Identification of Unknown Organic Compounds

Workbook to Accompany Organic Chemistry Courses

Introduction

This workbook is designed to train organic students in the art of spectral interpretation. A detailed discussion of the theory of spectroscopy (and spectometry for MS) may be found in most organic textbooks and that material should be studied before attempting the problems.
There are tables of data (correlation tables) which are used to interpret aspects of each spectrum. These are included as appendices in the back of the book.
Each compound is an "Unknown" and the spectral data are included: infrared (IR); nuclear magnetic resonance (NMR), both proton and 13C. Although not a spectroscopic technique, the low resolution mass spectrum (MS) is also included.

Problem Solving—The Strategy

There are four spectra for each compound:

1) **The Mass Spectrum**-This is a low resolution spectrum of the fragmentation patterns, resulting from the electron ionization of the compound. The molecular formula is also included on this page; by using the index of hydrogen deficiency, it is possible to determine the number of rings and/or double bonds in the compound.[1] The IHD does not distinguish rings *from* multiple bonds, but does indicate the total numbers of rings *and* multiple bonds. The mass spectrum itself, is a listing of the masses for the fragments, resulting from the ionization of the compound.

2) **The Infrared Spectrum**-This spectrum shows the vibrational frequencies of different types of bonding in an organic compound. This data is used to determine the *functional groups* present in the compound. There is a table of common vibrational frequencies in reciprocal centimeters (cm^{-1}) in Appendex B.

3) **The ^{1}H NMR**-this is used to determine the locations and the types of protons in the structure. The integration of the proton types is included on the spectra. The integration is the simplest ratio of *types of protons* in the structure; always cross check with the molecular formula to be sure that all the protons have been assigned. There is a correlation table of chemical shift values in Appendix C.

4) **The ^{13}C NMR**-analogous to proton NMR: this spectrum reveals the different types of carbon in the compound. These are the standard decoupled ^{13}C NMR spectra; there is also a correlation table of ^{13}C chemical shift data in appendix D.

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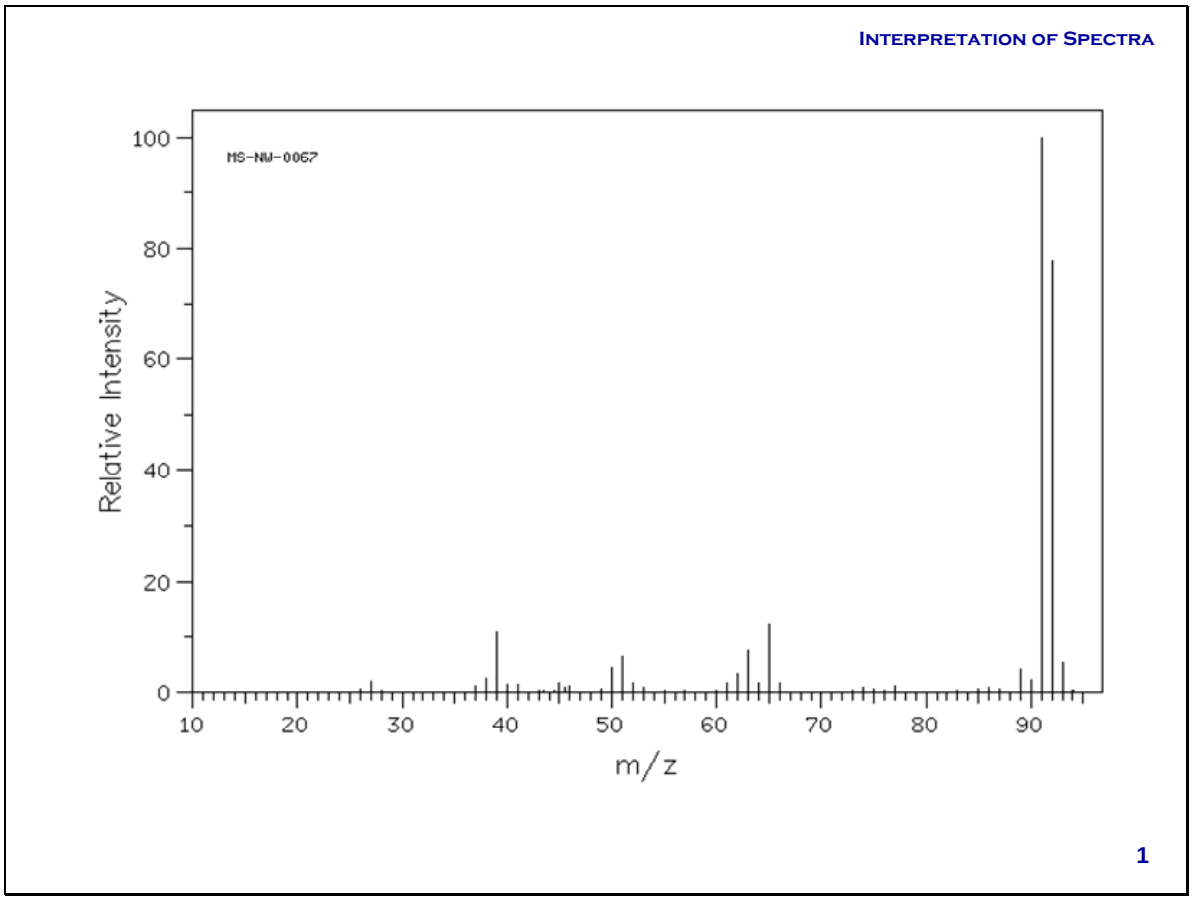
[1] IHD = (#Hs saturated Hydrocarbon) – (#Hs in the compound) / 2

Suggested Steps:

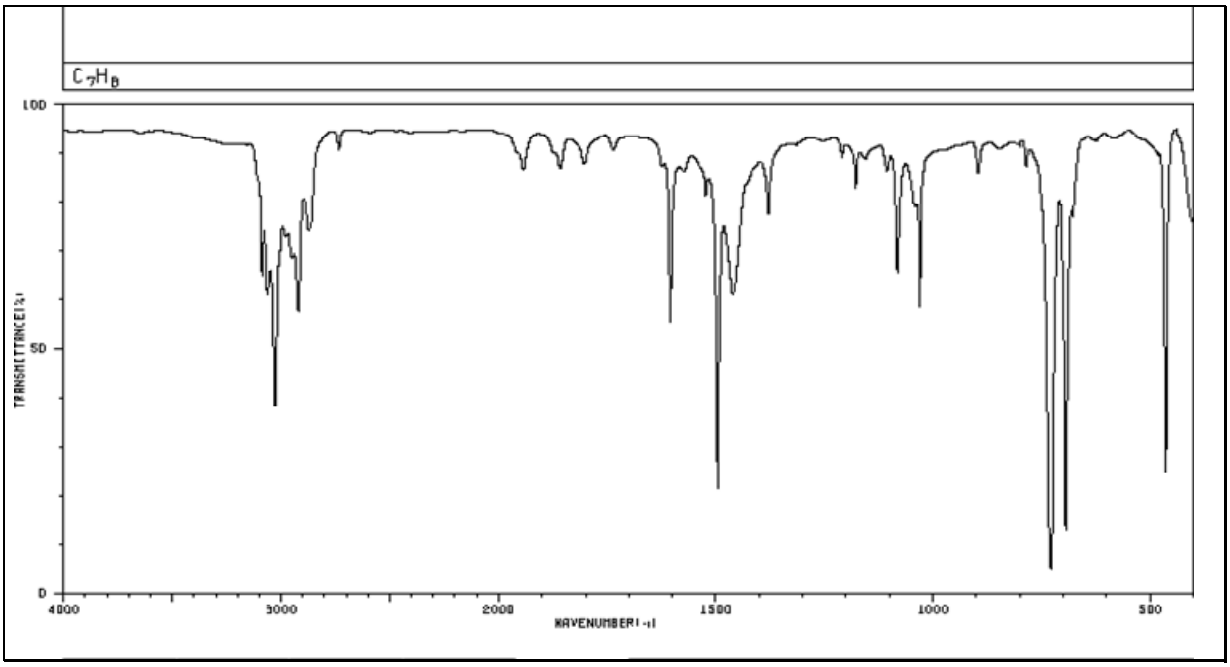
Use the mass spectrum and the molecular formula to determine structural sub-groups. The IR spectrum is used to determine the functional groups in the compound. On a separate worksheet, write down the molecular "pieces." It is also helpful to subtract these atoms from the molecular formula to determine how much of the structure is left. The ^{1}H NMR is the most valuable for determining the structure (including isomers). Begin assembling the subgroups and pieces to build a possible molecule. The NMR will indicate where, and how many protons are possible. At this point, there will be very few structures which are consistent with the data. The ^{13}C NMR will indicate the **types** of carbon atoms (not how many). Combining all the information from all the spectra, propose (draw) a structure. Go back to each spectra and test for consistency- all the spectral data will be consistent with the proper structure. The list of all unknowns is included on the last page of the appendix.

Unknown 1: Mass Spec

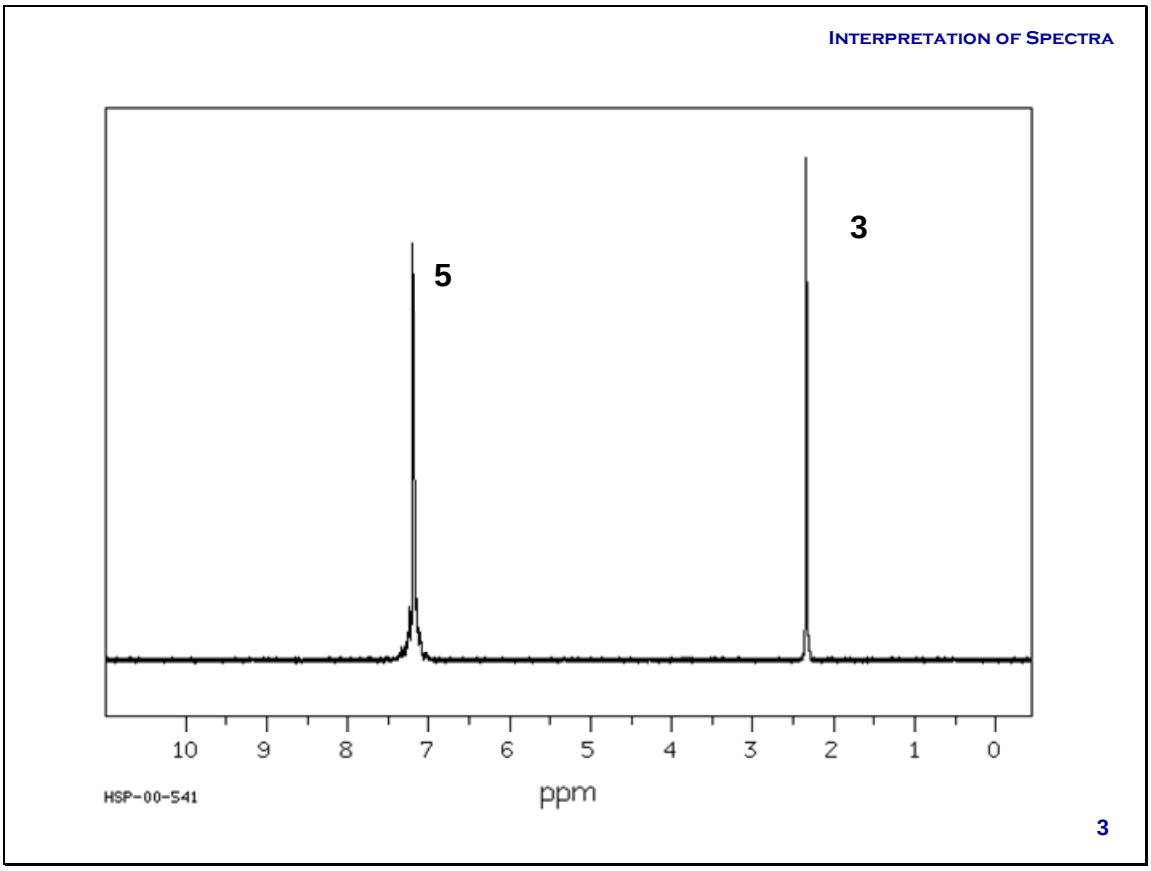
MF: C_7H_8



Unknown 1: IR



Unknown 1: NMR



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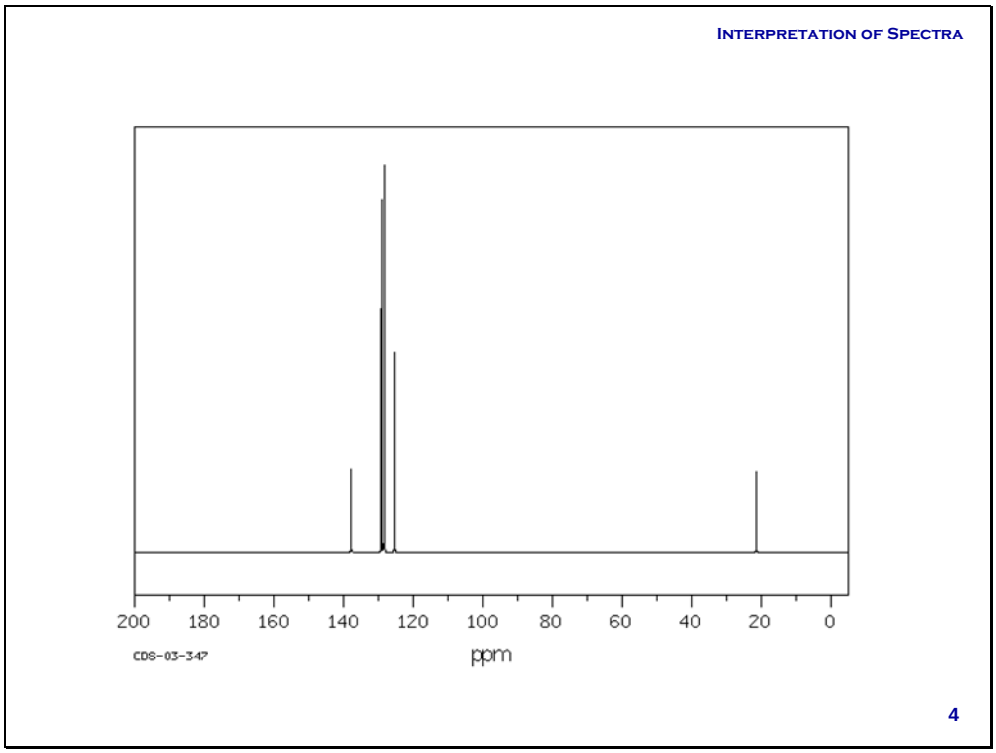
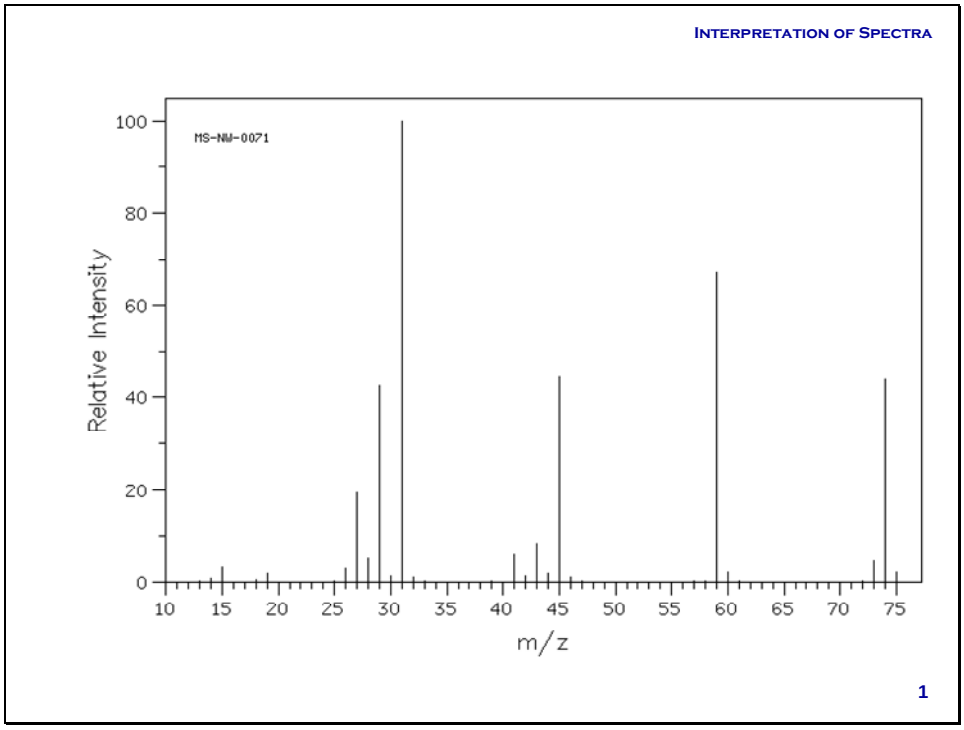


Unknown 2: MS

MF: $C_4H_{10}O$



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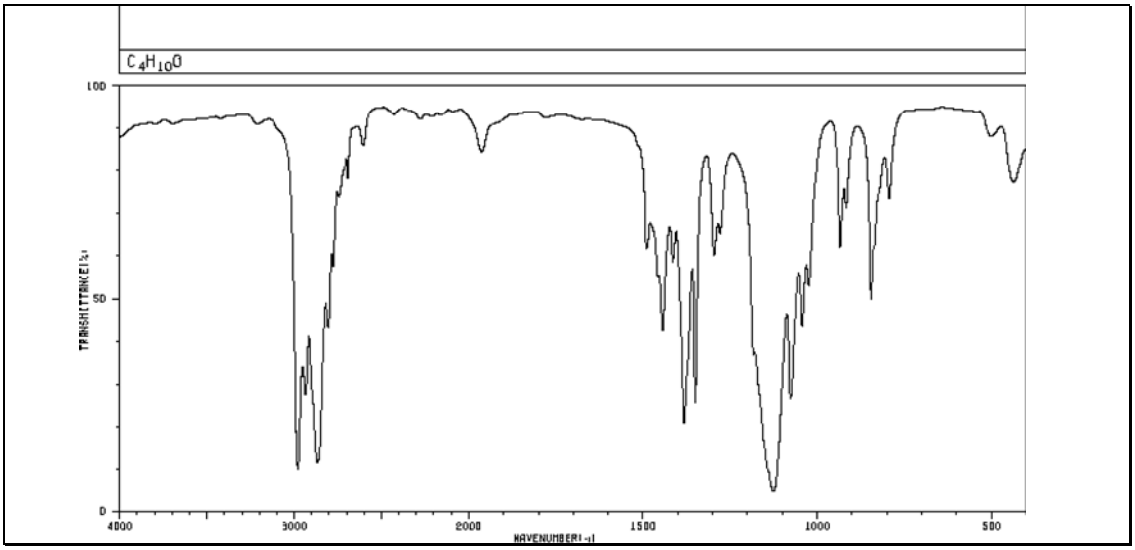

