Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

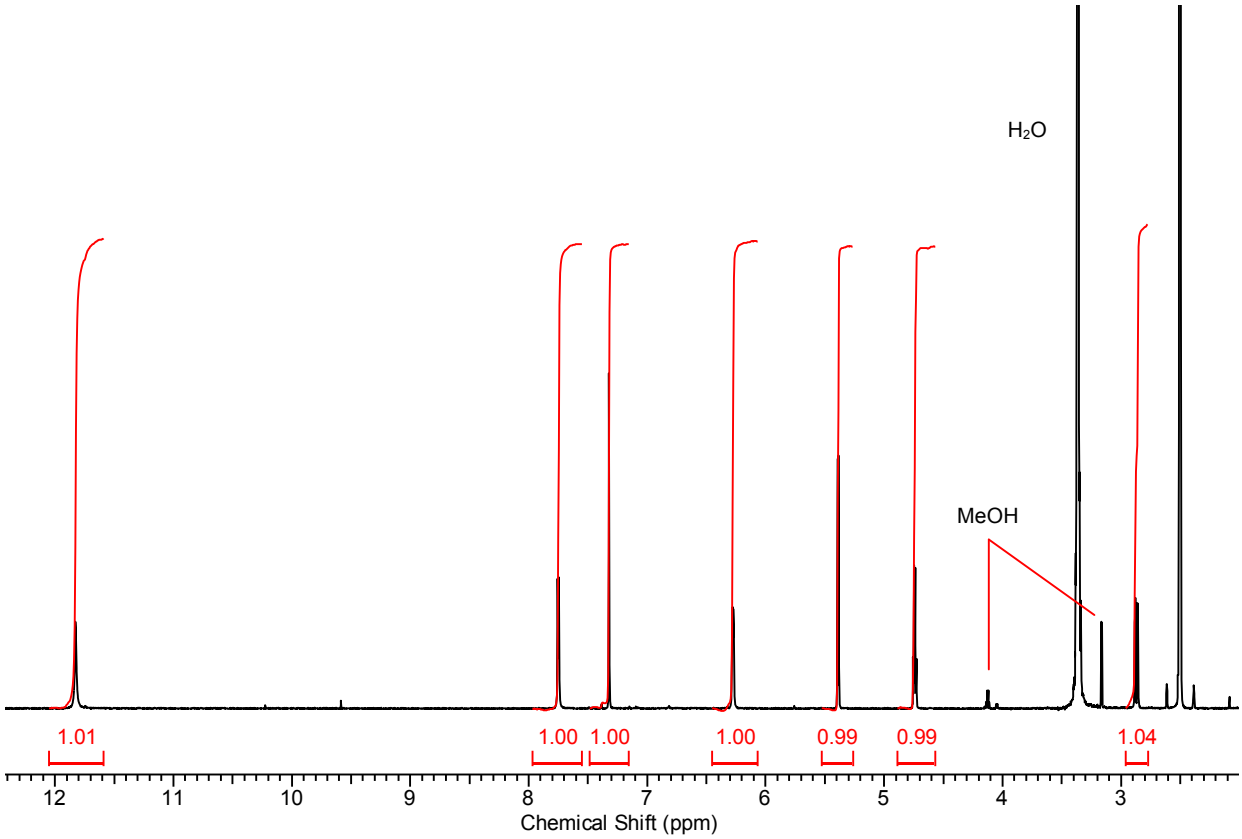
Supplementary information

Spectra

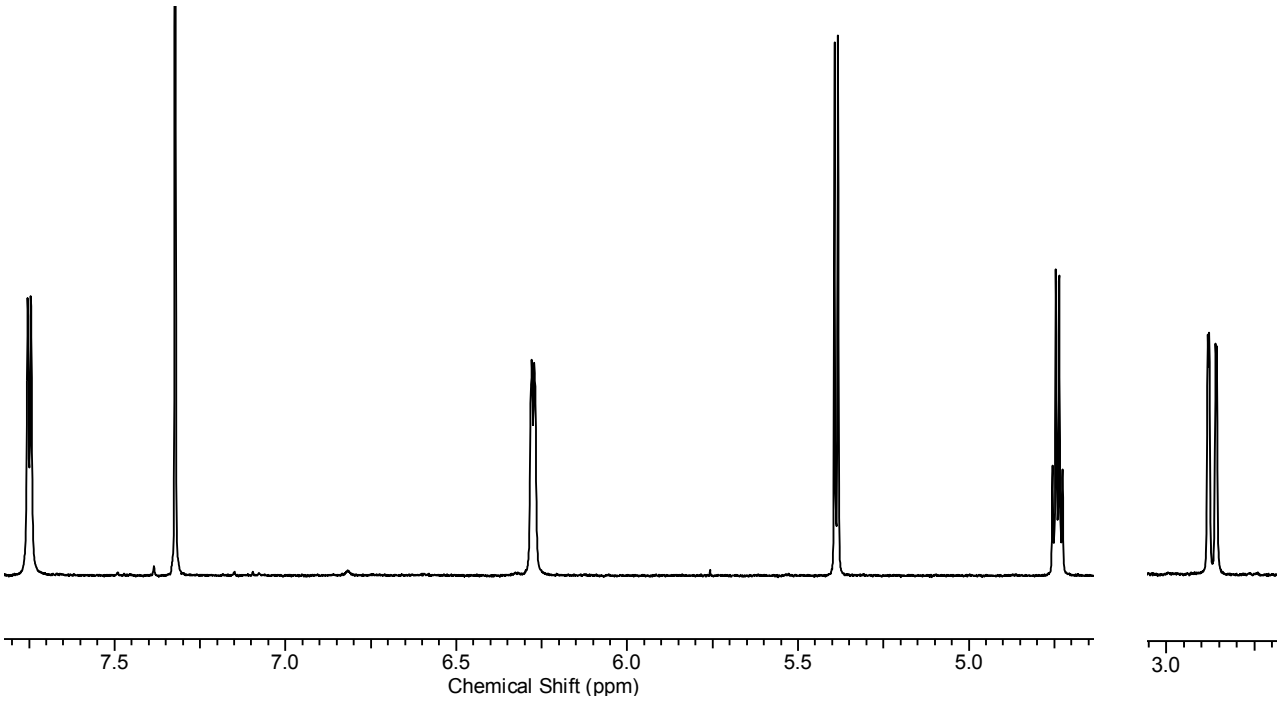
Crystallography

Spectra

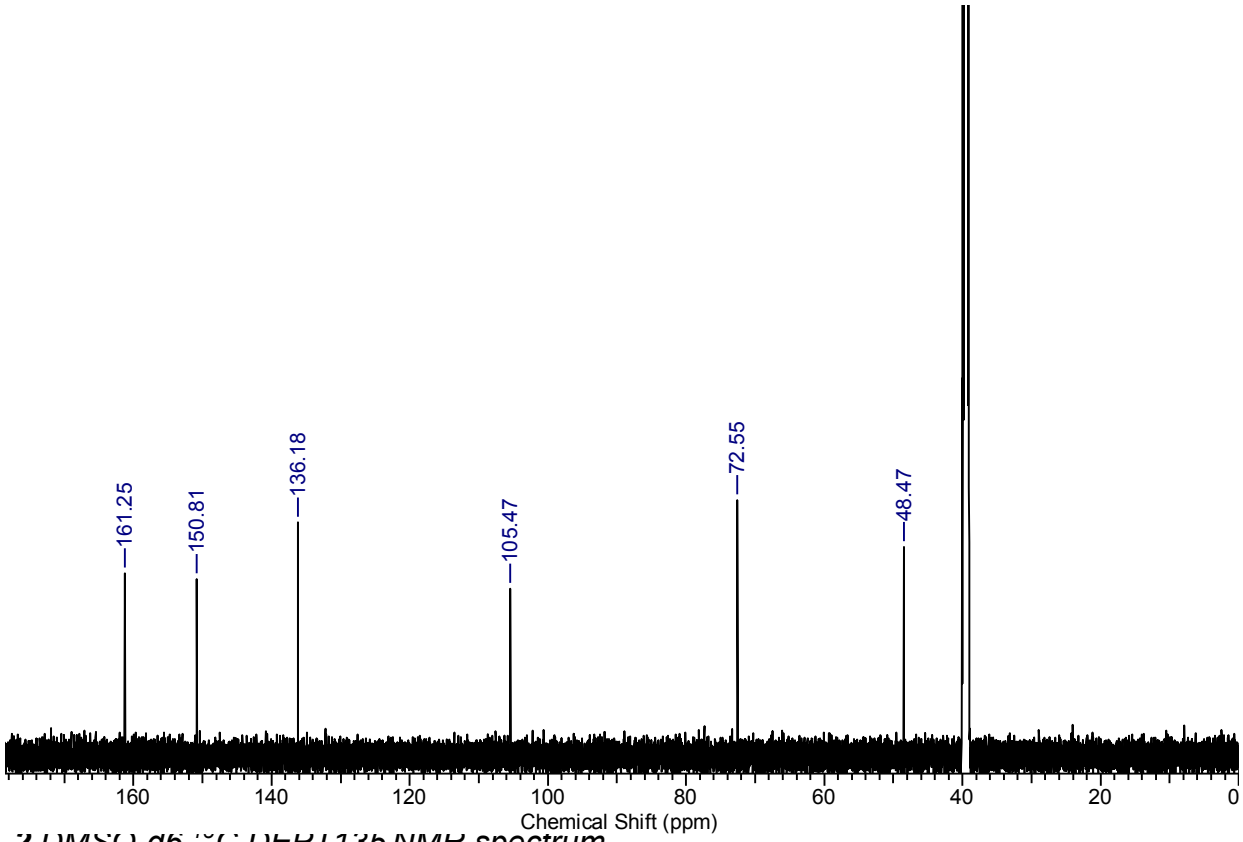
2 *DMSO-d6 ^{1}H NMR spectrum*



