Supporting Information

Studies of the Biosynthesis of DTX-5a and DTX-5b by the Dinoflagellate *Prorocentrum maculosum*: Regiospecificity of the Putative Baeyer-Villigerase and Insertion of a Single Amino Acid in a Polyketide Chain.

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Figure S1

DTX-5a ex[1,2-^{13}C] Acetate

^{13}C Spectrum in CD_3OD

^{1}H Decoupled

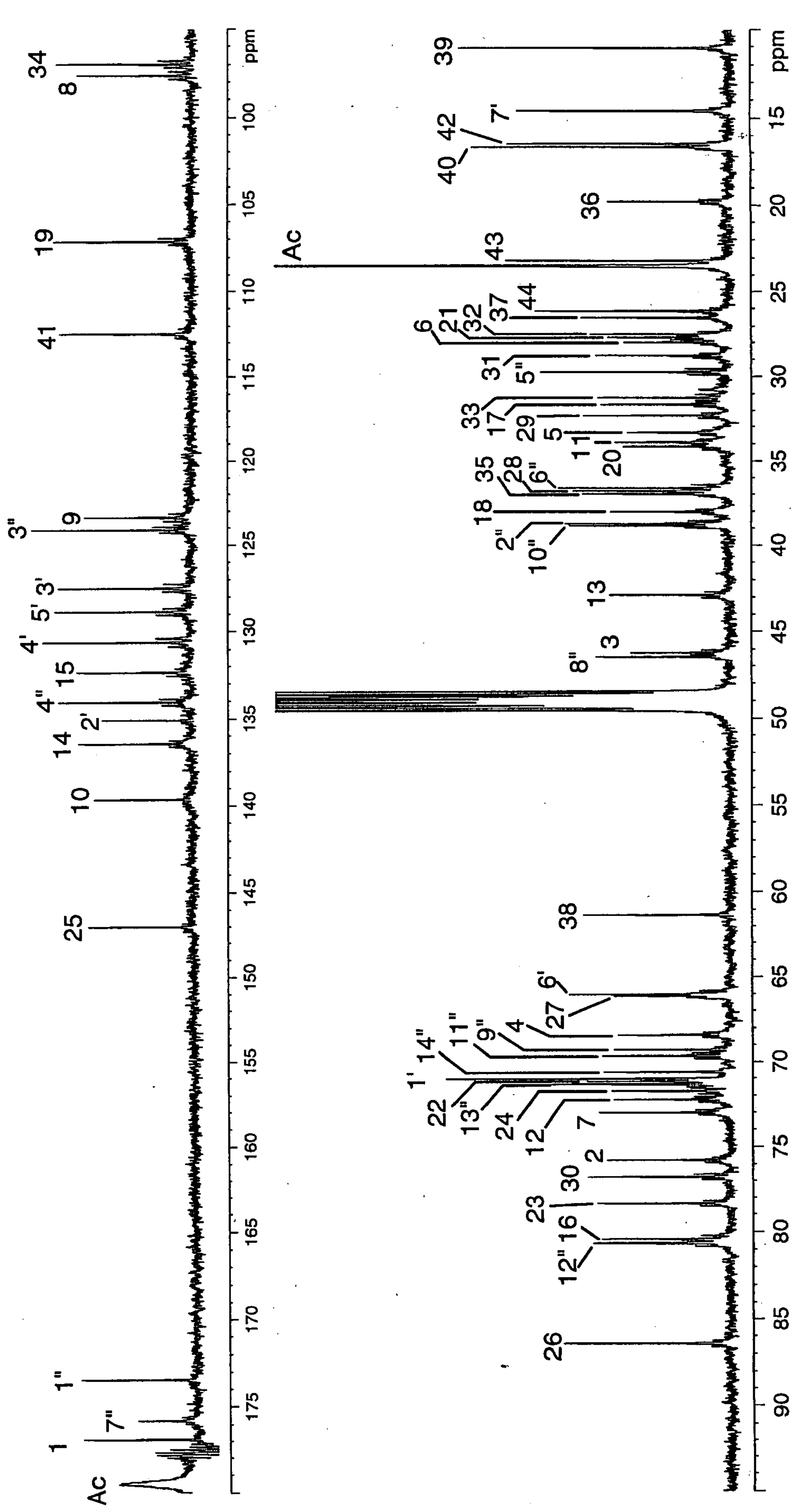

Figure S2
DTX-5a ex[2-$^{13}CD_3$] Acetate
^{13}C Spectrum in CD_3OD
^1H,D Decoupled