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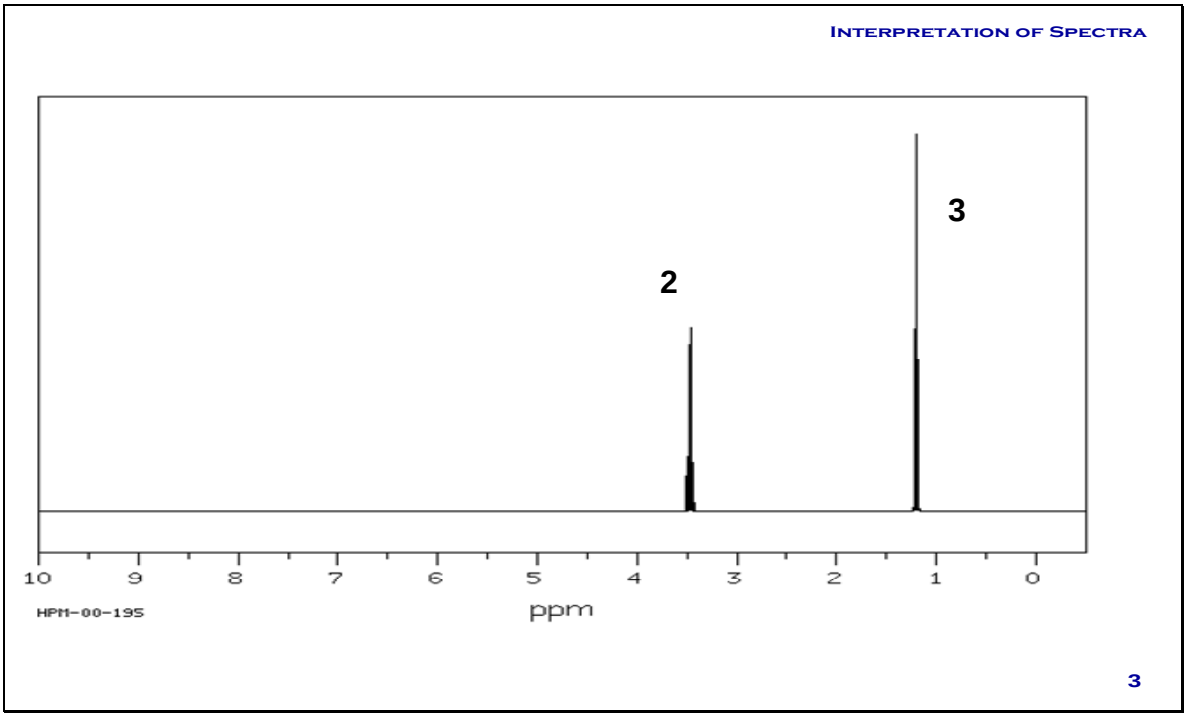
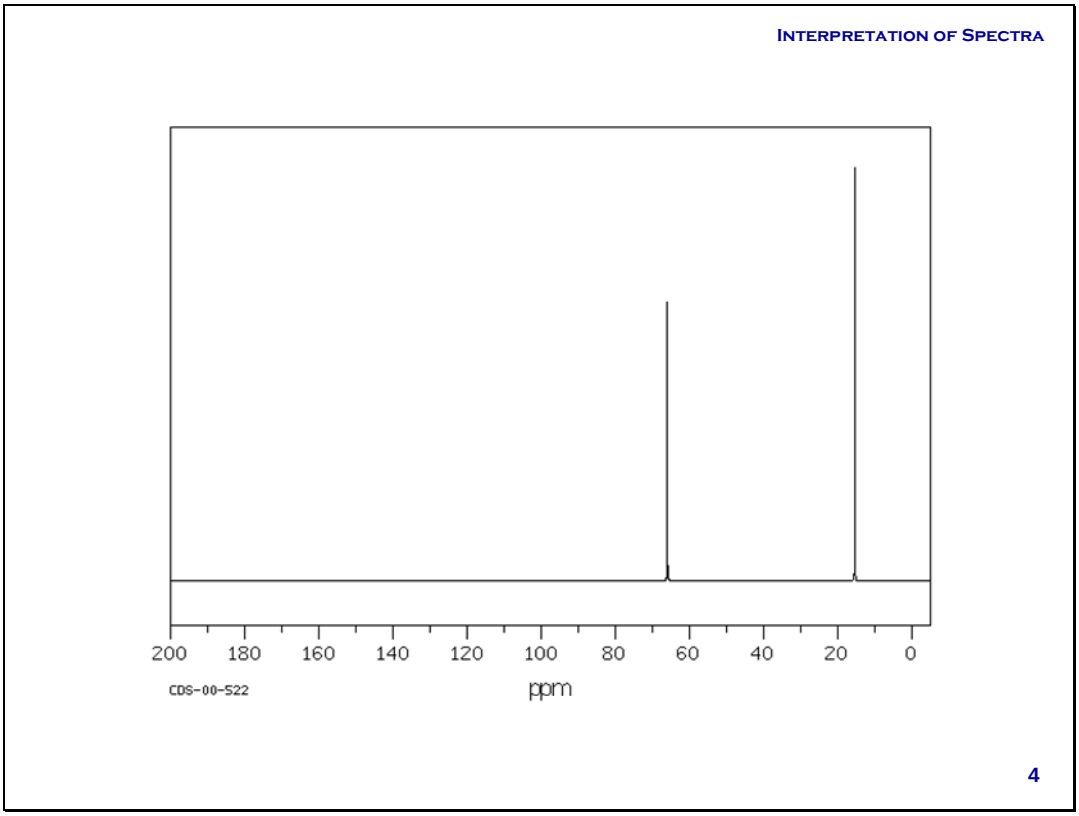
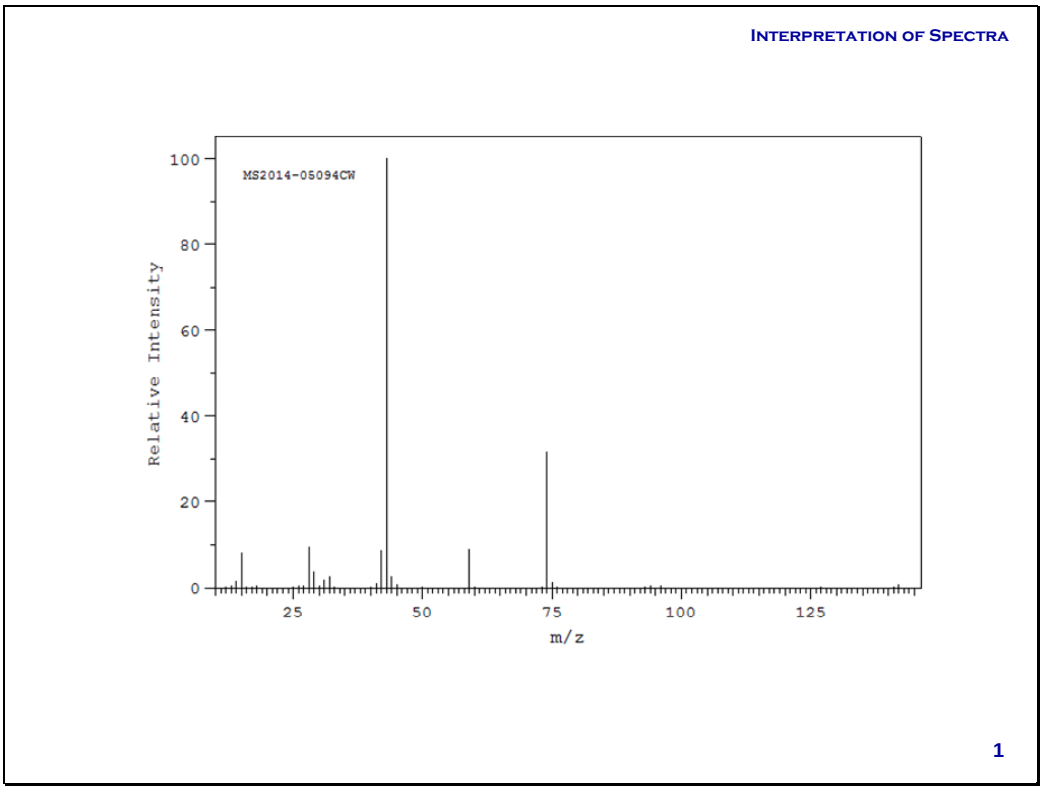


Unknown 2: C NMR



Unknown 3: MS

MF: $C_3H_6O_2$



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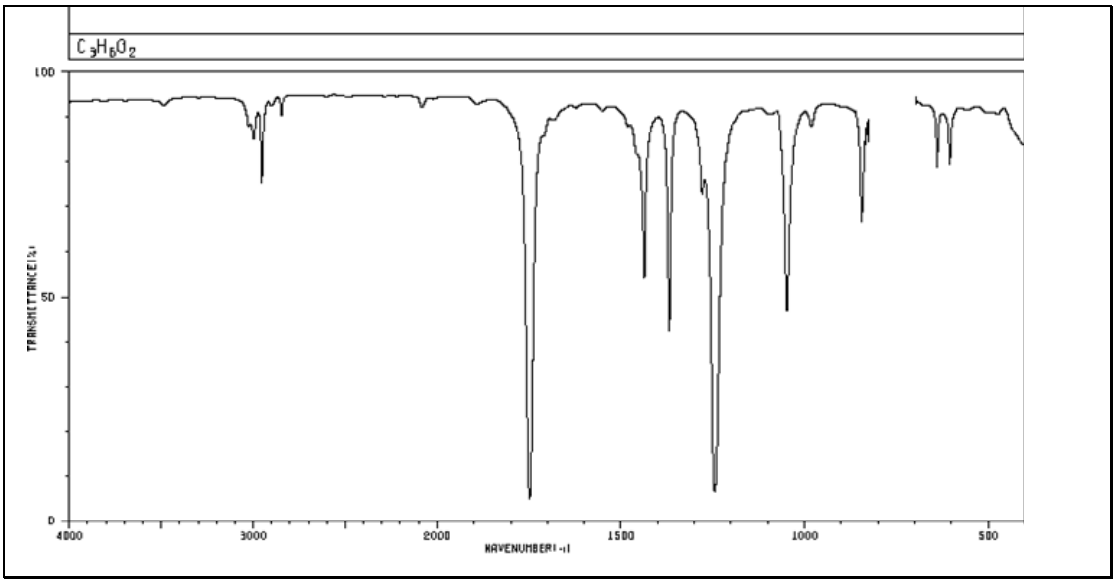
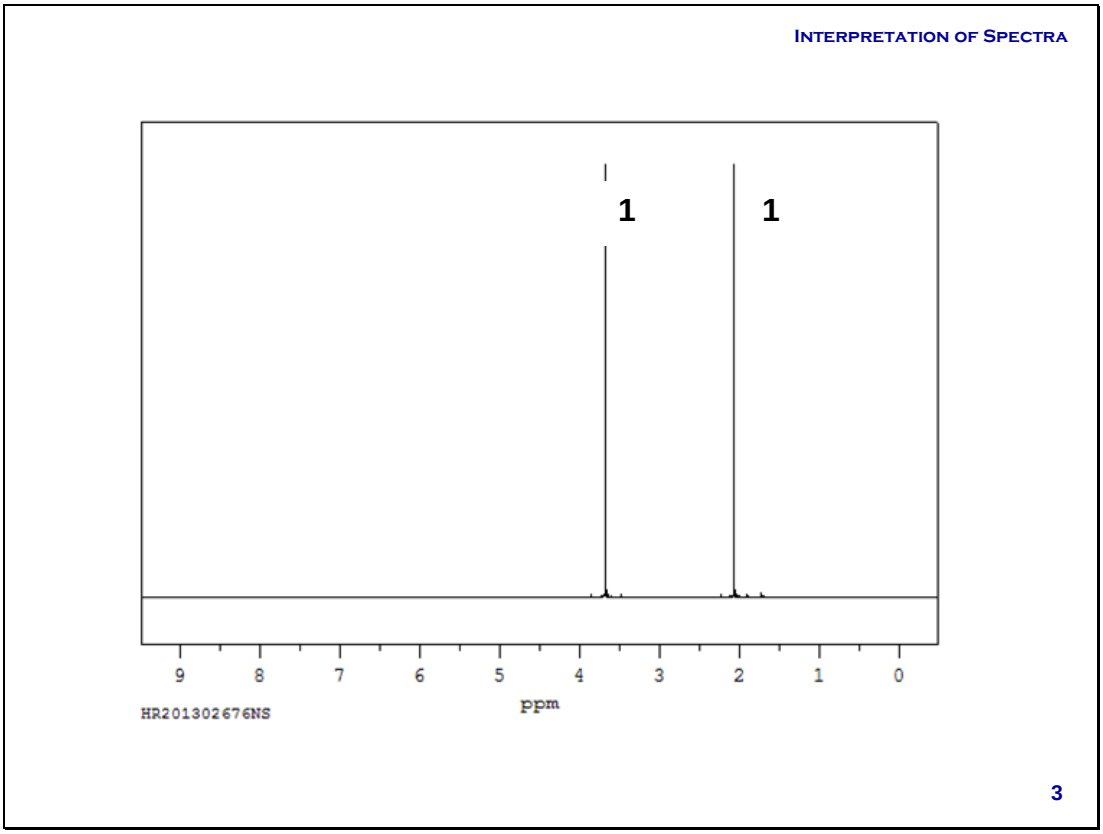


Unknown 3: NMR



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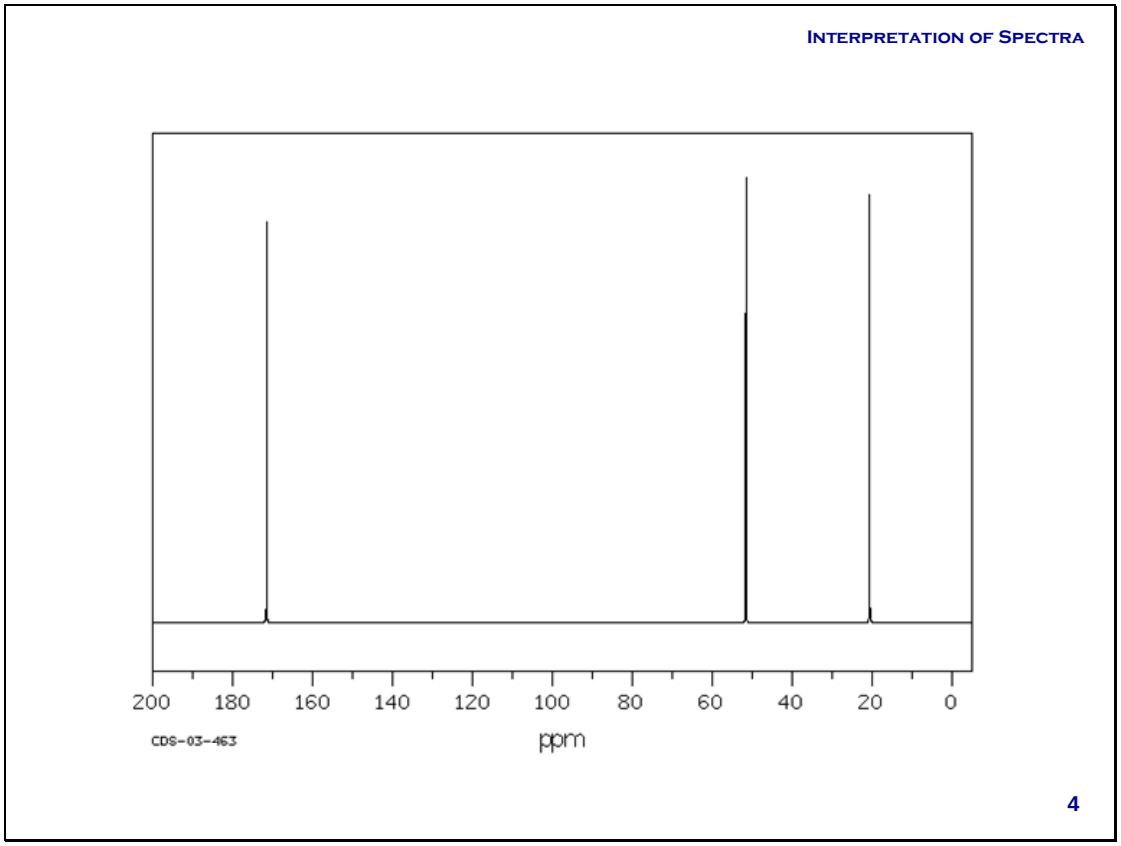
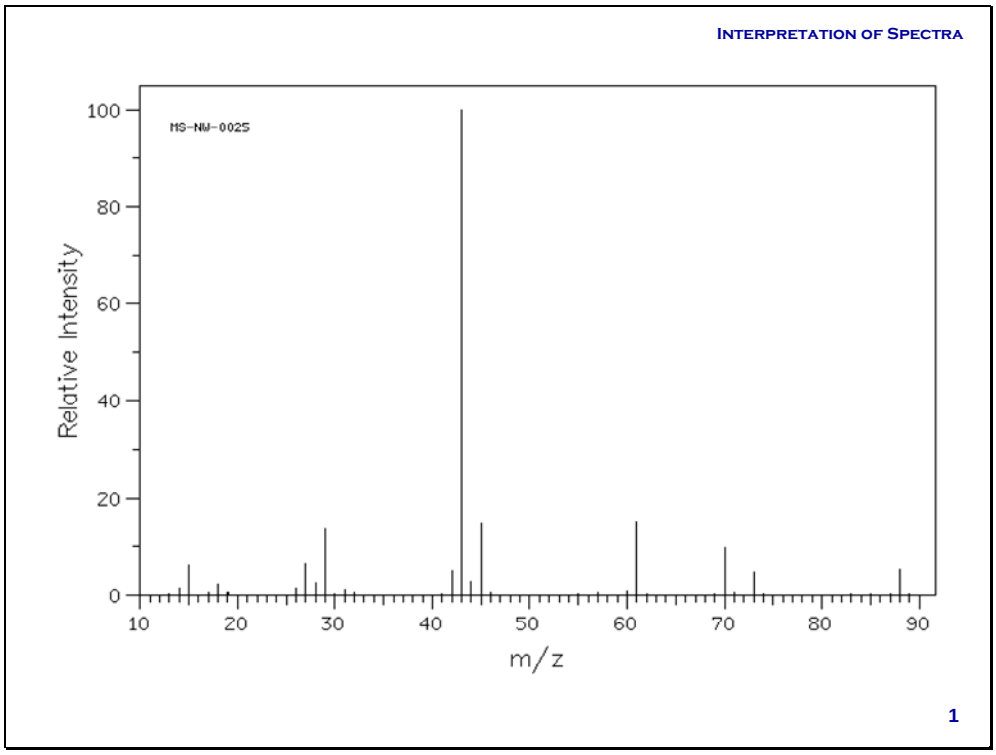


Unknown 4: MS

MF: $C_4H_8O_2$



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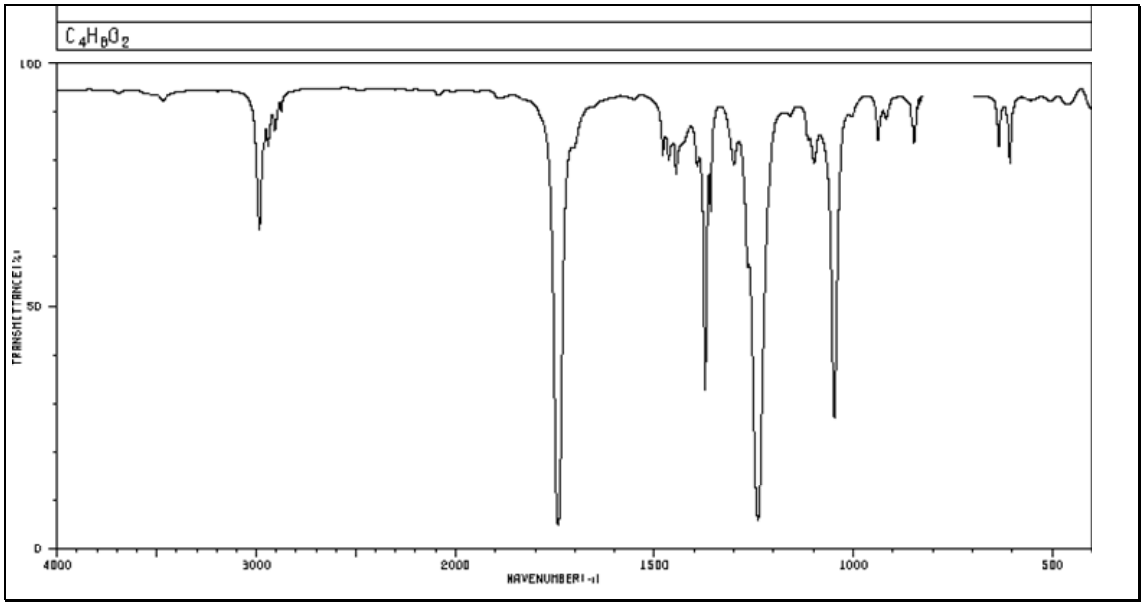
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1000
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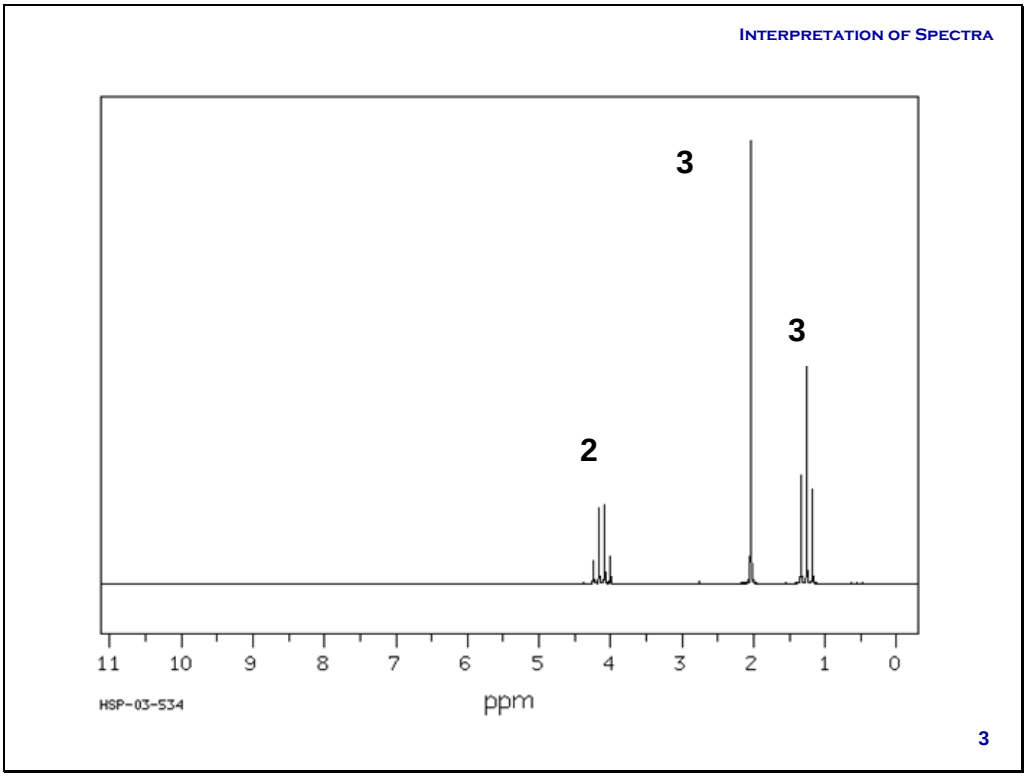
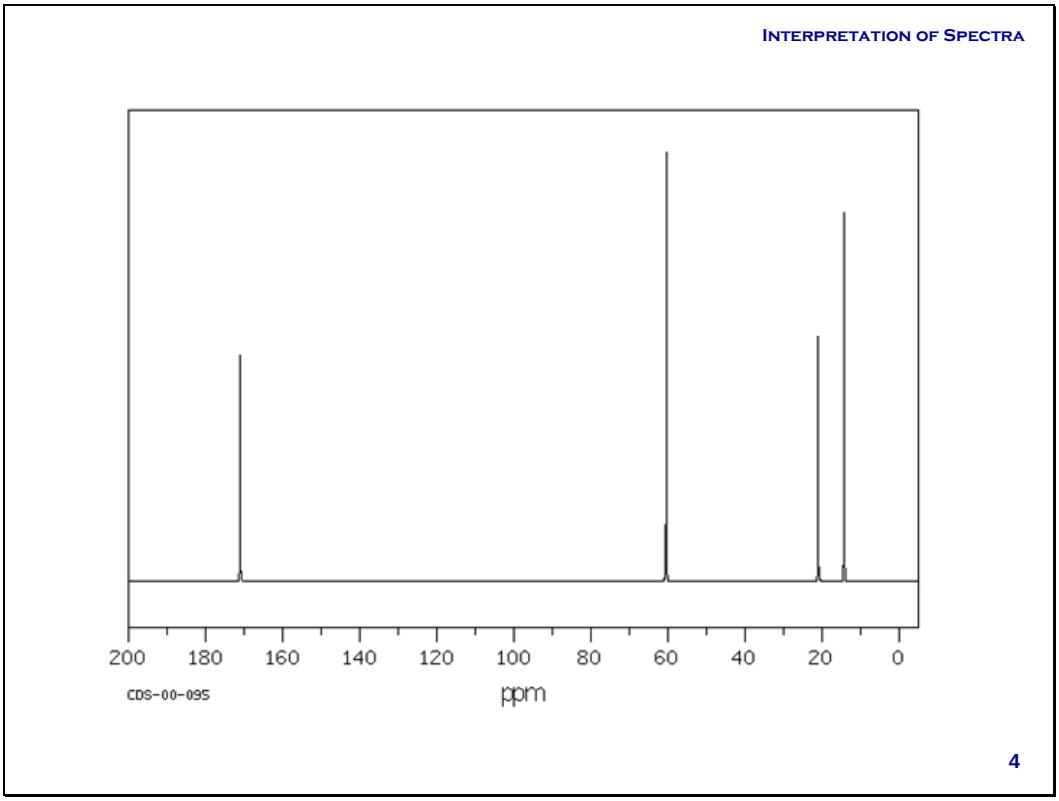
WAVENUMBER[-1]

