

Absolute Configuration of In Situ Crystallized (+)- γ -Decalactone

Michael Patzer, Nils Nöthling, Richard Goddard & Christian W. Lehmann*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an
der Ruhr, Germany.

lehmann@mpi-muelheim.mpg.de

Supporting Information

Single crystal structure analysis of (+)- γ -Decalactone, (γ -lac)

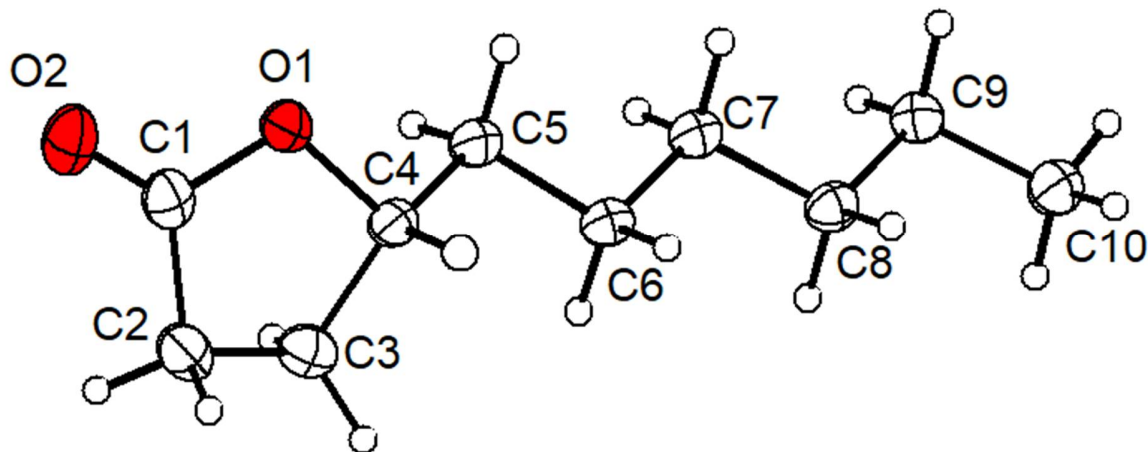


Figure S1: ORTEP-Plot of the molecular structure of (+)- γ -Decalactone.

X-ray Crystal Structure Analysis of γ -lac: $C_{10}H_{18}O_2$, $M_r = 170,24 \text{ g mol}^{-1}$, colorless capillary measurement, maximum size of crystal $1.078 \times 0.441 \times 0.411 \text{ mm}^3$, orthorhombic, space group $P 2_12_12_1$ [19], $a = 5.0543(6) \text{ \AA}$, $b = 5.3683(6) \text{ \AA}$, $c = 37.143(4) \text{ \AA}$, $V = 1007.8(2) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.122 \text{ g cm}^{-3}$, $\lambda = 1.54178 \text{ \AA}$, $\mu(\text{Cu-K}\alpha) = 0.603 \text{ mm}^{-1}$, analytical absorption correction ($T_{min} = 0.84565$, $T_{max} = 0.69343$), Bruker-AXS Kappa Mach3 with APEX-II detector and rotating anode X-ray source, $2.379^\circ < \theta < 71.877^\circ$, 33819 measured reflections, 1902 independent reflections, 1880 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0389$. The structure was solved by dual space methods (*SHELXT*) and refined by full-matrix least-squares (*SHELXL*) against F^2 to $R_1 = 0.0302$ [$I > 2\sigma(I)$], $wR_2 = 0.0688$, 110 parameters, 0 restraints, Absolute structure parameter Flack (x) = - 0.02(6).

