11-Azaartemisinin cocrystals with preserved lactam: acid heterosynthons ‡

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Supplementary Material

Submitted to CrystEngComm

October 2017

S1. Crystal Determination Summaries for 1-8

Table S1.1.1 Crystal data and structure refinement for 11-Aza 1

Identification code	madiha8cult
Empirical formula	$C_{15}H_{23}NO_4$
Formula weight	281.34
Temperature/K	100.00(10)
Crystal system	trigonal
Space group	$P3_2$
a/Å	11.71759(15)
b/Å	11.71759(15)
c/Å	9.48728(13)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1128.10(3)
Z	3
ρ_{calc}g/cm^3	1.242
μ/mm^{-1}	0.732
F(000)	456.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.714 to 134.57
Index ranges	$-13 \leq h \leq 14$, $-14 \leq k \leq 13$, $-11 \leq l \leq 11$
Reflections collected	5621
Independent reflections	2647 [R_{int} = 0.0144, R_{sigma} = 0.0187]
Data/restraints/parameters	2647/1/184
Completeness to theta = 66.5°	99.9%
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0238, wR_2 = 0.0579
Final R indexes [all data]	R_1 = 0.0243, wR_2 = 0.0582
Largest diff. peak/hole / e Å^{-3}	0.15/-0.13
Flack parameter	0.00(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza 1.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	1696.0(13)	4212.5(12)	6607.7(14)	21.1(3)
O2	348.4(12)	3208.3(12)	6993.5(14)	21.8(3)
O3	665.0(12)	1427.4(12)	6861.9(12)	18.5(3)
O10	229.7(13)	2450.5(13)	2362.9(14)	26.1(3)
N11	747.0(14)	1933.9(14)	4456.3(15)	17.6(3)
C1	2434.1(17)	3610.9(17)	6043.5(18)	17.1(4)
C2	1529.8(17)	2144.2(17)	5717.2(18)	16.8(4)
C3	429.5(19)	2242.3(18)	7812.7(19)	21.4(4)
C4	1505(2)	2843(2)	8945(2)	27.1(4)
C5	2829(2)	2993(2)	8505.5(19)	26.1(4)
C6	4546.4(19)	3561(2)	6584(2)	26.3(4)
C7	5125.5(19)	4345.8(19)	5235(2)	25.4(4)
C8	4090.6(18)	4080.2(18)	4114(2)	21.9(4)
C9	1980.9(18)	4233.4(17)	3657.4(19)	19.4(4)
C10	921.9(17)	2802.1(17)	3422.5(18)	18.5(4)
C11	3460.8(18)	3808.3(18)	7172(2)	22.1(4)
C12	3060.1(17)	4395.1(17)	4698.7(18)	17.6(4)
C13	-936(2)	1408(2)	8427(2)	26.8(4)
C14	5642(2)	3910(3)	7664(3)	42.8(6)
C15	2523(2)	4928(2)	2248(2)	28.1(4)

Table S1.1.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza 1.

Anisotropic displacement factor exponent has the form: $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	21.8(6)	14.2(6)	26.7(7)	-0.8(5)	5.4(5)	8.6(5)
O2	21.3(6)	18.4(6)	25.5(7)	2.9(5)	6.4(5)	9.7(5)
O3	22.8(7)	15.1(6)	17.6(6)	1.9(5)	3.8(5)	9.4(5)
O10	23.1(7)	24.2(7)	21.7(7)	2.6(5)	-4.5(5)	4.9(6)
N11	17.0(7)	13.0(7)	18.6(7)	-0.5(6)	-0.1(6)	4.4(6)
C1	19.9(9)	14.5(8)	18.4(9)	-3.0(6)	0.0(7)	9.7(7)
C2	17.7(8)	14.6(8)	17.6(8)	0.4(6)	1.5(7)	7.8(7)
C3	27.7(10)	18.1(9)	19.9(9)	0.3(7)	4.3(7)	12.5(8)
C4	35.5(11)	24.6(10)	17.9(9)	0.0(7)	1.4(8)	12.6(9)
C5	28.8(10)	23.8(10)	20.6(9)	0.5(7)	-5.8(8)	9.2(8)
C6	20.9(10)	23.3(10)	33.2(11)	2.3(8)	-3.6(8)	9.9(8)
C7	19.3(10)	20.8(9)	35.1(12)	1.2(8)	0.8(8)	9.2(8)
C8	20.0(9)	17.9(9)	25.7(9)	-0.7(7)	4.5(7)	7.9(8)
C9	20.7(9)	16.3(9)	20.9(9)	0.8(7)	-0.8(7)	9.0(8)
C10	16.9(8)	19.3(9)	19.0(9)	0.0(7)	2.3(7)	9.0(7)
C11	22.4(10)	17.4(9)	22.4(9)	-2.5(7)	-4.9(7)	6.9(8)
C12	18.1(9)	12.0(8)	21.0(9)	-1.1(6)	-0.2(7)	6.1(7)
C13	30.1(11)	24.6(10)	24.5(10)	1.4(8)	8.7(8)	12.7(9)
C14	27.3(12)	50.0(15)	47.5(15)	9.7(11)	-9.3(10)	16.6(11)
C15	26.7(11)	21.5(9)	25.4(10)	5.4(8)	-3.2(8)	4.0(8)

Table S1.1.4 Bond Lengths for 11-Aza 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.4676(18)	C3	C13	1.514(3)
O1	C1	1.463(2)	C4	C5	1.530(3)
O2	C3	1.415(2)	C5	C11	1.534(3)
O3	C2	1.435(2)	C6	C7	1.523(3)
O3	C3	1.437(2)	C6	C11	1.543(3)
O10	C10	1.226(2)	C6	C14	1.529(3)
N11	C2	1.452(2)	C7	C8	1.524(3)
N11	C10	1.353(2)	C8	C12	1.532(2)
C1	C2	1.533(2)	C9	C10	1.524(2)
C1	C11	1.539(2)	C9	C12	1.540(2)
C1	C12	1.528(2)	C9	C15	1.529(3)
C3	C4	1.533(3)			

Table S1.1.5 Bond Angles for 11-Aza 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	111.29(12)	C5	C4	C3	114.54(16)
C3	O2	O1	107.62(13)	C4	C5	C11	116.24(16)
C2	O3	C3	113.58(13)	C7	C6	C11	110.51(16)
C10	N11	C2	128.65(14)	C7	C6	C14	109.91(17)
O1	C1	C2	111.73(14)	C14	C6	C11	111.59(18)
O1	C1	C11	106.19(14)	C6	C7	C8	113.24(16)
O1	C1	C12	103.73(13)	C7	C8	C12	109.91(15)
C2	C1	C11	111.04(14)	C10	C9	C12	113.34(14)
C12	C1	C2	111.12(14)	C10	C9	C15	110.55(15)
C12	C1	C11	112.73(14)	C15	C9	C12	113.49(15)
O3	C2	N11	108.83(14)	O10	C10	N11	121.04(16)
O3	C2	C1	113.15(14)	O10	C10	C9	121.84(16)
N11	C2	C1	112.36(14)	N11	C10	C9	117.09(15)
O2	C3	O3	107.38(13)	C1	C11	C6	112.08(15)
O2	C3	C4	112.70(15)	C5	C11	C1	112.49(15)
O2	C3	C13	104.83(15)	C5	C11	C6	111.56(16)
O3	C3	C4	111.00(16)	C1	C12	C8	110.89(14)
O3	C3	C13	107.73(15)	C1	C12	C9	110.11(14)
C13	C3	C4	112.81(16)	C8	C12	C9	115.82(14)

Table S1.1.6 Torsion Angles for 11-Aza 1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-77.21(16)	C6	C7	C8	C12	57.8(2)
O1	O2	C3	C4	45.34(18)	C7	C6	C11	C1	50.9(2)
O1	O2	C3	C13	168.39(13)	C7	C6	C11	C5	178.12(15)
O1	C1	C2	O3	-49.49(19)	C7	C8	C12	C1	-56.27(19)
O1	C1	C2	N11	74.26(18)	C7	C8	C12	C9	177.32(15)
O1	C1	C11	C5	68.45(18)	C10	N11	C2	O3	142.19(17)
O1	C1	C11	C6	-164.88(14)	C10	N11	C2	C1	16.1(2)
O1	C1	C12	C8	168.93(14)	C10	C9	C12	C1	-49.69(19)
O1	C1	C12	C9	-61.56(16)	C10	C9	C12	C8	77.11(19)
O2	O1	C1	C2	12.13(18)	C11	C1	C2	O3	68.86(18)
O2	O1	C1	C11	-109.08(14)	C11	C1	C2	N11	-167.39(14)
O2	O1	C1	C12	131.91(13)	C11	C1	C12	C8	54.50(18)
O2	C3	C4	C5	-94.7(2)	C11	C1	C12	C9	-175.99(14)
O3	C3	C4	C5	25.8(2)	C11	C6	C7	C8	-55.0(2)
C1	O1	O2	C3	48.65(16)	C12	C1	C2	O3	-164.82(14)
C2	O3	C3	O2	37.59(19)	C12	C1	C2	N11	-41.07(18)
C2	O3	C3	C4	-86.00(17)	C12	C1	C11	C5	-178.62(15)
C2	O3	C3	C13	150.03(15)	C12	C1	C11	C6	-51.95(19)
C2	N11	C10	O10	174.58(17)	C12	C9	C10	O10	-157.90(16)
C2	N11	C10	C9	-7.3(3)	C12	C9	C10	N11	24.0(2)
C2	C1	C11	C5	-53.2(2)	C13	C3	C4	C5	146.85(17)
C2	C1	C11	C6	73.48(19)	C14	C6	C7	C8	-178.56(18)
C2	C1	C12	C8	-70.89(18)	C14	C6	C11	C1	173.56(16)
C2	C1	C12	C9	58.62(17)	C14	C6	C11	C5	-59.3(2)
C3	O3	C2	N11	-102.38(16)	C15	C9	C10	O10	-29.2(2)
C3	O3	C2	C1	23.28(19)	C15	C9	C10	N11	152.73(16)
C3	C4	C5	C11	56.9(2)	C15	C9	C12	C1	-176.87(15)
C4	C5	C11	C1	-36.2(2)	C15	C9	C12	C8	-50.1(2)
C4	C5	C11	C6	-163.17(16)					

Table S1.1.7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza 1.

Atom	*x*	*y*	*z*	U(eq)
H11	68	1135	4350	21
H2	2106	1755	5542	20
H4A	1642	3722	9202	32
H4B	1189	2283	9798	32
H5A	2706	2102	8361	31
H5B	3456	3403	9296	31
H6	4138	2603	6354	32
H7A	5776	4126	4846	31

H7B	5599	5297	5465	31
H8A	3656	3144	3823	26
H8B	4519	4632	3274	26
H9	1529	4675	4102	23
H11A	3903	4756	7459	26
H12	3548	5345	4978	21
H13A	-1597	1246	7703	40
H13B	-1052	1873	9224	40
H13C	-1044	566	8751	40
H14A	6345	3807	7234	64
H14B	5283	3321	8479	64
H14C	5998	4824	7971	64
H15A	2940	4501	1746	42
H15B	3177	5855	2417	42
H15C	1801	4874	1677	42

Experimental

Single crystals of $C_{15}H_{23}NO_4$ **11-Aza 1** were grown from evaporation of an ethyl acetate solution. A suitable crystal was selected and mounted on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector.. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza 1

Crystal Data for $C_{15}H_{23}NO_4$ (M =281.34 g/mol): trigonal, space group $P3_2$ (no. 145), a = 11.71759(15) Å, c = 9.48728(13) Å, V = 1128.10(3) Å^3, Z = 3, T = 100.00(10) K, μ(CuKα) = 0.732 mm^{-1}, *Dcalc* = 1.242 g/cm^3, 5621 reflections measured (8.714° ≤ 2Θ ≤ 134.57°), 2647 unique (R_{int} = 0.0144, R_{sigma} = 0.0187) which were used in all calculations. The final R_1 was 0.0238 (I > 2σ(I)) and wR_2 was 0.0582 (all data).

Refinement model description

Number of restraints - 1, constraints – listed below.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12)
2.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B)
2.c Aromatic/amide H refined with riding coordinates:
 N11(H11)
2.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)
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Table S1.2.1 Crystal data and structure refinement for 11-Aza:Ben 2

Identification code	madiha36CuLT
Empirical formula	$C_{22}H_{29}NO_6$
Formula weight	403.46
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.64312(19)
b/Å	9.3622(2)
c/Å	22.8165(4)
α/°	90
β/°	90.9437(18)
γ/°	90
Volume/Å^3	2059.60(7)
Z	4
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.776
F(000)	864.0
Crystal size/mm^3	0.18 × 0.15 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.75 to 134.998
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-26 \leq l \leq 27$
Reflections collected	11649
Independent reflections	7317 [R_{int} = 0.0339, R_{sigma} = 0.0514]
Data/restraints/parameters	7317/1/545
Completeness to theta = 66.5°	99.7%
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0785
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.0818
Largest diff. peak/hole / e Å^{-3}	0.18/-0.18
Flack parameter	-0.04(10)

Table S1.2.2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:Ben 2.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4500(2)	5659(2)	4125.2(8)	21.6(4)
O2	5959.6(19)	5856(2)	4304.1(8)	22.7(4)
O3	6451.5(19)	3462(2)	4414.7(8)	20.5(4)
O10	4043(2)	4837(2)	6008.7(8)	22.2(4)
N11	5037(2)	3900(2)	5214.4(9)	19.4(5)
C1	4034(3)	4190(3)	4214.5(11)	17.8(5)
C2	5065(3)	3392(3)	4609.8(11)	18.4(5)
C3	6732(3)	4707(3)	4071.5(12)	22.6(6)
C4	6376(3)	4447(3)	3420.8(12)	25.5(6)
C5	5306(3)	3265(3)	3315.5(11)	22.5(6)
C6	3061(3)	2082(3)	3618.5(12)	20.6(5)
C7	1700(3)	2246(3)	3944.8(13)	25.1(6)
C8	1908(3)	2889(3)	4554.8(12)	22.4(6)
C9	2807(3)	5145(3)	5100.4(12)	20.7(5)
C10	3997(3)	4585(3)	5470.7(12)	18.8(5)
C11	3887(3)	3493(3)	3602.5(11)	19.3(5)
C12	2629(3)	4350(3)	4515.1(11)	18.9(5)
C13	8232(3)	5103(4)	4186.6(14)	31.9(7)
C14	2766(3)	1524(3)	2996.2(13)	27.7(6)
C15	1478(3)	5250(4)	5454.5(13)	30.5(7)
O20	7260(2)	3334(2)	6092.4(8)	25.5(4)
O21	5527(2)	3371(2)	6737.4(8)	25.0(4)
C20	6760(3)	2960(3)	6555.6(12)	21.7(6)
C21	7481(3)	1984(3)	6978.0(12)	22.0(6)
C22	8781(3)	1448(3)	6838.7(12)	24.6(6)
C23	9438(3)	489(3)	7210.0(13)	29.5(7)
C24	8811(3)	55(4)	7724.5(14)	31.4(7)
C25	7519(3)	598(4)	7867.4(13)	31.1(7)
C26	6856(3)	1567(3)	7497.3(13)	25.6(6)
O1A	3403.6(19)	3676(2)	-638.7(8)	18.1(4)
O2A	2982.9(19)	3436(2)	-29.8(8)	19.0(4)
O3A	3001.6(18)	5804(2)	239.7(8)	18.6(4)
O10A	7570.5(18)	4566(2)	182.8(8)	20.7(4)
N11A	5383(2)	5408(2)	149.6(10)	17.7(5)
C1A	3862(3)	5137(3)	-737.4(11)	16.7(5)
C2A	4122(2)	5903(3)	-152.0(11)	16.5(5)
C3A	2122(3)	4588(3)	132.0(12)	19.5(5)
C4A	1010(3)	4925(3)	-336.9(12)	22.5(6)
C5A	1392(3)	6123(3)	-756.7(12)	22.6(6)
C6A	3226(3)	7295(3)	-1383.9(12)	22.1(6)
C7A	4610(3)	7109(3)	-1691.7(12)	23.5(6)
C8A	5713(3)	6420(3)	-1297.6(12)	21.6(6)

C9A	6276(3)	4138(3)	-708.1(11)	17.9(5)
C10A	6465(3)	4751(3)	-93.6(11)	16.2(5)
C11A	2726(3)	5888(3)	-1106.9(11)	18.9(5)
C12A	5213(3)	4973(3)	-1077.4(11)	16.8(5)
C13A	1513(3)	4150(3)	711.2(12)	24.3(6)
C14A	2138(3)	7885(3)	-1817.3(14)	30.2(7)
C15A	7665(3)	3925(3)	-1004.1(12)	23.3(6)
O20A	6290.4(19)	6131(2)	1429.4(8)	23.9(4)
O21A	8439.3(19)	6097(2)	1063.3(8)	22.4(4)
C20A	7497(3)	6511(3)	1444.4(12)	19.8(5)
C21A	8084(3)	7506(3)	1899.2(11)	19.4(5)
C22A	7286(3)	7875(4)	2378.0(13)	27.1(6)
C23A	7800(3)	8830(4)	2795.0(13)	33.5(7)
C24A	9104(3)	9433(4)	2727.9(13)	30.1(7)
C25A	9898(3)	9071(3)	2249.9(12)	23.5(6)
C26A	9398(3)	8100(3)	1840.4(11)	19.9(5)

Table S1.2.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:Ben 2. The exponent takes the form: $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	17.5(9)	18.1(9)	29.1(10)	2.3(8)	-0.6(7)	-2.1(7)
O2	16.1(9)	22.2(10)	29.9(10)	-5.6(8)	2.2(7)	-3.5(8)
O3	15.8(9)	24.5(10)	21.4(9)	-1.7(8)	3.4(7)	3.6(8)
O10	23.7(10)	24.9(10)	18.1(9)	-1.6(8)	1.8(7)	2.2(8)
N11	16.3(11)	23.6(12)	18.2(11)	0.3(9)	-1.4(9)	2.0(9)
C1	17.6(12)	15.4(12)	20.5(12)	1(1)	-0.1(10)	-0.5(10)
C2	16.6(12)	18.9(13)	19.8(12)	0.2(11)	0.6(10)	0.6(10)
C3	19.4(13)	22.9(14)	25.7(14)	-4.0(11)	5.5(10)	-1.5(11)
C4	24.4(14)	30.2(15)	22.1(13)	-1.8(11)	7.3(11)	-6.5(12)
C5	23.2(14)	26.9(14)	17.6(12)	-2.1(11)	1.9(10)	-3.2(12)
C6	19.2(13)	19.6(13)	22.9(13)	0.1(11)	-2.9(10)	-1.0(11)
C7	19.9(14)	27.3(15)	28.2(14)	-0.1(12)	-0.3(11)	-4.6(12)
C8	18.3(13)	24.6(14)	24.3(14)	2.0(11)	2.8(11)	-1.6(11)
C9	15.9(13)	20.6(13)	25.6(13)	0.1(11)	0.6(10)	1.7(10)
C10	17.7(12)	17.0(12)	21.8(13)	1.8(10)	1.7(10)	-2.3(10)
C11	19.6(13)	21.2(13)	17.1(12)	1.6(10)	-0.2(10)	-0.5(11)
C12	17.2(12)	21.1(13)	18.5(12)	2(1)	1(1)	0.6(10)
C13	22.4(14)	37.7(17)	35.7(16)	-11.0(14)	6.9(12)	-3.7(13)
C14	29.1(15)	28.5(15)	25.4(14)	-2.3(12)	-2.7(12)	-2.2(13)
C15	19.1(14)	44.4(18)	28.0(15)	-7.6(13)	2.5(11)	4.2(13)
O20	21.5(9)	30.4(11)	24.7(10)	-0.6(9)	1.2(8)	-0.7(9)
O21	21.4(10)	30.2(11)	23.5(9)	1.8(9)	2.1(8)	7.6(9)
C20	18.4(13)	22.8(14)	23.7(13)	-4.3(11)	-2.8(11)	0.2(11)
C21	19.1(13)	23.3(14)	23.4(13)	-7.1(11)	-3.2(11)	-1.2(11)

C22	20.4(13)	29.5(15)	23.9(14)	-7.5(12)	-1.3(11)	-0.5(12)
C23	23.8(15)	34.5(17)	30.0(15)	-11.7(13)	-5.6(12)	7.6(13)
C24	30.3(16)	31.7(16)	31.7(15)	-2.2(13)	-9.1(12)	9.1(13)
C25	29.6(16)	37.4(17)	26.4(15)	2.1(13)	-2.5(12)	1.9(13)
C26	22.1(14)	28.7(14)	25.8(14)	-1.8(12)	-3.0(11)	4.5(12)
O1A	20.7(9)	17.8(9)	15.9(8)	-0.8(7)	3.1(7)	-3.8(7)
O2A	17.9(8)	20.2(9)	18.9(8)	0.7(7)	4.9(7)	-1.2(7)
O3A	13.2(8)	22.4(9)	20.3(9)	-5.0(8)	3.4(7)	-1.3(7)
O10A	15.5(9)	24.6(10)	22.2(9)	0.1(8)	-0.4(7)	1.6(8)
N11A	15.1(10)	22.3(12)	15.5(11)	-2.7(9)	-0.3(8)	-2.1(9)
C1A	15.3(12)	15.4(12)	19.3(12)	0.4(10)	1.1(10)	-3(1)
C2A	12.0(11)	18.5(13)	19.0(12)	-2(1)	1.4(9)	-1.3(10)
C3A	14.3(12)	20.9(13)	23.3(13)	-2.8(11)	3.5(10)	-1.1(11)
C4A	12.2(12)	32.6(15)	22.9(13)	-4.0(12)	1.8(10)	-1.5(11)
C5A	17.7(13)	26.1(14)	23.7(13)	-2.0(11)	-3.8(10)	4.1(11)
C6A	24.9(14)	19.4(13)	21.8(13)	-0.4(11)	-3.8(11)	1.2(11)
C7A	29.0(15)	20.9(12)	20.8(13)	4.3(11)	0.2(11)	-3.5(12)
C8A	20.9(13)	22.9(14)	21.3(13)	2.2(11)	3(1)	-3.4(11)
C9A	15.9(12)	18.9(12)	18.8(12)	-1.7(10)	2.3(10)	-0.6(10)
C10A	12.5(11)	16.6(12)	19.6(12)	2.1(10)	2.9(9)	-2.7(10)
C11A	17.5(12)	20.5(13)	18.8(12)	-2.2(10)	-1.6(10)	0.8(11)
C12A	15.0(12)	19.8(13)	15.7(11)	-2.9(10)	1.0(9)	-0.7(10)
C13A	17.3(13)	29.4(15)	26.3(13)	-0.2(12)	5(1)	-0.8(11)
C14A	34.7(17)	26.0(15)	29.7(15)	3.2(12)	-7.7(13)	4.3(13)
C15A	15.7(13)	33.1(15)	21.2(12)	-3.2(11)	4.3(10)	2.9(11)
O20A	17.2(9)	27.4(10)	27.2(10)	3.8(8)	2.0(7)	-4.5(8)
O21A	16.9(9)	25.8(10)	24.4(9)	-3.3(8)	0.4(7)	1.3(8)
C20A	17.8(13)	19.6(12)	22.1(13)	7.3(11)	0.9(10)	2.8(11)
C21A	19.4(13)	21.0(13)	17.8(12)	4.3(10)	-0.2(10)	1.3(10)
C22A	17.7(13)	36.9(17)	26.8(14)	0.7(12)	4.7(11)	-3.7(12)
C23A	25.7(15)	50(2)	25.2(15)	-7.7(14)	7.7(12)	1.7(14)
C24A	26.1(15)	38.6(17)	25.6(14)	-7.4(13)	0.3(12)	-0.5(13)
C25A	18.5(13)	27.6(14)	24.3(13)	0.8(11)	-0.1(11)	-3.0(11)
C26A	17.0(12)	24.7(13)	18.1(12)	4.2(10)	1.6(10)	1.7(11)

Table S1.2.4 Bond Lengths for 11-Aza:Ben 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.470(3)	O1A	O2A	1.471(2)
O1	C1	1.462(3)	O1A	C1A	1.456(3)
O2	C3	1.417(3)	O2A	C3A	1.414(3)
O3	C2	1.418(3)	O3A	C2A	1.417(3)
O3	C3	1.433(4)	O3A	C3A	1.439(3)
O10	C10	1.250(3)	O10A	C10A	1.242(3)
N11	C2	1.460(3)	N11A	C2A	1.463(3)
N11	C10	1.333(4)	N11A	C10A	1.339(3)
C1	C2	1.526(4)	C1A	C2A	1.533(3)
C1	C11	1.546(3)	C1A	C11A	1.541(3)
C1	C12	1.536(3)	C1A	C12A	1.535(3)
C3	C4	1.538(4)	C3A	C4A	1.535(4)
C3	C13	1.512(4)	C3A	C13A	1.511(4)
C4	C5	1.529(4)	C4A	C5A	1.524(4)
C5	C11	1.542(4)	C5A	C11A	1.542(4)
C6	C7	1.528(4)	C6A	C7A	1.528(4)
C6	C11	1.543(4)	C6A	C11A	1.542(4)
C6	C14	1.535(4)	C6A	C14A	1.533(4)
C7	C8	1.526(4)	C7A	C8A	1.524(4)
C8	C12	1.538(4)	C8A	C12A	1.526(4)
C9	C10	1.508(4)	C9A	C10A	1.523(3)
C9	C12	1.536(4)	C9A	C12A	1.530(3)
C9	C15	1.530(4)	C9A	C15A	1.523(3)
O20	C20	1.220(4)	O20A	C20A	1.217(3)
O21	C20	1.322(4)	O21A	C20A	1.326(3)
C20	C21	1.492(4)	C20A	C21A	1.498(4)
C21	C22	1.392(4)	C21A	C22A	1.390(4)
C21	C26	1.393(4)	C21A	C26A	1.392(4)
C22	C23	1.381(4)	C22A	C23A	1.391(5)
C23	C24	1.390(5)	C23A	C24A	1.390(4)
C24	C25	1.389(5)	C24A	C25A	1.385(4)
C25	C26	1.388(4)	C25A	C26A	1.384(4)

Table S1.2.5 Bond Angles for 11-Aza:Ben 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	112.02(18)	C1A	O1A	O2A	112.26(17)
C3	O2	O1	107.87(18)	C3A	O2A	O1A	107.61(18)
C2	O3	C3	113.4(2)	C2A	O3A	C3A	113.45(19)
C10	N11	C2	126.6(2)	C10A	N11A	C2A	126.7(2)
O1	C1	C2	110.1(2)	O1A	C1A	C2A	110.5(2)
O1	C1	C11	107.2(2)	O1A	C1A	C11A	107.4(2)
O1	C1	C12	104.2(2)	O1A	C1A	C12A	104.3(2)
C2	C1	C11	112.1(2)	C2A	C1A	C11A	111.6(2)
C2	C1	C12	110.8(2)	C2A	C1A	C12A	111.0(2)
C12	C1	C11	112.1(2)	C12A	C1A	C11A	111.8(2)
O3	C2	N11	108.3(2)	O3A	C2A	N11A	108.6(2)
O3	C2	C1	113.6(2)	O3A	C2A	C1A	113.8(2)
N11	C2	C1	112.2(2)	N11A	C2A	C1A	112.6(2)
O2	C3	O3	108.0(2)	O2A	C3A	O3A	107.51(19)
O2	C3	C4	111.8(2)	O2A	C3A	C4A	112.4(2)
O2	C3	C13	104.8(2)	O2A	C3A	C13A	105.1(2)
O3	C3	C4	110.9(2)	O3A	C3A	C4A	111.1(2)
O3	C3	C13	107.0(2)	O3A	C3A	C13A	107.6(2)
C13	C3	C4	113.8(2)	C13A	C3A	C4A	112.9(2)
C5	C4	C3	113.9(2)	C5A	C4A	C3A	114.6(2)
C4	C5	C11	115.8(2)	C4A	C5A	C11A	115.7(2)
C7	C6	C11	111.9(2)	C7A	C6A	C11A	111.9(2)
C7	C6	C14	109.7(2)	C7A	C6A	C14A	109.8(2)
C14	C6	C11	110.9(2)	C14A	C6A	C11A	110.9(2)
C8	C7	C6	112.5(2)	C8A	C7A	C6A	112.5(2)
C7	C8	C12	110.5(2)	C7A	C8A	C12A	110.4(2)
C10	C9	C12	113.1(2)	C10A	C9A	C12A	112.6(2)
C10	C9	C15	111.3(2)	C10A	C9A	C15A	111.4(2)
C15	C9	C12	114.1(2)	C15A	C9A	C12A	114.1(2)
O10	C10	N11	120.4(2)	O10A	C10A	N11A	121.5(2)
O10	C10	C9	119.9(2)	O10A	C10A	C9A	120.2(2)
N11	C10	C9	119.5(2)	N11A	C10A	C9A	118.2(2)
C5	C11	C1	111.9(2)	C1A	C11A	C5A	111.9(2)
C5	C11	C6	110.7(2)	C1A	C11A	C6A	112.9(2)
C6	C11	C1	112.3(2)	C5A	C11A	C6A	111.1(2)
C1	C12	C8	110.0(2)	C8A	C12A	C1A	110.7(2)
C1	C12	C9	110.4(2)	C8A	C12A	C9A	115.0(2)
C9	C12	C8	115.1(2)	C9A	C12A	C1A	109.8(2)
O20	C20	O21	124.0(3)	O20A	C20A	O21A	124.2(3)
O20	C20	C21	123.3(3)	O20A	C20A	C21A	123.5(3)
O21	C20	C21	112.8(2)	O21A	C20A	C21A	112.4(2)
C22	C21	C20	119.0(3)	C22A	C21A	C20A	119.4(3)
C22	C21	C26	119.8(3)	C22A	C21A	C26A	119.5(3)
C26	C21	C20	121.2(3)	C26A	C21A	C20A	121.0(2)

C23	C22	C21	120.0(3)	C21A	C22A	C23A	120.1(3)
C22	C23	C24	120.4(3)	C24A	C23A	C22A	119.9(3)
C25	C24	C23	119.7(3)	C25A	C24A	C23A	120.0(3)
C26	C25	C24	120.1(3)	C26A	C25A	C24A	120.1(3)
C25	C26	C21	120.0(3)	C25A	C26A	C21A	120.3(3)

Table S1.2.6 Hydrogen Bonds for 11-Aza:Ben 2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O20	0.90(4)	2.06(3)	2.958(3)	170(3)
O21	H21	O10	0.87(4)	1.71(4)	2.572(3)	171(4)
N11A	H11B	O20A	0.89(4)	2.23(4)	3.109(3)	169(3)
O21A	H21A	O10A	0.91(5)	1.71(5)	2.596(3)	162(4)

Table S1.2.7 Torsion Angles for 11-Aza:Ben 2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-75.0(2)	O1A	O2A	C3A	O3A	-75.9(2)
O1	O2	C3	C4	47.3(3)	O1A	O2A	C3A	C4A	46.7(3)
O1	O2	C3	C13	171.1(2)	O1A	O2A	C3A	C13A	169.75(19)
O1	C1	C2	O3	-53.0(3)	O1A	C1A	C2A	O3A	-51.2(3)
O1	C1	C2	N11	70.3(3)	O1A	C1A	C2A	N11A	73.0(3)
O1	C1	C11	C5	69.1(3)	O1A	C1A	C11A	C5A	69.1(3)
O1	C1	C11	C6	-165.7(2)	O1A	C1A	C11A	C6A	-164.6(2)
O1	C1	C12	C8	171.6(2)	O1A	C1A	C12A	C8A	171.3(2)
O1	C1	C12	C9	-60.3(3)	O1A	C1A	C12A	C9A	-60.7(2)
O2	O1	C1	C2	14.7(3)	O2A	O1A	C1A	C2A	14.2(3)
O2	O1	C1	C11	-107.5(2)	O2A	O1A	C1A	C11A	-107.7(2)
O2	O1	C1	C12	133.51(19)	O2A	O1A	C1A	C12A	133.57(18)
O2	C3	C4	C5	-96.7(3)	O2A	C3A	C4A	C5A	-96.1(3)
O3	C3	C4	C5	23.9(3)	O3A	C3A	C4A	C5A	24.4(3)
C1	O1	O2	C3	46.1(3)	C1A	O1A	O2A	C3A	46.3(2)
C2	O3	C3	O2	35.7(3)	C2A	O3A	C3A	O2A	37.7(3)
C2	O3	C3	C4	-87.2(3)	C2A	O3A	C3A	C4A	-85.6(3)
C2	O3	C3	C13	148.1(2)	C2A	O3A	C3A	C13A	150.4(2)
C2	N11	C10	O10	172.7(2)	C2A	N11A	C10A	O10A	169.0(2)
C2	N11	C10	C9	-11.5(4)	C2A	N11A	C10A	C9A	-15.2(4)
C2	C1	C11	C5	-51.8(3)	C2A	C1A	C11A	C5A	-52.1(3)
C2	C1	C11	C6	73.4(3)	C2A	C1A	C11A	C6A	74.1(3)
C2	C1	C12	C8	-70.0(3)	C2A	C1A	C12A	C8A	-69.7(3)
C2	C1	C12	C9	58.1(3)	C2A	C1A	C12A	C9A	58.3(3)
C3	O3	C2	N11	-98.8(2)	C3A	O3A	C2A	N11A	-102.4(2)
C3	O3	C2	C1	26.5(3)	C3A	O3A	C2A	C1A	23.9(3)
C3	C4	C5	C11	59.1(3)	C3A	C4A	C5A	C11A	58.5(3)