Unknown 4: NMR

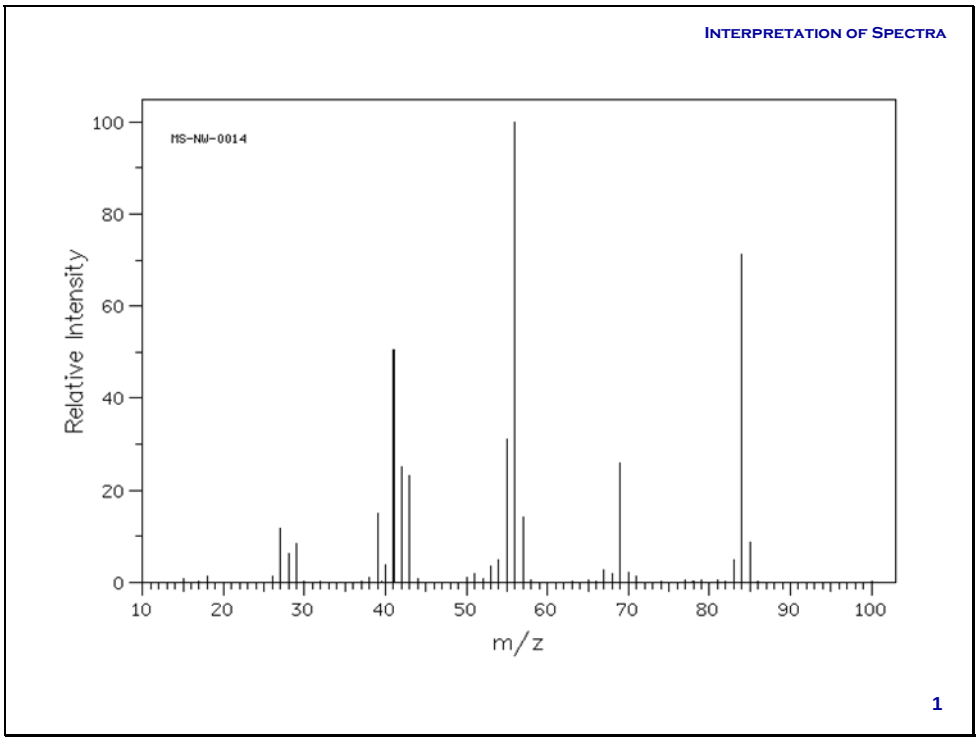


Unknown 4: C NMR



Unknown 5: MS

MF: C_6H_{12}



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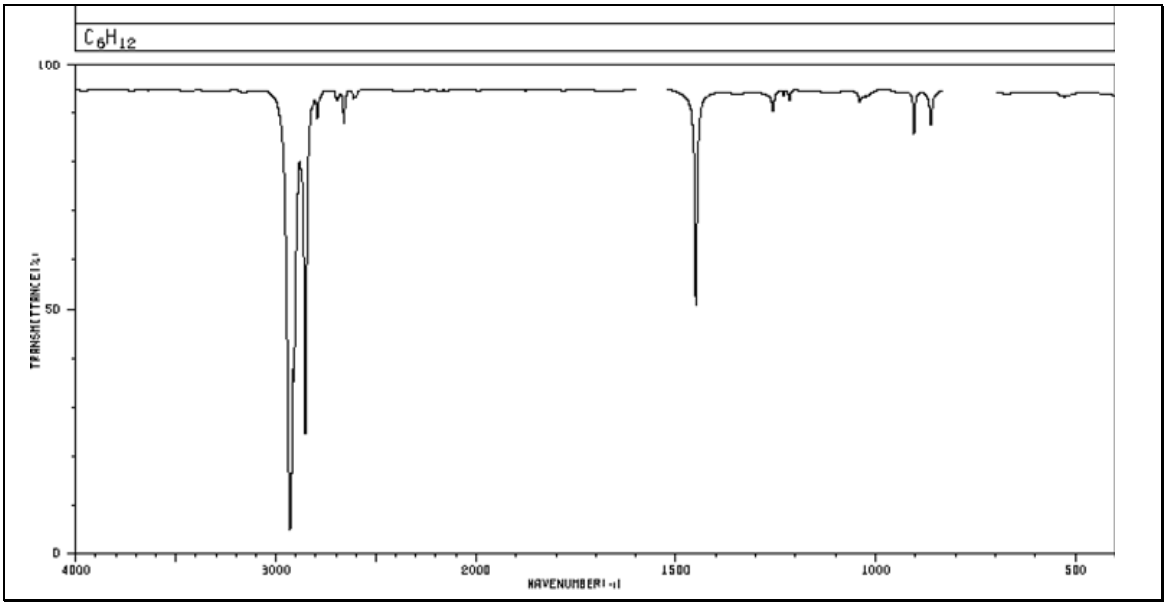

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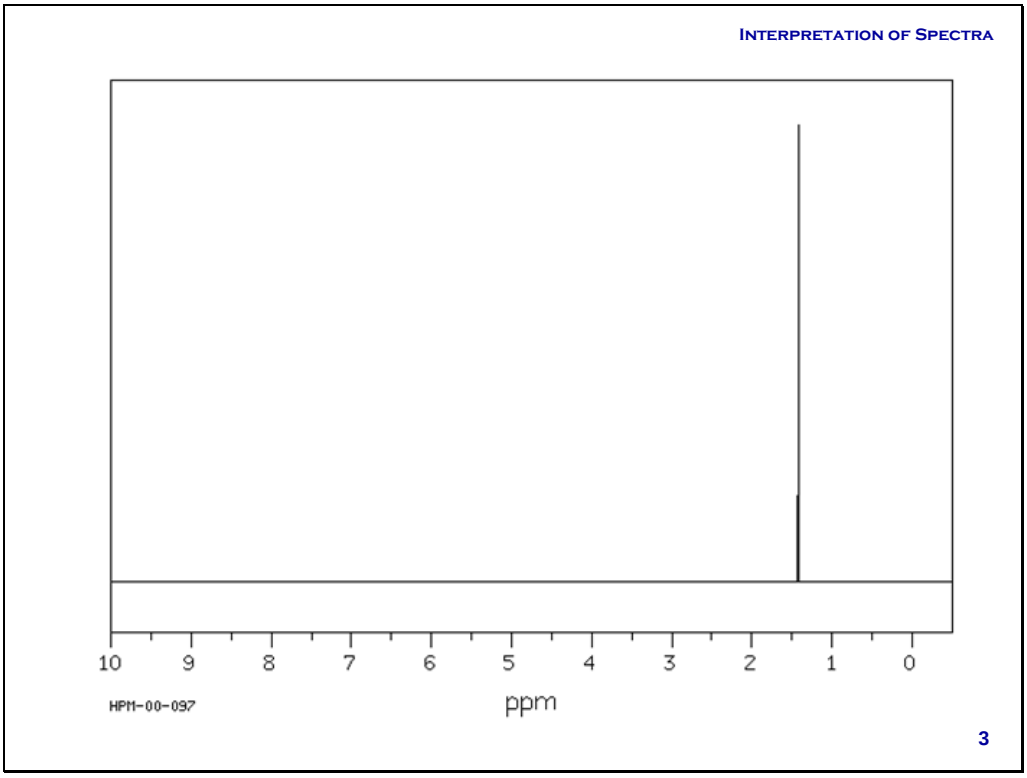

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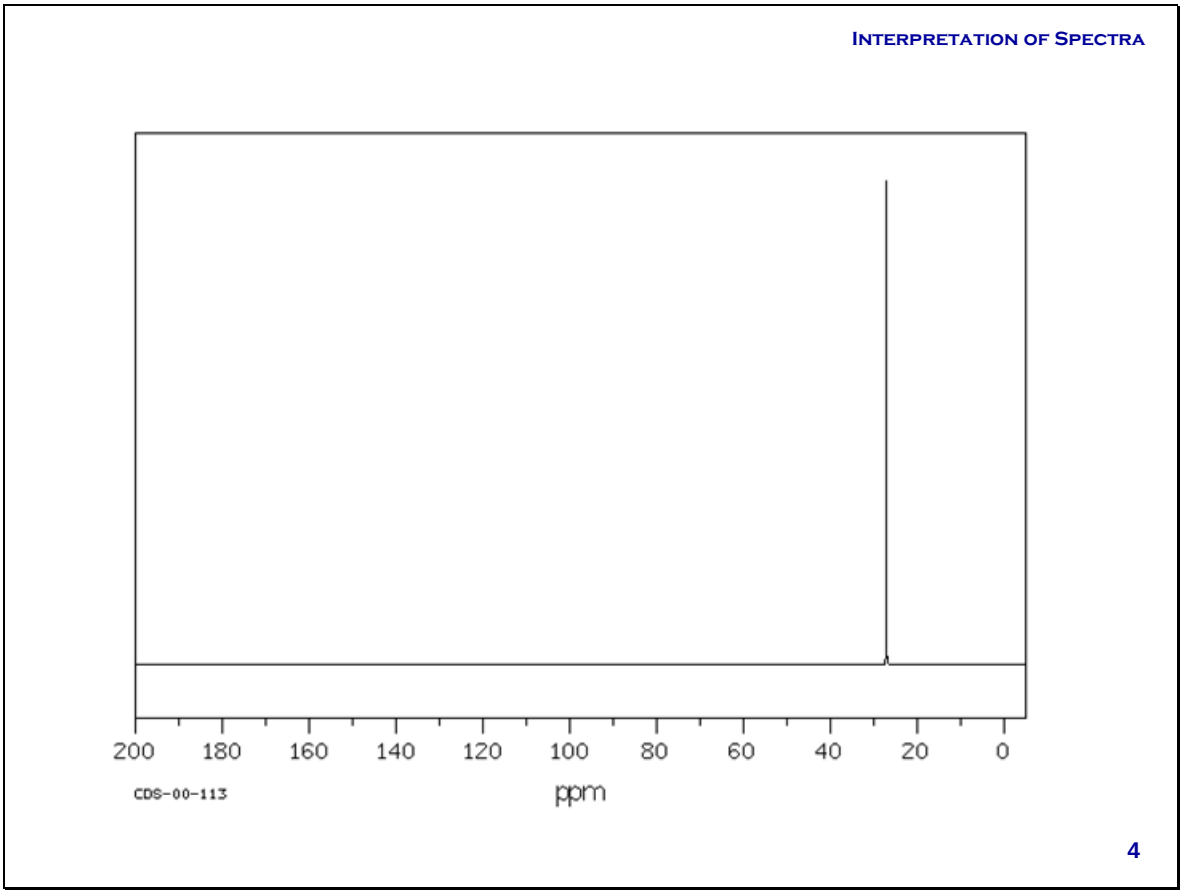
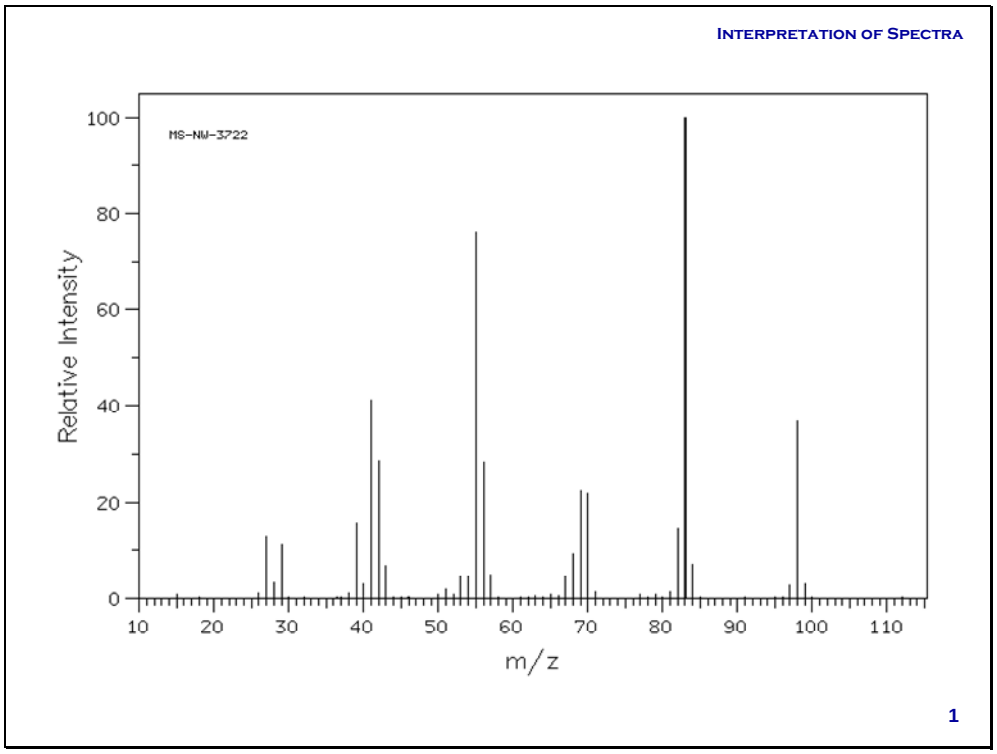


Unknown 6: MS

MF: C_7H_{14}



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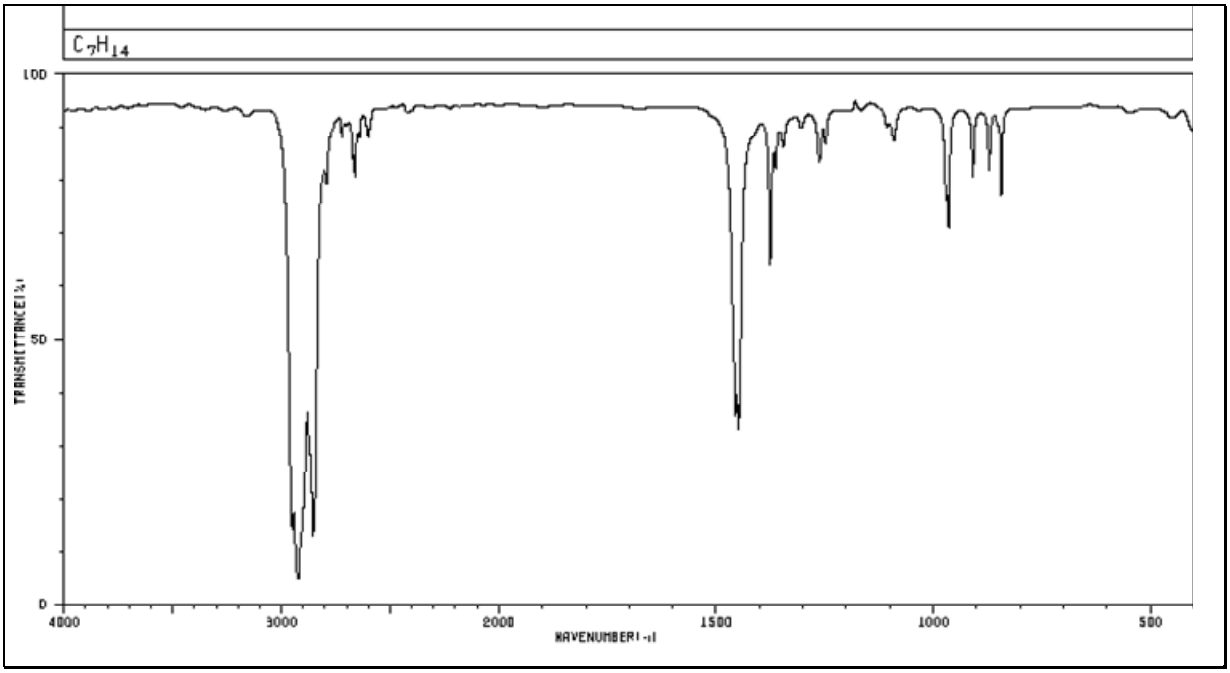
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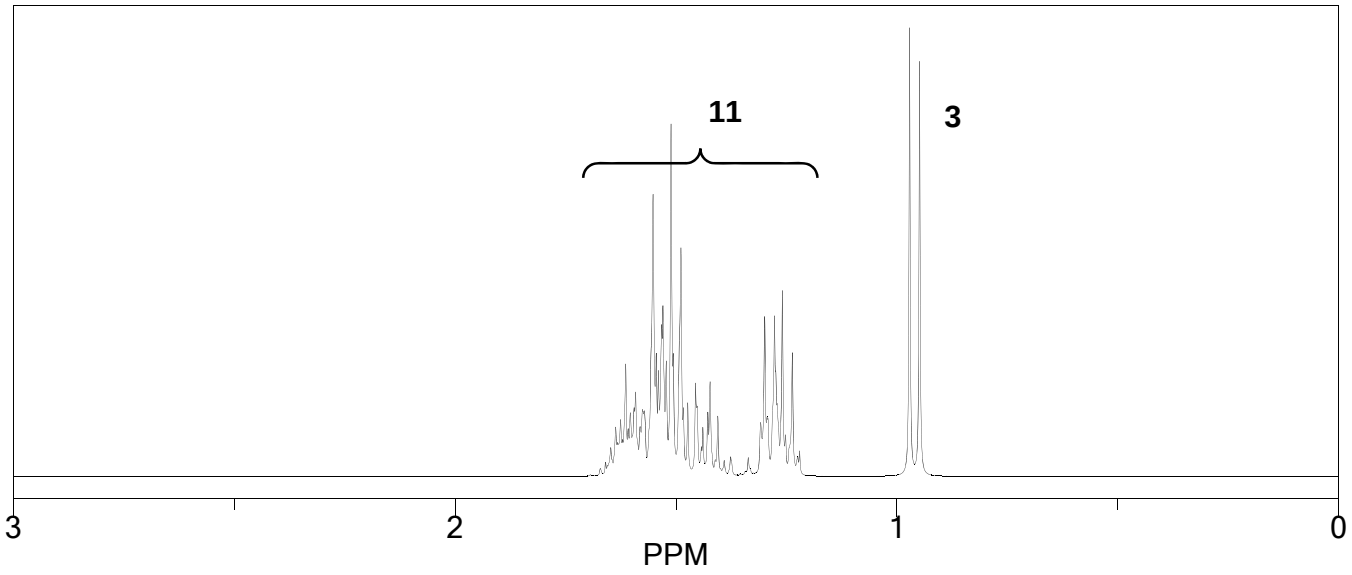
WAVENUMBER[-1]