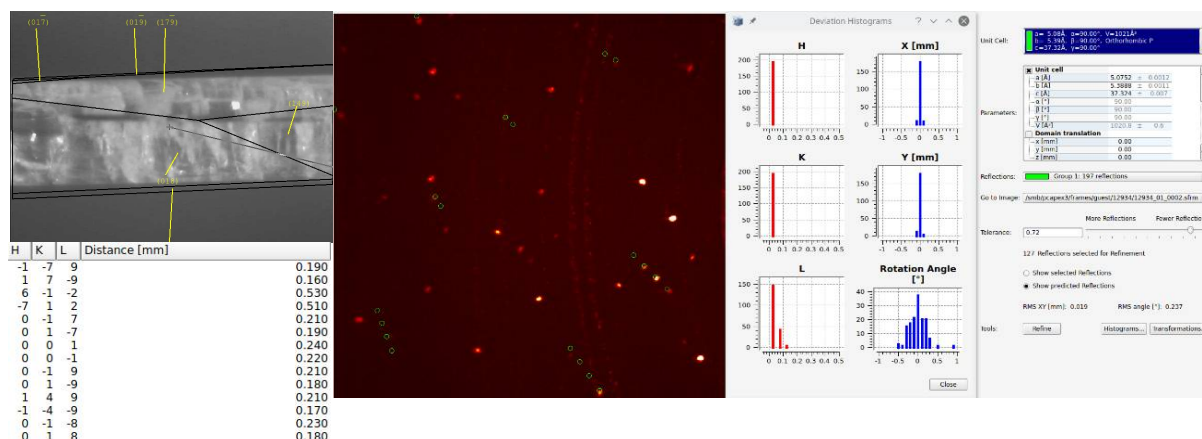


Figure S2: Screen shots of the capillary, face indexing and unit cell indexing.

Crystals were grown in a 0.3 mm diameter WJM borosilicate glass capillary by multiple melting and crystallization cycles. The maximum crystal size was estimated based on the diffraction geometry. For data acquisition, a fixed chi angle of 54.7 degree was chosen to ensure that the exposed crystalline volume was as small as possible consistent with a high redundancy.

Two reflections $[-5\ 2\ 14]$ and $[-5\ 3\ 6]$ were omitted from data set before final refinement cycles. Complete .cif-data of the compound are available under the CCDC number **CCDC- 2072278**.

Table S1: Crystal data and structure refinement.

Identification code	12934sadabs	
Empirical formula	$C_{10}H_{18}O_2$	
Color	colorless	
Formula weight	$170.24\text{ g}\cdot\text{mol}^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 \AA	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$, (no. 19)	
Unit cell dimensions	$a = 5.0543(6)\text{ \AA}$	$\alpha = 90^\circ$.
	$b = 5.3683(6)\text{ \AA}$	$\beta = 90^\circ$.
	$c = 37.143(4)\text{ \AA}$	$\gamma = 90^\circ$.
Volume	$1007.8(2)\text{ \AA}^3$	
Z	4	
Density (calculated)	$1.122\text{ Mg}\cdot\text{m}^{-3}$	

Absorption coefficient	0.603 mm ⁻¹	
F(000)	376 e	
Crystal size	1.078 x 0.441 x 0.411 mm ³	
θ range for data collection	2.379 to 71.877°.	
Index ranges	-5 ≤ h ≤ 4, -6 ≤ k ≤ 6, -45 ≤ l ≤ 45	
Reflections collected	33819	
Independent reflections	1902 [R _{int} = 0.0389]	
Reflections with I > 2σ(I)	1880	
Completeness to θ = 67.679°	97.1 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.84565 and 0.69343	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1902 / 0 / 128	
Goodness-of-fit on F ²	1.089	
Final R indices [I > 2σ(I)]	R ₁ = 0.0299	wR ² = 0.0687
R indices (all data)	R ₁ = 0.0302	wR ² = 0.0688
Absolute structure parameter	-0.02(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.106 and -0.144 e·Å ⁻³	

Table S2: Bond lengths [Å] and angles [°].

