Synthetic procedures and characterization:

Compound **1** was synthesized as reported previously. **(**F. Rodríguez-Llansola, J. F. Miravet, and B. Escuder, *Chem. Commun.*, 2009, 7303).

General procedure for the preparation of catalytic hydrogels:

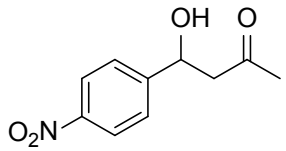
3 mg (0,008 mmol) of **1** were suspended in 4 mL of water in a screw-capped vial which was heated during 3 min in a bath at 100 ºC until complete dissolution. Then the vial was immersed in an ultrasounds bath for 1 min and then left at room temperature. After 1 hour, the formation of a hydrogel can be observed. Samples were aged for 24h at room temperature.

General procedure for the catalytic aldol reaction:

0,04 mmol of 4-nitrobenzaldehyde and 0,4 mmol of ketone were mixed and added simultaneously on top of the hydrogel and left to diffuse and react at room temperature. The reaction was quenched by addition of 2 mL of 0.1 M HCl and extracted twice with 2 mL of dichloromethane. The combined organic extracts were dried with anhydrous sodium sulfate and the solvent evaporated. The resulting yellow solid was analysed by ^{1}H-NMR in $CDCl_3$ in order to determine the yield. Afterwards, the crude product was purified by column chromatography on silica gel (hexane:ethyl acetate, 3:1) to give the aldol product. Then the enantioselectivity was determined by chiral phase HPLC.

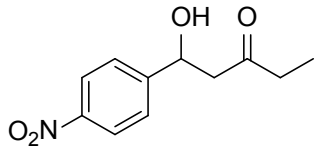
Characterization of aldol products:

1-(4-nitrophenyl)-1-hydroxy-3-butanone.



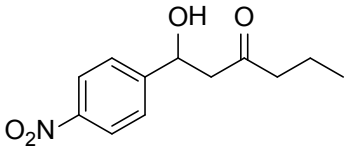
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.86 (d, *J*=1.8 Hz, 1H), 2.88 (s, 1H) 3.70 (s, 1H), 5.27 (dd, *J*=2.9, 3.3 Hz, 1H), 7.54 (d, *J*=8.8 Hz, 2H), 8.21 (d, *J*=8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$):δ 30.6, 51.4, 68.8, 123.7, 126.3, 147.3, 149.9, 208.2.

1-(4-nitrophenyl)-1-hydroxy-3-pentanone.



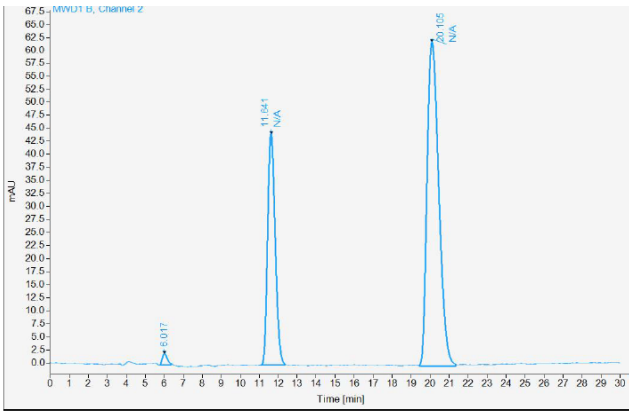
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, *J*=7.3 Hz, 3H), 2.48 (q, *J*=7.3 Hz, 2H), 2.82 (m, 2H), 3.67 (d, *J*=3.3 Hz, 1H), 5.27 (dt, *J*=3.5 Hz, 7.7, 1H), 7.53 (d, *J*=8.6 Hz, 2H), 8.21 (d, *J*=9.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.4, 36.8, 50.2, 69.1, 123.7, 126.4, 147.3, 150.1, 211.4.

1-(4-nitrophenyl)-1-hydroxy-3-hexanone.