Unknown 6: NMR



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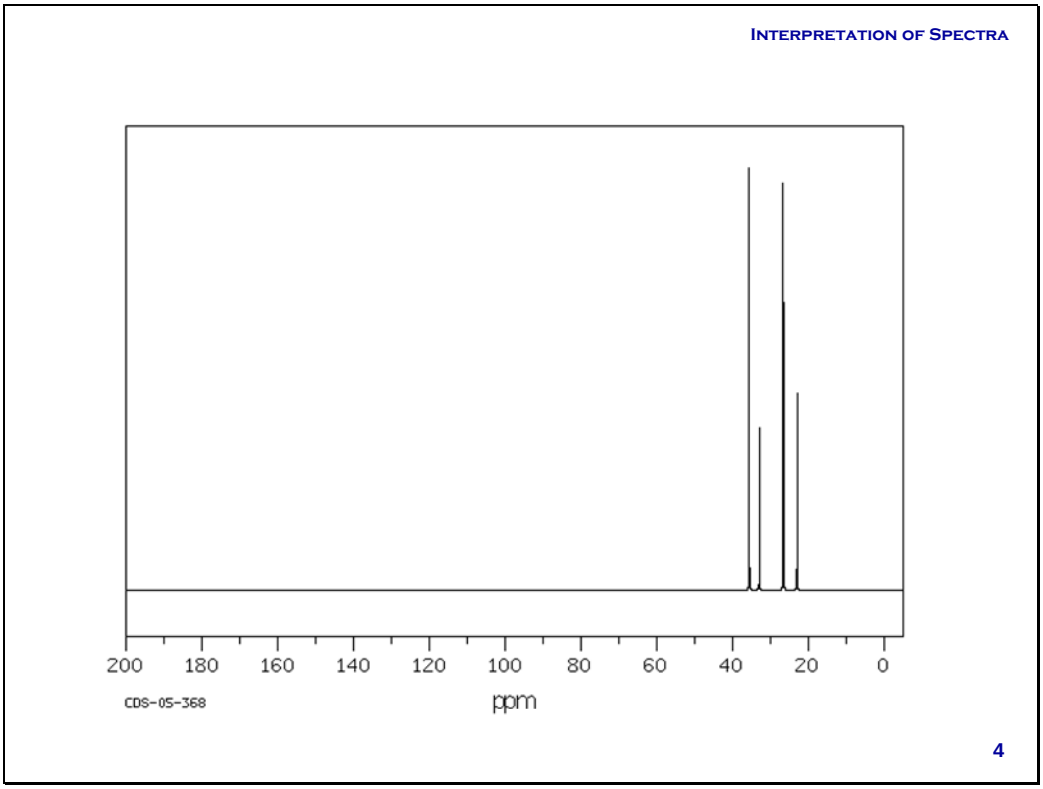
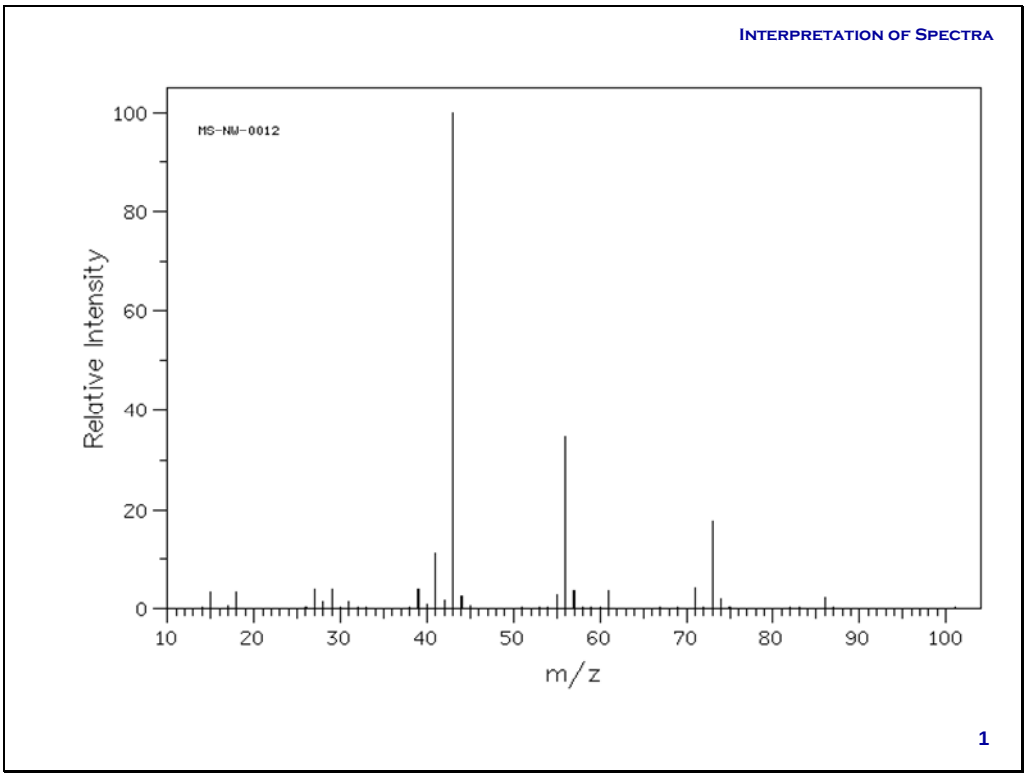


Unknown 7: MS

MF: $C_6H_{12}O_2$



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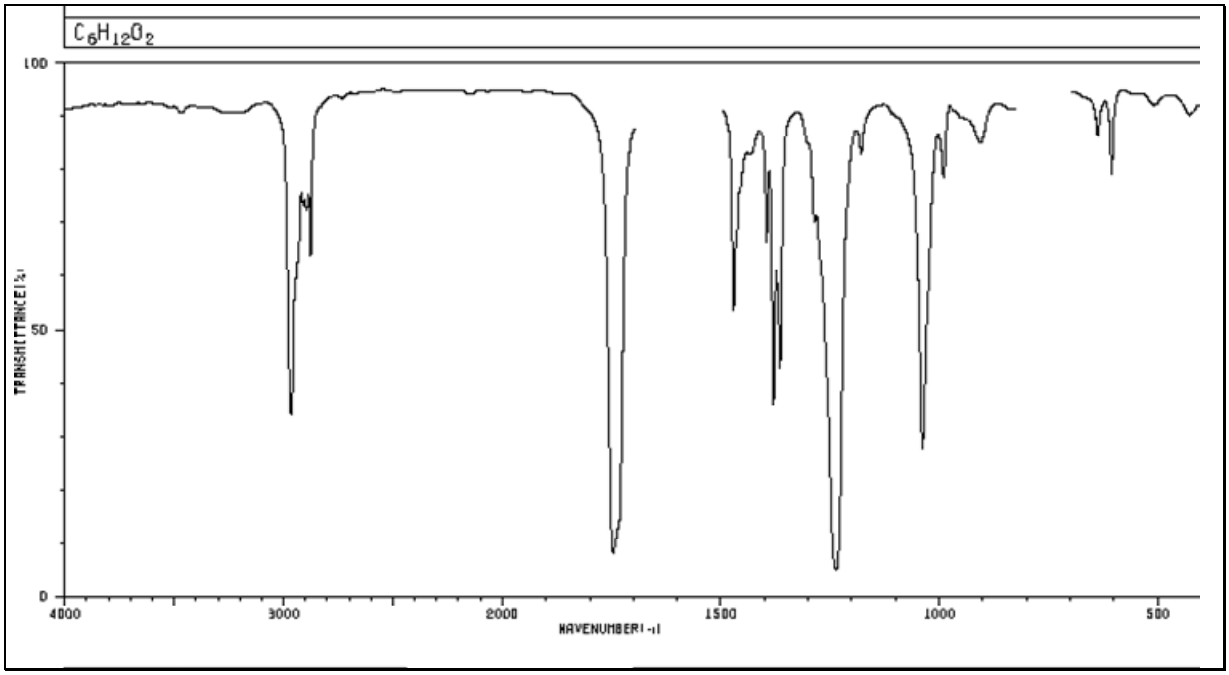
C6H12O2
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0
TRANSMITTANCE[%]
4000
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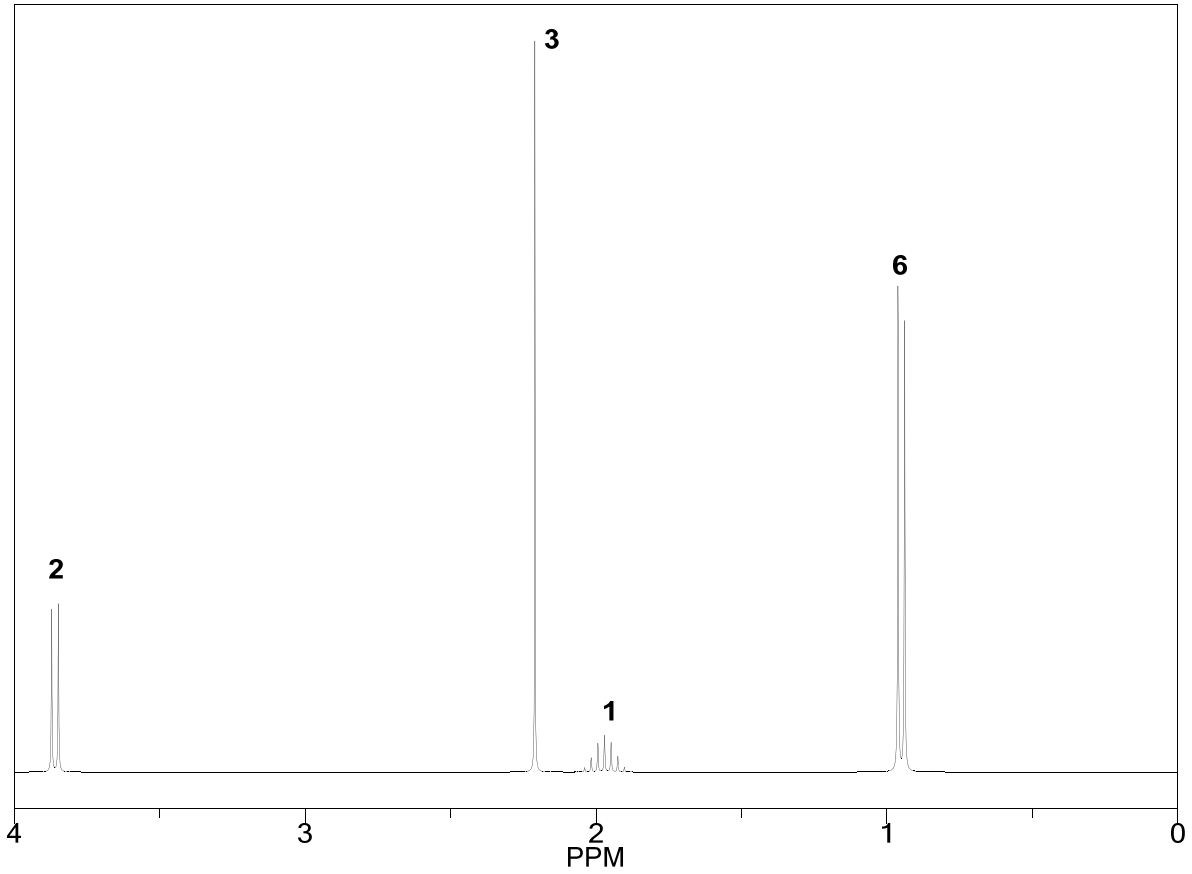
2000
1500
1000
500
WAVENUMBER[-1]

Unknown 7: NMR



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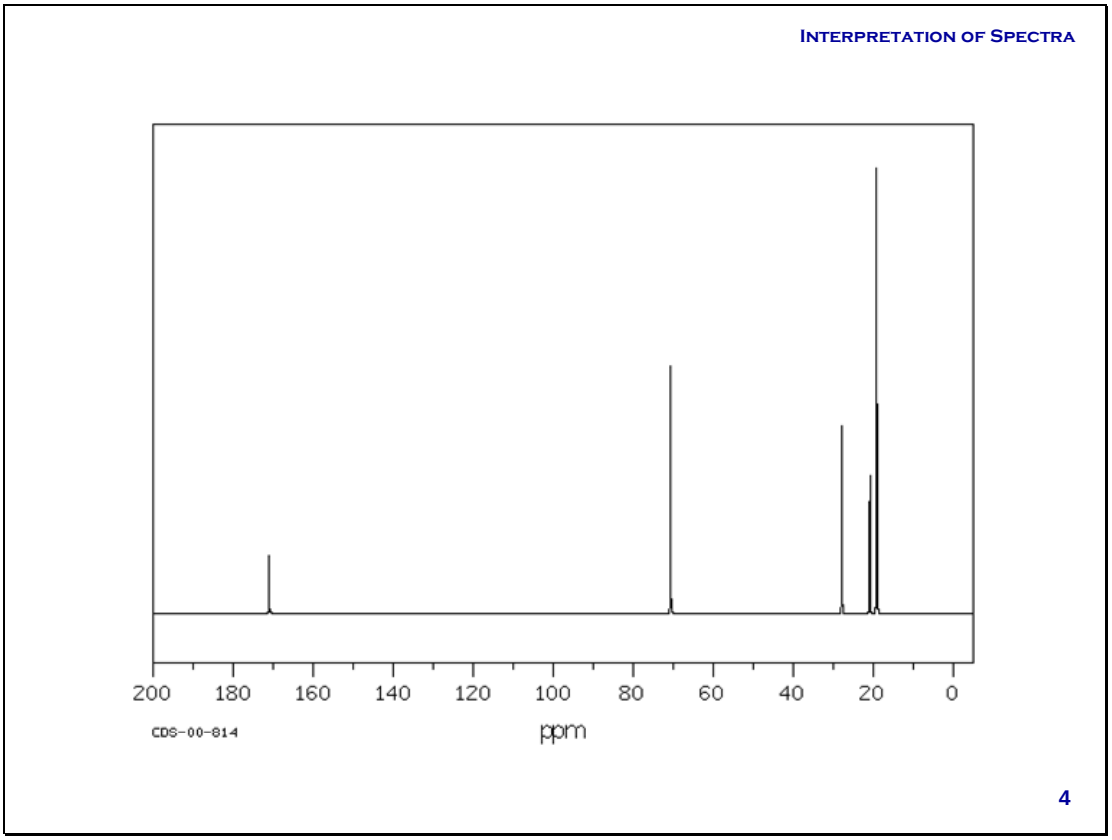
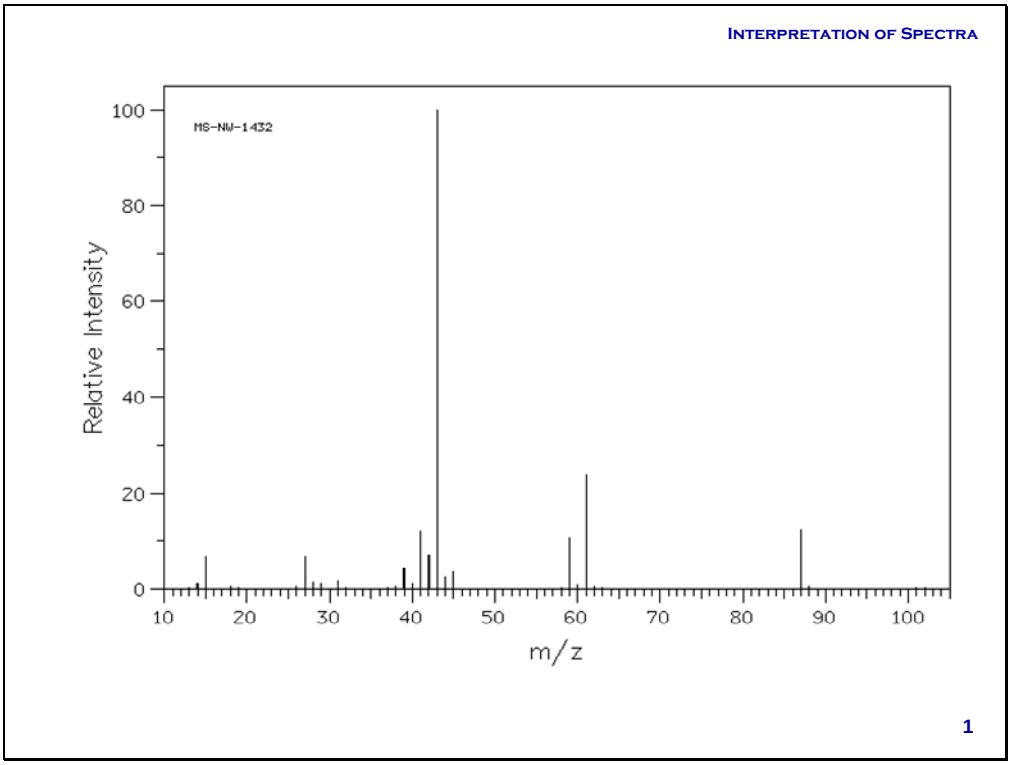


Unknown 8: MS

MF: $C_5H_{10}O_2$



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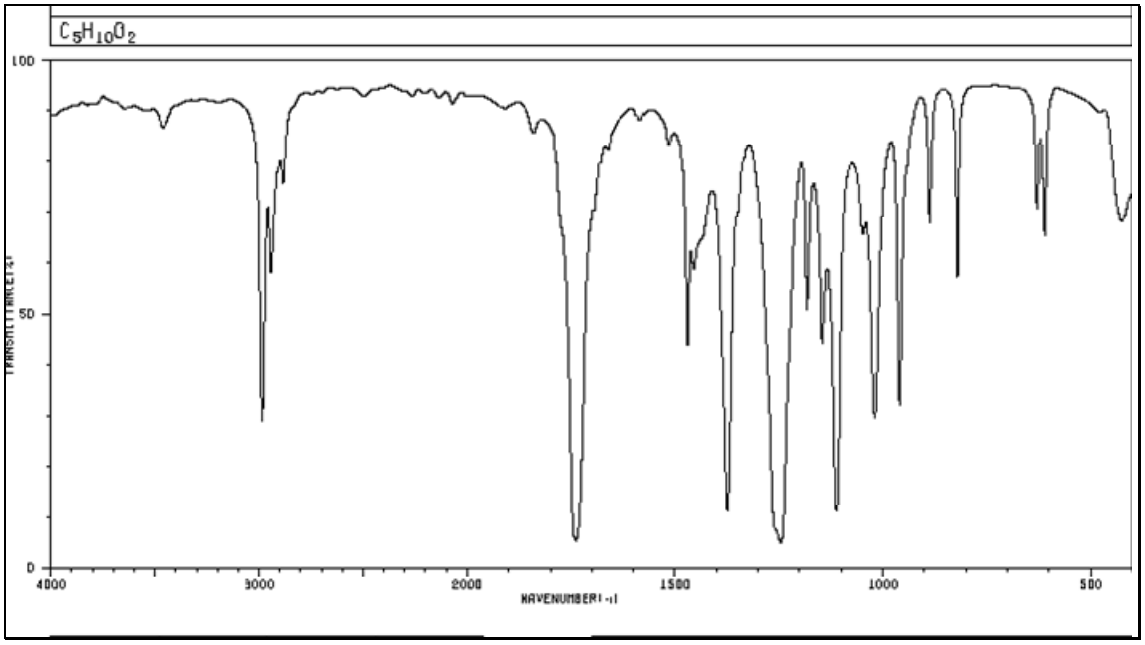

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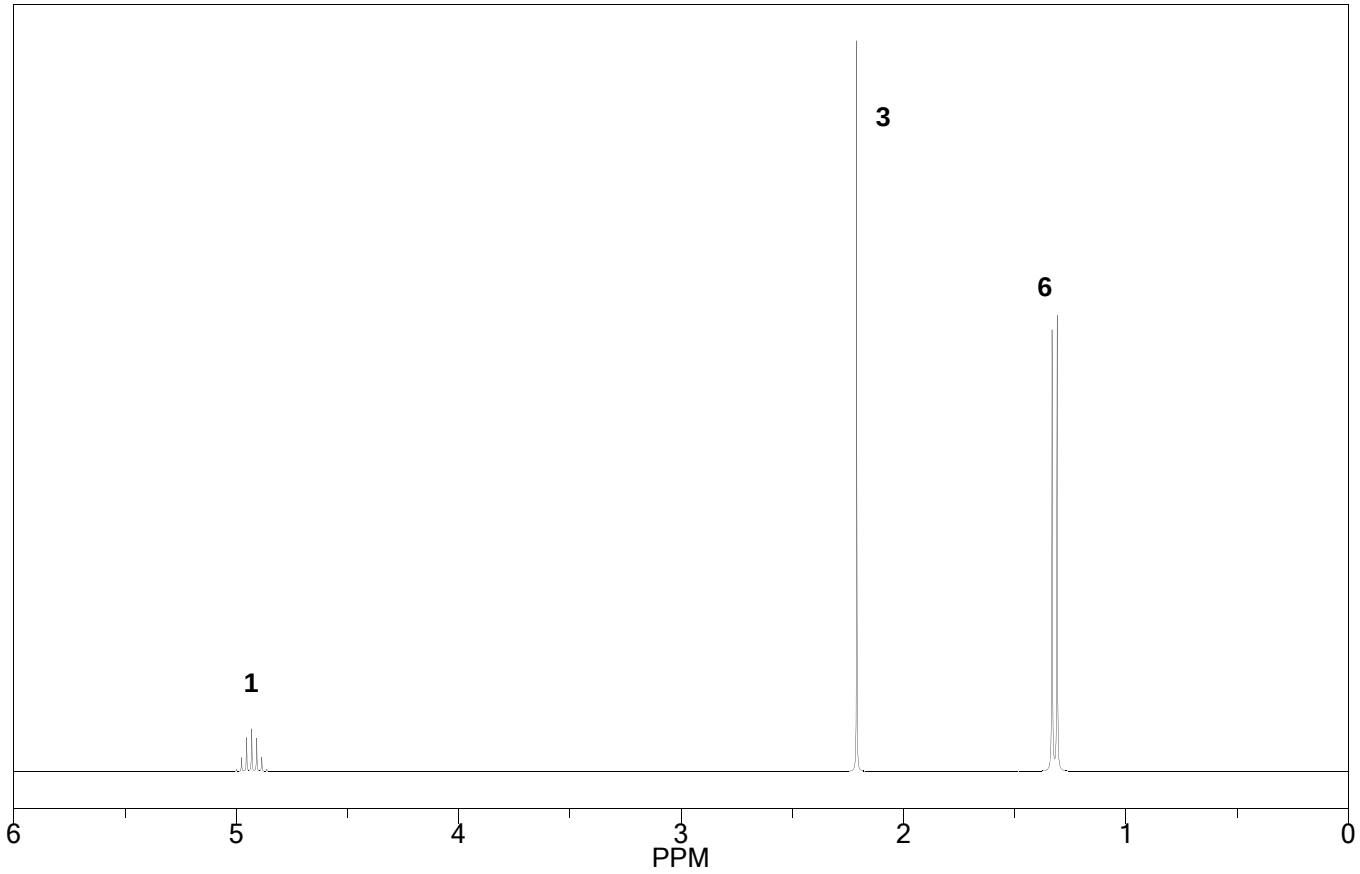