O(1)-C(1)	1.3489(19)	O(1)-C(4)	1.4688(19)
O(2)-C(1)	1.208(2)	C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900	C(6)-C(7)	1.525(2)
C(6)-C(5)	1.526(2)	C(1)-C(2)	1.501(3)
C(4)-H(4)	1.0000	C(4)-C(5)	1.510(2)
C(4)-C(3)	1.523(2)	C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900	C(7)-C(8)	1.521(2)
C(9)-H(9A)	0.9900	C(9)-H(9B)	0.9900
C(9)-C(8)	1.523(2)	C(9)-C(10)	1.517(2)
C(5)-H(5A)	0.9900	C(5)-H(5B)	0.9900
C(3)-H(3A)	0.9900	C(3)-H(3B)	0.9900
C(3)-C(2)	1.523(2)	C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900	C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900	C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800	C(10)-H(10C)	0.9800
C(1)-O(1)-C(4)	110.34(12)	H(6A)-C(6)-H(6B)	107.9
C(7)-C(6)-H(6A)	109.2	C(7)-C(6)-H(6B)	109.2
C(7)-C(6)-C(5)	111.91(13)	C(5)-C(6)-H(6A)	109.2
C(5)-C(6)-H(6B)	109.2	O(1)-C(1)-C(2)	109.83(15)
O(2)-C(1)-O(1)	120.84(16)	O(2)-C(1)-C(2)	129.33(16)
O(1)-C(4)-H(4)	109.2	O(1)-C(4)-C(5)	107.89(13)
O(1)-C(4)-C(3)	104.00(13)	C(5)-C(4)-H(4)	109.2
C(5)-C(4)-C(3)	117.18(14)	C(3)-C(4)-H(4)	109.2
C(6)-C(7)-H(7A)	108.8	C(6)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7	C(8)-C(7)-C(6)	113.86(13)
C(8)-C(7)-H(7A)	108.8	C(8)-C(7)-H(7B)	108.8
H(9A)-C(9)-H(9B)	107.7	C(8)-C(9)-H(9A)	108.9
C(8)-C(9)-H(9B)	108.9	C(10)-C(9)-H(9A)	108.9
C(10)-C(9)-H(9B)	108.9	C(10)-C(9)-C(8)	113.45(14)
C(6)-C(5)-H(5A)	109.0	C(6)-C(5)-H(5B)	109.0
C(4)-C(5)-C(6)	112.87(14)	C(4)-C(5)-H(5A)	109.0
C(4)-C(5)-H(5B)	109.0	H(5A)-C(5)-H(5B)	107.8
C(4)-C(3)-H(3A)	111.3	C(4)-C(3)-H(3B)	111.3

C(4)-C(3)-C(2)	102.15(14)	H(3A)-C(3)-H(3B)	109.2
C(2)-C(3)-H(3A)	111.3	C(2)-C(3)-H(3B)	111.3
C(1)-C(2)-C(3)	103.37(14)	C(1)-C(2)-H(2A)	111.1
C(1)-C(2)-H(2B)	111.1	C(3)-C(2)-H(2A)	111.1
C(3)-C(2)-H(2B)	111.1	H(2A)-C(2)-H(2B)	109.1
C(7)-C(8)-C(9)	113.11(13)	C(7)-C(8)-H(8A)	109.0
C(7)-C(8)-H(8B)	109.0	C(9)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8B)	109.0	H(8A)-C(8)-H(8B)	107.8
C(9)-C(10)-H(10A)	109.5	C(9)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5	H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5	H(10B)-C(10)-H(10C)	109.5

Table S3: Anisotropic displacement parameters (\AA^2).

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2 a^{*2}U_{11} + \dots + 2 h k a^* b^* U_{12}].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.028(1)	0.030(1)	0.024(1)	-0.001(1)	0.000(1)	-0.006(1)
O(2)	0.035(1)	0.038(1)	0.040(1)	-0.008(1)	-0.008(1)	-0.003(1)
C(6)	0.022(1)	0.025(1)	0.027(1)	0.001(1)	0.003(1)	0.001(1)
C(1)	0.027(1)	0.026(1)	0.028(1)	0.000(1)	-0.004(1)	0.008(1)
C(4)	0.020(1)	0.024(1)	0.025(1)	0.002(1)	0.000(1)	0.000(1)
C(7)	0.021(1)	0.025(1)	0.026(1)	0.001(1)	0.002(1)	0.001(1)
C(9)	0.024(1)	0.029(1)	0.025(1)	0.000(1)	0.001(1)	0.001(1)
C(5)	0.022(1)	0.027(1)	0.026(1)	-0.001(1)	0.002(1)	0.000(1)
C(3)	0.031(1)	0.028(1)	0.027(1)	0.003(1)	0.003(1)	0.003(1)
C(2)	0.033(1)	0.035(1)	0.023(1)	-0.001(1)	0.000(1)	0.006(1)
C(8)	0.021(1)	0.025(1)	0.028(1)	0.001(1)	0.001(1)	0.002(1)
C(10)	0.028(1)	0.036(1)	0.030(1)	-0.006(1)	0.001(1)	-0.002(1)

Table S4: Hydrogen coordinates and isotropic displacement parameters (\AA^2).