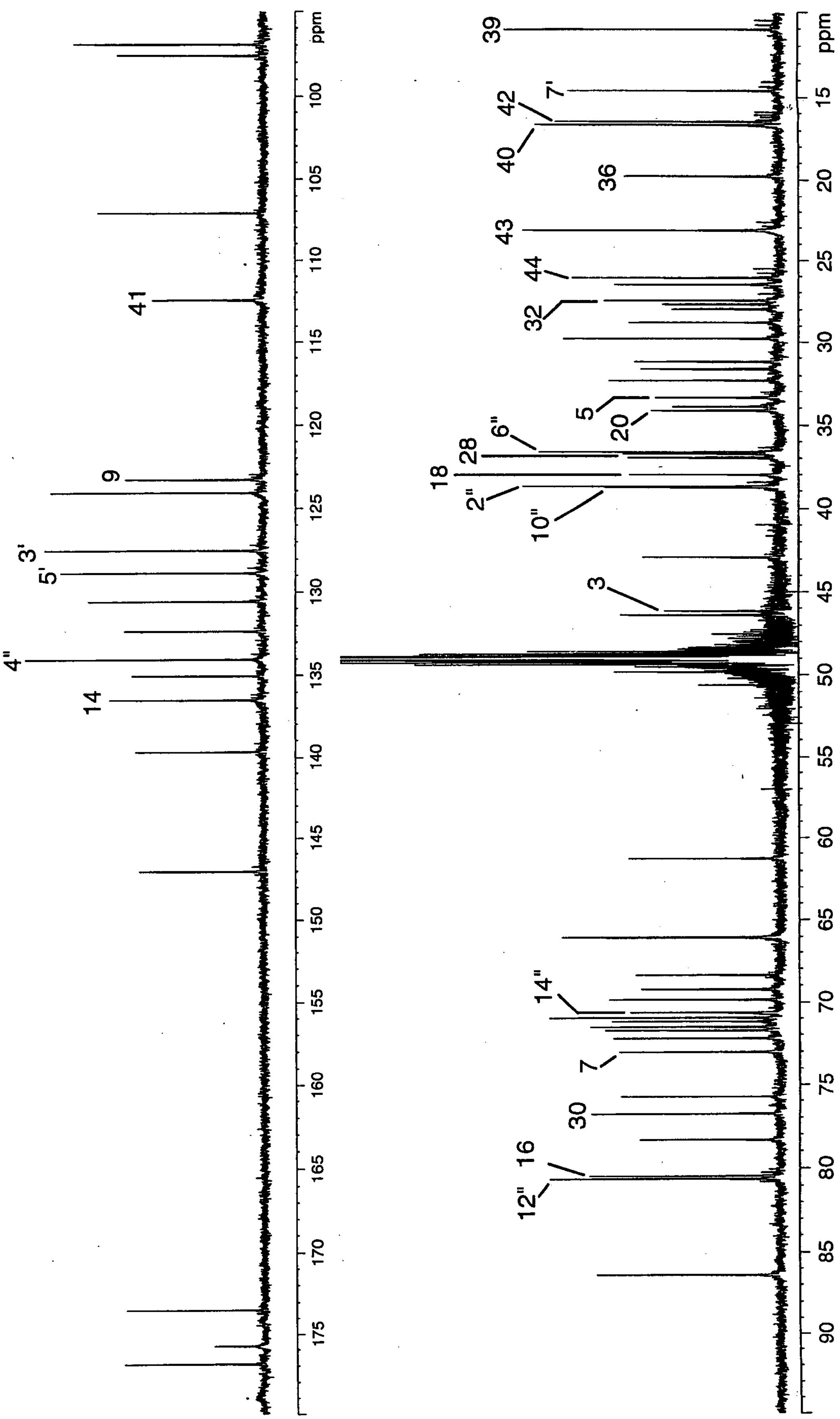

Figure S3
DTX-5a ex[2-$^{13}CD_3$] Acetate
^{13}C Spectrum in CD_3OD
^1H,D Decoupled (expansions)

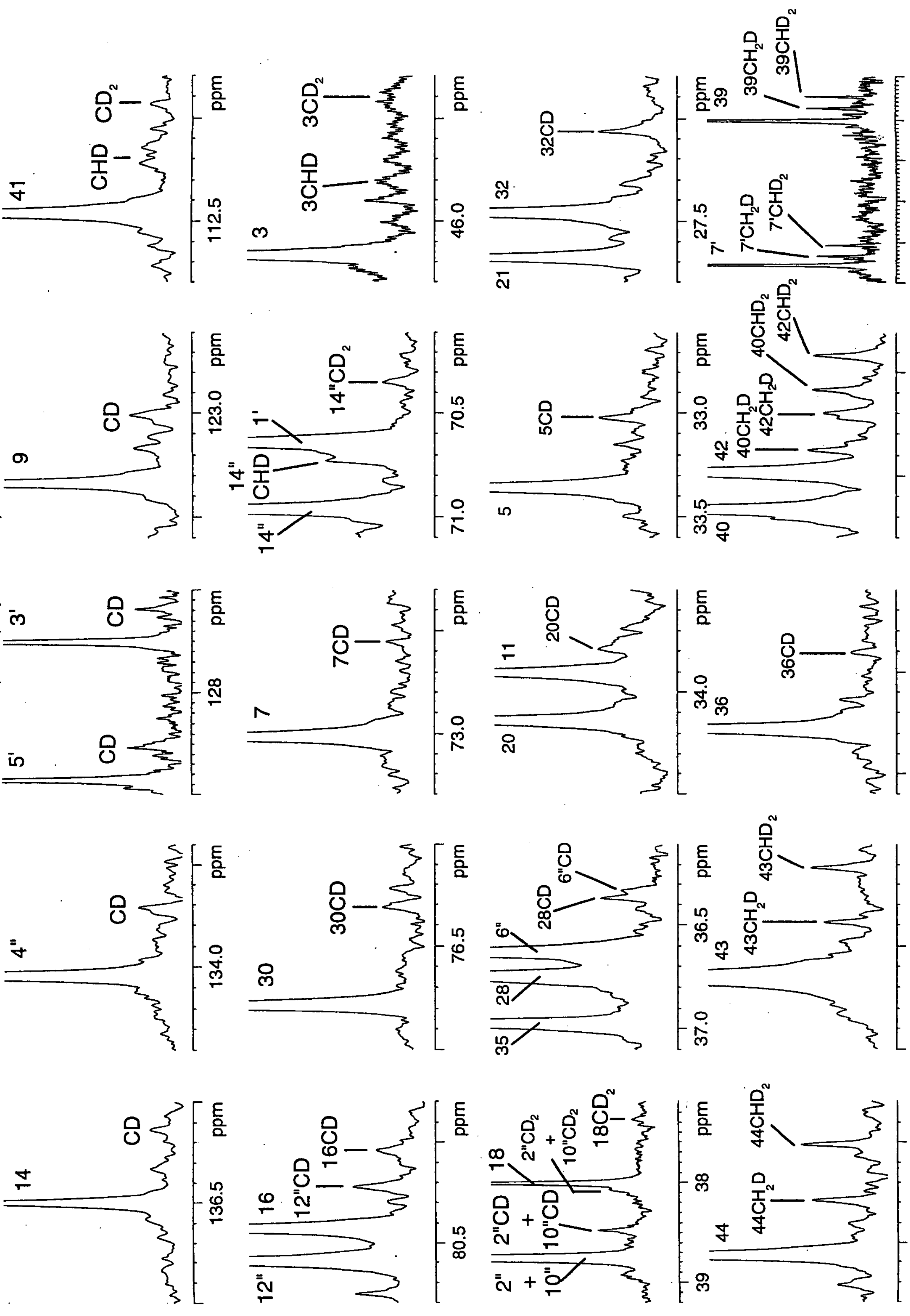

Figure S4
DTX-5a ex[2-^{13}C, ^{15}N] Glycine
^{13}C Spectrum in CD_3OD
^{1}H Decoupled