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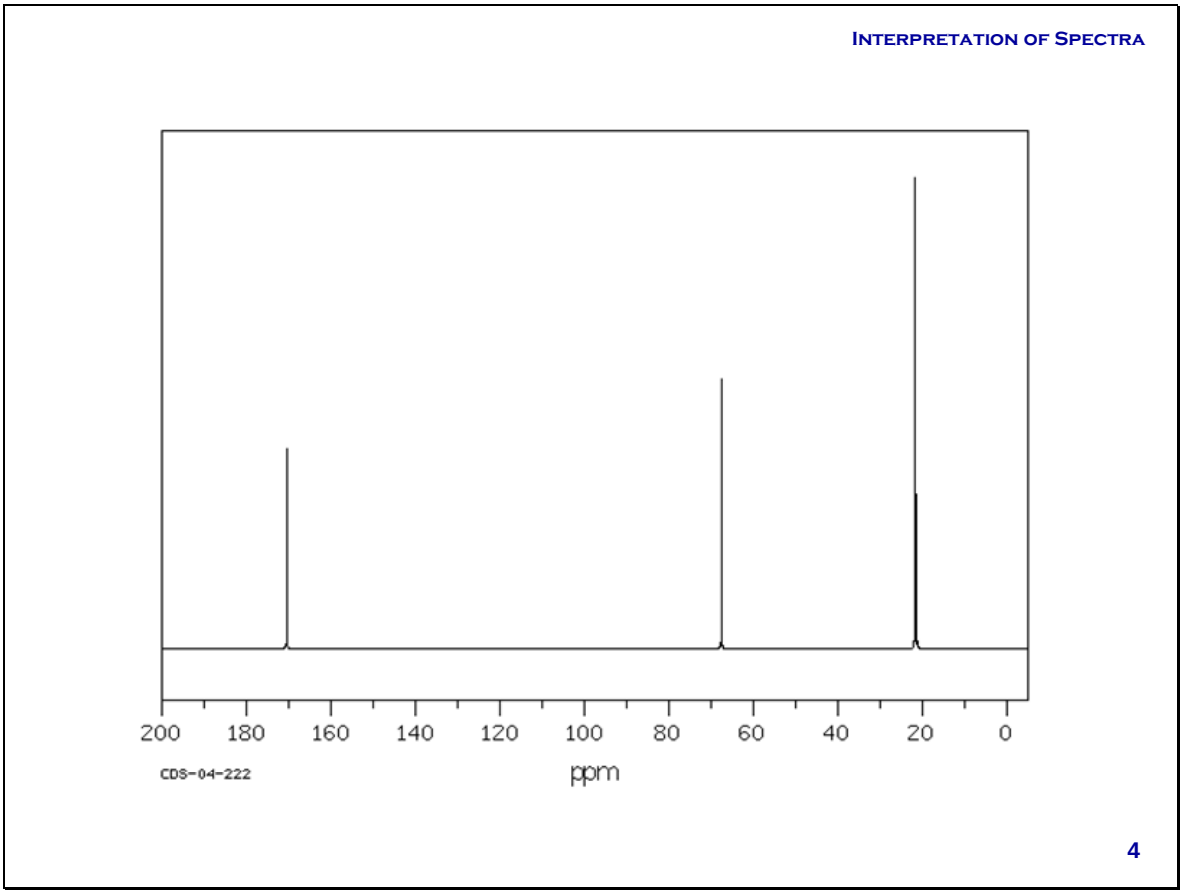
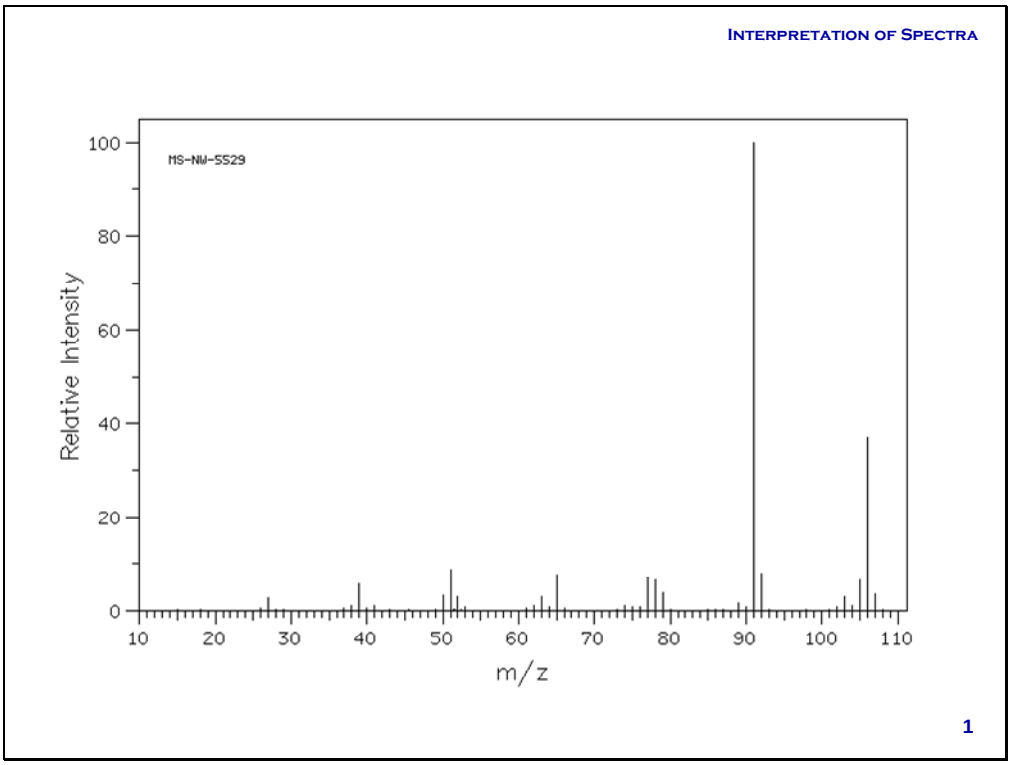


Unknown 9: MS

MF: C_8H_{10}



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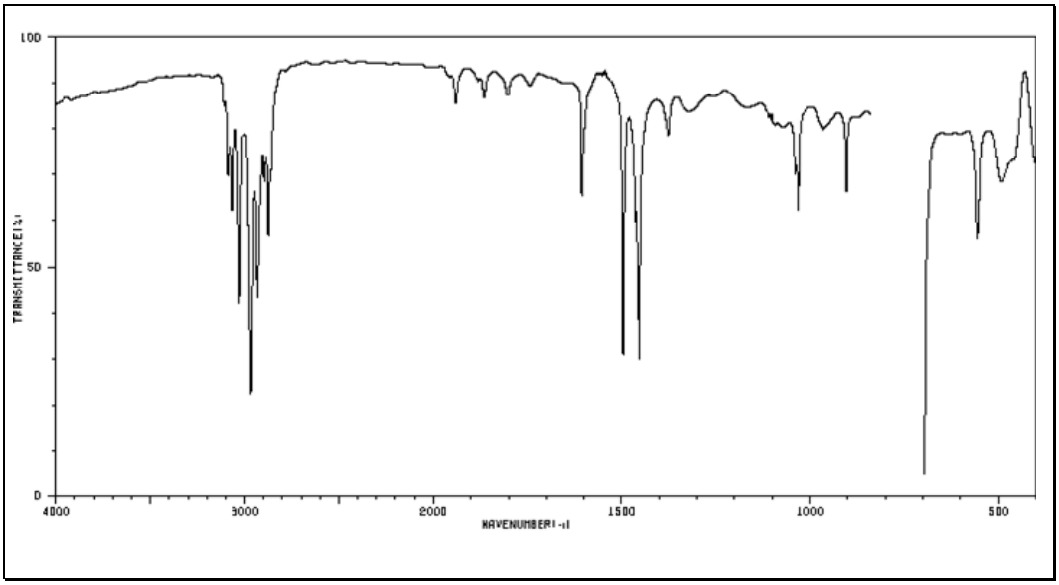

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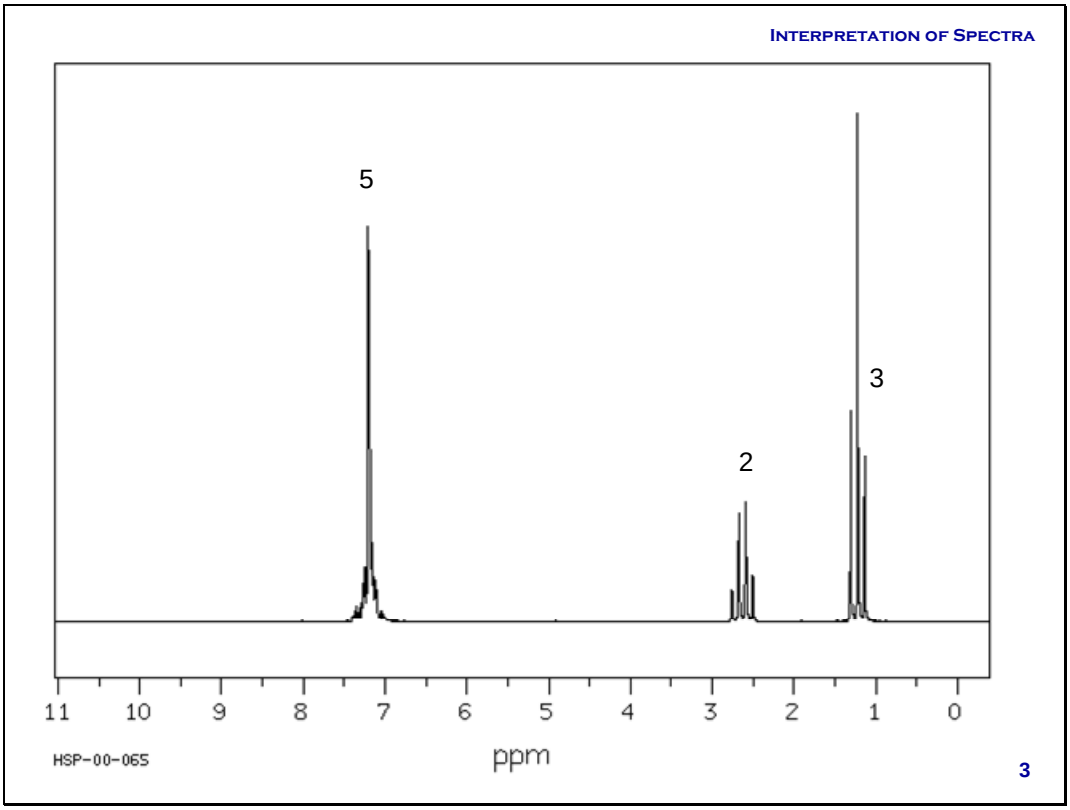

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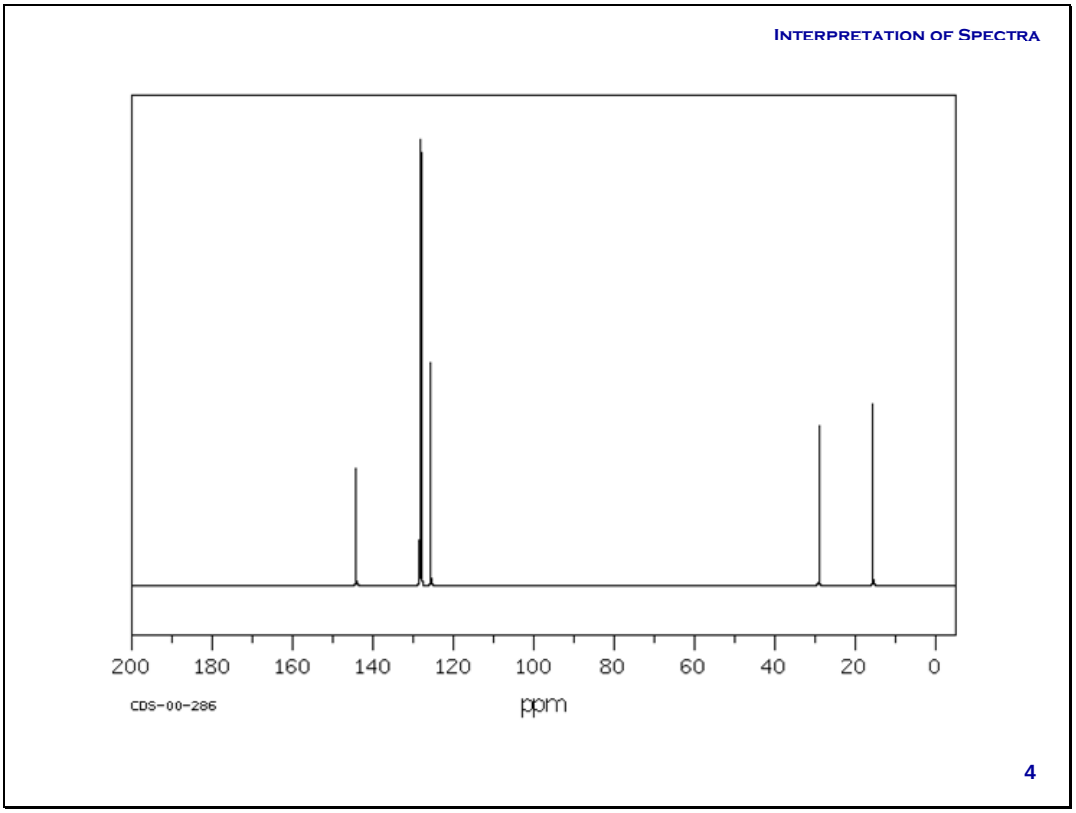
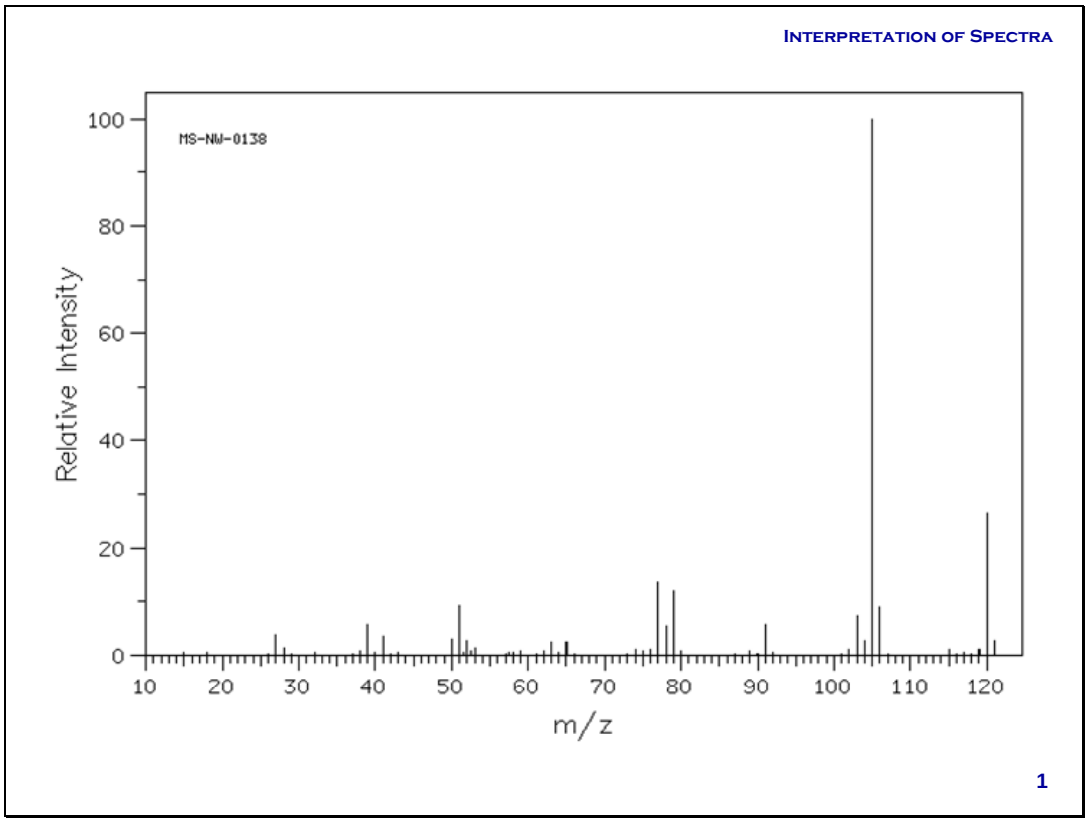


Unknown 10: MS

MF: C_9H_{12}



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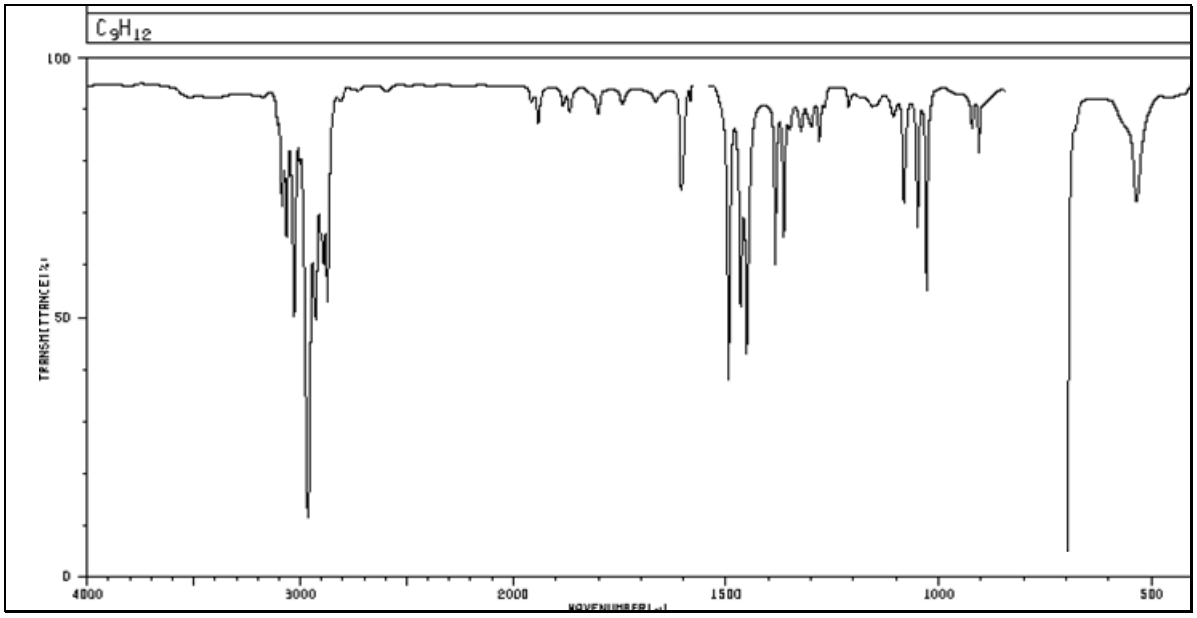
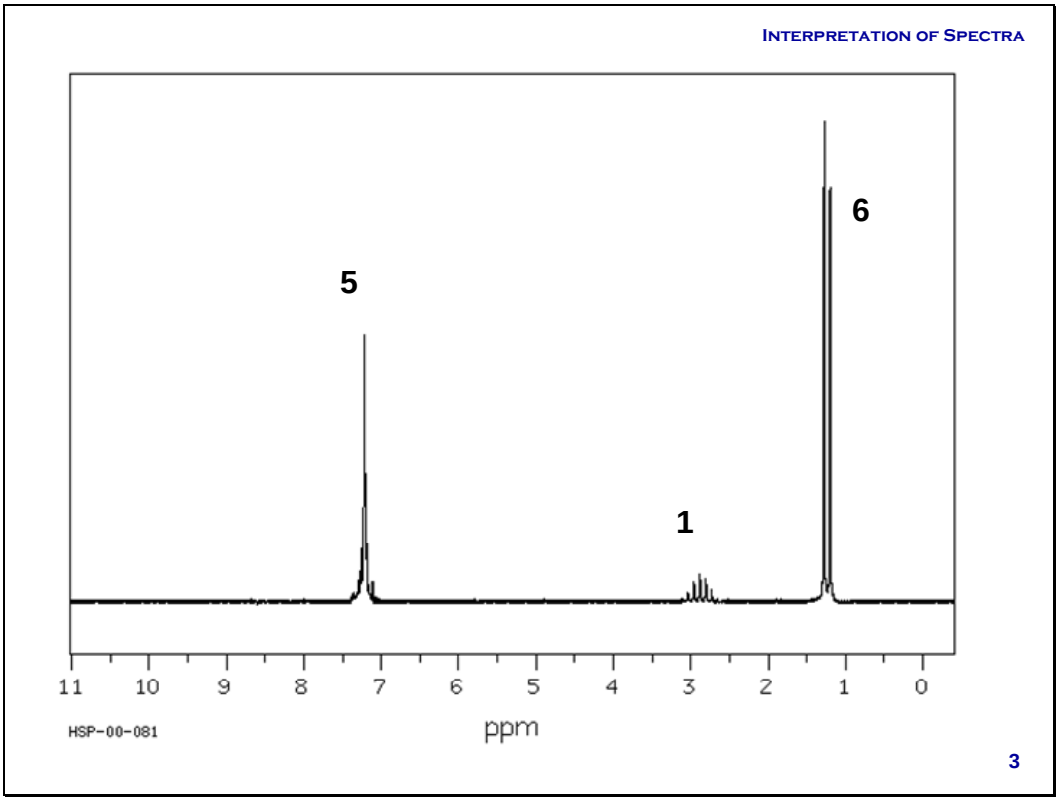