	x	y	z	U_{eq}
H(6A)	0.6927	0.3329	0.3891	0.030(5)
H(6B)	0.6189	0.5467	0.3608	0.034(5)
H(4)	0.5118	0.0070	0.3506	0.024(5)
H(7A)	0.3642	0.7538	0.4050	0.023(5)
H(7B)	0.4246	0.5368	0.4333	0.027(5)
H(9A)	0.5545	1.0781	0.4475	0.027(5)
H(9B)	0.6031	0.8613	0.4763	0.032(5)
H(5A)	0.2303	0.2259	0.3927	0.027(5)
H(5B)	0.1716	0.4259	0.3618	0.028(5)
H(3A)	0.5980	0.2320	0.3000	0.033(5)
H(3B)	0.3080	0.3579	0.2994	0.031(5)
H(2A)	0.2296	0.0454	0.2589	0.044(6)
H(2B)	0.4453	-0.1365	0.2771	0.035(5)
H(8A)	0.8196	0.8648	0.4051	0.035(5)
H(8B)	0.8771	0.6501	0.4339	0.024(5)
H(10A)	1.0042	1.1891	0.4503	0.049(7)
H(10B)	1.0592	0.9670	0.4780	0.041(6)
H(10C)	0.8788	1.1979	0.4898	0.047(6)

Table S5: Torsion angles [°].

O(1)-C(1)-C(2)-C(3)	-17.45(18)
O(1)-C(4)-C(5)-C(6)	169.19(12)
O(1)-C(4)-C(3)-C(2)	-31.04(17)
O(2)-C(1)-C(2)-C(3)	163.39(18)
C(6)-C(7)-C(8)-C(9)	179.01(14)
C(1)-O(1)-C(4)-C(5)	146.93(13)
C(1)-O(1)-C(4)-C(3)	21.82(17)
C(4)-O(1)-C(1)-O(2)	176.53(15)
C(4)-O(1)-C(1)-C(2)	-2.72(18)
C(4)-C(3)-C(2)-C(1)	29.21(17)
C(7)-C(6)-C(5)-C(4)	-174.87(13)
C(5)-C(6)-C(7)-C(8)	177.50(13)
C(5)-C(4)-C(3)-C(2)	-149.97(15)
C(3)-C(4)-C(5)-C(6)	-73.97(19)
C(10)-C(9)-C(8)-C(7)	178.34(14)

Table S6: Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2A)...O(2)#1	0.99	2.44	3.424(2)	172.9
C(2)-H(2B)...O(2)#2	0.99	2.59	3.423(2)	142.0

Symmetry transformations used to generate equivalent atoms:

#1 -x,y+1/2,-z+1/2 #2 x+1,y,z

Table S7: Asymmetry Parameters of the Five Membering Ring (Puckering Coordinates Analysis).

Atom	O1	C1	C2	C3	C4
	sp3	sp2	sp3	sp3	sp3
Dev. (Å)	0.0741	0.0489	-0.1532	0.1989	-0.1687
Cs(I)-Asym-Par (°)	36.85	38.8	25.28	3.35	19.83
C2(I)-Asym-Par (°)	19.84	11.65	38.59	50.85	43.67
Ring Bond Angle(°)	110.34	109.83	103.37	102.15	104.00
Tors(I-J) (°)	-2.72	-17.45	29.21	-31.04	21.82
Cs(I-J)-Asym-Par (°)	3.35	19.83	36.85	38.8	25.28
C2(I-J)-Asym-Par (°)	50.85	43.67	19.84	11.65	38.59
Ring Bond Distance (Å)	1.3489	1.5014	1.5231	1.5232	1.4688

Definitions:

Dev	Deviation of Atom I from Cremer&Pople Plane (Defined Differently from Least-Squares Plane)
Cs(I),C2(I)	Mirror Plane and 2-Axis Asym. Par. for Atom I (See Duax et al., Topics in Stereochemistry,V-9, (1976) pp.271-383)
Cs(I-J),C2(I-J)	Asymmetry Parameters for Bond I-J
Tors(I-J)	Torsion Angle for Bond I-J

Differential scanning calorimetry

(+)- γ -Decalactone (**γ -lac**) was initially investigated using differential scanning calorimetry (DSC) to determine the phase transition temperatures and the possible occurrence of polymorphism. Experiments were performed on a METTLER TOLEDO DSC 820 measuring module for thermal analysis. Two cycles with different cooling and heating rates were used for the sample.