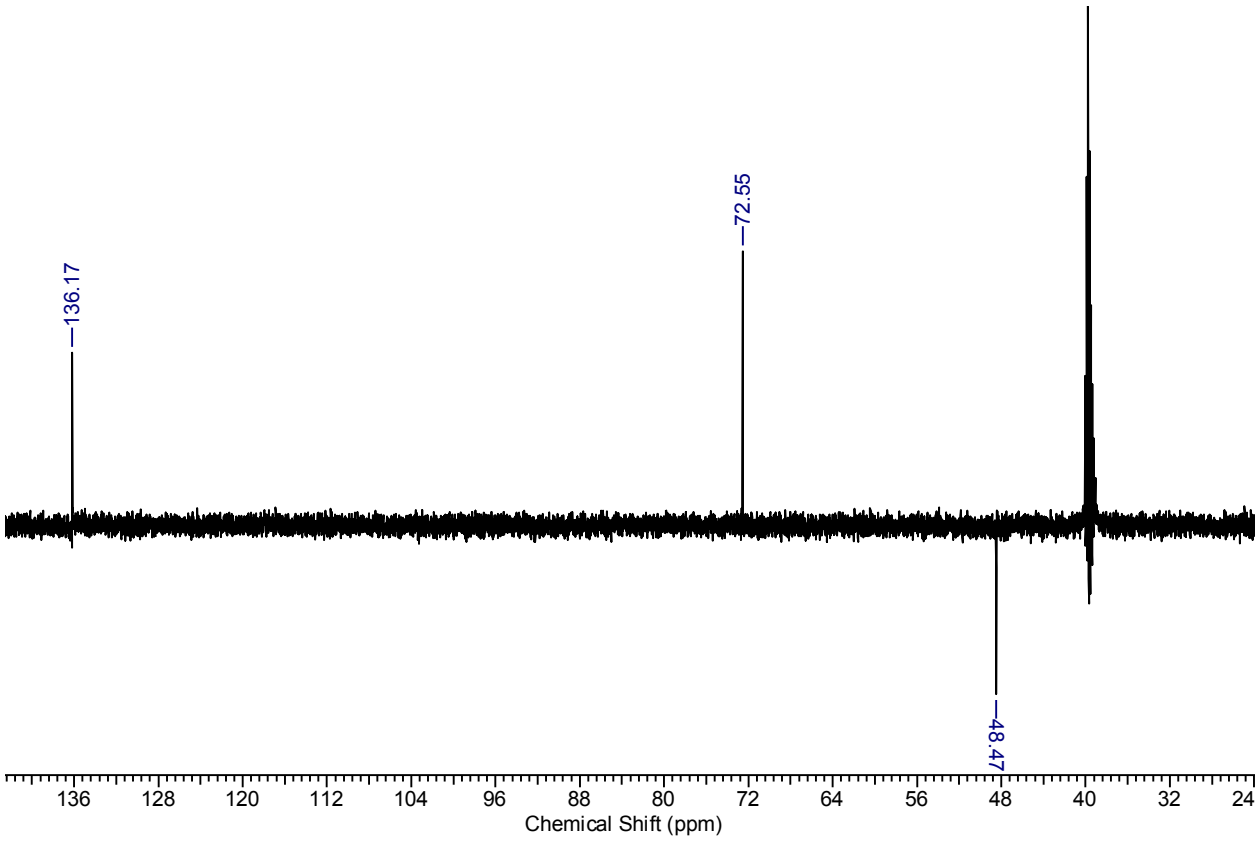
2 *DMSO-d6 ^{1}H NMR spectrum expanded*



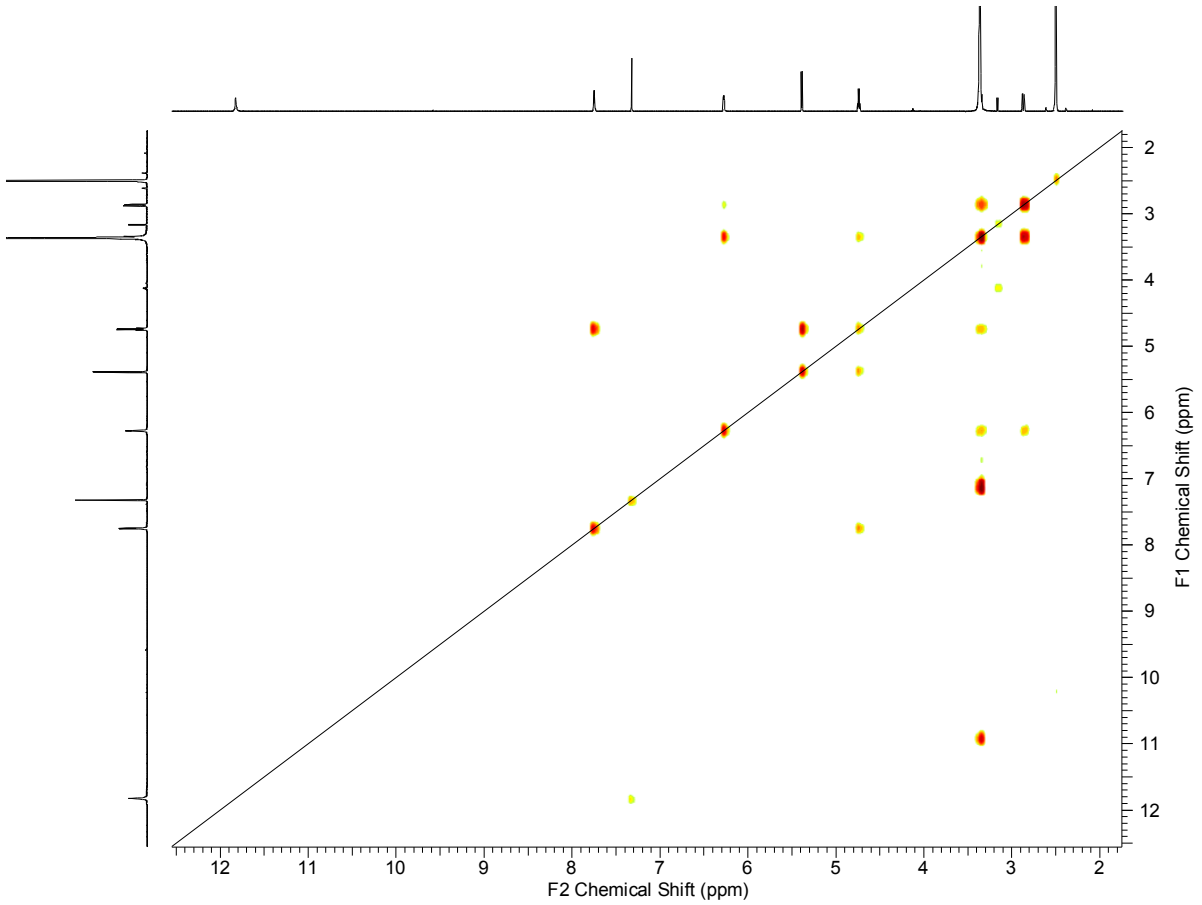
2 *DMSO-d6 ^{13}C NMR spectrum*



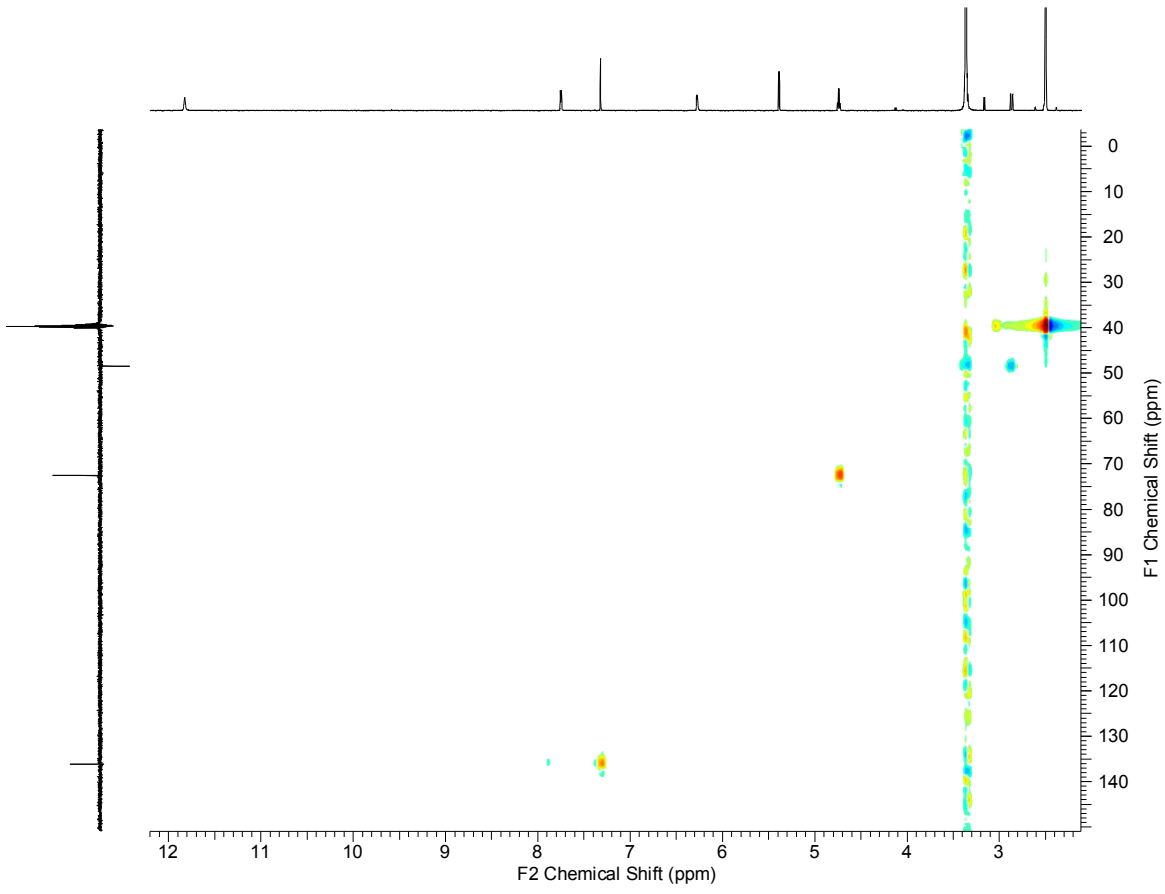
2 *DMSO-d6 ^{13}C DEPT 135 NMR spectrum*