C4	C5	C11	C1	-37.7(3)	C4A	C5A	C11A	C1A	-37.4(3)
C4	C5	C11	C6	-163.8(2)	C4A	C5A	C11A	C6A	-164.6(2)
C6	C7	C8	C12	57.4(3)	C6A	C7A	C8A	C12A	57.4(3)
C7	C6	C11	C1	49.5(3)	C7A	C6A	C11A	C1A	48.7(3)
C7	C6	C11	C5	175.4(2)	C7A	C6A	C11A	C5A	175.4(2)
C7	C8	C12	C1	-58.4(3)	C7A	C8A	C12A	C1A	-58.6(3)
C7	C8	C12	C9	176.2(2)	C7A	C8A	C12A	C9A	176.3(2)
C10	N11	C2	O3	148.3(3)	C10A	N11A	C2A	O3A	148.5(2)
C10	N11	C2	C1	22.1(4)	C10A	N11A	C2A	C1A	21.6(4)
C10	C9	C12	C1	-46.9(3)	C10A	C9A	C12A	C1A	-51.3(3)
C10	C9	C12	C8	78.4(3)	C10A	C9A	C12A	C8A	74.3(3)
C11	C1	C2	O3	66.2(3)	C11A	C1A	C2A	O3A	68.2(3)
C11	C1	C2	N11	-170.5(2)	C11A	C1A	C2A	N11A	-167.6(2)
C11	C1	C12	C8	56.1(3)	C11A	C1A	C12A	C8A	55.6(3)
C11	C1	C12	C9	-175.8(2)	C11A	C1A	C12A	C9A	-176.4(2)
C11	C6	C7	C8	-52.7(3)	C11A	C6A	C7A	C8A	-52.2(3)
C12	C1	C2	O3	-167.7(2)	C12A	C1A	C2A	O3A	-166.4(2)
C12	C1	C2	N11	-44.5(3)	C12A	C1A	C2A	N11A	-42.2(3)
C12	C1	C11	C5	-177.1(2)	C12A	C1A	C11A	C5A	-177.1(2)
C12	C1	C11	C6	-51.9(3)	C12A	C1A	C11A	C6A	-50.8(3)
C12	C9	C10	O10	-160.4(2)	C12A	C9A	C10A	O10A	-154.4(2)
C12	C9	C10	N11	23.7(3)	C12A	C9A	C10A	N11A	29.8(3)
C13	C3	C4	C5	144.6(3)	C13A	C3A	C4A	C5A	145.3(2)
C14	C6	C7	C8	-176.3(2)	C14A	C6A	C7A	C8A	-175.7(2)
C14	C6	C11	C1	172.4(2)	C14A	C6A	C11A	C1A	171.6(2)
C14	C6	C11	C5	-61.7(3)	C14A	C6A	C11A	C5A	-61.6(3)
C15	C9	C10	O10	-30.5(4)	C15A	C9A	C10A	O10A	-24.7(4)
C15	C9	C10	N11	153.6(3)	C15A	C9A	C10A	N11A	159.5(2)
C15	C9	C12	C1	-175.4(2)	C15A	C9A	C12A	C1A	-179.5(2)
C15	C9	C12	C8	-50.1(3)	C15A	C9A	C12A	C8A	-54.0(3)
O20	C20	C21	C22	-0.9(4)	O20A	C20A	C21A	C22A	9.2(4)
O20	C20	C21	C26	-178.9(3)	O20A	C20A	C21A	C26A	-168.8(3)
O21	C20	C21	C22	179.0(3)	O21A	C20A	C21A	C22A	-170.8(2)
O21	C20	C21	C26	1.0(4)	O21A	C20A	C21A	C26A	11.2(3)
C20	C21	C22	C23	-176.9(3)	C20A	C21A	C22A	C23A	-178.1(3)
C20	C21	C26	C25	176.6(3)	C20A	C21A	C26A	C25A	176.8(3)
C21	C22	C23	C24	-0.2(4)	C21A	C22A	C23A	C24A	1.0(5)
C22	C21	C26	C25	-1.4(4)	C22A	C21A	C26A	C25A	-1.1(4)
C22	C23	C24	C25	-0.4(5)	C22A	C23A	C24A	C25A	-0.7(5)
C23	C24	C25	C26	0.1(5)	C23A	C24A	C25A	C26A	-0.5(5)
C24	C25	C26	C21	0.7(5)	C24A	C25A	C26A	C21A	1.4(4)
C26	C21	C22	C23	1.1(4)	C26A	C21A	C22A	C23A	-0.1(4)

Table S1.2.8 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 11-Aza:Ben 2.

Atom	*x*	*y*	*z*	U(eq)
H11	5760(40)	3650(40)	5450(15)	28(9)
H2	4786	2364	4611	22
H4A	6018	5346	3247	31
H4B	7237	4194	3214	31
H5A	5701	2355	3462	27
H5B	5154	3162	2887	27
H6	3640	1355	3831	25
H7A	1065	2865	3713	30
H7B	1256	1297	3982	30
H8A	2479	2235	4800	27
H8B	997	3003	4743	27
H9	3060	6149	4997	25
H11A	3350	4172	3348	23
H12	2035	4965	4255	23
H13A	8365	5340	4602	48
H13B	8475	5930	3946	48
H13C	8828	4294	4086	48
H14A	2279	2261	2767	42
H14B	2187	666	3016	42
H14C	3643	1290	2808	42
H15A	1240	4305	5608	46
H15B	720	5598	5201	46
H15C	1623	5915	5782	46
H21	5100(40)	3910(50)	6478(19)	46(12)
H22	9217	1743	6488	30
H23	10324	123	7113	35
H24	9263	-609	7977	38
H25	7088	306	8219	37
H26	5978	1946	7598	31
H11B	5550(40)	5700(40)	514(16)	30(9)
H2A	4255	6939	-242	20
H4AA	823	4049	-568	27
H4AB	141	5188	-138	27
H5AA	1496	7017	-528	27
H5AB	611	6262	-1038	27
H6A	3361	8011	-1063	27
H7AA	4466	6509	-2045	28
H7AB	4946	8055	-1821	28
H8AA	5918	7053	-960	26
H8AB	6578	6293	-1519	26
H9A	5876	3162	-656	21
H11C	2480	5230	-1438	23
H12A	4992	4379	-1431	20

H13D	2257	3818	976	36
H13E	842	3377	646	36
H13F	1046	4970	887	36
H14D	1930	7165	-2118	45
H14E	2499	8749	-2004	45
H14F	1290	8120	-1607	45
H15D	8155	4840	-1024	35
H15E	7508	3555	-1402	35
H15F	8226	3241	-777	35
H21A	7960(50)	5620(50)	780(20)	53(13)
H22A	6388	7474	2420	32
H23A	7260	9069	3125	40
H24A	9452	10094	3010	36
H25A	10787	9490	2203	28
H26A	9954	7838	1518	24

Experimental

Single crystals of $C_{22}H_{29}NO_6$ **for 11-Aza:Ben 2** were **grown at room temperature by evaporation of a ethyl acetate solution**. A suitable crystal was selected and **mounted in Paratone with a cryo-loop** on a **SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas** detector. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst., 40, 786-790; Palatinus, L. & van der Lee, A. (2008). J. Appl. Cryst. 41, 975-984; Palatinus, L., Prathapa, S. J. & van Smaalen, S. (2012). J. Appl. Cryst. 45, 575-580.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza:Ben 2 Crystal Data for $C_{22}H_{29}NO_6$ (M =403.46 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 9.64312(19) Å, b = 9.3622(2) Å, c = 22.8165(4) Å, β = 90.9437(18)°, V = 2059.60(7) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 0.776 mm^{-1}, *Dcalc* = 1.301 g/cm^3, 11649 reflections measured (7.75° ≤ 2Θ ≤ 134.998°), 7317 unique (R_{int} = 0.0339, R_{sigma} = 0.0514) which were used in all calculations. The final R_1 was 0.0348 (I > 2σ(I)) and wR_2 was 0.0818 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12), C2A(H2A), C6A(H6A), C9A(H9A),
 C11A(H11C), C12A(H12A)
2.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B), C4A(H4AA,H4AB), C5A(H5AA,
 H5AB), C7A(H7AA,H7AB), C8A(H8AA,H8AB)
2.c Aromatic/amide H refined with riding coordinates:
 C22(H22), C23(H23), C24(H24), C25(H25), C26(H26), C22A(H22A), C23A(H23A),
 C24A(H24A), C25A(H25A), C26A(H26A)
2.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C), C13A(H13D,H13E,
 H13F), C14A(H14D,H14E,H14F), C15A(H15D,H15E,H15F)
```

Table S1.3.1. Crystal data & structure refinement for 11-Aza:Sal 3.

Identification code	madiha26CuLT
Empirical formula	$C_{22}H_{29}NO_7$
Formula weight	419.46
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.79451(14)
b/Å	9.30687(13)
c/Å	11.51291(16)
α/°	90
β/°	92.3070(12)
γ/°	90
Volume/Å^3	1048.62(3)
Z	2
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	0.820
F(000)	448.0
Crystal size/mm^3	0.38 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.686 to 133.992
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 10$, $-13 \leq l \leq 13$
Reflections collected	8079
Independent reflections	3602 [R_{int} = 0.0240, R_{sigma} = 0.0283]
Data/restraints/parameters	3602/1/286
Completeness to theta = 66.5°	99.4%
Goodness-of-fit on F^2	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0.0273, wR_2 = 0.0674
Final R indexes [all data]	R_1 = 0.0280, wR_2 = 0.0680
Largest diff. peak/hole / e Å^{-3}	0.16/-0.17
Flack parameter	0.06(9)

Table S1.3.2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 11-Aza:Sal 3.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4440.6(13)	8799.1(15)	3423.5(12)	17.4(3)
O2	5894.4(13)	8928.6(15)	3802.3(12)	18.8(3)
O3	6288.3(13)	6489.5(15)	3929.1(11)	17.0(3)
O10	3989.7(14)	7783.2(16)	7126.4(11)	21.3(3)
N11	4946.9(16)	6946.2(18)	5516.4(14)	15.8(3)
C1	3936.5(19)	7331(2)	3546.9(16)	14.7(4)
C2	4939.7(18)	6463(2)	4315.4(15)	14.9(4)
C3	6614(2)	7772(2)	3306.1(17)	18.4(4)
C4	6250(2)	7610(2)	2005.5(17)	21.8(4)
C5	5145(2)	6490(2)	1727.9(16)	19.4(4)
C6	2968(2)	5262(2)	2305.0(17)	20.0(4)
C7	1623(2)	5431(2)	2911.0(18)	22.8(4)
C8	1816(2)	6041(2)	4139.0(17)	19.9(4)
C9	2755.6(19)	8219(2)	5318.2(17)	16.6(4)
C10	3933.2(19)	7600(2)	6052.3(16)	16.0(4)
C11	3773(2)	6682(2)	2315.4(16)	17.7(4)
C12	2562.4(19)	7490(2)	4122.6(16)	15.8(4)
C13	8107(2)	8083(2)	3584(2)	25.6(5)
C14	2711(2)	4703(2)	1067.4(18)	25.2(5)
C15	1454(2)	8302(3)	6002.6(19)	25.6(5)
O20	7192.5(14)	6594.0(16)	7226.7(11)	20.6(3)
O21	5543.8(14)	6304.9(16)	8494.4(12)	22.3(3)
O22	9539.5(15)	5398.2(18)	7618.2(13)	24.7(3)
C20	6769(2)	6062(2)	8132.3(16)	18.3(4)
C21	7633(2)	5105(2)	8871.5(17)	18.1(4)
C22	8975(2)	4803(2)	8560.2(17)	19.4(4)
C23	9775(2)	3853(3)	9237.4(18)	24.0(4)
C24	9248(2)	3219(2)	10207.3(19)	26.0(5)
C25	7916(2)	3508(2)	10525.8(18)	24.2(5)
C26	7123(2)	4441(2)	9855.1(17)	20.8(4)

Table S1.3.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:Sal 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	15.7(6)	11.4(7)	24.9(7)	2.1(5)	-0.8(5)	-0.1(5)
O2	15.3(6)	15.7(7)	25.4(7)	-3.6(5)	0.9(5)	-1.7(5)
O3	15.8(6)	15.0(7)	20.2(6)	0.0(5)	1.1(5)	1.9(5)
O10	22.3(7)	24.5(8)	16.8(7)	-1.8(6)	-0.4(5)	5.5(6)
N11	14.5(8)	15.6(9)	17.2(8)	0.8(6)	-1.4(6)	2.7(6)
C1	18.3(9)	8.4(9)	17.3(9)	1.2(6)	-1.5(7)	-0.3(7)
C2	15.3(9)	13.2(10)	16.0(8)	0.0(7)	-0.9(7)	1.0(7)
C3	18.1(9)	13.4(10)	24.1(10)	-2.6(8)	4.7(7)	0.7(8)
C4	24.6(10)	20.6(11)	20.5(10)	0.3(8)	5.6(7)	-1.0(8)
C5	25.4(10)	16.5(10)	16.2(9)	-0.9(7)	-0.3(7)	0.9(8)
C6	22.7(10)	15.9(10)	21(1)	-1.9(7)	-5.0(8)	0.2(8)
C7	20.3(10)	19.3(11)	28.3(11)	-2.4(8)	-4.6(8)	-2.6(8)
C8	17.1(9)	18.2(10)	24.2(10)	0.4(8)	-0.3(7)	-2.3(8)
C9	15.9(9)	14.8(10)	19.1(9)	0.3(7)	-0.2(7)	1.4(7)
C10	16.2(9)	13.1(10)	18.8(9)	0.4(7)	1.0(7)	-1.2(7)
C11	19.9(9)	16.2(10)	16.8(9)	0.4(7)	-2.7(7)	2.1(7)
C12	15.9(9)	12.8(10)	18.4(9)	1.3(7)	-2.2(7)	1.5(7)
C13	20.3(11)	25.1(12)	31.8(11)	-7.5(9)	4.8(8)	-2.9(8)
C14	29.0(11)	20.5(11)	25.4(11)	-3.3(8)	-7.6(8)	-0.3(9)
C15	18.5(10)	34.1(13)	24.3(11)	-3.4(8)	0.9(8)	4.2(9)
O20	22.1(7)	18.7(7)	20.8(7)	1.0(5)	-2.2(5)	-0.3(6)
O21	20.4(7)	25.3(9)	21.1(7)	-0.8(6)	0.1(5)	5.7(6)
O22	18.8(7)	30.0(9)	25.5(8)	6.1(6)	1.6(6)	1.2(6)
C20	21.1(10)	14.8(10)	18.6(9)	-6.8(7)	-3.3(7)	-0.5(7)
C21	20.7(10)	15(1)	18.3(9)	-5.3(7)	-3.2(7)	-1.1(7)
C22	21.3(10)	18.4(11)	18.5(9)	-2.7(7)	-1.8(7)	-2.7(8)
C23	18.4(10)	27.4(12)	25.7(10)	-1.7(9)	-2.7(8)	2.4(9)
C24	27.3(11)	25.5(12)	24.5(11)	2.5(8)	-7.9(9)	3.6(9)
C25	30.4(11)	25.1(12)	17(1)	-0.1(8)	-1.4(8)	-0.9(9)
C26	21.9(10)	22.2(11)	18.3(9)	-5.0(8)	-0.1(7)	1.4(8)

Table S1.3.4 Bond Lengths for 11-Aza:Sal 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.4772(18)	C6	C14	1.528(3)
O1	C1	1.462(2)	C7	C8	1.528(3)
O2	C3	1.419(2)	C8	C12	1.534(3)
O3	C2	1.411(2)	C9	C10	1.516(3)
O3	C3	1.436(2)	C9	C12	1.540(3)
O10	C10	1.247(2)	C9	C15	1.527(3)
N11	C2	1.454(2)	O20	C20	1.241(2)
N11	C10	1.336(3)	O21	C20	1.306(2)
C1	C2	1.527(2)	O22	C22	1.355(3)
C1	C11	1.543(3)	C20	C21	1.475(3)
C1	C12	1.531(3)	C21	C22	1.405(3)
C3	C4	1.533(3)	C21	C26	1.400(3)
C3	C13	1.512(3)	C22	C23	1.398(3)
C4	C5	1.527(3)	C23	C24	1.381(3)
C5	C11	1.538(3)	C24	C25	1.396(3)
C6	C7	1.523(3)	C25	C26	1.380(3)
C6	C11	1.539(3)			

Table 1.3.5 Bond Angles for 11-Aza:Sal 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	111.90(13)	C10	C9	C12	113.22(16)
C3	O2	O1	107.94(13)	C10	C9	C15	111.32(16)
C2	O3	C3	113.72(14)	C15	C9	C12	114.10(16)
C10	N11	C2	127.21(16)	O10	C10	N11	121.05(18)
O1	C1	C2	109.82(15)	O10	C10	C9	120.21(17)
O1	C1	C11	107.42(15)	N11	C10	C9	118.58(16)
O1	C1	C12	104.96(14)	C5	C11	C1	112.92(15)
C2	C1	C11	111.44(15)	C5	C11	C6	110.70(16)
C2	C1	C12	110.89(15)	C6	C11	C1	112.16(16)
C12	C1	C11	112.03(15)	C1	C12	C8	110.36(15)
O3	C2	N11	109.00(14)	C1	C12	C9	110.55(15)
O3	C2	C1	113.37(15)	C8	C12	C9	114.71(15)
N11	C2	C1	111.45(15)	O20	C20	O21	122.80(18)
O2	C3	O3	107.78(14)	O20	C20	C21	121.49(18)
O2	C3	C4	111.58(16)	O21	C20	C21	115.71(18)
O2	C3	C13	105.20(16)	C22	C21	C20	119.65(18)
O3	C3	C4	111.00(16)	C26	C21	C20	121.18(18)
O3	C3	C13	106.62(16)	C26	C21	C22	119.12(18)
C13	C3	C4	114.25(16)	O22	C22	C21	122.57(19)
C5	C4	C3	114.01(16)	O22	C22	C23	117.84(18)
C4	C5	C11	116.92(16)	C23	C22	C21	119.58(19)

C7	C6	C11	111.15(16)	C24	C23	C22	120.10(19)
C7	C6	C14	110.43(17)	C23	C24	C25	120.9(2)
C14	C6	C11	111.39(17)	C26	C25	C24	119.1(2)
C6	C7	C8	112.61(16)	C25	C26	C21	121.24(19)
C7	C8	C12	110.90(16)				

Table 1.3.6 Hydrogen Bonds for 11-Aza:Sal 3.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O20	0.89(3)	2.05(3)	2.911(2)	163(3)
O21	H21	O10	0.95(4)	1.60(4)	2.5490(19)	173(3)
O22	H22	O20	0.84(3)	1.81(3)	2.577(2)	152(3)

Table 1.3.7 Torsion Angles for 11-Aza:Sal 3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-74.26(16)	C10	C9	C12	C1	-46.2(2)
O1	O2	C3	C4	47.85(19)	C10	C9	C12	C8	79.4(2)
O1	O2	C3	C13	172.26(14)	C11	C1	C2	O3	64.8(2)
O1	C1	C2	O3	-54.1(2)	C11	C1	C2	N11	-171.80(15)
O1	C1	C2	N11	69.29(19)	C11	C1	C12	C8	55.29(19)
O1	C1	C11	C5	66.16(19)	C11	C1	C12	C9	-176.73(15)
O1	C1	C11	C6	-167.93(15)	C11	C6	C7	C8	-53.7(2)
O1	C1	C12	C8	171.55(15)	C12	C1	C2	O3	-169.68(14)
O1	C1	C12	C9	-60.48(18)	C12	C1	C2	N11	-46.3(2)
O2	O1	C1	C2	14.66(19)	C12	C1	C11	C5	-179.08(15)
O2	O1	C1	C11	-106.70(15)	C12	C1	C11	C6	-53.2(2)
O2	O1	C1	C12	133.91(13)	C12	C9	C10	O10	-160.19(17)
O2	C3	C4	C5	-96.2(2)	C12	C9	C10	N11	24.4(2)
O3	C3	C4	C5	24.0(2)	C13	C3	C4	C5	144.59(18)
C1	O1	O2	C3	46.36(17)	C14	C6	C7	C8	-177.87(18)
C2	O3	C3	O2	34.0(2)	C14	C6	C11	C1	175.12(16)
C2	O3	C3	C4	-88.51(18)	C14	C6	C11	C5	-57.8(2)
C2	O3	C3	C13	146.48(15)	C15	C9	C10	O10	-30.1(3)
C2	N11	C10	O10	169.84(19)	C15	C9	C10	N11	154.46(18)
C2	N11	C10	C9	-14.7(3)	C15	C9	C12	C1	-174.86(16)
C2	C1	C11	C5	-54.2(2)	C15	C9	C12	C8	-49.3(2)
C2	C1	C11	C6	71.7(2)	O20	C20	C21	C22	1.1(3)
C2	C1	C12	C8	-69.92(19)	O20	C20	C21	C26	-176.24(18)
C2	C1	C12	C9	58.1(2)	O21	C20	C21	C22	-178.88(17)
C3	O3	C2	N11	-96.23(17)	O21	C20	C21	C26	3.8(3)
C3	O3	C2	C1	28.5(2)	O22	C22	C23	C24	179.9(2)
C3	C4	C5	C11	56.3(2)	C20	C21	C22	O22	2.4(3)
C4	C5	C11	C1	-33.9(2)	C20	C21	C22	C23	-177.60(18)

C4	C5	C11	C6	-160.56(17)	C20	C21	C26	C25	177.83(19)
C6	C7	C8	C12	56.7(2)	C21	C22	C23	C24	-0.1(3)
C7	C6	C11	C1	51.5(2)	C22	C21	C26	C25	0.5(3)
C7	C6	C11	C5	178.62(16)	C22	C23	C24	C25	0.2(3)
C7	C8	C12	C1	-56.6(2)	C23	C24	C25	C26	0.1(3)
C7	C8	C12	C9	177.72(16)	C24	C25	C26	C21	-0.4(3)
C10	N11	C2	O3	151.69(18)	C26	C21	C22	O22	179.75(18)
C10	N11	C2	C1	25.8(3)	C26	C21	C22	C23	-0.2(3)

Table S1.3.8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:Sal 3.

Atom	*x*	*y*	*z*	U(eq)
H11	5680(30)	6680(30)	5950(20)	35(7)
H2	4625	5440	4299	18
H4A	5936	8552	1696	26
H4B	7085	7343	1600	26
H5A	5516	5534	1947	23
H5B	4962	6484	876	23
H6	3531	4532	2745	24
H7A	1171	4482	2952	27
H7B	1014	6076	2444	27
H8A	2351	5354	4632	24
H8B	913	6168	4481	24
H9	3014	9237	5155	20
H11A	3224	7382	1832	21
H12	1990	8150	3621	19
H13A	8250	8229	4423	38
H13B	8378	8951	3170	38
H13C	8661	7269	3338	38
H14A	2227	5437	599	38
H14B	2155	3829	1086	38
H14C	3586	4486	723	38
H15A	705	8674	5499	38
H15B	1604	8943	6670	38
H15C	1218	7340	6277	38
H21	5020(30)	6860(40)	7940(30)	50(9)
H22	8910(30)	5890(30)	7300(20)	36(8)
H23	10683	3644	9030	29
H24	9800	2577	10664	31
H25	7560	3070	11194	29
H26	6213	4637	10065	25

Experimental

Single crystals of $C_{22}H_{29}NO_7$ **11-Aza:Sal 3** were grown at room temperature by evaporation of a ethyl acetate solution. A suitable crystal was selected and mounted in Paratone with a cryo-loop on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector. The crystal was kept at 100.01(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [11-Aza:Sal 3

Crystal Data for $C_{22}H_{29}NO_7$ (M =419.46 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 9.79451(14) Å, b = 9.30687(13) Å, c = 11.51291(16) Å, β = 92.3070(12)°, V = 1048.62(3) Å^3, Z = 2, T = 100.01(10) K, μ(CuKα) = 0.820 mm^{-1}, *Dcalc* = 1.328 g/cm^3, 8079 reflections measured (7.686° ≤ 2Θ ≤ 133.992°), 3602 unique (R_{int} = 0.0240, R_{sigma} = 0.0283) which were used in all calculations. The final R_1 was 0.0273 (I > 2σ(I)) and wR_2 was 0.0680 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12)
2.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B)
2.c Aromatic/amide H refined with riding coordinates:
 C23(H23), C24(H24), C25(H25), C26(H26)
2.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)
```

Table S1.4.1 Crystal data & structure refinement for 11-Aza:D-Man 4.

Identification code	madiha27CuLT
Empirical formula	$C_{23}H_{31}NO_7$
Formula weight	433.49
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.00907(10)
b/Å	10.09992(10)
c/Å	20.9254(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2115.37(4)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.830
F(000)	928.0
Crystal size/mm^3	0.3 × 0.12 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.452 to 135
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 12$, $-25 \leq l \leq 24$
Reflections collected	12213
Independent reflections	3723 [R_{int} = 0.0196, R_{sigma} = 0.0189]
Data/restraints/parameters	3723/0/295
Completeness to theta = 66.5°	97.9%
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0226, wR_2 = 0.0570
Final R indexes [all data]	R_1 = 0.0231, wR_2 = 0.0573
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15
Flack parameter	-0.03(4)

Table S1.4.2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:D-Man 4.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3175.7(10)	6904.6(11)	505.8(5)	16.0(2)
O2	1740.1(11)	6612.0(11)	576.7(5)	17.4(2)
O3	1590.7(10)	7311(1)	1622.4(5)	15.3(2)
O10	3439.4(11)	3301.8(10)	1631.6(6)	20.7(2)
N11	2897.2(12)	5426.7(13)	1784.3(6)	14.7(3)
C1	3819.9(14)	7225.4(14)	1114.2(7)	13.0(3)
C2	2929.9(15)	6850.1(14)	1678.7(7)	13.5(3)
C3	1181.0(15)	7597.2(16)	979.6(7)	17.0(3)
C4	1604.0(15)	8998.3(16)	784.4(8)	19.0(3)
C5	2804.9(15)	9542.8(15)	1155.3(8)	17.8(3)
C6	5095.0(15)	9130.4(15)	1642.8(7)	15.9(3)
C7	6344.0(16)	8265.0(15)	1622.8(8)	18.5(3)
C8	6023.5(16)	6795.4(15)	1662.7(8)	18.2(3)
C9	4769.7(15)	4909.9(14)	1068.9(8)	16.4(3)
C10	3662.3(15)	4481.4(15)	1519.8(7)	15.9(3)
C11	4099.7(14)	8724.7(14)	1112.8(7)	14.4(3)
C12	5101.3(14)	6394.2(14)	1110.5(7)	14.1(3)
C13	-315.7(15)	7373.5(17)	954.1(8)	21.5(3)
C14	5473.7(16)	10589.2(15)	1587.7(8)	19.5(3)
C15	5998.9(16)	4024.7(16)	1138.5(9)	22.4(3)
O20	823(1)	4555.3(11)	2631.3(5)	16.3(2)
O21	-1281.3(11)	4589.5(11)	2274.6(5)	17.2(2)
O22	1239.7(11)	2046.7(10)	2196.8(5)	15.4(2)
C21	-102.5(14)	4026.7(15)	2352.8(6)	13.1(3)
C22	-17.0(14)	2643.6(14)	2056.8(7)	14.1(3)
C23	-342.1(14)	2657.7(15)	1349.7(7)	14.8(3)
C24	180.5(17)	3619.3(16)	942.8(8)	20.1(3)
C25	-148.2(18)	3619.9(16)	299.5(8)	23.1(3)
C26	-992.3(17)	2654.7(18)	53.0(8)	23.7(4)
C27	-1495.5(17)	1679.5(16)	453.8(8)	21.9(3)
C28	-1168.4(15)	1678.8(15)	1099.9(8)	17.7(3)

Table S1.4.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:D-Man 4. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	10.8(5)	20.6(5)	16.5(5)	-0.7(4)	1.2(4)	-1.4(4)
O2	10.7(5)	20.1(5)	21.3(5)	-2.7(4)	-0.3(4)	-1.6(4)
O3	11.1(5)	17.3(5)	17.6(5)	0.9(4)	0.4(4)	2.6(4)
O10	17.9(5)	11.3(5)	33.0(6)	2.0(4)	3.6(5)	-0.3(4)
N11	13.1(6)	12.5(6)	18.6(6)	2.9(5)	3.7(5)	-0.4(5)
C1	12.3(7)	11.6(7)	15.1(7)	0.0(5)	-0.8(6)	0.2(5)
C2	11.3(7)	12.0(7)	17.4(7)	0.4(6)	-0.2(6)	1.2(5)
C3	14.2(7)	18.2(8)	18.8(7)	-0.9(6)	-1.4(6)	3.8(6)
C4	16.4(7)	16.1(7)	24.4(7)	3.9(6)	-3.3(6)	5.4(6)
C5	16.3(7)	11.5(6)	25.7(8)	2.1(6)	0.3(6)	1.3(6)
C6	15.1(7)	12.9(6)	19.8(7)	-0.6(6)	0.0(6)	-0.7(6)
C7	15.2(7)	15.4(7)	24.9(7)	0.0(6)	-4.6(6)	-0.6(6)
C8	14.9(7)	14.6(7)	25.2(8)	1.2(6)	-2.5(6)	1.8(5)
C9	14.4(7)	12.3(7)	22.3(7)	-1.3(6)	2.4(6)	0.8(5)
C10	13.6(7)	13.6(7)	20.6(7)	1.5(6)	-1.8(6)	0.2(6)
C11	13.2(7)	13.0(7)	17.0(7)	1.9(6)	1.2(5)	-0.1(5)
C12	12.0(7)	11.7(7)	18.6(7)	0.4(5)	2.1(6)	-0.1(5)
C13	13.7(8)	22.9(8)	27.8(8)	-0.5(7)	-2.4(6)	2.0(6)
C14	18.9(7)	14.9(7)	24.8(8)	-1.2(6)	0.9(6)	-2.5(6)
C15	16.4(7)	11.7(7)	39.1(9)	0.7(7)	5.1(6)	2.0(6)
O20	13.9(5)	14.8(5)	20.0(5)	-1.2(4)	-0.3(4)	-1.3(4)
O21	14.8(5)	13.0(5)	23.8(5)	-3.5(4)	-2.5(4)	3.0(4)
O22	11.9(5)	12.5(5)	21.9(5)	2.8(4)	0.6(4)	0.7(4)
C21	14.1(7)	11.0(6)	14.2(7)	2.2(5)	2.2(5)	-0.7(6)
C22	12.3(7)	10.2(6)	19.6(7)	0.9(5)	0.8(6)	1.1(5)
C23	13.3(6)	12.7(7)	18.5(7)	-0.6(6)	1.0(5)	3.8(6)
C24	21.8(8)	16.6(7)	21.8(8)	0.4(6)	0.4(6)	-0.3(6)
C25	30.1(9)	19.2(8)	19.9(8)	3.9(6)	2.5(6)	3.5(7)
C26	28.5(9)	23.4(9)	19.2(7)	-2.5(6)	-3.5(6)	9.0(7)
C27	20.4(8)	20.0(8)	25.1(8)	-5.4(6)	-3.9(7)	2.4(6)
C28	16.5(7)	14.4(7)	22.2(7)	-0.8(6)	0.5(6)	0.7(6)

Table S1.4.4 Bond Lengths for 11-Aza:D-Man 4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.4745(14)	C6	C14	1.526(2)
O1	C1	1.4635(18)	C7	C8	1.521(2)
O2	C3	1.4192(19)	C8	C12	1.533(2)
O3	C2	1.4238(18)	C9	C10	1.519(2)
O3	C3	1.4355(18)	C9	C12	1.538(2)
O10	C10	1.234(2)	C9	C15	1.528(2)
N11	C2	1.4549(19)	O20	C21	1.2177(19)
N11	C10	1.343(2)	O21	C21	1.3198(18)
C1	C2	1.527(2)	O22	C22	1.4253(17)
C1	C11	1.540(2)	C21	C22	1.530(2)
C1	C12	1.533(2)	C22	C23	1.515(2)
C3	C4	1.533(2)	C23	C24	1.393(2)
C3	C13	1.516(2)	C23	C28	1.391(2)
C4	C5	1.533(2)	C24	C25	1.386(2)
C5	C11	1.539(2)	C25	C26	1.389(3)
C6	C7	1.526(2)	C26	C27	1.388(3)
C6	C11	1.546(2)	C27	C28	1.391(2)

