

Supporting Information for:

Analysis of the Enol-Keto Tautomers of Indole-3-pyruvic Acid

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NMR data for: ¹H nmr IPyA in CD₃OD, t = 0 h

¹H nmr IPyA in CD₃OD, t = 24 h

¹³C nmr IPyA in CD₃OD, t = 24 h

¹H nmr IPyA in D₂O (NaHCO₃), pH ~9

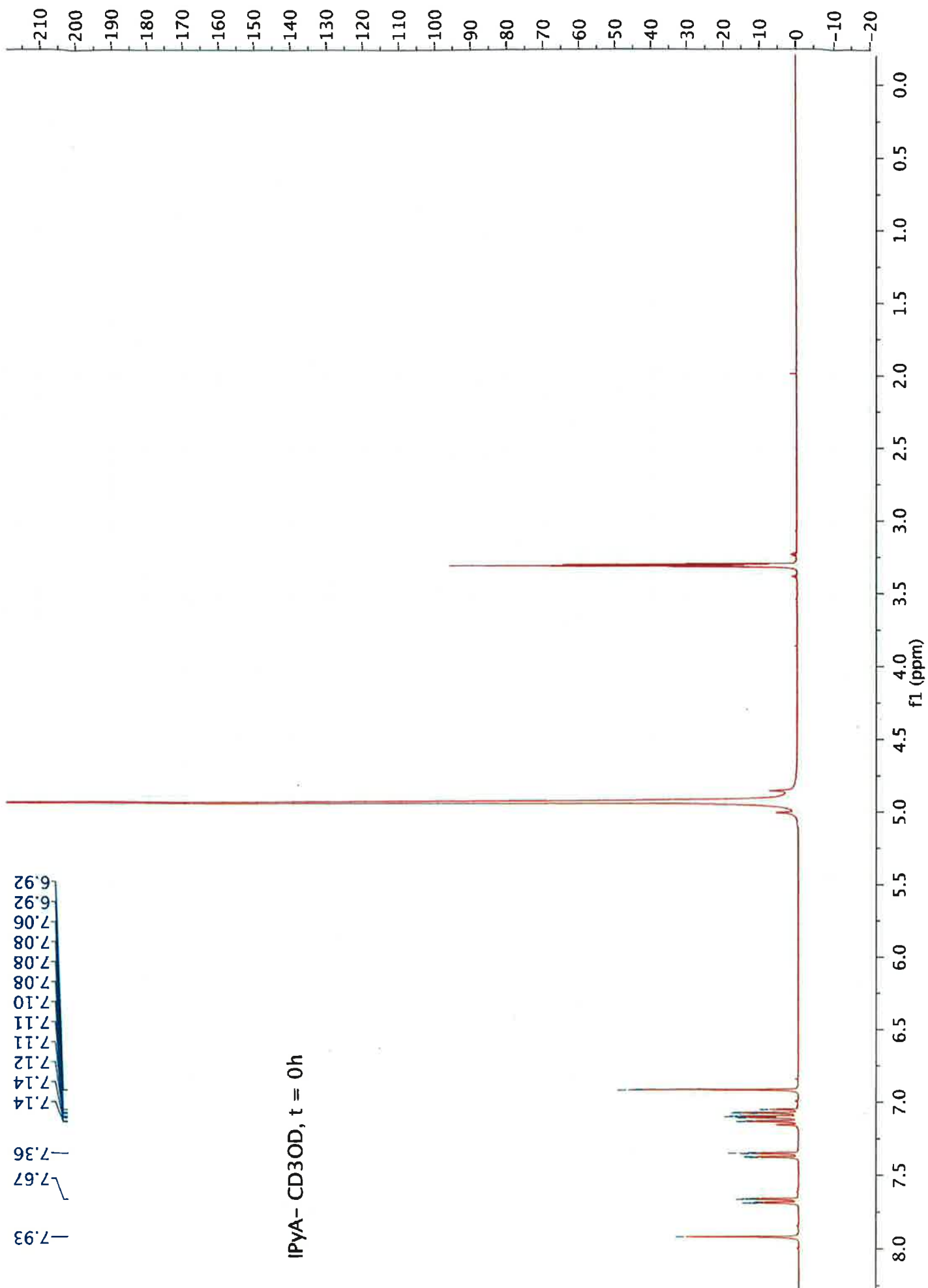
¹H nmr IPyA in D₂O (NaOH), pH ~12

¹H nmr IPyA in D₂O, KH₂PO₄/K₂HPO₄ buffer (pH 8.5), t = 0 h

¹H nmr IPyA in D₂O, KH₂PO₄/K₂HPO₄ buffer (pH 8.5), t = 24 h @ 40°C

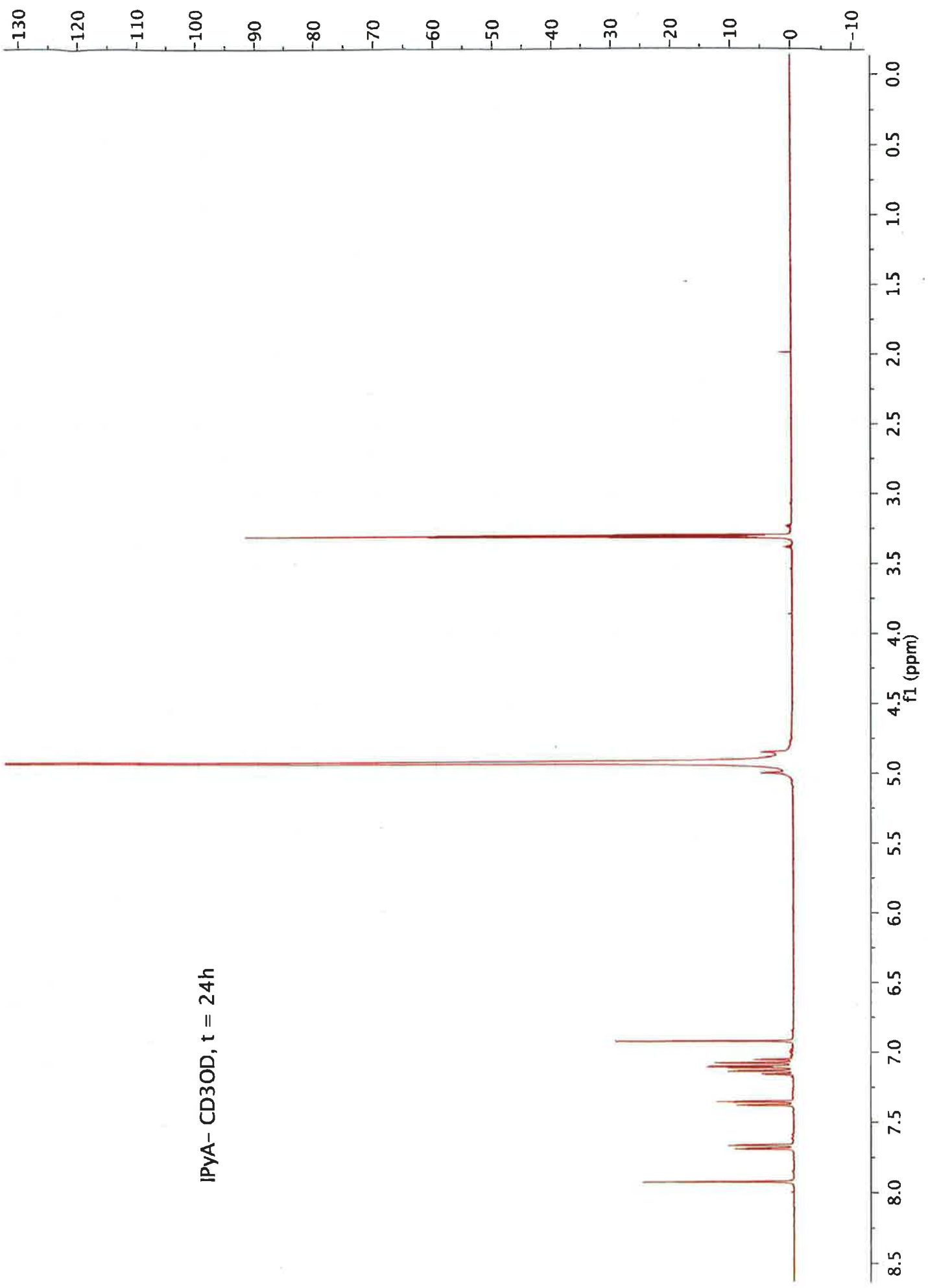
¹³C nmr IPyA in D₂O, KH₂PO₄/K₂HPO₄ buffer (pH 8.5), t = 24 h @ 40°C