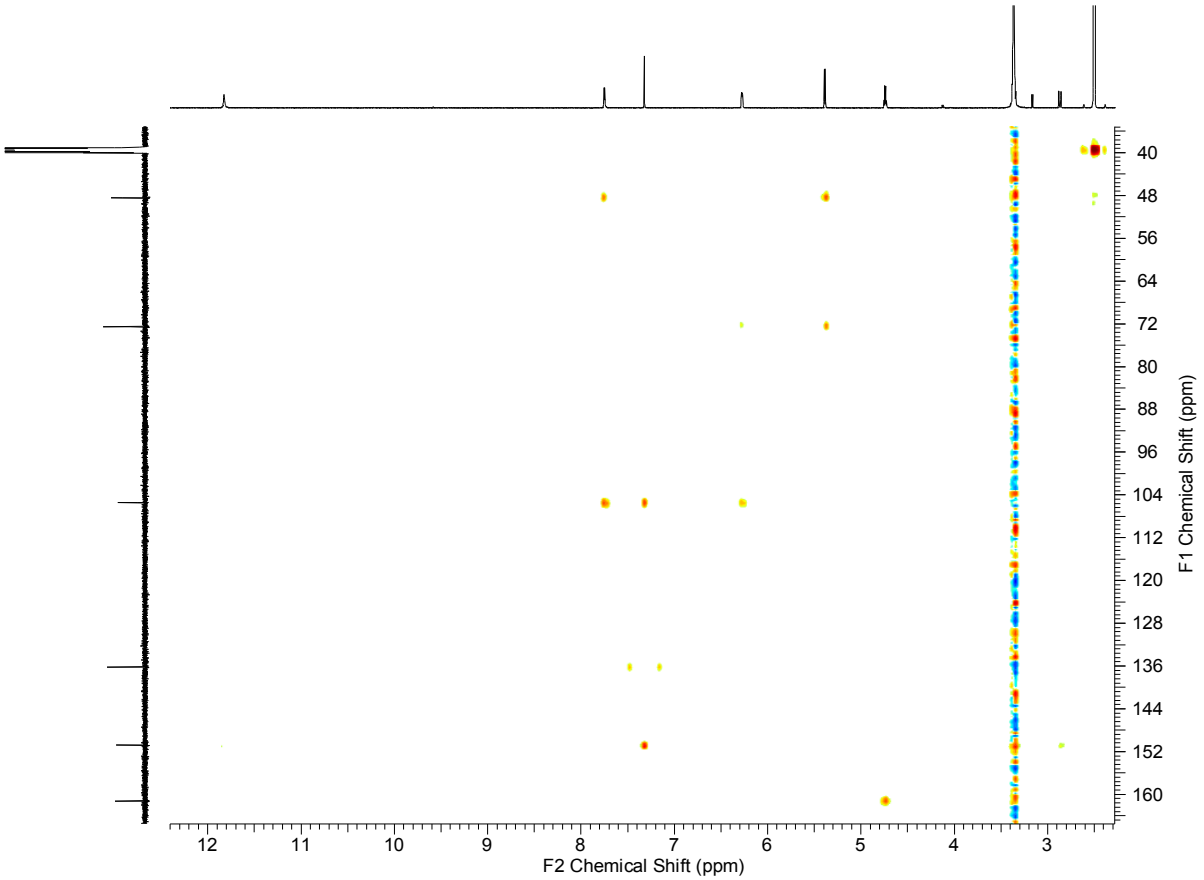
2 *DMSO-d6 ^{1}H-^{1}H COSY NMR spectrum*



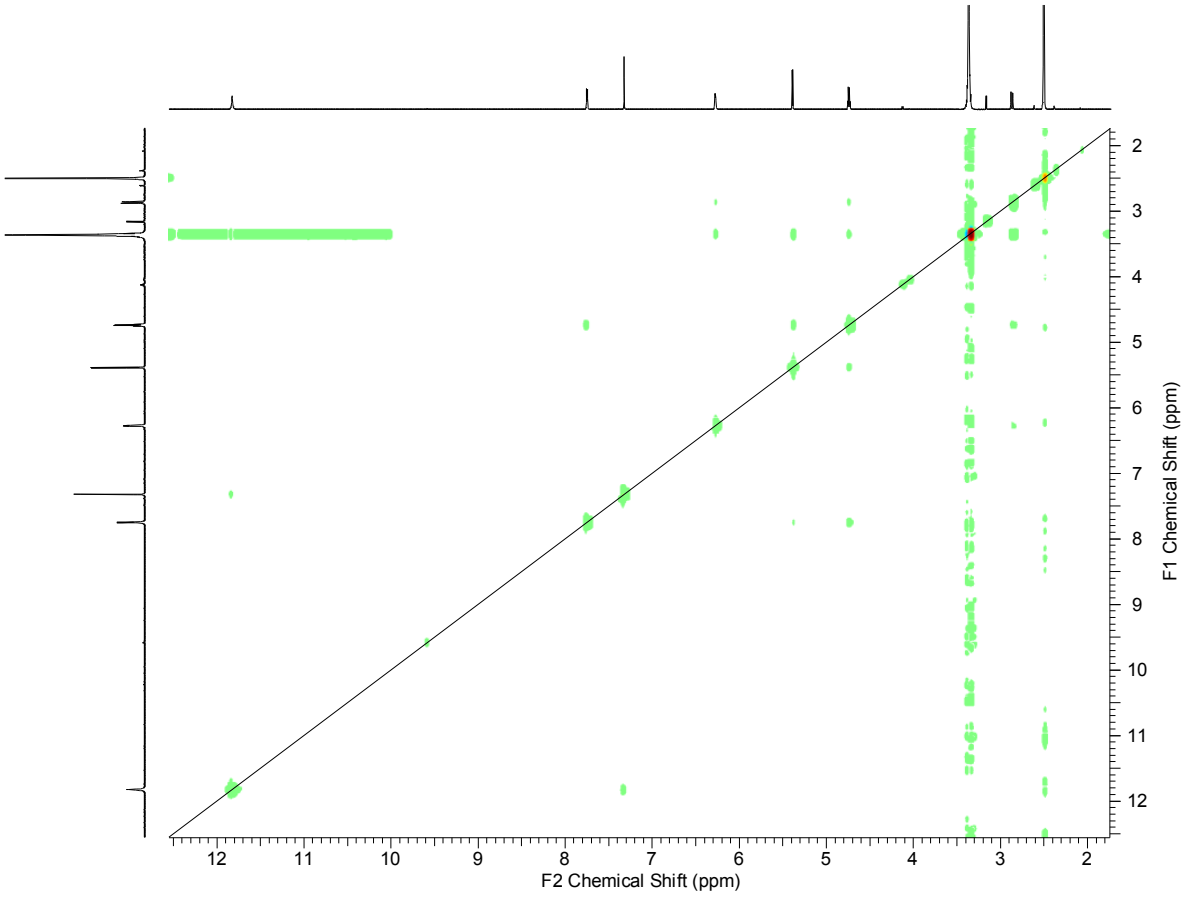
2 *DMSO-d6 ^{1}H-^{13}C HSQC NMR spectrum*



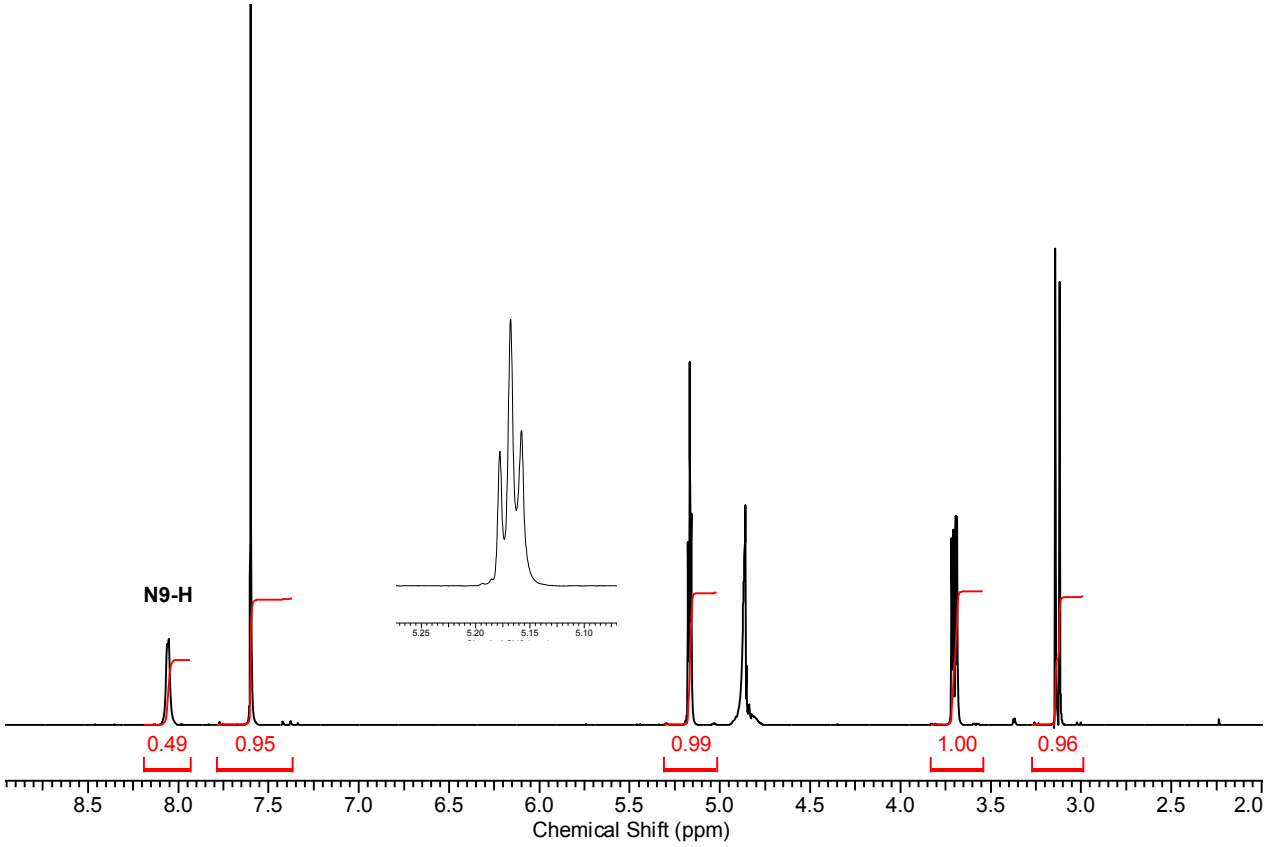
2 *DMSO-d6 ^{1}H-^{13}C HMBC NMR spectrum*