Unknown 10: NMR



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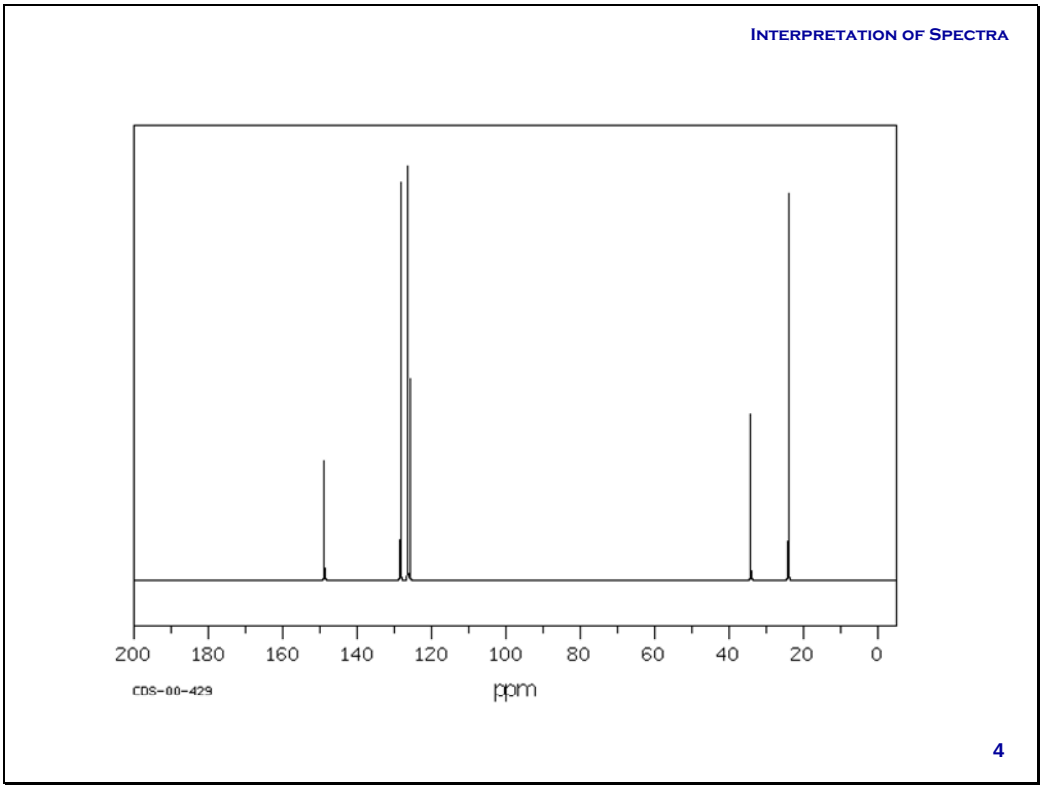
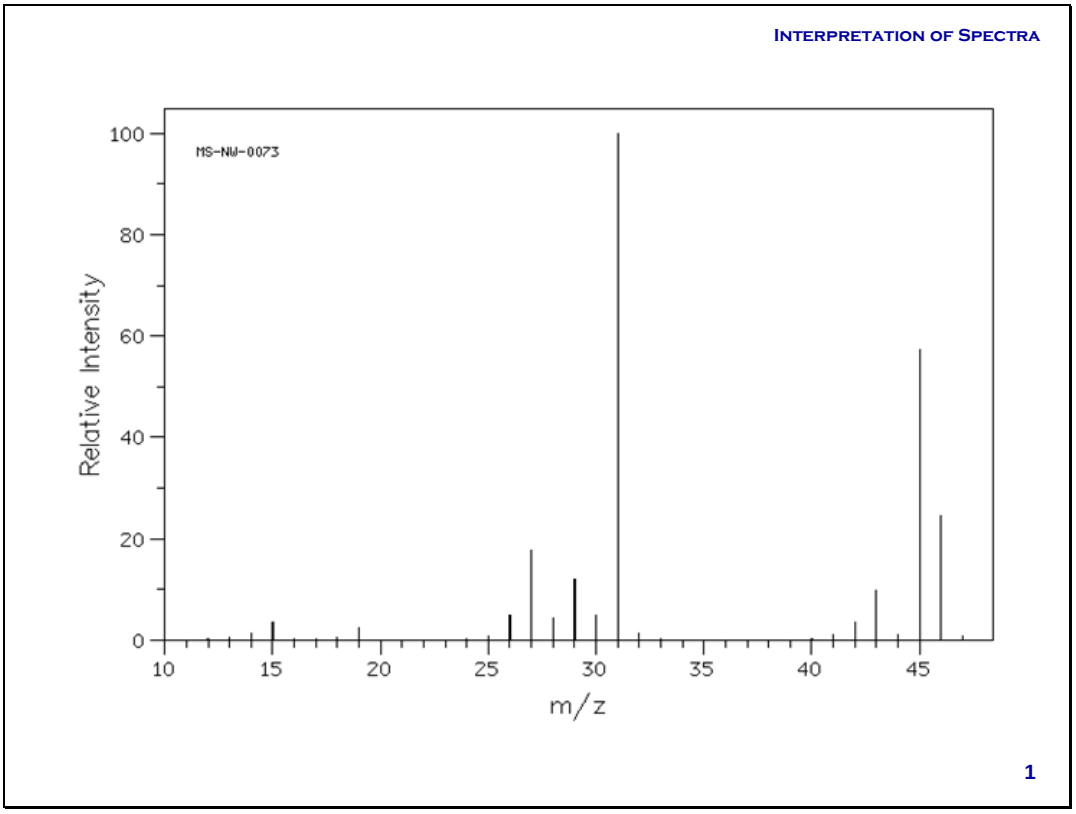
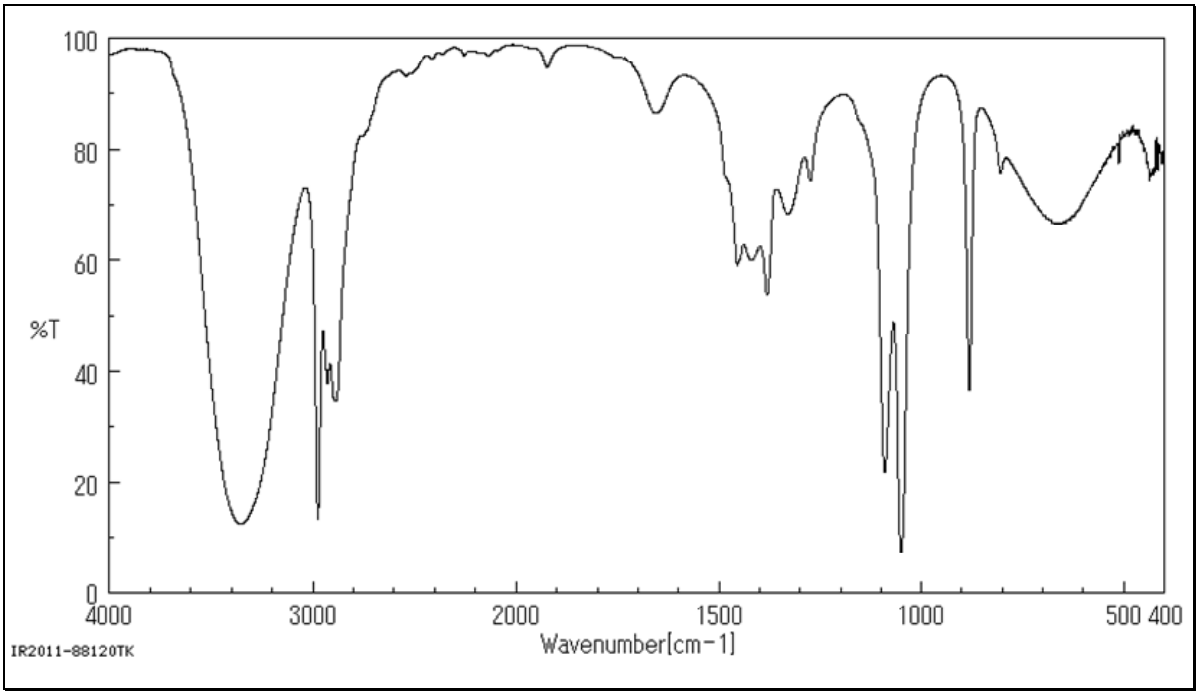


Unknown 11: MS

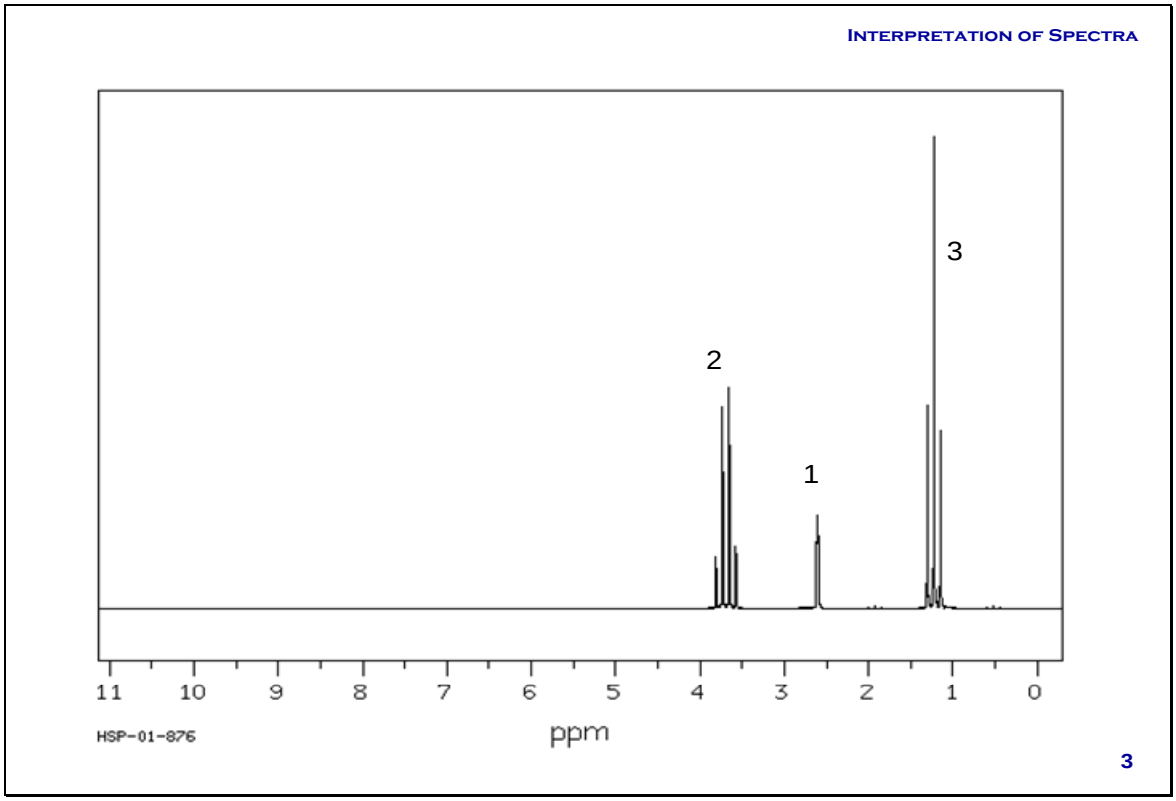
MF: C_2H_6O



Unknown 11: IR



Unknown 11: NMR



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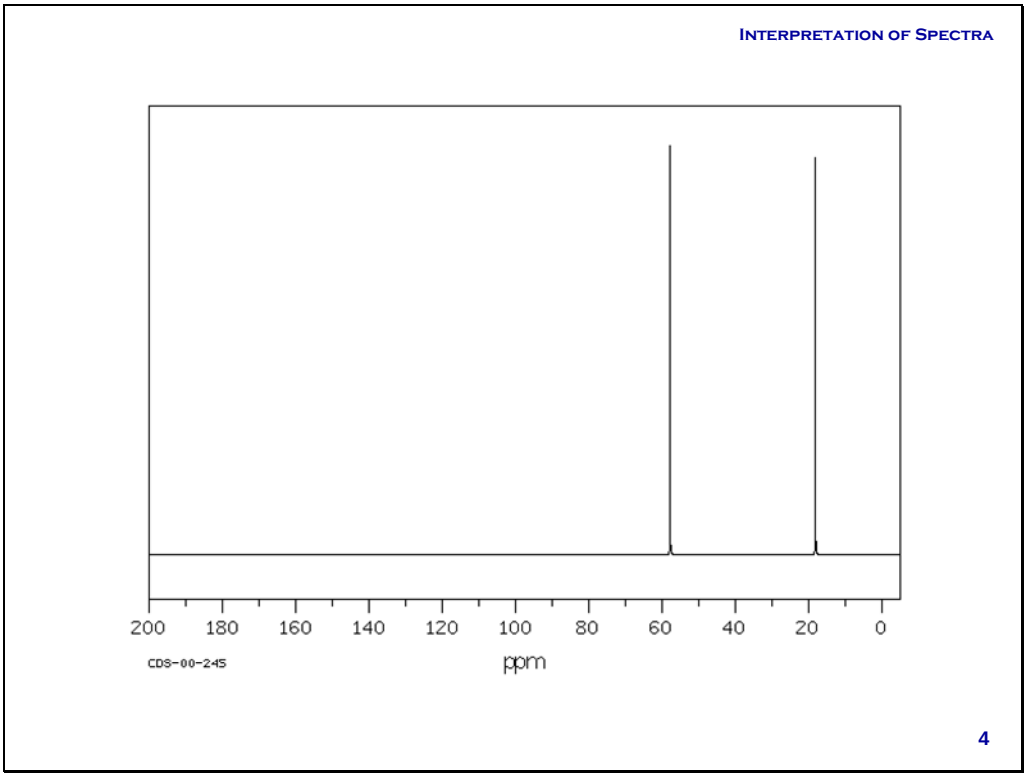
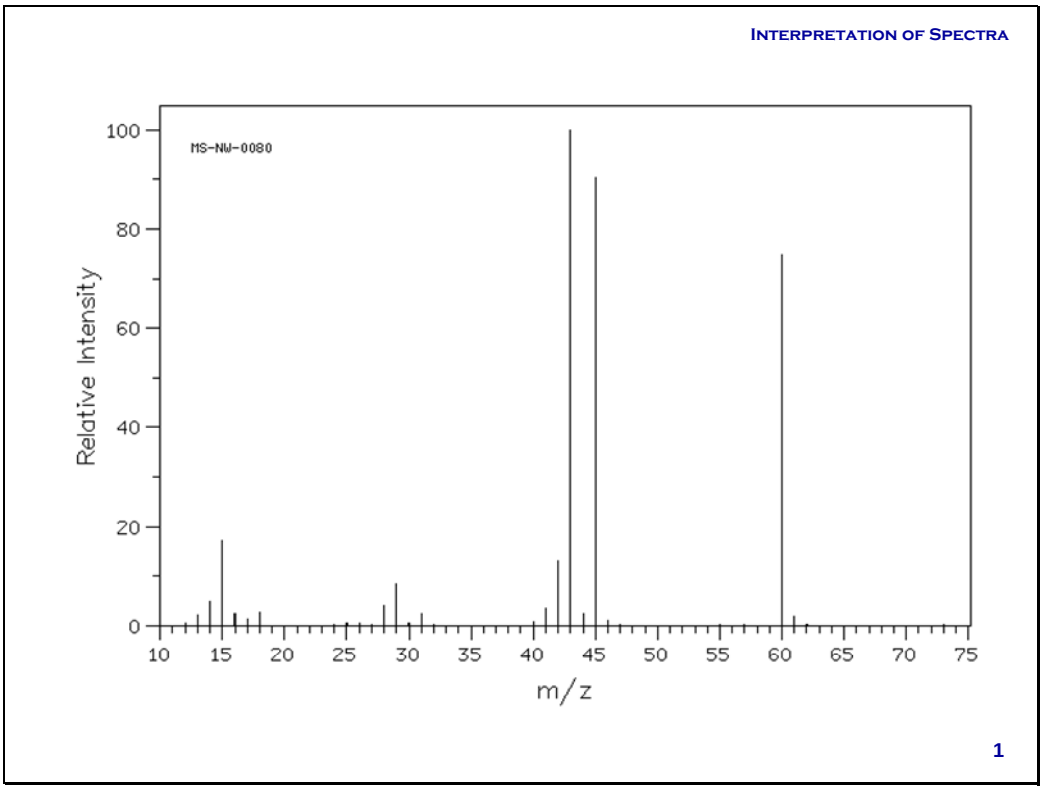


Unknown 12: MS

MF: $C_2H_4O_2$



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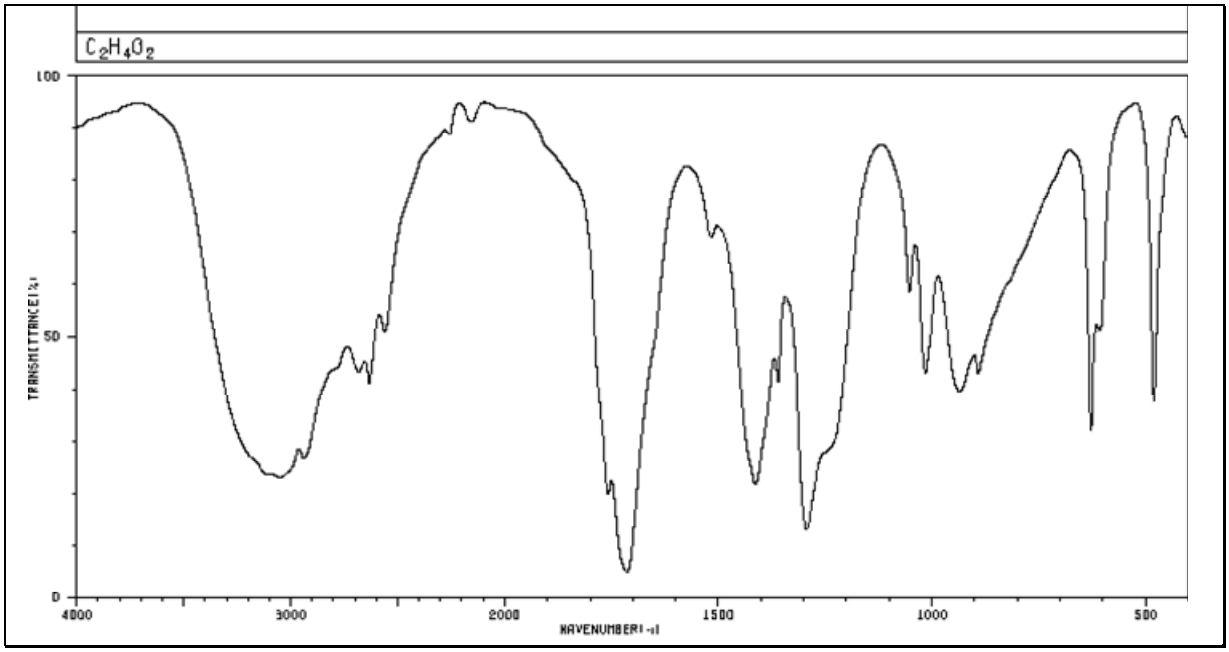
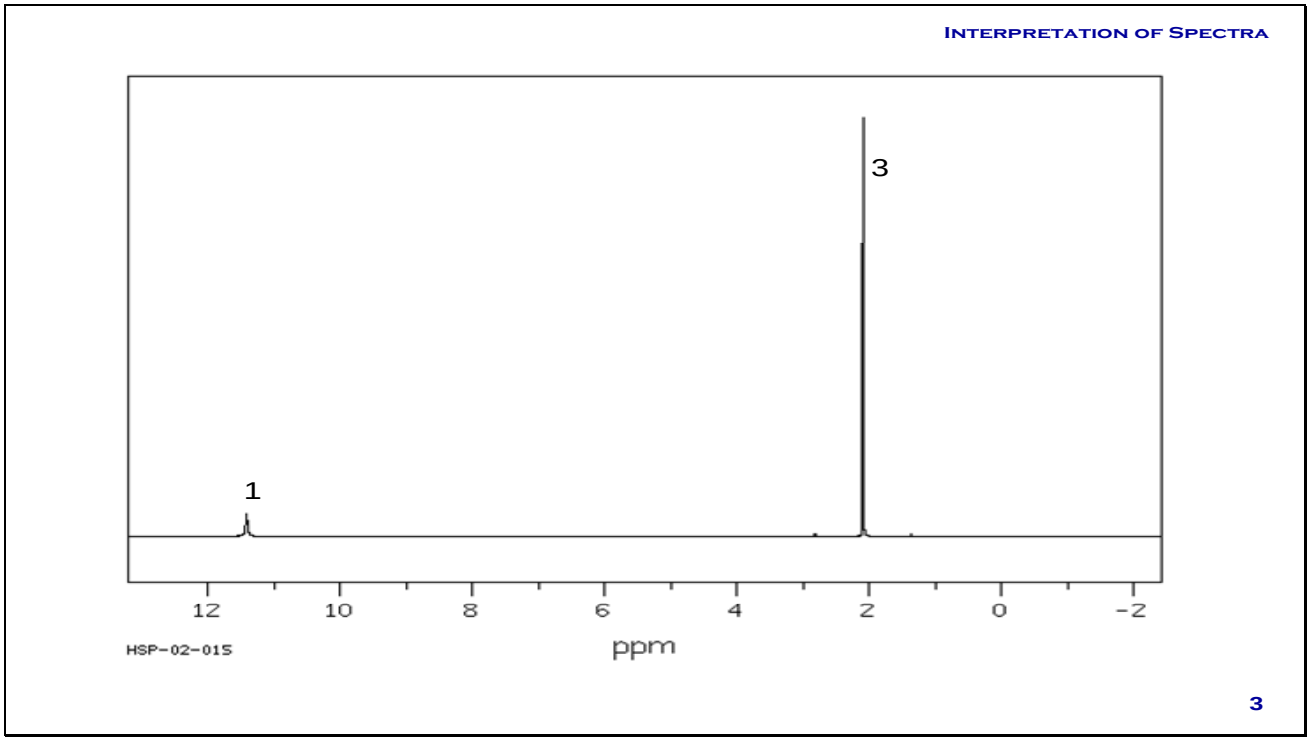
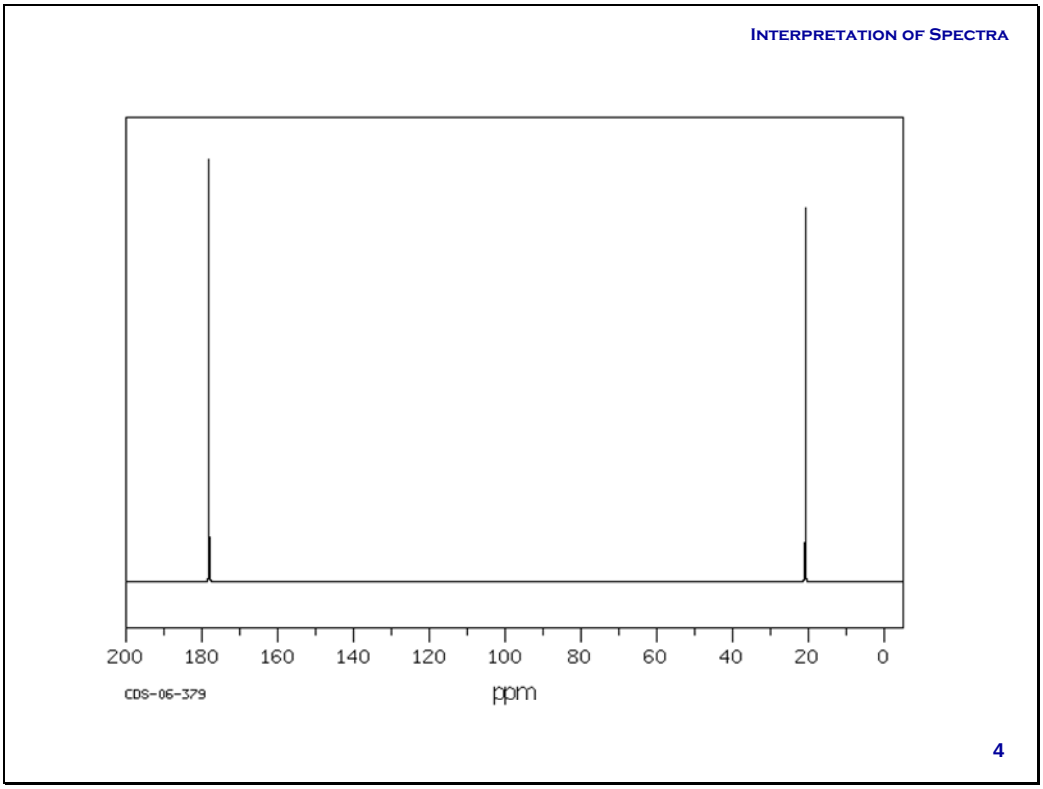