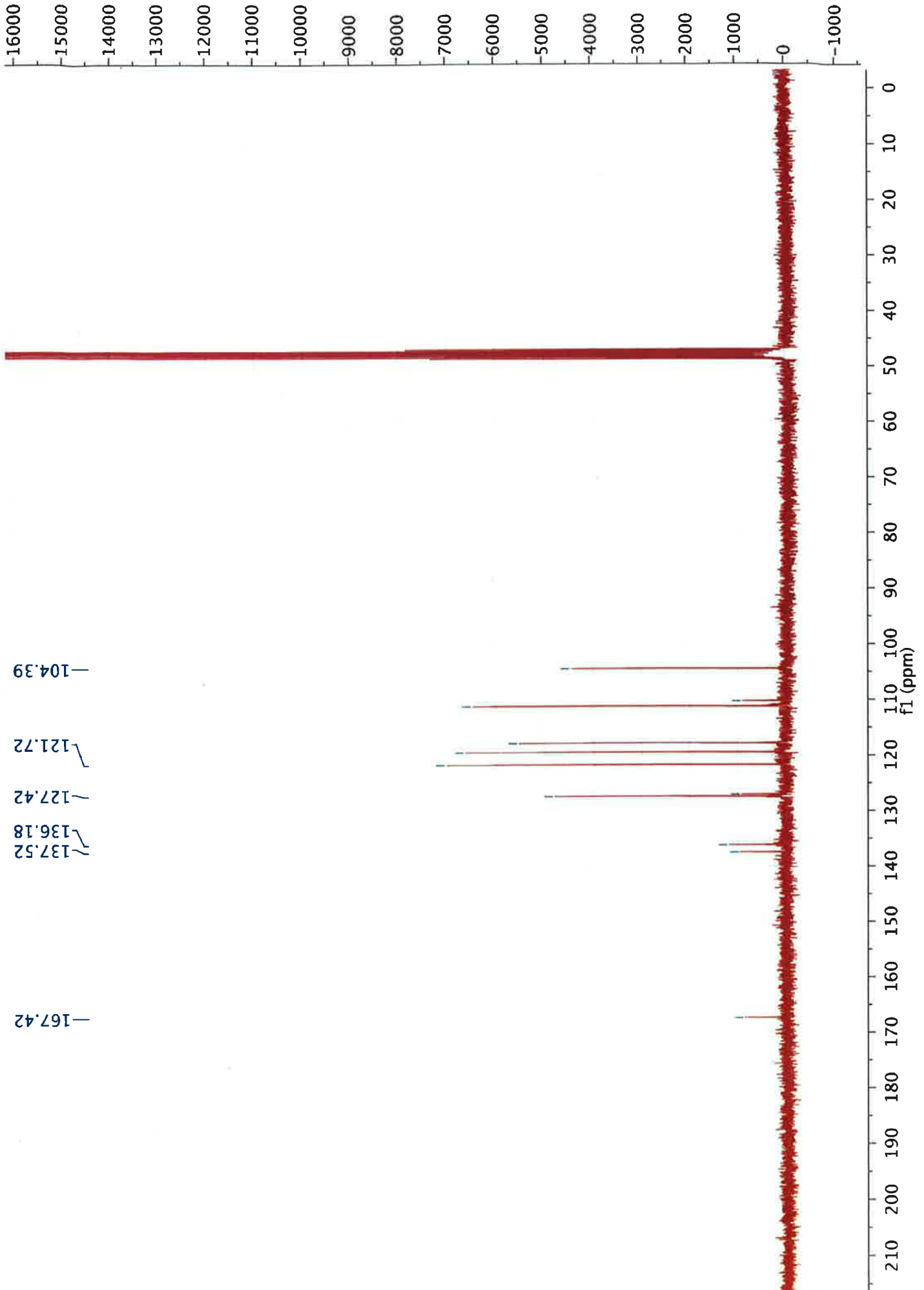
HSQC IPyA in D₂O, KH₂PO₄/K₂HPO₄ buffer (pH 8.5), t = 24 h @ 40°C