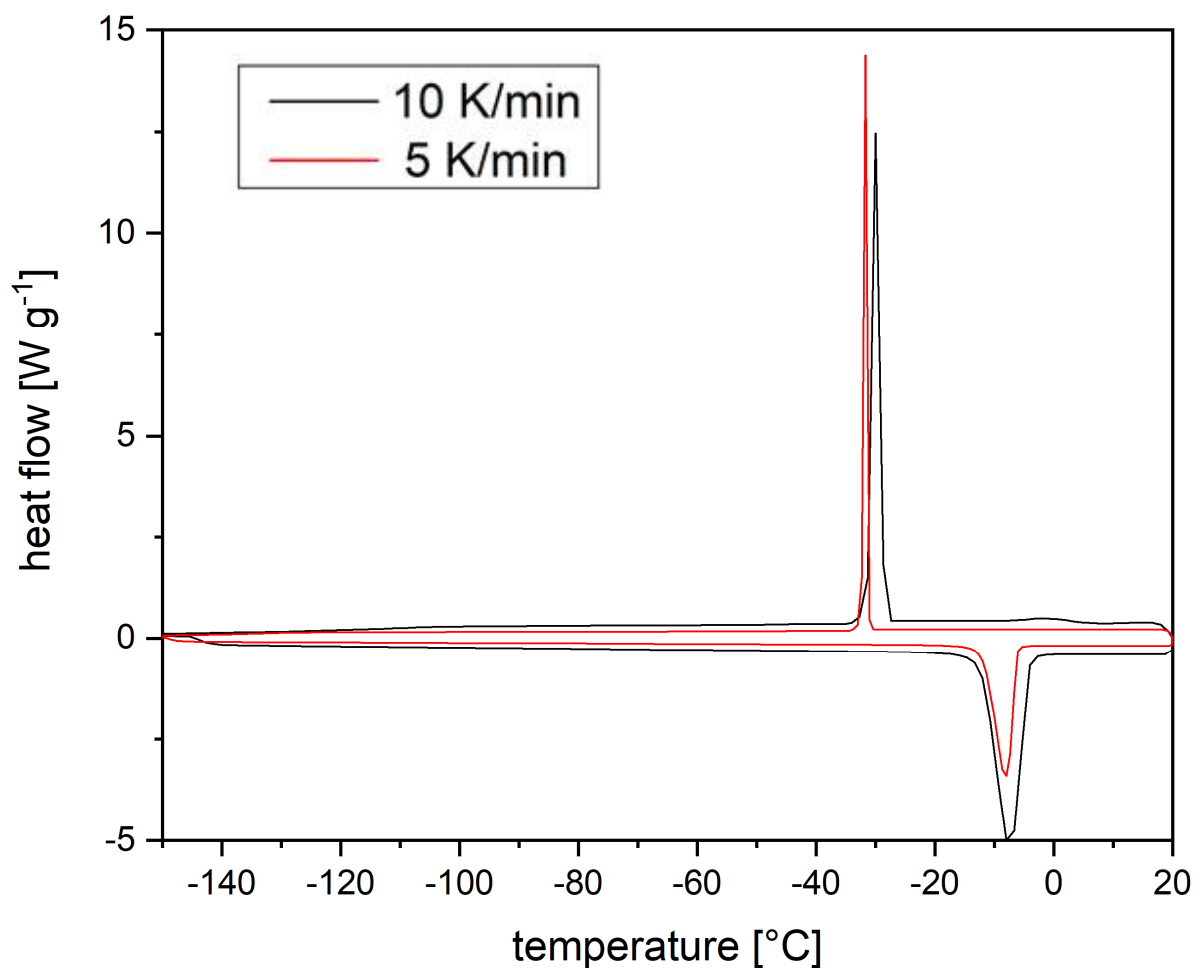


Figure S3: Recorded ambient to low temperature DSC curve of **γ -lac**.

Optical Rotation

The optical rotation of (+)- γ -Decalactone (**γ -lac**) was measured using a P8000-T polarimeter from A. Krüss Optronic GmbH at 24°C in chloroform with a concentration of $87\text{ mg}/100\text{ ml}$.

Vibrational Spectroscopy

The IR spectrum of liquid γ -lac was measured at room temperature on a Bruker Alpha Platinum-ATR spectrometer at a resolution of 4 cm^{-1} . 32 scans were accumulated and significant signals were observed. Some characteristic vibrational frequencies were identified and summarized in the table below.