Unknown 12: NMR

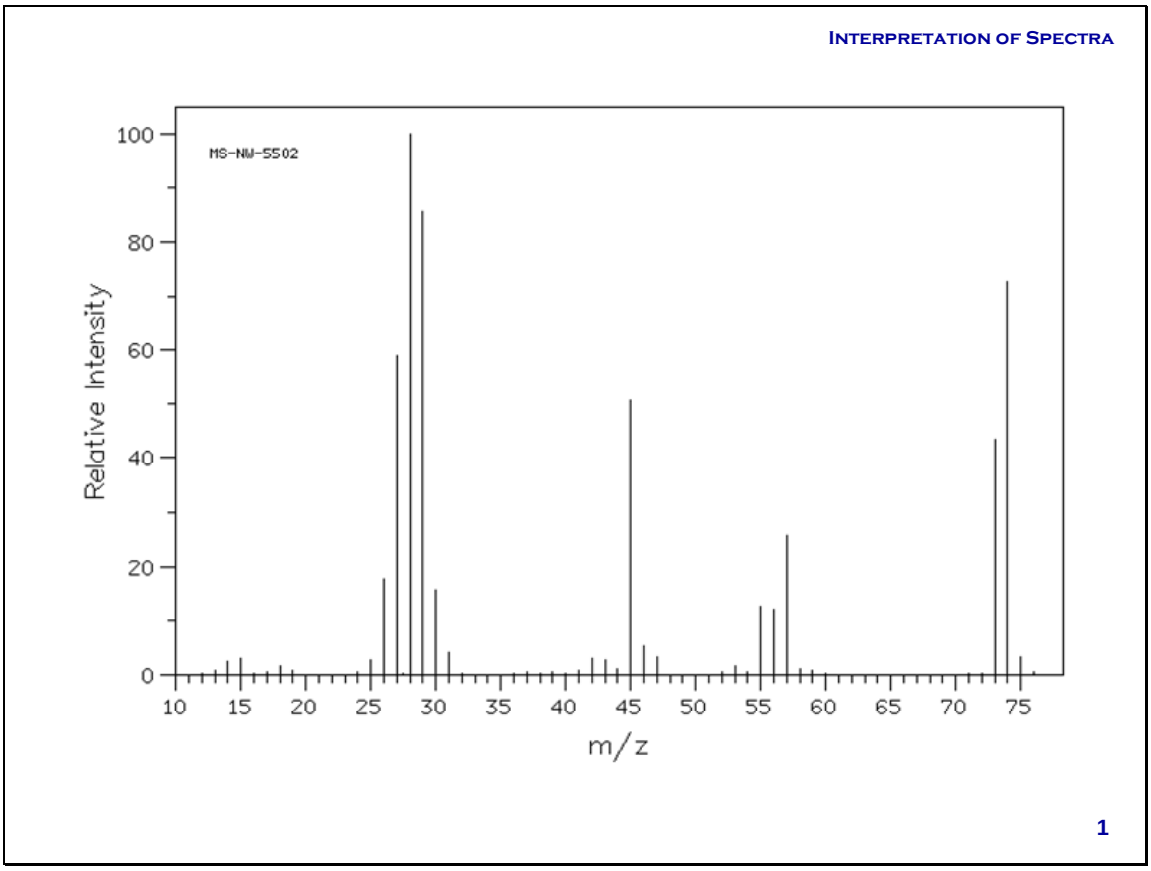


Unknown 12: CNMR



Unknown 13: MS

MF: $C_3H_6O_2$



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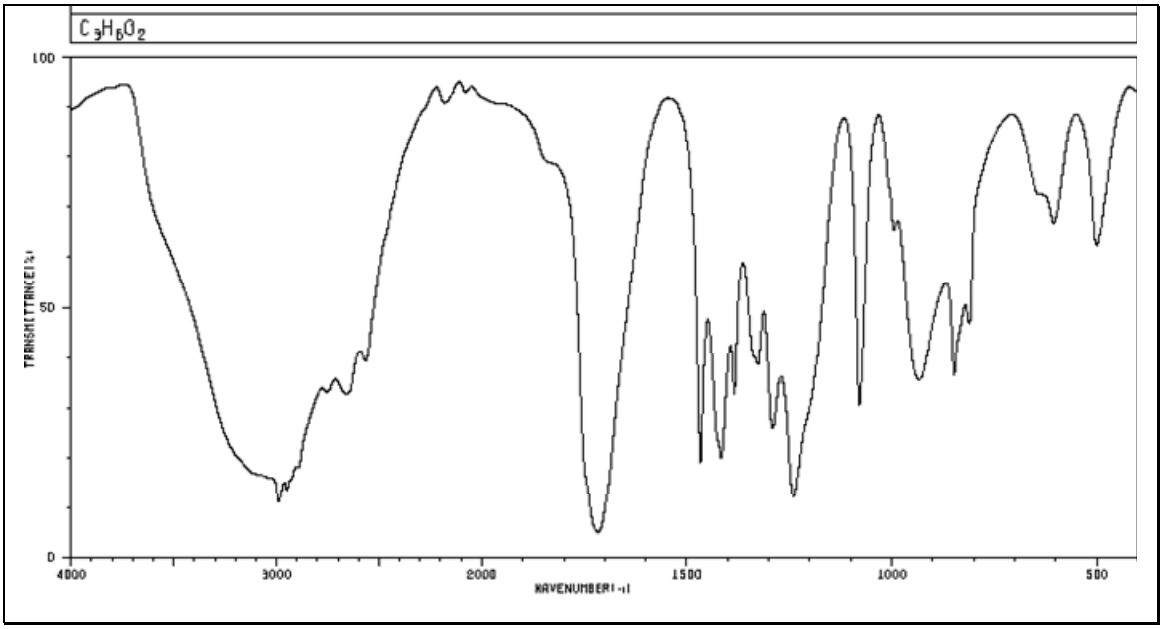
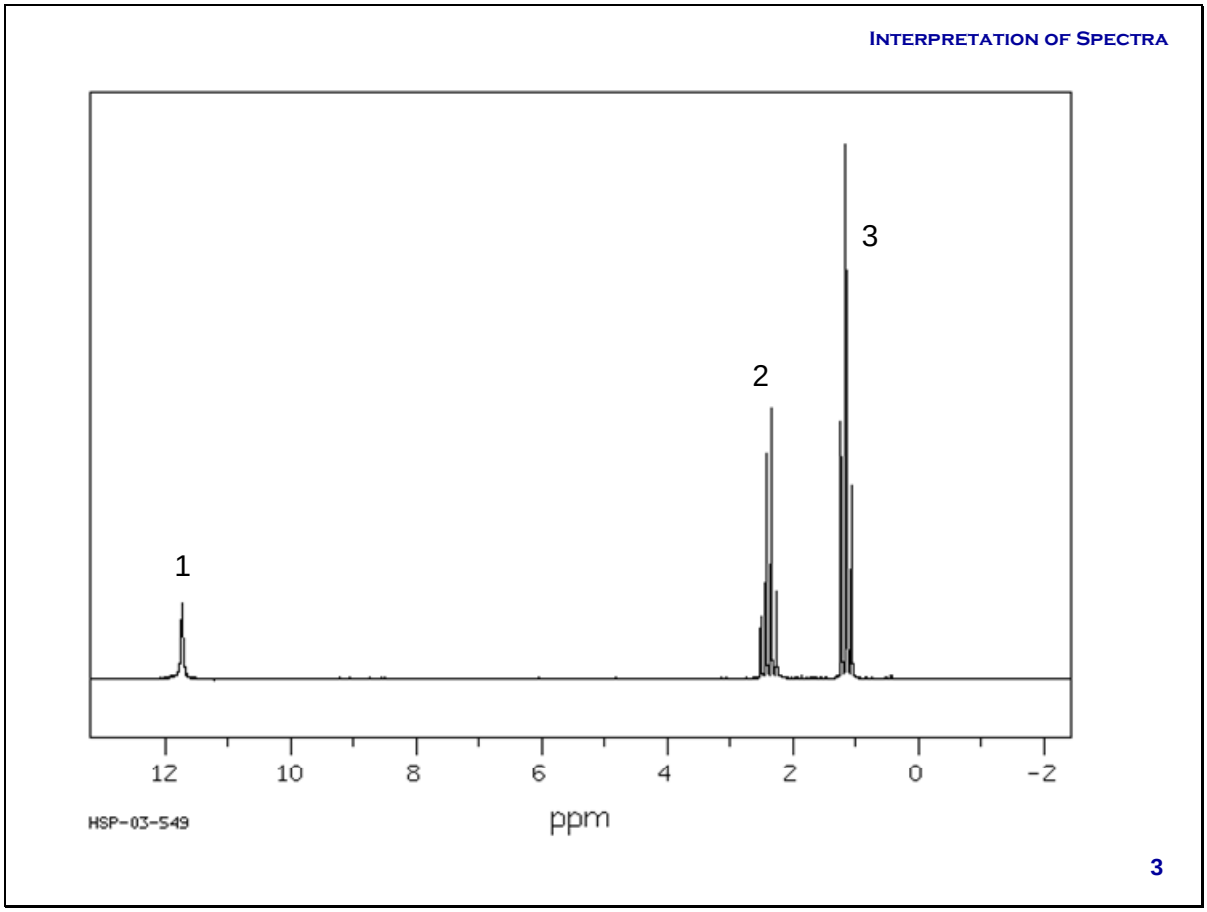
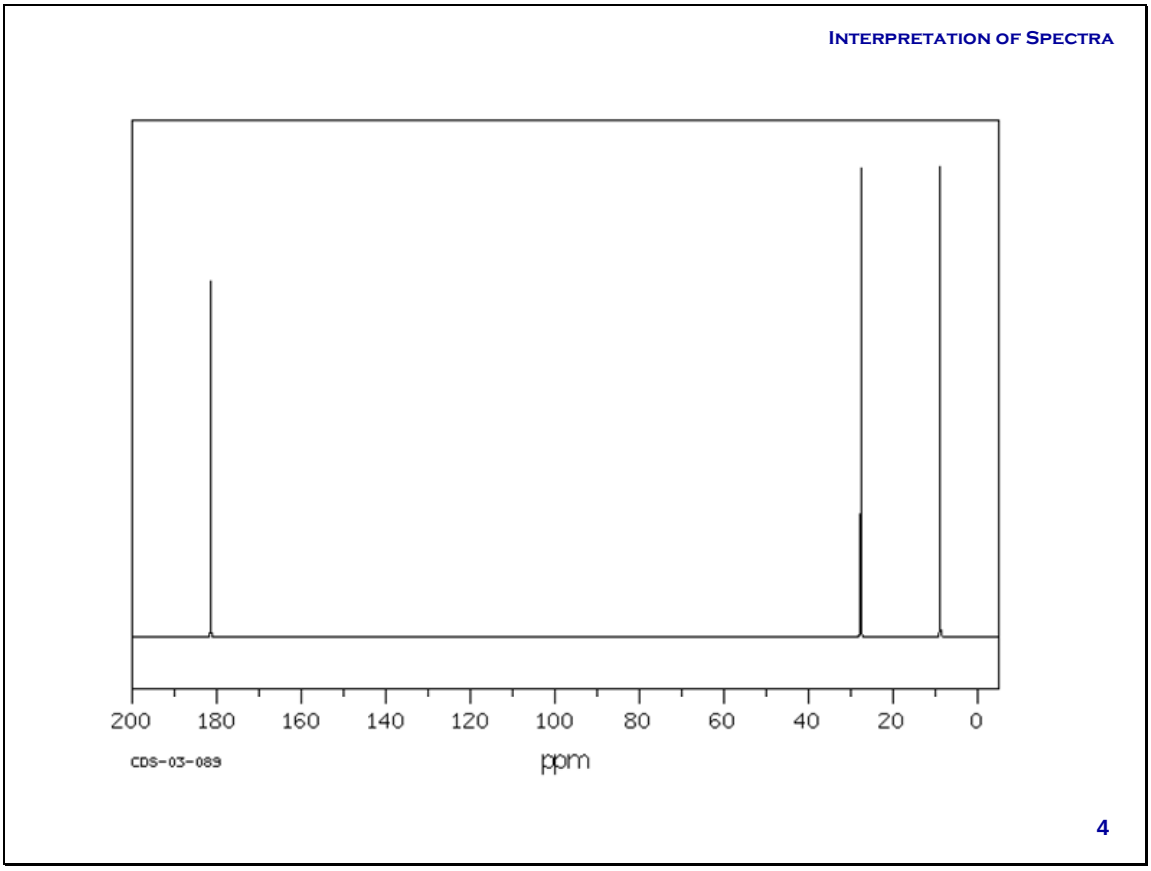


