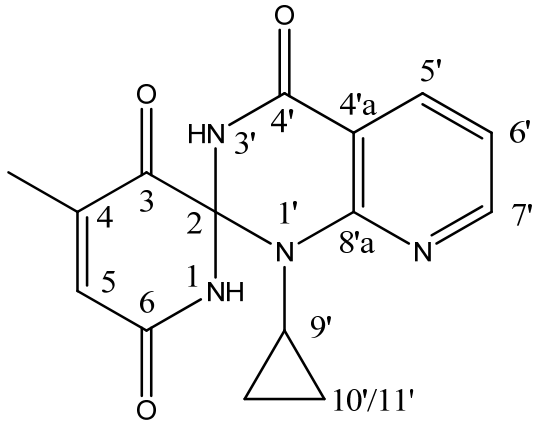
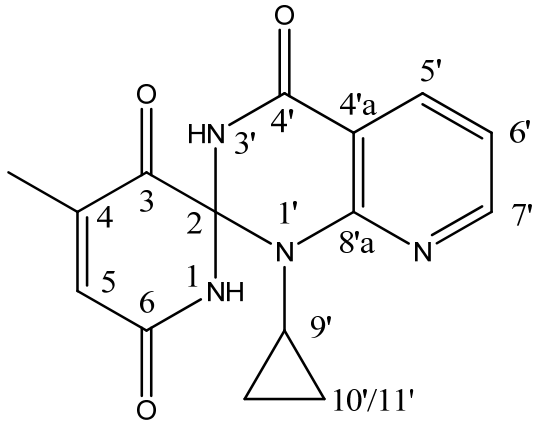
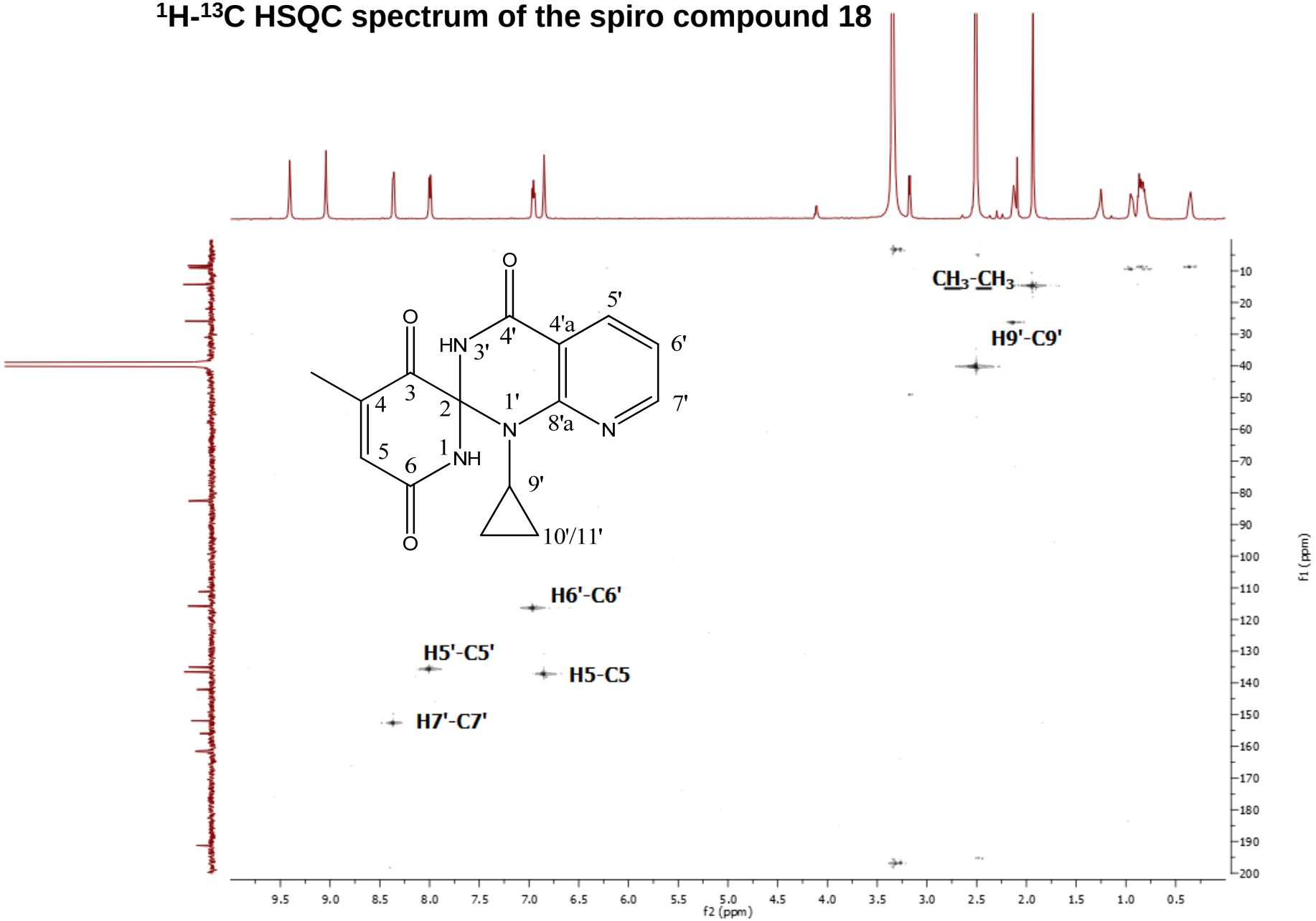
^{1}H NMR spectrum of the spiro compound 18



