

NMR - 2D

2. CORRELAZIONI ETERONUCLEARI SHIFT CORRELATE

	Technique	Principal Applications
1J	HSQC	Correlating coupled heteronuclear spins across a single bond and hence identifying directly connected nuclei. Employs detection of high-sensitivity nuclides, for example, ^1H , ^{19}F , ^{31}P (an 'inverse technique'). Favoured over HMQC as it can provide improved resolution.
1J	HMQC	Correlating coupled heteronuclear spins across a single bond and hence identifying directly connected nuclei, most often ^1H - ^{13}C . Employs detection of high-sensitivity nuclides, for example, ^1H , ^{19}F , ^{31}P (an 'inverse technique').
$^2J, ^3J$	HMBC	Correlating coupled spins across multiple bonds. Employs detection of high-sensitivity nuclides, for example, ^1H , ^{19}F , ^{31}P (an 'inverse technique'). This is HMQC tuned for the detection of small couplings. Most valuable in correlating ^1H - ^{13}C over two- or three-bonds. Powerful tool for linking together structural fragments.
2J	H2BC	Used to identify HMBC peaks that equate to two-bond ^1H - ^{13}C correlations and so distinguish them from three-bond correlations. Limited to correlations to protonated carbon centres only.
Long range	HSQMBC	Used for measurement of the magnitudes of long-range heteronuclear coupling constants, most often between proton and carbon centres.
Long range	LR-HSQMBC	Used for the detection of very long-range heteronuclear correlations. For ^1H - ^{13}C systems this may provide correlations over four, five and even six bonds and will likely prove most useful for proton-sparse structures.
1J	HETCOR	Correlating coupled heteronuclear spins across a single bond. Employs detection of the lower- γ nuclide, typically ^{13}C , so has significantly lower sensitivity than inverse techniques. Benefits from high resolution in the ^{13}C dimension, so may find use when this is critical, otherwise superseded by the aforementioned methods.

H,C-COSY

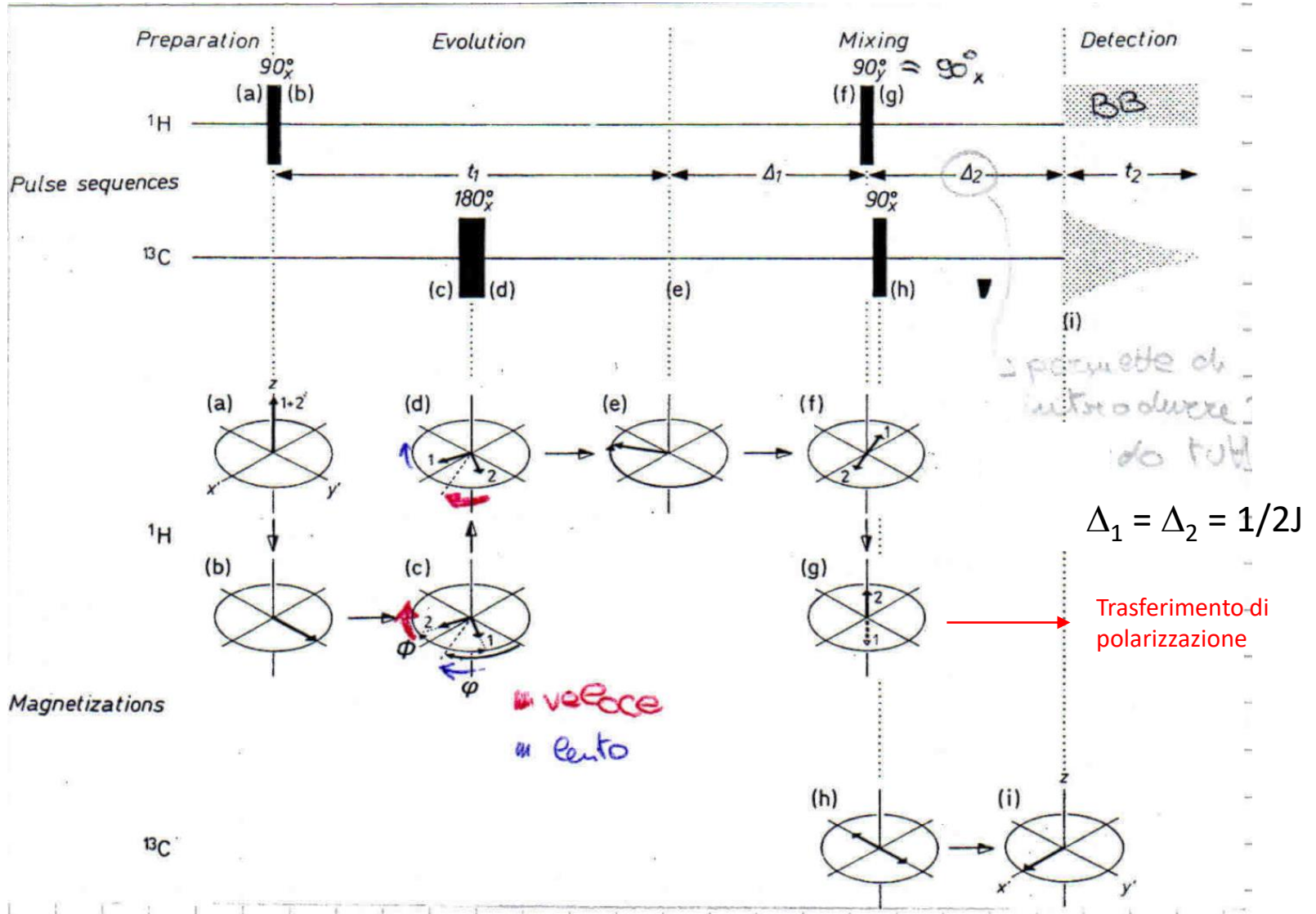
C,H-COSY

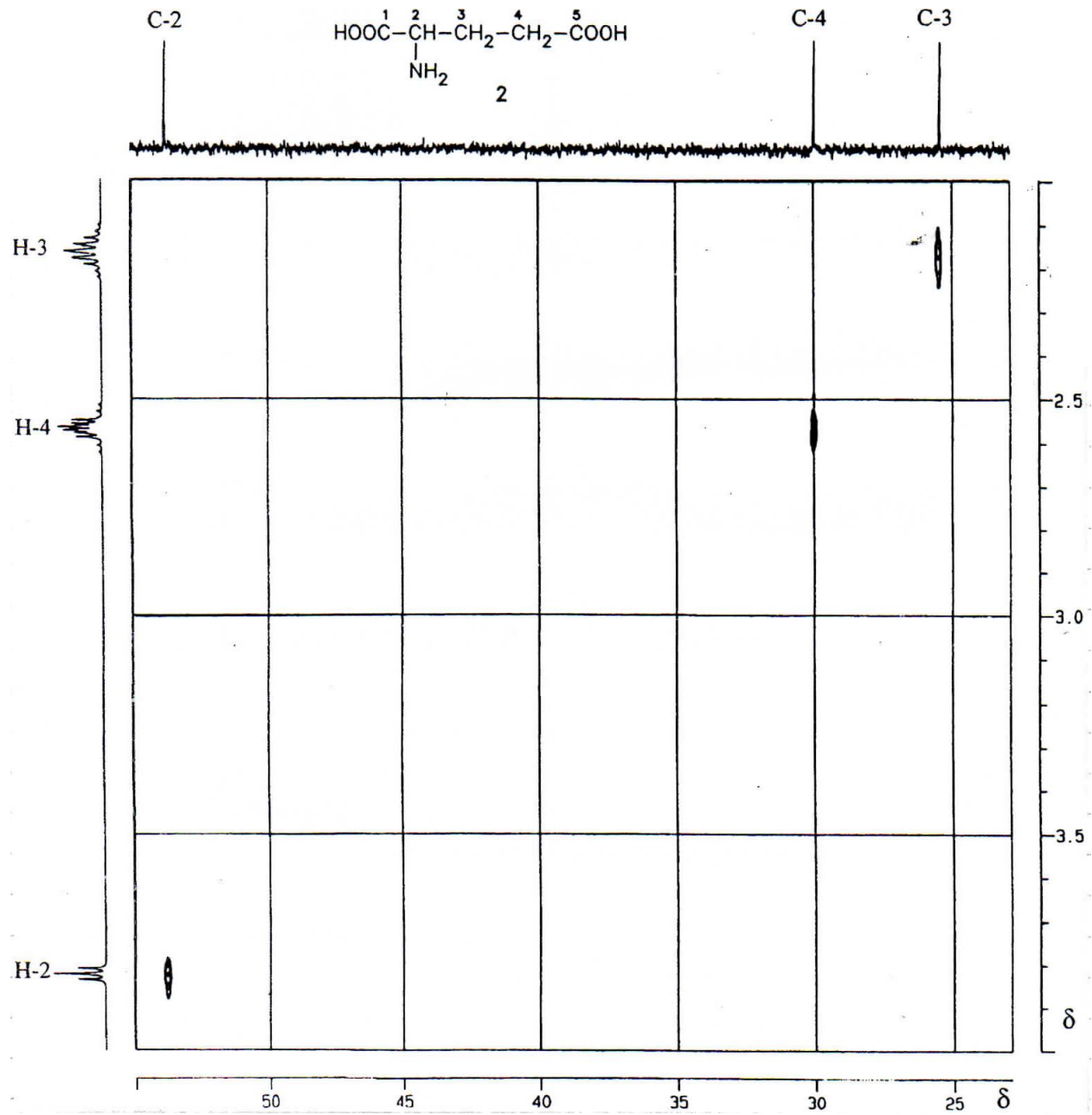
Informazione: quale C è attaccato a quale protone

- Differenza: nel primo caso il nucleo osservato (F2) è il ^{13}C (poco sensibile) **HETCOR**
- Nel secondo caso il nucleo osservato (F2) è il ^1H (molto sensibile) = **HSQC, HMQC** TECNICHE INVERSE

H,C-COSY: HETCOR

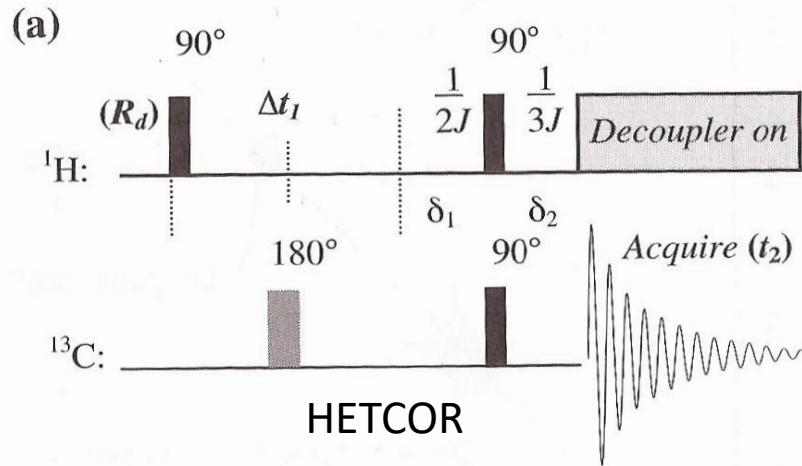
Heteronuclear Correlation



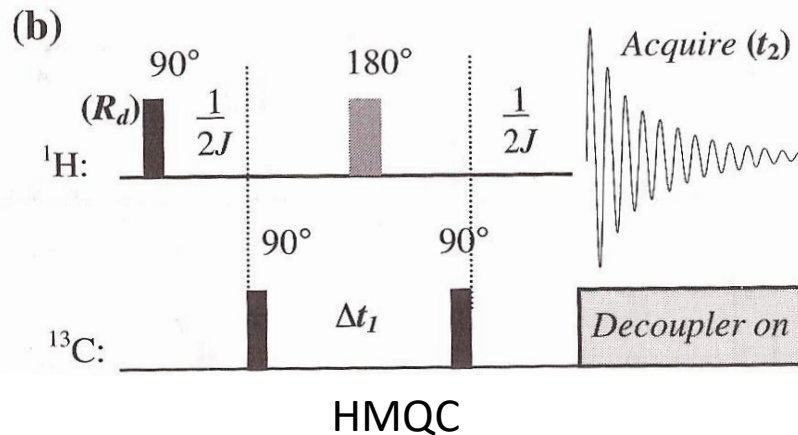


C,H-COSY: HMQC

Heteronuclear Multiple Quantum Correlation



Stesse informazioni di HETCOR
Minor tempo di acquisizione



Procedura inversa.
Si induce coerenza (90°) sul canale
del nucleo insensibile
Si rileva il nucleo più sensibile

