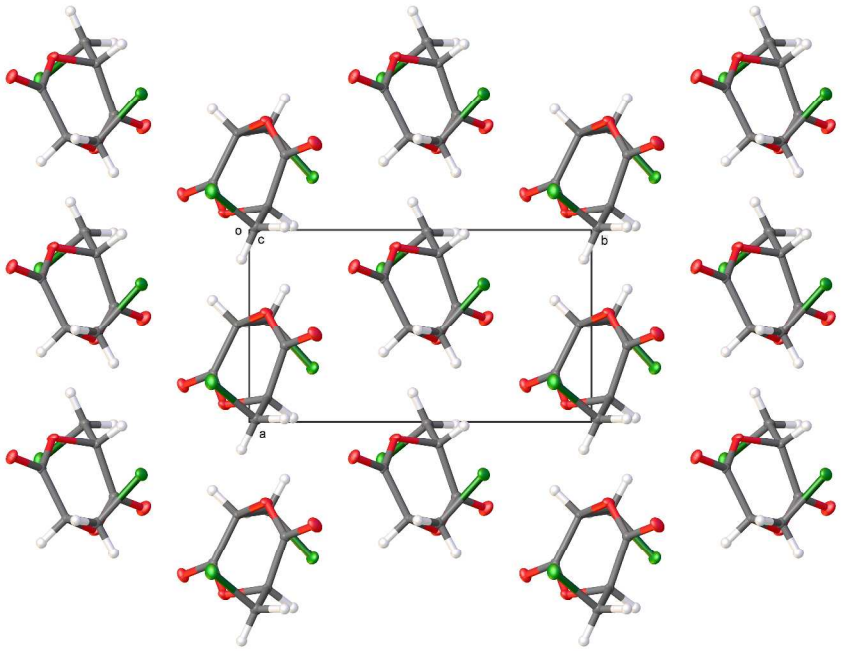


Figure S-12. Packing diagram viewed along the c-axis.

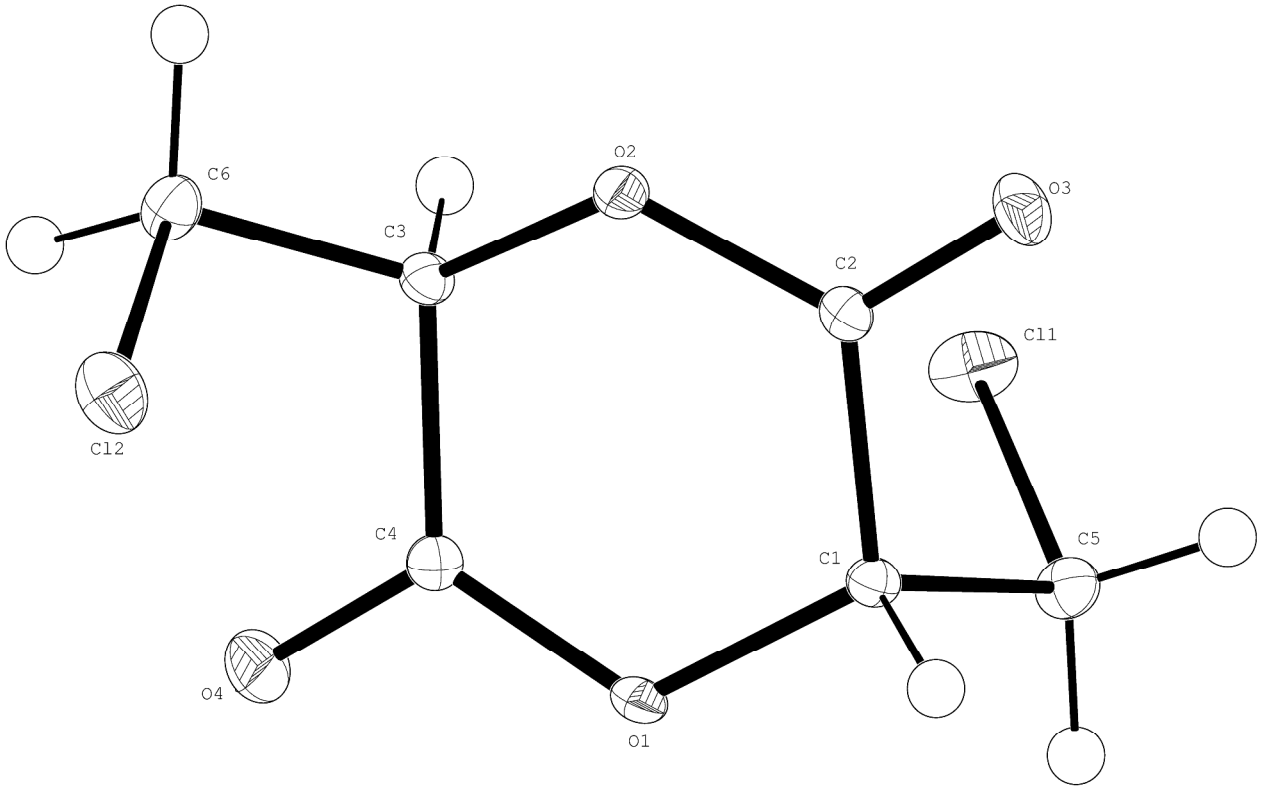
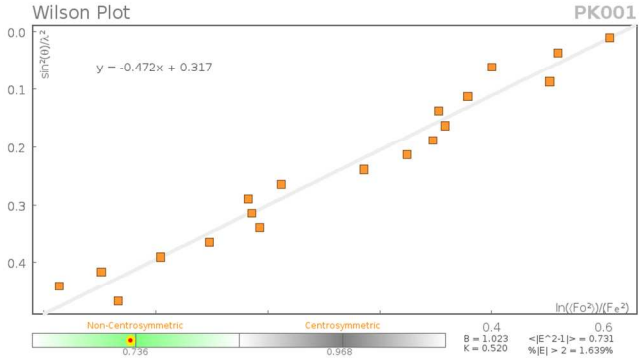
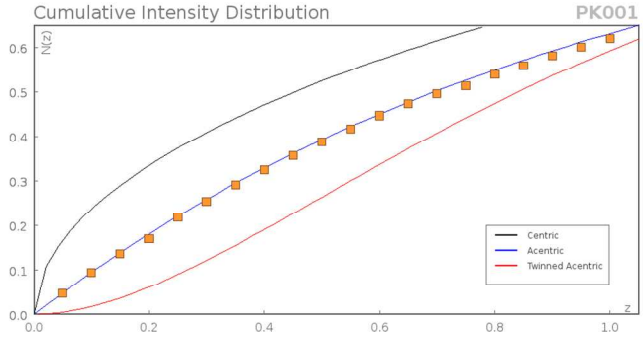
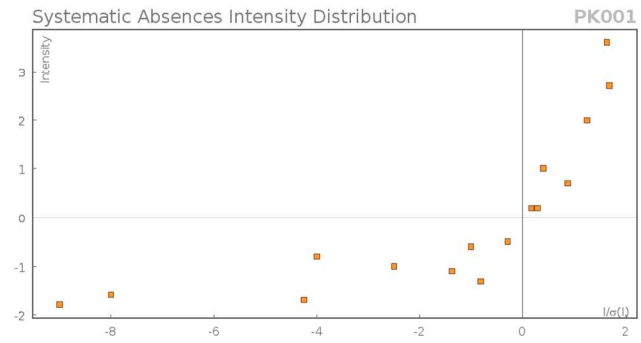