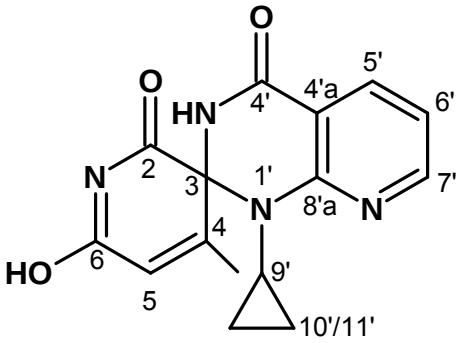
^{13}C NMR spectrum of the spiro compound 18



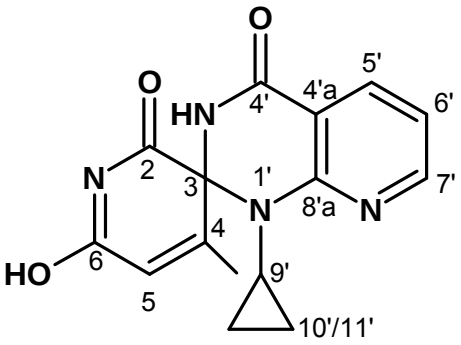
^{1}H-^{13}C HSQC spectrum of the spiro compound 18



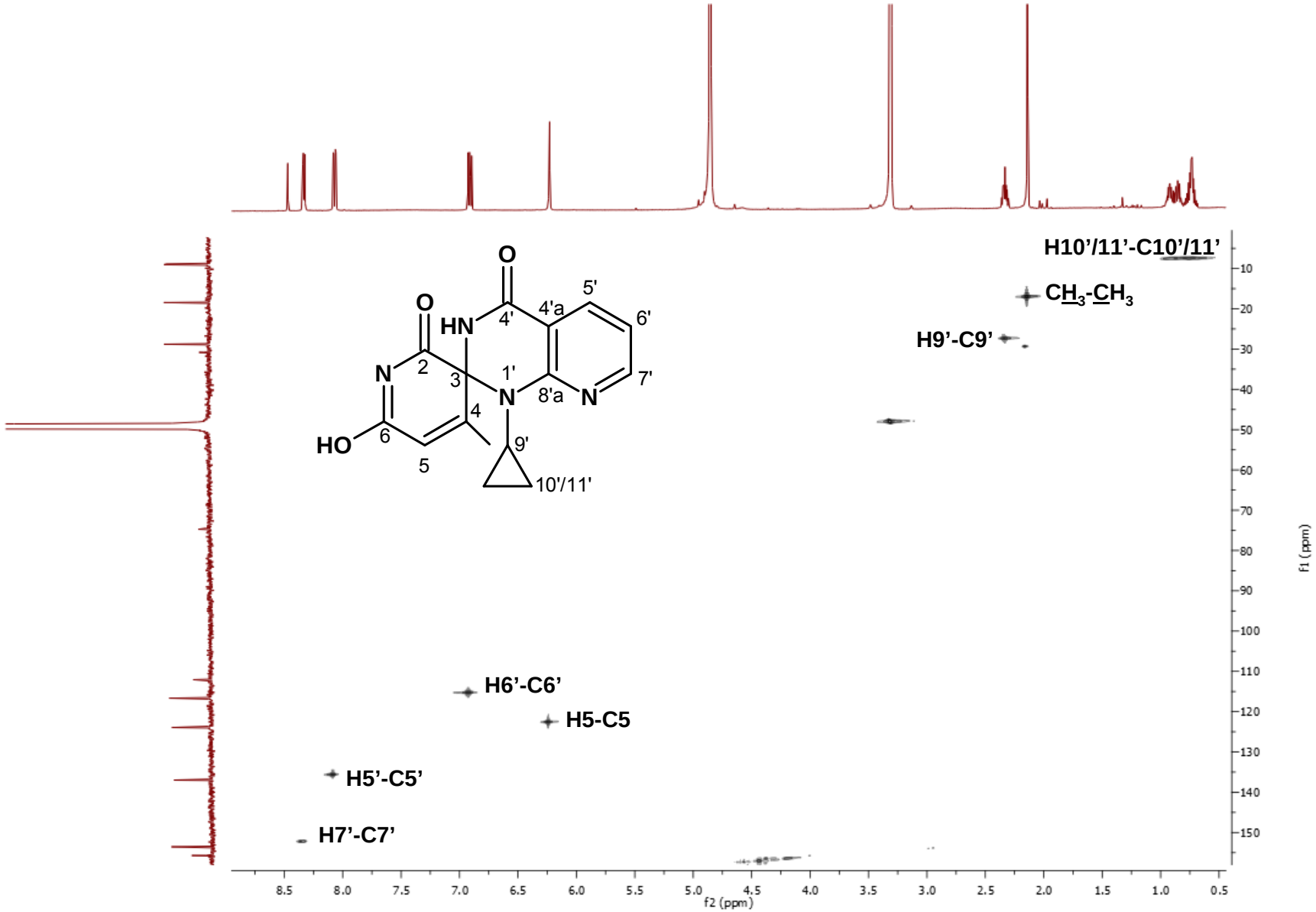
^{1}H NMR spectrum of the spiro compound 19