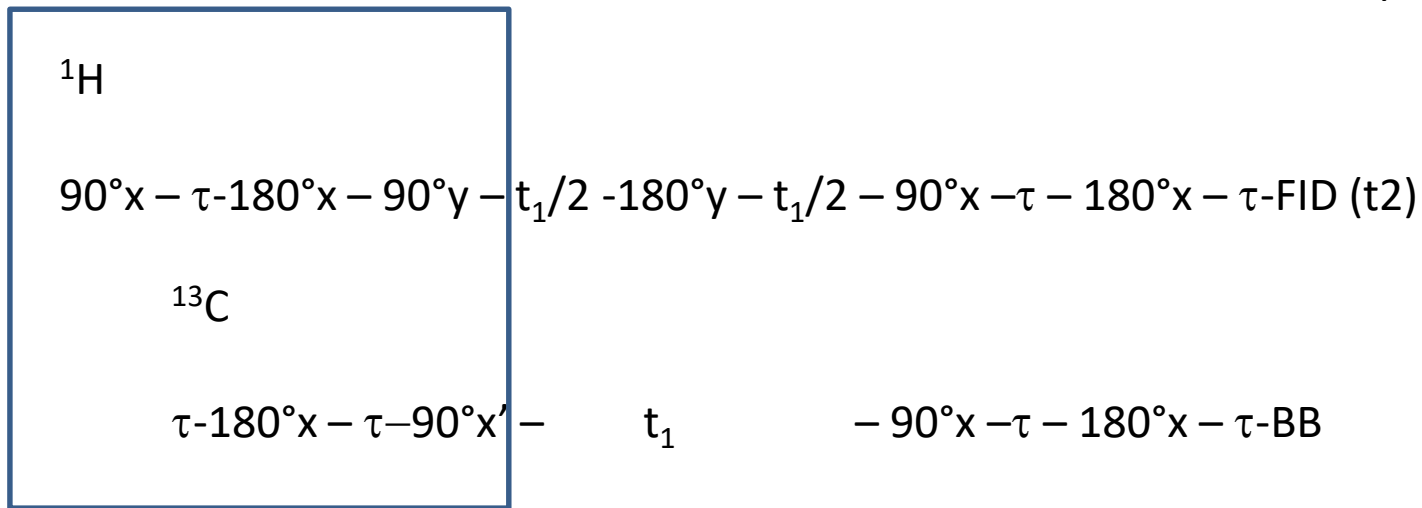
C,H-COSY: HSQC

Heteronuclear Single Quantum Correlation

Evolve solo la magnetizzazione del ^{13}C

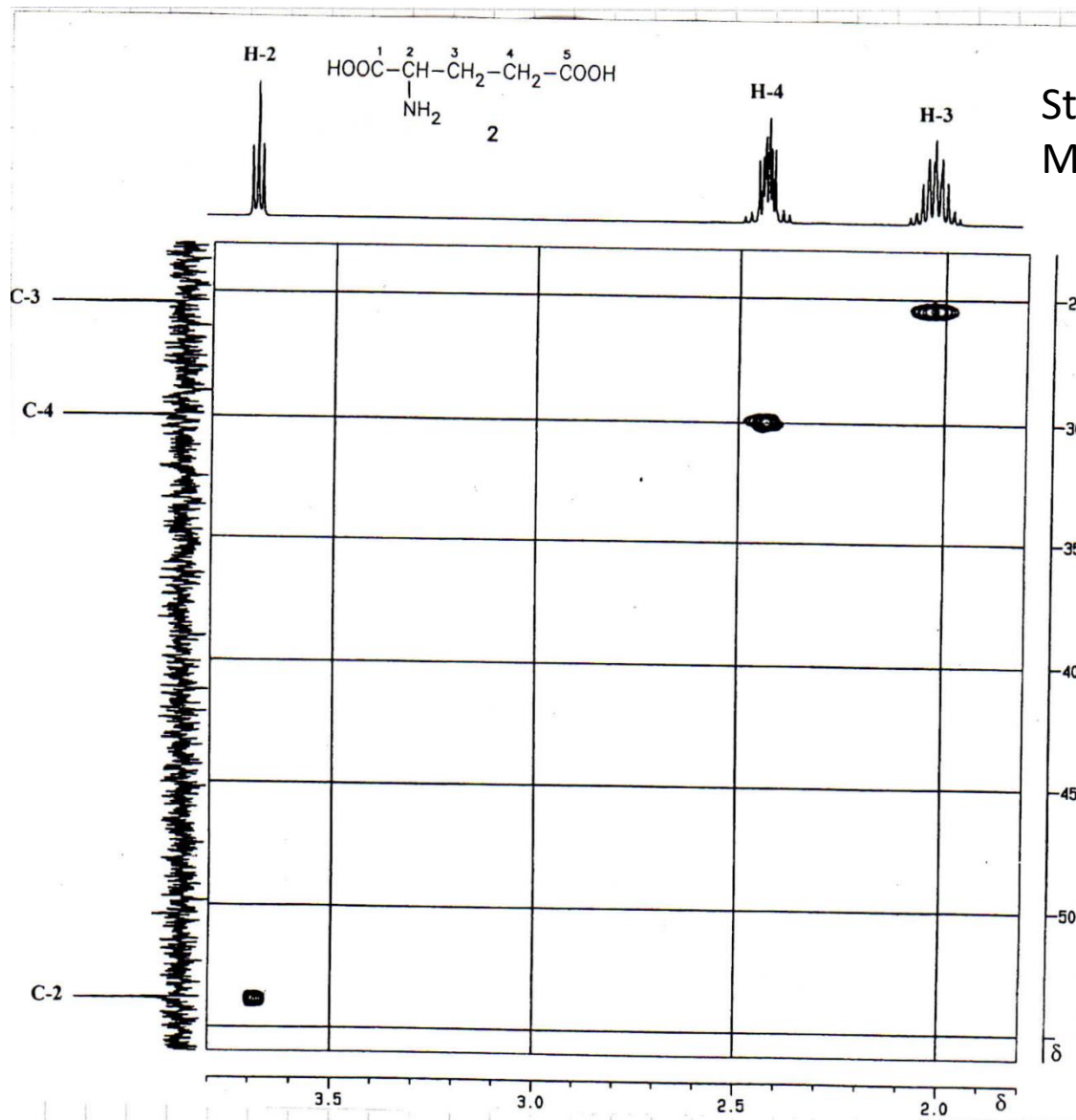
Stesse informazioni
Minor tempo di acquisizione

INEPT



C,H-COSY: HSQC

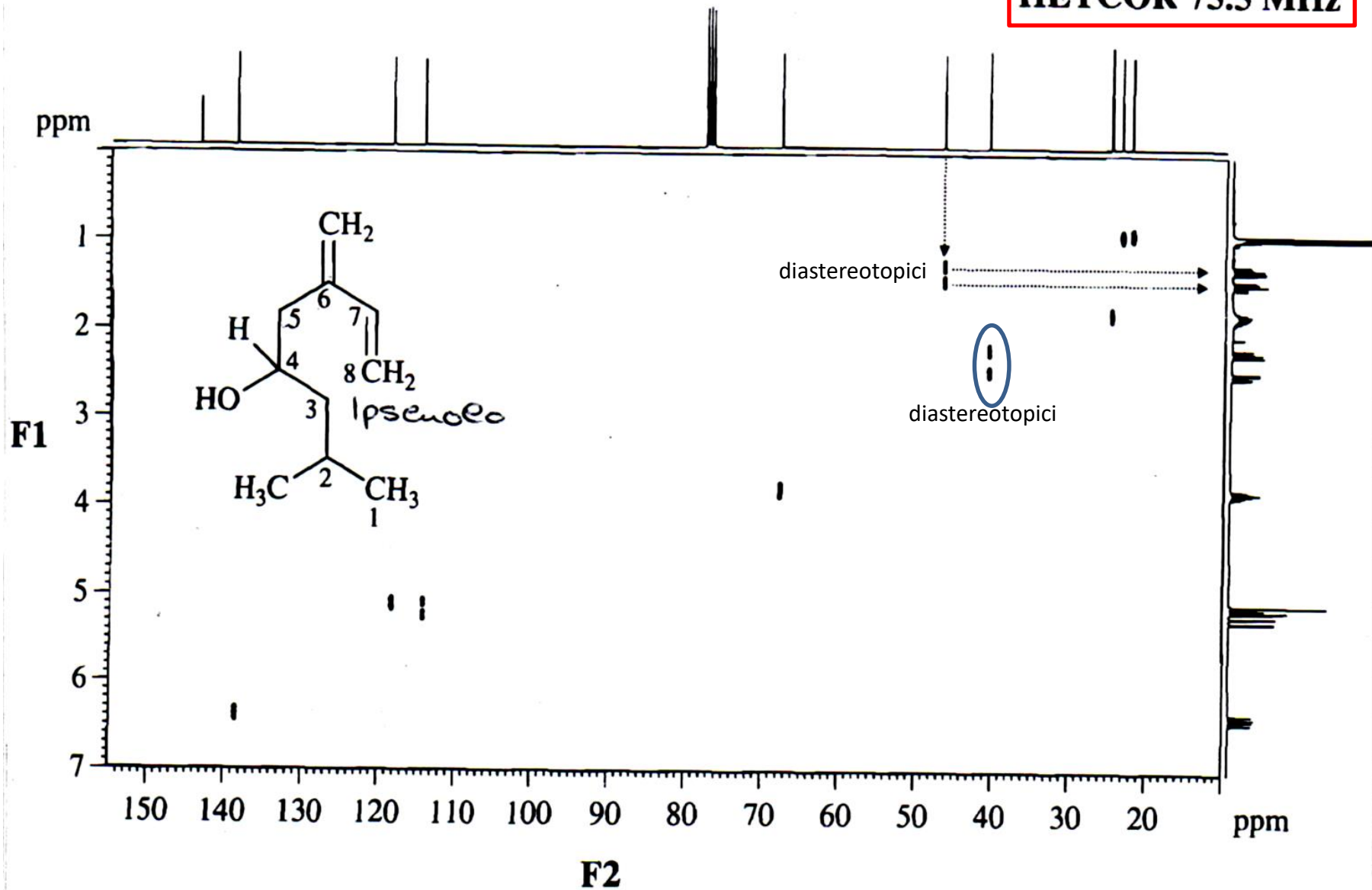
Heteronuclear Single Quantum Correlation



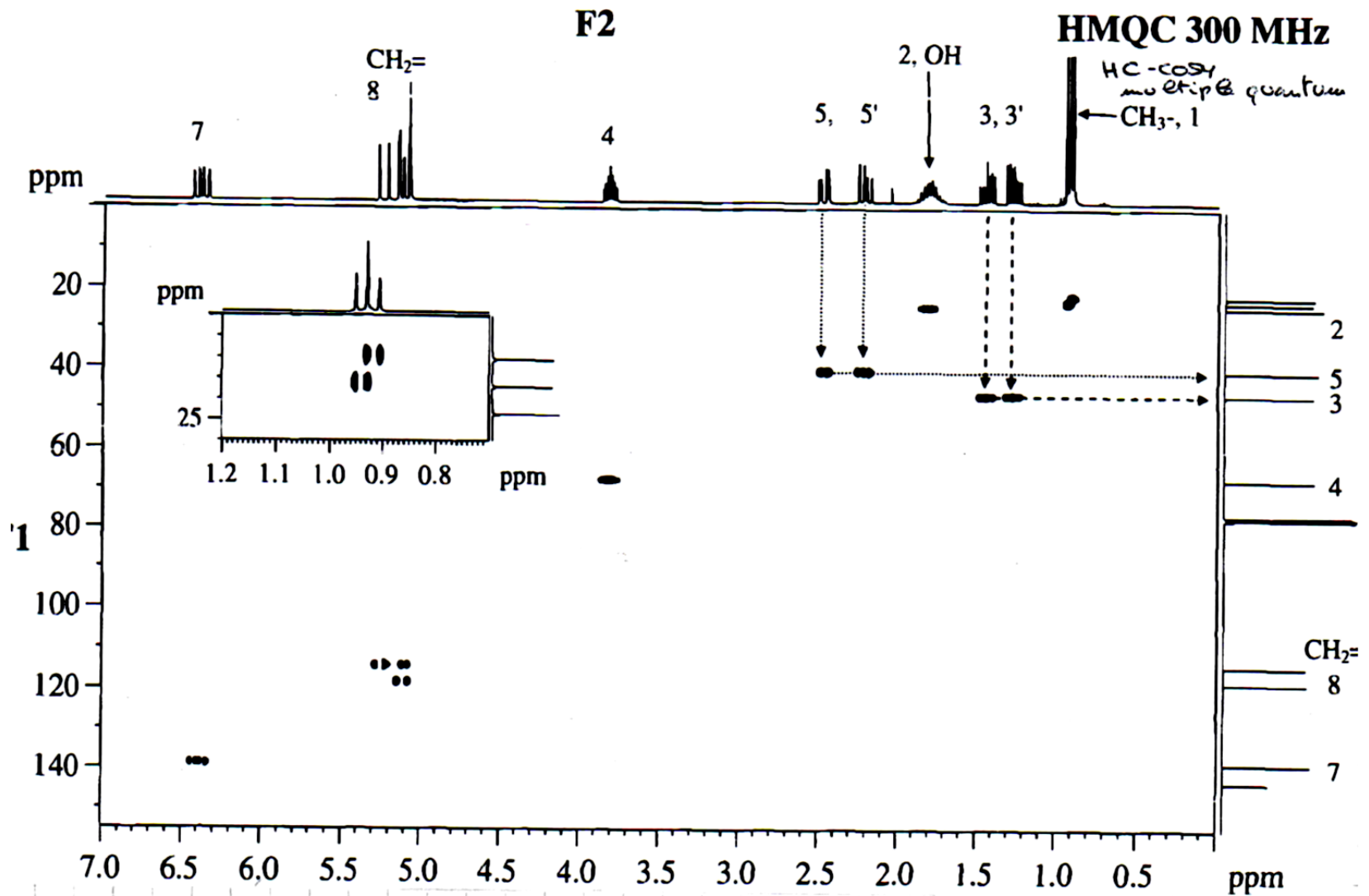
Stesse informazioni
Minor tempo di acquisizione