Table S1.4.5 Bond Angles for madiha27CuLT.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	112.72(10)	C10	C9	C12	113.59(12)
C3	O2	O1	107.67(10)	C10	C9	C15	111.21(13)
C2	O3	C3	114.35(11)	C15	C9	C12	113.03(13)
C10	N11	C2	128.82(13)	O10	C10	N11	120.32(14)
O1	C1	C2	111.15(11)	O10	C10	C9	121.65(14)
O1	C1	C11	107.22(11)	N11	C10	C9	118.01(13)
O1	C1	C12	104.06(11)	C1	C11	C6	112.11(12)
C2	C1	C11	110.59(12)	C5	C11	C1	112.00(12)
C2	C1	C12	110.86(12)	C5	C11	C6	111.02(12)
C12	C1	C11	112.73(12)	C1	C12	C8	110.79(12)
O3	C2	N11	108.33(12)	C1	C12	C9	110.71(12)
O3	C2	C1	113.83(12)	C8	C12	C9	115.48(13)
N11	C2	C1	112.08(12)	O20	C21	O21	123.41(14)
O2	C3	O3	107.62(11)	O20	C21	C22	123.45(13)
O2	C3	C4	112.33(13)	O21	C21	C22	113.14(12)
O2	C3	C13	105.32(12)	O22	C22	C21	110.63(11)
O3	C3	C4	110.91(12)	O22	C22	C23	113.22(12)
O3	C3	C13	106.58(13)	C23	C22	C21	112.00(12)
C13	C3	C4	113.65(13)	C24	C23	C22	121.51(14)
C3	C4	C5	114.39(13)	C28	C23	C22	119.21(14)
C4	C5	C11	115.99(13)	C28	C23	C24	119.27(14)
C7	C6	C11	110.88(12)	C25	C24	C23	120.31(15)
C14	C6	C7	110.34(12)	C24	C25	C26	120.31(16)
C14	C6	C11	111.22(12)	C27	C26	C25	119.63(15)
C8	C7	C6	112.63(13)	C26	C27	C28	120.13(15)
C7	C8	C12	110.10(13)	C23	C28	C27	120.33(15)

Table S1.4.6 Hydrogen Bonds for 11-Aza:D-Man 4.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O20	0.86(2)	2.01(2)	2.8681(17)	174.0(18)
O21	H21	O22[1]	0.84(3)	1.88(3)	2.7174(16)	174(2)
O22	H22	O10	0.78(3)	2.03(3)	2.8023(16)	174(2)

[1]-X,1/2+Y,1/2-Z

Table S1.4.7 Torsion Angles for 11-Aza:D-Man 4.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-74.96(13)	C10	C9	C12	C8	81.26(16)
O1	O2	C3	C4	47.41(14)	C11	C1	C2	O3	70.02(15)
O1	O2	C3	C13	171.62(11)	C11	C1	C2	N11	-166.60(12)
O1	C1	C2	O3	-48.95(15)	C11	C1	C12	C8	54.15(16)
O1	C1	C2	N11	74.43(15)	C11	C1	C12	C9	-176.40(12)
O1	C1	C11	C5	69.32(15)	C11	C6	C7	C8	-55.18(17)
O1	C1	C11	C6	-165.11(11)	C12	C1	C2	O3	-164.18(12)
O1	C1	C12	C8	169.98(11)	C12	C1	C2	N11	-40.80(16)
O1	C1	C12	C9	-60.56(14)	C12	C1	C11	C5	-176.75(12)
O2	O1	C1	C2	13.80(15)	C12	C1	C11	C6	-51.18(16)
O2	O1	C1	C11	-107.17(12)	C12	C9	C10	O10	-166.65(14)
O2	O1	C1	C12	133.18(11)	C12	C9	C10	N11	15.1(2)
O2	C3	C4	C5	-95.87(16)	C13	C3	C4	C5	144.66(14)
O3	C3	C4	C5	24.61(18)	C14	C6	C7	C8	-178.85(13)
C1	O1	O2	C3	45.55(14)	C14	C6	C11	C1	173.85(12)
C2	O3	C3	O2	38.86(15)	C14	C6	C11	C5	-60.04(16)
C2	O3	C3	C4	-84.38(14)	C15	C9	C10	O10	-37.8(2)
C2	O3	C3	C13	151.43(12)	C15	C9	C10	N11	143.99(14)
C2	N11	C10	O10	-175.06(15)	C15	C9	C12	C1	-173.57(13)
C2	N11	C10	C9	3.2(2)	C15	C9	C12	C8	-46.66(18)
C2	C1	C11	C5	-52.01(16)	O20	C21	C22	O22	4.42(19)
C2	C1	C11	C6	73.56(15)	O20	C21	C22	C23	-122.90(15)
C2	C1	C12	C8	-70.44(15)	O21	C21	C22	O22	-175.66(11)
C2	C1	C12	C9	59.02(16)	O21	C21	C22	C23	57.01(16)
C3	O3	C2	N11	-103.73(13)	O22	C22	C23	C24	-81.42(17)
C3	O3	C2	C1	21.66(16)	O22	C22	C23	C28	97.80(16)
C3	C4	C5	C11	58.42(18)	C21	C22	C23	C24	44.51(19)
C4	C5	C11	C1	-37.79(18)	C21	C22	C23	C28	-136.27(14)
C4	C5	C11	C6	-163.96(13)	C22	C23	C24	C25	-179.10(14)
C6	C7	C8	C12	58.47(17)	C22	C23	C28	C27	179.19(14)
C7	C6	C11	C1	50.69(17)	C23	C24	C25	C26	-0.6(3)
C7	C6	C11	C5	176.80(12)	C24	C23	C28	C27	-1.6(2)
C7	C8	C12	C1	-56.88(16)	C24	C25	C26	C27	-0.7(3)
C7	C8	C12	C9	176.26(13)	C25	C26	C27	C28	0.8(2)
C10	N11	C2	O3	136.65(15)	C26	C27	C28	C23	0.4(2)
C10	N11	C2	C1	10.2(2)	C28	C23	C24	C25	1.7(2)
C10	C9	C12	C1	-45.64(17)					

Table 8 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 11-Aza:D-Man 4.

Atom	*x*	*y*	*z*	U(eq)
H11	2320(20)	5160(20)	2059(9)	16(5)
H2	3322	7266	2070	16
H4A	837	9603	847	23
H4B	1824	8997	323	23
H5A	2550	9619	1611	21
H5B	2996	10447	998	21
H6	4649	8994	2065	19
H7A	6835	8441	1221	22
H7B	6935	8508	1983	22
H8A	5582	6600	2075	22
H8B	6861	6276	1642	22
H9	4423	4757	627	20
H11A	4528	8941	694	17
H12	5585	6624	707	17
H13A	-507	6431	1017	32
H13B	-658	7656	537	32
H13C	-750	7889	1292	32
H14A	5835	10763	1161	29
H14B	6150	10804	1910	29
H14C	4679	11138	1657	29
H15A	6329	4070	1579	34
H15B	6699	4327	845	34
H15C	5758	3109	1036	34
H21	-1280(20)	5330(30)	2464(11)	37(6)
H22	1810(20)	2440(20)	2032(10)	26(5)
H22A	-716	2091	2270	17
H24	765	4278	1107	24
H25	205	4283	26	28
H26	-1224	2662	-387	28
H27	-2064	1011	286	26
H28	-1511	1007	1372	21

Experimental

Single crystals of $C_{23}H_{31}NO_7$ **11-Aza:D-Man 4** were grown at room temperature by evaporation of a ethyl acetate solution. A suitable crystal was selected and mounted in Paratone with a cryo-loop on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector. The crystal was kept at 100.01(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza:D-Man 4

Crystal Data for $C_{23}H_{31}NO_7$ (M =433.49 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.00907(10) Å, b = 10.09992(10) Å, c = 20.9254(2) Å, V = 2115.37(4) Å^3, Z = 4, T = 100.01(10) K, μ(CuKα) = 0.830 mm^{-1}, $Dcalc$ = 1.361 g/cm^3, 12213 reflections measured (8.452° ≤ 2Θ ≤ 135°), 3723 unique (R_{int} = 0.0196, R_{sigma} = 0.0189) which were used in all calculations. The final R_1 was 0.0226 (I > 2σ(I)) and wR_2 was 0.0573 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12), C22(H22A)
2.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B)
2.c Aromatic/amide H refined with riding coordinates:
 C24(H24), C25(H25), C26(H26), C27(H27), C28(H28)
2.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)
```

Table S1.5.1 Crystal data and structure refinement for 11-Aza:Suc 5.

Identification code	madiha28a
Empirical formula	$C_{34}H_{52}N_2O_{12}$
Formula weight	680.77
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	17.9674(7)
b/Å	10.3025(4)
c/Å	9.3723(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1734.91(16)
Z	2
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.817
F(000)	732.0
Crystal size/mm^3	0.15 × 0.12 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.436 to 134.944
Index ranges	$-15 \leq h \leq 21$, $-12 \leq k \leq 12$, $-11 \leq l \leq 11$
Reflections collected	9822
Independent reflections	3114 [R_{int} = 0.0419, R_{sigma} = 0.0408]
Data/restraints/parameters	3114/0/228
Completeness to theta = 66.5°	99.4%
Goodness-of-fit on F^2	1.001
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1131
Final R indexes [all data]	R_1 = 0.0519, wR_2 = 0.1171
Largest diff. peak/hole / e Å^{-3}	0.17/-0.20
Flack parameter	-0.04(14)

Table S1.5.2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:Suc 5.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2715.0(12)	5050(2)	1678(3)	31.9(6)
O2	2971.5(12)	6404(2)	1587(3)	34.1(6)
O3	4231.5(12)	5943(2)	1652(3)	30.8(6)
O10	3322.4(14)	5779(2)	6080(3)	35.7(6)
N11	3901.4(16)	5464(3)	3982(4)	30.7(7)
C1	3322.8(18)	4166(3)	2053(4)	29.7(8)
C2	4004.5(18)	4921(3)	2574(4)	29.4(8)
C3	3636.1(18)	6424(3)	779(4)	32.2(8)
C4	3581(2)	5634(3)	-590(4)	37.3(9)
C5	3863(2)	4231(4)	-462(5)	39.5(9)
C6	3984.4(18)	2186(3)	1029(5)	39.1(10)
C7	3660(2)	1388(3)	2252(5)	40.5(10)
C8	3518.6(18)	2193(3)	3589(5)	37.6(9)
C9	2787.3(19)	4179(3)	4543(4)	31.1(8)
C10	3364.9(19)	5189(3)	4929(4)	29.6(7)
C11	3504.0(18)	3388(3)	699(5)	33.2(8)
C12	3000.6(18)	3332(3)	3256(4)	29.5(8)
C13	3783(2)	7860(3)	531(5)	37.3(9)
C14	4083(2)	1345(4)	-308(5)	46.8(11)
C15	2560(2)	3418(3)	5872(5)	41.2(9)
O21	4708.5(17)	7785(3)	4887(4)	60.4(10)
O22	3889.9(14)	8023(2)	6659(3)	39.3(6)
C21	4414(2)	8445(3)	5801(5)	38.4(9)
C22	4595(2)	9863(4)	6004(6)	52.2(12)

Table S1.5.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:Suc 5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	21.1(10)	14.5(10)	60.1(16)	-0.4(11)	-1.6(11)	-0.5(8)
O2	25.7(11)	14.3(10)	62.3(17)	-0.1(11)	1.7(12)	-0.2(8)
O3	21.7(11)	18.9(10)	51.8(16)	2.8(11)	0.3(11)	-1.5(9)
O10	35.2(12)	21.0(11)	50.9(16)	-0.3(11)	1.6(12)	-5.3(10)
N11	23.9(13)	16.9(12)	51.4(19)	-1.5(12)	0.0(13)	-5.0(11)
C1	18.8(14)	16.6(13)	54(2)	-1.4(14)	-0.4(15)	1.3(12)
C2	21.6(15)	14.9(14)	52(2)	2.6(15)	-1.9(14)	-2.2(12)
C3	23.0(15)	22.0(15)	51(2)	2.4(16)	0.9(16)	4.4(13)
C4	34.0(18)	27.0(18)	51(2)	-1.5(16)	1.4(17)	-0.3(15)
C5	34.3(19)	27.0(17)	57(3)	-11.1(16)	2.4(17)	-1.5(15)
C6	21.8(16)	19.8(16)	76(3)	-11.5(18)	2.1(17)	-0.2(13)
C7	27.0(17)	16.1(14)	79(3)	-5.0(17)	-2.2(18)	-1.0(13)
C8	26.5(16)	17.2(15)	69(3)	2.4(17)	1.0(17)	-1.4(13)
C9	26.5(16)	17.5(14)	49(2)	1.5(15)	-1.2(15)	-4.5(13)
C10	24.5(15)	16.4(14)	48(2)	1.7(15)	-0.7(14)	-1.2(13)
C11	21.3(15)	21.0(15)	57(2)	-8.7(16)	-0.6(15)	-3.6(13)
C12	22.2(14)	13.9(14)	52(2)	-0.1(14)	-2.4(15)	-3.5(11)
C13	34.5(19)	21.9(16)	55(2)	3.7(16)	2.4(17)	1.2(15)
C14	33.4(19)	27.5(18)	79(3)	-19.9(19)	2(2)	-0.6(16)
C15	43(2)	23.7(16)	56(3)	4.4(18)	2.7(19)	-10.6(15)
O21	47.1(16)	34.5(15)	100(3)	-28.8(18)	33.8(17)	-20.1(13)
O22	36.3(13)	19.0(11)	62.5(18)	-3.5(12)	11.3(13)	-6.6(10)
C21	29.4(16)	23.8(17)	62(3)	-5.7(18)	6.5(18)	-5.1(15)
C22	48(3)	21.4(18)	87(3)	-14(2)	26(2)	-12.3(16)

Table S1.5.4 Bond Lengths for 11-Aza:Suc 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.472(3)	C5	C11	1.535(6)
O1	C1	1.465(4)	C6	C7	1.527(6)
O2	C3	1.414(4)	C6	C11	1.541(5)
O3	C2	1.422(4)	C6	C14	1.533(6)
O3	C3	1.435(4)	C7	C8	1.523(6)
O10	C10	1.240(4)	C8	C12	1.530(4)
N11	C2	1.444(5)	C9	C10	1.513(4)
N11	C10	1.341(5)	C9	C12	1.538(5)
C1	C2	1.531(4)	C9	C15	1.527(5)
C1	C11	1.536(5)	O21	C21	1.214(5)
C1	C12	1.531(5)	O22	C21	1.312(5)
C3	C4	1.523(5)	C21	C22	1.509(5)
C3	C13	1.521(4)	C22	C22[1]	1.484(8)
C4	C5	1.537(5)			

[1]1-X,2-Y,+Z

Table S1.5.5 Bond Angles for 11-Aza:Suc 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	111.7(2)	C7	C6	C11	111.6(3)
C3	O2	O1	108.0(2)	C7	C6	C14	110.7(3)
C2	O3	C3	112.9(2)	C14	C6	C11	110.8(4)
C10	N11	C2	127.9(3)	C8	C7	C6	112.9(3)
O1	C1	C2	110.9(2)	C7	C8	C12	110.5(3)
O1	C1	C11	106.5(3)	C10	C9	C12	114.0(3)
O1	C1	C12	104.1(3)	C10	C9	C15	110.0(3)
C2	C1	C11	111.1(3)	C15	C9	C12	114.5(3)
C12	C1	C2	110.7(3)	O10	C10	N11	121.1(3)
C12	C1	C11	113.3(3)	O10	C10	C9	120.2(3)
O3	C2	N11	107.8(2)	N11	C10	C9	118.7(3)
O3	C2	C1	114.3(3)	C1	C11	C6	111.9(3)
N11	C2	C1	112.7(3)	C5	C11	C1	112.3(3)
O2	C3	O3	108.6(3)	C5	C11	C6	111.2(3)
O2	C3	C4	112.9(3)	C1	C12	C9	110.7(3)
O2	C3	C13	104.1(3)	C8	C12	C1	110.5(3)
O3	C3	C4	110.1(3)	C8	C12	C9	115.3(3)
O3	C3	C13	107.1(3)	O21	C21	O22	124.1(3)
C13	C3	C4	113.8(3)	O21	C21	C22	122.5(4)
C3	C4	C5	114.6(3)	O22	C21	C22	113.4(3)
C11	C5	C4	116.7(3)	C22[1]	C22	C21	113.3(4)

[1]1-X,2-Y,+Z

Table S1.5.6 Hydrogen Bonds for 11-Aza:Suc 5.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O21	0.80(5)	2.13(5)	2.923(4)	170(5)
O22	H22	O10	0.99(6)	1.61(6)	2.585(3)	167(5)

Table S1.5.7 Torsion Angles for 11-Aza:Suc 5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-75.5(3)	C7	C6	C11	C1	49.7(4)
O1	O2	C3	C4	46.9(4)	C7	C6	C11	C5	176.1(3)
O1	O2	C3	C13	170.7(3)	C7	C8	C12	C1	-56.4(4)
O1	C1	C2	O3	-50.7(4)	C7	C8	C12	C9	177.2(3)
O1	C1	C2	N11	72.8(4)	C10	N11	C2	O3	140.3(3)
O1	C1	C11	C5	69.1(3)	C10	N11	C2	C1	13.2(4)
O1	C1	C11	C6	-165.1(2)	C10	C9	C12	C1	-44.2(4)
O1	C1	C12	C8	169.8(3)	C10	C9	C12	C8	82.2(3)
O1	C1	C12	C9	-61.2(3)	C11	C1	C2	O3	67.5(3)
O2	O1	C1	C2	12.9(4)	C11	C1	C2	N11	-169.0(3)
O2	O1	C1	C11	-108.0(3)	C11	C1	C12	C8	54.5(4)
O2	O1	C1	C12	132.0(3)	C11	C1	C12	C9	-176.5(3)
O2	C3	C4	C5	-94.2(4)	C11	C6	C7	C8	-53.5(4)
O3	C3	C4	C5	27.3(4)	C12	C1	C2	O3	-165.7(3)
C1	O1	O2	C3	46.7(4)	C12	C1	C2	N11	-42.2(3)
C2	O3	C3	O2	36.4(4)	C12	C1	C11	C5	-177.0(3)
C2	O3	C3	C4	-87.6(3)	C12	C1	C11	C6	-51.2(4)
C2	O3	C3	C13	148.2(3)	C12	C9	C10	O10	-167.6(3)
C2	N11	C10	O10	-176.4(3)	C12	C9	C10	N11	15.0(4)
C2	N11	C10	C9	1.0(5)	C13	C3	C4	C5	147.5(3)
C2	C1	C11	C5	-51.8(4)	C14	C6	C7	C8	-177.5(3)
C2	C1	C11	C6	74.1(3)	C14	C6	C11	C1	173.6(3)
C2	C1	C12	C8	-71.0(4)	C14	C6	C11	C5	-60.0(4)
C2	C1	C12	C9	58.0(3)	C15	C9	C10	O10	-37.4(4)
C3	O3	C2	N11	-101.3(3)	C15	C9	C10	N11	145.2(3)
C3	O3	C2	C1	24.8(4)	C15	C9	C12	C1	-172.0(3)
C3	C4	C5	C11	56.0(4)	C15	C9	C12	C8	-45.7(4)
C4	C5	C11	C1	-36.2(4)	O21	C21	C22	C22[1]	-46.5(5)
C4	C5	C11	C6	-162.4(3)	O22	C21	C22	C22[1]	136.4(3)
C6	C7	C8	C12	57.0(4)					

[1] 1-X,2-Y,+Z

Table S1.5.8 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 11-Aza:Suc 5.

Atom	*x*	*y*	*z*	U(eq)
H11	4170(30)	6060(40)	4170(50)	43(13)
H2	4427	4292	2635	35
H4A	3870	6080	-1344	45
H4B	3054	5614	-899	45
H5A	3787	3796	-1393	47
H5B	4406	4258	-284	47
H6	4488	2496	1329	47
H7A	3185	994	1937	49
H7B	4007	674	2488	49
H8A	3997	2526	3962	45
H8B	3291	1639	4333	45
H9	2335	4675	4245	37
H11A	3021	3065	308	40
H12	2527	2949	2884	35
H13A	3759	8324	1443	56
H13B	3407	8211	-121	56
H13C	4279	7972	112	56
H14A	3593	1094	-677	70
H14B	4367	564	-64	70
H14C	4352	1839	-1038	70
H15A	2181	2775	5616	62
H15B	2357	4016	6586	62
H15C	2997	2974	6267	62
H22	3740(30)	7120(60)	6420(60)	86(19)
H22A	4356	10369	5231	63
H22B	4380	10159	6921	63

Experimental

Single crystals of $C_{34}H_{52}N_2O_{12}$ **11-Aza:Suc 5** were grown at room temperature by evaporation of a ethyl acetate solution. A suitable crystal was selected and mounted in Paratone with a cryo-loop on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza:Suc 5

Crystal Data for $C_{34}H_{52}N_2O_{12}$ (M =680.77 g/mol): orthorhombic, space group $P2_12_12$ (no. 18), a = 17.9674(7) Å, b = 10.3025(4) Å, c = 9.3723(7) Å, V = 1734.91(16) Å^3, Z = 2, T = 100.00(10) K, μ(CuKα) = 0.817 mm^{-1}, $Dcalc$ = 1.303 g/cm^3, 9822 reflections measured (9.436° ≤ 2Θ ≤ 134.944°), 3114 unique (R_{int} = 0.0419, R_{sigma} = 0.0408) which were used in all calculations. The final R_1 was 0.0455 (I > 2σ(I)) and wR_2 was 0.1171 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12)
2.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B), C22(H22A,H22B)
2.c Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)
```

Table S1.6.1 Crystal data & structure refinement for 11-Aza:L-Mal 6.

Identification code	madiha16a
Empirical formula	$C_{34}H_{52}N_2O_{13}$
Formula weight	696.77
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	17.7811(3)
b/Å	10.3174(2)
c/Å	9.49693(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1742.26(5)
Z	2
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	0.848
F(000)	748.0
Crystal size/mm^3	0.25 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.56 to 134.83
Index ranges	$-21 \leq h \leq 21$, $-11 \leq k \leq 12$, $-6 \leq l \leq 11$
Reflections collected	4942
Independent reflections	3094 [R_{int} = 0.0148, R_{sigma} = 0.0247]
Data/restraints/parameters	3094/58/281
Completeness to theta = 66.5°	98.5%
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0743
Final R indexes [all data]	R_1 = 0.0268, wR_2 = 0.0752
Largest diff. peak/hole / e Å^{-3}	0.18/-0.14
Flack parameter	-0.01(6)

Table S1.6.2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:L-Mal 6.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2690.0(6)	4981.8(11)	3254.7(12)	23.1(3)
O2	2944.5(7)	3630.9(12)	3378.1(13)	25.6(3)
O3	4219.2(6)	4080.1(12)	3334.3(12)	21.6(3)
O10	3346.4(7)	4200.7(12)	-1083.9(12)	24.7(3)
N11	3902.9(8)	4517.0(14)	1009.3(14)	19.6(3)
C1	3308.2(9)	5846.0(17)	2881.2(16)	20.0(3)
C2	4002.3(9)	5085.0(15)	2399.3(16)	19.4(3)
C3	3610.5(10)	3615.7(18)	4196.7(18)	26.2(4)
C4	3546.9(12)	4435(2)	5529.1(18)	34.2(4)
C5	3841.9(12)	5820(2)	5381.3(18)	32.4(4)
C6	3980.8(10)	7839.5(18)	3873(2)	32.2(4)
C7	3659.0(11)	8620.2(18)	2649(2)	33.8(4)
C8	3522.9(10)	7798.2(17)	1336(2)	27.4(4)
C9	2787.3(9)	5805.9(16)	407.1(16)	21.1(3)
C10	3377.7(9)	4794.8(15)	59.2(16)	19.4(3)
C11	3485.9(10)	6652.1(17)	4207.1(19)	26.3(4)
C12	2996.3(8)	6669.3(15)	1671.8(18)	20.8(3)
C13	3760.6(12)	2187(2)	4463.1(19)	32.4(4)
C14	4075.5(13)	8695(2)	5183(3)	45.2(6)
C15	2565.6(12)	6562.1(18)	-914.1(19)	31.2(4)
O20	4696(12)	2208(16)	220(20)	33(2)
O21	3944(19)	1980(20)	-1720(20)	31(4)
O22	3981.4(15)	-587(3)	-1549(3)	32.2(6)
O23	6062(18)	-2050(30)	-1630(20)	28(3)
O24	5377(12)	-2081(16)	265(19)	31(2)
C21	4379(10)	1554(16)	-644(14)	22.4(18)
C22	4511(2)	77(4)	-720(5)	20.6(8)
C23	5310(3)	-187(4)	-1213(5)	23.8(9)
C24	5554(10)	-1542(16)	-837(14)	25(2)

Table S1.6.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:L-Mal 6. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	17.5(5)	23.0(5)	29.0(6)	0.7(5)	3.5(4)	0.6(5)
O2	24.5(6)	23.2(6)	29.2(6)	4.1(5)	0.1(5)	-0.3(5)
O3	19.8(5)	24.7(6)	20.3(5)	1.6(5)	-1.2(4)	3.2(5)
O10	31.6(6)	23.5(6)	18.9(5)	-0.6(5)	-3.2(4)	6.5(5)
N11	19.3(6)	19.7(6)	19.9(6)	-2.1(5)	0.7(5)	4.5(5)
C1	15.3(7)	22.1(7)	22.6(7)	-3.5(6)	0.0(6)	0.5(6)
C2	17.0(7)	21.0(7)	20.2(7)	-1.2(6)	-1.0(6)	1.5(6)
C3	25.7(8)	31.2(9)	21.8(8)	3.0(7)	-0.2(7)	1.0(7)
C4	36.7(10)	46.2(12)	19.8(8)	0.5(7)	1.9(7)	7.2(9)
C5	34.4(10)	40.5(10)	22.3(8)	-12.0(7)	-5.2(7)	7.8(8)
C6	22.9(8)	26.6(9)	47.2(11)	-16.5(8)	-7.7(7)	4.2(7)
C7	25.6(8)	21.5(8)	54.2(11)	-8.6(8)	-4.4(8)	1.8(7)
C8	22.0(8)	20.3(8)	40.0(9)	0.9(7)	0.3(7)	0.9(6)
C9	19.3(8)	20.9(7)	23.2(7)	-0.3(6)	-2.2(6)	3.4(6)
C10	22.1(7)	15.9(7)	20.1(7)	1.8(6)	1.0(6)	0.0(6)
C11	21.7(8)	29.3(9)	27.8(8)	-10.0(7)	-2.5(7)	6.0(7)
C12	15.7(7)	19.8(8)	26.8(8)	-1.8(6)	0.2(6)	2.5(6)
C13	33.7(10)	32.4(10)	31.1(9)	9.4(7)	-1.0(8)	2.1(8)
C14	34.8(11)	40.1(11)	60.8(14)	-29.2(11)	-15.9(10)	9.7(9)
C15	38.3(10)	27.3(8)	28.0(9)	1.6(7)	-4.6(8)	12.0(7)
O20	24(3)	27(3)	46(3)	-11(2)	-12(3)	9(2)
O21	33(6)	20(3)	40(5)	-4(3)	-14(5)	8(3)
O22	33.4(13)	25.3(12)	37.8(13)	-2.4(10)	-12.1(11)	2.2(10)
O23	30(5)	26(4)	27(3)	8(2)	9(3)	9(3)
O24	31(5)	31(3)	31(2)	9(2)	8(2)	9(3)
C21	15(3)	21.0(17)	31(4)	-2.3(18)	-1(3)	3.9(14)
C22	19.6(15)	20.7(14)	21.3(19)	-2.2(13)	-0.4(12)	4.5(11)
C23	23.1(16)	23.2(16)	25(2)	2.5(13)	1.9(12)	4.1(12)
C24	22(4)	25.8(18)	26(3)	4(2)	4(3)	5(2)

Table S1.6.4 Bond Lengths for 11-Aza:L-Mal 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.4701(17)	C6	C11	1.541(3)
O1	C1	1.459(2)	C6	C14	1.535(3)
O2	C3	1.417(2)	C7	C8	1.527(3)
O3	C2	1.4186(19)	C8	C12	1.528(2)
O3	C3	1.439(2)	C9	C10	1.516(2)
O10	C10	1.248(2)	C9	C12	1.541(2)
N11	C2	1.455(2)	C9	C15	1.529(2)
N11	C10	1.330(2)	O20	C21	1.205(17)
C1	C2	1.533(2)	O21	C21	1.36(2)
C1	C11	1.542(2)	O22	C22	1.405(5)
C1	C12	1.532(2)	O23	C24	1.29(3)
C3	C4	1.526(2)	O24	C24	1.226(16)
C3	C13	1.519(3)	C21	C22	1.544(14)
C4	C5	1.529(3)	C22	C23	1.520(6)
C5	C11	1.543(3)	C23	C24	1.507(12)
C6	C7	1.526(3)			

Table S1.6.5 Bond Angles for 11-Aza:L-Mal 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	111.52(11)	C6	C7	C8	112.85(15)
C3	O2	O1	108.16(12)	C7	C8	C12	110.48(15)
C2	O3	C3	113.27(12)	C10	C9	C12	113.61(13)
C10	N11	C2	127.88(14)	C10	C9	C15	110.53(13)
O1	C1	C2	111.48(13)	C15	C9	C12	114.00(14)
O1	C1	C11	106.59(13)	O10	C10	N11	121.05(15)
O1	C1	C12	104.38(12)	O10	C10	C9	119.77(14)
C2	C1	C11	110.80(13)	N11	C10	C9	119.12(14)
C12	C1	C2	110.58(13)	C1	C11	C5	111.97(14)
C12	C1	C11	112.78(14)	C6	C11	C1	112.18(15)
O3	C2	N11	107.85(12)	C6	C11	C5	110.91(15)
O3	C2	C1	113.98(13)	C1	C12	C9	110.55(13)
N11	C2	C1	112.30(12)	C8	C12	C1	110.93(13)
O2	C3	O3	108.22(13)	C8	C12	C9	115.19(14)
O2	C3	C4	112.77(15)	O20	C21	O21	127.0(19)
O2	C3	C13	104.42(15)	O20	C21	C22	120.9(12)
O3	C3	C4	110.08(15)	O21	C21	C22	111.8(14)
O3	C3	C13	106.60(15)	O22	C22	C21	113.9(6)
C13	C3	C4	114.34(15)	O22	C22	C23	111.4(3)
C3	C4	C5	114.59(15)	C23	C22	C21	109.5(8)
C4	C5	C11	116.47(16)	C24	C23	C22	111.3(7)
C7	C6	C11	111.25(15)	O23	C24	C23	116.1(14)
C7	C6	C14	110.80(16)	O24	C24	O23	119.8(15)
C14	C6	C11	110.66(18)	O24	C24	C23	123.3(13)

Table S1.6.6 Hydrogen Bonds for 11-Aza:L-Mal 6.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O20	0.83(3)	2.05(3)	2.868(18)	168(2)
N11	H11	O24[1]	0.83(3)	2.10(3)	2.908(18)	164(2)
O21	H21	O10	0.95(5)	1.66(5)	2.60(2)	168(9)
O23	H23	O10[1]	0.91(3)	1.62(5)	2.51(3)	164(11)

[1]1-X,-Y,+Z

Table S1.6.7 Torsion Angles for 11-Aza:L-Mal 6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-75.44(15)	C7	C8	C12	C9	177.24(14)
O1	O2	C3	C4	46.57(17)	C10	N11	C2	O3	141.14(16)
O1	O2	C3	C13	171.29(12)	C10	N11	C2	C1	14.7(2)
O1	C1	C2	O3	-50.33(17)	C10	C9	C12	C1	-44.76(18)
O1	C1	C2	N11	72.70(16)	C10	C9	C12	C8	81.96(17)
O1	C1	C11	C5	69.35(18)	C11	C1	C2	O3	68.21(17)
O1	C1	C11	C6	-165.20(13)	C11	C1	C2	N11	-168.76(14)
O1	C1	C12	C8	169.43(13)	C11	C1	C12	C8	54.14(18)
O1	C1	C12	C9	-61.51(15)	C11	C1	C12	C9	-176.81(13)
O2	O1	C1	C2	12.83(15)	C11	C6	C7	C8	-54.0(2)
O2	O1	C1	C11	-108.20(13)	C12	C1	C2	O3	-165.97(13)
O2	O1	C1	C12	132.23(12)	C12	C1	C2	N11	-42.95(17)
O2	C3	C4	C5	-94.44(19)	C12	C1	C11	C5	-176.69(14)
O3	C3	C4	C5	26.5(2)	C12	C1	C11	C6	-51.24(18)
C1	O1	O2	C3	46.91(15)	C12	C9	C10	O10	-166.67(14)
C2	O3	C3	O2	36.40(18)	C12	C9	C10	N11	16.2(2)
C2	O3	C3	C4	-87.25(16)	C13	C3	C4	C5	146.46(17)
C2	O3	C3	C13	148.22(13)	C14	C6	C7	C8	-177.59(17)
C2	N11	C10	O10	-177.92(15)	C14	C6	C11	C1	173.94(15)
C2	N11	C10	C9	-0.9(2)	C14	C6	C11	C5	-60.03(19)
C2	C1	C11	C5	-52.11(19)	C15	C9	C10	O10	-37.1(2)
C2	C1	C11	C6	73.34(17)	C15	C9	C10	N11	145.85(16)
C2	C1	C12	C8	-70.56(17)	C15	C9	C12	C1	-172.61(14)
C2	C1	C12	C9	58.49(17)	C15	C9	C12	C8	-45.89(19)
C3	O3	C2	N11	-101.19(15)	O20	C21	C22	O22	166.1(18)
C3	O3	C2	C1	24.23(18)	O20	C21	C22	C23	-68(2)
C3	C4	C5	C11	56.7(2)	O21	C21	C22	O22	-20(2)
C4	C5	C11	C1	-36.6(2)	O21	C21	C22	C23	105(2)
C4	C5	C11	C6	-162.76(15)	O22	C22	C23	C24	-72.6(8)
C6	C7	C8	C12	57.2(2)	C21	C22	C23	C24	160.4(8)
C7	C6	C11	C1	50.31(19)	C22	C23	C24	O23	153(2)
C7	C6	C11	C5	176.34(15)	C22	C23	C24	O24	-37(2)
C7	C8	C12	C1	-56.23(18)					

Table S1.6.8 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 11-Aza:L-Mal 6.