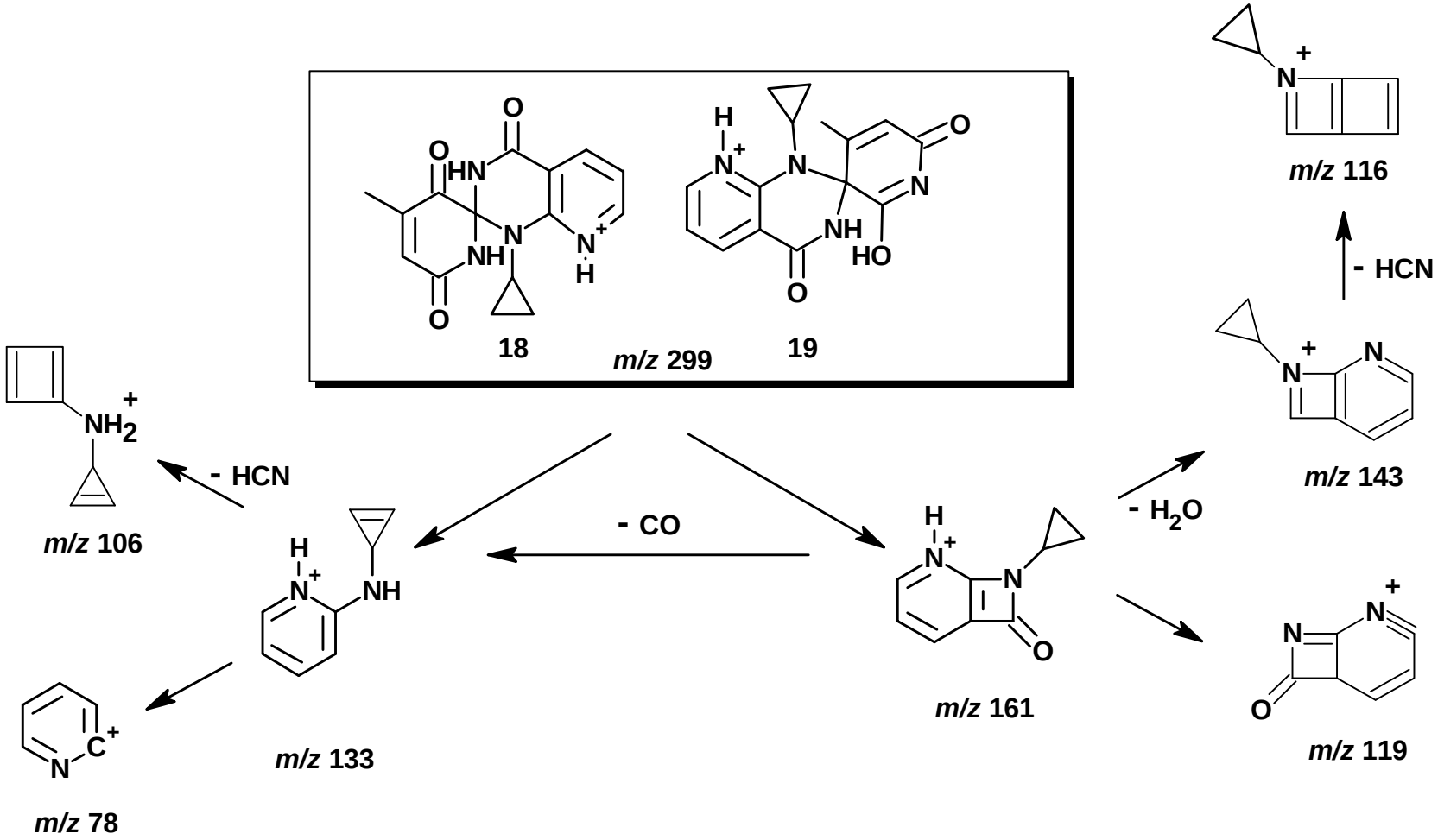


^{13}C NMR spectrum of the spiro compound 19



^{1}H-^{13}C HSQC spectrum of the spiro compound 19





Scheme S1. ESI-MS/MS fragmentation mechanism proposed for the protonated molecules (*m/z* 299) of **18** and **19**.

Table S1. Crystal and structure refinement data for compound 18.