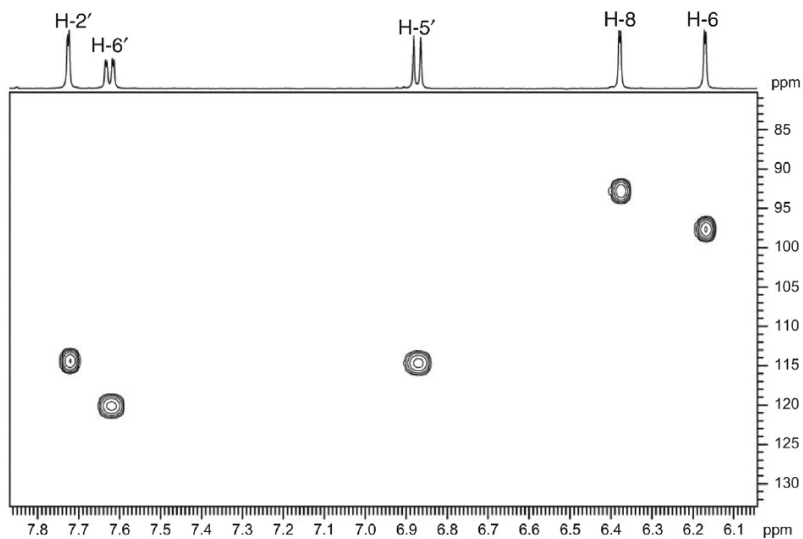
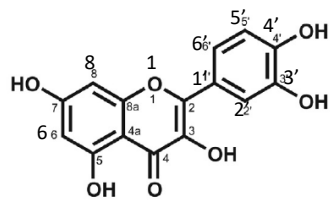
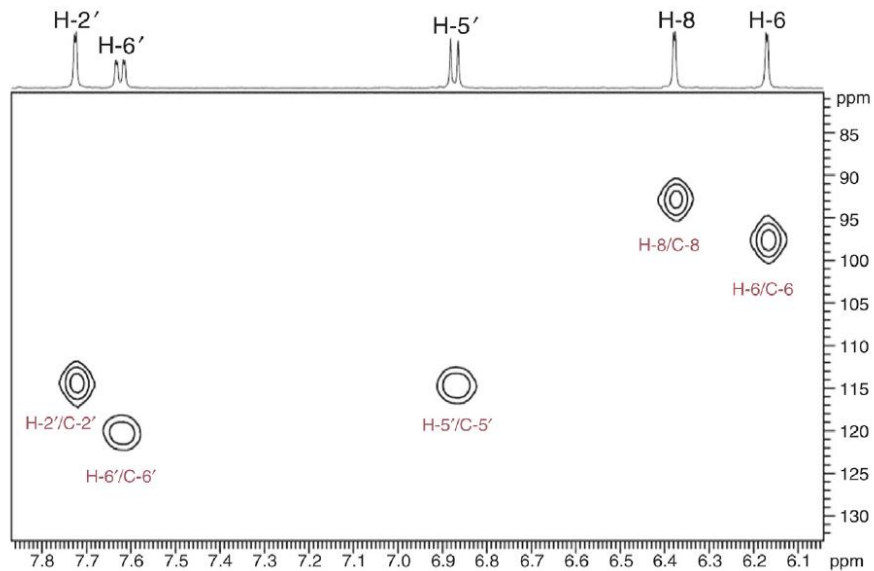
H,C-COSY

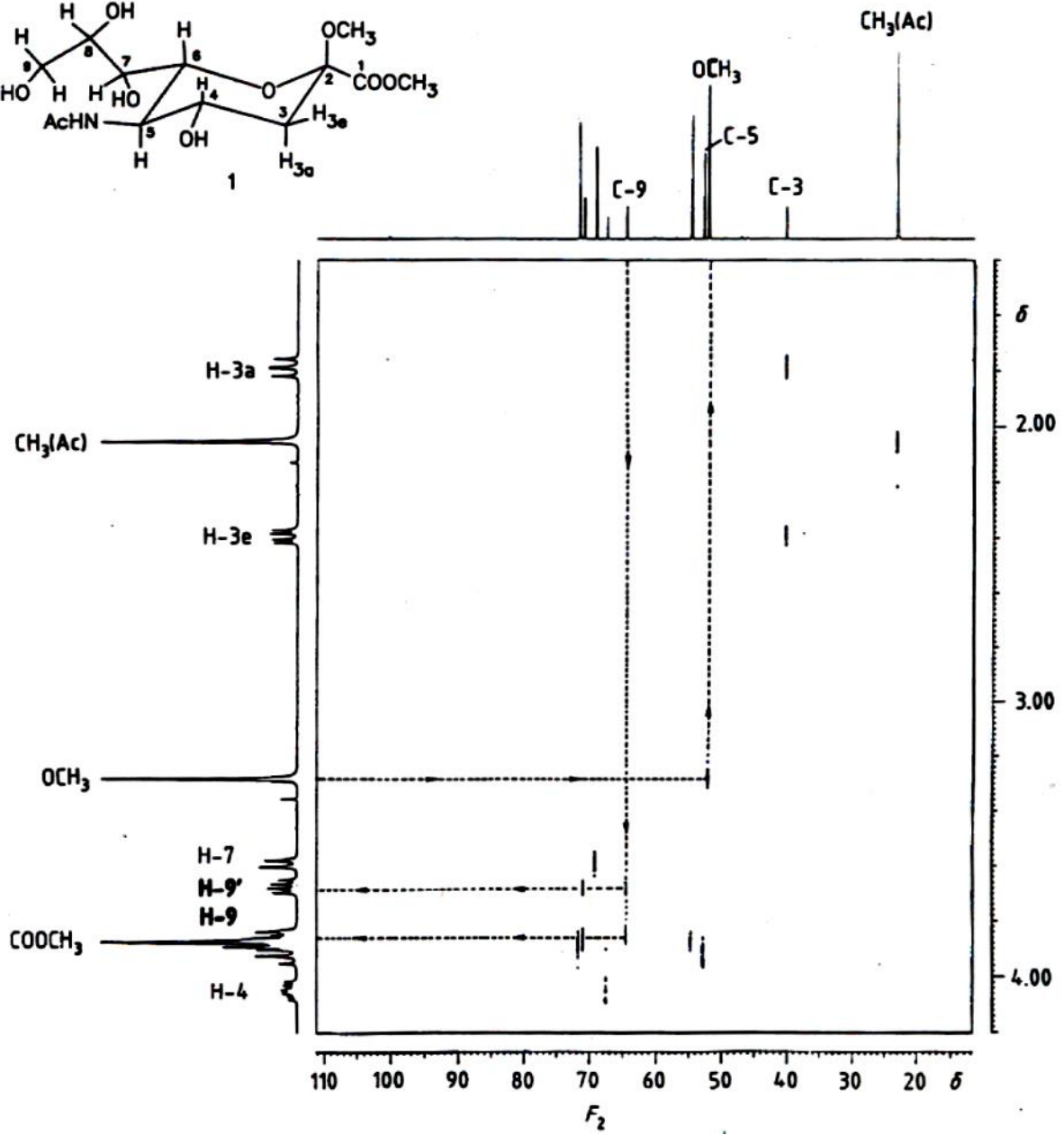
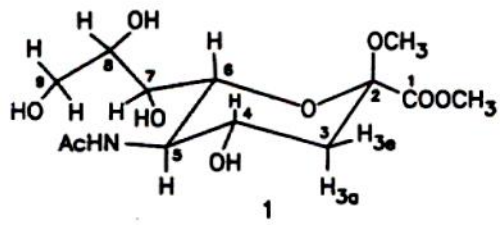
HETCOR 75.5 MHz



C,H-COSY

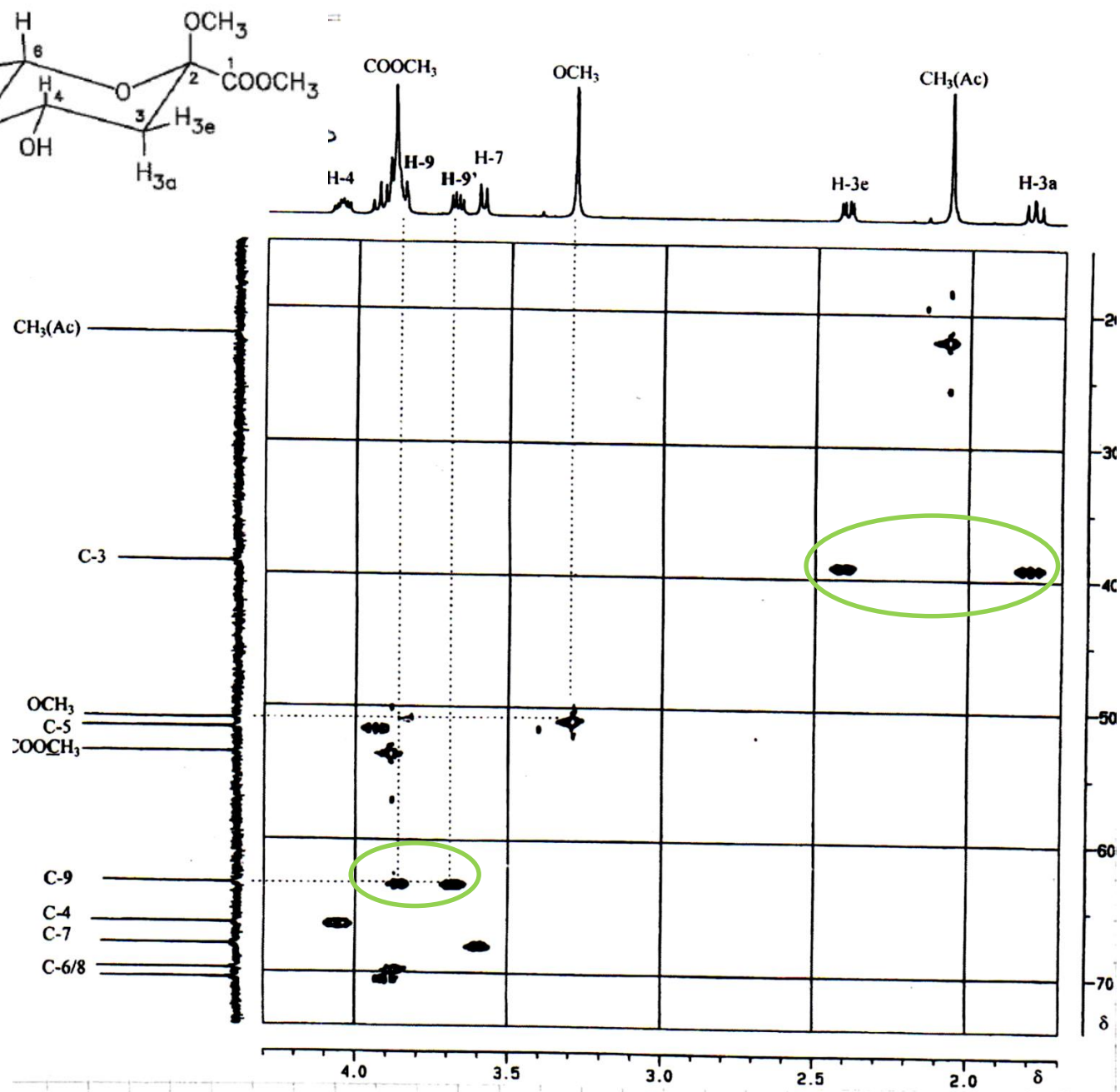
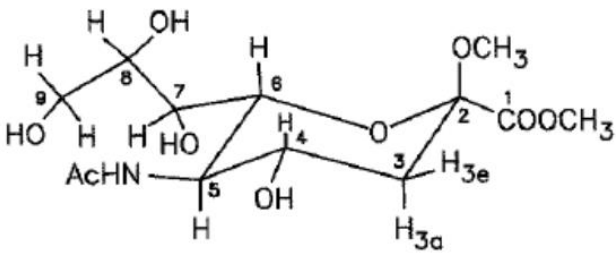