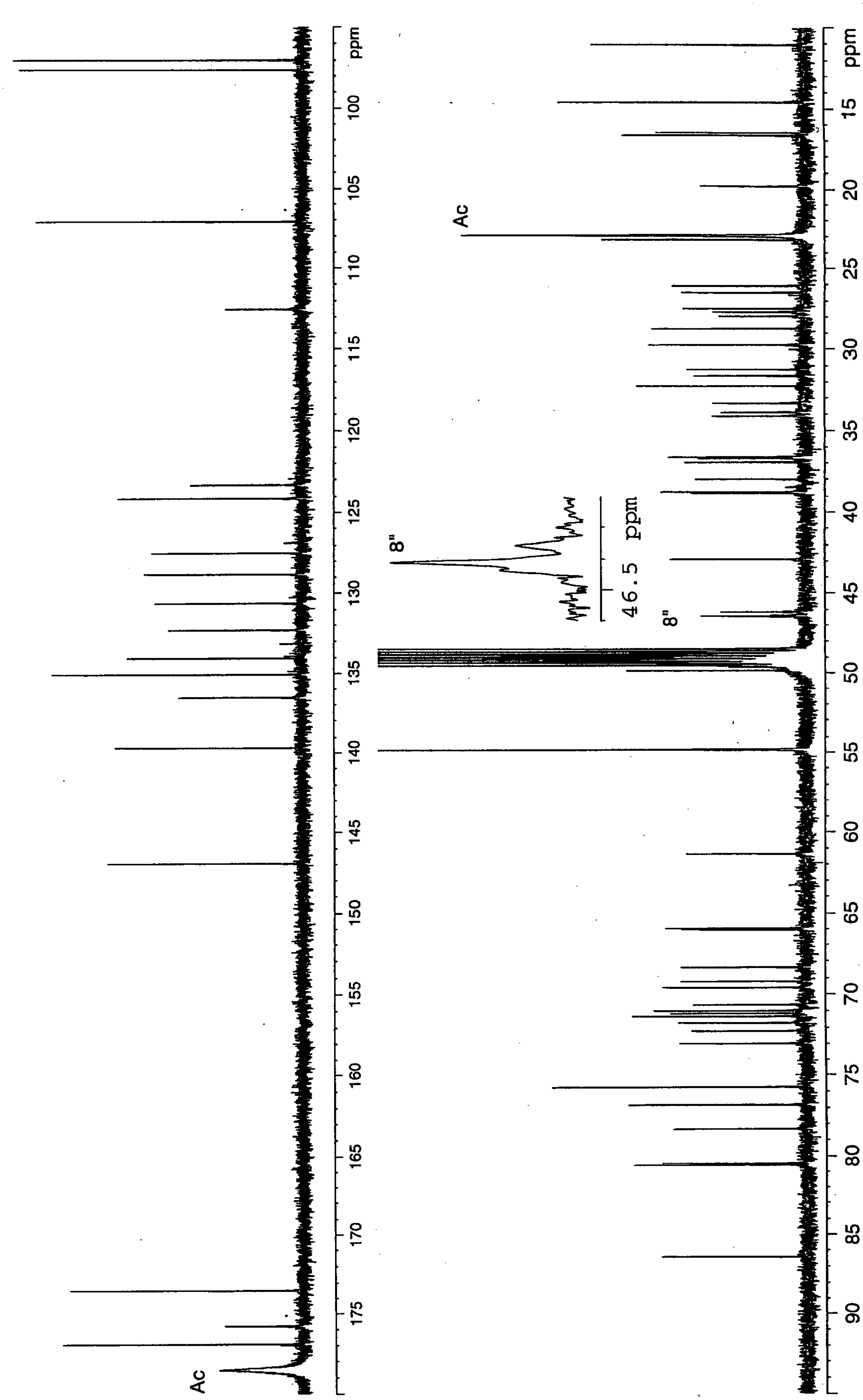

Figure S5

DTX-5a ex[1,2- ^{13}C] Glycine
^{13}C Spectrum in CD_3OD
^{1}H Decoupled

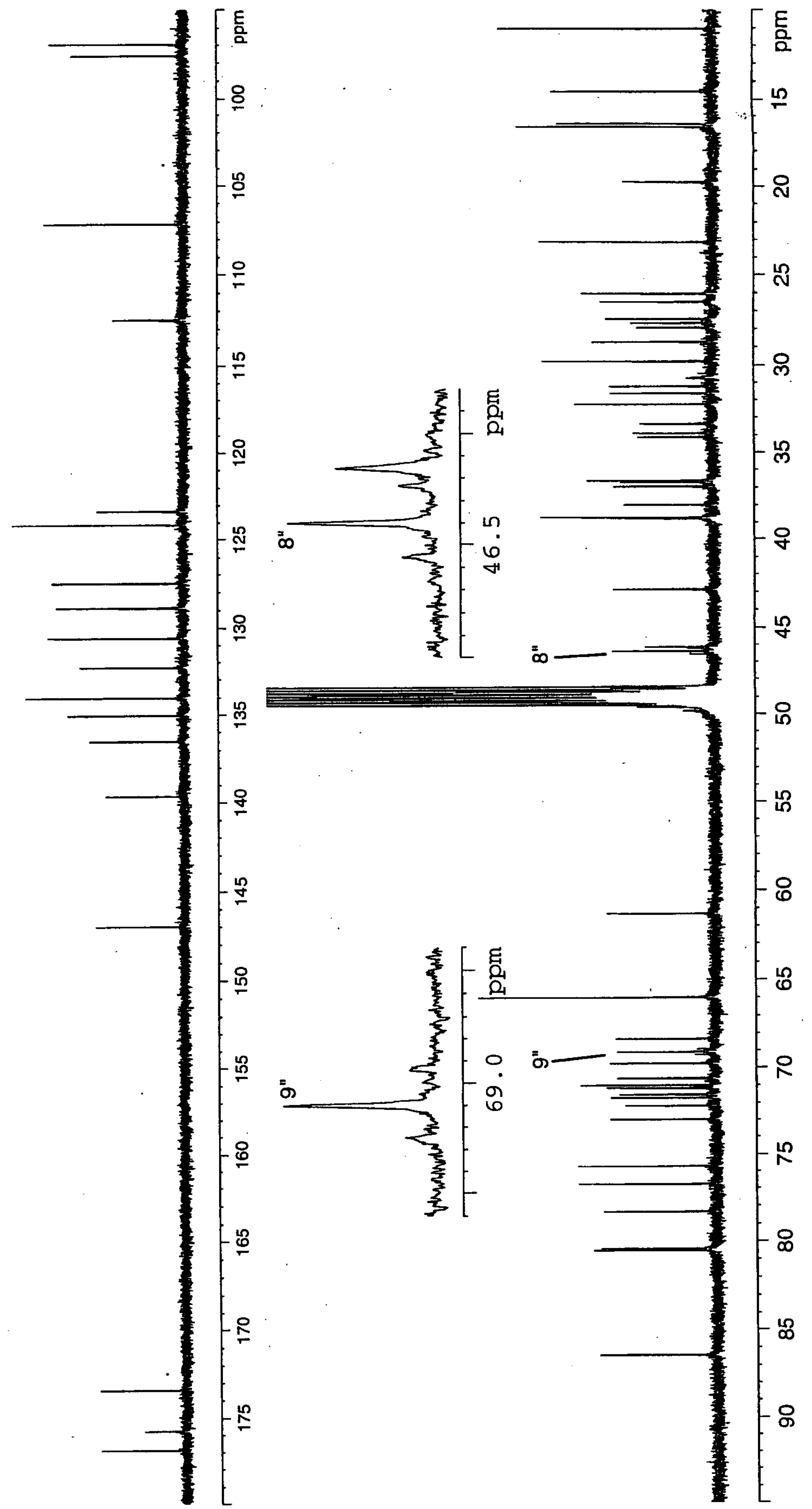

Figure S6