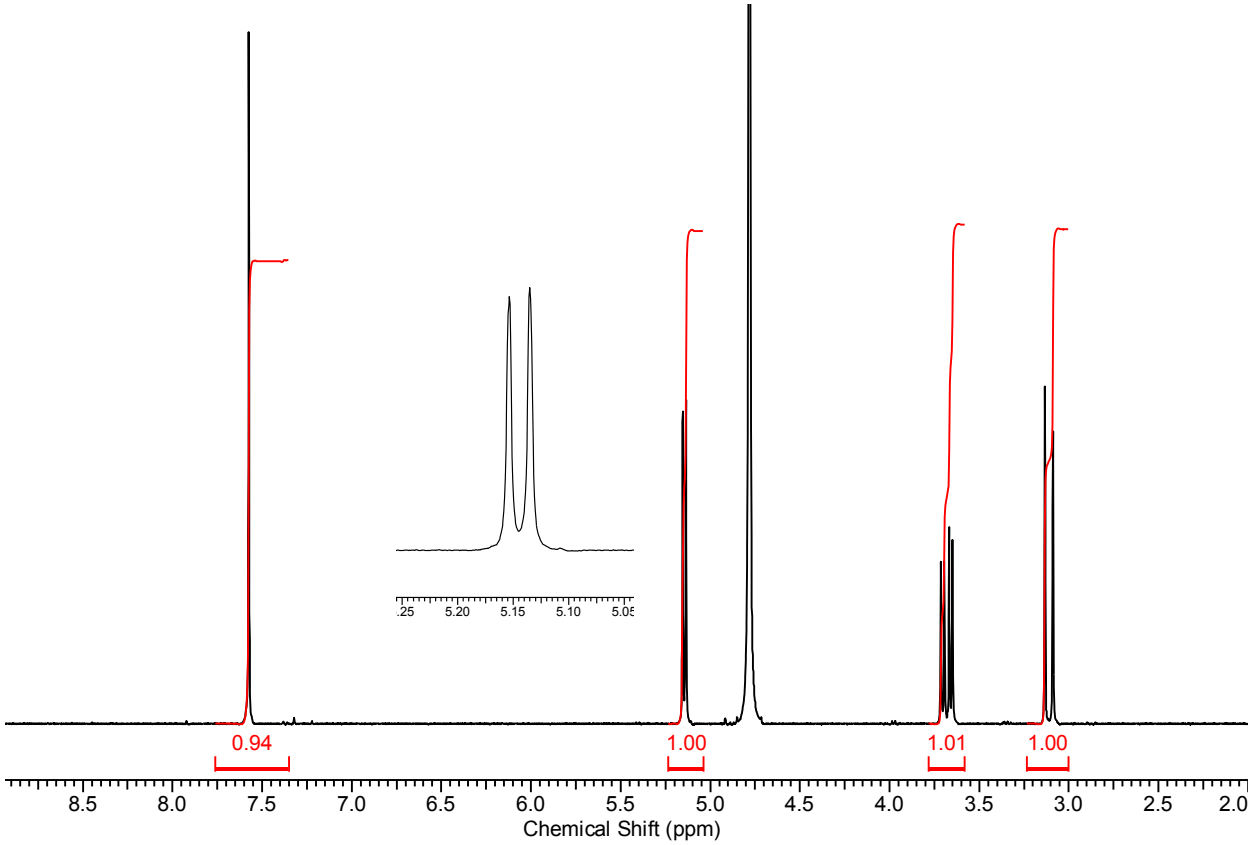
2 *DMSO-d6 ^{1}H-^{1}H NOESY NMR spectrum*