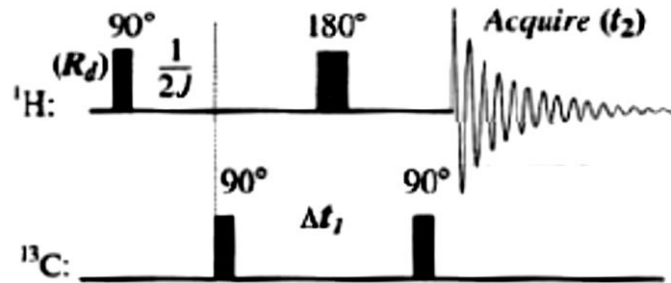
HETCOR

HSQC



HMBC

Heteronuclear Multiple Bond Coherence

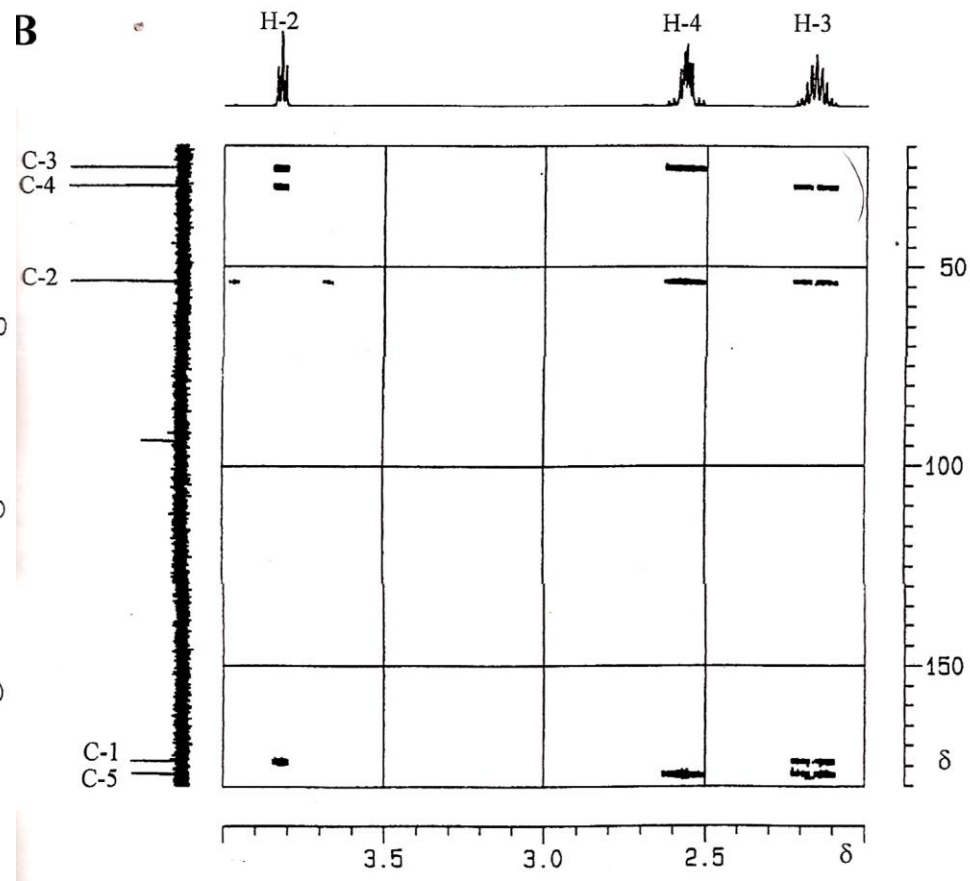
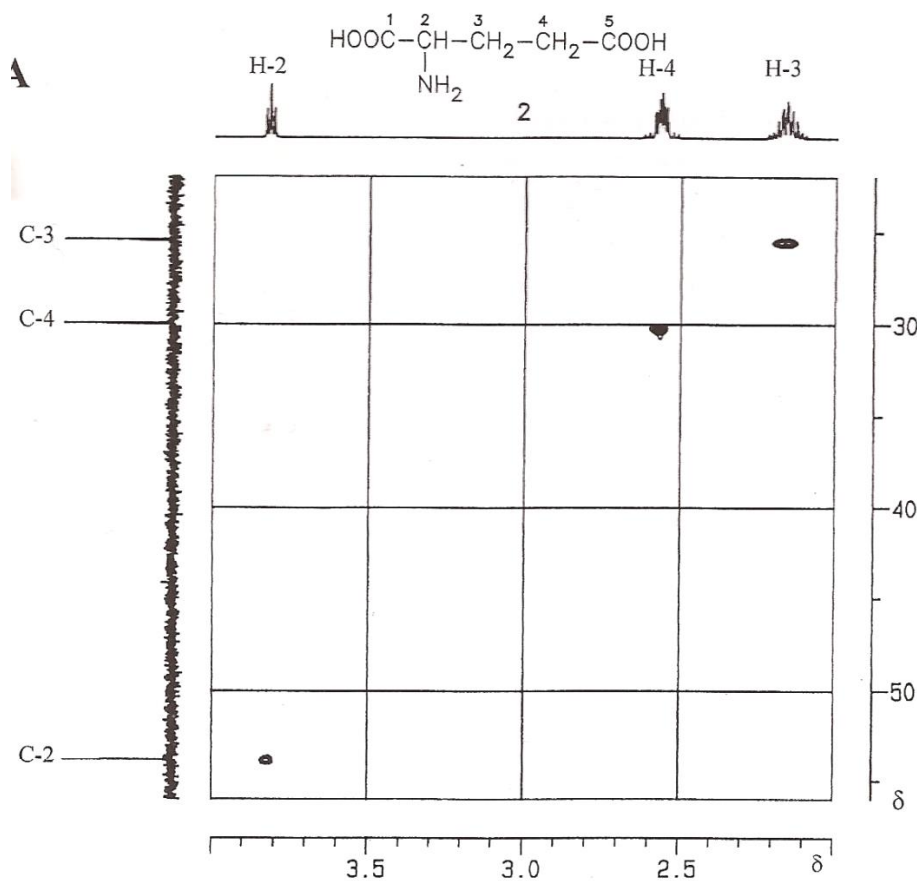


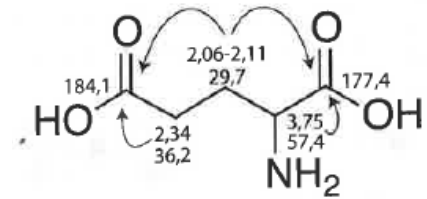
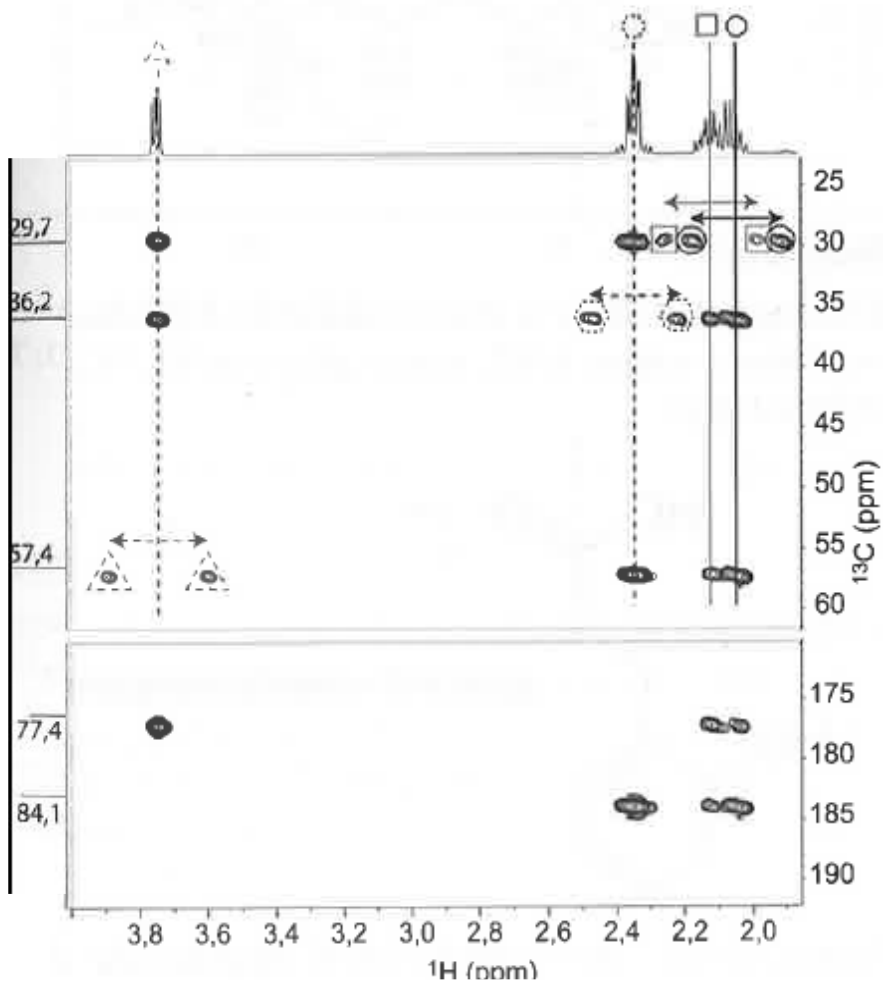
FILTRA GLI ACCOPPIAMENTI $^1J_{\text{CH}}$

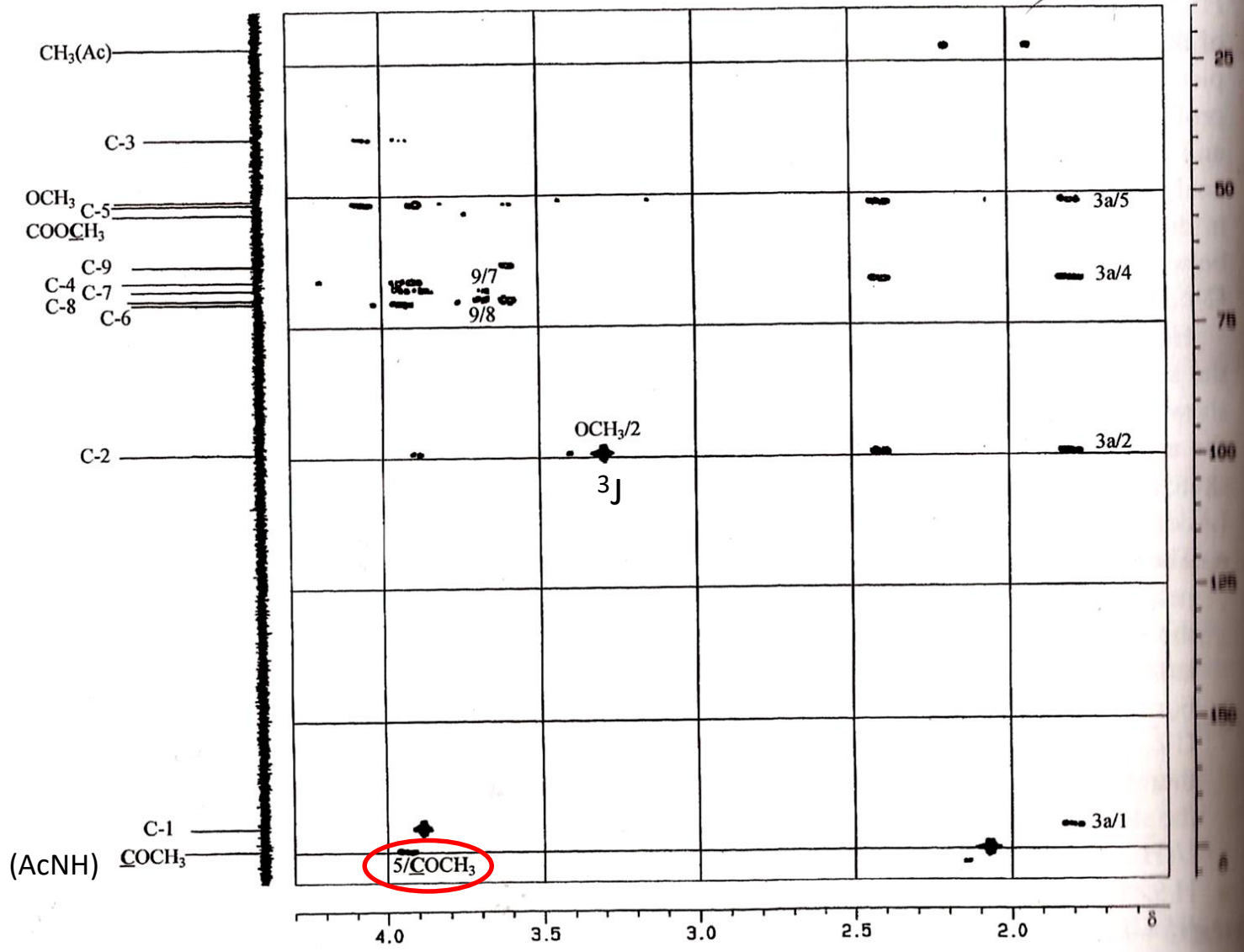
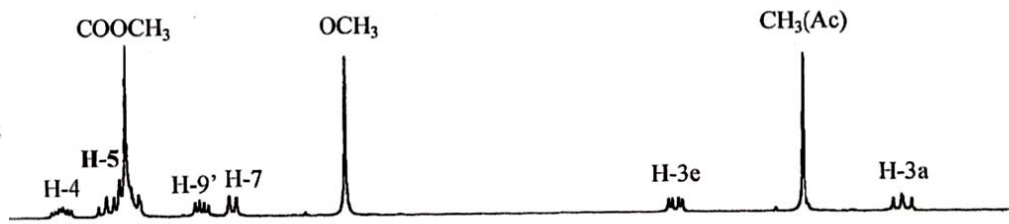
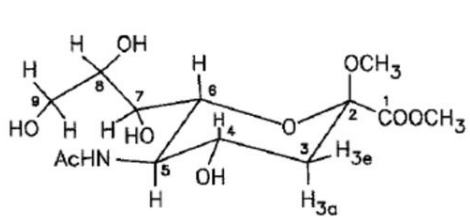
SI VEDONO GLI ACCOPPIAMENTI $^2J_{\text{CH}}$ e $^3J_{\text{CH}}$