DTX-5a ex[1,2-^{13}C] Acetate
^{13}C INADEQUATE Spectrum in CD_3OD

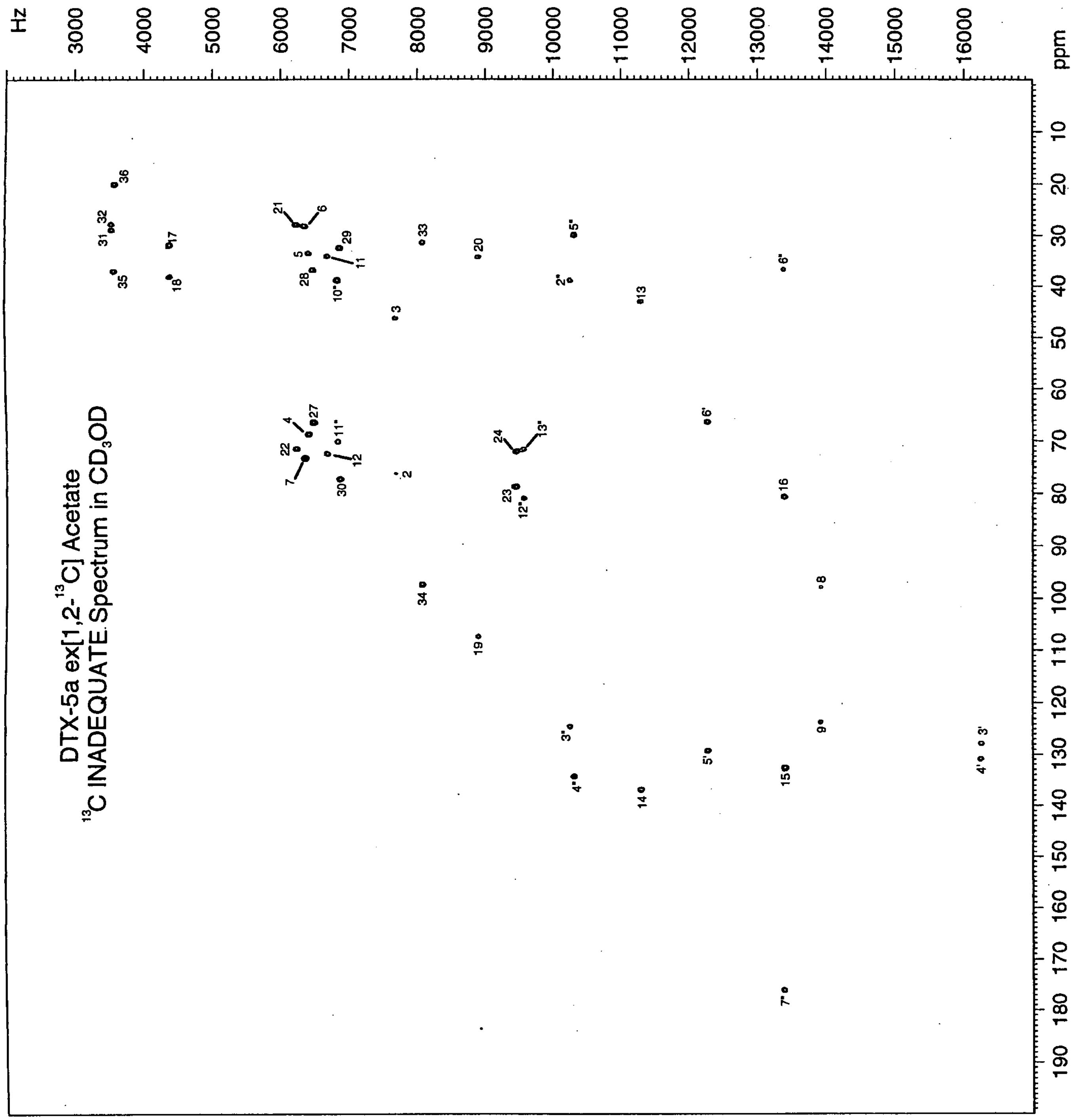

Figure S7
DTX-5b ex[1,2-^{13}C] Acetate
^{13}C Spectrum in CD_3OD
^{1}H Decoupled