Chem. Formula	$C_{33}\ H_{34}\ N_8\ O_7$ (2molecules + 1 solvent)
Mol. wt.	654.68
Temperature (K)	150(2)
Wavelenght (Å)	0.71073
Color/shape	Orange/prism
Cryst size (mm)	0.22 x 0.1 x 0.05
Cryst Syst	Monoclinic
Space group	*C*2/*c*
a (Å)	21.528(10)
b (Å)	8.433(4)
c (Å)	17.211(8)
α (°)	----------
β (°)	94.650(16)
γ (°)	----------
V (Å^3)	3114(3)
Z	4
$\rho_{calcd.}$ (g cm^{-3})	1.396
Absorption coefficient (mm^{-1})	0.101
F_{000}	1376
θ range (°)	3.57 to 25.88
Data collected (h,k,l)	-26 to 25, ±10, -19 to 20
Reflections collected / unique	13236 / 2973
$R_{(int)}$	0.1230
Completeness to Θ max (%)	97.9
Max. and min. transmission	0.9950 and 0.9782
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2973 / 0 / 229
Goodness-of-fit on F^2	0.954
Final R indices [I>2sigma(I)]	R_1 = 0.0591, wR_2 = 0.1096
R indices (all data)	R_1 = 0.1389, wR_2 = 0.1384
Extinction coefficient	0.0042(5)
Largest diff. peak and hole (e. Å^{-3})	0.262 and -0.288

Table S2. Selected bond lengths and angles for compound **18**

Bonds (Å)			
C2-C3	1.555(4)	N8'-C7'	1.346(3)
C3-C4	1.470(4)	C7'-C6'	1.385(4)
C4-C5	1.337(4)	C5'-C6'	1.382(4)
C5-C6	1.469(4)	C4'a-C5'	1.376(4)
C6-N1	1.358(4)	O8-C3	1.229(3)
N1-C2	1.435(3)	O9-C6	1.234(3)
C2-N1'	1.486(4)	O12'-C4'	1.235(4)
N1'-C8'a	1.404(3)	C7-C4	1.499(4)
C8'a-C4'a	1.398(4)	N1'-C9'	1.451(4)
C4'a-C4'	1.472(4)	C9'-C11'	1.491(4)
C4'-N3'	1.350(4)	C9'-C10'	1.503(4)
N3'-C2	1.440(4)	C11'-C10'	1.489(4)
N8'-C8'a	1.351(4)		
Angles (º)			
N1-C2-N1'	110.3(2)	C5'-C6'-C7'	117.3(3)
N3'-C2-N1	110.2(2)	C4'a-C5'-C6'	119.7(3)
N1-C2-C3	111.3(2)	C5'-C4'a-C8'a	119.1(3)
N3'-C2-C3	111.1(2)	C5'-C4'a-C4'	121.1(3)
N1-C2-N3'	106.5(2)	O8-C3-C4	122.5(3)
N1'-C2-C3	107.4(2)	O8-C3-C2	117.4(3)
C6-N1-C2	125.6(3)	C5-C4-C7	124.6(3)
N1-C6-C5	118.1(3)	C3-C4-C7	117.2(3)
C4-C5-C6	123.6(3)	O9-C6-N1	121.1(3)
C5-C4-C3	118.2(3)	O9-C6-C5	120.8(3)
C4-C3-C2	120.0(3)	O12'-C4'-N3'	122.0(3)
C4'-N3'-C2	124.9(3)	O12'-C4'-C4'a	122.8(3)
N3'-C4'-C4'a	115.1(3)	C8'a-N1'-C9'	117.3(2)
C8'a-C4'a-C4'	119.7(3)	C9'-N1'-C2	114.7(2)
C4'a-C8'a-N1'	121.3(3)	N1'-C9'-C11'	118.3(3)
C8'a-N1'-C2	115.2(2)	N1'-C9'-C10'	119.8(3)
N8'-C8'a-N1'	116.1(3)	C11'-C9'-C10'	59.67(19)
N8'-C8'a-C4'a	122.6(3)	C10'-C11'-C9'	60.57(19)
C7'-N8'-C8'a	116.1(3)	C11'-C10'-C9'	59.76(19
N8'-C7'-C6'	125.2(3)		