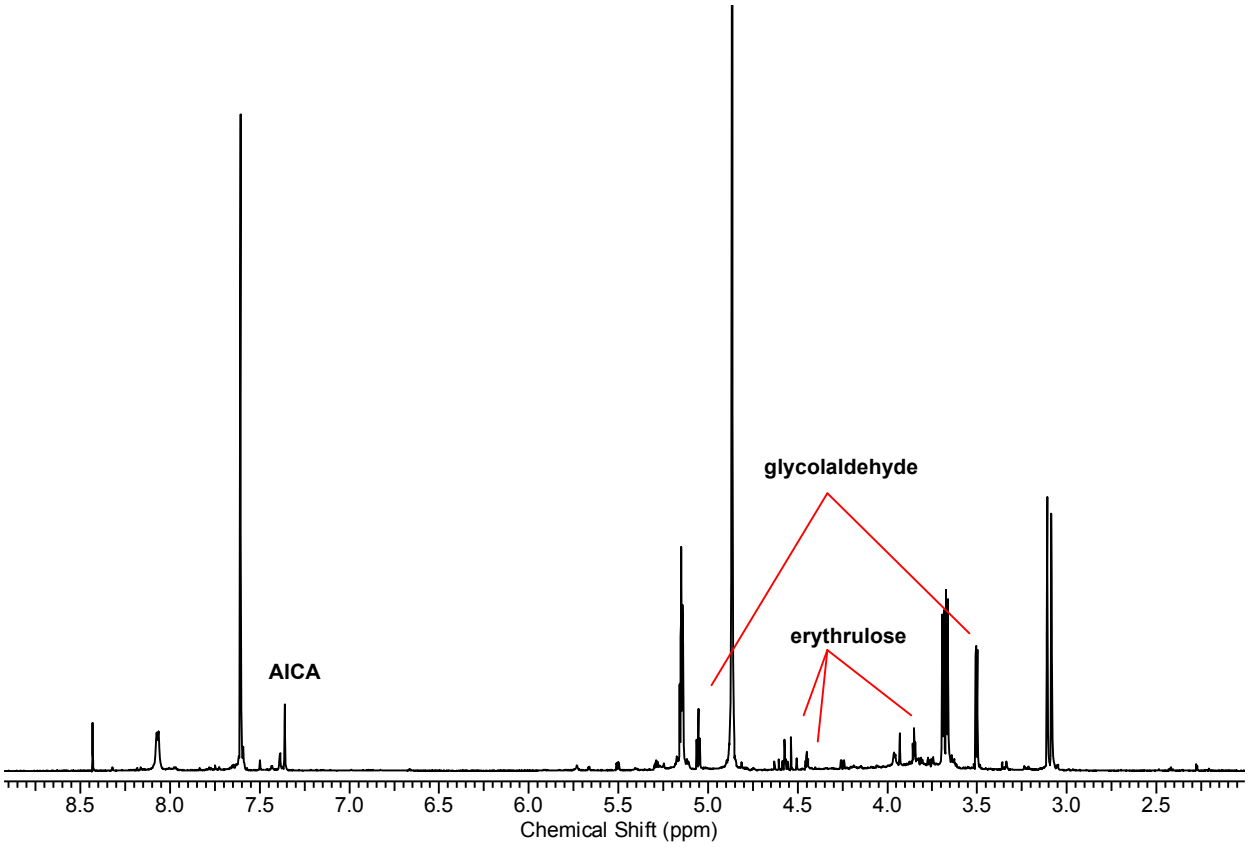
2 *10% D_2O/H_2O ^1H NMR spectrum*



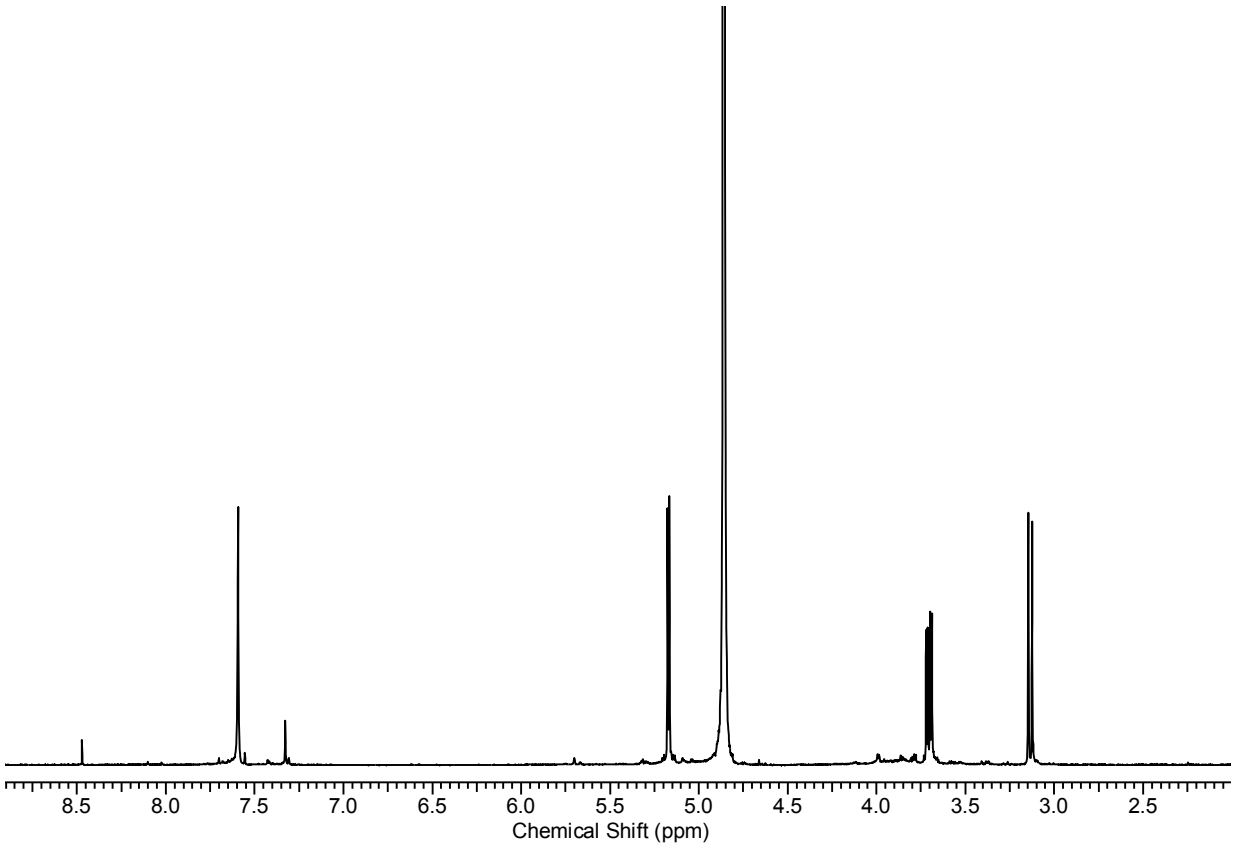
2 *D_2O ^1H NMR spectrum*



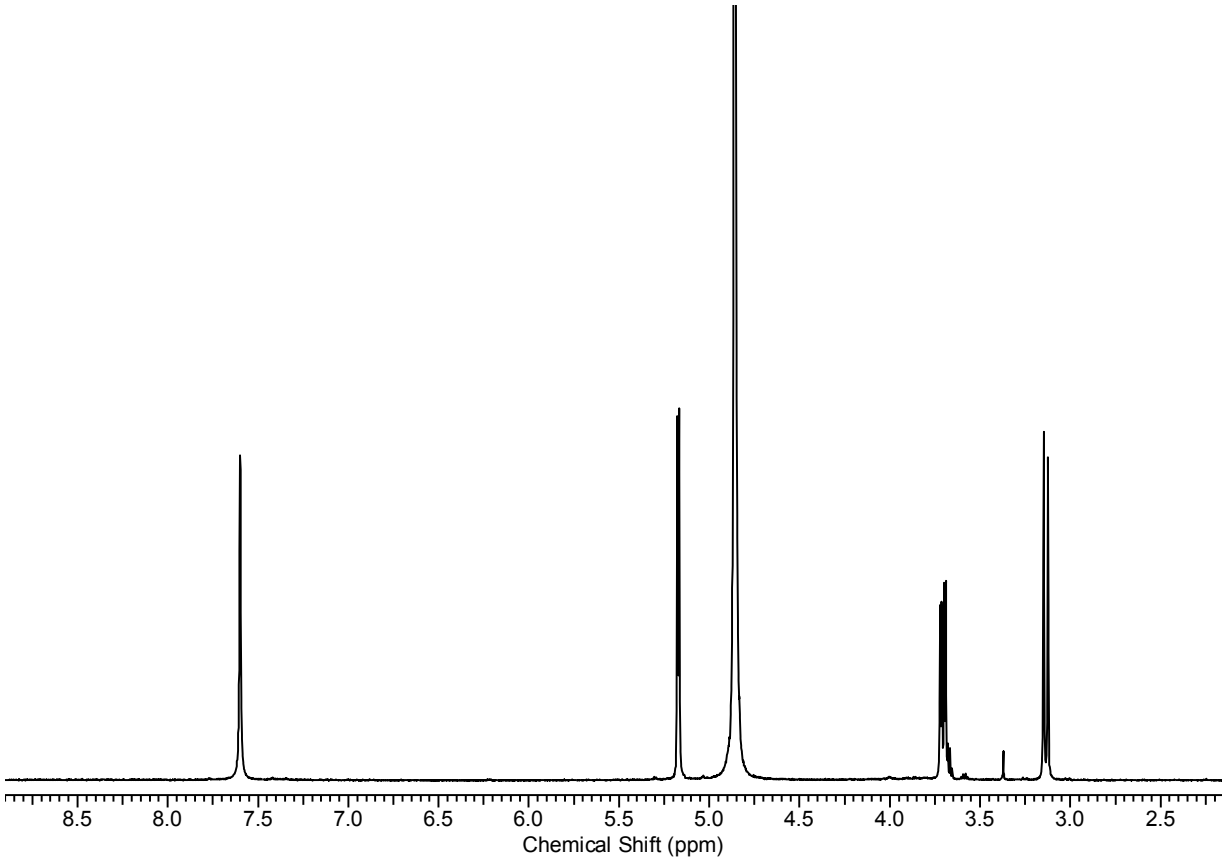
2 *Reaction mixture, 28 h, 10% D_2O/H_2O ^1H NMR spectrum*



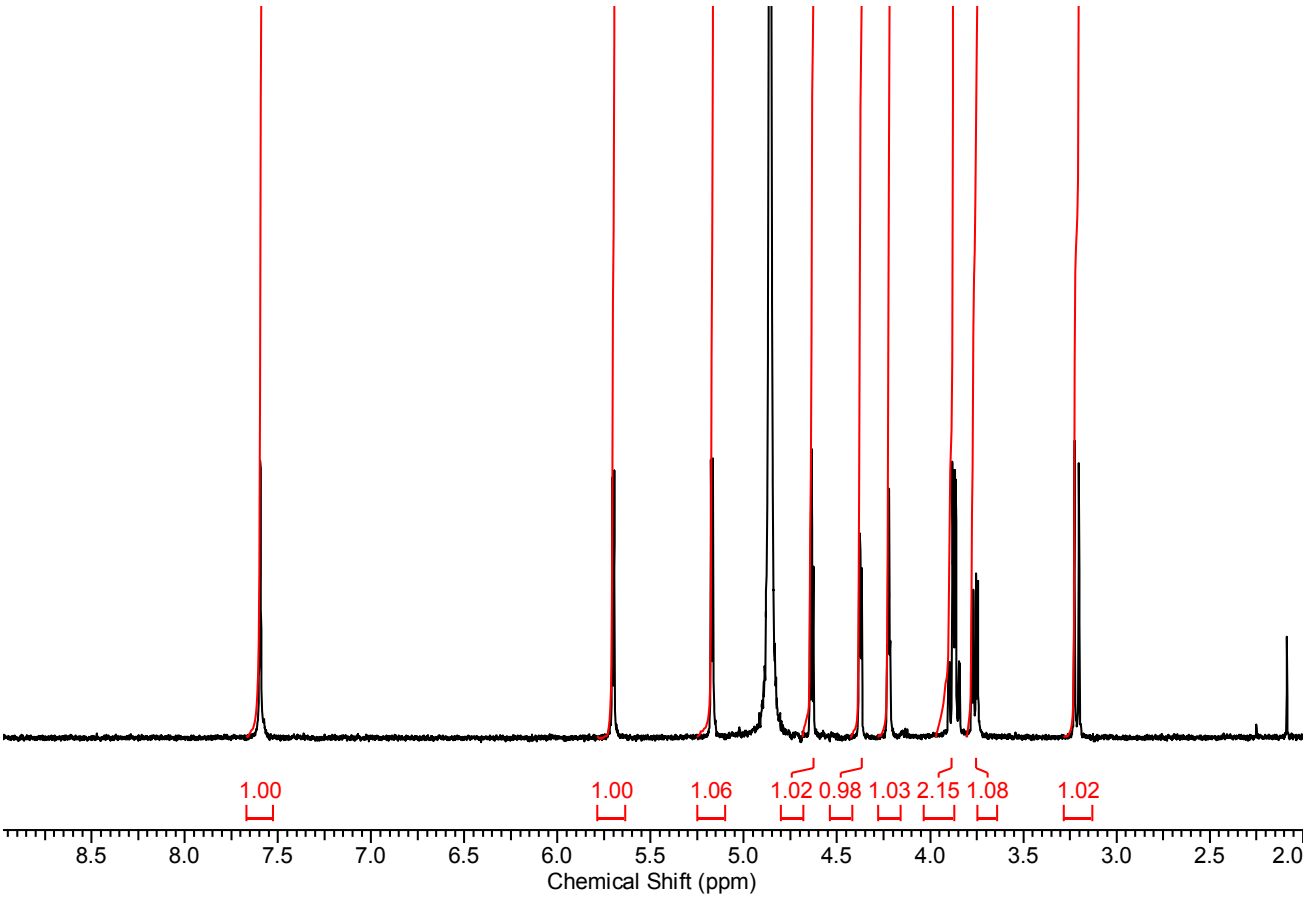
2 *Crude product after Dowex exchange and lyophilisation, D_2O ^1H NMR spectrum*



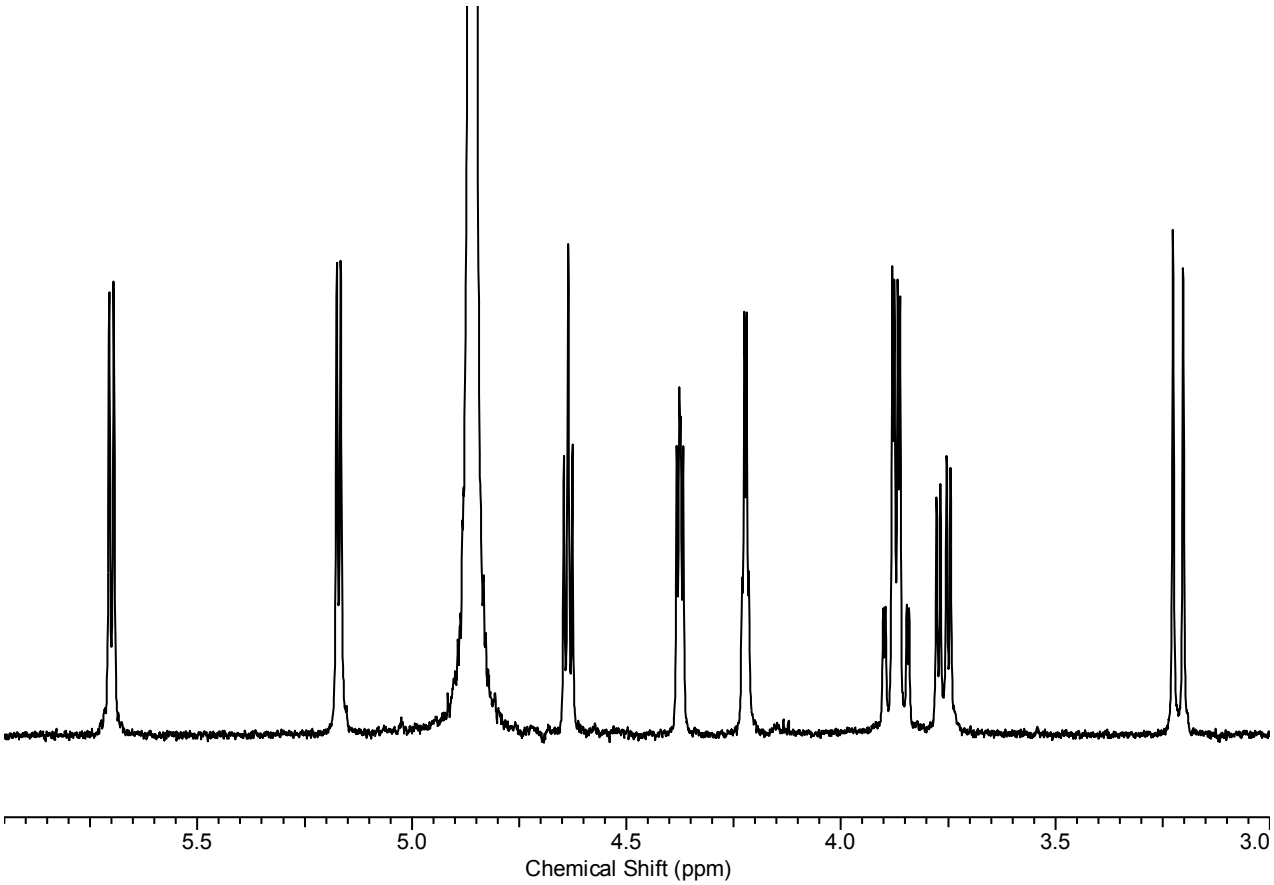
2 *after precipitation from H_2O/EtOH, D_2O ^1H NMR spectrum*