Atom	*x*	*y*	*z*	U(eq)
H11	4189(15)	3900(30)	830(30)	32(6)
H2	4431	5710	2339	23
H4A	3828	3998	6294	41
H4B	3012	4471	5814	41
H5A	4391	5778	5213	39
H5B	3765	6271	6290	39
H6	4490	7519	3590	39
H7A	4012	9330	2412	41
H7B	3178	9018	2946	41
H8A	4008	7458	983	33
H8B	3298	8343	588	33
H9	2328	5313	698	25
H11A	2996	6987	4577	32
H12	2516	7060	2020	25
H13A	3727	1710	3573	49
H13B	3386	1849	5125	49
H13C	4265	2082	4863	49
H14A	4367	9469	4937	68
H14B	4341	8208	5916	68
H14C	3579	8955	5532	68
H15A	2180	7203	-673	47
H15B	2367	5962	-1622	47
H15C	3009	7006	-1294	47
H21	3700(50)	2740(70)	-1380(90)	30(20)
H22	3820(50)	-60(80)	-2180(90)	90(30)
H23	6190(60)	-2880(50)	-1410(130)	60(40)
H22A	4467	-268	261	25
H23A	5338	-72	-2246	29
H23B	5655	445	-771	29

Table S1.6.9 Atomic Occupancy for 11-Aza:L-Mal 6.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O20	0.5	O21	0.5	H21	0.5
O22	0.5	H22	0.5	O23	0.5
H23	0.5	O24	0.5	C21	0.5
C22	0.5	H22A	0.5	C23	0.5
H23A	0.5	H23B	0.5	C24	0.5

Experimental

Single crystals of $C_{34}H_{52}N_2O_{13}$ **11-Aza:L-Mal 6** were grown at room temperature by evaporation of a ethyl acetate solution. A suitable crystal was selected and mounted in Paratone with a cryo-loop on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector. The crystal was kept at 100.01(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza:L-Mal 6

Crystal Data for $C_{34}H_{52}N_2O_{13}$ (M =696.77 g/mol): orthorhombic, space group $P2_12_12$ (no. 18), a = 17.7811(3) Å, b = 10.3174(2) Å, c = 9.49693(15) Å, V = 1742.26(5) Å^3, Z = 2, T = 100.01(10) K, μ(CuKα) = 0.848 mm^{-1}, $Dcalc$ = 1.328 g/cm^3, 4942 reflections measured (10.56° ≤ 2Θ ≤ 134.83°), 3094 unique (R_{int} = 0.0148, R_{sigma} = 0.0247) which were used in all calculations. The final R_1 was 0.0258 (I > 2σ(I)) and wR_2 was 0.0752 (all data).

Refinement model description

Number of restraints - 58, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 O23-H23
 0.9 with sigma of 0.02
 O21-H21 = O23-H23
 0.9 with sigma of 0.05
 C22-C24 ≈ C21-C23
 with sigma of 0.02
3. Rigid body (RIGU) restrains
 O20, O21, H21, O22, O23, H23, O24, C21, C22, C23, C24
 with sigma for 1-2 distances of 0.001 and sigma for 1-3 distances of 0.001
4. Others
 Fixed Sof: O20(0.5) O21(0.5) H21(0.5) O22(0.5) H22(0.5) O23(0.5) H23(0.5)
 O24(0.5) C21(0.5) C22(0.5) H22A(0.5) C23(0.5) H23A(0.5) H23B(0.5) C24(0.5)
5.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12), C22(H22A)
5.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B), C23(H23A,H23B)
5.c Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)
```

Table S1.7.1 Crystal data and structure refinement for 11-Aza:D-Mal 7.

Identification code	madiha30CuLT
Empirical formula	$C_{34}H_{52}N_2O_{13}$
Formula weight	696.77
Temperature/K	99.97(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.43733(12)
b/Å	18.04445(19)
c/Å	18.6345(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3509.55(7)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	0.842
F(000)	1496.0
Crystal size/mm^3	0.2 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.818 to 135
Index ranges	$-10 \leq h \leq 12$, $-18 \leq k \leq 21$, $-22 \leq l \leq 22$
Reflections collected	19371
Independent reflections	6284 [R_{int} = 0.0215, R_{sigma} = 0.0219]
Data/restraints/parameters	6284/26/487
Completeness to theta = 66.5°	98.9%
Goodness-of-fit on F^2	1.001
Final R indexes [I>=2σ (I)]	R_1 = 0.0284, wR_2 = 0.0715
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0725
Largest diff. peak/hole / e Å^{-3}	0.18/-0.16
Flack parameter	-0.06(5)

Table S1.7.2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:D-Mal 7.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7246.8(13)	7326.4(8)	3385.0(8)	25.1(3)
O2	8544.0(14)	7030.3(8)	3293.1(8)	28.4(3)
O3	7963.0(13)	5794.0(8)	3264.4(8)	25.7(3)
O10	8173.9(14)	6606.0(8)	5506.0(7)	25.7(3)
N11	7636.5(16)	6075.6(9)	4463.3(9)	21.5(3)
C1	6334.3(18)	6738.7(10)	3557.6(10)	20.1(4)
C2	7019.1(18)	6024.8(11)	3764.6(10)	19.8(4)
C3	8471(2)	6397.2(13)	2846.6(11)	30.3(5)
C4	7638(2)	6525.0(14)	2182.4(11)	35.7(5)
C5	6249(2)	6270.5(13)	2262.2(11)	31.2(5)
C6	4291(2)	6156.6(11)	3065.1(11)	24.8(4)
C7	3566(2)	6503.4(11)	3686.7(11)	26.3(4)
C8	4401.3(19)	6573.9(11)	4356.3(11)	23.9(4)
C9	6479.8(18)	7191.1(11)	4841.8(10)	21.6(4)
C10	7483.7(19)	6595.7(10)	4958.7(10)	20.2(4)
C11	5493(2)	6617.8(11)	2886.3(10)	23.4(4)
C12	5583.7(18)	7049.1(10)	4195.4(10)	20.1(4)
C13	9852(2)	6207.0(16)	2683.9(14)	41.4(6)
C14	3416(2)	6059.9(13)	2412.3(12)	32.2(5)
C15	5760(2)	7340.3(14)	5545.4(12)	32.5(5)
O1A	6619.9(13)	2791.2(7)	3321.1(7)	22.5(3)
O2A	5324.6(13)	3108.9(7)	3321.7(8)	23.3(3)
O3A	5956.4(13)	4333.0(7)	3403.3(7)	20.5(3)
O10A	6182.8(14)	3322.0(8)	5581.4(7)	25.0(3)
N11A	6503.8(16)	3936.9(9)	4549.6(9)	20.6(3)
C1A	7588.7(19)	3339.1(10)	3510.9(10)	20.0(4)
C2A	6979.3(18)	4043.1(10)	3822.3(10)	19.0(4)
C3A	5363(2)	3789.3(10)	2945.1(10)	22.2(4)
C4A	6101(2)	3740.3(11)	2234.1(11)	24.7(4)
C5A	7516(2)	3953.2(11)	2279.2(10)	24.9(4)
C6A	9614.8(19)	3906.3(12)	2965.7(11)	25.6(4)
C7A	10383(2)	3489.4(12)	3538.7(12)	28.3(4)
C8A	9628(2)	3381.3(12)	4231.5(11)	26.4(4)
C9A	7583(2)	2741.6(11)	4736.3(10)	22.6(4)
C10A	6713.4(18)	3361.3(11)	4986.6(10)	20.9(4)
C11A	8332.1(19)	3512.3(11)	2817.5(10)	22.7(4)
C12A	8405.6(19)	2943.3(10)	4077.3(10)	21.9(4)
C13A	3970(2)	3997.5(12)	2861.4(12)	28.8(4)
C14A	10414(2)	3992.6(13)	2279.7(12)	33.2(5)
C15A	8356(2)	2435.3(13)	5368.6(11)	30.8(5)
O20	-115.1(18)	5230.3(10)	4691.1(12)	51.8(5)
O21	406.6(15)	6008.8(8)	5572.0(8)	29.1(3)

O22	2236(2)	4808.2(13)	4456.2(11)	46.8(5)
O22A	1660(14)	4190(8)	5673(9)	35(3)
O23	4071.6(16)	3969.8(9)	5937.4(8)	32.0(3)
O24	4683.8(16)	4954.8(9)	5299.7(10)	38.2(4)
C21	662(2)	5503.5(11)	5098.4(11)	26.3(4)
C22	2060(2)	5274.0(13)	5053.3(11)	27.2(4)
C23	2499(5)	4901(2)	5731(4)	34.5(11)
C23A	2590(50)	4770(20)	5690(40)	24(5)
C24	3875(2)	4618.1(12)	5628.1(11)	28.8(4)

Table S1.7.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:D-Mal 7.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	25.0(7)	20.4(7)	29.8(7)	1.5(5)	2.3(6)	-6.0(6)
O2	23.5(7)	32.5(8)	29.3(7)	-4.8(6)	4.8(6)	-7.9(6)
O3	24.0(7)	26.1(7)	27.1(7)	-6.3(6)	6.4(6)	-1.4(6)
O10	25.9(7)	30.4(7)	20.8(7)	-1.9(6)	-3.2(5)	3.7(6)
N11	20.1(8)	19.7(8)	24.6(8)	0.4(6)	-2.0(7)	2.7(7)
C1	21.9(9)	17.6(9)	20.9(9)	1.2(7)	-0.2(7)	-5.3(8)
C2	19.6(8)	19.8(9)	20.1(9)	-2.4(7)	1.2(7)	-1.5(8)
C3	30.1(11)	35.3(11)	25.7(10)	-7.7(9)	7.5(9)	-7.3(9)
C4	39.5(12)	46.8(13)	20.6(9)	-2.9(9)	6.9(9)	-11.3(11)
C5	37.0(12)	35.2(11)	21.3(9)	-2.6(9)	-1.8(9)	-7.4(10)
C6	25.3(10)	21.1(9)	28.1(10)	1.3(8)	-7.1(8)	-3.1(8)
C7	21.6(10)	25.6(10)	31.7(11)	4.0(8)	-3.2(8)	-2.1(8)
C8	22.1(9)	24.2(9)	25.3(9)	0.5(8)	1.4(8)	-0.4(8)
C9	22.1(9)	21.5(9)	21.3(9)	-3.1(7)	0.0(8)	2.4(8)
C10	20.2(8)	21.3(9)	19.2(8)	1.0(7)	2.0(7)	-0.7(8)
C11	27.5(10)	21.3(9)	21.4(9)	2.4(8)	-3.4(8)	-2.5(8)
C12	20.1(9)	17.2(8)	23.1(9)	0.8(7)	-0.1(7)	1.0(7)
C13	30.6(12)	55.0(15)	38.5(13)	-11.4(12)	13.8(10)	-8.6(11)
C14	33.3(11)	28.7(11)	34.7(11)	1.6(9)	-12.7(9)	-5.0(9)
C15	28.1(10)	44.4(13)	24.9(10)	-9.0(9)	-0.3(8)	9.1(9)
O1A	21.9(7)	17.0(6)	28.4(7)	-2.0(5)	-1.8(5)	0.2(5)
O2A	21.1(7)	21.8(7)	27.1(7)	1.2(6)	-1.1(6)	-2.3(5)
O3A	20.5(6)	18.7(6)	22.3(6)	0.3(5)	-4.3(5)	1.0(5)
O10A	26.7(7)	28.1(7)	20.3(6)	2.3(6)	0.9(5)	4.3(6)
N11A	23.0(8)	17.3(7)	21.5(8)	-1.3(6)	-0.3(6)	2.6(7)
C1A	20.8(9)	17.0(8)	22.2(9)	-2.3(7)	-1.2(7)	-0.6(7)
C2A	17.5(8)	17.9(9)	21.7(9)	0.0(7)	-2.9(7)	0.4(7)
C3A	24.7(10)	19.6(9)	22.5(9)	0.5(7)	-4.3(8)	-4.7(8)
C4A	25.9(10)	26.8(10)	21.3(9)	1.1(8)	-2.9(8)	-1.9(8)

C5A	25.3(9)	27.2(10)	22.1(9)	1.9(8)	0.0(8)	-0.1(9)
C6A	21.3(9)	25.7(10)	29.8(10)	3.9(8)	2.6(8)	1.0(8)
C7A	20.2(9)	31.6(11)	33.2(11)	1.7(9)	0.2(8)	1.9(8)
C8A	21.8(9)	28(1)	29.4(10)	3.8(8)	-2.1(8)	2.6(9)
C9A	24.9(9)	20.2(9)	22.5(9)	0.9(7)	0.3(8)	3.7(8)
C10A	20.3(9)	20.7(9)	21.8(9)	-1.2(8)	-3.6(7)	-1.0(7)
C11A	23.8(10)	22.0(9)	22.3(9)	-1.7(7)	1.7(8)	1.9(8)
C12A	23.1(9)	19.9(9)	22.7(9)	1.1(7)	0.2(8)	3.8(8)
C13A	22.8(10)	31.9(10)	31.8(10)	3.3(9)	-5.2(8)	-2.3(9)
C14A	26(1)	39.2(12)	34.5(11)	6.1(10)	6.2(9)	1.7(10)
C15A	32.9(11)	34.4(11)	25.2(10)	6.7(8)	2.9(9)	12.0(9)
O20	36.6(9)	44.4(10)	74.6(13)	-29.8(10)	-22.1(9)	16.8(8)
O21	25.7(7)	34.8(8)	26.7(7)	-5.8(6)	-3.0(6)	5.2(7)
O22	42.3(12)	59.9(13)	38.2(10)	-21.4(10)	-2.8(9)	14.1(10)
O22A	32(4)	35(4)	38(7)	4(4)	4(4)	4(3)
O23	31.8(8)	32.7(8)	31.6(7)	9.6(7)	6.4(6)	9.5(7)
O24	31.1(8)	30.0(8)	53.7(10)	11.0(7)	9.9(7)	6.4(7)
C21	29.1(10)	22.0(9)	27.7(10)	-0.3(8)	-3.5(8)	1.0(8)
C22	27.6(10)	29.9(10)	24.1(9)	-1.0(8)	2.8(8)	4.4(8)
C23	31.0(15)	41(2)	31(2)	8(2)	10.4(13)	14.3(16)
C23A	31(6)	29(8)	13(10)	6(7)	5(5)	7(5)
C24	29(1)	32.1(11)	25.2(10)	2.9(9)	2.0(9)	5.2(9)

Table S1.7.4 Bond Lengths for 11-Aza:D-Mal 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.466(2)	N11A	C2A	1.456(2)
O1	C1	1.461(2)	N11A	C10A	1.338(3)
O2	C3	1.415(3)	C1A	C2A	1.535(3)
O3	C2	1.419(2)	C1A	C11A	1.539(3)
O3	C3	1.440(3)	C1A	C12A	1.533(3)
O10	C10	1.249(2)	C3A	C4A	1.535(3)
N11	C2	1.456(2)	C3A	C13A	1.511(3)
N11	C10	1.326(3)	C4A	C5A	1.529(3)
C1	C2	1.523(3)	C5A	C11A	1.538(3)
C1	C11	1.544(3)	C6A	C7A	1.532(3)
C1	C12	1.530(3)	C6A	C11A	1.541(3)
C3	C4	1.530(3)	C6A	C14A	1.534(3)
C3	C13	1.512(3)	C7A	C8A	1.525(3)
C4	C5	1.529(3)	C8A	C12A	1.528(3)
C5	C11	1.539(3)	C9A	C10A	1.513(3)
C6	C7	1.519(3)	C9A	C12A	1.542(3)
C6	C11	1.542(3)	C9A	C15A	1.531(3)
C6	C14	1.531(3)	O20	C21	1.215(3)
C7	C8	1.528(3)	O21	C21	1.297(3)
C8	C12	1.532(3)	O22	C22	1.406(3)
C9	C10	1.516(3)	O22A	C23A	1.43(3)
C9	C12	1.546(3)	O23	C24	1.320(3)
C9	C15	1.535(3)	O24	C24	1.207(3)
O1A	O2A	1.4685(19)	C21	C22	1.519(3)
O1A	C1A	1.458(2)	C22	C23	1.503(8)
O2A	C3A	1.415(2)	C22	C23A	1.60(6)
O3A	C2A	1.422(2)	C23	C24	1.536(5)
O3A	C3A	1.440(2)	C23A	C24	1.37(5)
O10A	C10A	1.241(2)			

Table S1.7.5 Bond Angles for 11-Aza:D-Mal 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	111.30(13)	C12A	C1A	C2A	110.84(15)
C3	O2	O1	108.26(14)	C12A	C1A	C11A	113.09(16)
C2	O3	C3	112.90(15)	O3A	C2A	N11A	107.67(15)
C10	N11	C2	127.88(17)	O3A	C2A	C1A	114.08(15)
O1	C1	C2	111.33(15)	N11A	C2A	C1A	112.61(15)
O1	C1	C11	107.15(14)	O2A	C3A	O3A	108.02(14)
O1	C1	C12	103.83(14)	O2A	C3A	C4A	113.11(16)
C2	C1	C11	110.65(16)	O2A	C3A	C13A	103.86(16)

C2	C1	C12	110.70(15)	O3A	C3A	C4A	109.60(15)
C12	C1	C11	112.95(16)	O3A	C3A	C13A	107.80(16)
O3	C2	N11	107.38(15)	C13A	C3A	C4A	114.09(17)
O3	C2	C1	114.08(16)	C5A	C4A	C3A	115.00(16)
N11	C2	C1	112.40(15)	C4A	C5A	C11A	116.16(16)
O2	C3	O3	108.19(16)	C7A	C6A	C11A	110.66(17)
O2	C3	C4	112.62(19)	C7A	C6A	C14A	110.24(17)
O2	C3	C13	104.47(18)	C14A	C6A	C11A	111.71(17)
O3	C3	C4	110.01(17)	C8A	C7A	C6A	112.49(17)
O3	C3	C13	106.7(2)	C7A	C8A	C12A	109.77(17)
C13	C3	C4	114.43(19)	C10A	C9A	C12A	113.88(16)
C5	C4	C3	114.53(18)	C10A	C9A	C15A	110.21(16)
C4	C5	C11	115.95(18)	C15A	C9A	C12A	113.84(17)
C7	C6	C11	110.37(16)	O10A	C10A	N11A	120.99(18)
C7	C6	C14	110.80(17)	O10A	C10A	C9A	120.03(17)
C14	C6	C11	112.05(17)	N11A	C10A	C9A	118.95(17)
C6	C7	C8	111.88(16)	C1A	C11A	C6A	112.41(16)
C7	C8	C12	110.28(16)	C5A	C11A	C1A	111.93(16)
C10	C9	C12	114.36(15)	C5A	C11A	C6A	111.06(16)
C10	C9	C15	109.85(16)	C1A	C12A	C9A	110.39(16)
C15	C9	C12	113.49(16)	C8A	C12A	C1A	110.66(16)
O10	C10	N11	120.65(18)	C8A	C12A	C9A	115.93(16)
O10	C10	C9	120.36(17)	O20	C21	O21	125.0(2)
N11	C10	C9	118.98(17)	O20	C21	C22	119.72(19)
C5	C11	C1	112.23(17)	O21	C21	C22	115.27(18)
C5	C11	C6	111.13(16)	O22	C22	C21	109.40(19)
C6	C11	C1	111.34(15)	O22	C22	C23	111.0(3)
C1	C12	C8	111.07(15)	C21	C22	C23A	116.7(19)
C1	C12	C9	110.86(15)	C23	C22	C21	111.6(2)
C8	C12	C9	115.30(16)	C22	C23	C24	109.2(4)
C1A	O1A	O2A	111.93(12)	O22A	C23A	C22	99(3)
C3A	O2A	O1A	108.19(13)	C24	C23A	O22A	122(4)
C2A	O3A	C3A	113.41(14)	C24	C23A	C22	113(4)
C10A	N11A	C2A	127.81(17)	O23	C24	C23	112.7(3)
O1A	C1A	C2A	111.45(15)	O23	C24	C23A	107(2)
O1A	C1A	C11A	106.48(14)	O24	C24	O23	124.0(2)
O1A	C1A	C12A	103.69(14)	O24	C24	C23	123.4(3)
C2A	C1A	C11A	111.00(15)	O24	C24	C23A	129(2)

Table S1.7.6 Hydrogen Bonds for 11-Aza:D-Mal 7.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O20[1]	0.83(3)	2.03(3)	2.831(2)	164(3)
N11A	H11B	O24	0.89(3)	2.12(3)	2.989(2)	165(2)
O21	H21	O10[2]	0.92(3)	1.67(3)	2.570(2)	165(3)
O23	H23	O10A	0.89(3)	1.70(3)	2.581(2)	169(3)

[1]1+X,+Y,+Z; [2]-1+X,+Y,+Z

Table S1.7.7 Torsion Angles for 11-Aza:D-Mal 7.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-75.51(19)	O1A	C1A	C12A	C9A	-61.42(19)
O1	O2	C3	C4	46.3(2)	O2A	O1A	C1A	C2A	12.86(19)
O1	O2	C3	C13	171.05(17)	O2A	O1A	C1A	C11A	-108.32(15)
O1	C1	C2	O3	-51.2(2)	O2A	O1A	C1A	C12A	132.15(14)
O1	C1	C2	N11	71.32(19)	O2A	C3A	C4A	C5A	-93.6(2)
O1	C1	C11	C5	69.0(2)	O3A	C3A	C4A	C5A	27.0(2)
O1	C1	C11	C6	-165.67(15)	C1A	O1A	O2A	C3A	46.68(17)
O1	C1	C12	C8	168.59(15)	C2A	O3A	C3A	O2A	37.4(2)
O1	C1	C12	C9	-61.85(18)	C2A	O3A	C3A	C4A	-86.21(18)
O2	O1	C1	C2	13.3(2)	C2A	O3A	C3A	C13A	149.08(16)
O2	O1	C1	C11	-107.80(16)	C2A	N11A	C10A	O10A	-175.62(17)
O2	O1	C1	C12	132.45(14)	C2A	N11A	C10A	C9A	2.6(3)
O2	C3	C4	C5	-95.2(2)	C2A	C1A	C11A	C5A	-51.0(2)
O3	C3	C4	C5	25.5(3)	C2A	C1A	C11A	C6A	74.8(2)
C1	O1	O2	C3	46.85(19)	C2A	C1A	C12A	C8A	-71.4(2)
C2	O3	C3	O2	36.1(2)	C2A	C1A	C12A	C9A	58.3(2)
C2	O3	C3	C4	-87.3(2)	C3A	O3A	C2A	N11A	-102.89(17)
C2	O3	C3	C13	148.00(17)	C3A	O3A	C2A	C1A	22.9(2)
C2	N11	C10	O10	-172.89(18)	C3A	C4A	C5A	C11A	57.1(2)
C2	N11	C10	C9	5.5(3)	C4A	C5A	C11A	C1A	-37.9(2)
C2	C1	C11	C5	-52.5(2)	C4A	C5A	C11A	C6A	-164.47(17)
C2	C1	C11	C6	72.8(2)	C6A	C7A	C8A	C12A	59.4(2)
C2	C1	C12	C8	-71.8(2)	C7A	C6A	C11A	C1A	50.1(2)
C2	C1	C12	C9	57.7(2)	C7A	C6A	C11A	C5A	176.33(17)
C3	O3	C2	N11	-100.28(18)	C7A	C8A	C12A	C1A	-57.4(2)
C3	O3	C2	C1	25.0(2)	C7A	C8A	C12A	C9A	175.92(16)
C3	C4	C5	C11	57.4(3)	C10A	N11A	C2A	O3A	137.66(18)
C4	C5	C11	C1	-36.5(3)	C10A	N11A	C2A	C1A	11.0(3)
C4	C5	C11	C6	-161.93(19)	C10A	C9A	C12A	C1A	-45.0(2)
C6	C7	C8	C12	58.9(2)	C10A	C9A	C12A	C8A	81.8(2)
C7	C6	C11	C1	53.5(2)	C11A	C1A	C2A	O3A	69.2(2)
C7	C6	C11	C5	179.42(16)	C11A	C1A	C2A	N11A	-167.74(15)
C7	C8	C12	C1	-55.4(2)	C11A	C1A	C12A	C8A	54.0(2)

C7	C8	C12	C9	177.45(16)	C11A	C1A	C12A	C9A	-176.33(15)
C10	N11	C2	O3	138.63(19)	C11A	C6A	C7A	C8A	-55.4(2)
C10	N11	C2	C1	12.4(3)	C12A	C1A	C2A	O3A	-164.30(15)
C10	C9	C12	C1	-40.4(2)	C12A	C1A	C2A	N11A	-41.2(2)
C10	C9	C12	C8	86.9(2)	C12A	C1A	C11A	C5A	-176.30(16)
C11	C1	C2	O3	67.8(2)	C12A	C1A	C11A	C6A	-50.5(2)
C11	C1	C2	N11	-169.64(15)	C12A	C9A	C10A	O10A	-166.76(17)
C11	C1	C12	C8	52.9(2)	C12A	C9A	C10A	N11A	15.0(3)
C11	C1	C12	C9	-177.58(15)	C13A	C3A	C4A	C5A	147.95(18)
C11	C6	C7	C8	-57.9(2)	C14A	C6A	C7A	C8A	-179.47(18)
C12	C1	C2	O3	-166.19(15)	C14A	C6A	C11A	C1A	173.29(17)
C12	C1	C2	N11	-43.6(2)	C14A	C6A	C11A	C5A	-60.4(2)
C12	C1	C11	C5	-177.24(16)	C15A	C9A	C10A	O10A	-37.4(3)
C12	C1	C11	C6	-51.9(2)	C15A	C9A	C10A	N11A	144.37(18)
C12	C9	C10	O10	-172.36(17)	C15A	C9A	C12A	C1A	-172.47(17)
C12	C9	C10	N11	9.2(3)	C15A	C9A	C12A	C8A	-45.7(2)
C13	C3	C4	C5	145.7(2)	O20	C21	C22	O22	6.4(3)
C14	C6	C7	C8	177.41(17)	O20	C21	C22	C23	-116.8(3)
C14	C6	C11	C1	177.51(17)	O20	C21	C22	C23A	-108.1(17)
C14	C6	C11	C5	-56.6(2)	O21	C21	C22	O22	-171.56(19)
C15	C9	C10	O10	-43.4(2)	O21	C21	C22	C23	65.3(3)
C15	C9	C10	N11	138.19(19)	O21	C21	C22	C23A	74.0(17)
C15	C9	C12	C1	-167.48(17)	O22	C22	C23	C24	52.5(4)
C15	C9	C12	C8	-40.2(2)	O22A	C23A	C24	O23	-33(6)
O1A	O2A	C3A	O3A	-75.53(16)	O22A	C23A	C24	O24	140(3)
O1A	O2A	C3A	C4A	45.96(19)	C21	C22	C23	C24	174.8(2)
O1A	O2A	C3A	C13A	170.18(14)	C21	C22	C23A	O22A	53(3)
O1A	C1A	C2A	O3A	-49.4(2)	C21	C22	C23A	C24	-176.7(19)
O1A	C1A	C2A	N11A	73.75(19)	C22	C23	C24	O23	-141.8(2)
O1A	C1A	C11A	C5A	70.47(19)	C22	C23	C24	O24	38.3(5)
O1A	C1A	C11A	C6A	-163.73(15)	C22	C23A	C24	O23	-151.3(19)
O1A	C1A	C12A	C8A	168.88(15)	C22	C23A	C24	O24	22(4)

Table S1.7.8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:D-Mal 7.

Atom	*x*	*y*	*z*	U(eq)
H11	8190(30)	5757(17)	4539(16)	43(8)
H2	6359	5624	3794	24
H4A	7644	7061	2067	43
H4B	8028	6260	1772	43
H5A	6244	5726	2324	37
H5B	5791	6382	1810	37
H6	4582	5653	3219	30
H7A	2807	6195	3800	32
H7B	3259	7001	3543	32

H8A	4675	6075	4517	29
H8B	3900	6804	4748	29
H9	6960	7656	4729	26
H11A	5193	7117	2723	28
H12	5256	7545	4042	24
H13A	10342	6191	3132	62
H13B	10216	6585	2366	62
H13C	9892	5722	2448	62
H14A	2663	5768	2549	48
H14B	3883	5803	2030	48
H14C	3140	6548	2240	48
H15A	5317	6888	5698	49
H15B	5132	7737	5470	49
H15C	6372	7491	5917	49
H11B	6020(30)	4301(14)	4716(14)	27(6)
H2A	7662	4431	3843	23
H4AA	6039	3226	2052	30
H4AB	5678	4068	1880	30
H5AA	7572	4485	2406	30
H5AB	7899	3894	1797	30
H6A	9422	4413	3154	31
H7AA	10634	2999	3348	34
H7AB	11176	3769	3645	34
H8AA	9405	3870	4438	32
H8AB	10159	3110	4585	32
H9A	7005	2331	4578	27
H11C	8540	3027	2587	27
H12A	8683	2464	3858	26
H13D	3549	3984	3331	43
H13E	3549	3645	2538	43
H13F	3907	4498	2661	43
H14D	10630	3502	2090	50
H14E	11204	4264	2390	50
H14F	9919	4268	1921	50
H15D	8891	2830	5570	46
H15E	8903	2029	5202	46
H15F	7769	2251	5738	46
H21	-440(30)	6146(16)	5575(16)	42(8)
H22	1520(40)	4730(20)	4265(19)	49(10)
H22A	1317	4175	5265	53
H23	4850(30)	3802(17)	5819(16)	48(8)
H22C	2179	4939	4638	33
H22B	2593	5720	4973	33
H23A	2509	5274	6121	41
H23B	1919	4489	5865	41
H23C	2468	5047	6147	29

Table S1.7.9 Atomic Occupancy for 11-Aza:D-Mal 7.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O22	0.9	H22	0.9	O22A	0.1
H22A	0.1	H22C	0.1	C23	0.9
H23A	0.9	H23B	0.9	C23A	0.1
H23C	0.1				

Experimental

Single crystals of $C_{34}H_{52}N_2O_{13}$ **11-Aza:D-Mal 7** were grown at room temperature by evaporation of a ethyl acetate solution. A suitable crystal was selected and mounted in Paratone with a cryo-loop on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector. The crystal was kept at 99.97(10) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst., 40, 786-790; Palatinus, L. & van der Lee, A. (2008). J. Appl. Cryst. 41, 975-984; Palatinus, L., Prathapa, S. J. & van Smaalen, S. (2012). J. Appl. Cryst. 45, 575-580.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza:D-Mal 7

Crystal Data for $C_{34}H_{52}N_2O_{13}$ (M =696.77 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.43733(12) Å, b = 18.04445(19) Å, c = 18.6345(2) Å, V = 3509.55(7) Å^3, Z = 4, T = 99.97(10) K, μ(CuKα) = 0.842 mm^{-1},*Dcalc* = 1.319 g/cm^3, 19371 reflections measured (6.818° ≤ 2Θ ≤ 135°), 6284 unique (R_{int} = 0.0215, R_{sigma} = 0.0219) which were used in all calculations. The final R_1 was 0.0284 (I > 2σ(I)) and wR_2 was 0.0725 (all data).

Refinement model description

Number of restraints - 26, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 O22A-C23
 1.38 with sigma of 0.02
 O22A-C23A
 1.4 with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
Uanis(C23) ≈ Ueq: with sigma of 0.02 and sigma for terminal atoms of 0.003
4. Rigid body (RIGU) restrains
 O22A, C22, C23A, C24
 with sigma for 1-2 distances of 0.003 and sigma for 1-3 distances of 0.001
5. Others
 Fixed Sof: O22(0.9) H22(0.9) O22A(0.1) H22A(0.1) H22C(0.1) C23(0.9) H23A(0.9)
 H23B(0.9) C23A(0.1) H23C(0.1)
6.a Riding coordinates:
 C22(H22C,H22B), C23(H23A,H23B)
6.b Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12), C2A(H2A), C6A(H6A), C9A(H9A),
 C11A(H11C), C12A(H12A), C23A(H23C)
6.c Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B), C4A(H4AA,H4AB), C5A(H5AA,
 H5AB), C7A(H7AA,H7AB), C8A(H8AA,H8AB)
6.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C), C13A(H13D,H13E,
 H13F), C14A(H14D,H14E,H14F), C15A(H15D,H15E,H15F)
6.e Idealised tetrahedral OH refined as rotating group:
 O22A(H22A)
```

Table S1.8.1 Crystal data and structure refinement for 11-Aza:Pim 8.