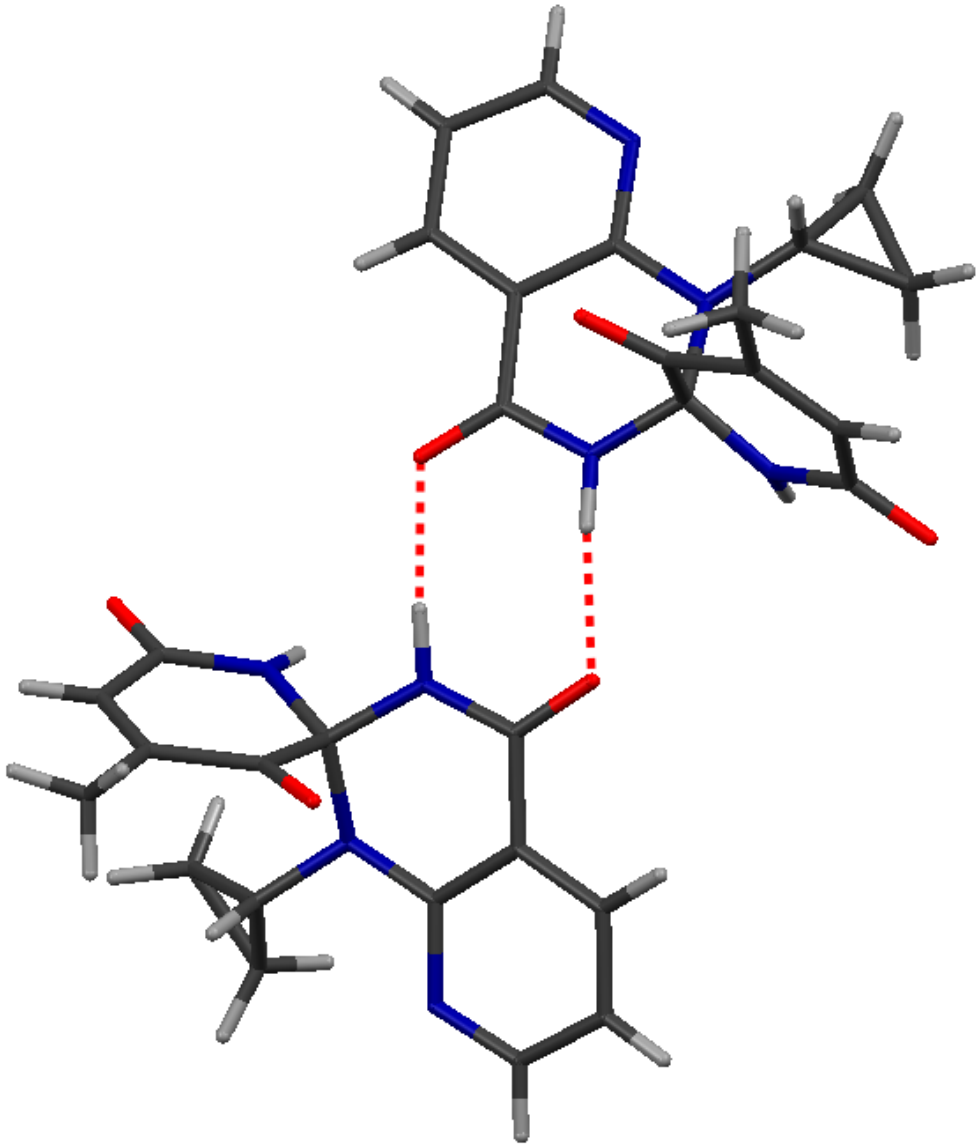
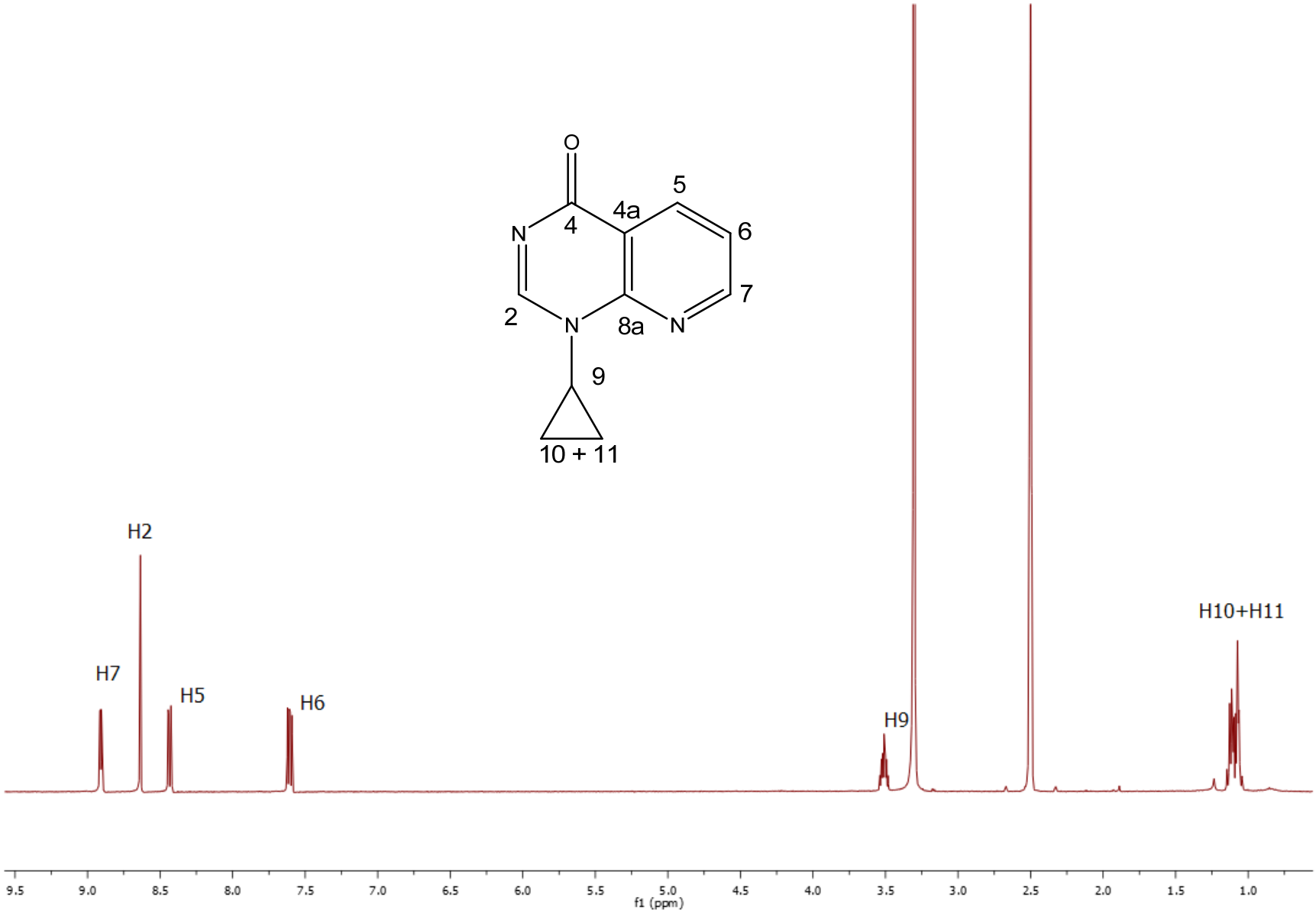
