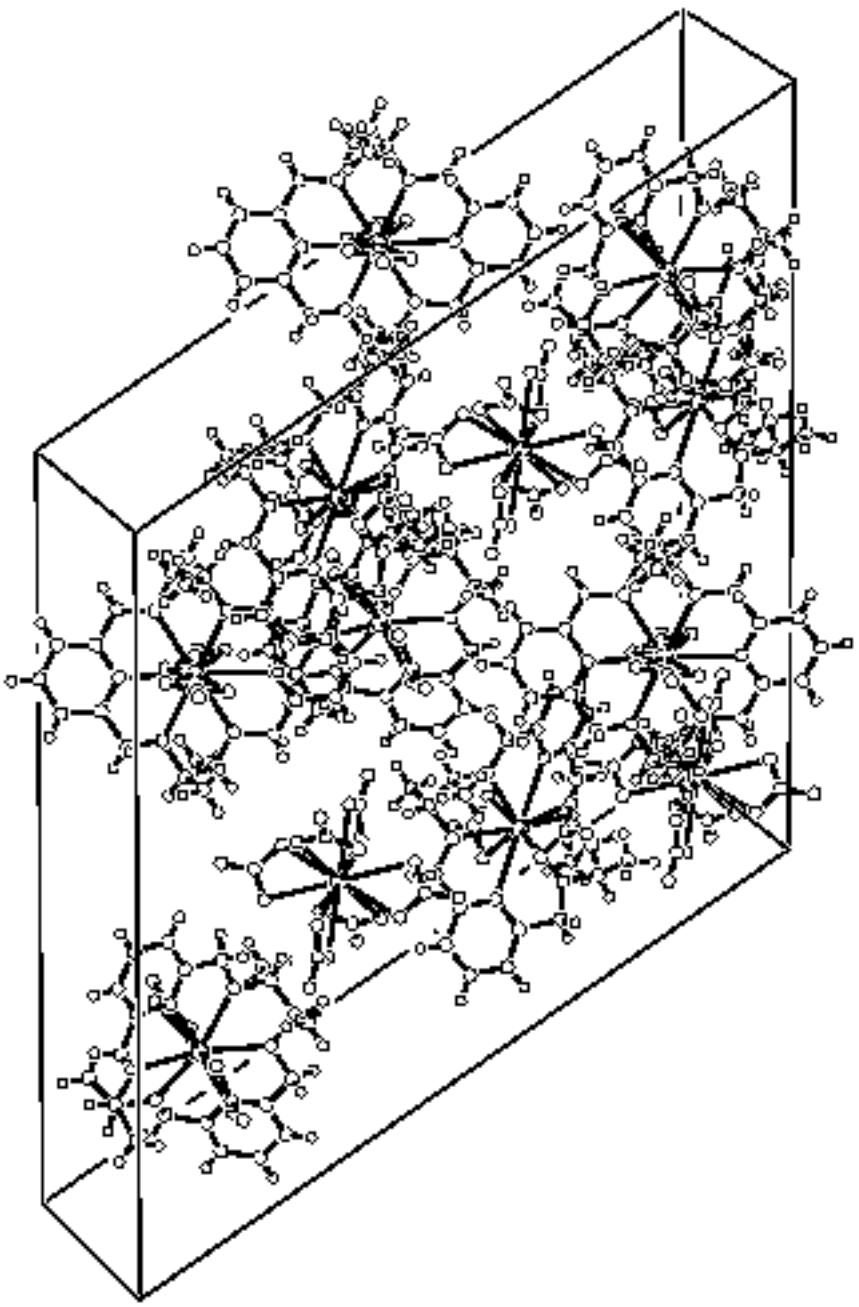
General procedure of the asymmetric aldol reaction: To a solution of $Ln(OTf)_3$ (10–20 mol %) in water/ethanol (1/9, 0.1 mL) at 0 or –10 °C was added a solution of **1** (12–24 mol %) in water/ethanol (1/9, 0.4 mL). Then, a solution of an aldehyde (0.2 mmol) in water/ethanol (1/9, 0.3 mL) and a solution of **2** (0.3 mmol) in water/ethanol (1/9, 0.3 mL). The whole was stirred for 18 h at the same temperature. The reaction was quenched by addition of aq. $NaHCO_3$. The mixture was extracted with methylene chloride 3 times, dried over Na_2SO_4, and concentrated. The desired product was purified by silica gel chromatography (AcOEt/hexane 1/6).