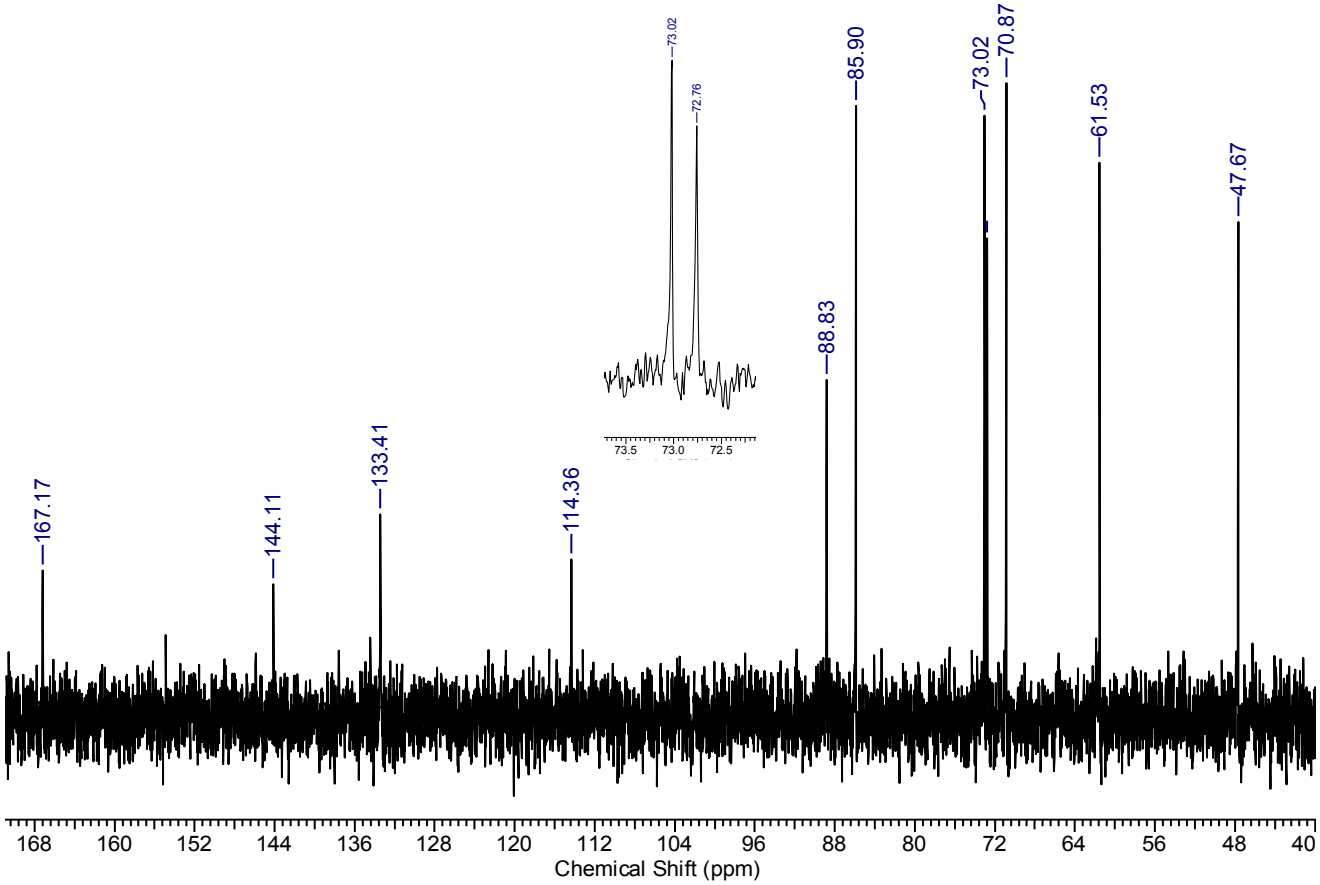
5$_A$ *D_2O ^1H NMR spectrum*



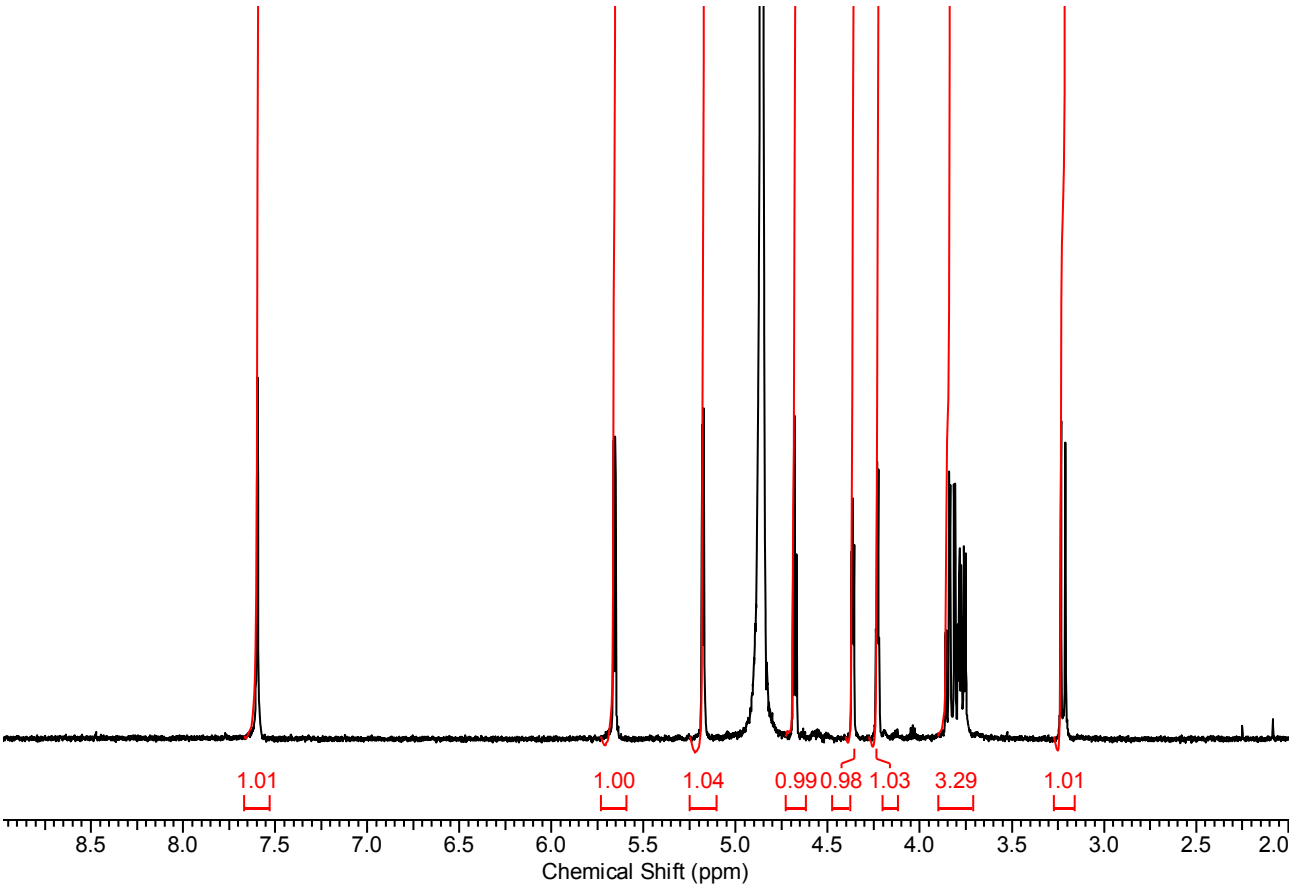
5A *D_2O ^{1}H NMR spectrum expanded*



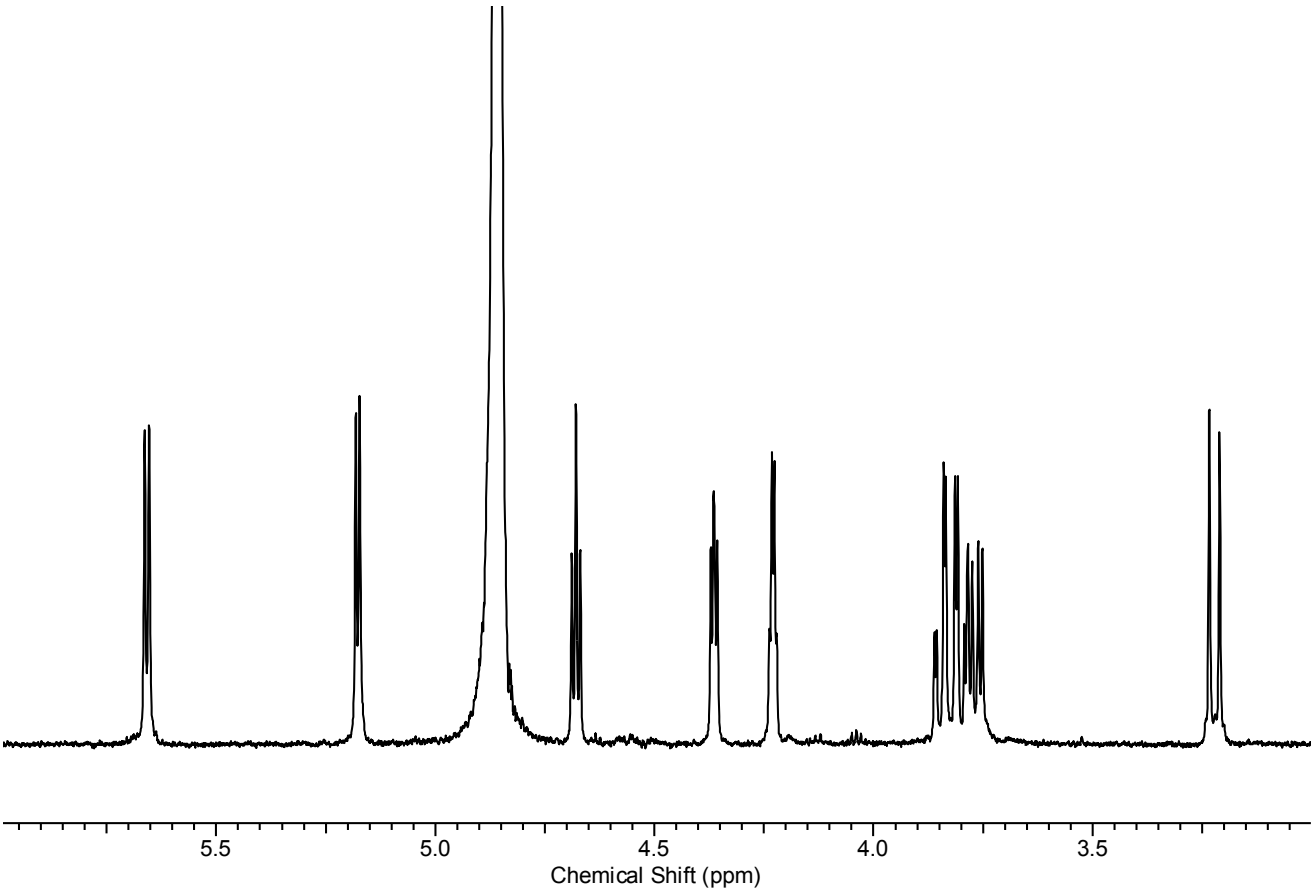
5A *D_2O ^{13}C NMR spectrum*



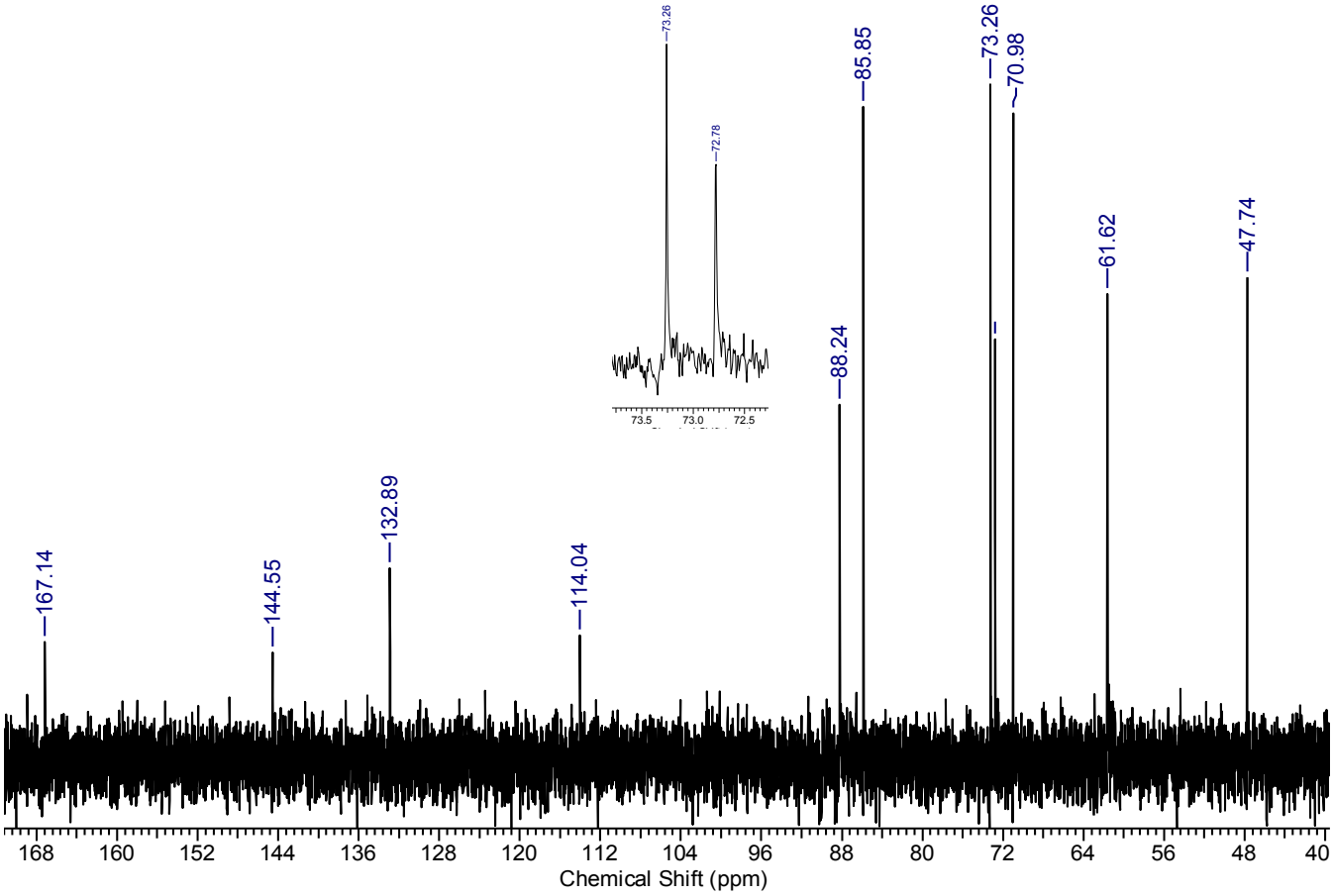
***5*$_B$** *D_2O ^1H NMR spectrum*



***5*$_B$** *D_2O ^1H NMR spectrum expanded*

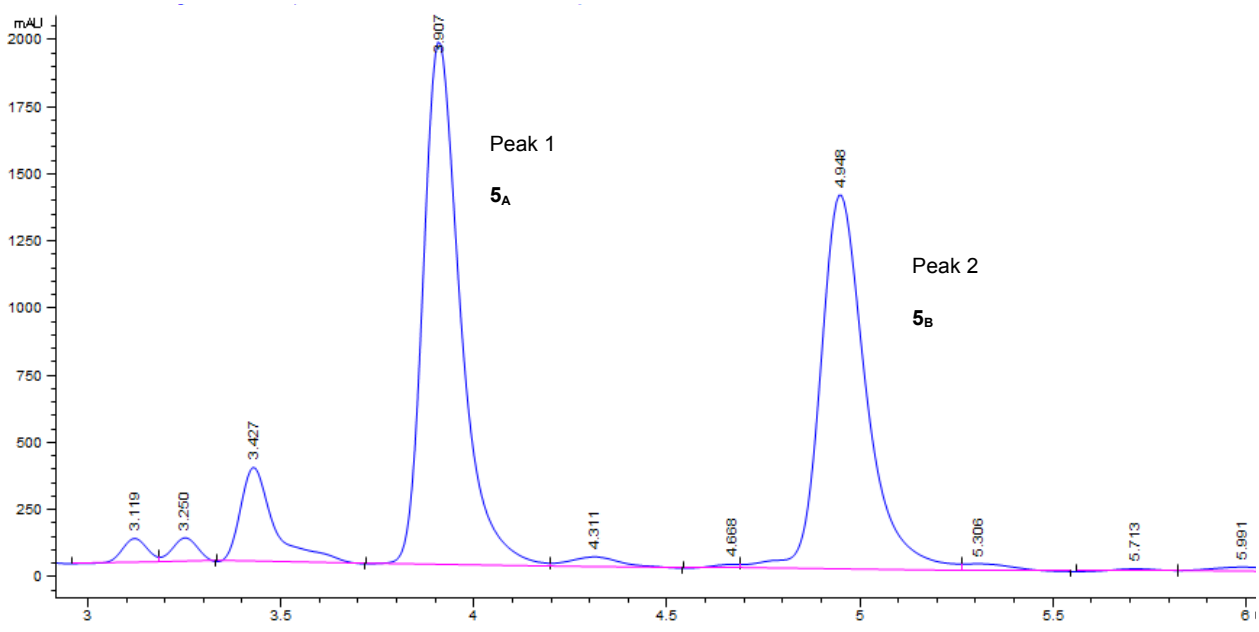


5$_B$ *D_2O ^{13}C NMR spectrum*

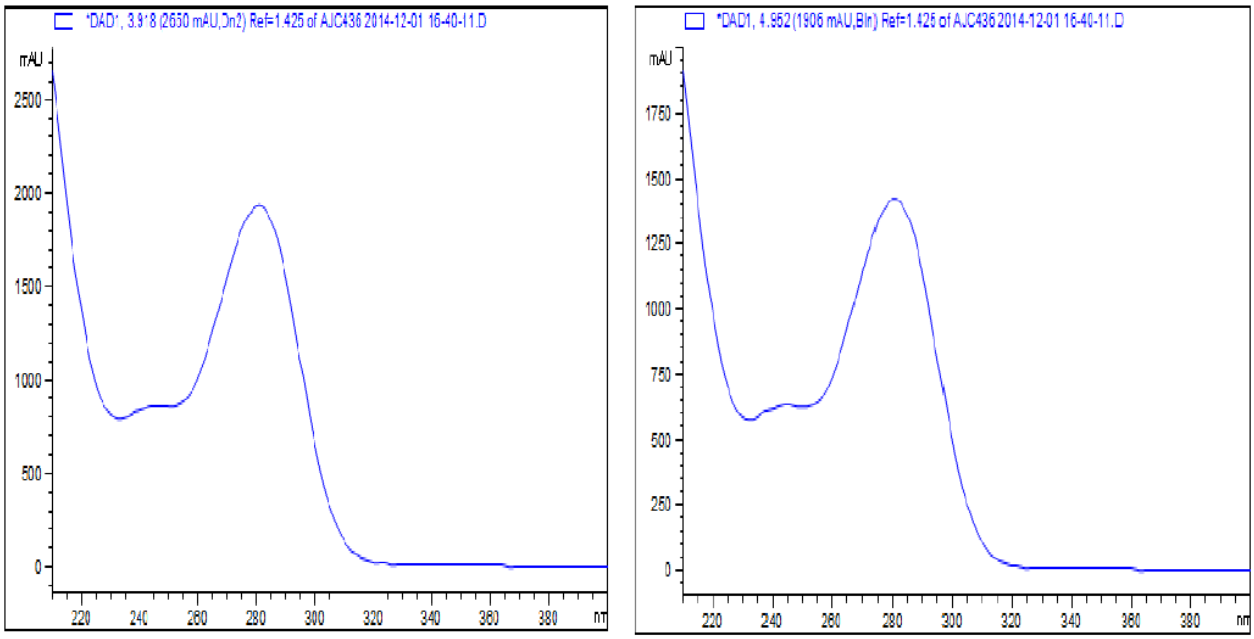


HPLC traces

*Crude **5** HPLC trace, isocratic water*

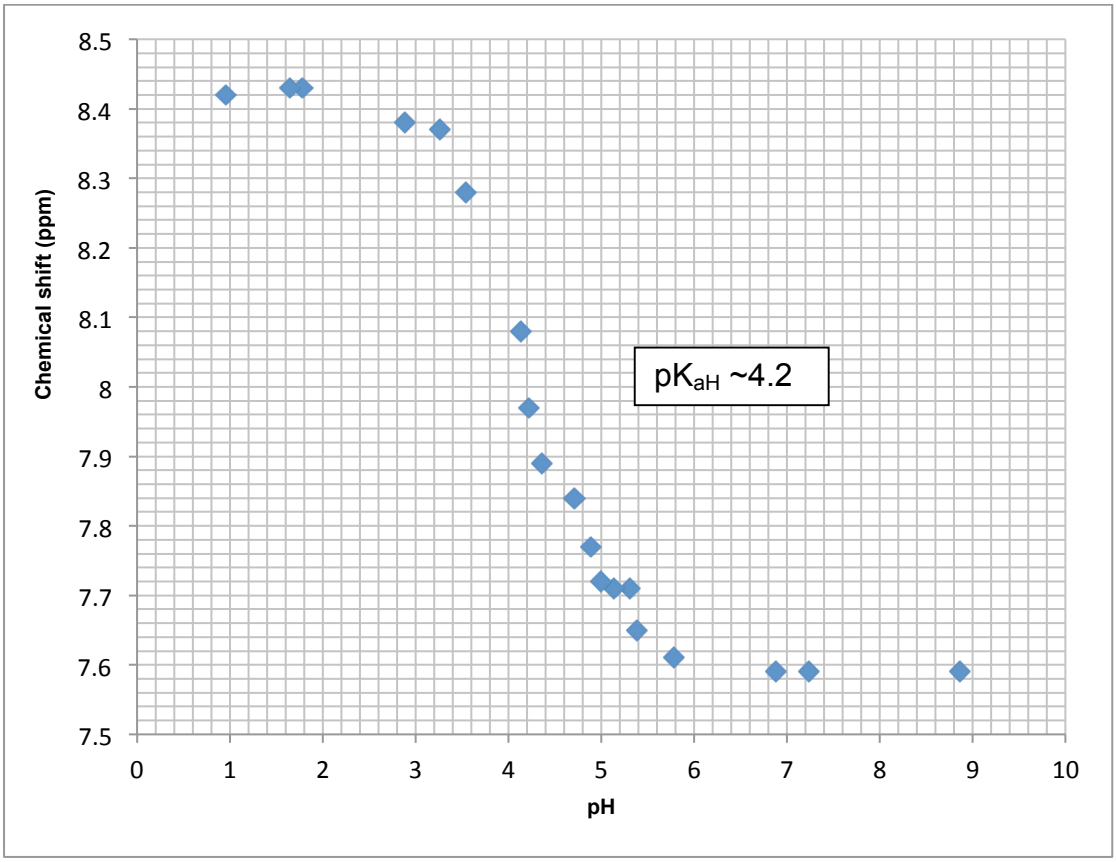


UV traces for peak 1 and peak 2



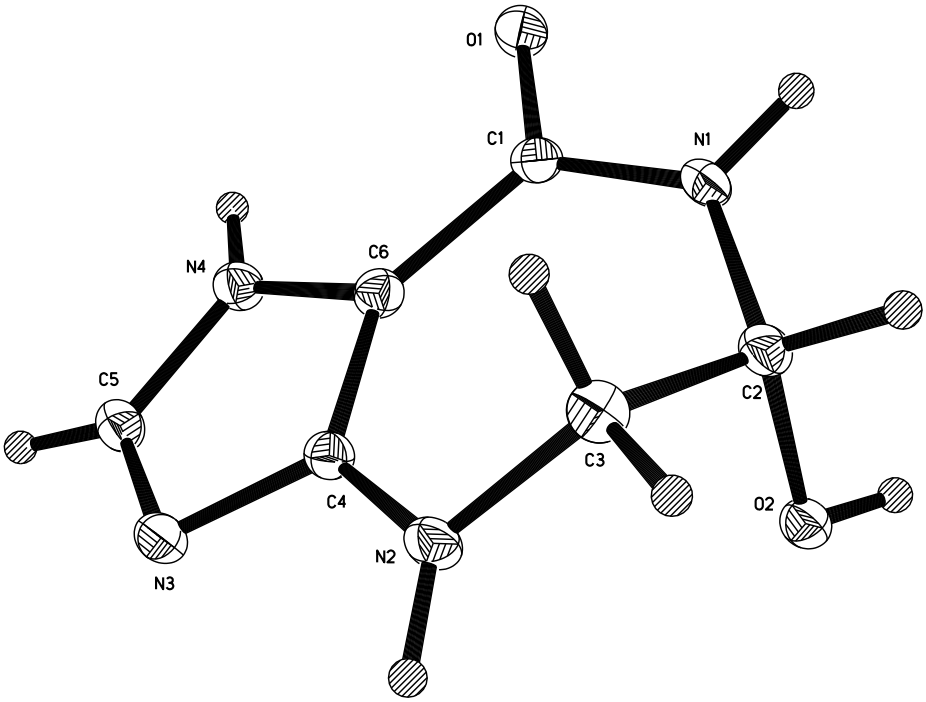
pH titration of azepinomycin (2)

*NMR titration curve (measuring shift of C2-**H** peak vs pH) with calculated pK_{aH} for **2***

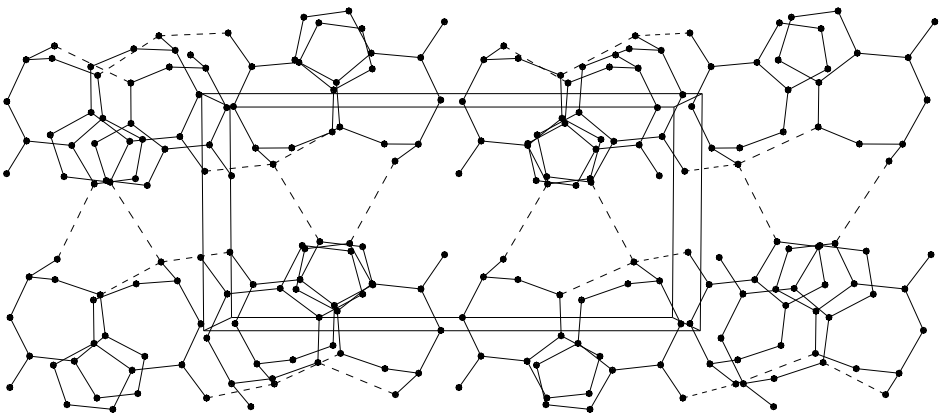