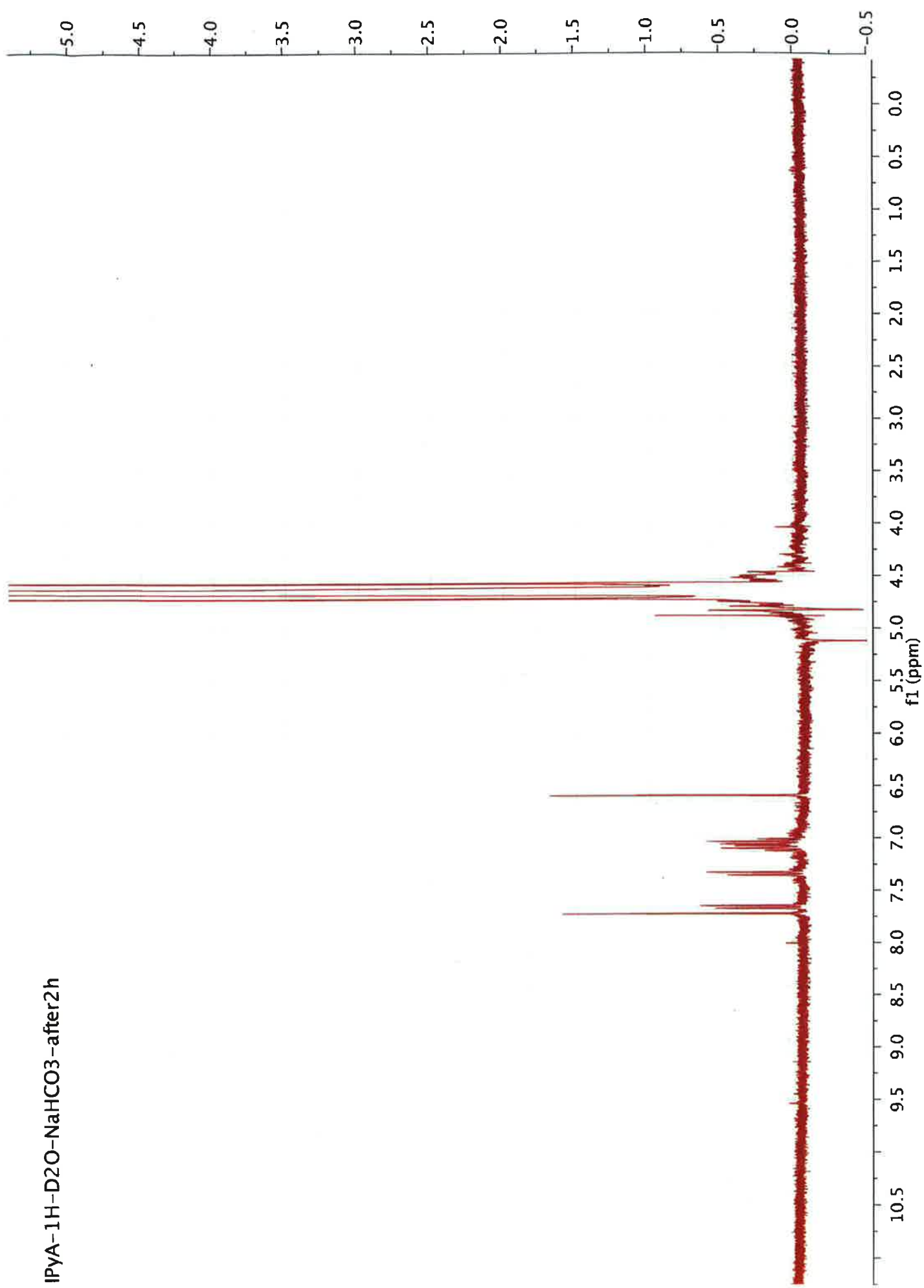
IPyA- CD3OD, t = 0h

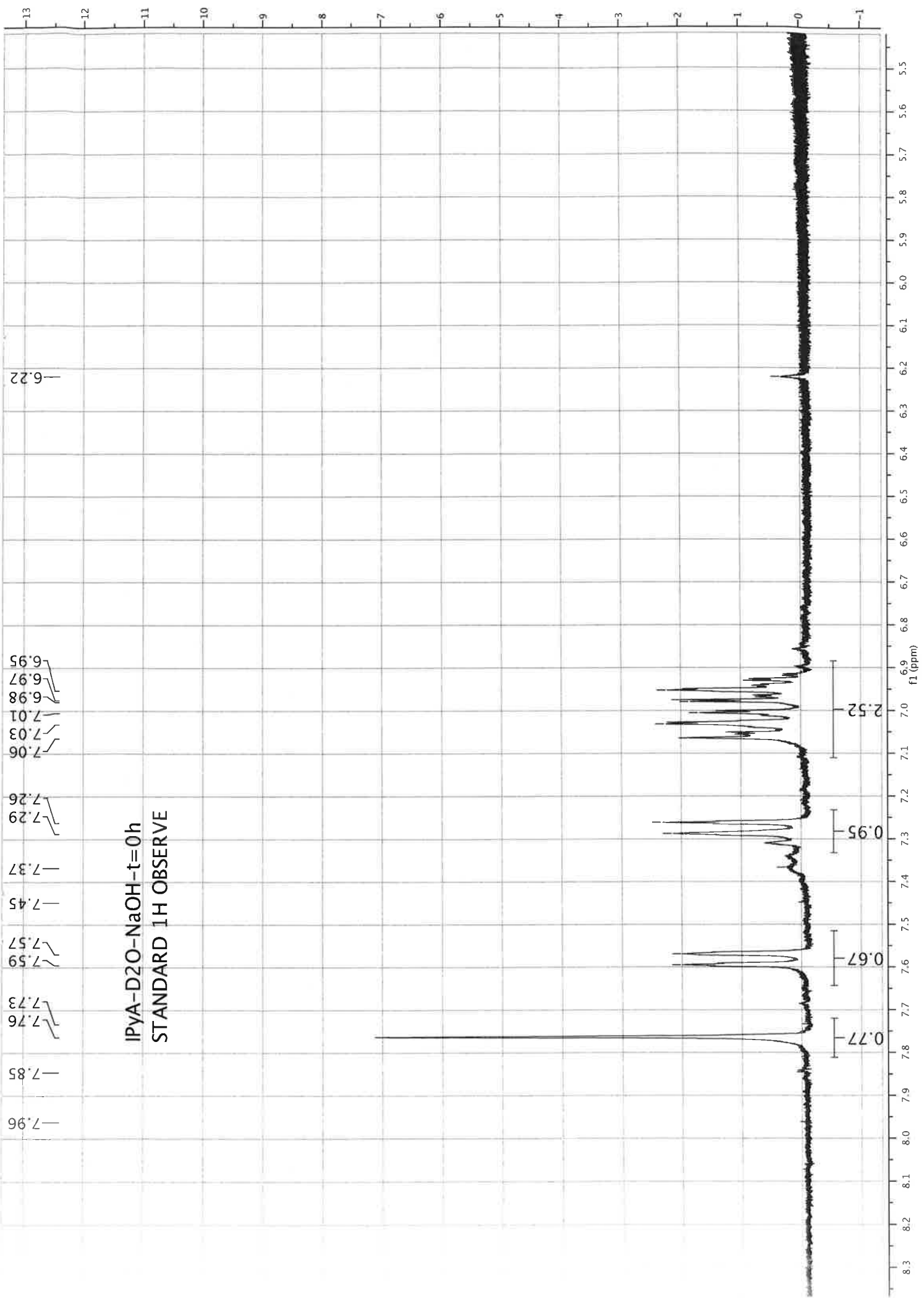
IPyA- CD3OD, t = 24h





IPyA-1H-D2O-NaHCO3--after2h

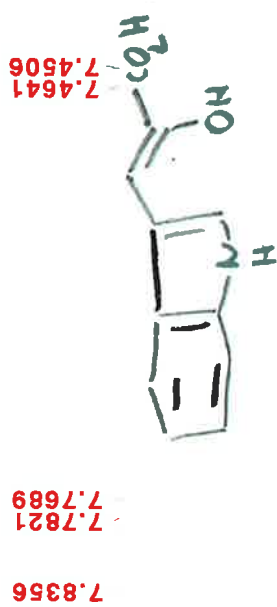