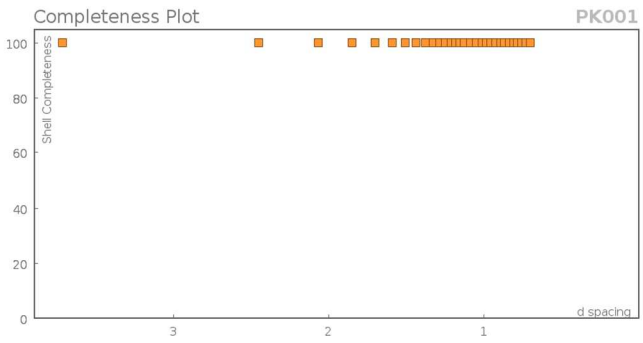
Figure S-13. Ortep plot.

Data Plots: Diffraction Data

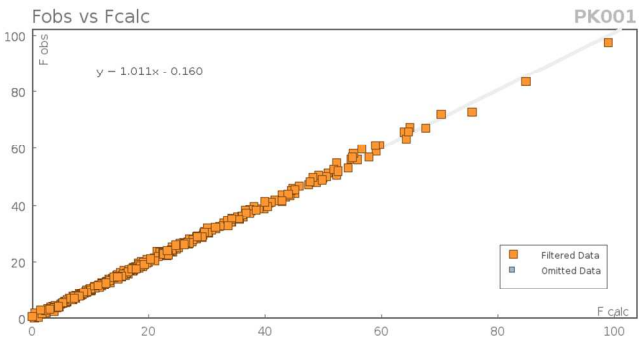


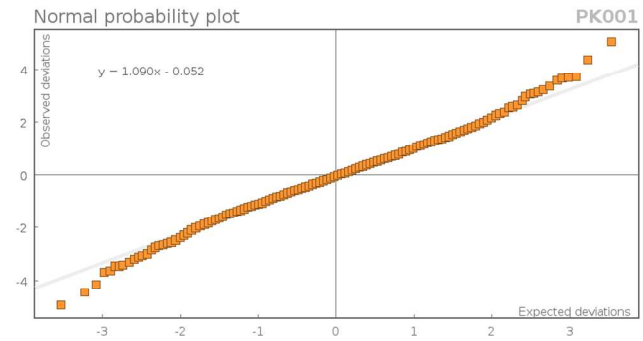






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	6986	Unique reflections	2428
Completeness	0.991	Mean I/σ	31.62
hklsub>max</sub> collected	(7, 13, 11)	hklsub>min</sub> collected	(-7, -13, -11)
hkl_{max} used	(7, 13, 11)	hkl_{min} used	(-7, -13, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	9.36	d_{min} used	0.7
Friedel pairs	2093	Friedel pairs merged	0
Inconsistent equivalents	0	R_{int}	0.0252
R_{sigma}	0.0253	Intensity transformed	0

Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2469, 1732, 279, 54)	Maximum mulitplicity	6
Removed systematic absences	16	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **PK001**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Cl2	2072.9(8)	3896.5(5)	2605.9(5)	15.66(9)
Cl1	2798.2(7)	6853.8(4)	9188.2(5)	15.53(10)
O1	5748(2)	5504.9(13)	6350.9(15)	10.2(2)
O2	877(2)	4268.9(13)	6215.1(15)	10.4(2)
O4	4567(2)	6923.1(15)	4284.5(16)	16.9(3)
O3	1890(2)	3068.9(13)	8484.9(15)	12.7(2)
C4	3964(3)	6057.7(17)	5266(2)	9.4(3)
C1	5093(3)	4657.8(17)	7723.0(19)	7.9(3)
C2	2498(3)	3937.7(19)	7514.6(17)	7.9(2)
C6	139(3)	5208.4(18)	3520(2)	11.5(3)
C3	1215(3)	5531.7(17)	5252(2)	8.6(3)
C5	5339(3)	5562.2(18)	9269(2)	11.1(3)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **PK001**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl2	20.43(18)	14.05(17)	12.97(17)	-3.08(14)	4.16(13)	-0.34(15)
Cl1	13.57(16)	12.59(17)	20.49(19)	-7.17(15)	1.82(14)	1.66(14)
O1	7.0(5)	13.0(5)	10.8(5)	3.5(4)	2.0(4)	-1.7(4)
O2	8.3(5)	11.8(5)	11.0(5)	3.8(4)	-0.3(4)	-2.7(4)
O4	17.6(5)	17.1(6)	15.7(6)	7.1(5)	0.6(5)	-5.3(5)
O3	16.7(6)	11.5(5)	10.0(5)	1.8(4)	2.1(4)	-4.2(4)
C4	9.2(6)	9.9(7)	9.1(6)	0.0(5)	0.8(5)	-0.3(5)
C1	7.4(6)	7.8(6)	8.7(7)	0.4(5)	1.2(5)	-0.2(5)
C2	9.2(6)	7.3(6)	7.3(6)	-1.8(5)	1.6(5)	-0.4(5)
C6	11.2(6)	12.0(7)	11.1(7)	0.4(6)	-0.7(5)	1.4(5)
C3	8.0(6)	8.2(6)	9.8(7)	1.8(5)	1.3(5)	-0.5(5)
C5	10.6(6)	11.7(7)	10.9(7)	-3.0(6)	0.2(5)	-0.1(5)

Table 3: Bond Lengths in Å for **PK001**.

Atom	Atom	Length/Å
Cl2	C6	1.7955(17)
Cl1	C5	1.7958(17)
O1	C4	1.3370(19)
O1	C1	1.4390(19)
O2	C2	1.3391(19)
O2	C3	1.4398(19)
O4	C4	1.201(2)

Atom	Atom	Length/Å
O3	C2	1.198(2)
C4	C3	1.522(2)
C1	C2	1.515(2)
C1	C5	1.518(2)
C6	C3	1.509(2)

Table 4: Bond Angles in ° for **PK001**.

Atom	Atom	Atom	Angle/°
C4	O1	C1	122.08(12)
C2	O2	C3	121.67(13)
O1	C4	C3	119.20(13)
O4	C4	O1	119.71(15)
O4	C4	C3	121.04(15)
O1	C1	C2	115.39(13)
O1	C1	C5	109.47(13)
C2	C1	C5	110.70(13)

Atom	Atom	Atom	Angle/°
O2	C2	C1	119.29(14)
O3	C2	O2	119.75(14)
O3	C2	C1	120.96(14)
C3	C6	Cl2	110.41(11)
O2	C3	C4	114.96(13)
O2	C3	C6	107.16(13)
C6	C3	C4	110.48(13)
C1	C5	Cl1	109.55(11)

Table 5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **PK001**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5A	5200(50)	4930(20)	10170(20)	13(4)
H5B	6940(30)	6040(20)	9350(30)	13(4)
H1	6360(30)	3930(20)	7840(30)	10(4)
H3	220(40)	6278(19)	5660(30)	10(4)
H6A	-1500(30)	4780(30)	3570(30)	18(4)
H6B	160(50)	6034(19)	2840(30)	18(4)

Citations

APEX2 suite for crystallographic software v2014.11, Bruker axs, Madison, WI (2014).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

SAINT-8.34A-2013 •Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (2013).

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

Sheldrick, G.M., ShelXT, *Acta Cryst.*, (2014), **A71**, 3-8.

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#      Reported C6 H6 Cl2 O4
#    SumFormula C6 H6 Cl2 O4
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 2 ALERT_Level_A = In General: Serious Problem
 3 ALERT_Level_B = Potentially Serious Problem
 2 ALERT_Level_C = Check & Explain

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 1 ALERT_Type_2 Indicator that the Structure Model may be Wrong or Deficient.
 1 ALERT_Type_3 Indicator that the Structure Quality may be Low.
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