Identification code	madiha38CuLT
Empirical formula	$C_{37}H_{58}N_2O_{12}$
Formula weight	722.85
Temperature/K	99.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	17.5836(7)
b/Å	10.3594(4)
c/Å	9.9524(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1812.89(12)
Z	2
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.812
F(000)	780.0
Crystal size/mm^3	0.4 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.886 to 134.972
Index ranges	$-19 \leq h \leq 21$, $-12 \leq k \leq 10$, $-11 \leq l \leq 11$
Reflections collected	16856
Independent reflections	3259 [R_{int} = 0.0422, R_{sigma} = 0.0287]
Data/restraints/parameters	3259/55/289
Completeness to theta = 66.5°	99.6%
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0715
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0729
Largest diff. peak/hole / e Å^{-3}	0.12/-0.17
Flack parameter	0.08(10)

Table S1.8.2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11-Aza:Pim 8.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7347.7(8)	1947.5(15)	1885.7(15)	28.4(3)
O2	7059.8(9)	617.9(15)	1748.9(16)	32.0(4)
O3	5786.3(9)	1162.9(16)	1780.4(17)	34.8(4)
O10	6627(1)	1328.3(16)	6085.7(15)	37.0(4)
N11	6127.0(11)	1536.0(19)	4016(2)	30.0(4)
C1	6742.5(12)	2846(2)	2242(2)	24.9(4)
C2	6030.7(13)	2121(2)	2693(2)	29.1(5)
C3	6389.8(15)	655(2)	961(2)	34.8(5)
C4	6491.1(18)	1474(3)	-307(2)	42.1(6)
C5	6226.3(17)	2874(3)	-167(3)	43.2(6)
C6	6111.3(15)	4879(2)	1295(3)	40.6(6)
C7	6433.6(14)	5628(2)	2494(3)	36.1(6)
C8	6552.5(12)	4786(2)	3725(2)	30.5(5)
C9	7266.0(12)	2780(2)	4599(2)	24.7(4)
C10	6641.4(13)	1839(2)	4954(2)	27.4(5)
C11	6590.1(14)	3666(2)	977(2)	33.1(5)
C12	7072.2(11)	3647(2)	3392(2)	24.2(4)
C13	6195.5(17)	-747(3)	699(3)	44.3(6)
C14	6043.7(19)	5771(3)	86(3)	58.6(9)
C15	7524.2(13)	3527(2)	5846(2)	31.8(5)
O20	5502(11)	8646(14)	4944(14)	31.8(19)
O21	5880(12)	9350(19)	6963(16)	25.0(19)
O22	4025(12)	653(18)	7141(16)	24(2)
O23	4441(12)	1147(15)	5088(14)	35(2)
C21	5563(13)	8470(14)	6140(20)	28(3)
C22	5523(3)	7187(5)	6887(5)	26.6(11)
C23	5072(6)	6163(10)	6122(15)	26(2)
C24	5176(2)	4836(5)	6736(4)	23.8(11)
C25	4703(6)	3759(9)	6117(14)	21(2)
C26	4825(3)	2490(5)	6877(5)	23.2(10)
C27	4357(12)	1391(13)	6258(16)	19(2)

Table S1.8.3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 11-Aza:Pim 8.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	31.3(8)	20.2(8)	33.6(8)	-0.3(7)	1.6(6)	1.8(6)
O2	43.8(8)	18.1(8)	33.9(8)	-2.1(6)	-2.3(7)	3.4(7)
O3	38.1(8)	22.8(8)	43.4(9)	-5.8(7)	-5.7(7)	-5.1(7)
O10	55.3(10)	26.1(9)	29.7(8)	-2.1(7)	8.5(7)	-16.2(8)
N11	32(1)	21.2(10)	36.8(10)	-3.7(8)	6.0(8)	-9.4(8)
C1	26(1)	17.5(10)	31.2(10)	-0.5(9)	-1.7(8)	1.0(9)
C2	28.8(11)	19.2(11)	39.3(12)	-4.6(9)	-2.6(9)	-2.0(9)
C3	45.7(13)	24.0(12)	34.7(12)	-4.4(10)	-6.5(10)	0.9(10)
C4	65.0(17)	31.2(14)	30.2(12)	0.5(10)	-10.4(11)	-3.8(13)
C5	59.3(16)	28.0(13)	42.4(14)	5.5(11)	-22.1(12)	-6.9(12)
C6	36.4(12)	20.8(12)	64.7(17)	5.9(12)	-22.5(12)	-3.2(10)
C7	32.9(12)	17.7(11)	57.8(16)	1.2(11)	-11.2(11)	0.9(9)
C8	27.1(10)	18.4(11)	45.9(13)	-3.4(10)	-1.7(10)	-0.7(8)
C9	25.4(10)	19.1(11)	29.7(11)	2.0(9)	2.4(8)	-0.7(8)
C10	34.7(11)	18(1)	29.6(11)	-6.1(9)	5.8(9)	-2.4(8)
C11	39.4(12)	22.8(12)	37.0(12)	5.7(11)	-12.9(10)	-4.5(10)
C12	22.8(9)	17.7(10)	32.2(10)	0.4(9)	-1.6(8)	-1.0(8)
C13	67.0(17)	24.6(13)	41.3(14)	-5.8(11)	-6.0(13)	-1.6(12)
C14	72.7(19)	25.3(14)	78(2)	11.4(14)	-49.4(18)	-6.7(13)
C15	36.6(12)	26.0(12)	32.9(11)	3.7(10)	-3.8(10)	-7.5(10)
O20	41(4)	28(4)	26(3)	3(3)	-8(2)	-10(3)
O21	31(5)	22(3)	22(4)	6(2)	-5(3)	-5(2)
O22	30(4)	20(3)	21(3)	3(2)	10(2)	-10(3)
O23	49(4)	36(5)	19(3)	-1(2)	12(2)	-24(3)
C21	20(4)	30(5)	34(4)	-5(3)	-9(3)	-10(3)
C22	32(3)	23(2)	25(2)	0.9(17)	-1(2)	-4(2)
C23	28(6)	19(3)	30(3)	-5(2)	1(4)	-5(3)
C24	30(3)	20(3)	22.0(17)	0.2(18)	-1.0(16)	-3(2)
C25	24(5)	16(3)	22(3)	-4(2)	-3(4)	-5(3)
C26	30(3)	20(2)	20(2)	2.5(17)	0(2)	-4.9(19)
C27	23(5)	19(4)	16(3)	2(3)	2(3)	-13(3)

Table S1.8.4 Bond Lengths for 11-Aza:Pim 8.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	O2	1.474(2)	C6	C14	1.522(4)
O1	C1	1.457(3)	C7	C8	1.519(3)
O2	C3	1.416(3)	C8	C12	1.529(3)
O3	C2	1.412(3)	C9	C10	1.511(3)
O3	C3	1.438(3)	C9	C12	1.538(3)
O10	C10	1.245(3)	C9	C15	1.531(3)
N11	C2	1.459(3)	O20	C21	1.213(19)
N11	C10	1.337(3)	O21	C21	1.344(16)
C1	C2	1.527(3)	O22	C27	1.303(15)
C1	C11	1.543(3)	O23	C27	1.200(17)
C1	C12	1.528(3)	C21	C22	1.523(14)
C3	C4	1.531(3)	C22	C23	1.528(11)
C3	C13	1.515(3)	C23	C24	1.515(12)
C4	C5	1.530(4)	C24	C25	1.522(10)
C5	C11	1.542(3)	C25	C26	1.531(12)
C6	C7	1.532(3)	C26	C27	1.534(12)
C6	C11	1.545(4)			

Table S1.8.5 Bond Angles for 11-Aza:Pim 8.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	O2	111.62(14)	C7	C8	C12	110.51(19)
C3	O2	O1	108.14(16)	C10	C9	C12	113.47(18)
C2	O3	C3	113.40(17)	C10	C9	C15	110.63(18)
C10	N11	C2	127.65(19)	C15	C9	C12	113.82(17)
O1	C1	C2	110.85(17)	O10	C10	N11	121.2(2)
O1	C1	C11	106.27(18)	O10	C10	C9	120.0(2)
O1	C1	C12	104.59(16)	N11	C10	C9	118.7(2)
C2	C1	C11	111.63(18)	C1	C11	C6	112.0(2)
C2	C1	C12	110.97(18)	C5	C11	C1	112.42(19)
C12	C1	C11	112.20(17)	C5	C11	C6	111.0(2)
O3	C2	N11	108.90(18)	C1	C12	C8	110.79(17)
O3	C2	C1	113.95(18)	C1	C12	C9	110.62(17)
N11	C2	C1	111.98(18)	C8	C12	C9	114.42(18)
O2	C3	O3	108.05(18)	O20	C21	O21	122.1(13)
O2	C3	C4	112.0(2)	O20	C21	C22	127.3(13)
O2	C3	C13	104.9(2)	O21	C21	C22	108.4(14)
O3	C3	C4	110.5(2)	C21	C22	C23	112.8(9)
O3	C3	C13	106.4(2)	C24	C23	C22	111.5(9)
C13	C3	C4	114.6(2)	C23	C24	C25	115.8(5)
C5	C4	C3	114.5(2)	C24	C25	C26	110.7(8)
C4	C5	C11	116.4(2)	C25	C26	C27	111.3(9)
C7	C6	C11	111.71(19)	O22	C27	C26	113.8(12)
C14	C6	C7	109.7(2)	O23	C27	O22	125.9(13)
C14	C6	C11	111.9(2)	O23	C27	C26	118.6(12)
C8	C7	C6	112.87(19)				

Table S1.8.6 Hydrogen Bonds for 11-Aza:Pim 8.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N11	H11	O20[1]	0.86(3)	2.55(4)	3.320(14)	150(3)
N11	H11	O23[2]	0.86(3)	2.38(4)	3.141(15)	149(3)
O21	H21	O10[3]	0.84	1.81	2.586(17)	153.0
O22	H22	O10[2]	0.84	1.74	2.575(17)	174.6

[1]+X,-1+Y,+Z; [2]1-X,-Y,+Z; [3]+X,1+Y,+Z

Table S1.8.7 Torsion Angles for 11-Aza:Pim 8.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	O2	C3	O3	-74.8(2)	C7	C8	C12	C9	176.52(18)
O1	O2	C3	C4	47.2(2)	C10	N11	C2	O3	146.1(2)
O1	O2	C3	C13	172.06(18)	C10	N11	C2	C1	19.2(3)
O1	C1	C2	O3	-51.9(2)	C10	C9	C12	C1	-46.4(2)
O1	C1	C2	N11	72.3(2)	C10	C9	C12	C8	79.5(2)
O1	C1	C11	C5	68.6(2)	C11	C1	C2	O3	66.4(2)
O1	C1	C11	C6	-165.57(18)	C11	C1	C2	N11	-169.44(18)
O1	C1	C12	C8	170.60(17)	C11	C1	C12	C8	55.8(2)
O1	C1	C12	C9	-61.4(2)	C11	C1	C12	C9	-176.20(18)
O2	O1	C1	C2	13.4(2)	C11	C6	C7	C8	-52.6(3)
O2	O1	C1	C11	-108.07(17)	C12	C1	C2	O3	-167.64(18)
O2	O1	C1	C12	133.07(16)	C12	C1	C2	N11	-43.5(2)
O2	C3	C4	C5	-95.0(3)	C12	C1	C11	C5	-177.6(2)
O3	C3	C4	C5	25.6(3)	C12	C1	C11	C6	-51.8(2)
C1	O1	O2	C3	46.8(2)	C12	C9	C10	O10	-161.1(2)
C2	O3	C3	O2	35.2(3)	C12	C9	C10	N11	21.3(3)
C2	O3	C3	C4	-87.7(2)	C13	C3	C4	C5	145.7(2)
C2	O3	C3	C13	147.3(2)	C14	C6	C7	C8	-177.3(2)
C2	N11	C10	O10	174.6(2)	C14	C6	C11	C1	173.0(2)
C2	N11	C10	C9	-7.9(3)	C14	C6	C11	C5	-60.4(3)
C2	C1	C11	C5	-52.3(3)	C15	C9	C10	O10	-31.7(3)
C2	C1	C11	C6	73.5(2)	C15	C9	C10	N11	150.7(2)
C2	C1	C12	C8	-69.8(2)	C15	C9	C12	C1	-174.14(17)
C2	C1	C12	C9	58.2(2)	C15	C9	C12	C8	-48.2(2)
C3	O3	C2	N11	-99.7(2)	O20	C21	C22	C23	-25(3)
C3	O3	C2	C1	26.1(3)	O21	C21	C22	C23	172.0(14)
C3	C4	C5	C11	56.4(3)	C21	C22	C23	C24	168.4(12)
C4	C5	C11	C1	-35.8(3)	C22	C23	C24	C25	175.5(9)
C4	C5	C11	C6	-162.2(2)	C23	C24	C25	C26	-176.7(9)
C6	C7	C8	C12	56.6(3)	C24	C25	C26	C27	-179.5(10)
C7	C6	C11	C1	49.5(3)	C25	C26	C27	O22	-137.4(15)
C7	C6	C11	C5	176.0(2)	C25	C26	C27	O23	56(2)
C7	C8	C12	C1	-57.6(2)					

Table S1.8.8 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 11-Aza:Pim 8.

Atom	*x*	*y*	*z*	U(eq)
H11	5802(19)	950(30)	4230(30)	56(10)
H2	5611	2769	2769	35
H4A	7036	1472	-558	51
H4B	6205	1065	-1050	51
H5A	5668	2872	-32	52

H5B	6329	3324	-1026	52
H6	5587	4586	1540	49
H7A	6926	6018	2233	43
H7B	6081	6339	2726	43
H8A	6055	4460	4046	37
H8B	6783	5306	4454	37
H9	7711	2245	4316	30
H11A	7095	3974	643	40
H12	7563	4018	3062	29
H13A	6549	-1102	32	66
H13B	5674	-808	357	66
H13C	6238	-1237	1537	66
H14A	6550	6079	-172	88
H14B	5721	6509	317	88
H14C	5816	5298	-667	88
H15A	7092	4004	6221	48
H15B	7927	4135	5596	48
H15C	7719	2921	6519	48
H21	5999	10008	6517	37
H22	3816	29	6749	35
H22A	5284	7326	7776	32
H22B	6046	6866	7041	32
H23A	4526	6393	6133	31
H23B	5242	6145	5174	31
H24A	5051	4890	7704	29
H24B	5719	4596	6663	29
H25A	4849	3644	5164	25
H25B	4158	3997	6148	25
H26A	4675	2606	7828	28
H26B	5371	2259	6854	28

Table S1.8.9 Atomic Occupancy for 11-Aza:Pim 8.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O20	0.5	O21	0.5	H21	0.5
O22	0.5	H22	0.5	O23	0.5
C21	0.5	C22	0.5	H22A	0.5
H22B	0.5	C23	0.5	H23A	0.5
H23B	0.5	C24	0.5	H24A	0.5
H24B	0.5	C25	0.5	H25A	0.5
H25B	0.5	C26	0.5	H26A	0.5
H26B	0.5	C27	0.5		

Experimental

Single crystals of $C_{37}H_{58}N_2O_{12}$ **11-Aza:Pim** were grown at room temperature by evaporation of a ethyl acetate solution. A suitable crystal was selected and mounted in Paratone with a cryo-loop on a SuperNova, Dual wavelength diffractometer, Cu Ka radiation Atlas detector. The crystal was kept at 99.99(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 11-Aza:Pim

Crystal Data for $C_{37}H_{58}N_2O_{12}$ (M =722.85 g/mol): orthorhombic, space group $P2_12_12$ (no. 18), a = 17.5836(7) Å, b = 10.3594(4) Å, c = 9.9524(3) Å, V = 1812.89(12) Å^3, Z = 2, T = 99.99(10) K, μ(CuKα) = 0.812 mm^{-1}, $Dcalc$ = 1.324 g/cm^3, 16856 reflections measured (8.886° ≤ 2Θ ≤ 134.972°), 3259 unique (R_{int} = 0.0422, R_{sigma} = 0.0287) which were used in all calculations. The final R_1 was 0.0312 (I > 2σ(I)) and wR_2 was 0.0729 (all data).