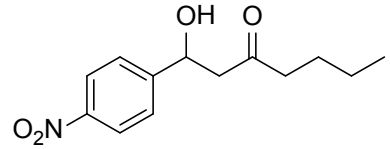


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 5.32 – 5.21 (m, 1H), 3.62 (d, *J* = 3.3 Hz, 1H), 2.81 (m, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.63 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 211.0, 150.2, 147.2, 126.4, 123.7, 69.0, 50.5, 45.4, 17.0, 13.6.

HPLC conditions Chiralpak IA (*n*-hexane/*THF*: 80/20, 1.0 mL/min, λ=250 nm), t_R=11.639 (minor), t_R=20.108 (major).

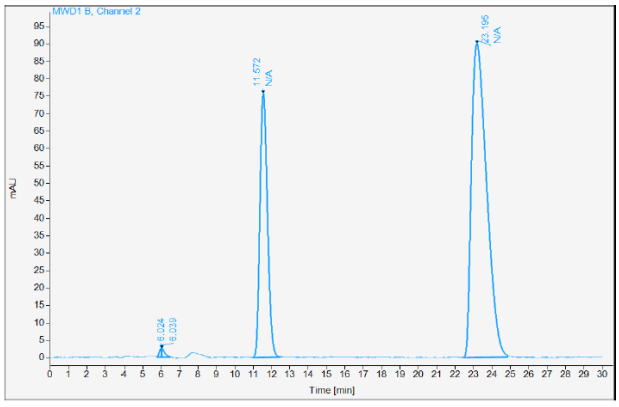


1-(4-nitrophenyl)-1-hydroxy-3-heptanone.

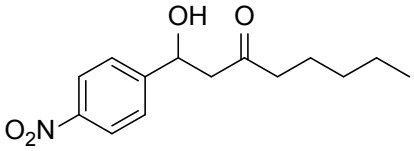


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 5.29 – 5.24 (m, 1H), 3.63 (d, *J* = 3.0 Hz, 1H), 2.82 (m, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 1.59 (m, 2H), 1.32 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 211.0, 150.2, 147.2, 126.4, 123.7, 69.0, 50.5, 43.3, 25.5, 22.2, 13.8.

HPLC conditions Chiralpak IA (*n*-hexane/*THF*: 80/20, 1.0 mL/min, λ=250 nm), t_R=11.572 (minor), t_R=23.195 (major).

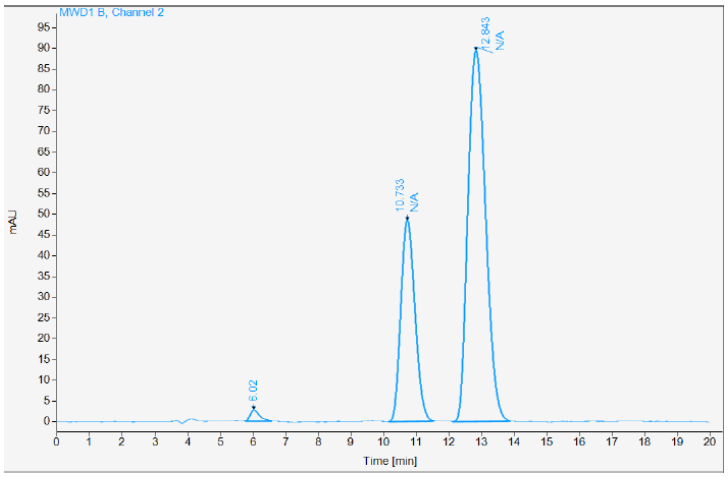


1-(4-nitrophenyl)-1-hydroxy-3-octanone.