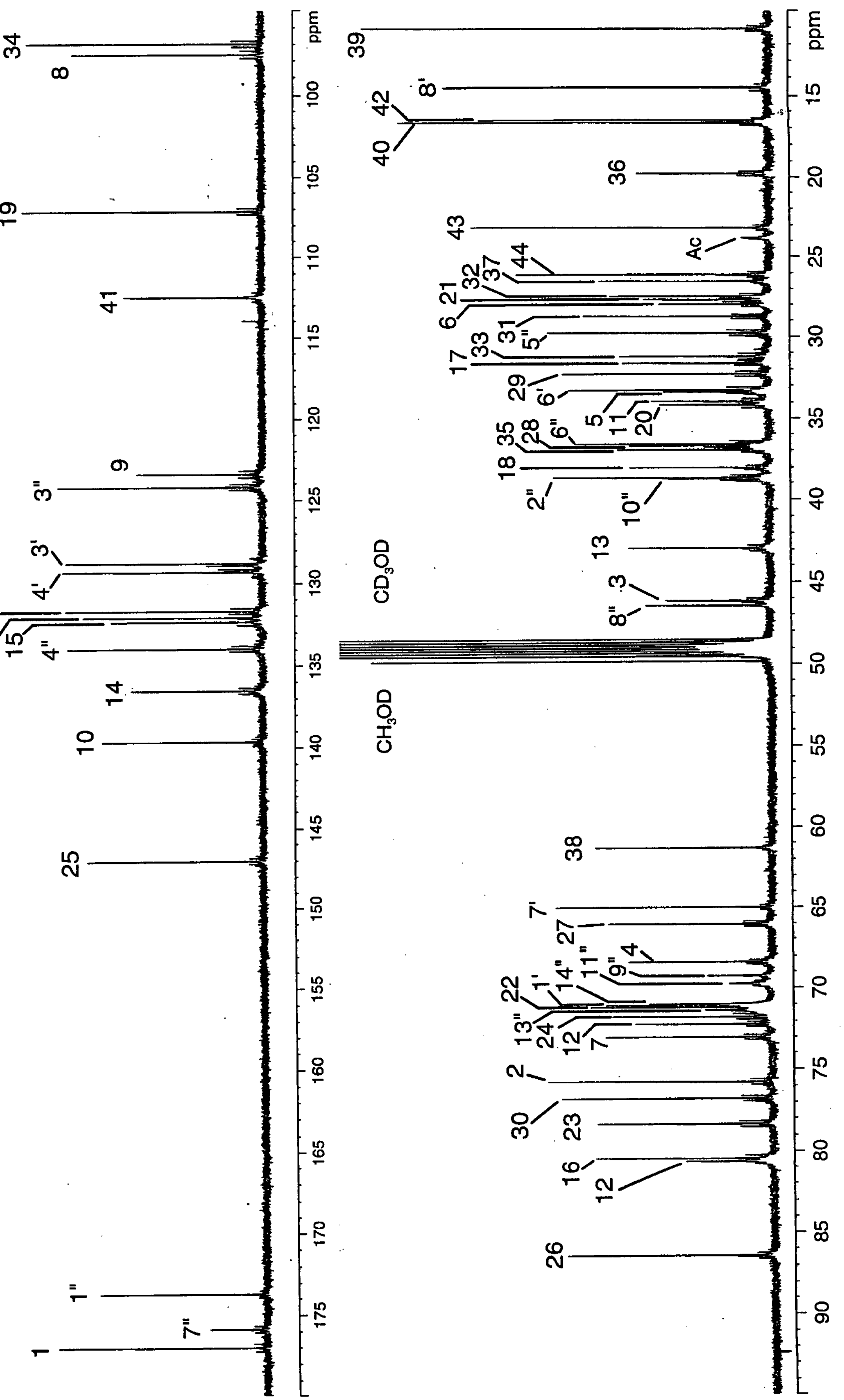

Figure S8

DTX-5b ex[2-$^{13}CD_3$] Acetate

^{13}C Spectrum in CD_3OD

^{1}H,D Decoupled

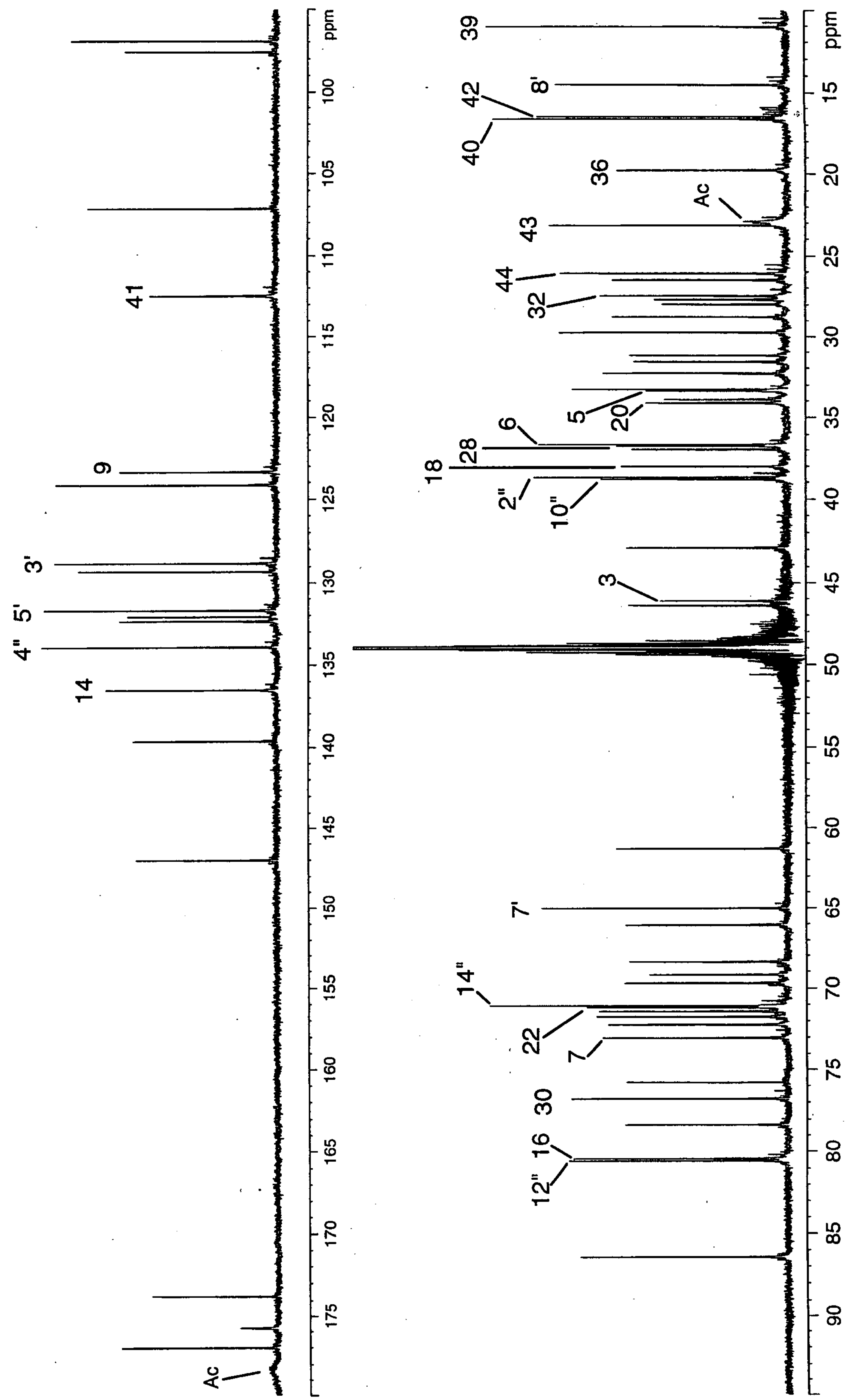

Figure S9
DTX-5b ex[2-$^{13}CD_3$] Acetate
^{13}C Spectrum in CD_3OD
^{1}H,D Decoupled (expansions)

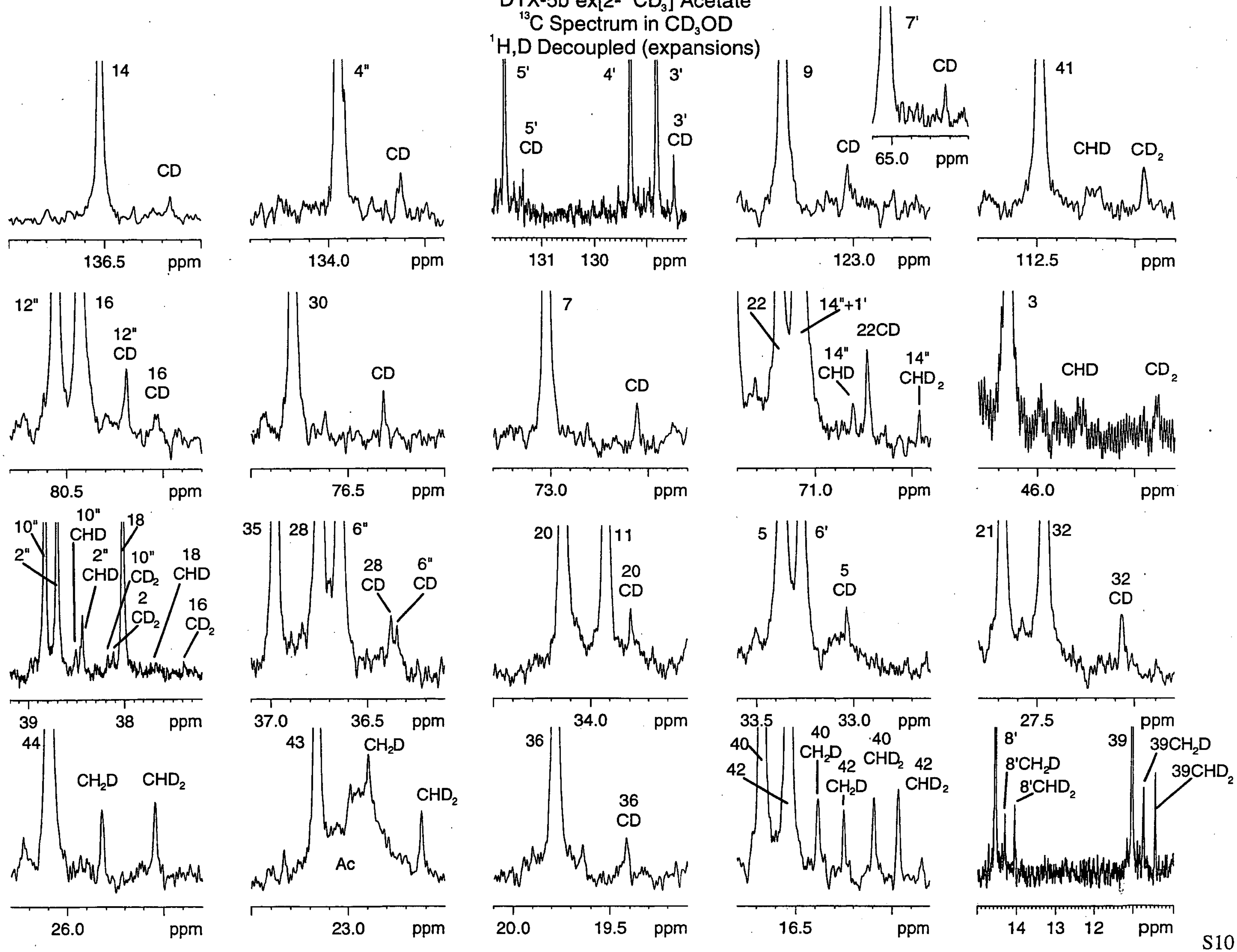

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Figure S10

DTX-5b ex[2-^{13}C, ^{15}N] Glycine
^{13}C Spectrum in CD_3OD
^{1}H Decoupled (expansions)