IPyA-D2O-NaOH-t=0h
STANDARD 1H OBSERVE

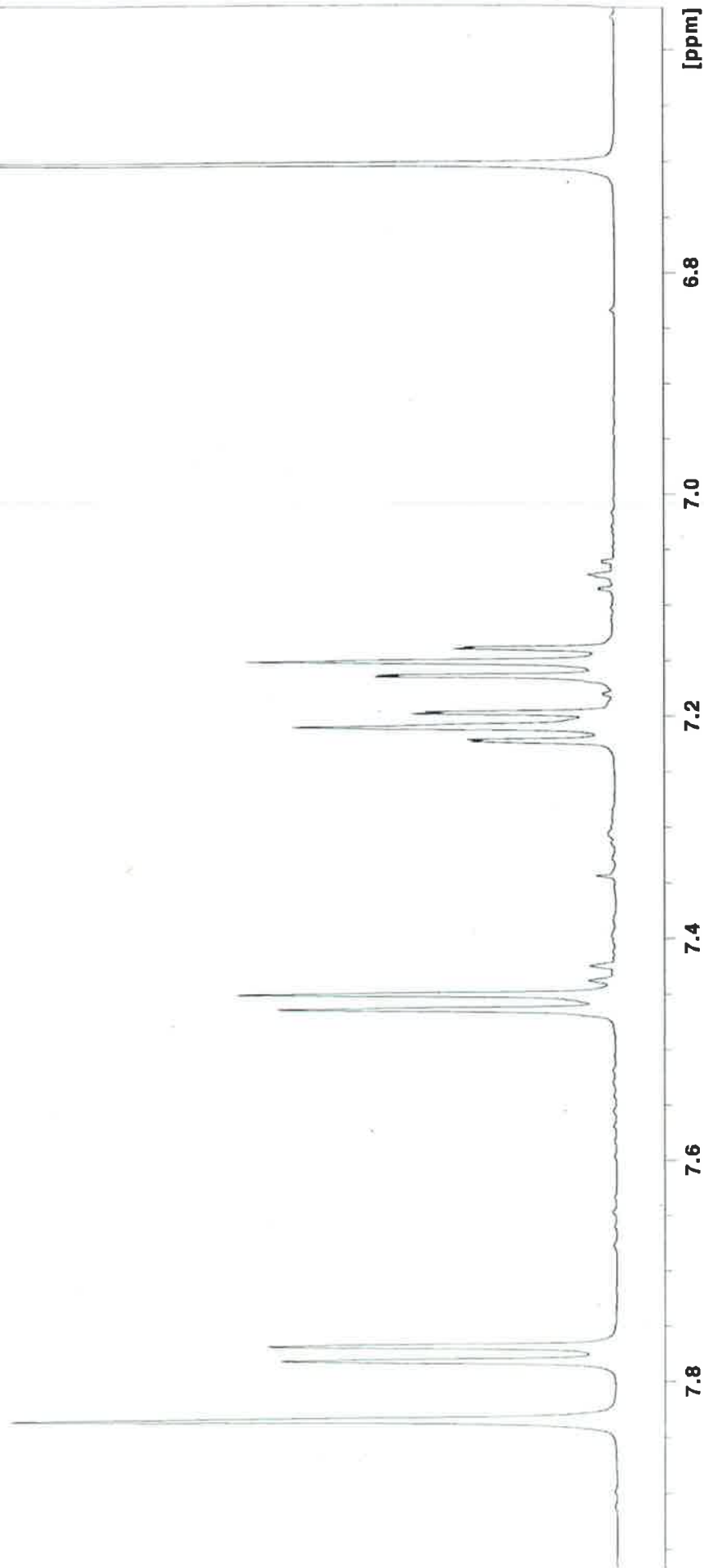
IpyA_repeat 2 1 /opt/data/hjh
IpyA_repeat for publication

$D_2O/K_2H_2PO_4/K_2HPO_4$ BUFFER, $t=0h$



7.2230
7.2214
7.2096
7.1978