HMBC

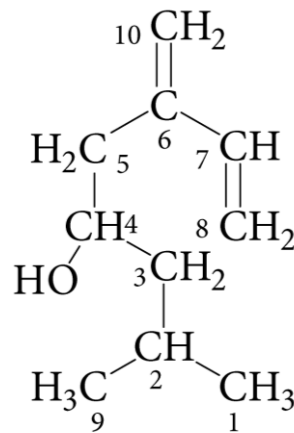
Heteronuclear Multiple Bond Coherence







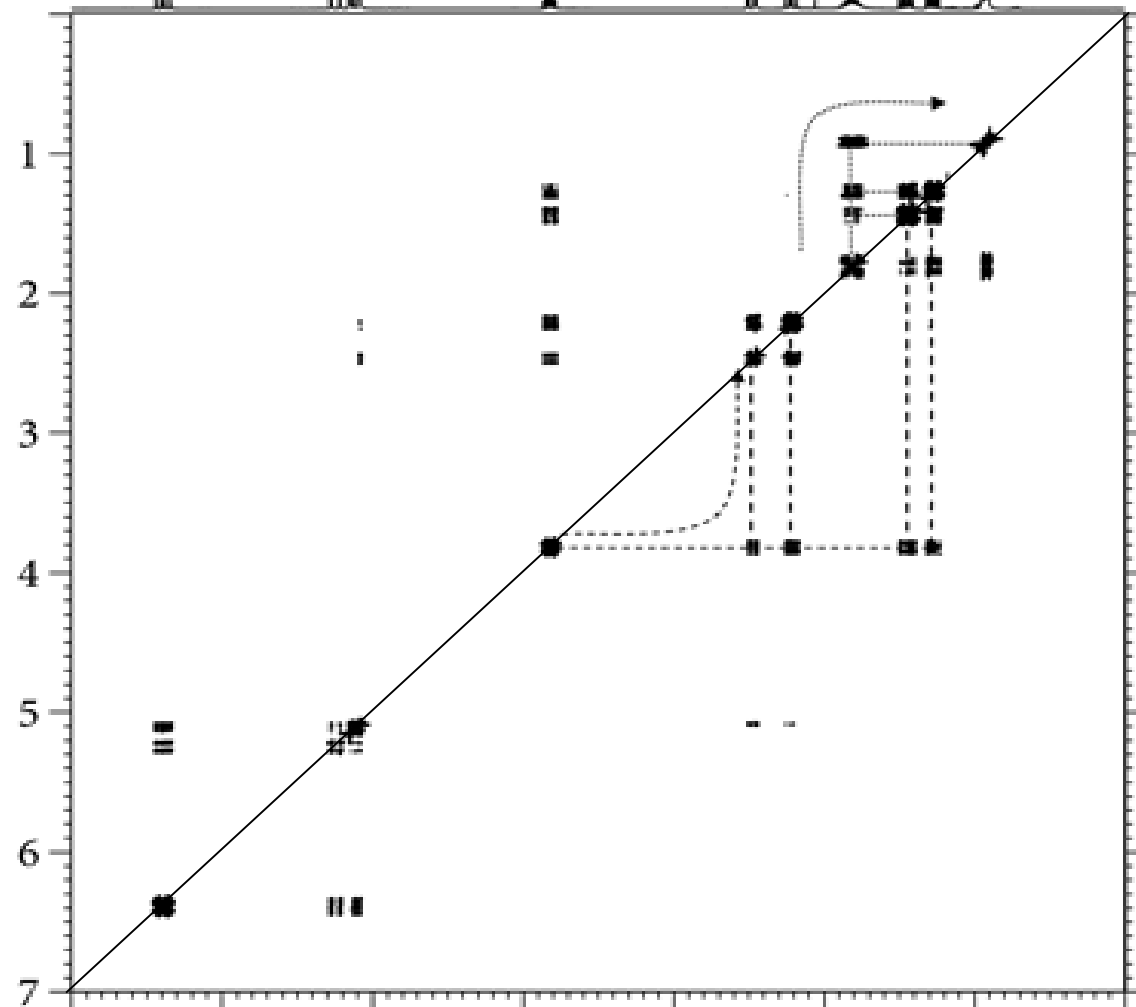
Esercizio: identificare i segnali dei =CH₂ nelle posizioni 8 e 10.



Ipsenolo - COSY

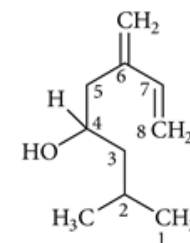
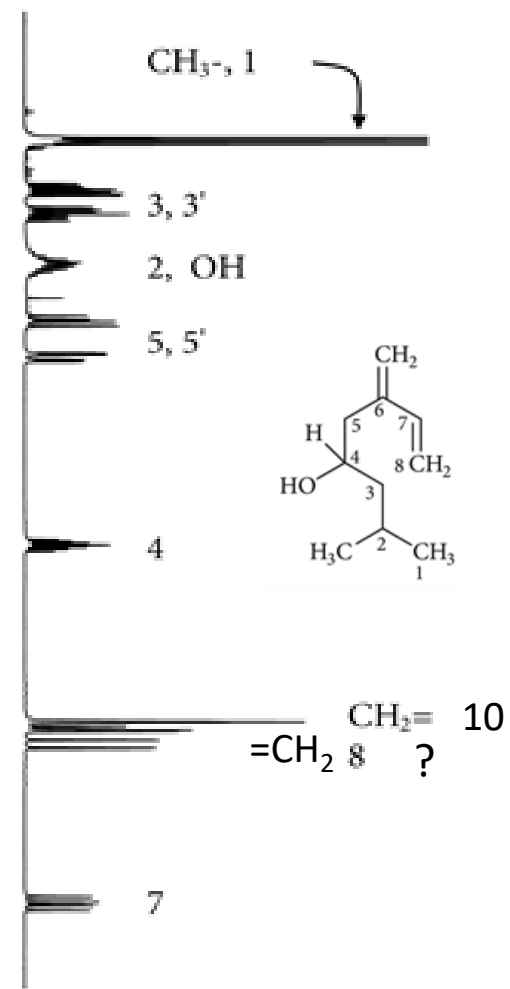
F2

ppm

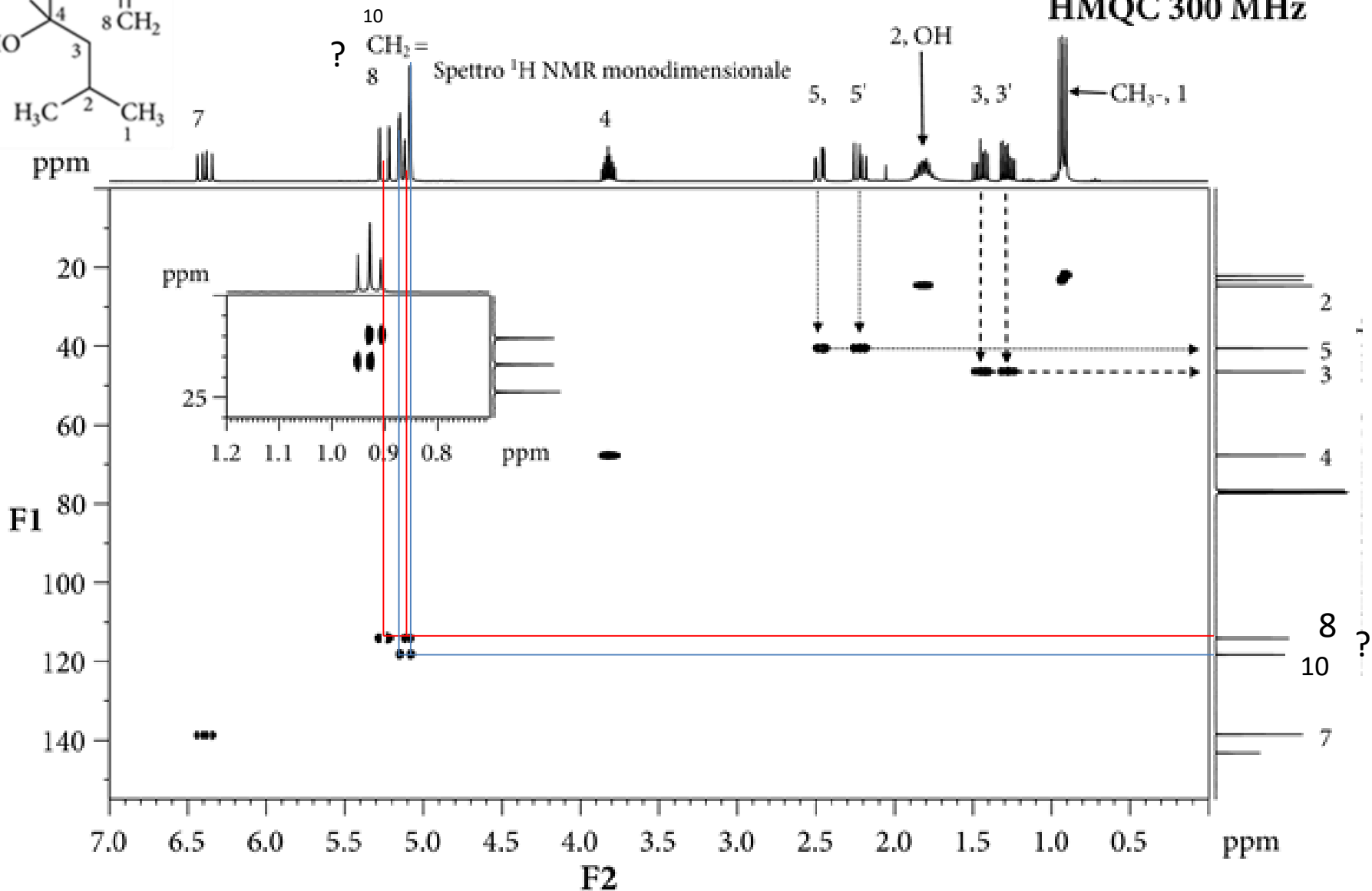
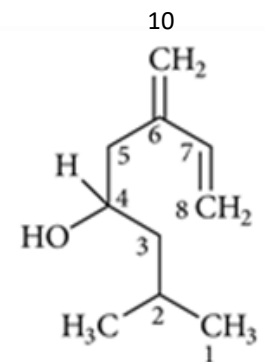