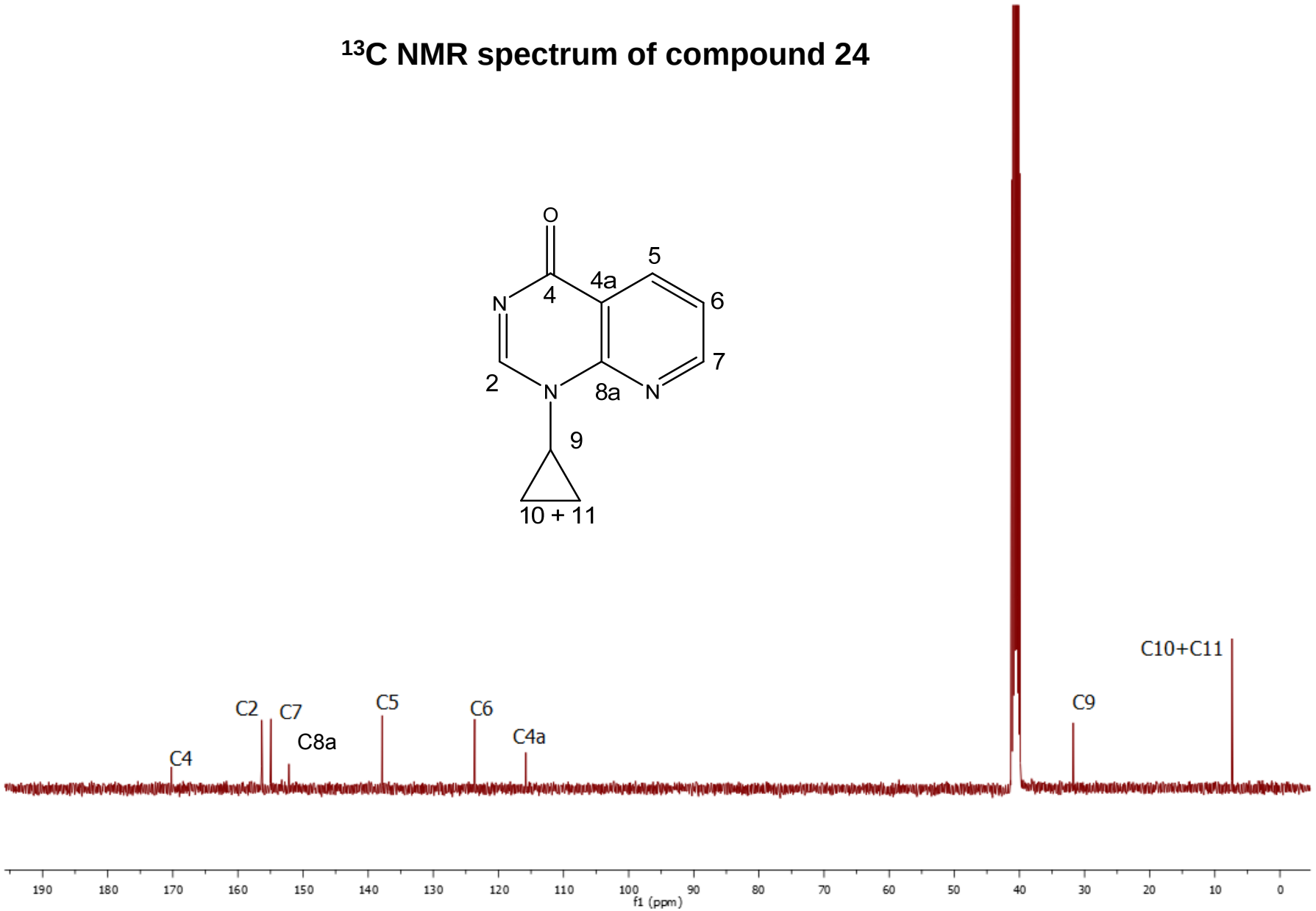