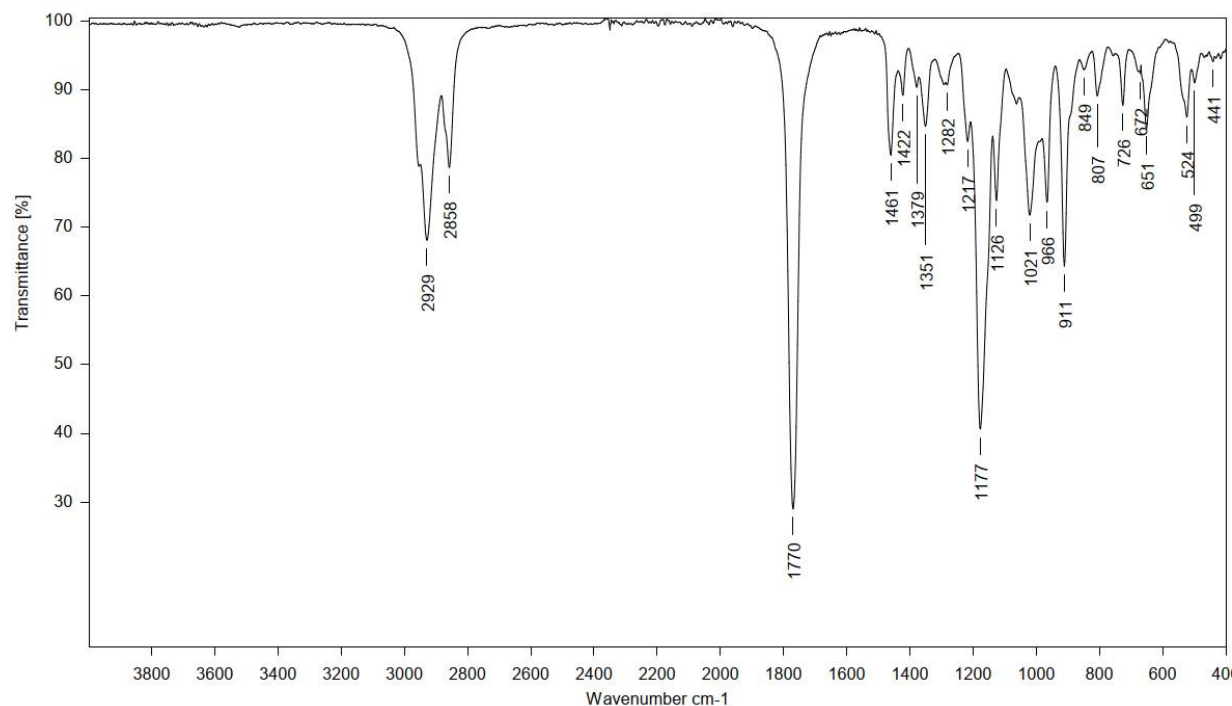


Figure S4: ATR-FT-IR spectra of γ -lac.

Bond type vibration	Literature [^a]	Experimental
C=O <i>st</i>	1790 – 1650	1770
C-O <i>st as</i>	≈ 1180	1177
C-H <i>st</i>	3000 – 2840	2929, 2858
CH ₃ δ <i>as</i>	1470 – 1430	1461
CH ₂ δ	1475 – 1450	

[^a] „Spektroskopische Daten zur Strukturaufklärung organischer Verbindungen“; Ernö Pretsch, Philippe Bühlmann, Martin Badertscher, 6. Auflage, **2019** Springer-Verlag GmbH Berlin, Germany
 ISBN 978-3-662-60949-1
 ISBN 978-3-662-60950-7 (eBook)

Flack-Parameter determination via Parsons' method

The Flack Parameter was determined according to Parsons' method. The experimental quotients q_{exp} are plotted against the theoretical ones q_{calc} in the following figures. The theoretical intensities of the Bijvoet pairs were calculated using SHELXL_2018/3. The Flack-Parameter was obtained from the slope by a linear fit using Origin_2019b (Fig S5).