F2

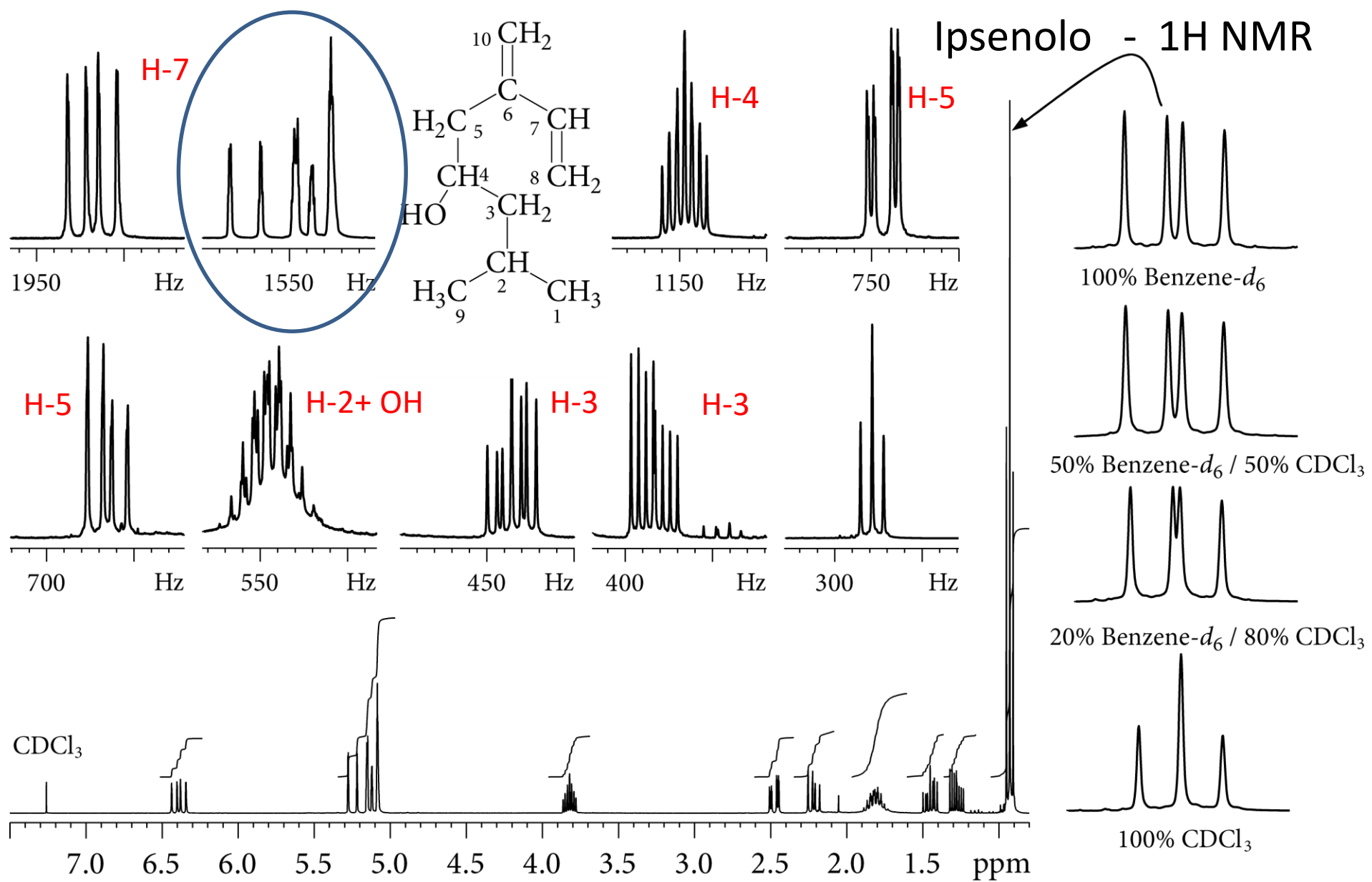
DQF-COSY 300 MHz



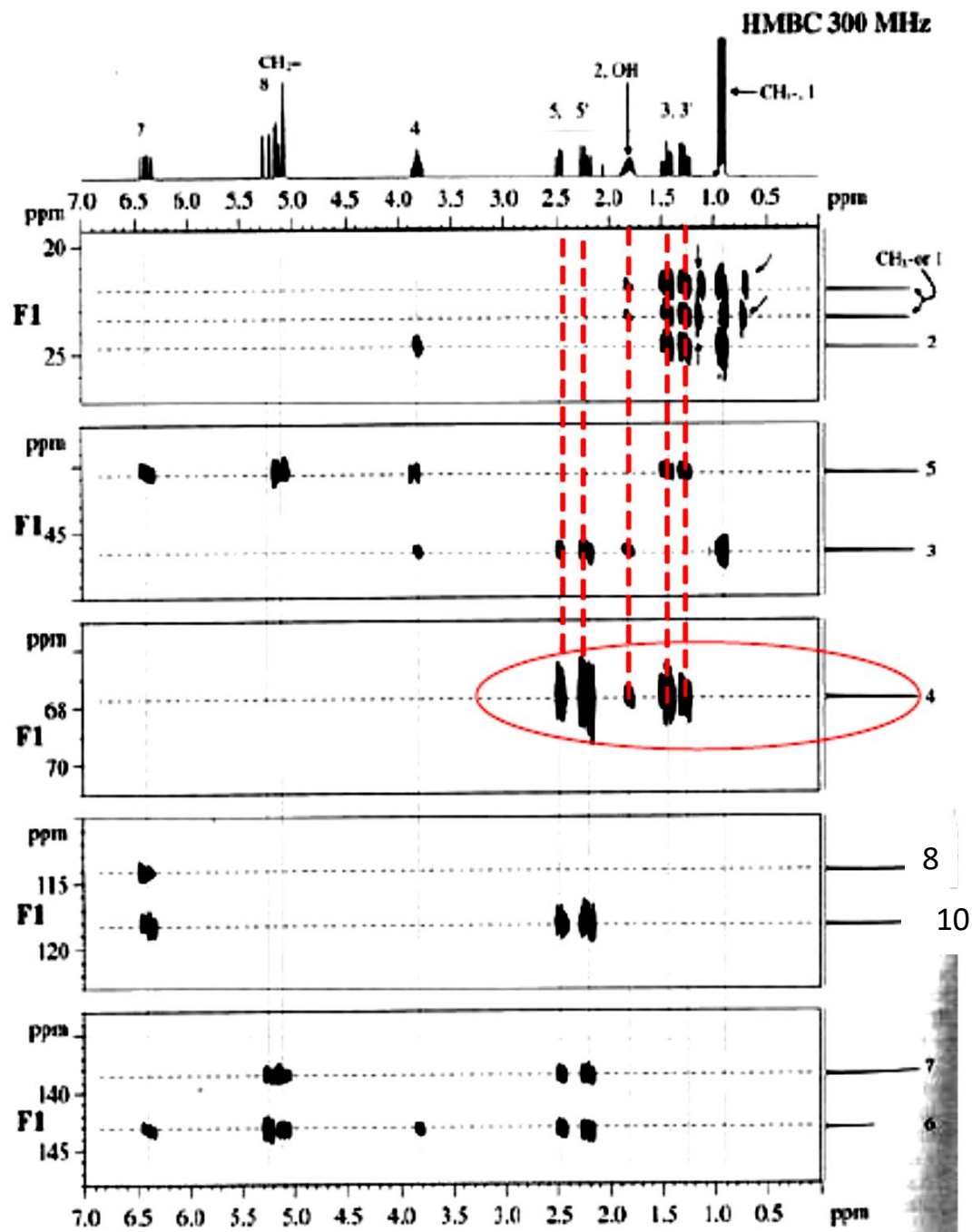
Ipsenolo - HMQC



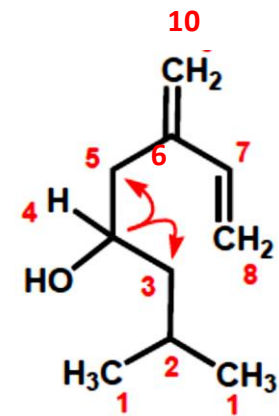
Ipsenolo - 1H NMR



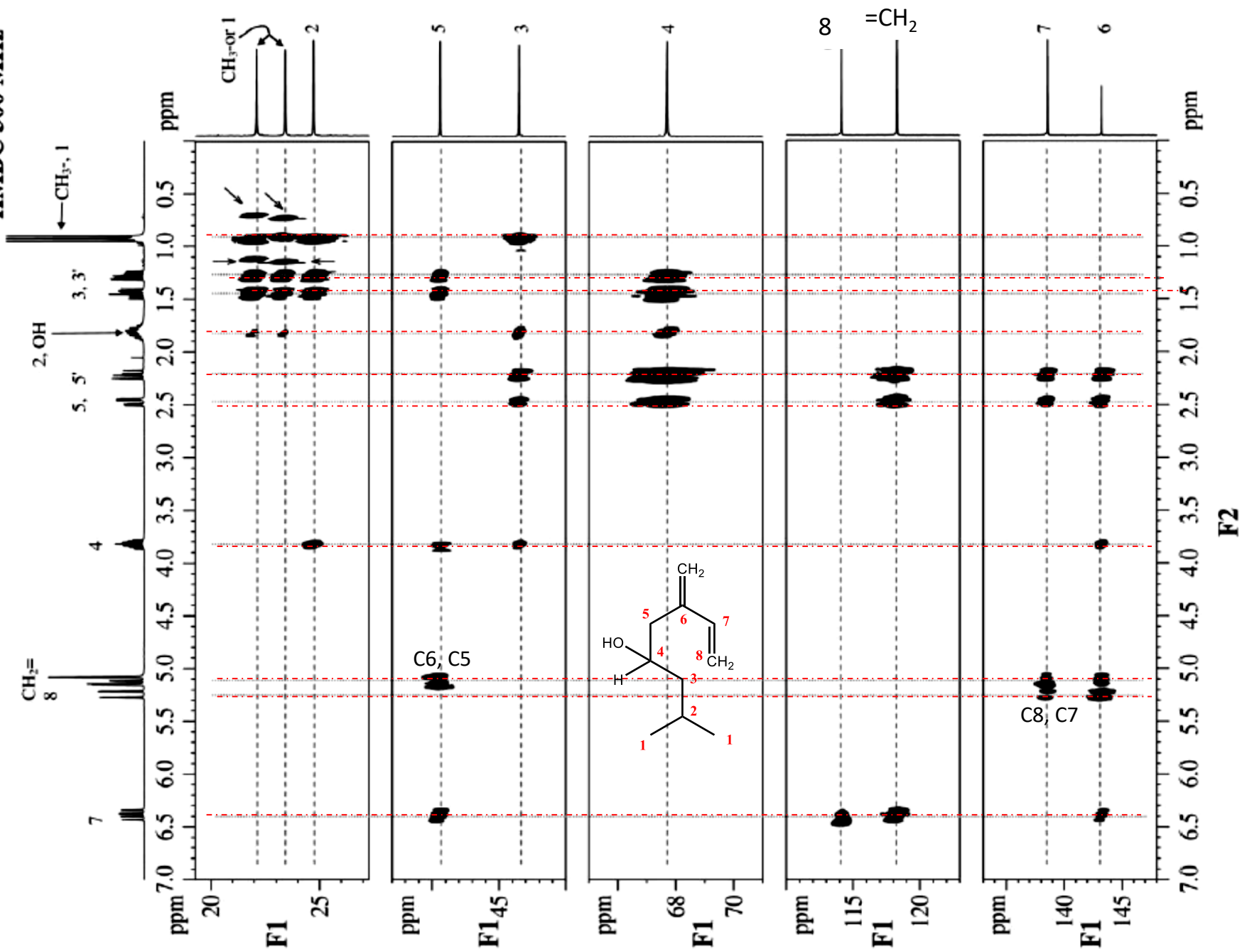
Spettro protonico NMR di 2-metil-6-metilen-7-otten-4-olo (ipesenolo) in CDCl₃ a 300 MHz ed effetto della titolazione con benzene-d₆.



Non si osservano costanti dirette



HMBC 300 MHz



J RESOLVED NMR 2D

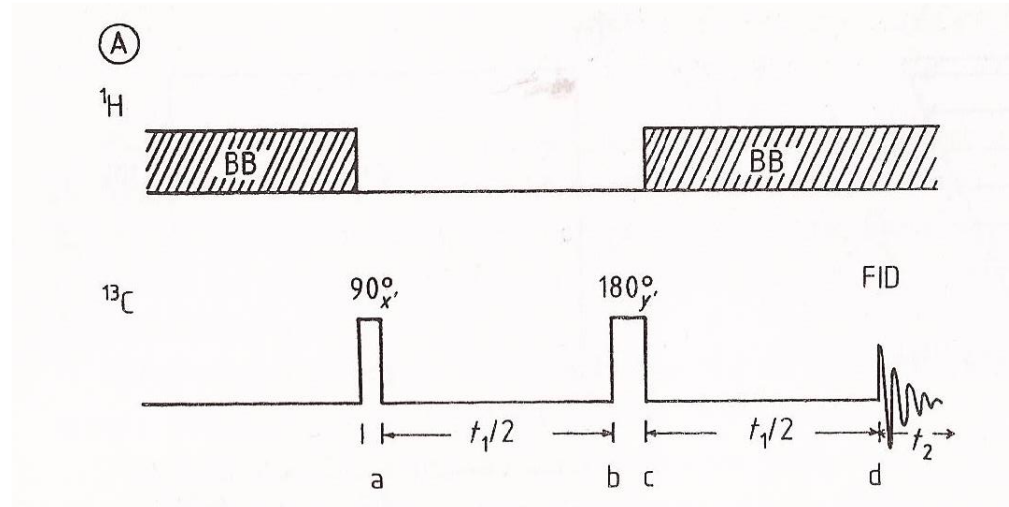
Gli esperimenti J resolved separano l'informazione del chemical shift (ν_1) da quella della J (ν_2) lungo le due dimensioni dello spettro consentendo l'assegnazione esatta di chemical shift e J di multipletti sovrapposti nello spettro 1D.

Versioni omo- ed eteronucleari

1. HETERONUCLEAR (C-H) J-RESOLVED 2D

Derivano dalla variazione periodica del segnale del ^{13}C durante t_1 ad opera della J_{CH} (frequenza di modulazione)

Si usa una sequenza uguale alla 1D J-MODULATED SPIN ECHO, con t_1 variabile in maniera incrementale. Il decoupler è acceso ad intermittenza, in particolare viene spento durante la prima metà del t_1 .



J RESOLVED NMR 2D

Seconda trasformata di Fourier in t_1 dà, per il sistema AX (CHCl_3) due segnali separati da $J/2$