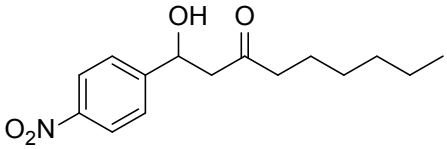


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 5.29 – 5.23 (m, 1H), 3.63 (d, *J* = 3.3 Hz, 1H), 2.87 – 2.75 (m, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 1.60 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.35 – 1.19 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H): ^{13}C NMR (126 MHz, cdcl$_3$) δ 211.07, 150.04, 126.38, 123.74, 69.06, 50.51, 43.62, 31.24, 23.22, 22.35, 13.82. (ESI-TOF, positive mode) m/z exp $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_4^+$ 288.1206; found, 288.1210 $[M+Na]^+$ (Δ=0.7 ppm).

HPLC conditions Chiralpak IA (*n*-hexane/*THF*: 80/20, 1.0 mL/min, λ=250 nm), t_R=10.733 (minor), t_R=12.843 (major).

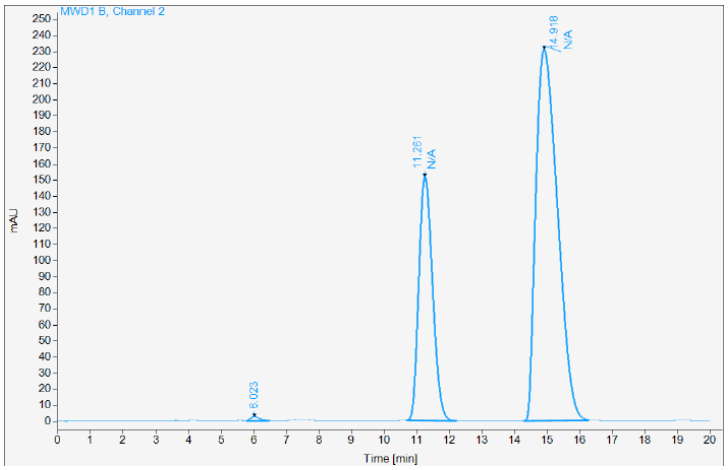


1-(4-nitrophenyl)-1-hydroxy-3-nonanone.

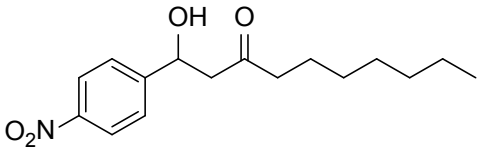


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 5.28 (m, 1H), 3.65 (s, 1H), 2.83 (m, 2H), 2.45 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.56 (m, 2H), 1.29 (s, 6H), 0.89 (t, *J* = 5.5 Hz, 3H); 13C NMR (CDCl3, 75 MHz) δ = 211.33, 150.21, 147.43, 126.47, 123.80, 69.02, 50.46, 43.60, 31.41, 28.66, 23.40, 22.32, 13.85.

HPLC conditions Chiralpak IA (*n*-hexane/*THF*: 80/20, 1.0 mL/min, λ=250 nm), t_R=11.261 (minor), t_R=14.918 (major).

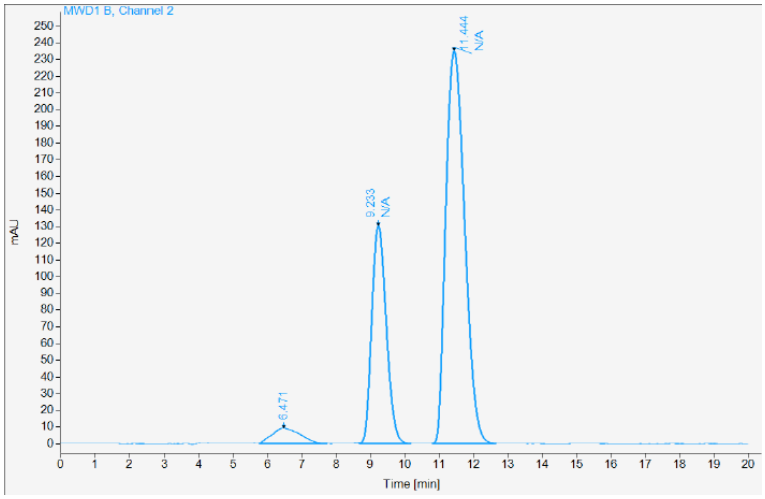


1-(4-nitrophenyl)-1-hydroxy-3-decanone.