Refinement model description

Number of restraints - 55, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 C22-C21 ≈ C23-C22 ≈ C24-C23 ≈ C24-C25 ≈ C25-C26 ≈ C26-C27
 with sigma of 0.02
 C21-C23 ≈ C25-C27
 C22-C24 ≈ C23-C25
 C23-C25 ≈ C24-C26
 with sigma of 0.02
3. Rigid body (RIGU) restrains
 O22, O23, C26, C27
 O20, O21, C21, C22
 with sigma for 1-2 distances of 0.003 and sigma for 1-3 distances of 0.001
4. Others
 Fixed Sof: O20(0.5) O21(0.5) H21(0.5) O22(0.5) H22(0.5) O23(0.5) C21(0.5)
 C22(0.5) H22A(0.5) H22B(0.5) C23(0.5) H23A(0.5) H23B(0.5) C24(0.5) H24A(0.5)
 H24B(0.5) C25(0.5) H25A(0.5) H25B(0.5) C26(0.5) H26A(0.5) H26B(0.5) C27(0.5)
5.a Ternary CH refined with riding coordinates:
 C2(H2), C6(H6), C9(H9), C11(H11A), C12(H12)
5.b Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C8(H8A,H8B), C22(H22A,H22B), C23(H23A,
 H23B), C24(H24A,H24B), C25(H25A,H25B), C26(H26A,H26B)
5.c Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C15(H15A,H15B,H15C)
5.d Idealised tetrahedral OH refined as rotating group:
 O21(H21), O22(H22)
```

S2. Powder XRD from Liquid Assisted Grinding (LAG) experiments:

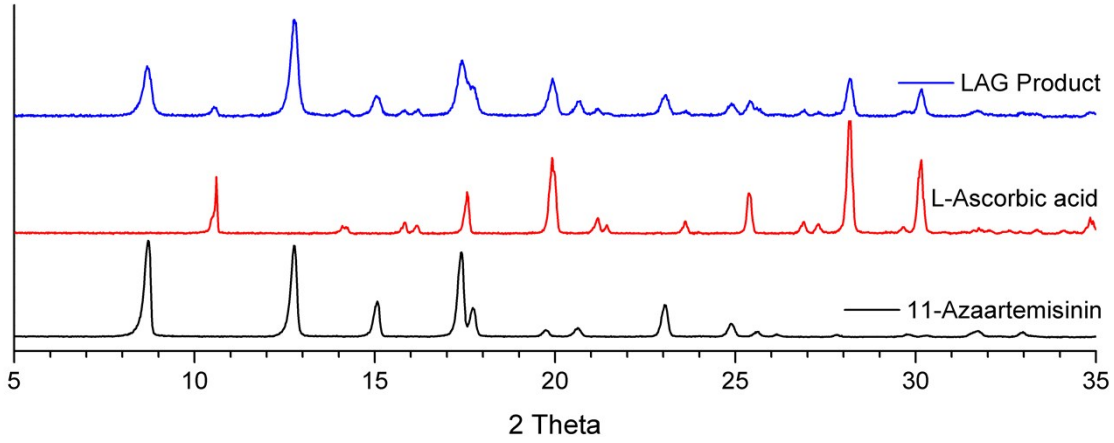


Figure S2.1: P-XRD patterns from LAG of 11-Azaartemisinin and L-Ascorbic acid.

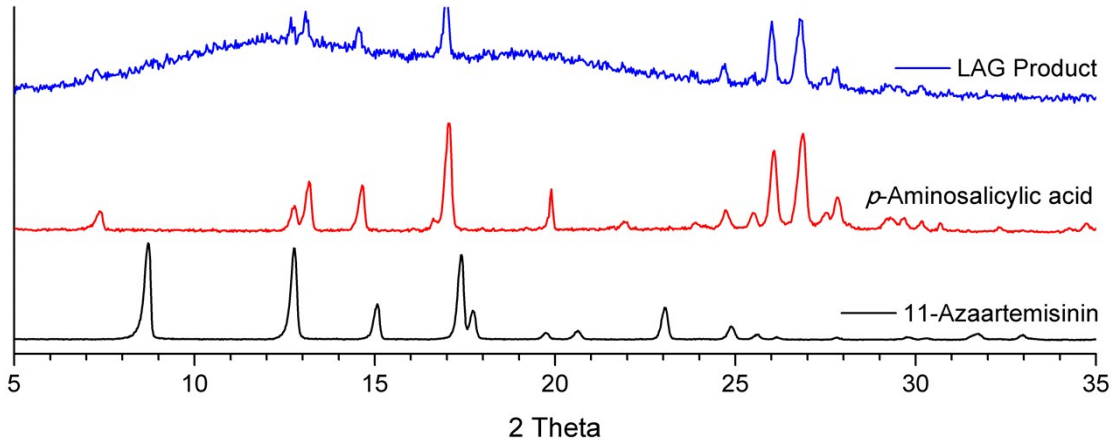


Figure S2.2: P-XRD patterns of from LAG of 11-Azaartemisinin and *p*-Aminosalicylic acid.

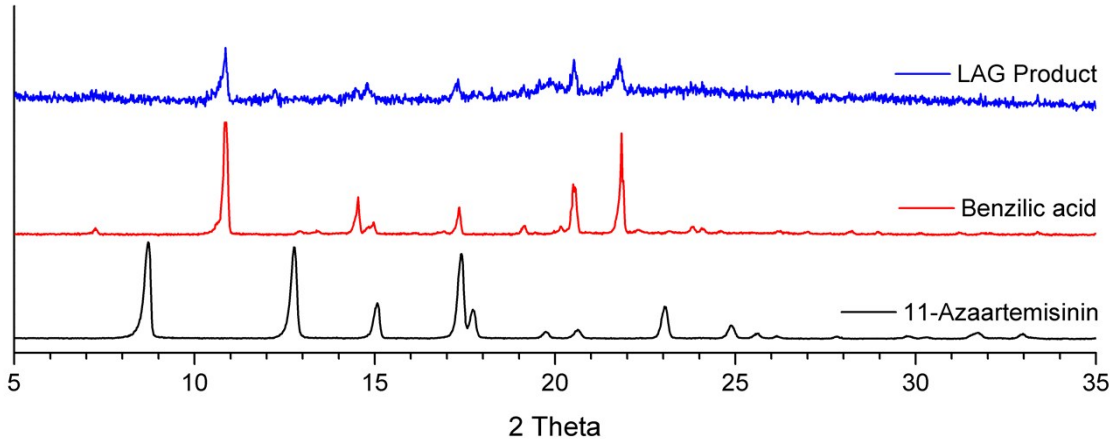


Figure S2.3: P-XRD patterns from LAG of 11-Azaartemisinin and Benzilic acid.

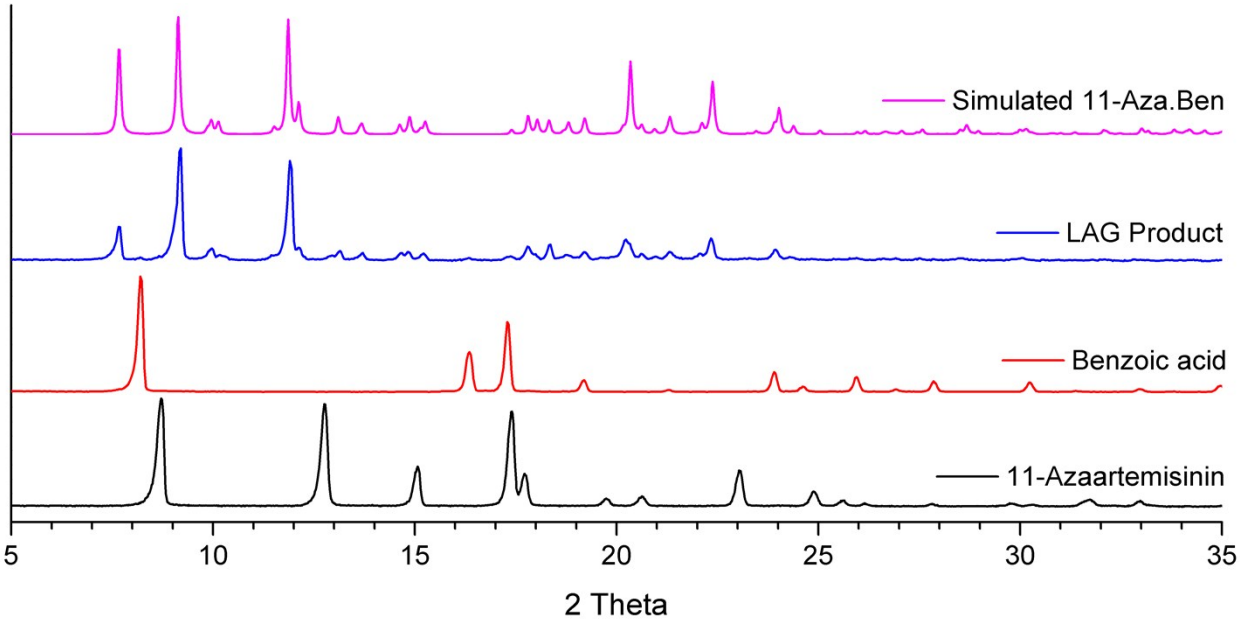


Figure S2.4: P-XRD patterns from LAG of 11-Azaartemisinin and Benzoic acid.

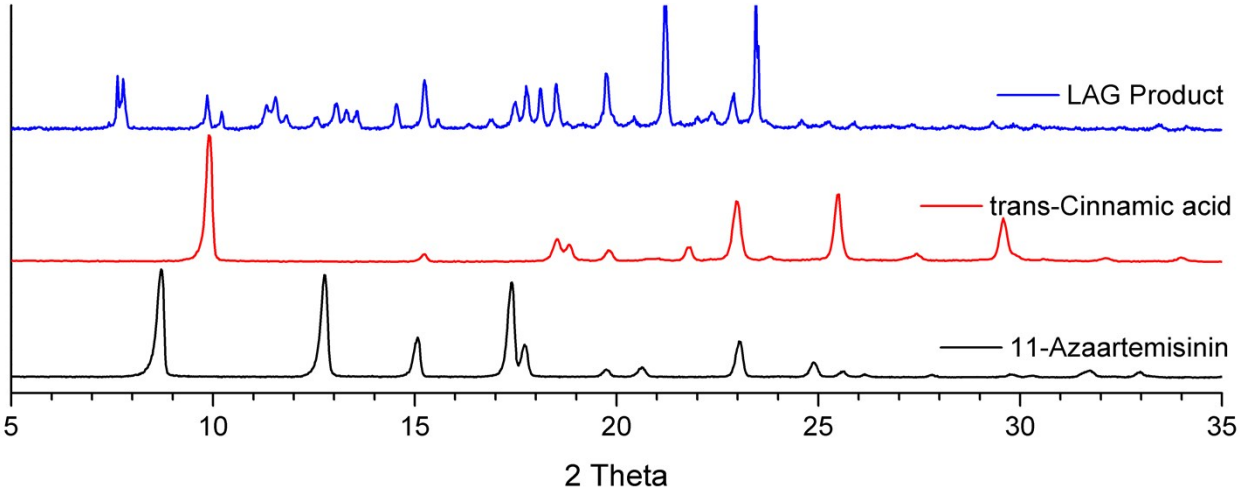


Figure S2.5: P-XRD patterns from LAG of 11-Azaartemisinin and *trans*-Cinnamic acid.

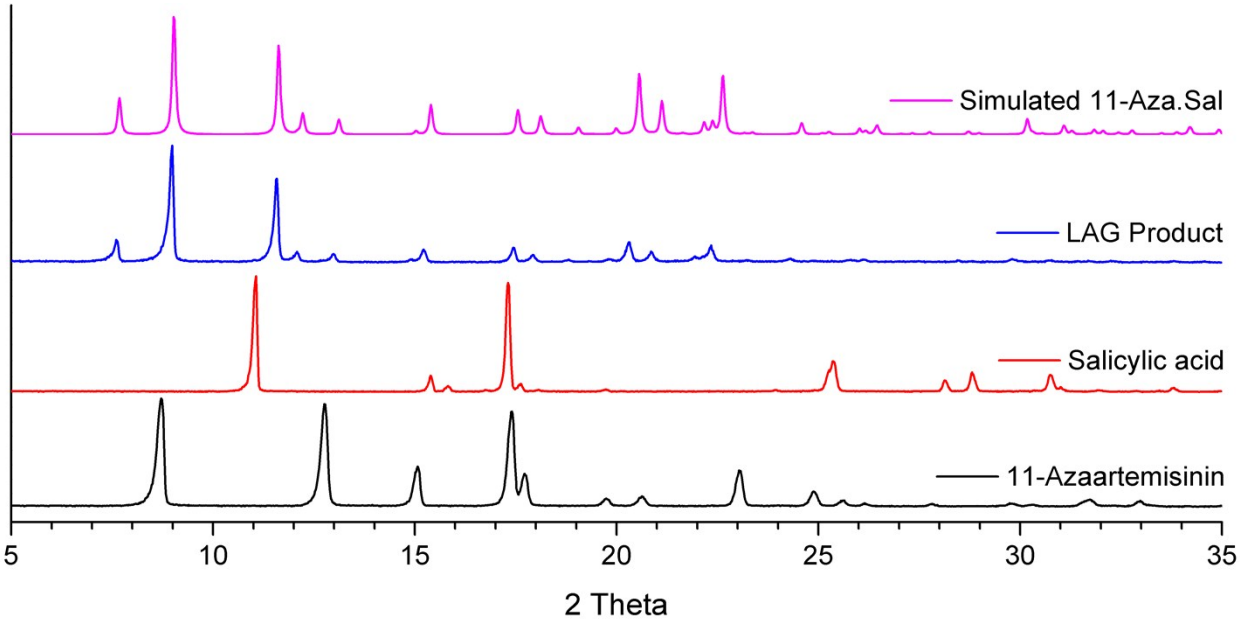


Figure S2.6: P-XRD patterns from LAG of 11-Azaartemisinin and Salicylic acid.

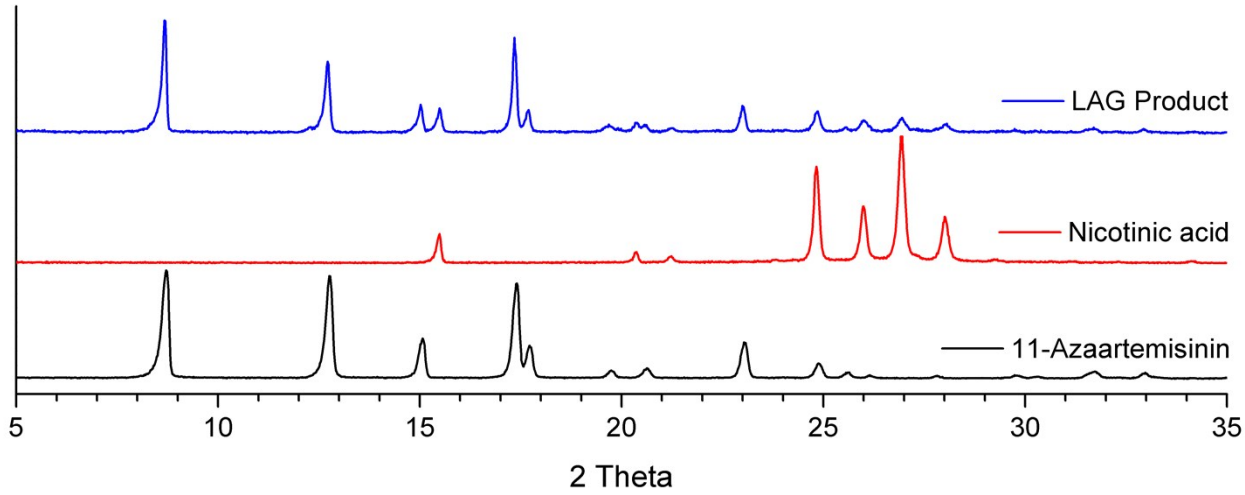


Figure S2.7: P-XRD patterns from LAG of 11-Azaartemisinin and Nicotinic acid.

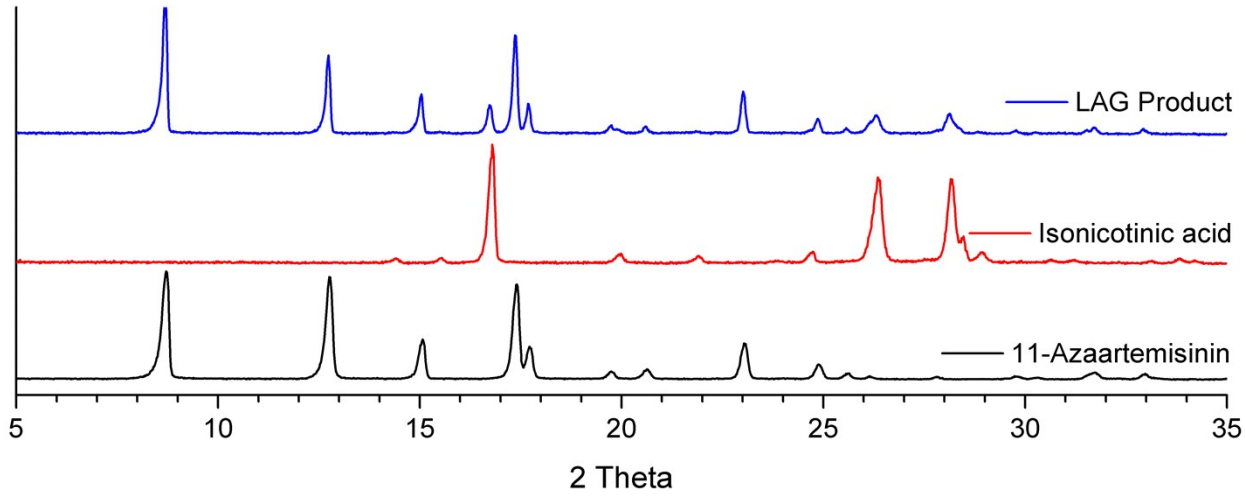


Figure S2.8: P-XRD patterns from LAG of 11-Azaartemisinin and Isonicotinic acid.

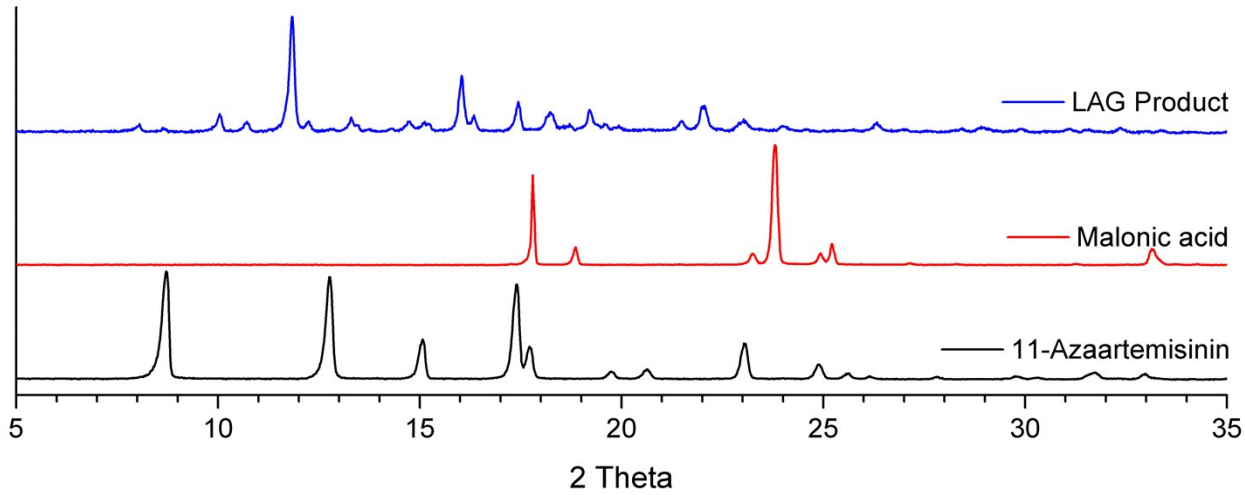


Figure S2.9: P-XRD patterns from LAG of 11-Azaartemisinin and Malonic acid.

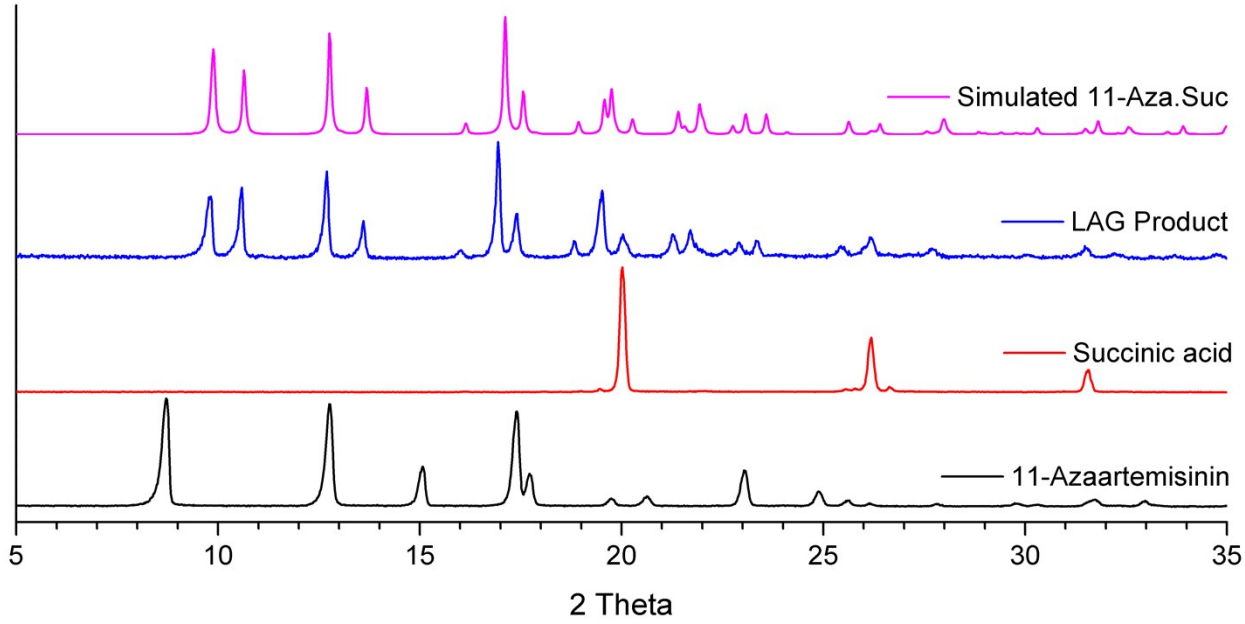


Figure S2.10: P-XRD patterns from LAG of 11-Azaartemisinin and Succinic acid.

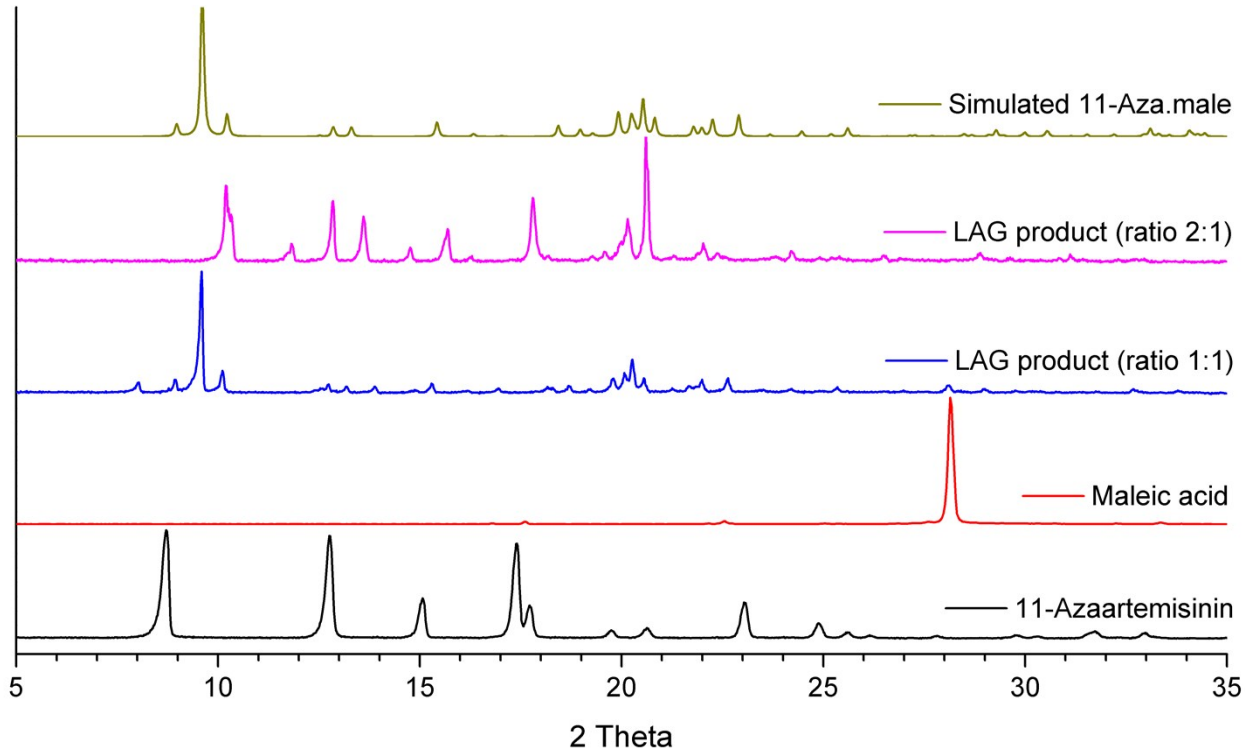


Figure S2.11: P-XRD patterns from LAG of 11-Azaartemisinin and Maleic acid.

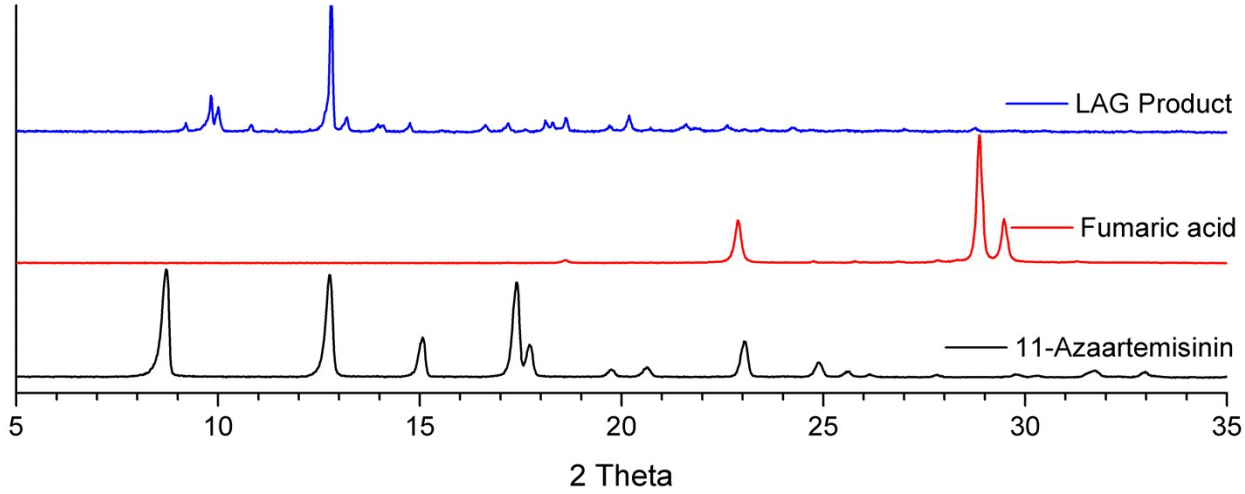


Figure S2.12: P-XRD patterns from LAG of 11-Azaartemisinin and Fumaric acid.

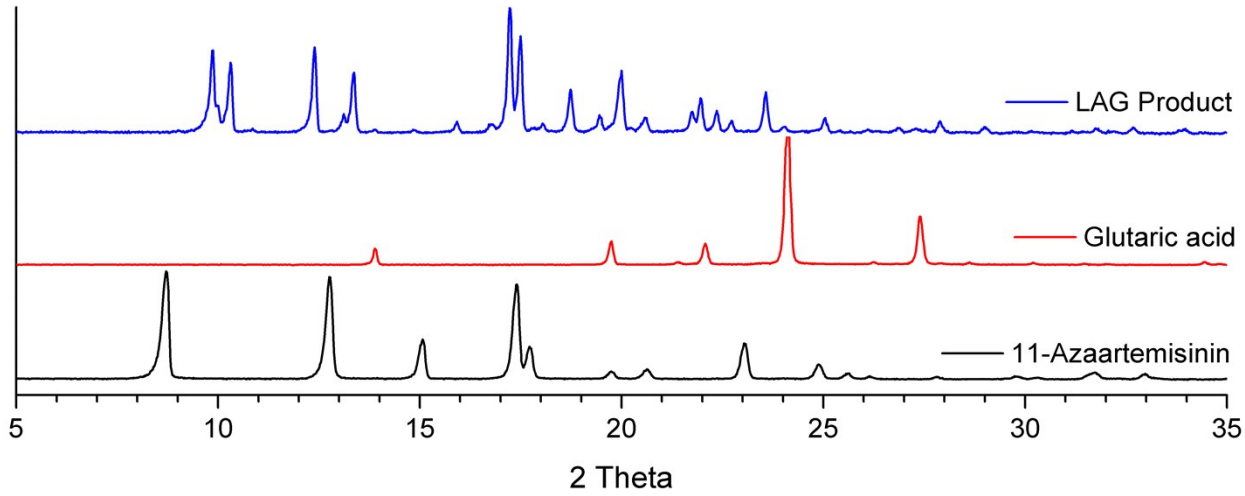


Figure S2.13: P-XRD patterns from LAG of 11-Azaartemisinin and Glutaric acid.

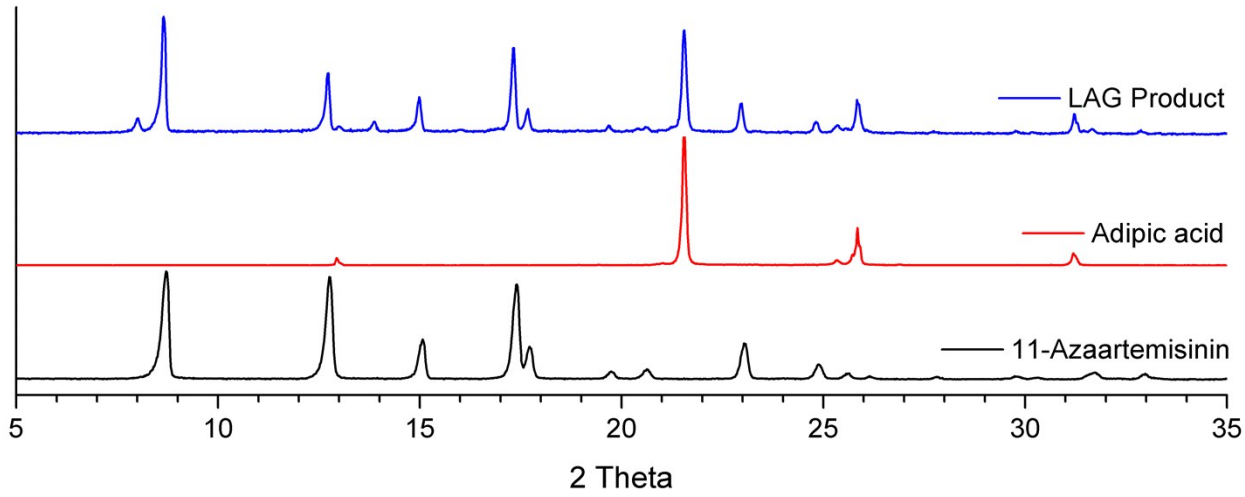


Figure S2.14: P-XRD patterns from LAG of 11-Azaartemisinin and Adipic acid.

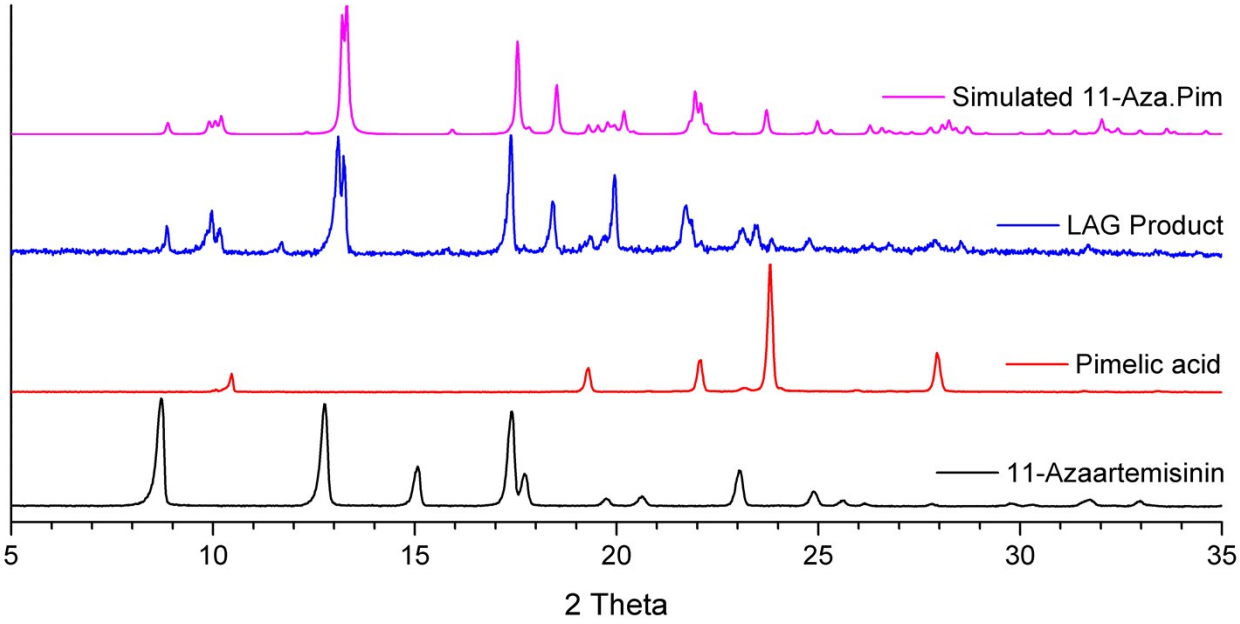


Figure S2.15: P-XRD patterns from LAG of 11-Azaartemisinin and Pimelic acid.

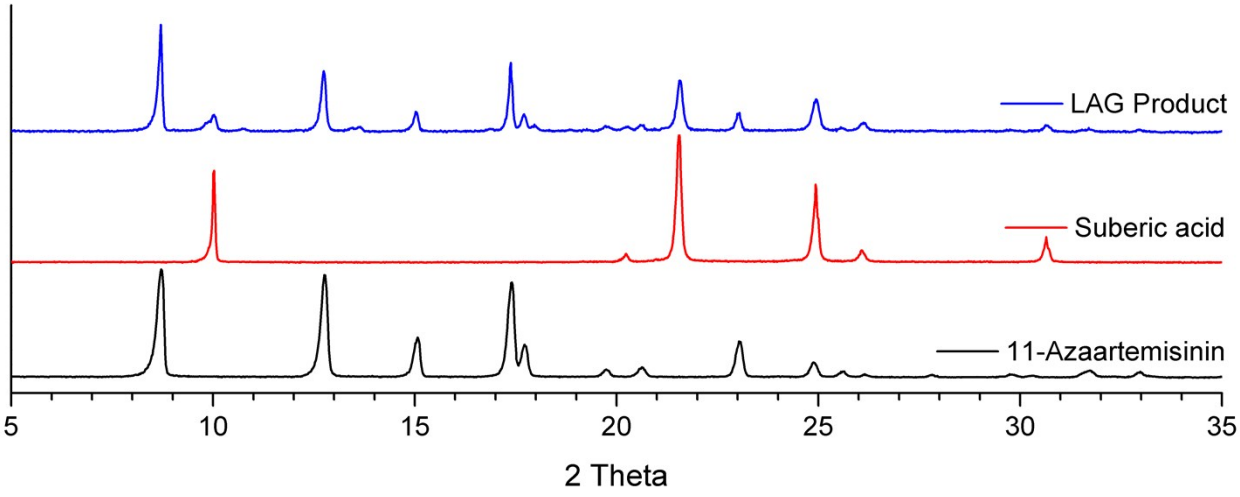


Figure S2.16: P-XRD patterns from LAG of 11-Azaartemisinin and Suberic acid.

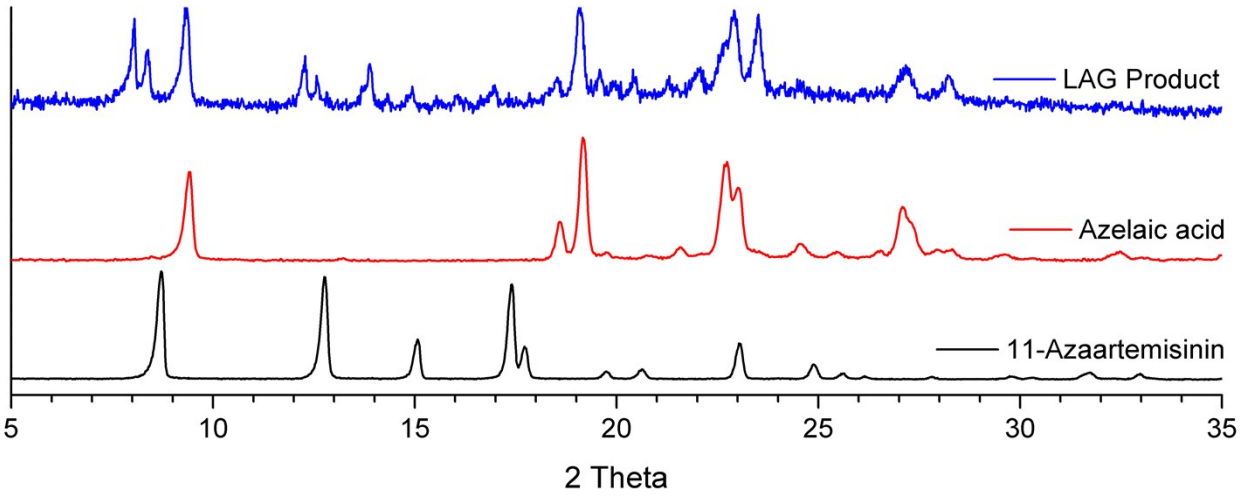


Figure S2.17: P-XRD patterns from LAG of 11-Azaartemisinin and Azelaic acid.

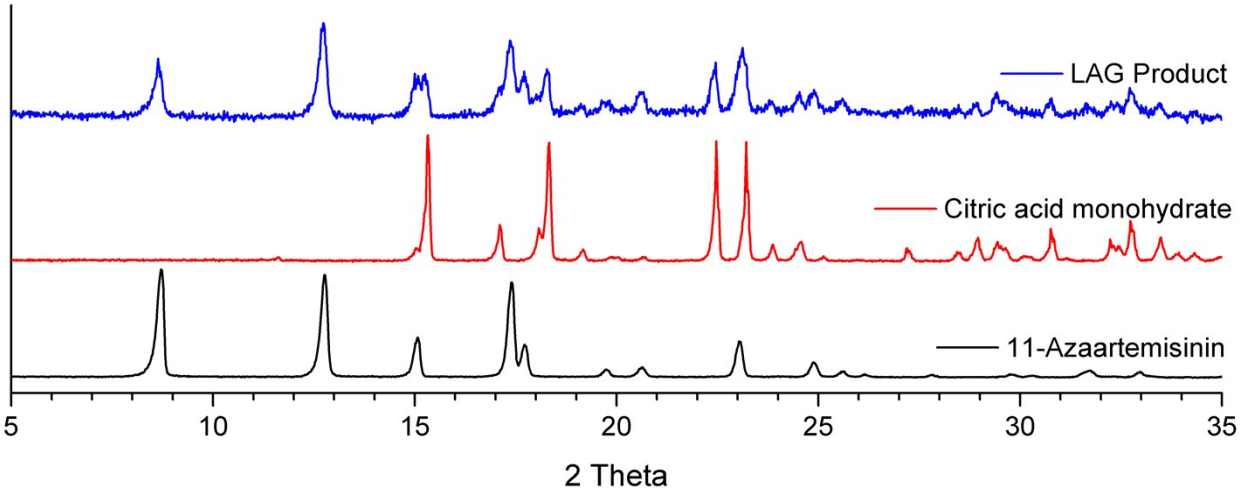


Figure S2.18: P-XRD patterns from LAG of 11-Azaartemisinin and Citric acid monohydrate.

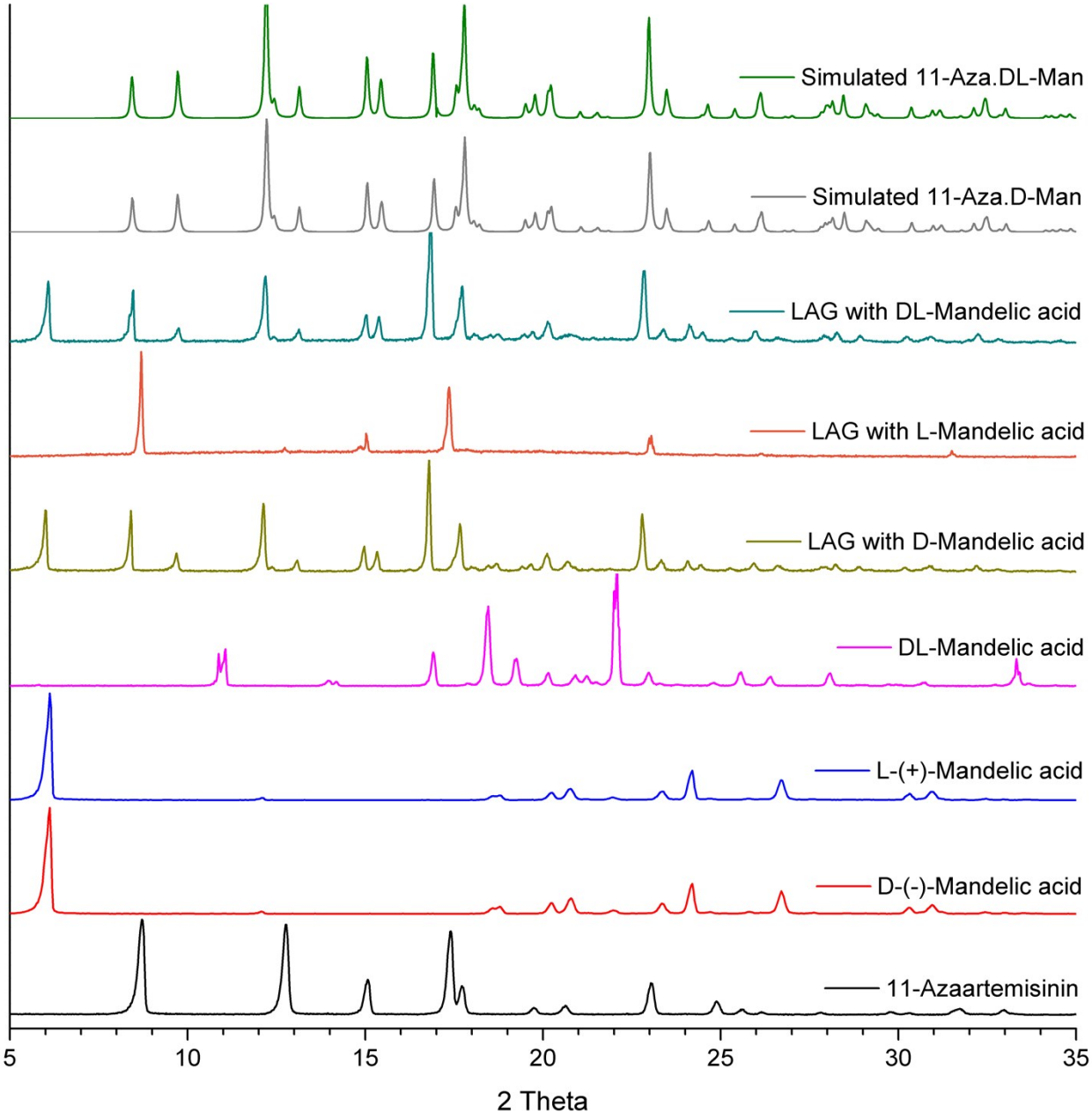


Figure S2.19: P-XRD patterns from LAG of 11-Azaartemisinin with D-(–)-Mandelic acid, L-(+)-Mandelic acid and DL-Mandelic acid.

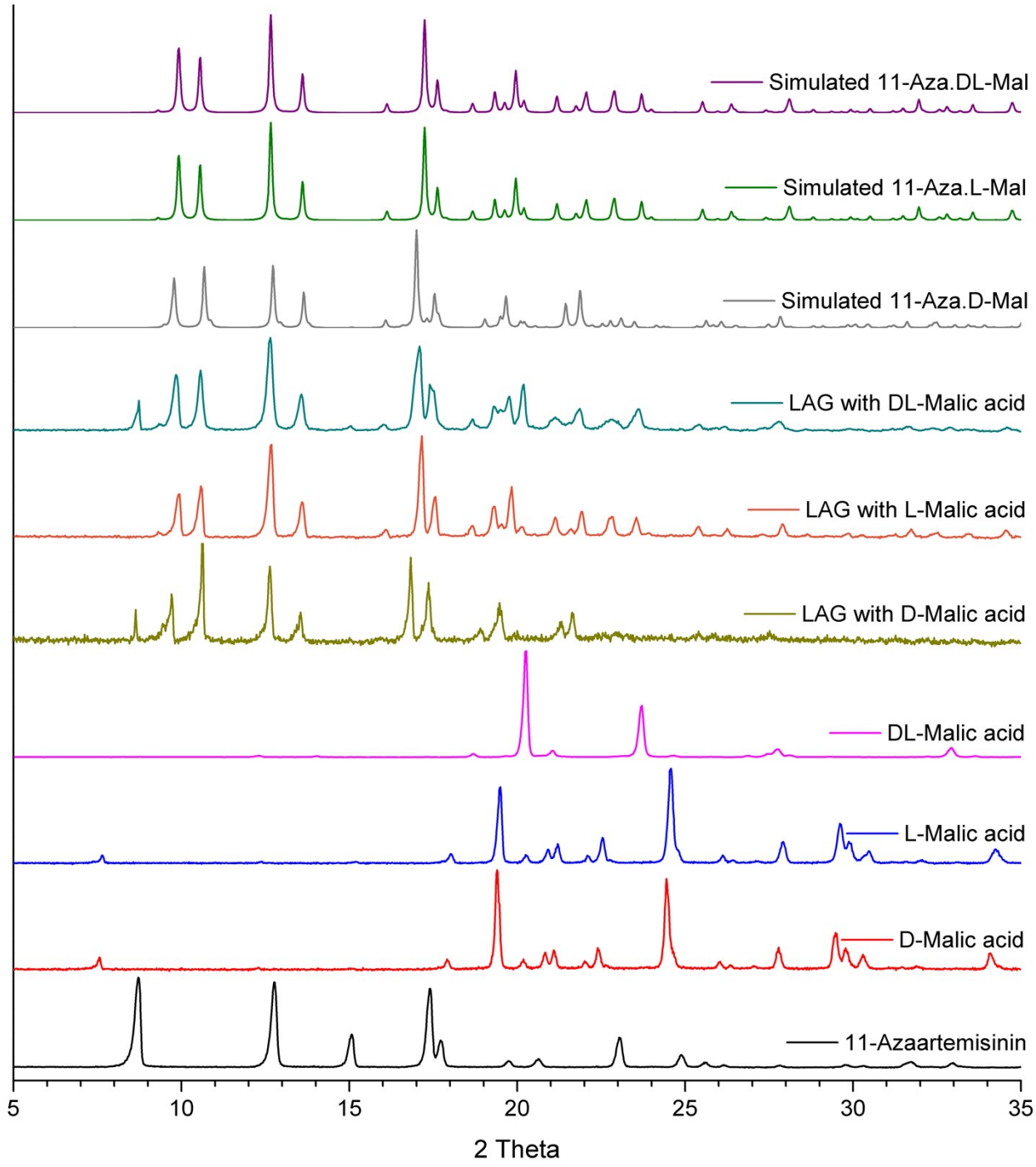


Figure S2.19: P-XRD patterns from LAG of 11-Azaartemisinin with D-(+)-Malic acid, L-(–)-Malic acid and DL-Malic acid.

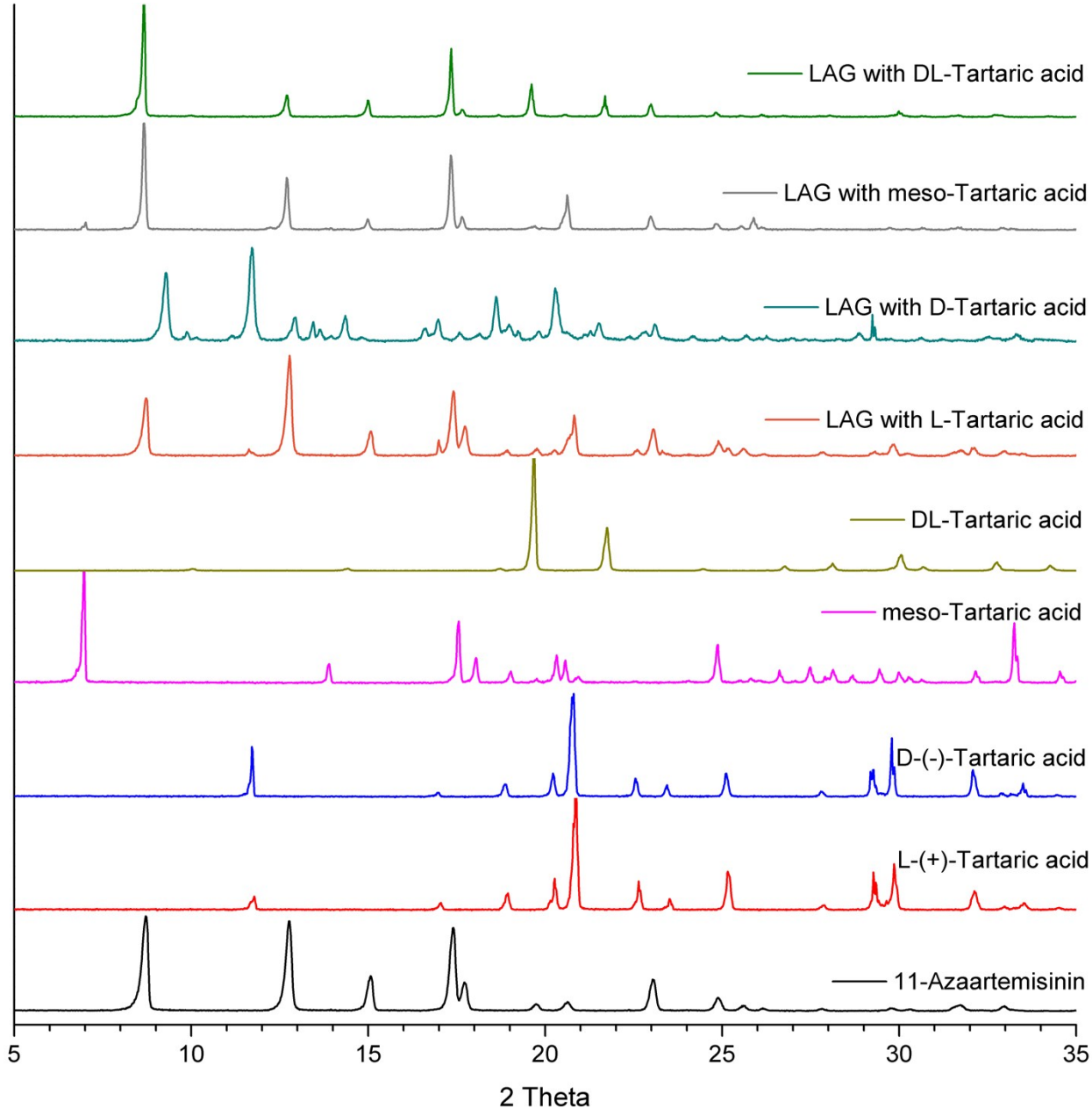


Figure S2.21: P-XRD patterns from LAG of 11-Azaartemisinin with L-(+)-Tartaric acid, D-(–)-Tartaric acid, *meso*-Tartaric acid monohydrate and DL-Tartaric acid.

S3. Differential Scanning Calorimetry (DSC) data

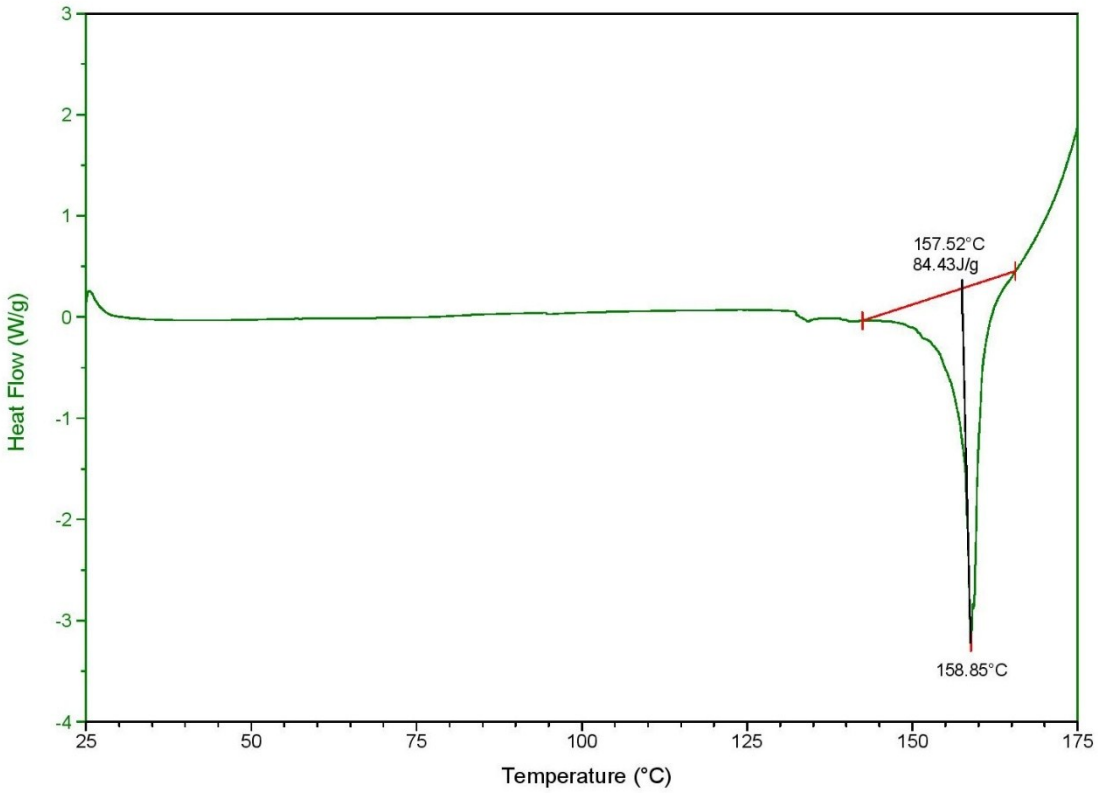


Figure S3.1: DSC thermogram for 11-Azaartemisinin (11-Aza) **1** heated at a rate of 10 °C min^{-1} under N_2.

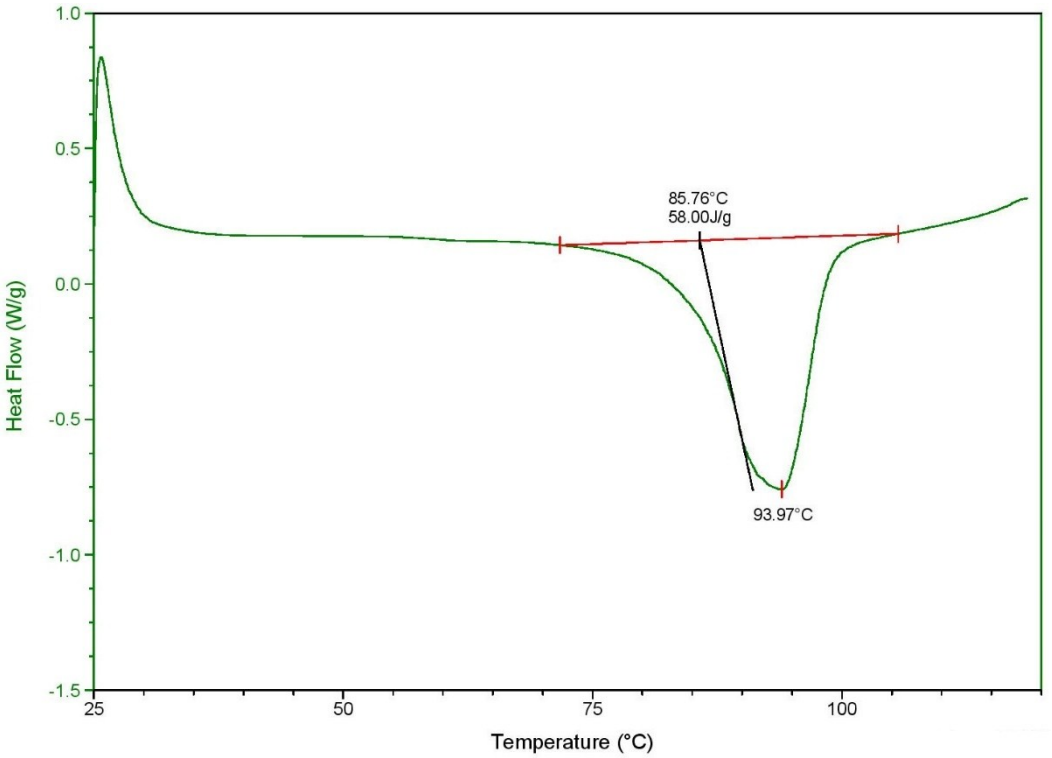


Figure S3.1: DSC thermogram for cocrystal of 11-Azaartemisinin and Benzoic acid, 11-Aza:Ben **2** heated at a rate of 10 °C min^{-1} under N_2.