Diagram displaying the interactions between two molecules of the same enantiomer of the spiro compound **18**.

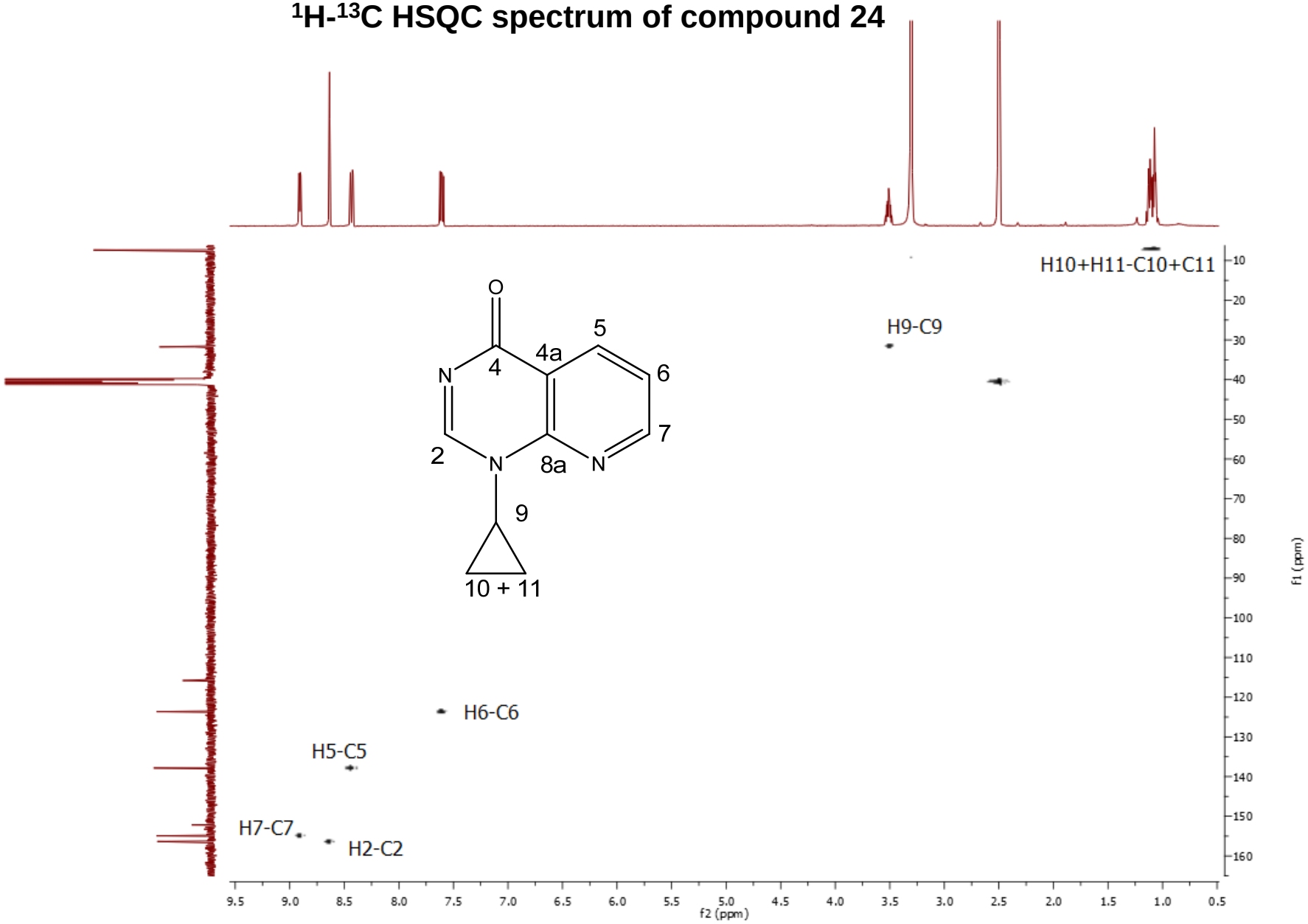
^{1}H NMR spectrum of compound 24



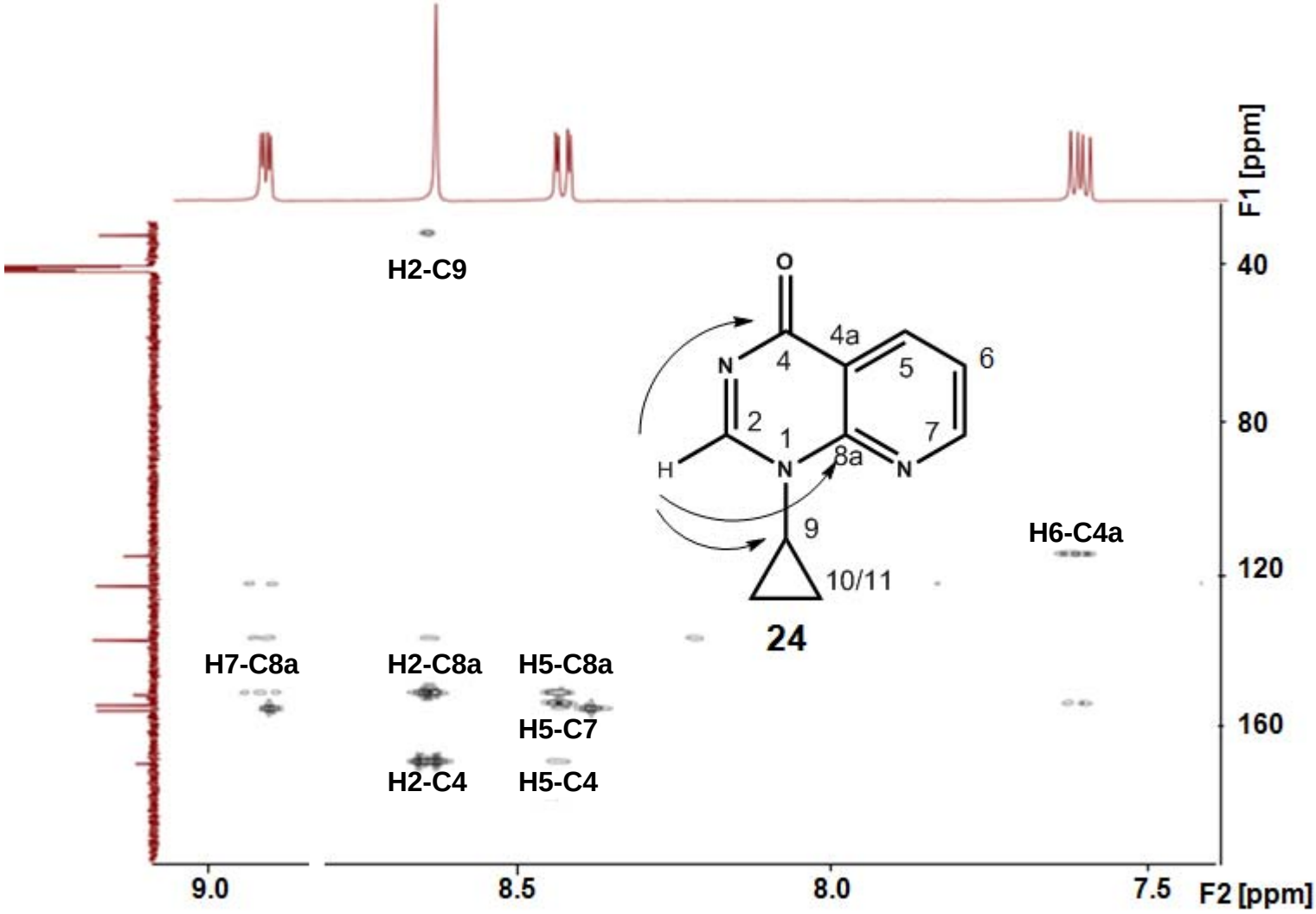
^{13}C NMR spectrum of compound 24

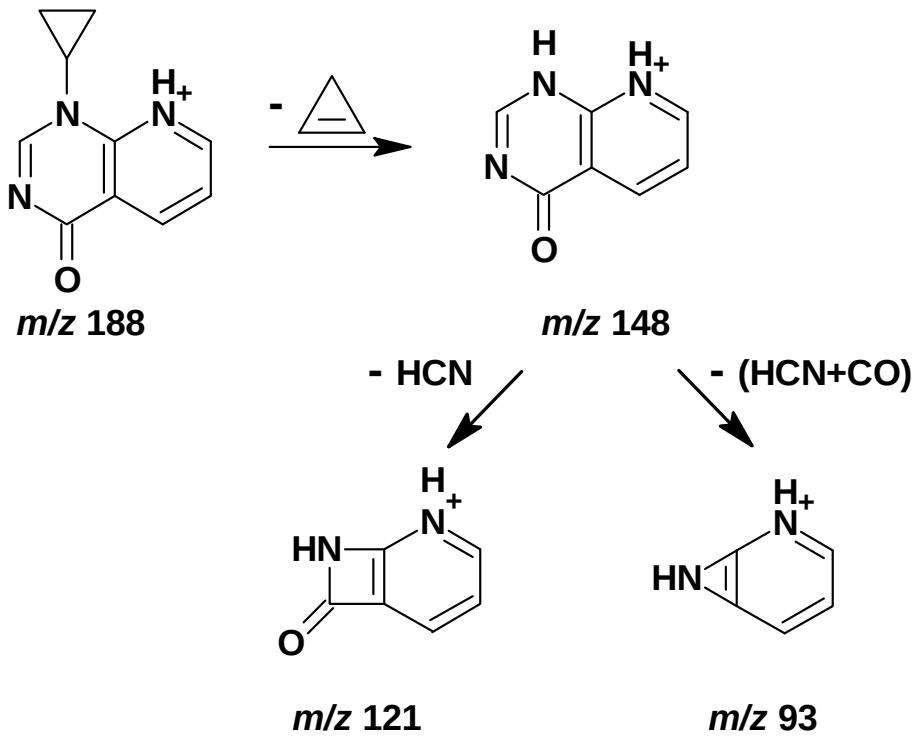


^{1}H-^{13}C HSQC spectrum of compound 24



Expanded region of the ^{1}H-^{13}C HMBC spectrum of compound **24**, displaying the 3-bond connectivities between the imine H2 proton and carbons C4, C8a, and C9.





Scheme S2. ESI-MS/MS Fragmentation mechanism proposed for the protonated molecule (*m/z* 188) of **24**.