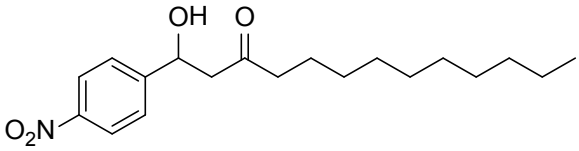


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.21 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 5.26 (m, 1H), 3.64 (s, 1H), 2.82 (m, 2H), 2.44 (t, J = 7.4 Hz, 2H), 1.60 (m, 2H), 1.28 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, cdcl$_3$) δ 209.64, 150.76, 147.43, 126.38, 123.74, 69.05, 50.49, 43.65, 31.58, 29.67, 23.54, 22.54, 13.99.(ESI-TOF, positive mode) m/z exp $[M+Na]^+$ calcd for $C_{16}H_{23}NNaO_4^+$ 316.1519; found, 316.1529 $[M+Na]^+$ (Δ=1.3 ppm).

HPLC conditions Chiralpak IA (*n*-hexane/*THF*: 80/20, 1.0 mL/min, λ=250 nm), t_R=9.233 (minor), t_R=11.444 (major).

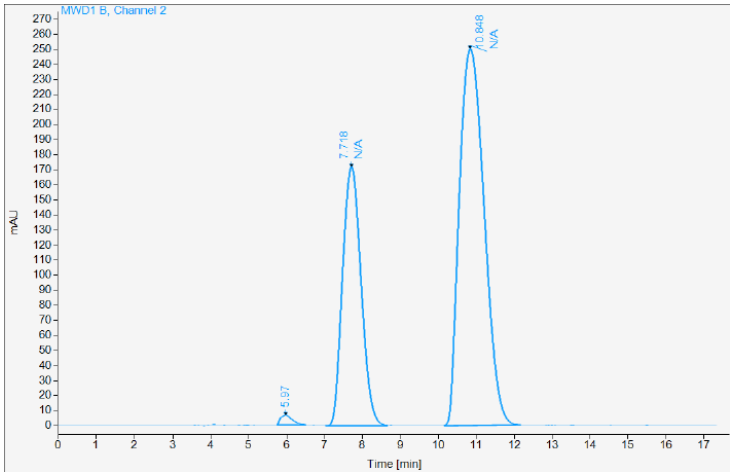


1-(4-nitrophenyl)-1-hydroxy-3-tridecanone.



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 3H), 5.26 (m, 1H), 3.64 (s, 1H), 2.81 (m, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.26 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 210.85, 150.14, 147.43, 126.25, 123.51, 68.86, 50.39, 43.49, 31.68, 29.34, 29.24, 29.15, 29.09, 28.92, 23.36, 13.89.

HPLC conditions Chiralpak IA (*n*-hexane/*THF*: 80/20, 1.0 mL/min, λ=250 nm), t_R=7.718 (minor), t_R=10.848 (major).



Crystal data collection and refinement for **1**·HCl·2H_2O

Table ESI1 Crystal data and structure refinement for 1·HCl·2H_2O	
Identification code	CCDC 951964
Empirical formula	$C_{22}H_{48}N_3O_4Cl$
Formula weight	454.08
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.83104(13)
b/Å	7.1526(2)
c/Å	38.7650(12)
α/°	90.00
β/°	90.420(3)
γ/°	90.00
Volume/Å^3	1339.47(7)
Z	2
ρ_{calc}mg/mm^3	1.126
m/mm^{-1}	1.491
F(000)	500.0
Crystal size/mm^3	0.533 × 0.044 × 0.038
2Θ range for data collection	9.12 to 130.98°
Index ranges	-5 ≤ h ≤ 5, -8 ≤ k ≤ 8, -45 ≤ l ≤ 45
Reflections collected	7253
Independent reflections	4335[R(int) = 0.0434]
Data/restraints/parameters	4335/1/288
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.1543
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1916
Largest diff. peak/hole / e Å^{-3}	0.31/-0.35
Flack parameter	-0.02(2)