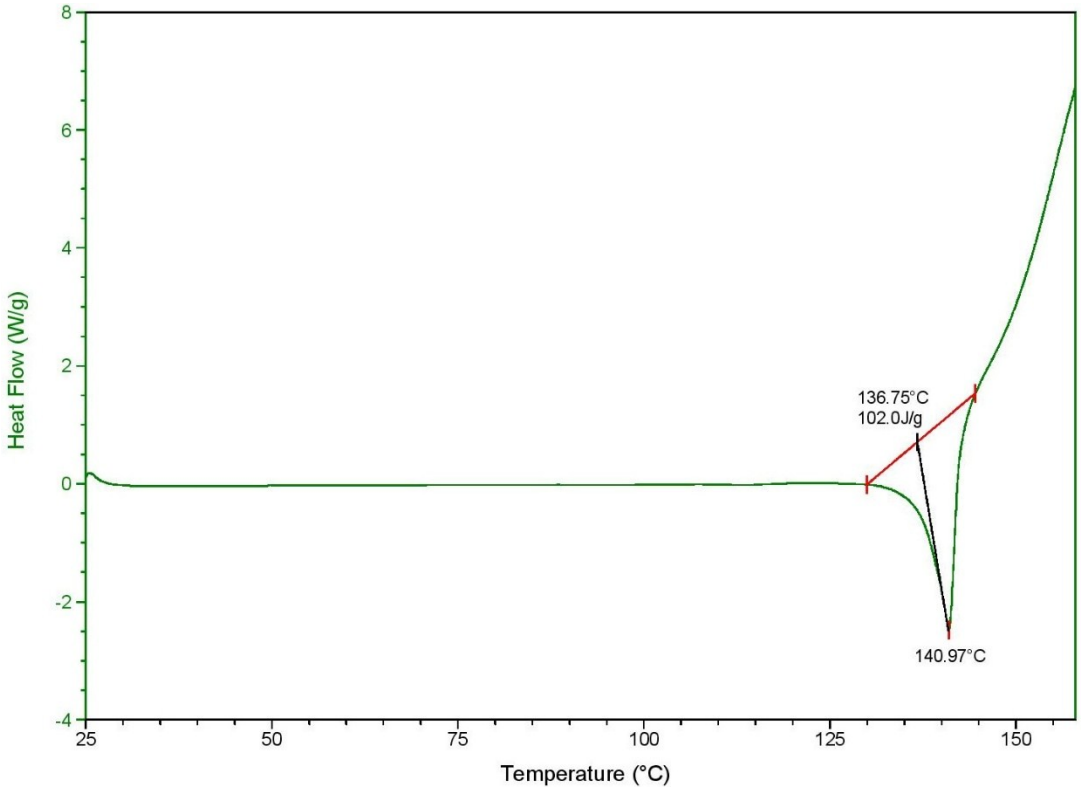


Figure S3.2: DSC thermogram for cocrystal of 11-Azaartemisinin and Salicylic acid, 11-Aza:Sal **3** heated at a rate of 10 °C min^{-1} under N_2.

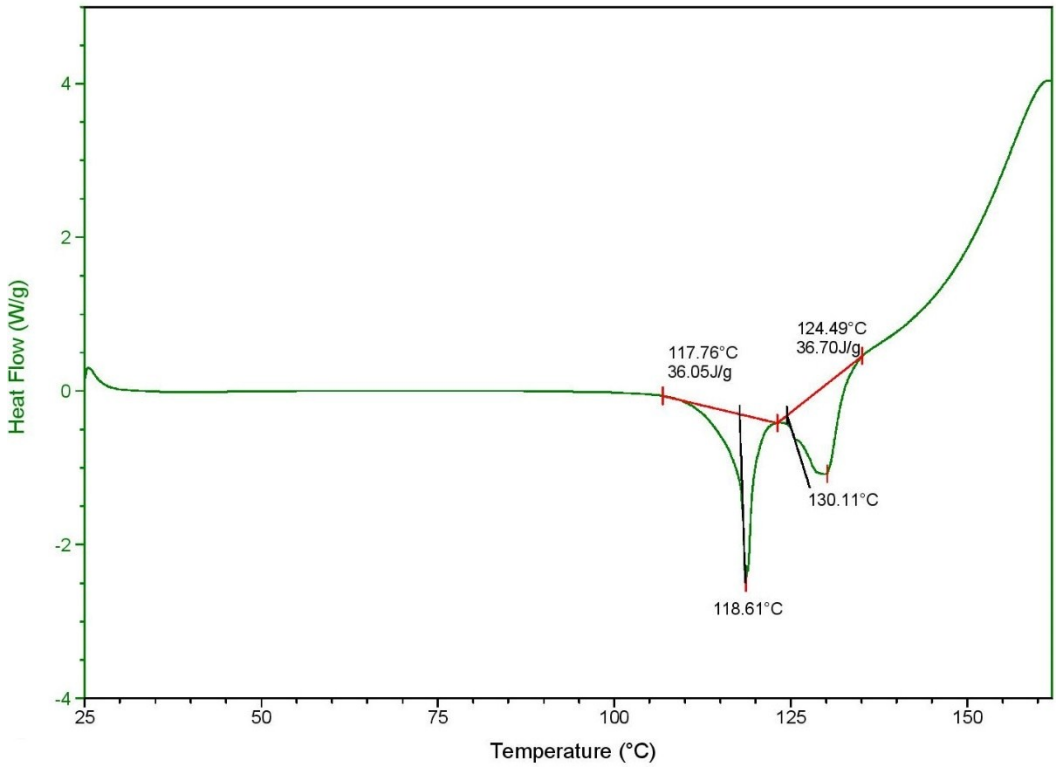


Figure S3.4: DSC thermogram for cocrystal of 11-Azaartemisinin and D-(–)-Mandelic acid, 11-Aza:D-Man **4** heated at a rate of 10 °C min^{-1} under N_2.

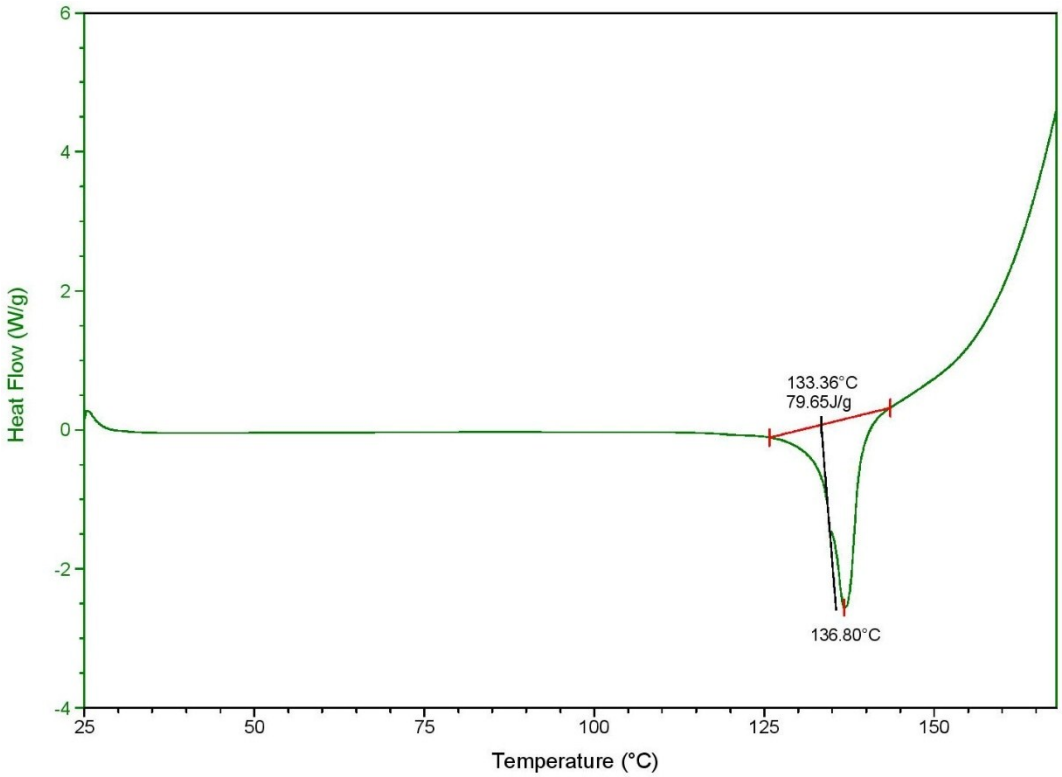


Figure S3.5: DSC thermogram for cocrystal of 11-Azaartemisinin and Succinic acid, 11-Aza:Suc **5** heated at a rate of 10 °C min^{-1} under N_2.

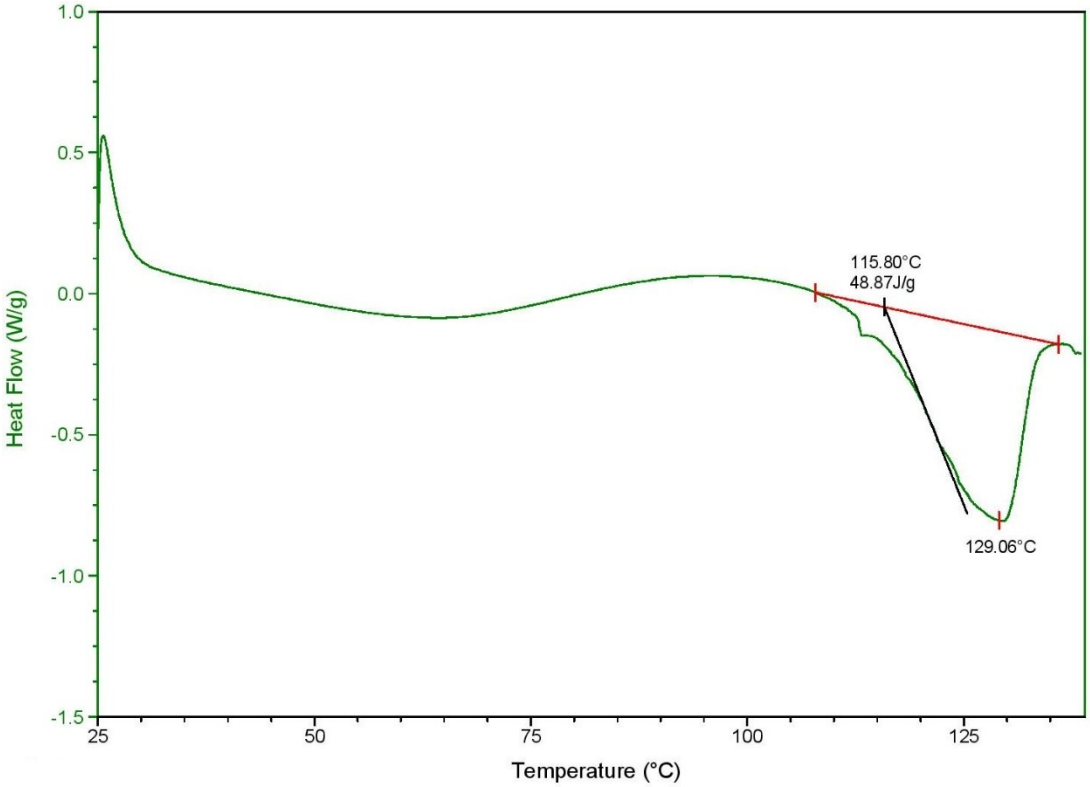


Figure S3.6: DSC thermogram for cocrystal of 11-Azaartemisinin and L-(–)-Malic acid, 11-Aza:L-Mal **6** heated at a rate of 10 °C min^{-1} under N_2.

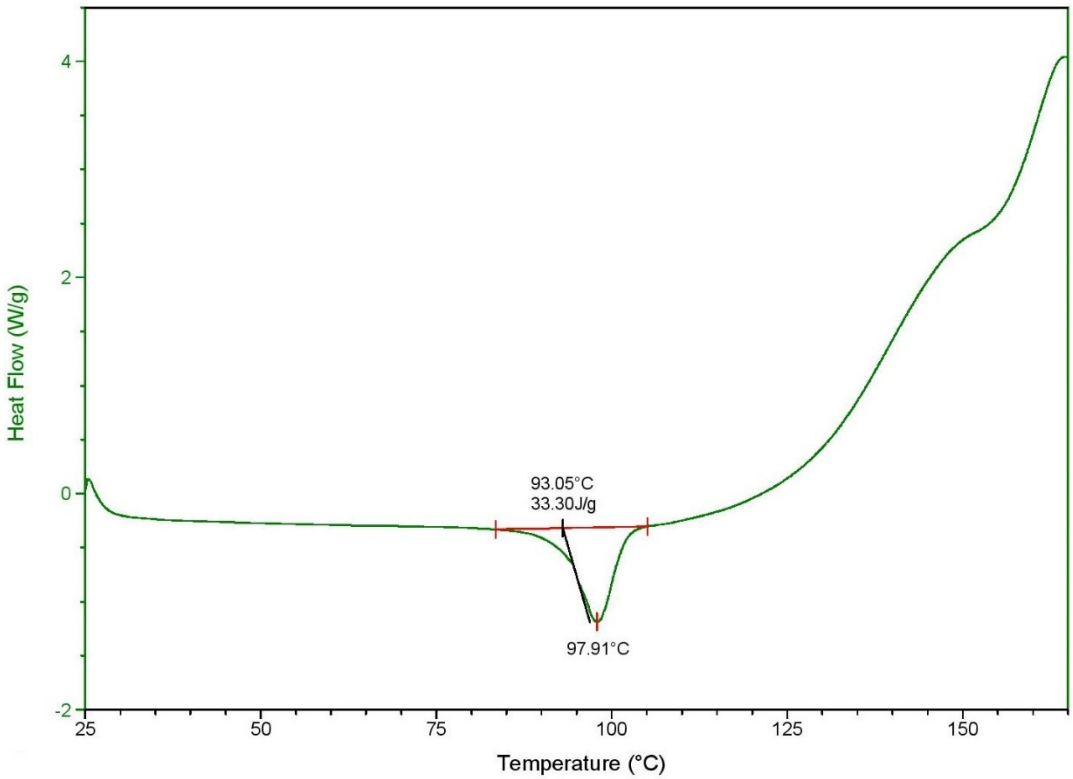


Figure S3.7: DSC thermogram for cocrystal of 11-Azaartemisinin and D-(+)-Malic acid, 11-Aza:D-Mal **7** heated at a rate of 10 °C min^{-1} under N_2.

S4. Thermal Gravimetric Analyses (TGA)

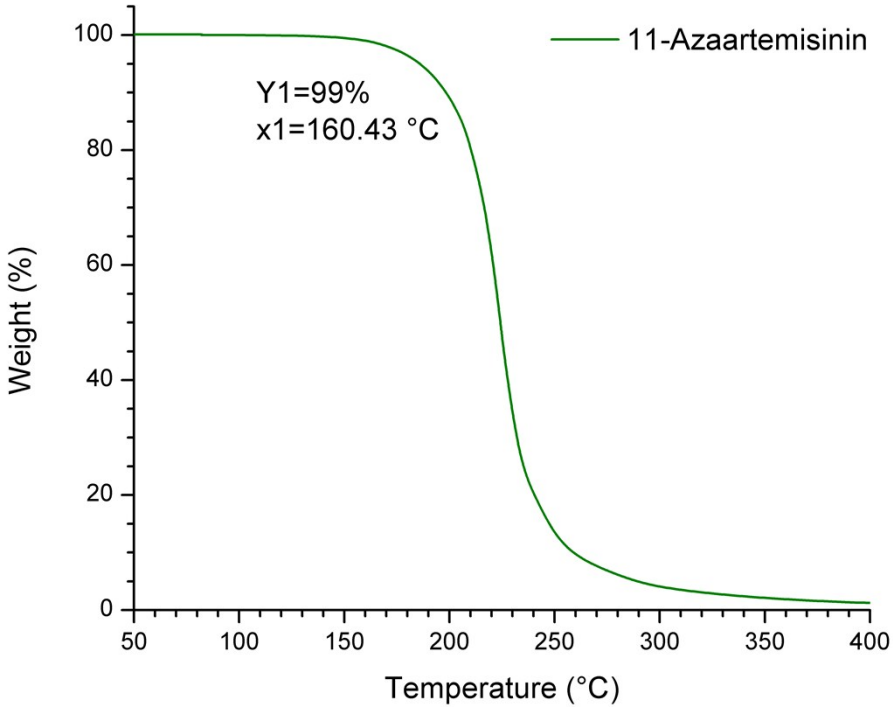


Figure S4.1 : TGA result of 11-Azaartemisinin **1**, heated at a rate of 10 °C min^{-1} under N_2. X1 and Y1 respectively refer to temperature and weight of the sample at the incipient decomposition event.

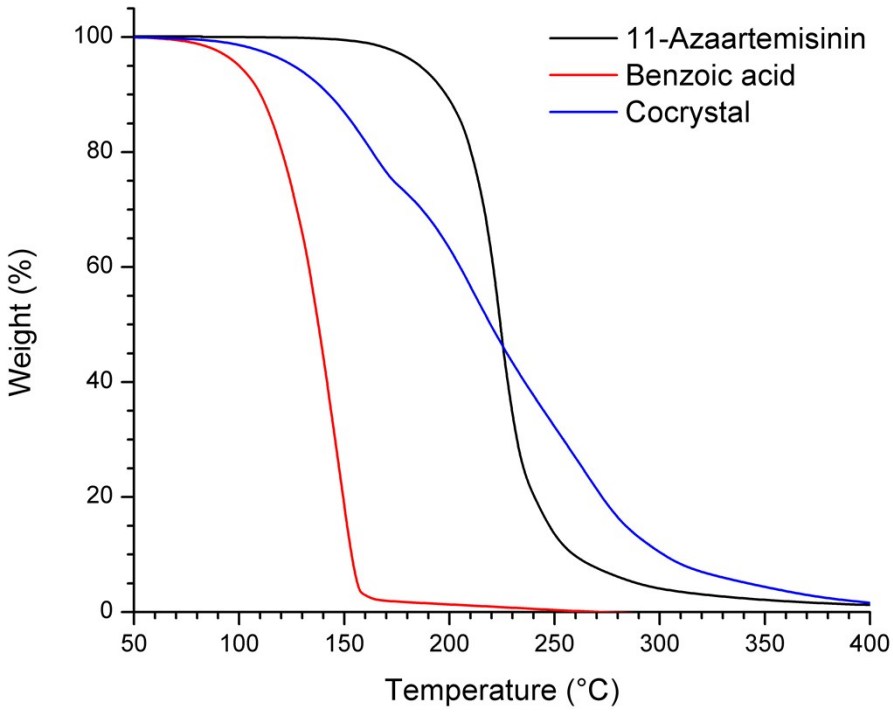


Figure S4.2: TGA overlay of 11-Azaartemisinin, coformer (Benzoic acid) and cocrystal, 11-Aza:Ben **2** heated at a rate of 10 °C min^{-1} under N_2.

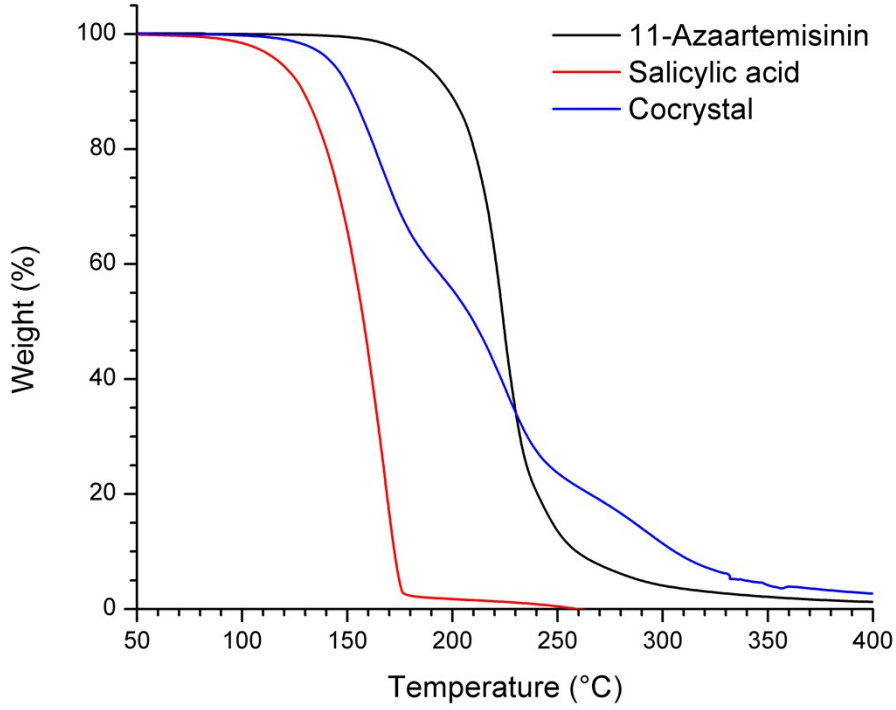


Figure S4.3: TGA overlay of 11-Azaartemisinin, coformer (Salicylic acid) and cocrystal 11-Aza:Sal **3**, heated at a rate of 10 °C min^{-1} under N_2.

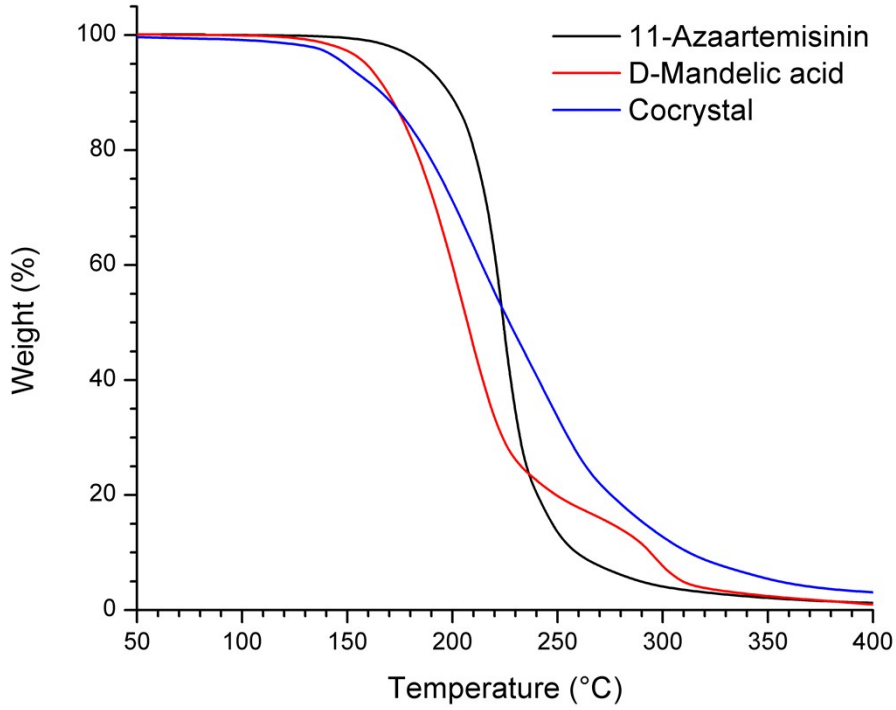


Figure S4.4: TGA overlay of 11-Azaartemisinin, coformer (D-(–)-Mandelic acid) and cocrystal, 11-Aza:D-Man **4** heated at a rate of 10 °C min^{-1} under N_2.

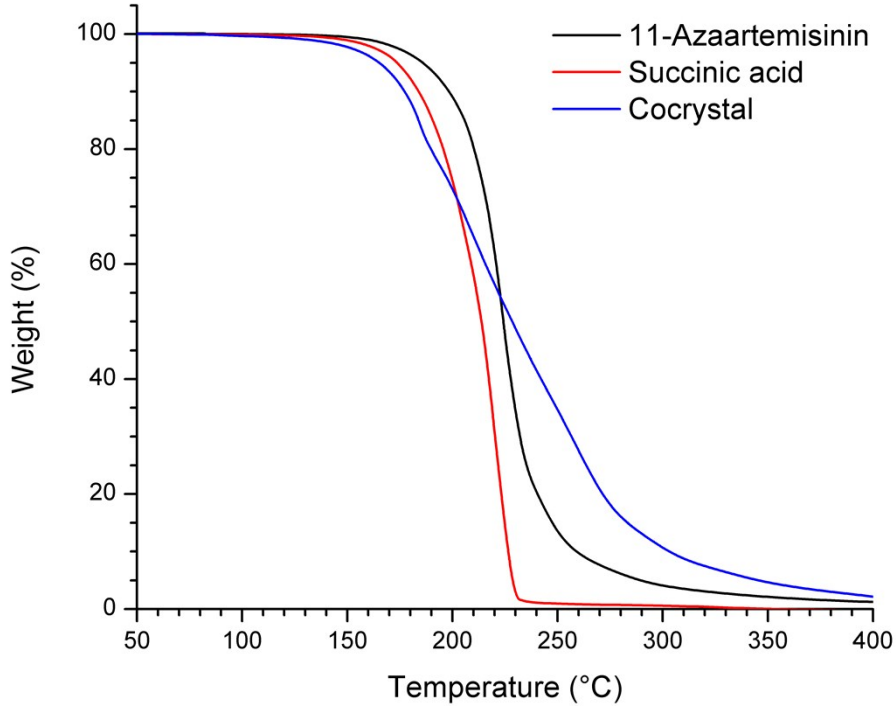


Figure S4.5: TGA overlay of 11-Azaartemisinin, coformer (Succinic acid) and cocrystal 11-Aza:Suc **5**, heated at a rate of 10 °C min^{-1} under N_2.

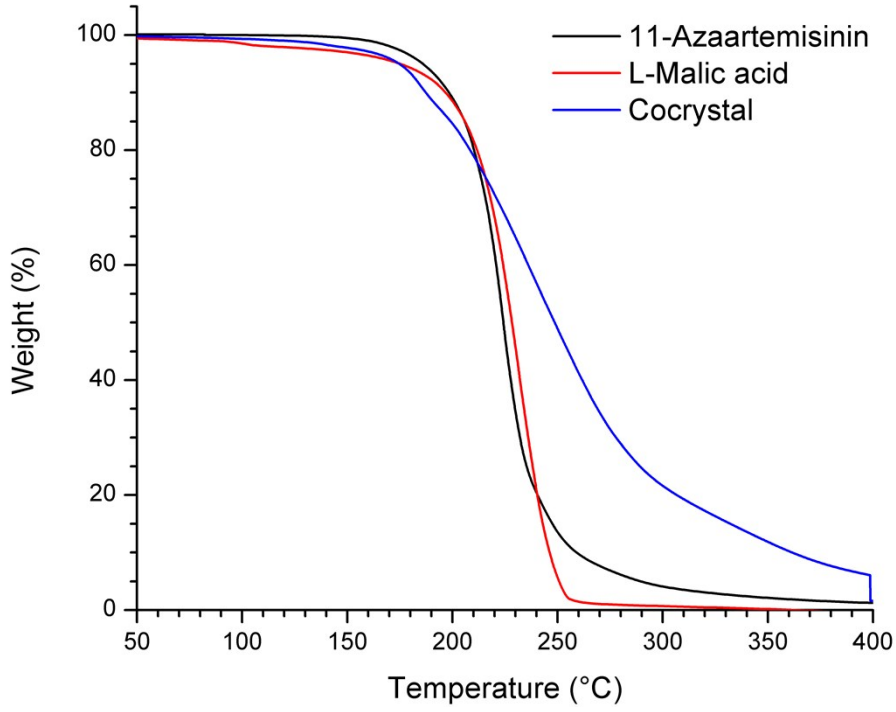


Figure S4.6: TGA overlay of 11-Azaartemisinin, coformer (L-(–)-Malic acid) and cocrystal **6** 11-Aza:L-Mal , heated at a rate of 10 °C min^{-1} under N_2.

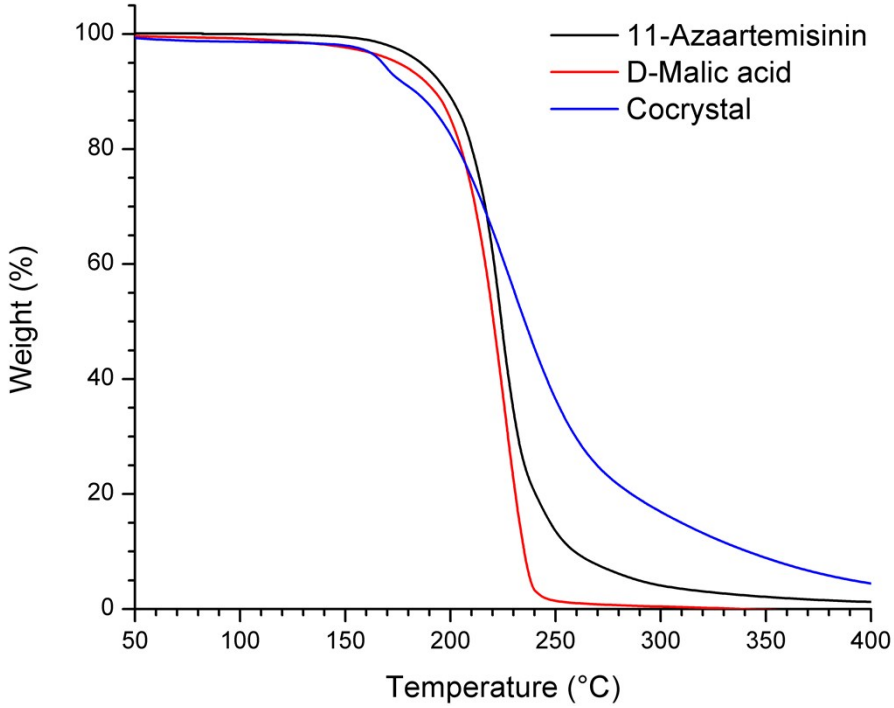


Figure S4.7: TGA overlay of 11-Azaartemisinin, coformer (D-(+)-Malic acid) and cocrystal **7** 11-Aza:D-Mal, heated at a rate of 10 °C min^{-1} under N_2.

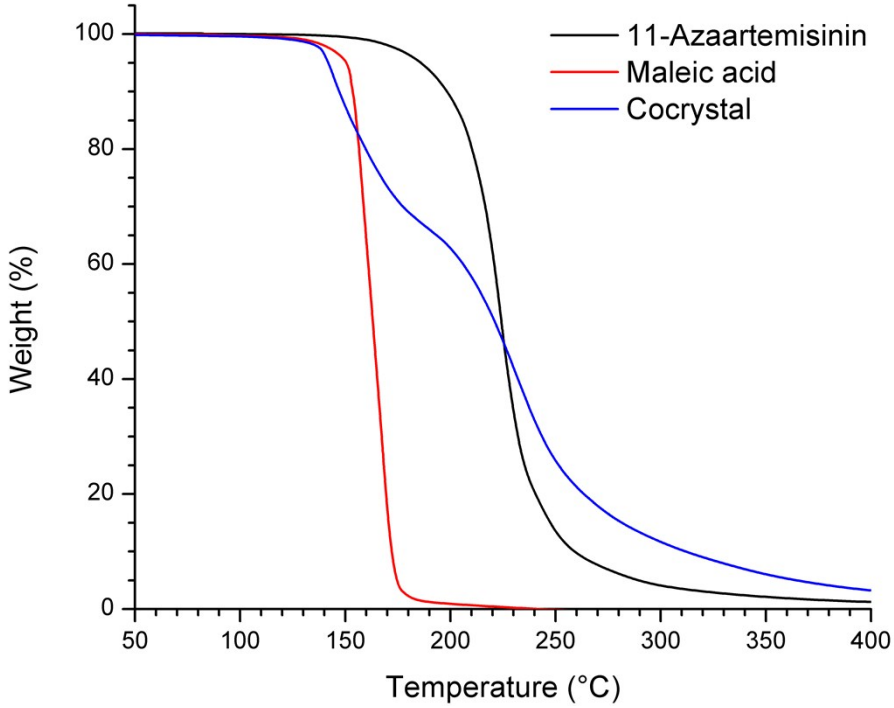
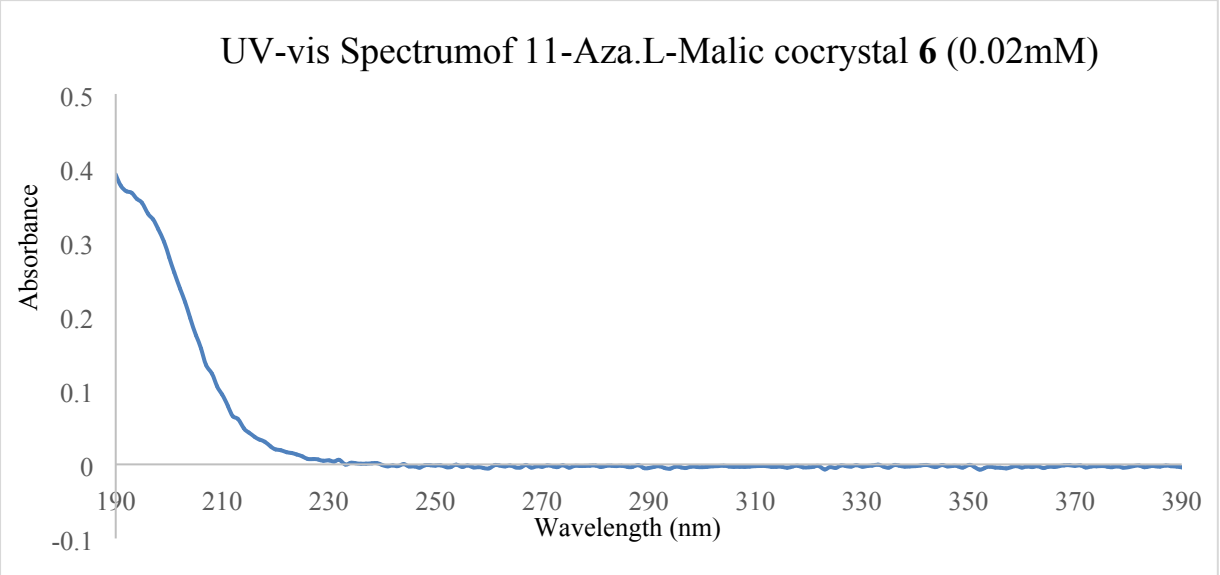
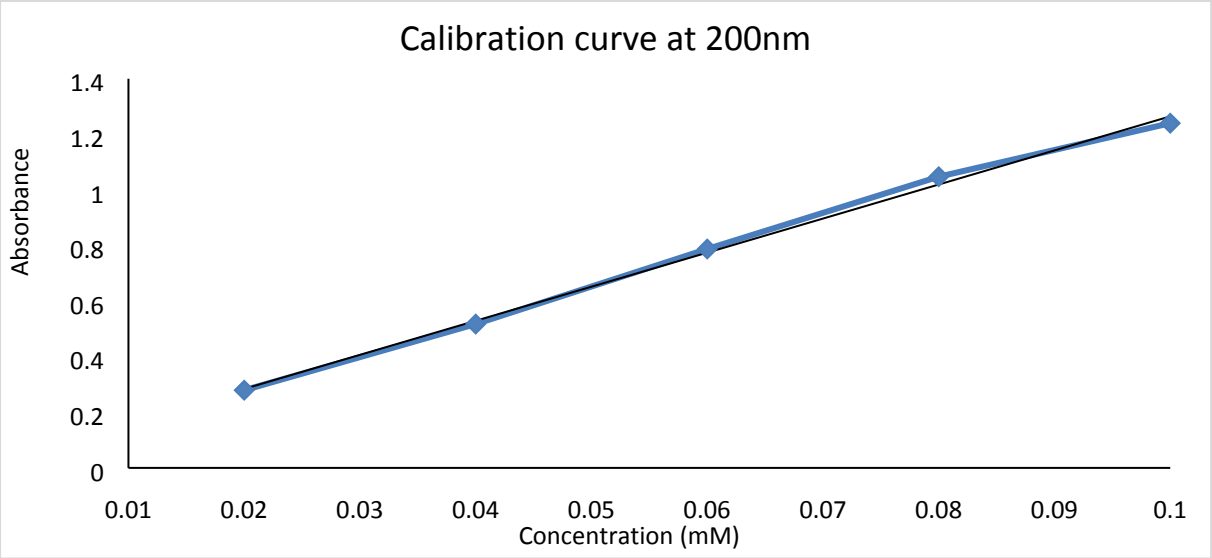


Figure S4.8: TGA overlay of 11-Azaartemisinin, coformer (Maleic acid) and 1:1 cocrystal, heated at a rate of 10 °C min^{-1} under N_2.

S5. Solubility Data – Example Compound **6**





Concentration (mM)	Absorbance
0.020	0.2795
0.040	0.5174
0.060	0.7874
0.080	1.0475
0.100	1.240
100x Diluted satur. soln.	0.2235

Slope, m = 12.2559 Intercept, c = 0.0390

Concentration of unknown, x= (y-c)/ m = 0.015049 mM

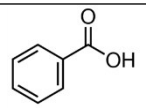
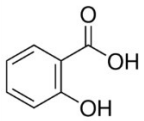
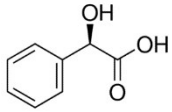
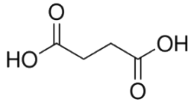
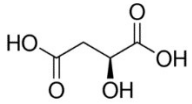
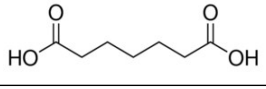
Dilution factor = 100 x = 100 x 0.015049 = 1.5049 mM (= 3mM 11-Aza)

weight (of unknown) in grams = Molarity x M.W = 0.0015049 x 696.7

= 1.0486 g/L = 0.1049 g/100mL

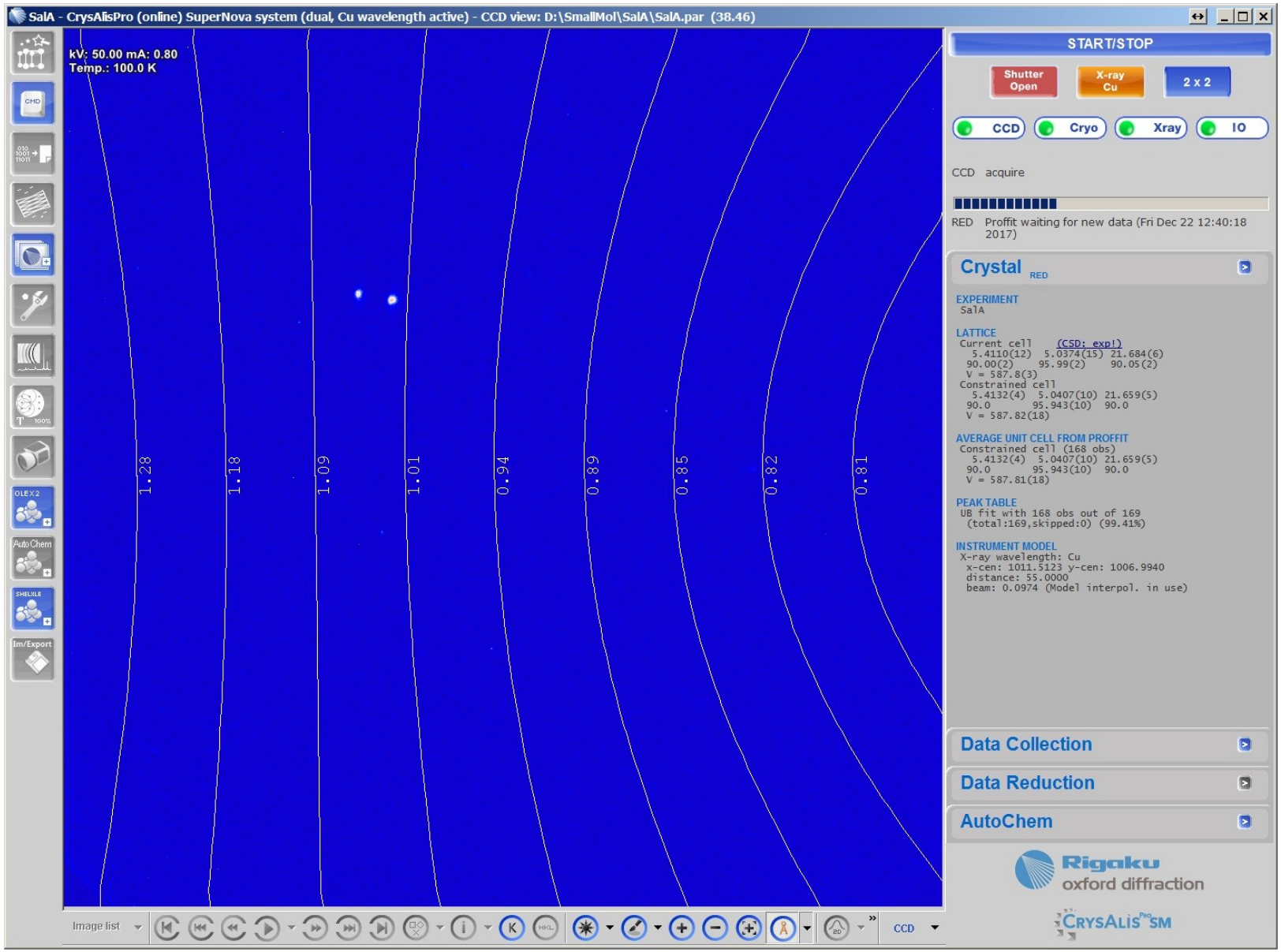
S6. Unit Cell Data for Coformer Acids at 100K (Data used for Specific Volumes in Table 5.)

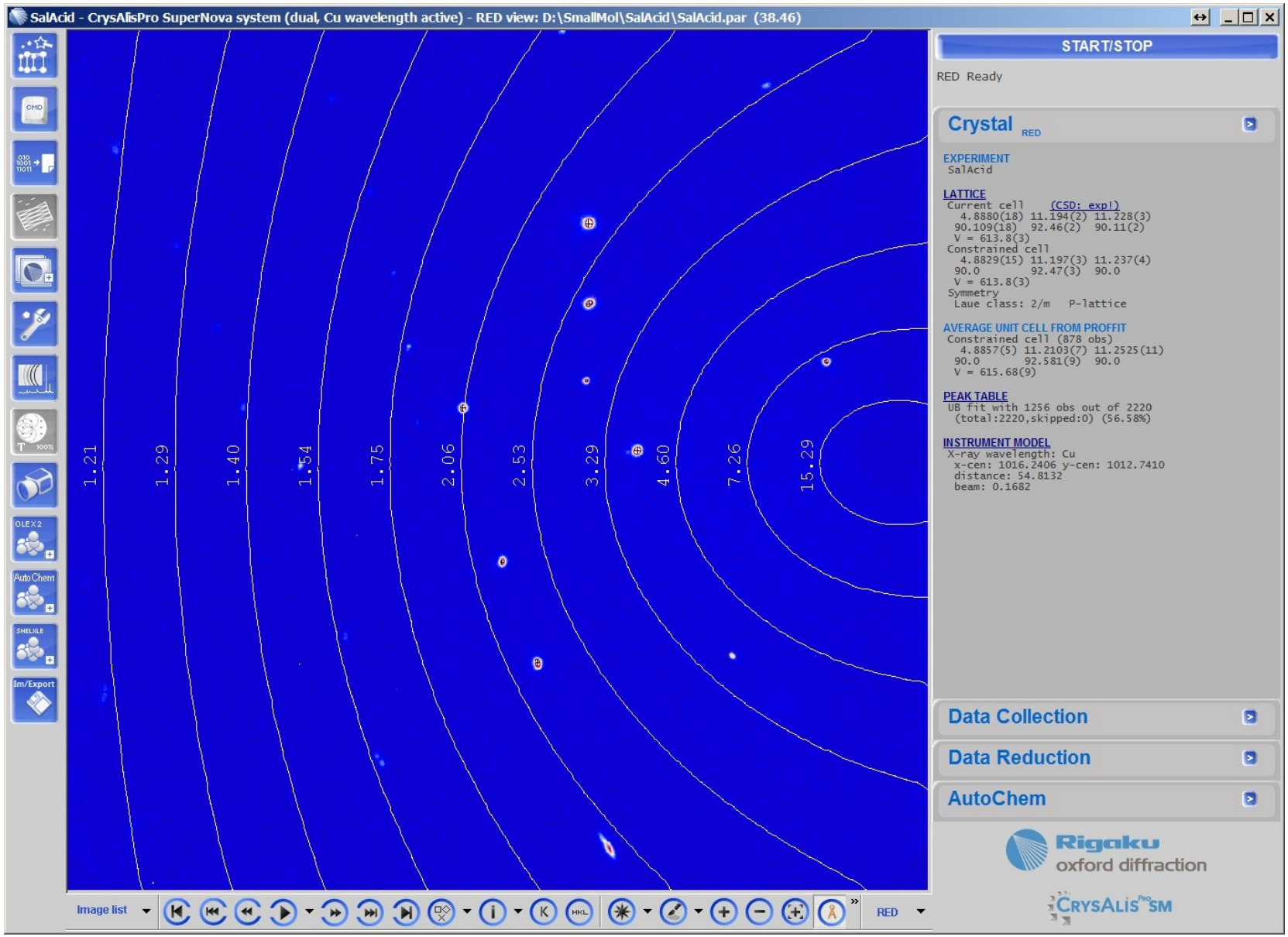
Data in green measured at HKUST under same experimental conditions as compounds **1-8** and used in Table 5.
The other literature values listed for comparison only are in good agreement.

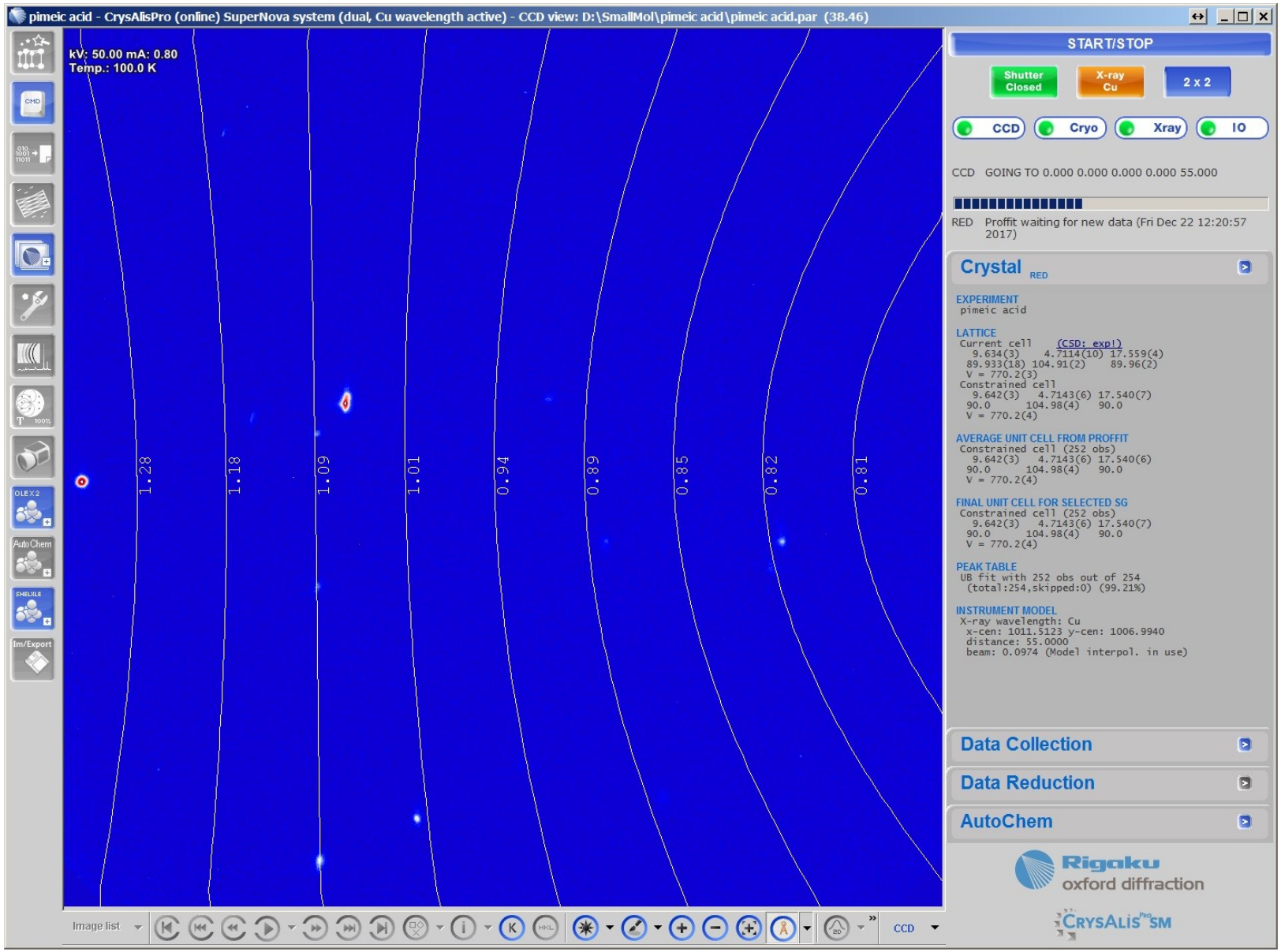
Sample	Acid	Structure	a	b	c	beta	V (Å^3)	SG	CCDC	Z	Z'	T (K)
2-A	Benzoic		5.429(2)	5.042(1)	21.746(12)	98.04(3)	589.4(4)	$P2_1/c$	1108741	4	1	100
			5.4132(4)	5.0407(10)	21.695(5)	95.943(10)	587.81(18)		This work			100
3-A	Salicylic		4.8848(10)	11.201(2)	11.244(2)	92.49(3)	614.6(2)	$P2_1/c$	737930	4	1	100
			4.8857(5)	11.2103(7)	11.2525(11)	92.581(9)	615.68(9)		This work			100