La dimensione ν_2 contiene il ^{13}C chemical shift

La dimensione ν_1 contiene le costanti di accoppiamento

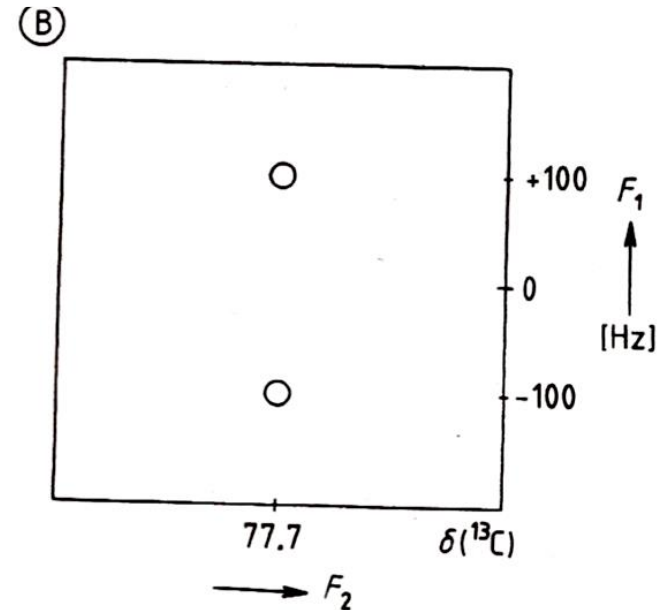
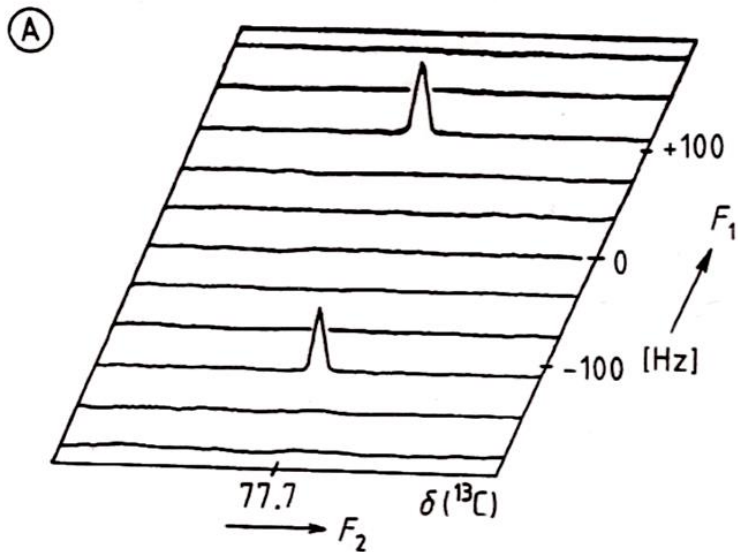
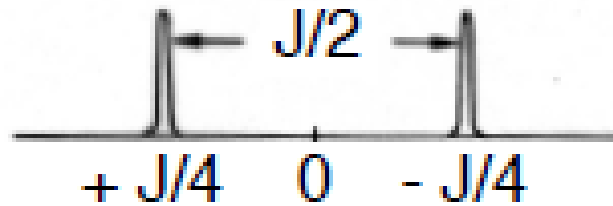
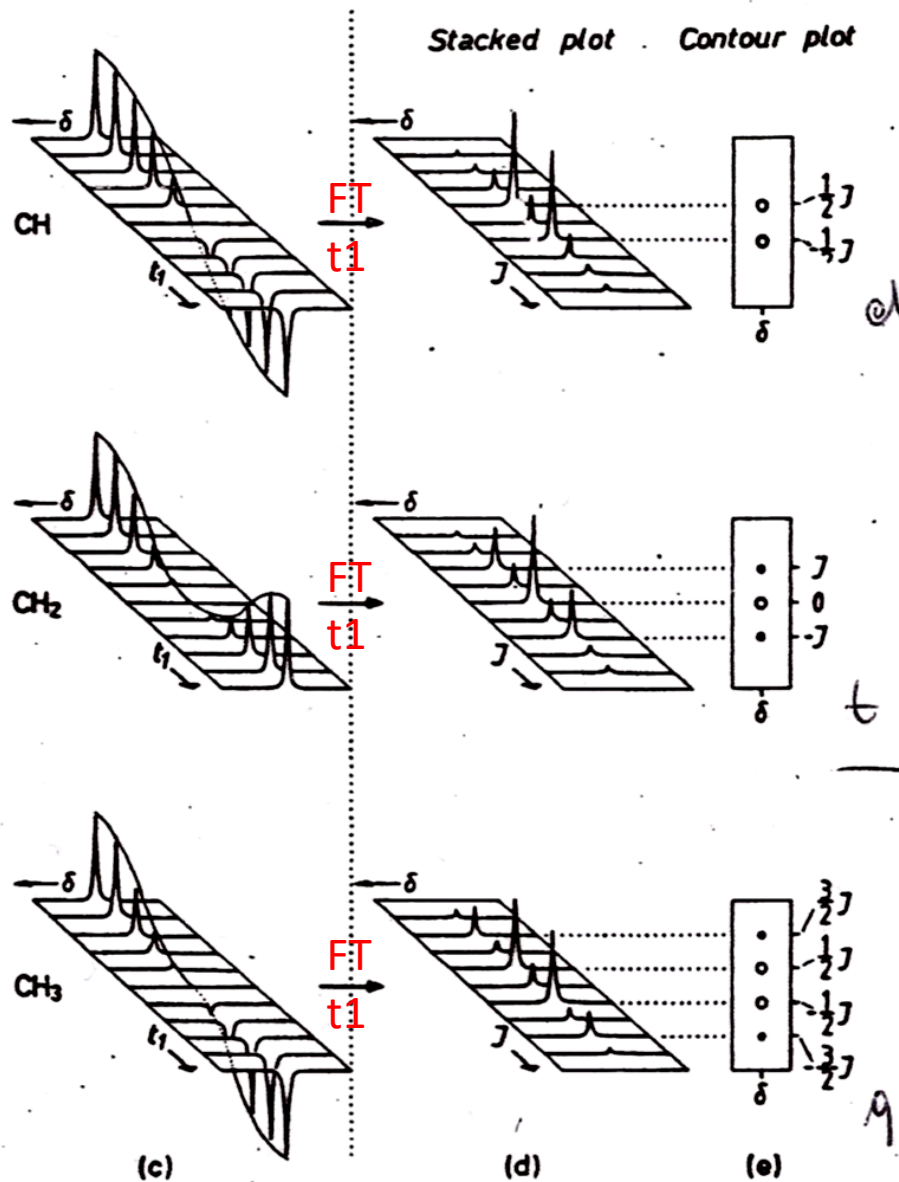
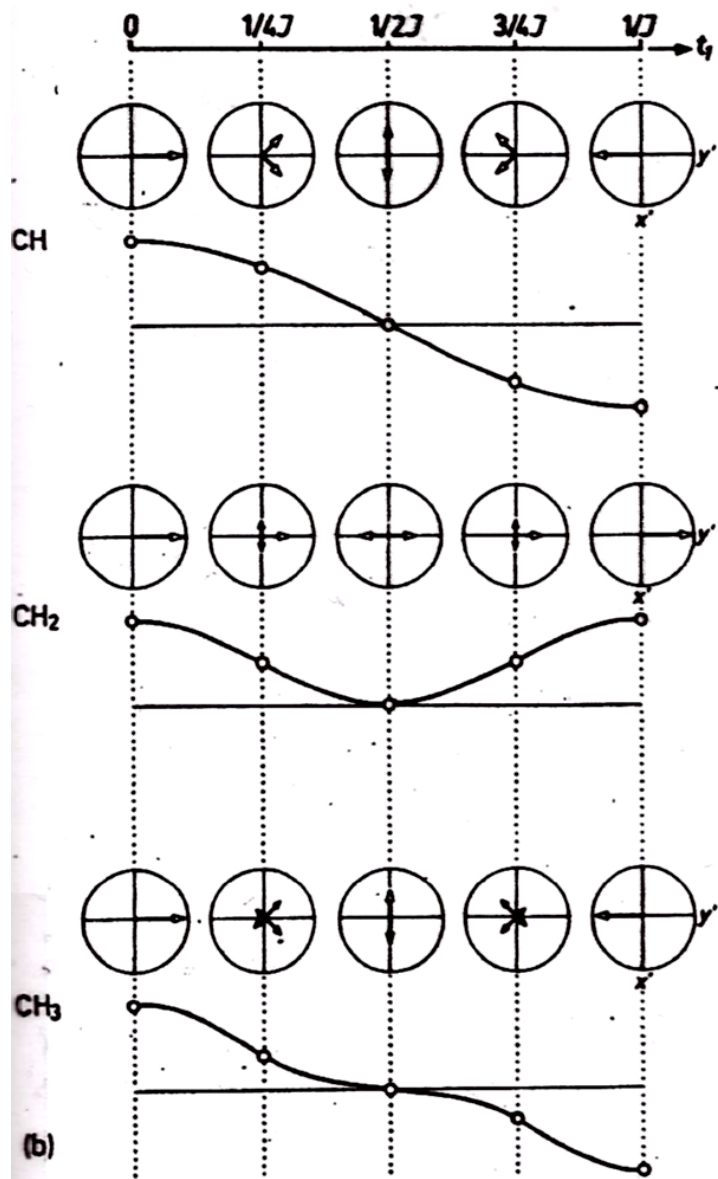
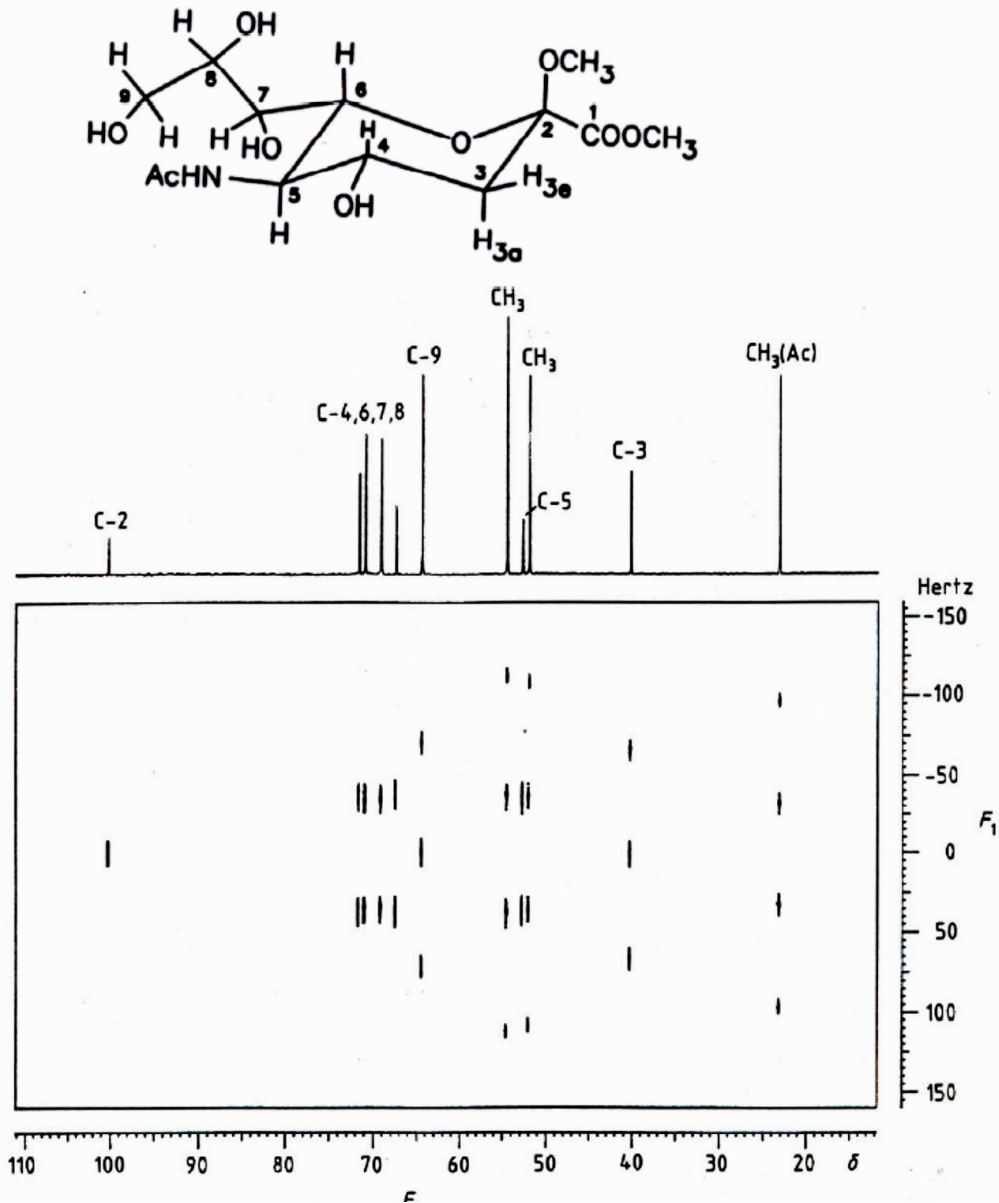


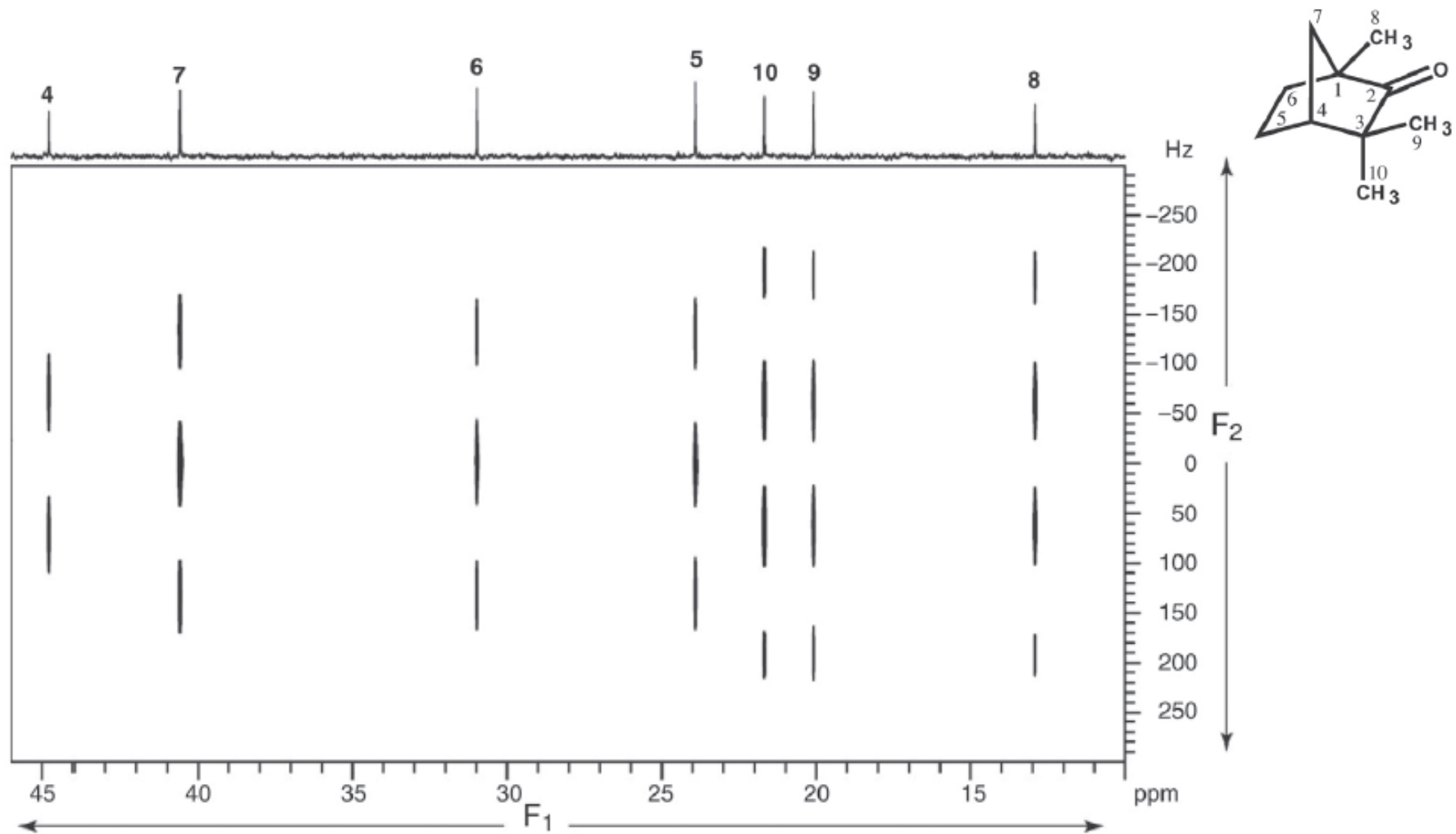
Figure 9-3.