Table ESI2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $\mathbf{1}\cdot HCl\cdot 2H_2O$. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
C4	-7745(11)	3444(7)	-4329.2(10)	45.6(11)
C22	-7281(15)	-1099(8)	-2477.1(13)	66.5(16)
C20	-6240(10)	-172(7)	-2805.7(10)	43.1(9)
C6	-7142(7)	1876(5)	-2816.4(8)	23.9(7)
C21	-7235(16)	-1214(7)	-3123.6(13)	70.1(18)
C11	-8121(7)	3615(5)	-991.2(8)	24.2(7)
C15	-8095(7)	3617(5)	326.2(8)	22.5(7)
C3	-7194(10)	5462(6)	-4255.3(10)	40.2(10)
C13	-8124(7)	3622(5)	-333.1(8)	22.0(7)
C14	-6909(7)	4437(5)	-5.1(8)	22.0(7)
C9	-8006(7)	3566(5)	-1649.7(9)	25.7(7)
C17	-8077(7)	3661(5)	984.8(8)	22.5(7)
C16	-6862(7)	4454(5)	653.2(8)	22.4(7)
C7	-5963(7)	2909(5)	-2506.1(8)	24.6(7)
C2	-7777(9)	5690(6)	-3871.3(10)	35.3(9)
C18	-6852(7)	4538(6)	1310.1(8)	28.2(8)
C5	-7989(7)	3271(5)	-3382.9(8)	21.1(7)
C1	-6682(7)	3872(5)	-3722.0(9)	24.5(7)
C12	-6941(7)	4457(5)	-662.5(8)	22.6(7)
C8	-6983(8)	4552(6)	-1970.3(9)	29.2(8)
C10	-6974(7)	4480(5)	-1319.7(8)	23.9(7)
C19	-8116(9)	3759(7)	1640.2(9)	39.5(10)
N3	-7799(6)	3634(5)	-2287.4(7)	26.3(6)
N1	-7428(6)	2434(4)	-3991.1(7)	24.7(7)
N2	-6216(6)	2775(4)	-3132.9(7)	22.0(6)
O1	-10514(5)	3225(5)	-3354.8(6)	35.8(6)
O2	-3441(5)	3041(6)	-2463.1(7)	49.3(9)
Cl1	-2502.0(17)	-251.0(14)	-3981.6(2)	36.5(3)
O4	-12510(6)	4973(5)	-4939.3(8)	45.1(7)
O3	-7545(6)	3780(5)	-5223.1(8)	43.5(7)