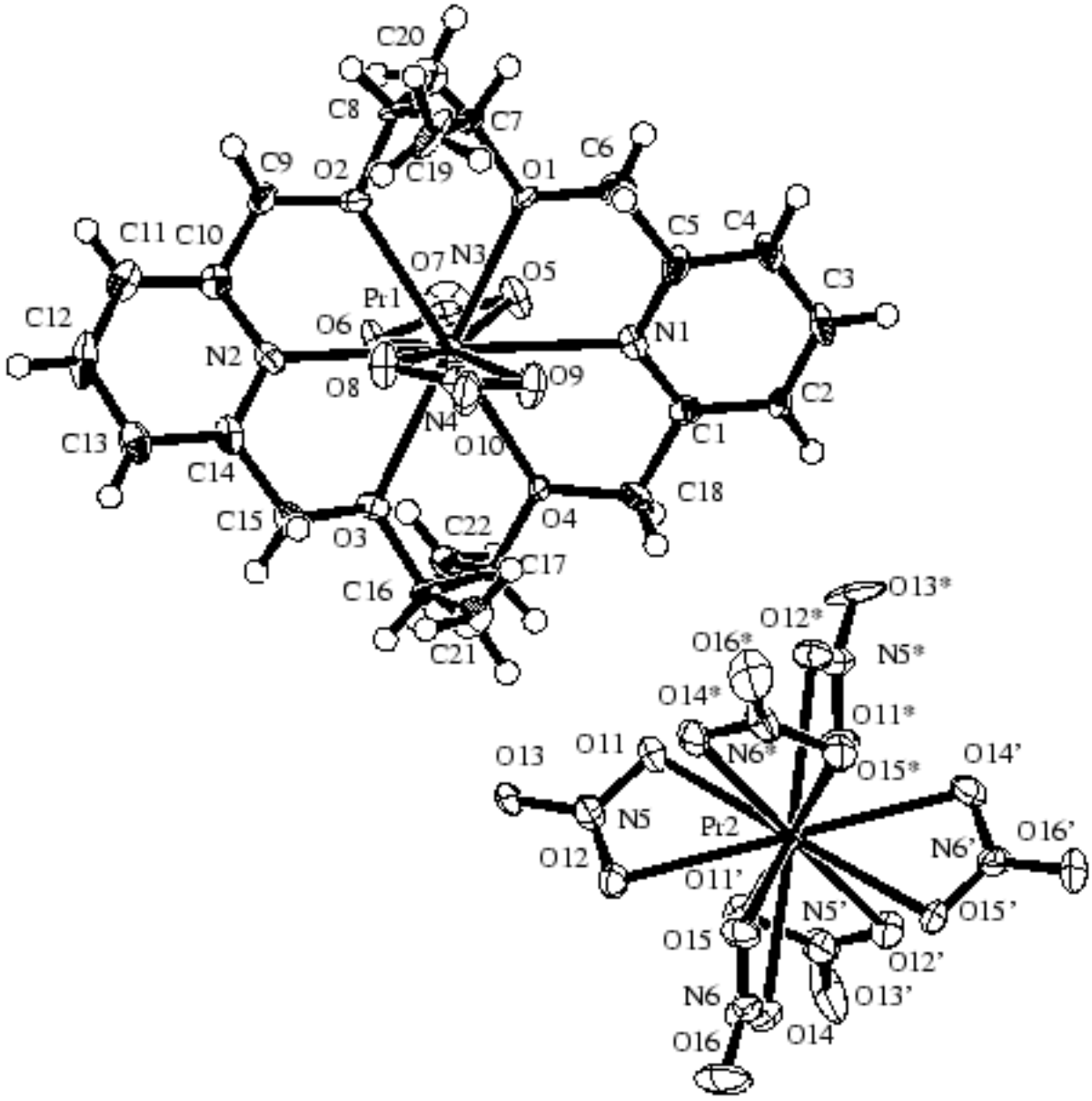
For the recovery of $Ln(OTf)_3$ and **1**, the following work-up procedure was used: After the aldol reaction was completed, water (10 mL) was added. The organic materials were extracted with methylene chloride 3 times, and the combined organic layers were washed with water, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography. The $Ln(OTf)_3$ used was recovered by concentration of the combined aqueous layers and drying in vacuo at 150 °C.