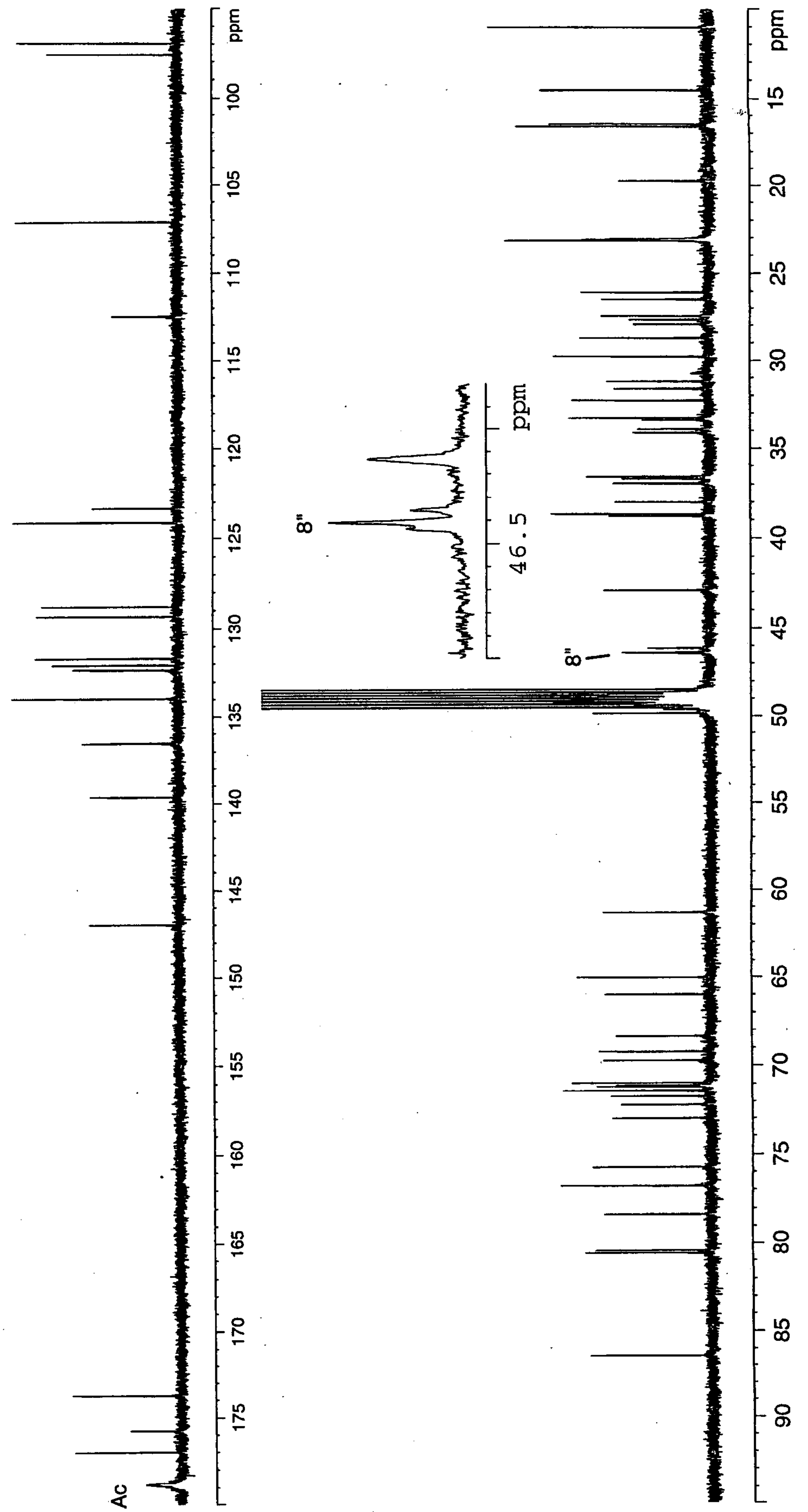


Figure S11

DTX-5b ex[1,2-^{13}C] Glycine
^{13}C Spectrum in CD_3OD
^{1}H Decoupled