Table ESI3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $1 \cdot HCl \cdot 2H_2O$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C4	70(3)	48(2)	19.6(17)	2.6(18)	-4.9(19)	-7(2)
C22	116(5)	49(3)	35(2)	17(2)	6(3)	-1(3)
C20	60(3)	43(2)	26.4(18)	5.2(19)	6.1(17)	2(2)
C6	16.3(16)	41.7(18)	13.8(14)	0.4(14)	6.2(12)	-4.6(14)
C21	135(6)	39(2)	37(2)	-7(2)	4(3)	-6(3)
C11	23.8(17)	27.6(17)	21.1(16)	1.4(13)	1.9(13)	-1.6(14)
C15	18.6(16)	29.2(18)	19.6(15)	2.6(14)	2.4(13)	1.0(13)
C3	56(3)	39(2)	25.9(18)	4.5(16)	2.5(18)	-1.3(19)
C13	22.8(16)	27.1(17)	16.1(15)	-0.4(13)	3.9(13)	1.0(13)
C14	19.2(16)	26.0(17)	20.7(16)	3.9(13)	3.5(13)	-1.2(13)
C9	26.9(18)	28.5(17)	21.8(16)	0.4(14)	1.4(13)	-5.2(14)
C17	20.4(16)	27.4(17)	19.7(16)	0.0(13)	2.6(13)	-0.5(14)
C16	21.1(17)	25.3(17)	20.8(16)	1.8(13)	2.0(13)	-0.2(13)
C7	13.8(16)	42.9(19)	17.0(15)	0.3(13)	4.8(12)	-1.3(14)
C2	48(2)	30.3(19)	28.1(18)	0.0(16)	9.3(17)	1.2(17)
C18	25.4(17)	38(2)	21.3(16)	-1.8(15)	0.6(13)	1.0(15)
C5	16.1(15)	31.5(17)	15.8(14)	-3.5(12)	7.0(12)	-1.9(13)
C1	17.8(16)	34.6(18)	21.1(16)	-1.1(14)	5.1(13)	-4.3(14)
C12	23.1(17)	26.8(18)	18.0(15)	2.7(13)	2.9(12)	0.0(13)
C8	28.8(18)	38(2)	20.8(15)	-2.6(15)	6.0(13)	-10.9(17)
C10	25.1(17)	26.7(17)	19.9(16)	2.5(13)	3.2(12)	-2.4(14)
C19	43(2)	55(3)	21.0(17)	3.2(17)	1.0(16)	5(2)
N3	14.1(13)	46.3(18)	18.4(13)	-2.1(13)	2.6(11)	-2.7(12)
N1	24.0(16)	29.6(16)	20.5(14)	0.4(11)	8.0(12)	0.3(12)
N2	12.1(13)	38.4(15)	15.6(12)	3.3(11)	4.9(10)	-1.2(11)
O1	14.9(12)	66.7(18)	25.8(12)	7.8(12)	4.7(10)	-1.2(12)
O2	13.0(13)	97(3)	37.7(15)	-17.5(16)	0.1(11)	-2.4(15)
Cl1	25.4(4)	34.4(4)	49.9(5)	-4.7(4)	6.3(4)	0.8(4)
O4	37.6(15)	47.9(17)	49.7(16)	-4.4(14)	0.1(13)	-1.0(14)
O3	33.5(16)	50.0(16)	47.0(17)	0.7(15)	4.1(13)	3.9(13)

Table ESI4 Bond Lengths for $\mathbf{1}\cdot HCl\cdot 2H_2O$.					
Atom	Atom	Length/Å	Atom	Atom	Length/Å
C4	C3	1.495(7)	C9	C8	1.515(5)
C4	N1	1.503(5)	C9	C10	1.518(5)
C22	C20	1.525(6)	C17	C16	1.526(4)
C20	C6	1.529(6)	C17	C18	1.524(4)
C20	C21	1.515(7)	C7	N3	1.336(5)
C6	C7	1.519(5)	C7	O2	1.232(4)
C6	N2	1.458(4)	C2	C1	1.517(5)
C11	C12	1.517(4)	C18	C19	1.527(5)
C11	C10	1.524(5)	C5	C1	1.524(4)
C15	C14	1.527(4)	C5	N2	1.336(4)
C15	C16	1.520(4)	C5	O1	1.226(4)
C3	C2	1.526(5)	C1	N1	1.507(4)
C13	C14	1.514(4)	C8	N3	1.446(5)
C13	C12	1.524(4)			