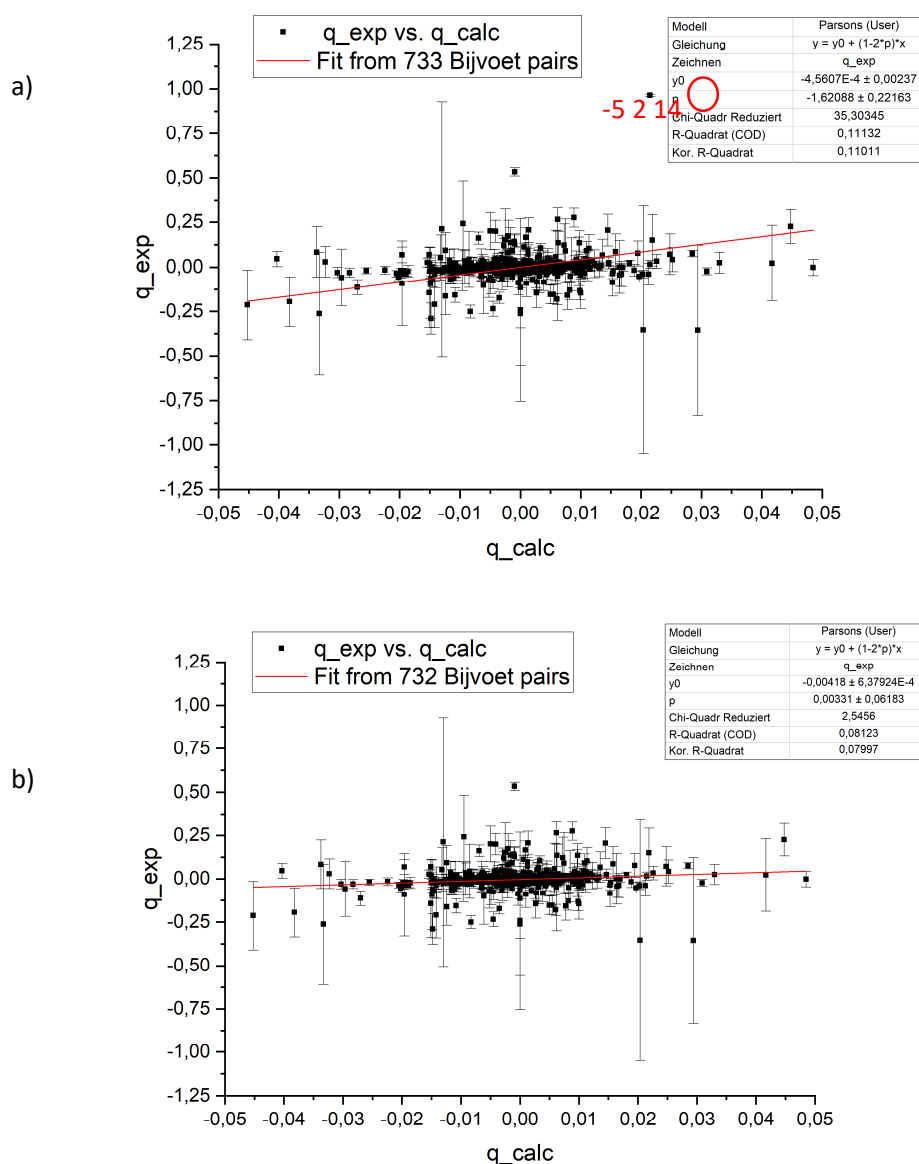


Figure S5: Determination of the Flack-Parameter by Parsons' method; a) The full data-set of 733 Bijvoet-Pairs was used for determination of the Flack-Parameter (variable p in linear regression), the quotient with highest difference from theory is marked with a red circle; b) Linear regression of 732 Bijvoet pairs, the red marked quotient in a) was omitted.

An outlier was clearly evident in the HKLF4 file, which is noticeable through the clear deviation from the predicted intensity of ca. $19 \sigma(I)$ according to the FCF and extremely large difference between the Bijvoet-pairs (Fig. S6).

-5	-2	-14	270.37	13.30
-5	-2	14	6.10	2.00
-5	-2	14	3.20	2.10
-5	2	-14	5.70	1.50
-5	-2	14	5.30	1.50
-5	-2	14	4.30	3.40
-5	-2	14	2.40	3.10
-5	-2	14	4.80	3.70

Figure S6: Excerpt from the HKLF4 file for γ -lac. Symmetry-equivalent reflections are marked with colored boxes (point group 2 2 2: $h\ k\ l = -h\ -k\ -l = h\ k\ -l = h\ -k\ -l$). The reflection (-5 -2 -14) in the blue box strongly deviates from its Bijvoet-pairs (red box).