The diastereoselectivity and the enantioselectivity of the aldol adduct formed from benzaldehyde with **2** were determined by ^1H NMR and HPLC analysis, respectively, according to the literature method (Denmark, S. E.; Wong, K.-T.; Stavenger, R. A. *J. Am. Chem. Soc*. **1997**, *119*, 2333.).

Crystallographic data for $[Pr(NO_3)_2•\mathbf{1}]_3[Pr(NO_3)_6]$

Crystallization of $[Pr(NO_3)_2•\mathbf{1}]_3[Pr(NO_3)_6]$ was carried out as follows: To a solution of **1** (5.2 mg) in ethanol (0.24 mL) was added a solution of $Pr(NO_3)_3$ (6.0 mg) in ethanol (0.11 mL) at rt. A white precipitate was immediately formed, and dissolved by addition of water (0.08 mL) at 80 °C (oil bath temperature). The resulting solution was allowed to stand at 5 °C under ethanol vapor to give the crystals.




C20
C8
C7
C9
O2
C19
O1
C6
C11
C10
C5
C4
O7
N3
O5
C3
Pt1
C12
O6
N1
N2
O8
O9
C2
N4
C13
O10
C1
C14
C18
C15
O3
C22
O4
C17
C16
C21
O13*
O12*
O16*
N5*
O14*
O11*
O13
O11
N6*
O15*
O14'
N5
Pt2
O16'
O12
N6'
O11'
N5'
O15'
O15
O12'
N6
O13'
O16
O14

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{66}H_{90}N_{18}O_{48}Pr_4$
Formula Weight	2467.16
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.30 X 0.20 X 0.10 mm
Crystal System	trigonal
Lattice Type	R-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	10575 (4.2 - 55.0°)
Indexing Images	2 oscillations at 1.0 minutes
Camera Radius	127.40 mm
Lattice Parameters	a = 27.396(1) $\AA$ c = 10.7569(8) $\AA$ V = 6991.7(6) $\AA^3$
Space Group	R3 (#146)
Z value	3
D_{calc}	1.758 g/cm^3
F_{000}	3696.00
μ(MoKα)	21.53 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation	MoKα (λ = 0.71069 $\AA$) graphite monochromated
Temperature	-150.0 °C

Voltage, Current	50 kV, 100 mA
Collimator Size	0.5 mm
Detector Aperture	270.0 mm x 256.0 mm
Data Images	37 exposures at 0.2 minutes per degree
Oscillation Range (ϕ=0.0°,χ=45.0°)	ω 130.0 - 190.0° with 5.0° step
Oscillation Range (ϕ=180.0°,χ=45.0°)	ω 0.0 - 160.0° with 5.0° step
Camera Radius	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 11558 Unique: 1178 (R_{int} = 0.022)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo^2)}$
p-factor	0.0260
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.40σ(I))	3242
No. Variables	408
Reflection/Parameter Ratio	7.95
Residuals: R; Rw	0.048 ; 0.082
Residuals: R1	0.091
No. of Reflections to calc R1	2176
Goodness of Fit Indicator	1.25

Max Shift/Error in Final Cycle	12.109
Maximum peak in Final Diff. Map	96.69 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-82.35 $e^-/\AA^3$