Table ESI5 Bond Angles for $\mathbf{1}\cdot HCl\cdot 2H_2O$.							
Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	C4	N1	106.3(3)	O2	C7	C6	120.6(3)
C22	C20	C6	110.1(4)	O2	C7	N3	123.0(3)
C21	C20	C22	111.1(5)	C1	C2	C3	102.4(3)
C21	C20	C6	111.2(4)	C17	C18	C19	112.8(3)
C7	C6	C20	109.9(3)	N2	C5	C1	115.6(3)
N2	C6	C20	110.9(3)	O1	C5	C1	120.2(3)
N2	C6	C7	109.7(3)	O1	C5	N2	124.1(3)
C12	C11	C10	113.8(3)	C2	C1	C5	115.2(3)
C16	C15	C14	113.8(3)	N1	C1	C2	103.9(3)
C4	C3	C2	104.8(3)	N1	C1	C5	107.8(3)
C14	C13	C12	114.0(3)	C11	C12	C13	114.0(3)
C13	C14	C15	114.4(3)	N3	C8	C9	113.4(3)
C8	C9	C10	112.6(3)	C9	C10	C11	114.2(3)
C18	C17	C16	113.3(3)	C7	N3	C8	122.5(3)
C15	C16	C17	113.9(3)	C4	N1	C1	107.3(3)
N3	C7	C6	116.4(3)	C5	N2	C6	121.9(3)

Table ESI6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $\mathbf{1}\cdot HCl\cdot 2H_2O$.

Atom	*x*	*y*	*z*	U(eq)
H1A	-5770(100)	1450(70)	-3996(13)	43(13)
H1B	-9110(90)	1720(60)	-3943(12)	31(11)
H4A	-6434	2969	-4496	55
H4B	-9603	3281	-4421	55
H22A	-6677	-389	-2280	100
H22B	-6555	-2346	-2462	100
H22C	-9267	-1147	-2482	100
H20	-4212	-209	-2802	52
H6	-9167	1932	-2808	29
H21A	-6855	-2524	-3097	105
H21B	-6289	-748	-3323	105
H21C	-9192	-1031	-3152	105
H11A	-10116	3767	-991	29
H11B	-7731	2284	-993	29
H15A	-10081	3816	327	27
H15B	-7772	2279	328	27
H3A	-8406	6256	-4392	48
H3B	-5287	5779	-4306	48
H13A	-10111	3817	-333	26
H13B	-7797	2284	-334	26
H14A	-7224	5777	-5	26
H14B	-4923	4236	-5	26
H9A	-7394	2275	-1654	31
H9B	-10014	3568	-1651	31
H17A	-10063	3861	983	27
H17B	-7753	2323	991	27
H16A	-7157	5796	650	27
H16B	-4880	4237	654	27
H2A	-6801	6760	-3776	42
H2B	-9743	5830	-3829	42
H18A	-7149	5879	1303	34
H18B	-4871	4319	1315	34
H1	-4666	3942	-3695	29
H12A	-7299	5792	-664	27
H12B	-4950	4283	-661	27
H8A	-7694	5820	-1972	35

H8B	-4979	4623	-1960	35
H10A	-7467	5795	-1325	29
H10B	-4970	4400	-1312	29
H19A	-10094	3883	1629	59
H19B	-7415	4442	1835	59
H19C	-7635	2463	1664	59
H3	-9532	3551	-2337	32
H2	-4480	2992	-3160	26
H4C	-12531	6153	-4915	68
H4D	-13879	4639	-5064	68
H3C	-9038	4104	-5125	65
H3D	-7678	3990	-5438	65

Experimental

Single crystals of $C_{22}H_{48}N_3O_4Cl$ (**1**·HCl·2H_2O) were obtained from an acidic aqueous solution. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 200.00(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. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122

Crystal structure determination of $C_{22}H_{48}N_3O_4Cl$ (**1**·HCl·2H_2O)

Crystal Data. $C_{22}H_{48}N_3O_4Cl$, M =454.08, monoclinic, a = 4.83104(13) Å, b = 7.1526(2) Å, c = 38.7650(12) Å, β = 90.420(3)°, V = 1339.47(7) Å^3, T = 200.00(10), space group $P2_1$ (no. 4), Z = 2, μ(Cu Kα) = 1.491, 7253 reflections measured, 4335 unique (R_{int} = 0.0434) which were used in all calculations. The final wR_2 was 0.1916 (all data) and R_1 was 0.0495 (>2sigma(I)).

Deposition number: CCDC 951964.