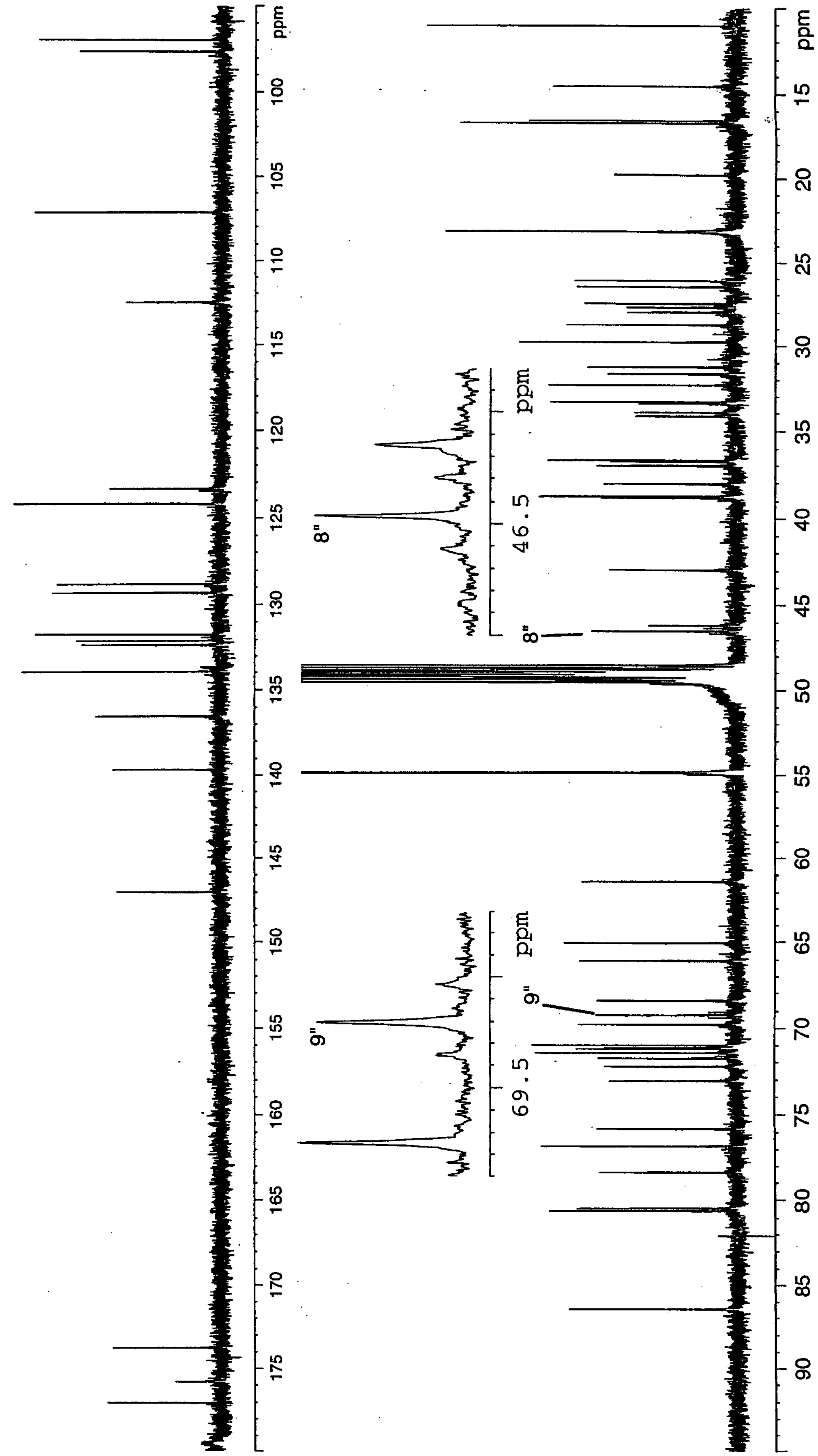
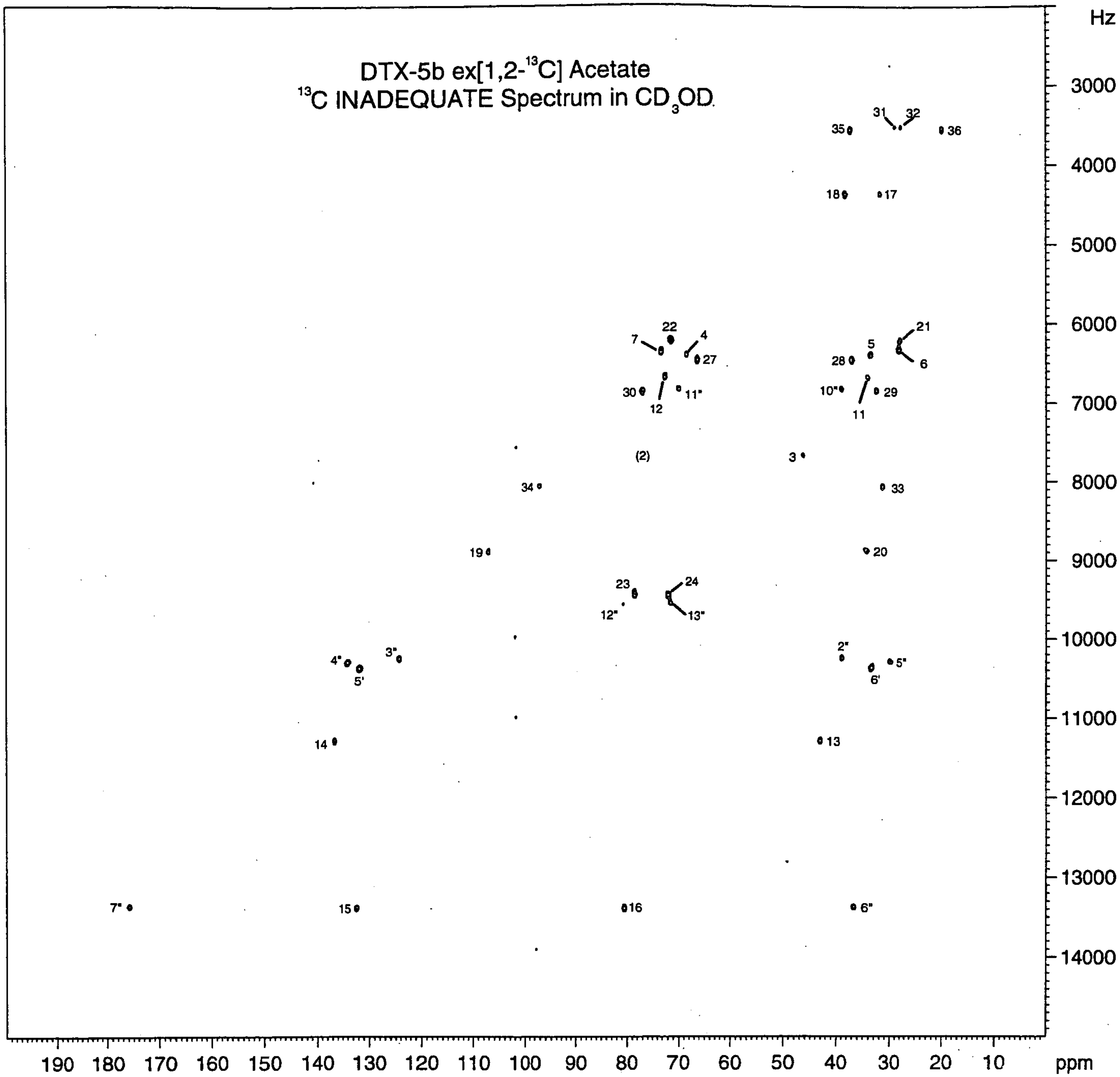
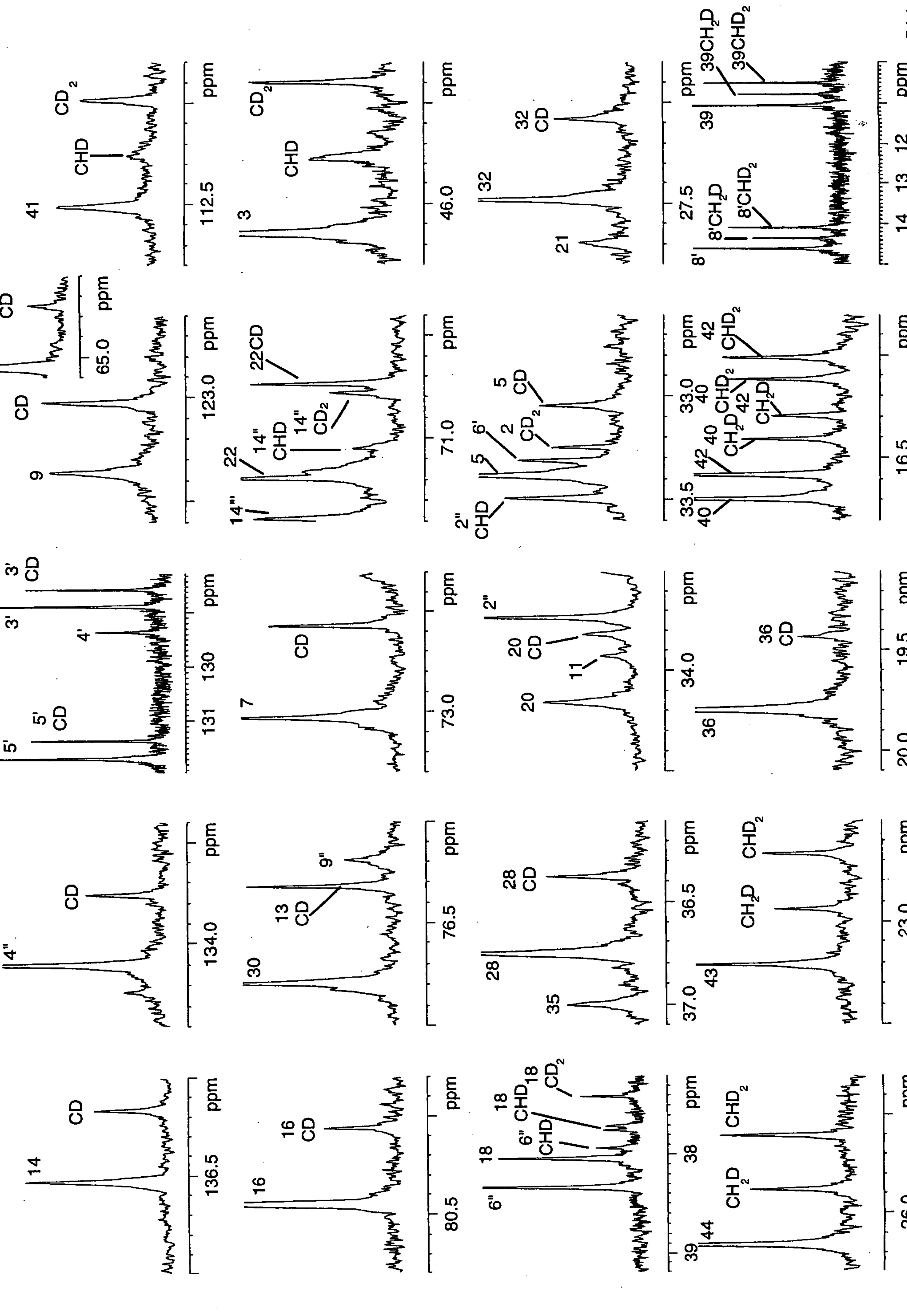