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

atom	x	y	z	B_{eq}	occ
Pr(1)	0.83402(3)	0.66543(3)	0.5000	1.26(1)	1.0000
Pr(2)	0.6667	0.3333	0.1667(1)	1.37(1)	0.3333
O(1)	0.7917(3)	0.7275(3)	0.4628(7)	1.6(1)	1.0000
O(2)	0.8793(3)	0.7632(3)	0.6011(7)	1.7(2)	1.0000
O(3)	0.8877(3)	0.6121(3)	0.4782(6)	1.5(2)	1.0000
O(4)	0.7785(3)	0.5588(3)	0.4839(6)	1.3(1)	1.0000
O(5)	0.7626(3)	0.6364(3)	0.6704(7)	2.4(2)	1.0000
O(6)	0.8442(3)	0.6538(3)	0.7305(8)	2.0(2)	1.0000
O(7)	0.7749(4)	0.6219(4)	0.8629(7)	2.5(2)	1.0000
O(8)	0.9067(3)	0.7154(3)	0.3236(7)	2.2(2)	1.0000
O(9)	0.8199(3)	0.6598(3)	0.2665(9)	2.4(2)	1.0000
O(10)	0.8857(3)	0.7070(4)	0.1263(8)	2.7(2)	1.0000
O(11)	0.7263(3)	0.3950(3)	0.3501(8)	2.3(2)	1.0000
O(12)	0.7699(3)	0.3606(3)	0.2451(8)	2.0(2)	1.0000
O(13)	0.8117(4)	0.4147(4)	0.4021(10)	4.4(3)	1.0000
O(14)	0.6954(4)	0.2578(3)	0.0961(8)	2.4(2)	1.0000
O(15)	0.7301(3)	0.3340(3)	-0.0165(7)	2.2(2)	1.0000
O(16)	0.7491(4)	0.2689(4)	-0.0604(9)	3.9(3)	1.0000
N(1)	0.7277(4)	0.6152(4)	0.4207(8)	1.5(2)	1.0000
N(2)	0.9401(4)	0.7153(4)	0.5700(9)	1.6(2)	1.0000
N(3)	0.7939(4)	0.6365(4)	0.762(1)	2.2(2)	1.0000
N(4)	0.8720(4)	0.6945(4)	0.2368(9)	1.6(2)	1.0000
N(5)	0.7707(4)	0.3904(4)	0.333(1)	2.7(3)	1.0000
N(6)	0.7256(4)	0.2872(4)	0.0023(9)	2.1(2)	1.0000

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

atom	x	y	z	B_{eq}	occ
C(1)	0.6943(4)	0.5592(4)	0.4155(9)	1.6(2)	1.0000
C(2)	0.6373(4)	0.5326(4)	0.3879(9)	1.5(2)	1.0000
C(3)	0.6142(5)	0.5656(5)	0.361(1)	2.2(2)	1.0000
C(4)	0.6481(4)	0.6245(4)	0.3645(10)	2.2(2)	1.0000
C(5)	0.7043(4)	0.6471(4)	0.3921(9)	1.9(2)	1.0000
C(6)	0.7429(5)	0.7109(4)	0.390(1)	2.4(2)	1.0000
C(7)	0.8234(4)	0.7870(4)	0.482(1)	2.3(2)	1.0000
C(8)	0.8518(5)	0.7966(4)	0.6062(10)	1.9(2)	1.0000
C(9)	0.9258(4)	0.7833(4)	0.6842(9)	1.9(2)	1.0000
C(10)	0.9648(4)	0.7649(4)	0.6355(10)	1.7(2)	1.0000
C(11)	1.0210(5)	0.7959(5)	0.6573(9)	2.0(2)	1.0000
C(12)	1.0550(4)	0.7764(5)	0.6104(10)	2.6(2)	1.0000
C(13)	1.0327(4)	0.7251(5)	0.5434(10)	2.2(2)	1.0000
C(14)	0.9736(4)	0.6963(4)	0.5279(9)	1.5(2)	1.0000
C(15)	0.9458(4)	0.6406(4)	0.4555(9)	1.6(2)	1.0000
C(16)	0.8599(4)	0.5528(4)	0.4383(10)	1.7(2)	1.0000
C(17)	0.8062(4)	0.5259(4)	0.5080(8)	1.3(2)	1.0000
C(18)	0.7222(4)	0.5255(4)	0.442(1)	2.4(2)	1.0000
C(19)	0.8665(6)	0.8145(5)	0.375(1)	3.4(3)	1.0000
C(20)	0.8131(5)	0.7827(6)	0.714(1)	2.9(3)	1.0000
C(21)	0.8531(5)	0.5481(5)	0.301(1)	2.6(3)	1.0000
C(22)	0.8108(5)	0.5208(5)	0.649(1)	2.0(2)	1.0000
H(2)	0.6155	0.4931	0.3919	2.0213	1.0000
H(3)	0.5747	0.5492	0.3448	2.5764	1.0000