7.1961
7.1644
7.1630
7.1512
7.1395
7.1380

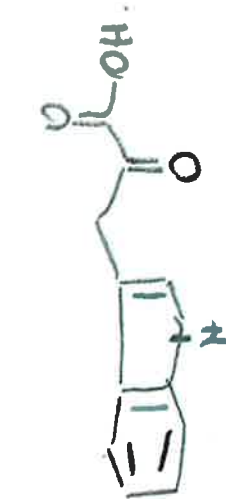
6.7037



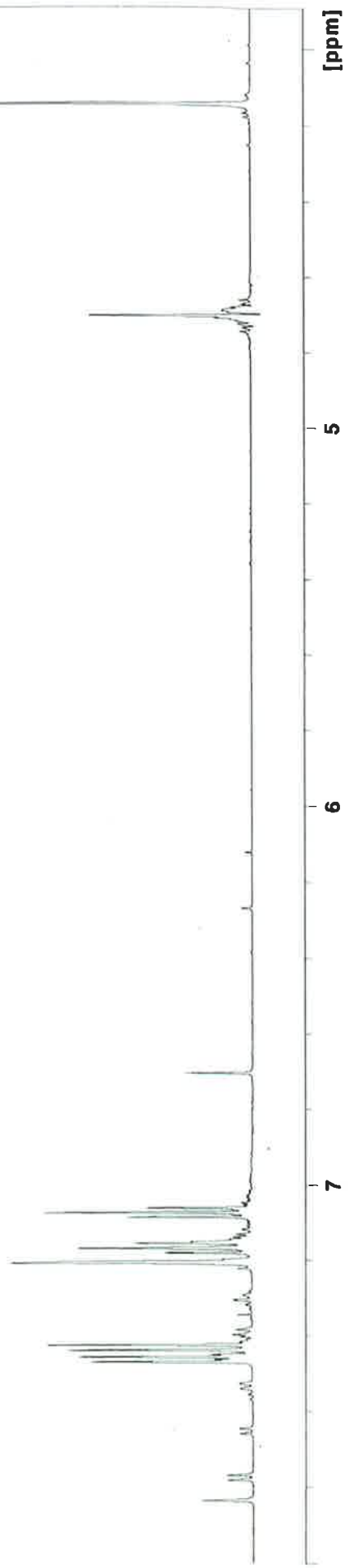
IpYA_repeat 12 1 /opt/data/hjh
IpYA_repeat for publication - overnight