Figure S12



Intact units for C3', C4' and C8, C9 confirmed in ^{13}C spectrum but not visible in INADEQUATE as J_{CC} (56.7 Hz) not optimal.

Figure S13
DTX-4 ex[2-$^{13}CD_3$] Acetate
^{13}C Spectrum in CD_3OD
^1H,D Decoupled (expansions)



Supplementary data for Macpherson et al. " Studies of the Biosynthesis of DTX-5a and DTX-5b..."

13C chemical shifts (solvent CD3OD, reference to 13CD3OD = 49.0 ppm) and JCC coupling constants (Hz) for DTX-4,-5a and -5b ex [1,2-13C] Acetate, DTX-4 ex [1,2-13C] Glycolate and DTX-5a/5b ex [1,2-13C] Glycine

Error in JCC ca +/- 0.3 Hz

Carbon #	DTX-4 13C ppm	DTX-5a 13C ppm	DTX-5b 13C ppm	13C pairs Ca #	Cb #	DTX-4 J(Ca,Cb) Hz	OA J(Ca,Cb) Hz	DTX-5a J(Ca,Cb) Hz	DTX-5b J(Ca,Cb) Hz
1	177.0	177.0	177.0	1	2	61.0	54.9	61.5	61.3
2	75.8	75.8	75.8	2	44	39.1	39.5	39.1	39.1
3	46.2	46.2	46.2	2	3	37.5	36.1	37.7	37.3
4	68.4	68.4	68.4	3	4				
5	33.4	33.4	33.4	4	5	35.8	36.0	35.3	35.0
6	28.0	28.0	28.0	5	6				
7	73.0	73.0	73.0	6	7	36.2	38.1	35.8	36.5
8	97.6	97.6	97.6	7	8				
9	123.4	123.4	123.4	8	9	56.5	56.2	57.0	56.6
10	139.6	139.6	139.6	9	10				
11	34.0	34.0	34.0	10	43	43.2	43.1	43.4	43.6
12	72.3	72.3	72.3	10	11				
13	42.9	42.9	42.9	11	12	38.1	37.9	38.0	38.8
14	136.5	136.5	136.5	12	13				
15	132.4	132.4	132.4	13	14	43.4	43.6	42.7	42.5
16	80.4	80.4	80.4	13	42		34.8		34.2
17	31.7	31.7	31.7	14	15				
18	38.0	38.0	38.0	15	16	50.5	50.5	50.5	49.8
19	107.1	107.1	107.1	16	17				
20	34.2	34.2	34.2	17	18	32.9	32.9	32.9	32.8
21	27.7	27.7	27.7	18	19				
22	71.2	71.2	71.2	19	20	45.3	45.3	45.3	45.5
23	78.4	78.4	78.4	20	21				
24	71.8	71.8	71.8	21	22	38.0	38.2	38.0	37.7
25	147.0	147.0	147.0	22	23				
26	86.4	86.4	86.4	23	24	40.5	39.8	40.1	40.0
27	66.1	66.1	66.1	24	25				
28	36.8	36.8	36.8	25	26				
29	32.2	32.2	32.2	25	41	74.4	73.7	74.9	73.2
30	76.8	76.8	76.8	26	27				
31	28.8	28.8	28.8	27	28	40.5	40.6	40.1	40.1
32	27.5	27.5	27.5	28	29				
33	31.3	31.3	31.3	29	30	40.5	40.7	40.6	40.3
34	97.0	97.0	97.0	29	40		37.6		35.5
35	37.0	37.0	37.0	30	31				
36	19.8	19.8	19.8	31	32	32.8	32.8	33.4	32.6
37	26.5	26.5	26.5	31	39	35.3	35.3	33.0	35.1
38	61.4	61.4	61.4	32	33				
39	11.1	11.1	11.1	33	34	45.8	45.4	45.8	45.8
40	16.6	16.6	16.6	34	35				
41	112.5	112.5	112.5	35	36	32.7	32.6	32.5	32.7
42	16.6	16.6	16.6	36	37				
43	23.2	23.2	23.2	37	38	35.4	34.9		35.8
44	26.1	26.1	26.1						
1'	71.1	71.1	71.8						
2'	132.1	135.1	132.0	1'	2'	47.9			
3'	128.8	127.5	128.8	2'	3'				
4'	129.4	130.6	129.3	2'	8'	43.3			43.2
5'	131.7	128.9	131.7	3'	4'	56.5		56.5	56.7
6'	33.3	66.0	33.3	4'	5'				
7'	65.1	14.6	65.1	5'	6'	43.5		48.6	43.4
8'	14.6		14.6	6'	7'	38.6			38.6
1"	173.8	173.5	173.8						
2"	33.8	38.7	38.7						
3"	122.4	124.4	124.4	1"	2"	57.9		58.0	
4"	134.0	134.0	134.0	2"	3"	43.2		43.9	43.8
5"	24.7	29.8	29.8	3"	4"				
6"	38.3	36.6	36.6	4"	5"	42.9		43.2	43.0
7"	69.1	175.8	175.8	5"	6"				
8"	44.4	46.4	46.4	6"	7"	38.3		51.0	49.6
9"	76.2	69.3	69.3	7"	8"				
10"	39.6	38.8	38.8	8"	9"	39.6		40.2	40.2
11"	68.5	69.9	69.9	9"	10"				
12"	82.0	80.7	80.7	10"	11"	39.1		37.2	38.9
13"	71.7	71.5	71.4	11"	12"				
14"	70.4	70.7	71.0	12"	13"	43.8		overlap	40.0
				13"	14"	40.5			