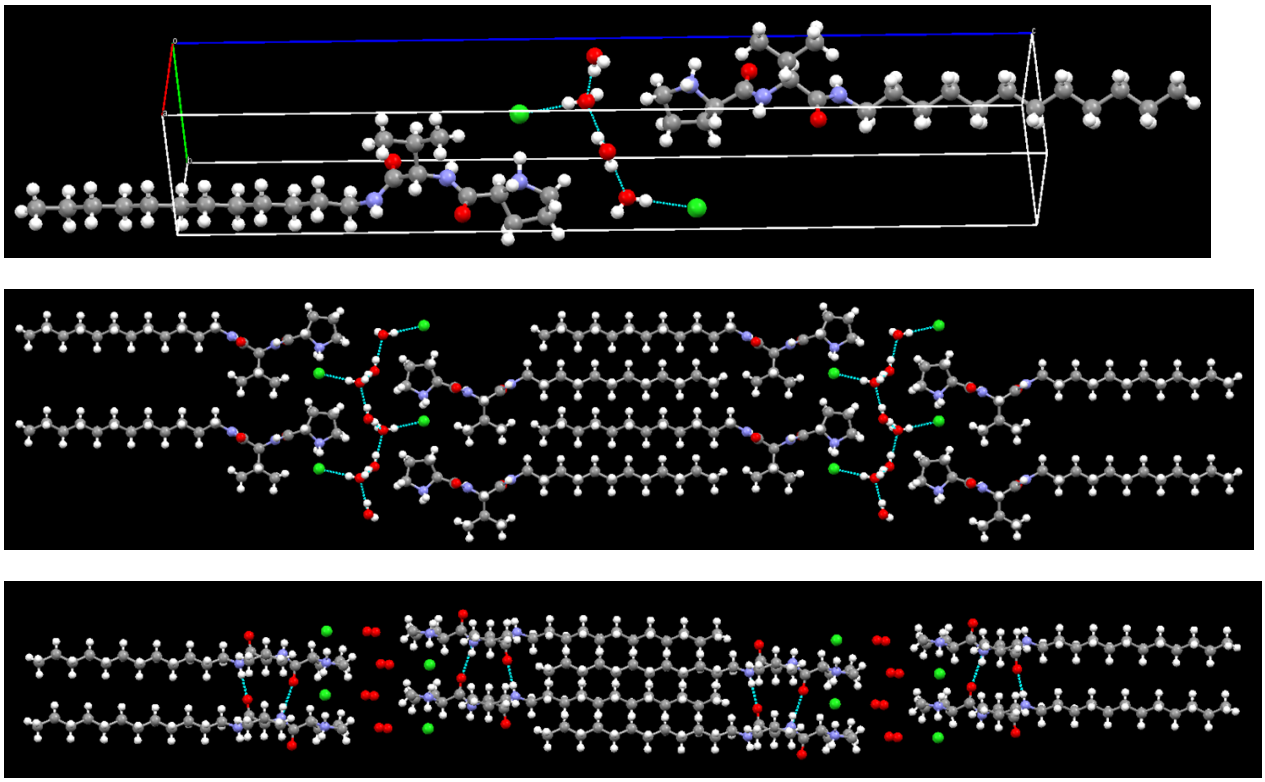


Fig. ESI1. Single crystal X-ray structure of compound **1**·HCl·2H_2O.

Table ESI7 H-bonding parameters for 1·HCl·2H_2O.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/Å	Symmetry operation for A
N2-H2···O1	0.86	2.071	2.910	164.68	-1-x, 1/2+y, -z
N3-H3···O2	0.86	1.981	2.837	173.17	-x, 1/2+y, -z
O3-H3C···O4	0.852	1.931	2.780	174.45	1+x, y, 1+z
O3-H3D···Cl1	0.848	2.317	3.160	172.70	-x, 1/2+y, -z
O4-H4C···O3	0.849	1.954	2.795	170.32	-x, 1/2+y, -z
O4-H4D···O3	0.850	1.970	2.796	163.59	1+x, y, 1+z