4-A	D-(–)-Mandelic		8.377(4)	5.859(2)	15.047(5)	103.08(2)	719.36	$P2_1$	1001991	4	2	100
			8.372(10)	5.866(7)	15.039(18)	102.90(10)	720(1)		This work			100
5-A	Succinic		5.464(1)	8.766(3)	5.004(1)	93.29(3)	239.28	$P2_1/c$	1263471	2	0.5	77
			5.4712(15)	8.775(2)	5.012(12)	93.07(2)	240.3(4)		This work			100
6-A/ 7-A	L-(–)-Malic		5.041(3)	9.188(3)	11.792(5)	94.06(4)	544.8	$P2_1$	1128608	4	2	293
			5.010(2)	9.131(17)	11.572(3)	92.50(4)	529(2)		This work			100
8-A	Pimelic		17.692(6)	4.7069(16)	9.626(3)	106.776(5)	767.5(4)	C2/c	1233869	4	0.5	100
			17.559(4)	4.7114(10)	9.634(2)	104.98(4)	770.2(4)		This work			100

References:

2-A. C. C.Wilson, N. Shankland, A. J. Florence*, J. Chem.Soc., Faraday Trans*., 1996, **92**, 5051. M. Nieger, *CSD Communication*, 2010, DOI: 10.5517/ccvfcxj.
3-A. N.Hamdi, P.Valerga, M.C.Puerta, *CSD Communication*, 2009, DOI: 10.5517/ccsrw6l.
4-A. S-W, Zhang, M. T. Harasimowicz, M. M. de Villiers and L. Yu, *J. Am. Chem. Soc*., 2013, **135**, 18981–18989.
5-A. R. S. Gopalan, P. Kumaradhas, G. U. Kulkarni and C. N. R. Rao, *J. Mol. Struct*., 2000, **521**, 97–106.
6-A. P. van der Sluis and J. Kroon, *Acta Cryst. C*, 1989, **45**, 1406-1408.
8-A. C. A. Mitchell, L. Yu and M. D. Ward, *J. Am. Chem. Soc.*, 2001, **123**, 10830–10839.


SalA - CrysAlisPro (online) SuperNova system (dual, Cu wavelength active) - CCD view: D:\SmallMol\SalA\SalA.par (38.46)
kV: 50.00 mA: 0.80
Temp.: 100.0 K
1.28
1.18
1.09
1.01
0.94
0.89
0.85
0.82
0.81
START/STOP
Shutter Open
X-ray Cu
2 x 2
CCD
Cryo
Xray
IO
CCD acquire
RED Proffit waiting for new data (Fri Dec 22 12:40:18 2017)
Crystal RED
EXPERIMENT
SalA
LATTICE
Current cell (CSD: exp!)
5.4110(12) 5.0374(15) 21.684(6)
90.00(2) 95.99(2) 90.05(2)
V = 587.8(3)
Constrained cell
5.4132(4) 5.0407(10) 21.659(5)
90.0 95.943(10) 90.0
V = 587.82(18)
AVERAGE UNIT CELL FROM PROFFIT
Constrained cell (168 obs)
5.4132(4) 5.0407(10) 21.659(5)
90.0 95.943(10) 90.0
V = 587.81(18)
PEAK TABLE
UB fit with 168 obs out of 169
(total:169,skipped:0) (99.41%)
INSTRUMENT MODEL
X-ray wavelength: Cu
x-cen: 1011.5123 y-cen: 1006.9940
distance: 55.0000
beam: 0.0974 (Model interpol. in use)
Data Collection
Data Reduction
AutoChem
Rigaku
oxford diffraction
CrysAlis Pro SM
Image list
CCD


SalAcid - CrysAlisPro SuperNova system (dual, Cu wavelength active) - RED view: D:\SmallMol\SalAcid\SalAcid.par (38.46)
START/STOP
RED Ready
Crystal RED
EXPERIMENT
SalAcid
LATTICE
Current cell (CSD: exp!)
4.8880(18) 11.194(2) 11.228(3)
90.109(18) 92.46(2) 90.11(2)
V = 613.8(3)
Constrained cell
4.8829(15) 11.197(3) 11.237(4)
90.0 92.47(3) 90.0
V = 613.8(3)
Symmetry
Laue class: 2/m P-lattice
AVERAGE UNIT CELL FROM PROFFIT
Constrained cell (878 obs)
4.8857(5) 11.2103(7) 11.2525(11)
90.0 92.581(9) 90.0
V = 615.68(9)
PEAK TABLE
UB fit with 1256 obs out of 2220
(total:2220,skipped:0) (56.58%)
INSTRUMENT MODEL
X-ray wavelength: Cu
x-cen: 1016.2406 y-cen: 1012.7410
distance: 54.8132
beam: 0.1682
1.21
1.29
1.40
1.54
1.75
2.06
2.53
3.29
4.60
7.26
15.29
Data Collection
Data Reduction
AutoChem
Rigaku
oxford diffraction
CrysAlis Pro SM
Image list
RED


pimeic acid - CrysAlisPro (online) SuperNova system (dual, Cu wavelength active) - CCD view: D:\SmallMol\pimeic acid\pimeic acid.par (38.46)
kV: 50.00 mA: 0.80
Temp.: 100.0 K
1.28
1.18
1.09
1.01
0.94
0.89
0.85
0.82
0.81
START/STOP
Shutter Closed
X-ray Cu
2 x 2
CCD
Cryo
Xray
IO
CCD GOING TO 0.000 0.000 0.000 0.000 55.000
RED Proffit waiting for new data (Fri Dec 22 12:20:57 2017)
Crystal RED
EXPERIMENT
pimeic acid
LATTICE
Current cell (CSD: exp!)
9.634(3) 4.7114(10) 17.559(4)
89.933(18) 104.91(2) 89.96(2)
V = 770.2(3)
Constrained cell
9.642(3) 4.7143(6) 17.540(7)
90.0 104.98(4) 90.0
V = 770.2(4)
AVERAGE UNIT CELL FROM PROFFIT
Constrained cell (252 obs)
9.642(3) 4.7143(6) 17.540(6)
90.0 104.98(4) 90.0
V = 770.2(4)
FINAL UNIT CELL FOR SELECTED SG
Constrained cell (252 obs)
9.642(3) 4.7143(6) 17.540(7)
90.0 104.98(4) 90.0
V = 770.2(4)
PEAK TABLE
UB fit with 252 obs out of 254
(total:254,skipped:0) (99.21%)
INSTRUMENT MODEL
X-ray wavelength: Cu
x-cen: 1011.5123 y-cen: 1006.9940
distance: 55.0000
beam: 0.0974 (Model interpol. in use)
Data Collection
Data Reduction
AutoChem
Rigaku
oxford diffraction
CrysAlis Pro SM
Image list
CCD