D₂O/H₂O K₂HPO₄/K₂HPO₄ BUFFER, t = 24 h @ 40°C.

7.8356
7.7825
7.7693
7.6609
7.6476
7.5417
7.5292
7.4705
7.4572
7.4390
7.4254
7.2071
7.1818
7.1803
7.1684
7.1564
7.1548
7.1519
7.1519
7.0870
7.0738
7.0620



4.1442



lpyA_repeat 15 1 /opt/data/hjh

Avance III - 13C with 1H Power-gated Decoupling

D₂O/H₂O PHOSPHATE BUFFER, t = 24h @ 40°C

204.3738

170.5596

136.2726

126.8778

125.3016

121.9741

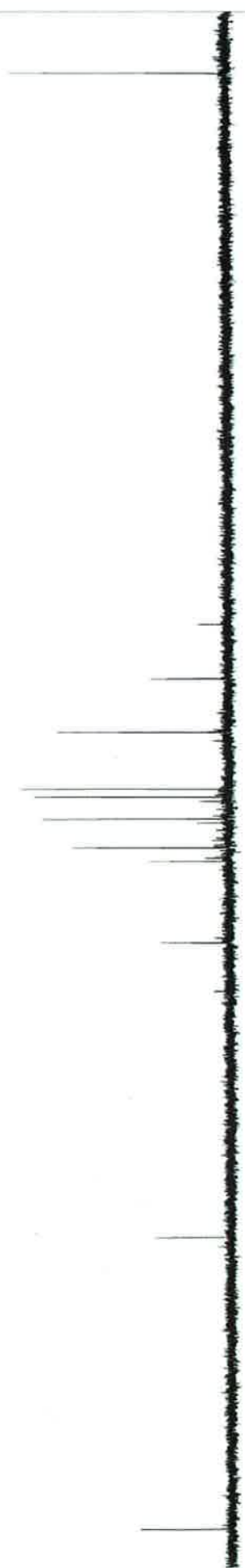
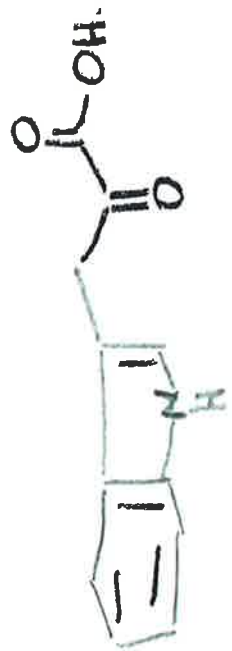
119.4274