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

atom	x	y	z	B_{eq}	occ
H(4)	0.6326	0.6475	0.3465	2.7501	1.0000
H(6A)	0.7535	0.7201	0.3017	3.0304	1.0000
H(6B)	0.7221	0.7269	0.4143	3.0304	1.0000
H(7)	0.7995	0.8027	0.4790	2.4745	1.0000
H(8)	0.8806	0.8361	0.6085	2.5708	1.0000
H(9A)	0.9139	0.7686	0.7618	2.2819	1.0000
H(9B)	0.9455	0.8234	0.6839	2.2819	1.0000
H(11)	1.0388	0.8302	0.6984	2.1942	1.0000
H(12)	1.0964	0.7964	0.6183	2.7019	1.0000
H(13)	1.0550	0.7113	0.5093	2.3884	1.0000
H(15A)	0.9549	0.6489	0.3728	2.6285	1.0000
H(15B)	0.9628	0.6191	0.4872	2.6285	1.0000
H(16)	0.8817	0.5369	0.4667	2.3253	1.0000
H(17)	0.7824	0.4886	0.4772	1.9242	1.0000
H(18A)	0.7004	0.4975	0.5049	2.6640	1.0000
H(18B)	0.7213	0.5053	0.3685	2.6640	1.0000
H(19C)	0.8794	0.8540	0.3686	3.7394	1.0000
H(19A)	0.8491	0.7978	0.2951	3.7394	1.0000
H(19B)	0.8979	0.8093	0.3853	3.7394	1.0000
H(20C)	0.8333	0.7884	0.7863	3.4702	1.0000
H(20A)	0.7845	0.7436	0.7057	3.4702	1.0000
H(20B)	0.7956	0.8050	0.7104	3.4702	1.0000
H(21C)	0.8895	0.5665	0.2631	3.0951	1.0000
H(21A)	0.8341	0.5093	0.2778	3.0951	1.0000

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

atom	x	y	z	B_{eq}	occ
H(21B)	0.8324	0.5650	0.2734	3.0951	1.0000
H(22C)	0.7740	0.5004	0.6840	2.5945	1.0000
H(22A)	0.8310	0.5567	0.6836	2.5945	1.0000
H(22B)	0.8299	0.5001	0.6631	2.5945	1.0000

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr(1)	0.0134(3)	0.0151(3)	0.0195(2)	0.0072(3)	-0.0005(2)	0.0001(3)
Pr(2)	0.0143(3)	0.0143	0.0235(5)	0.0071	0.0000	0.0000
O(1)	0.021(4)	0.009(3)	0.029(4)	0.005(3)	-0.009(3)	-0.006(3)
O(2)	0.026(4)	0.018(4)	0.025(4)	0.015(3)	-0.005(3)	-0.006(3)
O(3)	0.021(4)	0.024(4)	0.018(4)	0.014(3)	0.007(3)	0.002(3)
O(4)	0.014(3)	0.013(3)	0.025(4)	0.008(3)	-0.008(3)	-0.002(3)
O(5)	0.020(4)	0.049(6)	0.027(4)	0.021(4)	-0.002(3)	0.000(4)
O(6)	0.013(4)	0.037(5)	0.028(5)	0.013(4)	0.002(3)	0.011(4)
O(7)	0.041(5)	0.047(5)	0.009(4)	0.023(4)	0.015(3)	0.008(4)
O(8)	0.017(4)	0.037(5)	0.020(4)	0.006(4)	-0.001(3)	0.004(3)
O(9)	0.016(4)	0.036(5)	0.025(4)	0.004(4)	0.001(3)	-0.002(3)
O(10)	0.022(4)	0.042(5)	0.034(5)	0.012(4)	-0.009(4)	-0.014(4)
O(11)	0.024(4)	0.034(5)	0.036(5)	0.018(4)	-0.010(4)	-0.005(4)
O(12)	0.023(5)	0.031(5)	0.025(5)	0.014(4)	-0.006(3)	-0.007(4)
O(13)	0.047(6)	0.050(6)	0.091(8)	0.041(5)	-0.054(6)	-0.043(6)
O(14)	0.024(5)	0.015(4)	0.049(6)	0.006(4)	-0.002(4)	-0.005(4)
O(15)	0.025(5)	0.027(5)	0.034(5)	0.015(4)	0.013(4)	0.003(4)
O(16)	0.052(6)	0.038(6)	0.069(7)	0.030(5)	0.027(5)	-0.003(5)
N(1)	0.016(5)	0.025(5)	0.015(5)	0.010(4)	0.002(4)	0.007(4)
N(2)	0.018(5)	0.023(5)	0.023(6)	0.013(4)	0.002(4)	0.005(4)
N(3)	0.027(6)	0.015(5)	0.043(7)	0.011(5)	-0.006(5)	-0.007(4)
N(4)	0.019(5)	0.022(5)	0.018(5)	0.010(4)	0.012(4)	0.005(4)
N(5)	0.022(6)	0.025(6)	0.057(8)	0.013(5)	-0.008(5)	-0.001(5)
N(6)	0.024(6)	0.021(5)	0.027(6)	0.005(5)	0.008(4)	-0.005(4)