Crystallography

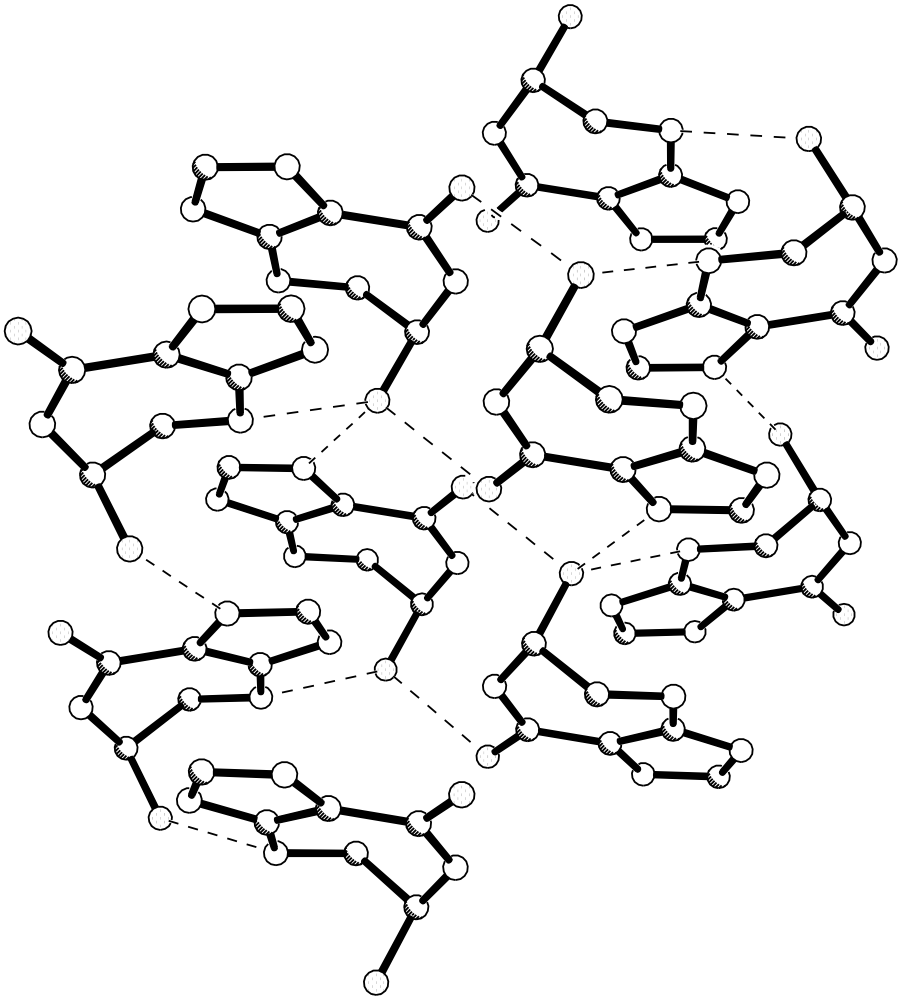
*ORTEP plot of azepinomycin (**2**)*



*Cell packing of azepinomycin **2**, viewed down the c-axis*



Intermolecular hydrogen bonding interactions of azepinomycin ***2***



Crystal data structure refinement table

Identification code	xstr0044
Empirical formula	$C_6N_4O_2H_8$
Formula weight	168.16
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.68948(7)
b/Å	14.04389(15)
c/Å	7.22458(9)
α/°	90
β/°	93.8750(11)
γ/°	90
Volume/Å^3	677.171(13)
Z	4
ρ_{calc}mg/mm^3	1.649
m/mm^{-1}	1.090
F(000)	352.0
Crystal size/mm^3	0.28 × 0.26 × 0.15
Radiation	Cu Kα (λ = 1.5418)
2Θ range for data collection	12.606 to 147.344°
Index ranges	-8 ≤ h ≤ 8, -17 ≤ k ≤ 17, -8 ≤ l ≤ 8
Reflections collected	9206
Independent reflections	1328[R(int) = 0.0198]
Data/restraints/parameters	1328/0/110
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.1007
Largest diff. peak/hole / e Å^{-3}	0.69/-0.66

Bond lengths table

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.2558(17)	N3	C5	1.3307(18)
O2	C2	1.4235(16)	N4	C5	1.3338(19)
N1	C1	1.3498(18)	N4	C6	1.3909(17)
N1	C2	1.4477(17)	C1	C6	1.4477(19)
N2	C3	1.4482(18)	C2	C3	1.5326(19)
N2	C4	1.3678(18)	C4	C6	1.3922(18)
N3	C4	1.3680(18)			

Bond angles table

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C2	127.73(11)	N1	C2	C3	114.13(11)
C4	N2	C3	117.48(11)	N2	C3	C2	112.87(11)
C5	N3	C4	104.93(11)	N2	C4	N3	120.91(12)
C5	N4	C6	107.52(11)	N2	C4	C6	128.62(13)
O1	C1	N1	120.63(12)	N3	C4	C6	110.47(12)
O1	C1	C6	119.56(12)	N3	C5	N4	112.67(12)
N1	C1	C6	119.80(12)	N4	C6	C1	119.71(12)
O2	C2	N1	112.05(11)	N4	C6	C4	104.40(12)
O2	C2	C3	108.33(10)	C4	C6	C1	135.80(13)