118.4921

111.9412

105.7273

35.7702



200

150

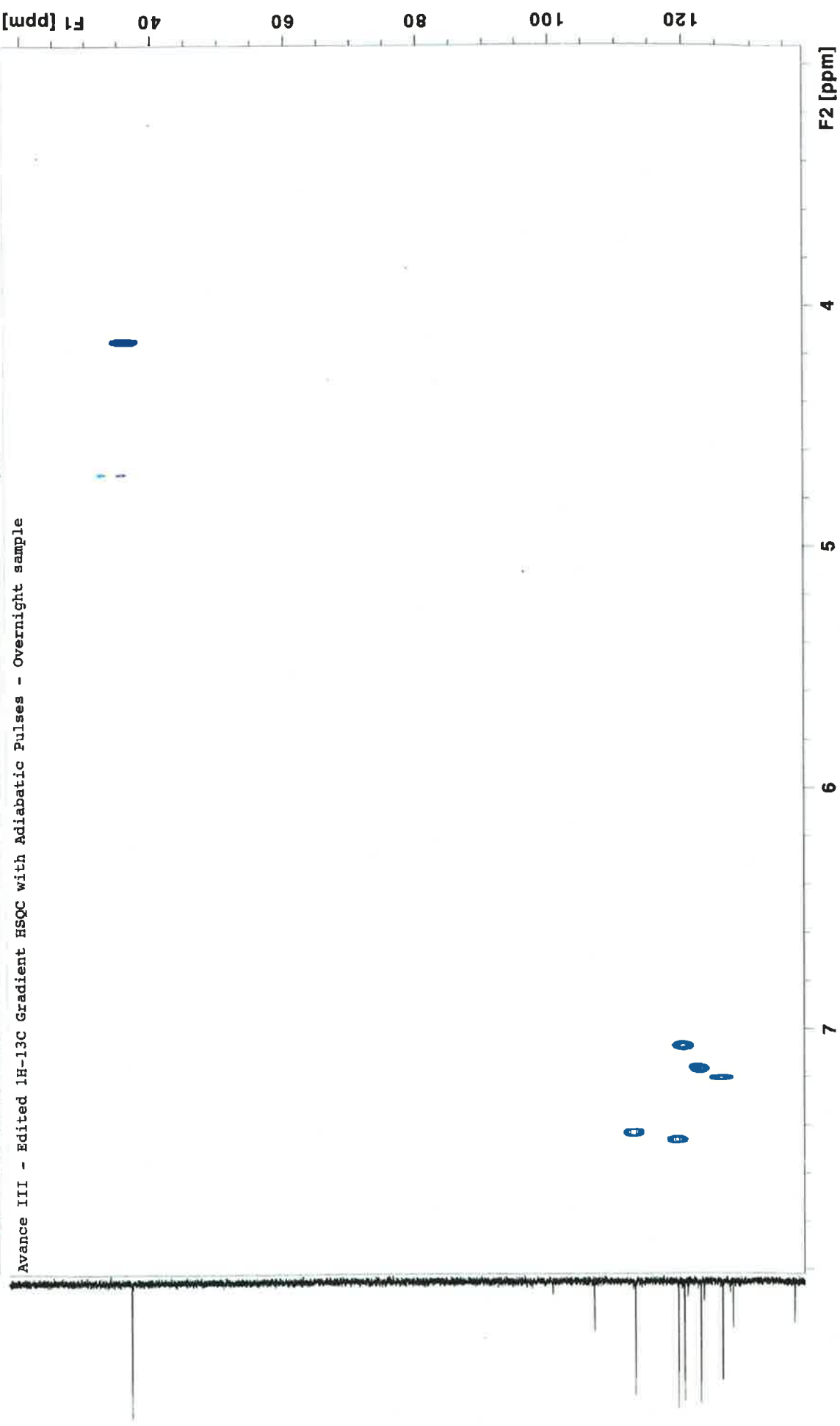
100

50

[ppm]

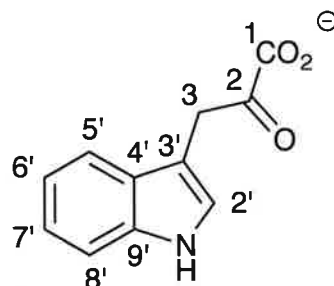
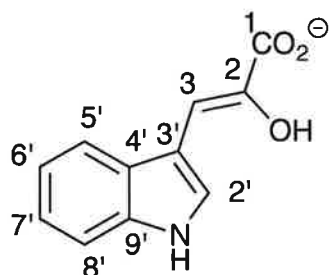
IpyA_repeat 9 1 /opt/data/hjh

D₂O/H₂O PHOSPHATE BUFFER, t=24 h @ 40°C



Avance III - Edited 1H-13C Gradient HSQC with Adiabatic Pulses - Overnight sample

Assignment of enol and keto tautomers of IPyA, pH = 8.5



Solvent	Enol tautomer	Keto tautomer		
KH ₂ PO ₄ /K ₂ HPO ₄ buffer (pH 8.5)	δ_H (multiplicity)	δ_H (multiplicity)	δ_C	
	1	-	-	170.6
	2	-	-	204.4
	3	6.92 (s)	-	35.8
	2'	7.93 (s)	7.20 (s)	126.9
	3'	-	-	
	4'	-	-	
	5'	7.77 (d)	7.43 (d)	111.9
	6'	7.15(t)	7.07 (t)	119.4
	7'	7.21 (t)	7.17(m)	122.0
8'	7.46 (d)	7.46 (d)	118.5	
9'	-	-		