Table 2. Anisotropic Displacement Parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.023(6)	0.019(5)	0.018(6)	0.011(5)	0.003(4)	0.000(4)
C(2)	0.012(5)	0.015(5)	0.028(6)	0.004(4)	-0.001(4)	-0.001(4)
C(3)	0.017(5)	0.037(7)	0.031(7)	0.013(5)	-0.007(5)	0.006(5)
C(4)	0.023(5)	0.030(6)	0.034(6)	0.015(5)	-0.011(4)	0.008(5)
C(5)	0.017(5)	0.018(5)	0.028(6)	0.002(4)	-0.001(4)	0.004(4)
C(6)	0.031(7)	0.018(5)	0.043(7)	0.013(5)	-0.005(5)	0.006(5)
C(7)	0.019(6)	0.008(5)	0.057(8)	0.004(4)	-0.013(5)	-0.007(5)
C(8)	0.031(6)	0.013(5)	0.033(6)	0.013(5)	-0.006(5)	-0.012(4)
C(9)	0.022(5)	0.016(5)	0.031(6)	0.006(4)	-0.008(4)	-0.004(4)
C(10)	0.022(5)	0.017(5)	0.022(6)	0.007(5)	0.003(4)	0.012(4)
C(11)	0.028(6)	0.025(6)	0.014(5)	0.006(5)	-0.002(4)	0.004(4)
C(12)	0.015(5)	0.041(7)	0.015(5)	-0.005(5)	-0.001(4)	0.018(5)
C(13)	0.019(5)	0.035(6)	0.028(6)	0.012(5)	0.004(4)	0.008(5)
C(14)	0.017(5)	0.022(5)	0.014(5)	0.006(4)	0.003(4)	0.014(4)
C(15)	0.019(5)	0.030(6)	0.015(6)	0.014(5)	0.010(4)	0.004(4)
C(16)	0.022(5)	0.018(5)	0.026(6)	0.011(4)	-0.001(4)	-0.010(4)
C(17)	0.030(6)	0.013(5)	0.014(5)	0.017(4)	-0.005(4)	-0.005(4)
C(18)	0.016(5)	0.018(5)	0.057(8)	0.010(5)	0.004(5)	0.002(5)
C(19)	0.049(9)	0.016(6)	0.039(8)	-0.003(6)	-0.020(7)	0.001(5)
C(20)	0.036(8)	0.034(7)	0.040(8)	0.019(6)	0.001(6)	-0.004(6)
C(21)	0.032(7)	0.031(7)	0.027(7)	0.010(6)	0.013(5)	0.001(5)
C(22)	0.029(6)	0.026(6)	0.026(6)	0.018(5)	-0.005(5)	0.001(5)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$