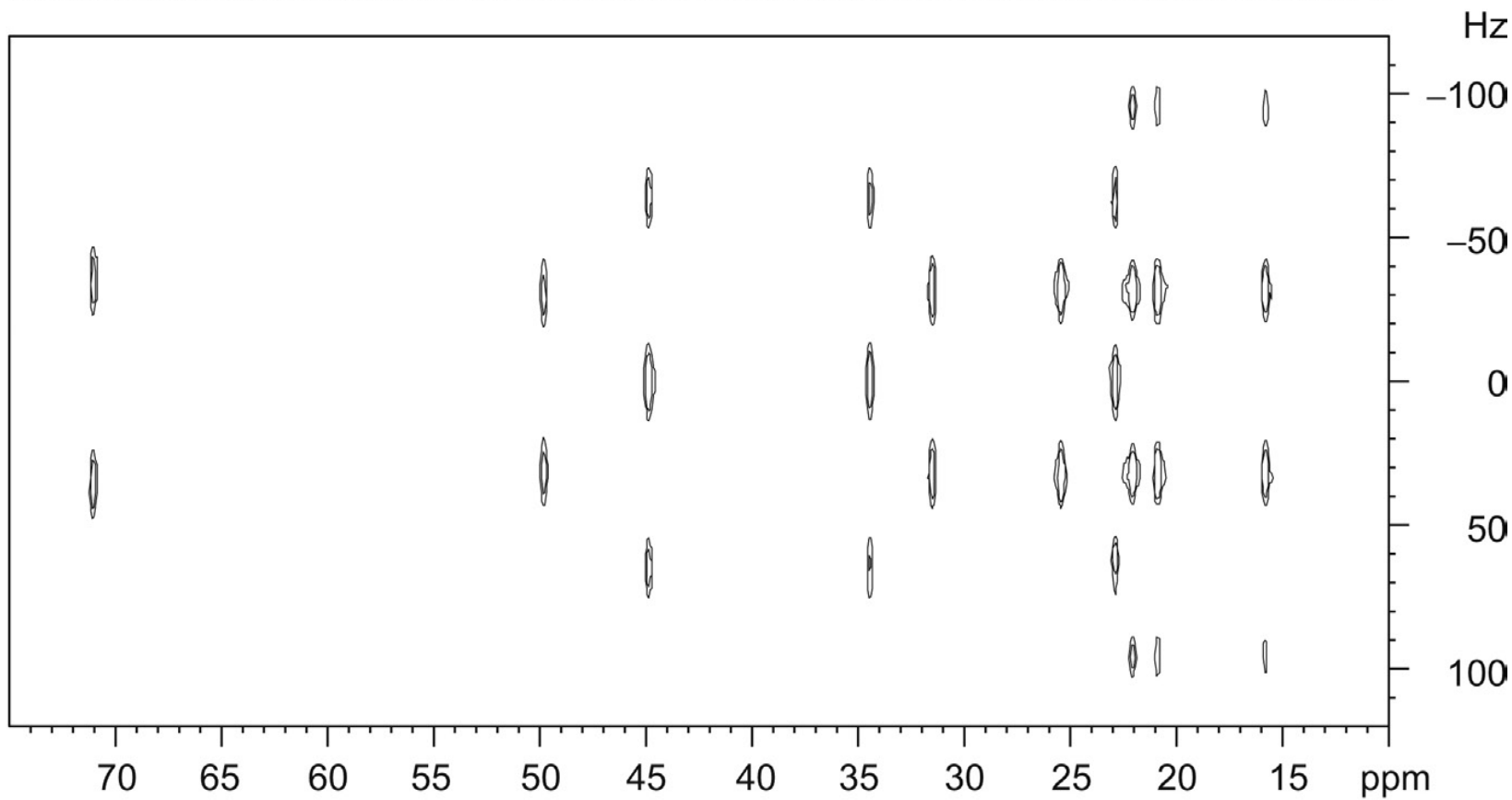
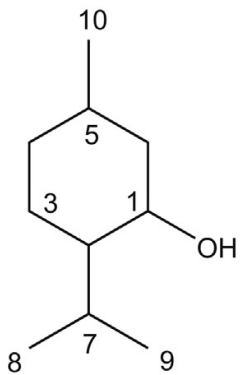
EVOLUZIONE DEI MULTIPLETTI CH_x SOTTO L'INFLUENZA DELLA J



J RESOLVED NMR 2D



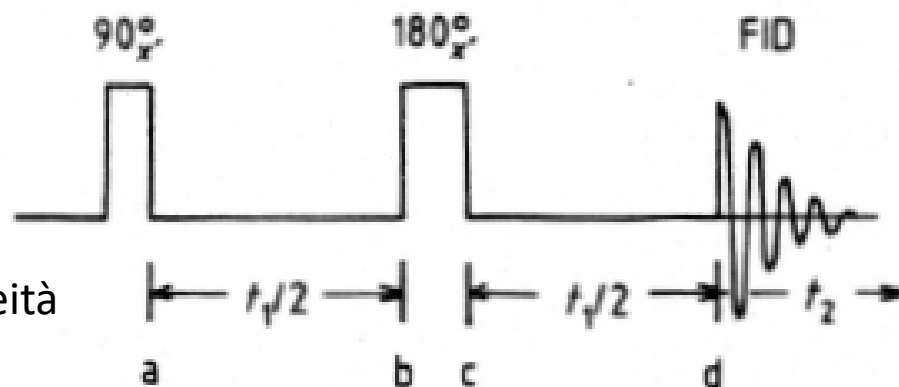




J RESOLVED NMR 2D

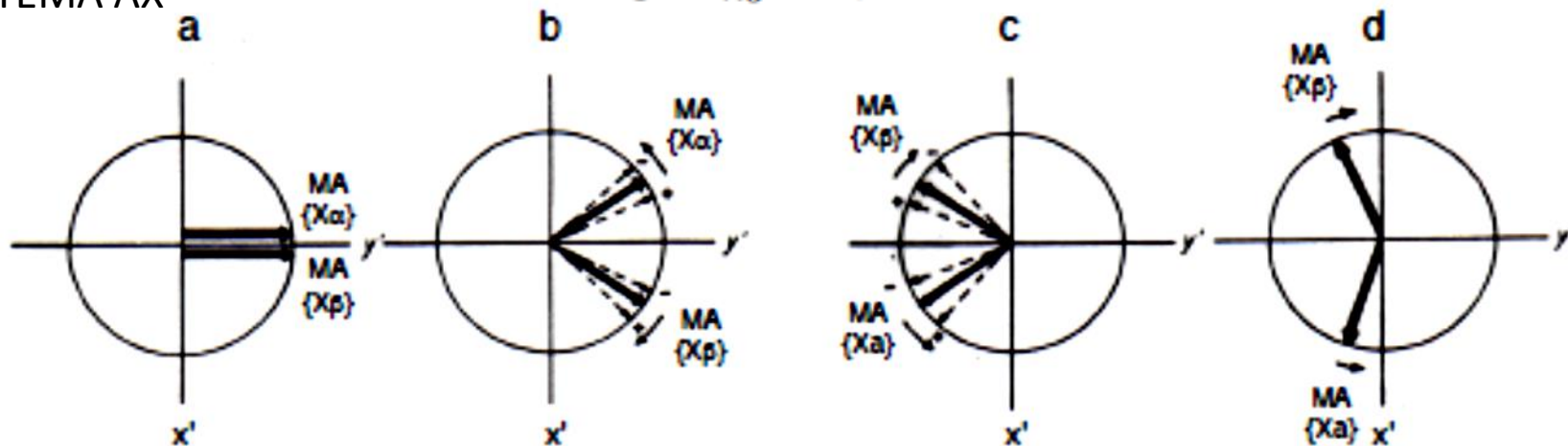
2. HOMONUCLEAR (HH) J-RESOLVED 2D

- Esperimento simile a J-MOD spin echo con t_1 variabile
- Ovviamente non si può usare il BB
- Gli impulsi sono applicati su entrambi gli spin A e X
- J coupling evolvono durante entrambi i $t_1/2$
- Evoluzione del chemical shift e le inomogeneità sono rifocalizzate con 180°



SISTEMA AX

$$\Theta = 2\pi J_{AX} t_1$$



J RESOLVED NMR 2D

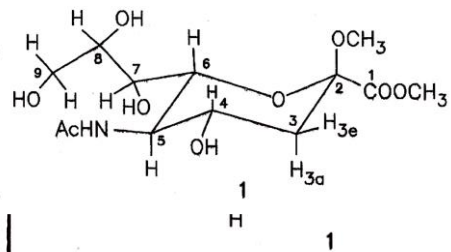
2. HOMONUCLEAR (HH) J-RESOLVED 2D

Per un sistema ^1H AX:

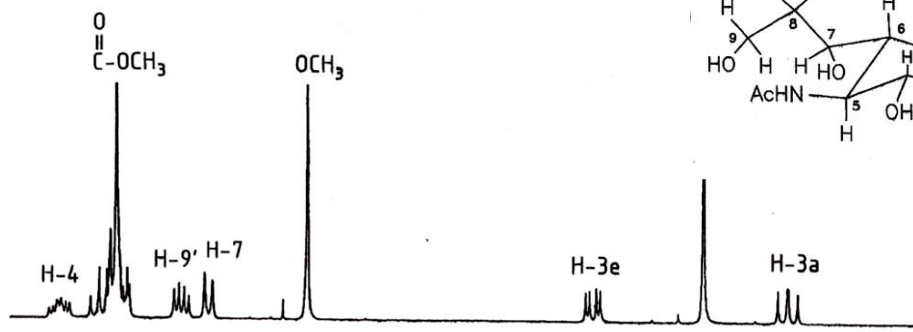
Il segnale nel receiver dipende dalla somma dei due vettori, che dipende da J_{AX} .

Dopo FT(t_2) otteniamo 1 picco in ν_2

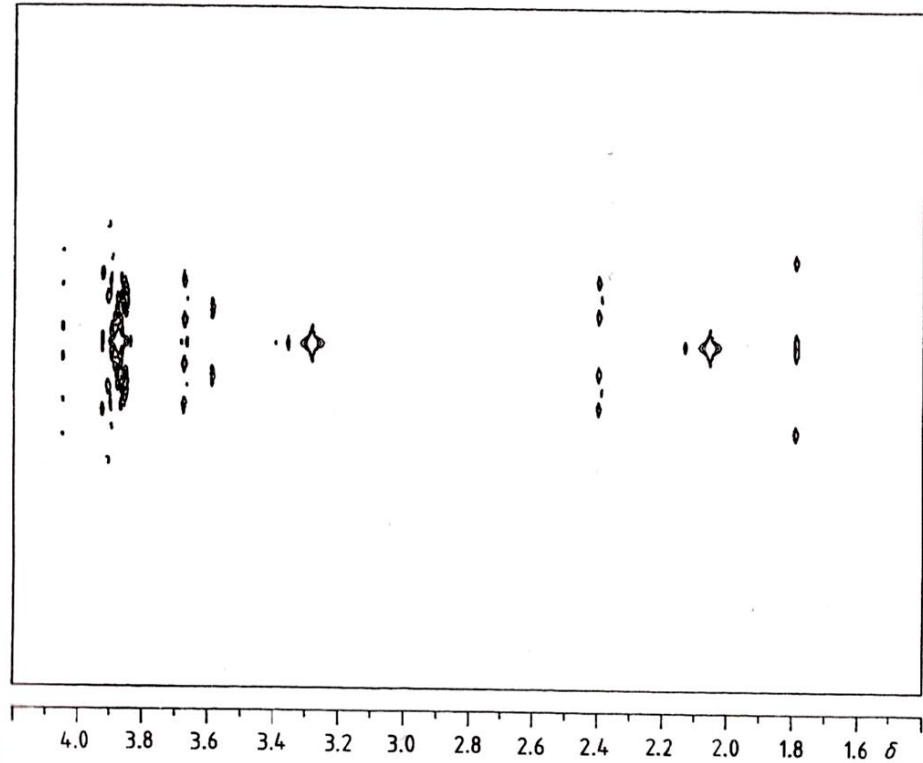
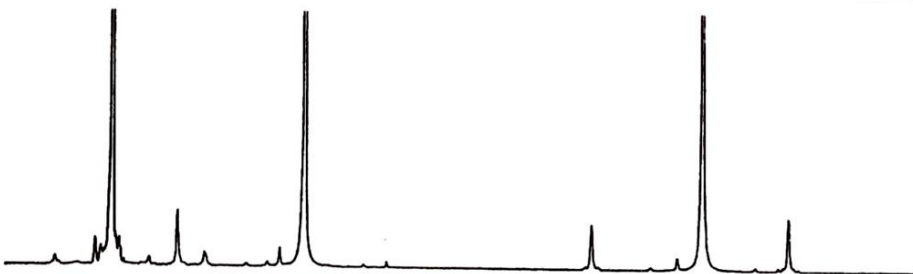
I segnali ^1H NMR sono modulati da J_{AX} in t_1 . Dopo FT(t_1) si osserva un doppietto in t_1 con separazione J_{AX}



B)



A)



J RESOLVED HH-2D