Unknown 13: NMR

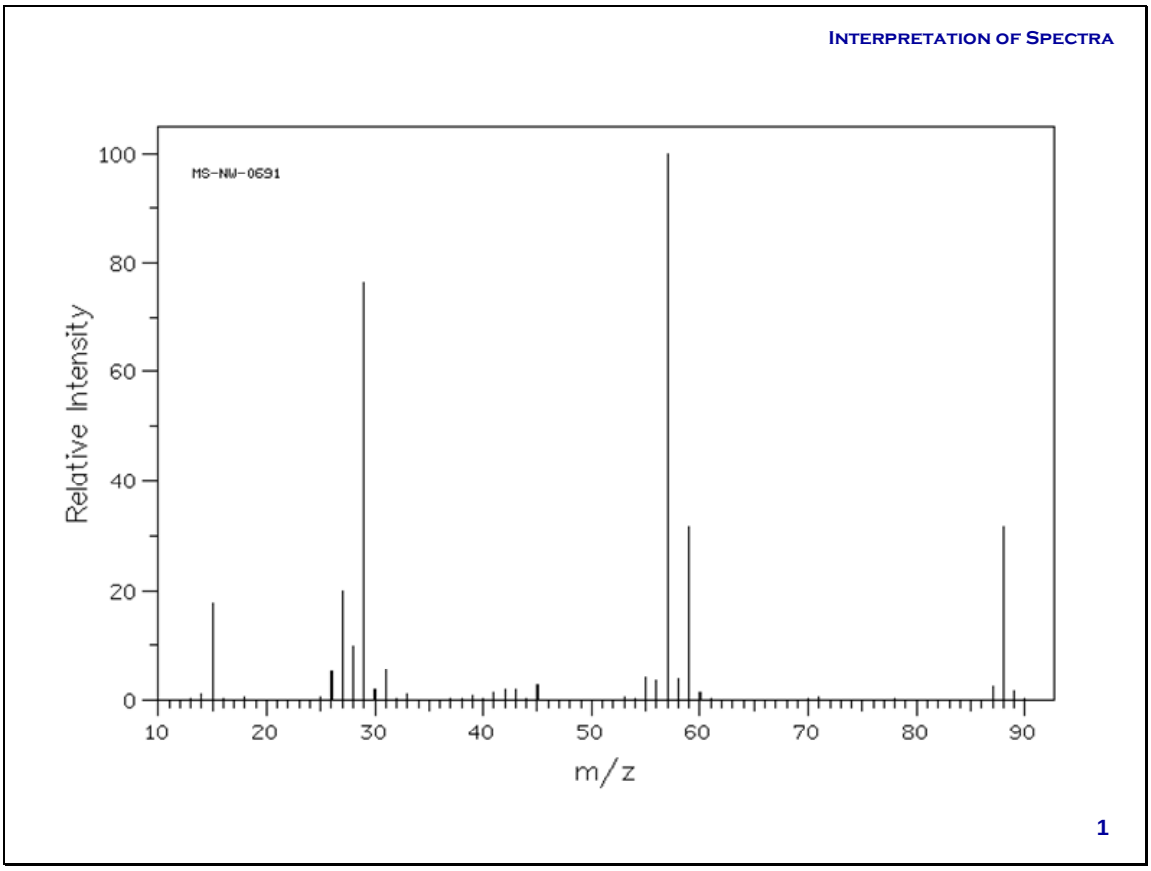


Unknown 13: CNMR

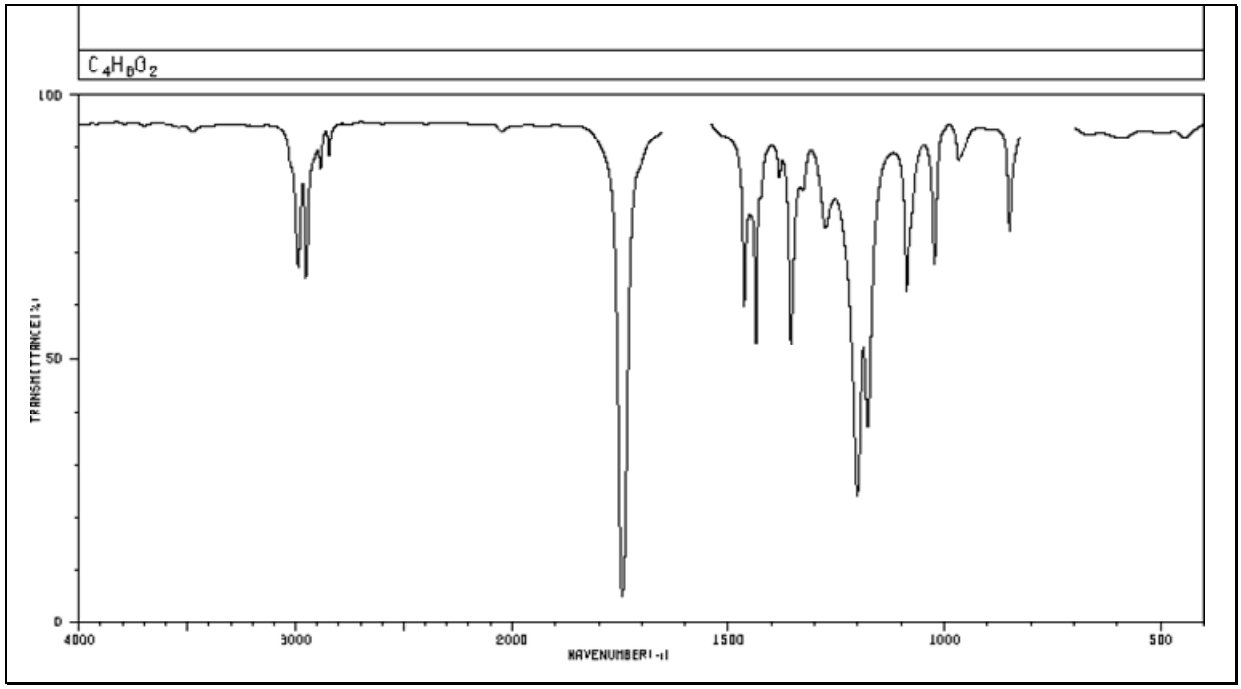


Unknown 14: MS

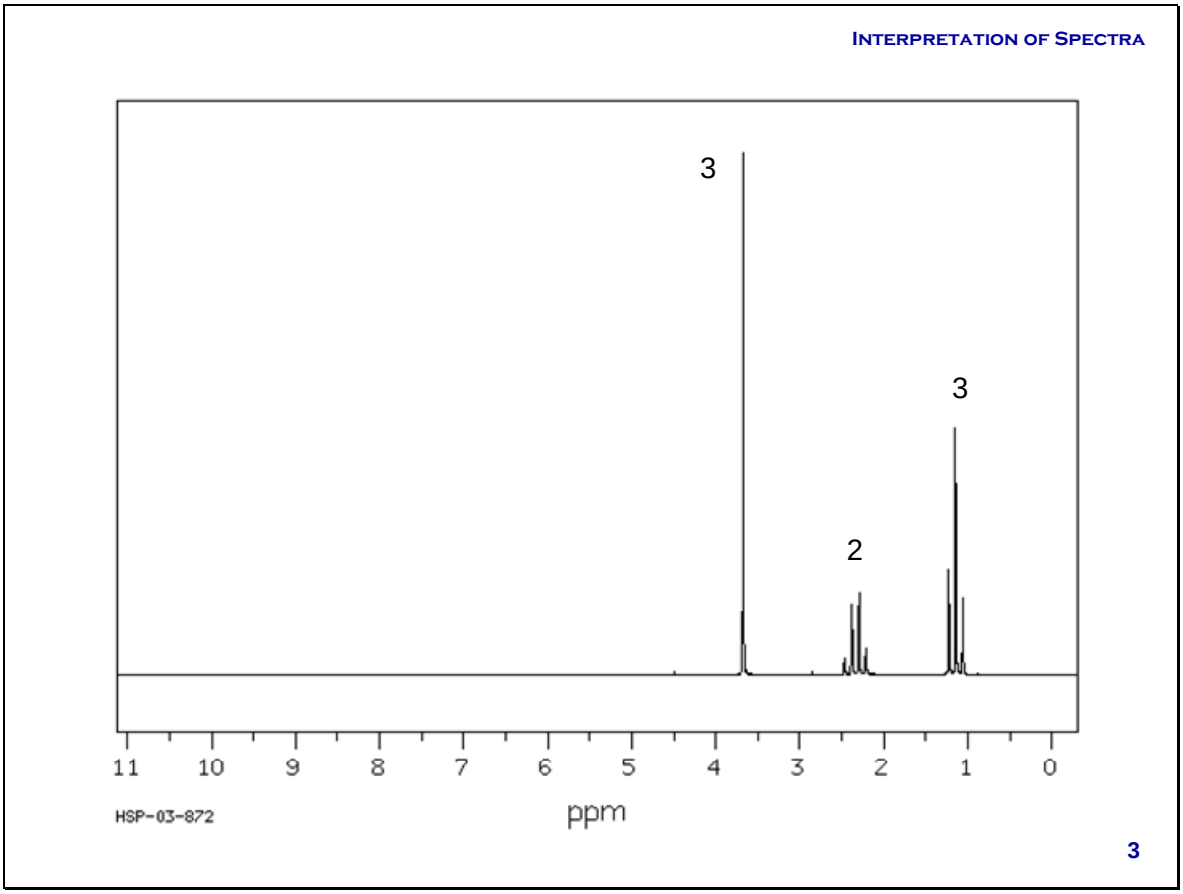
MF: $C_4H_8O_2$



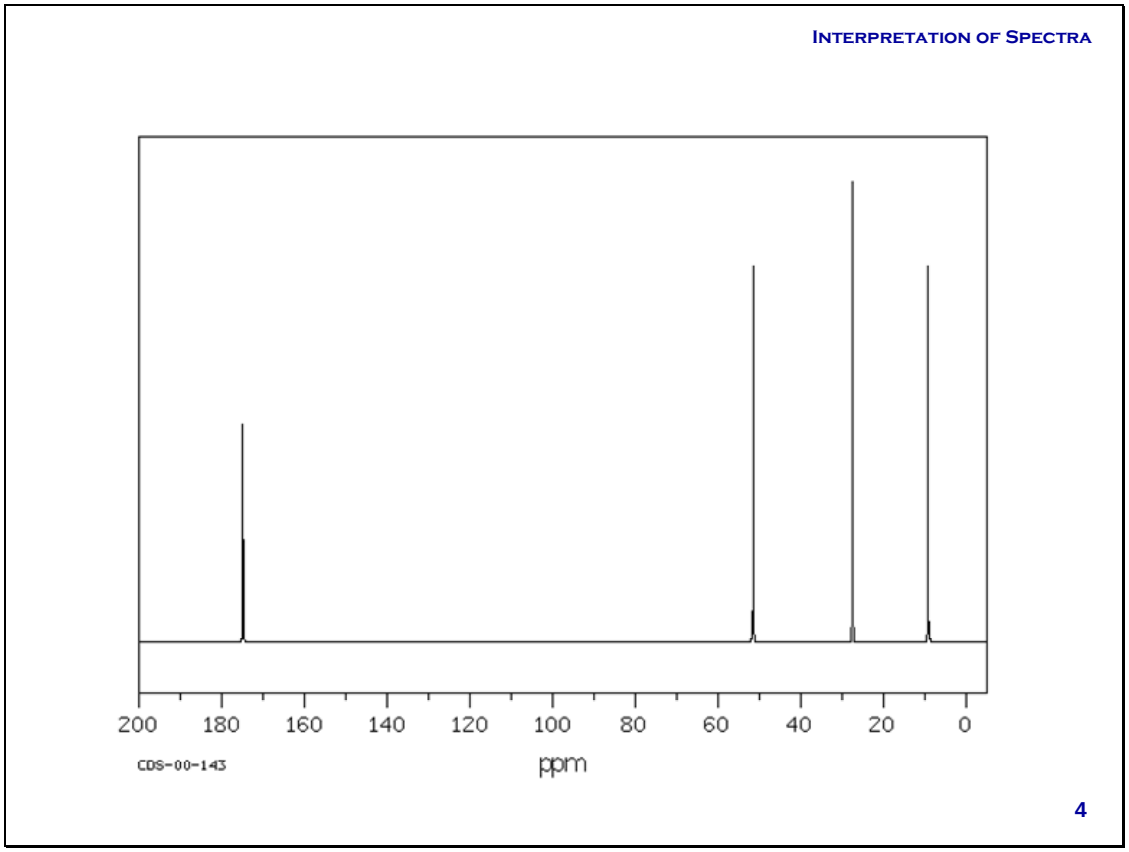
Unknown 14: IR



Unknown 14: NMR

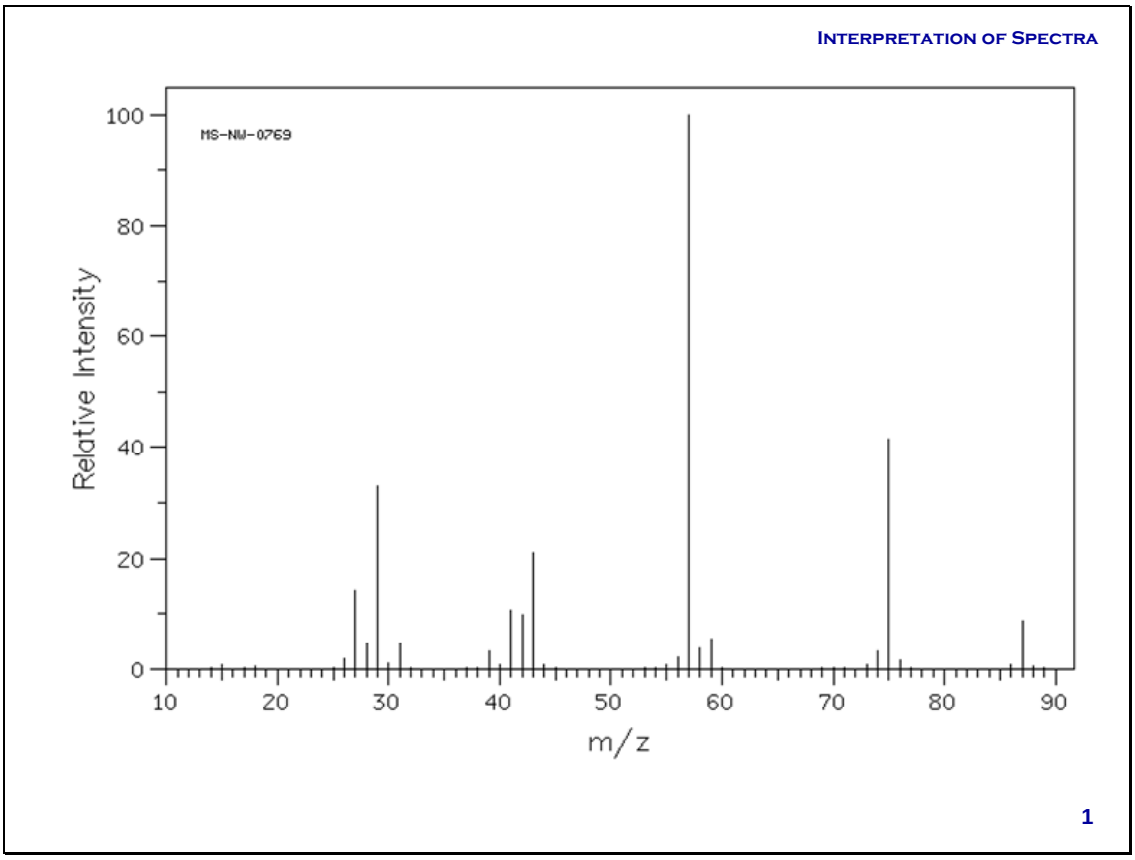


Unknown 14: CNMR

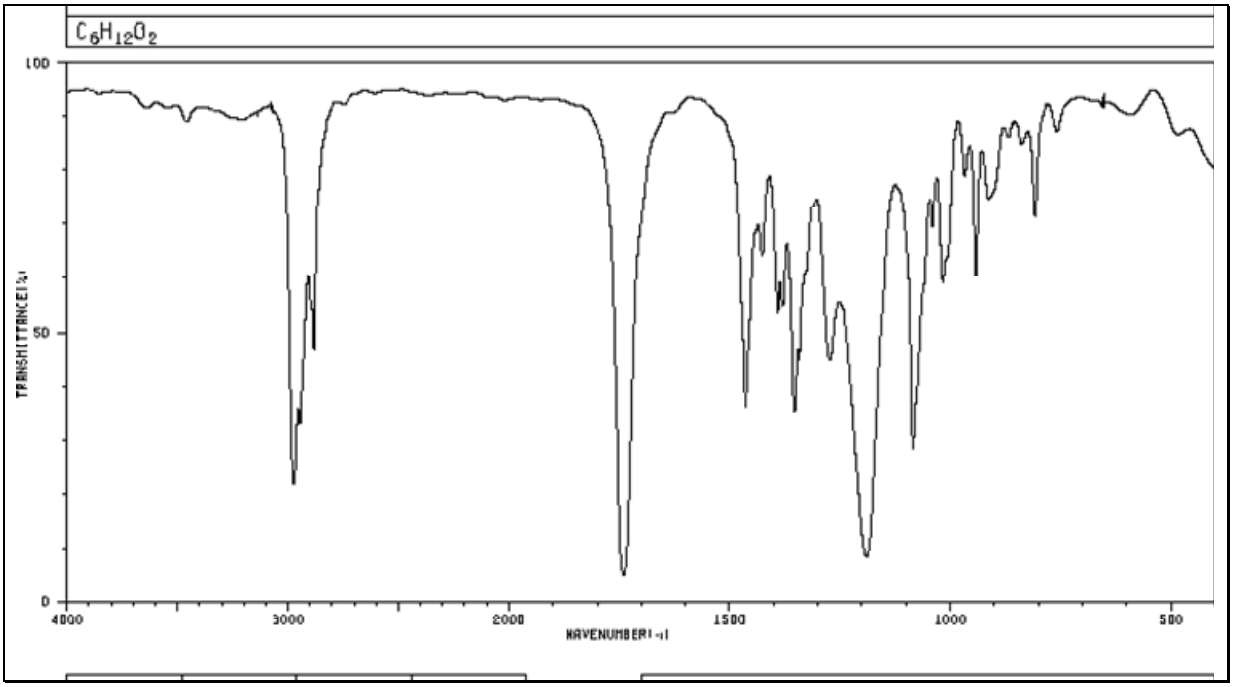


Unknown 15: MS

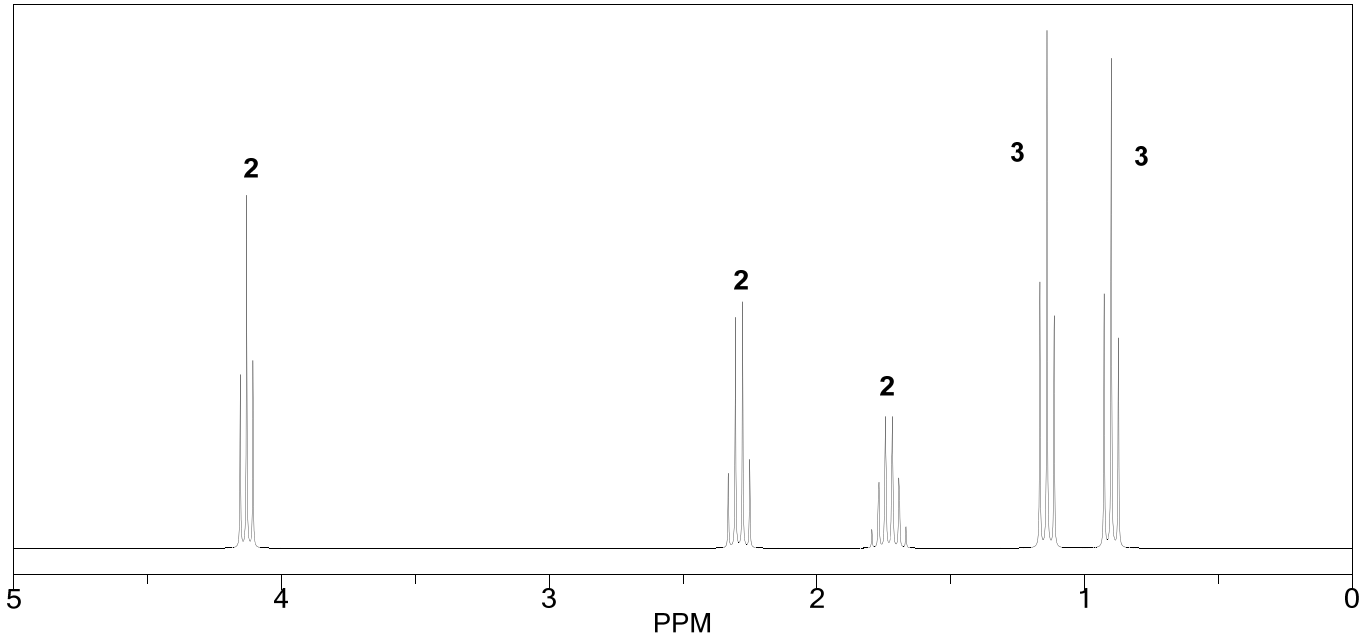
MF: $C_6H_{12}O_2$



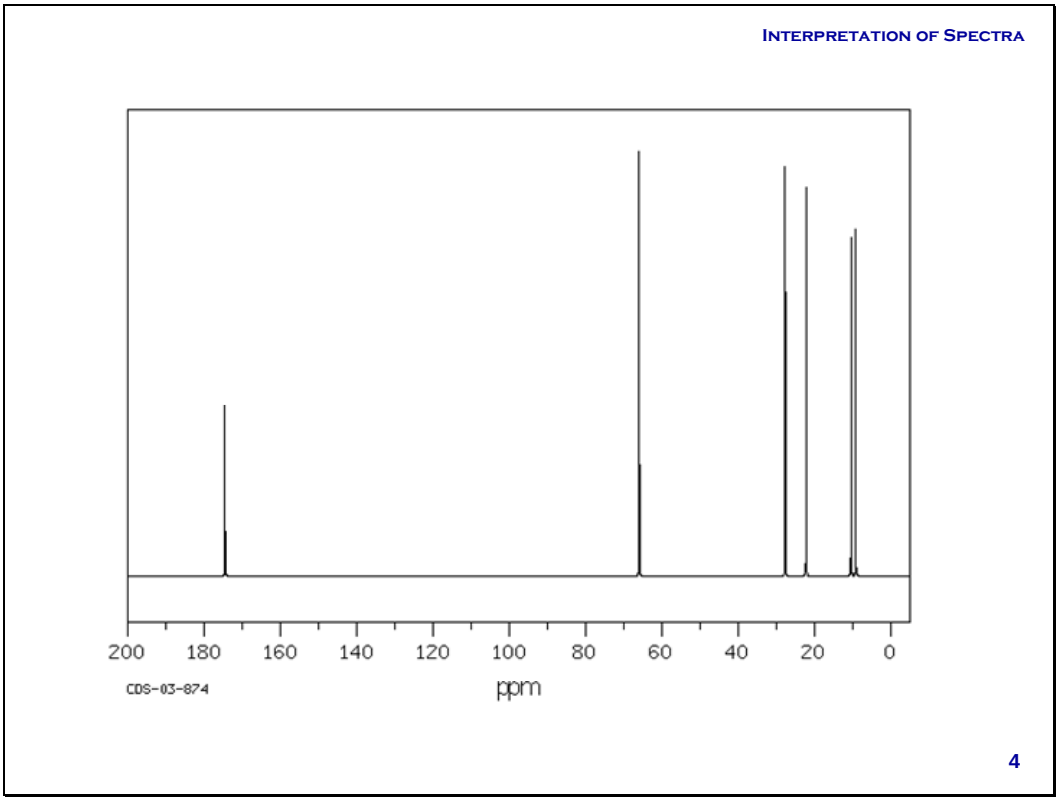
Unknown 15: IR



Unknown 15: NMR

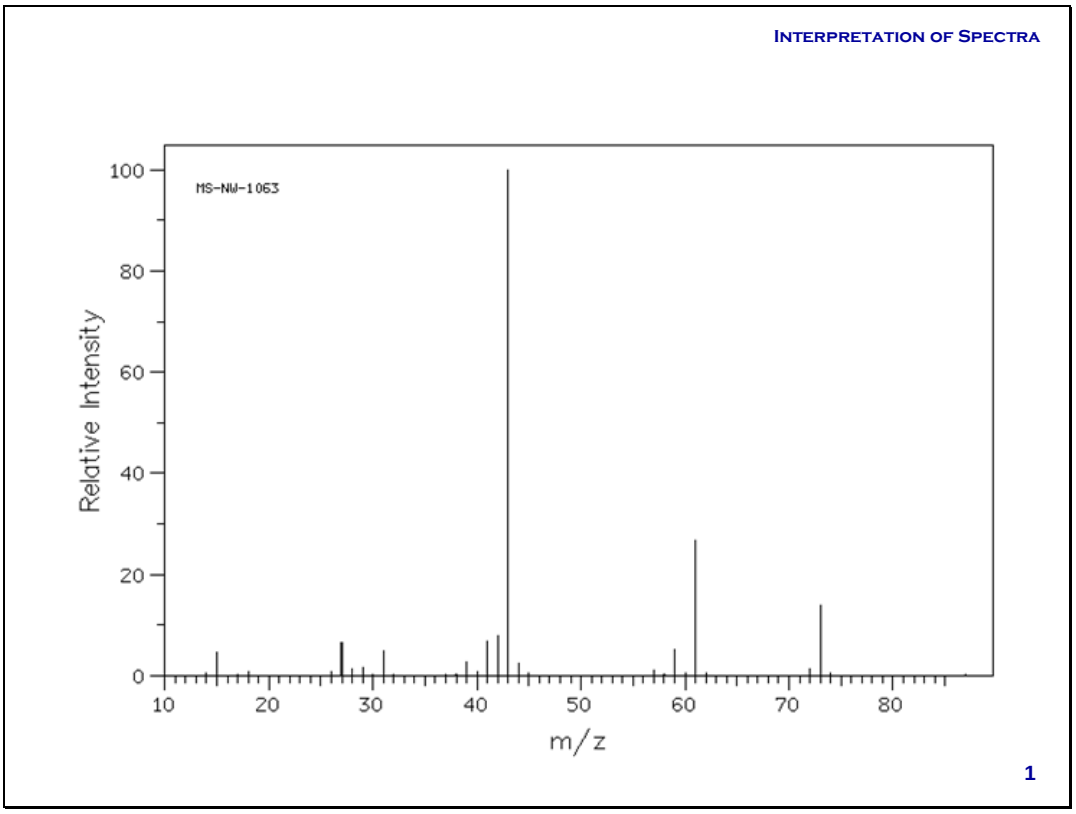


Unknown 15: CNMR

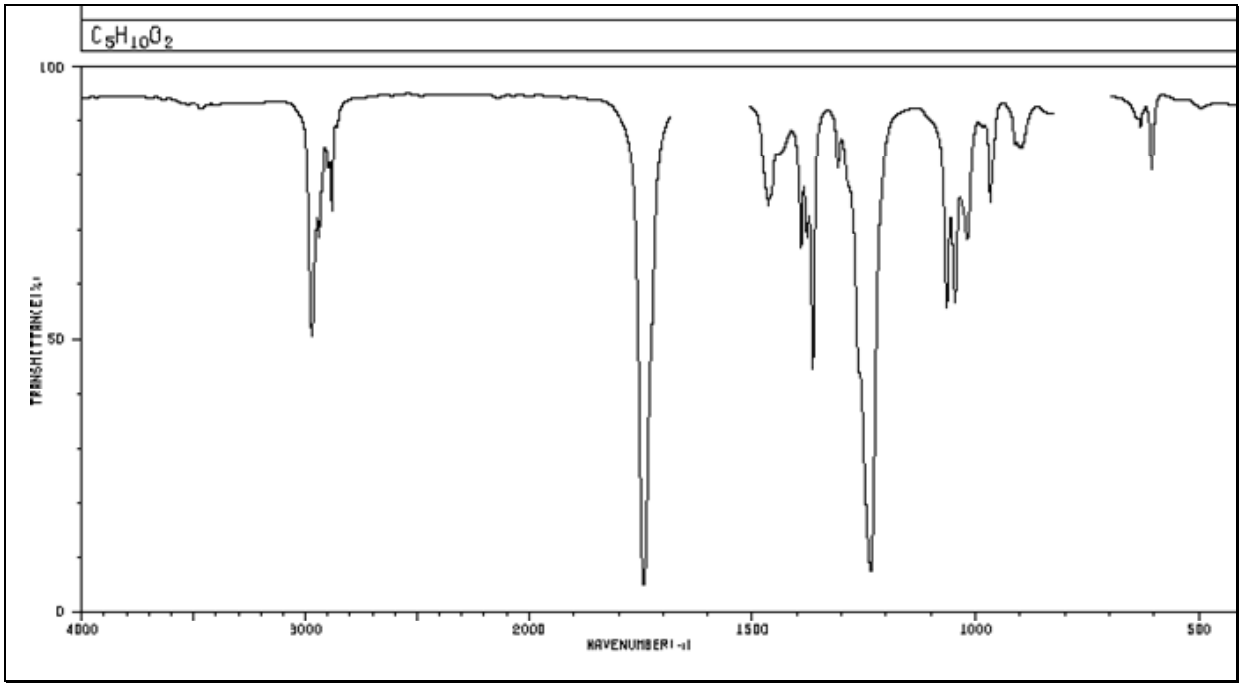


Unknown 16: MS

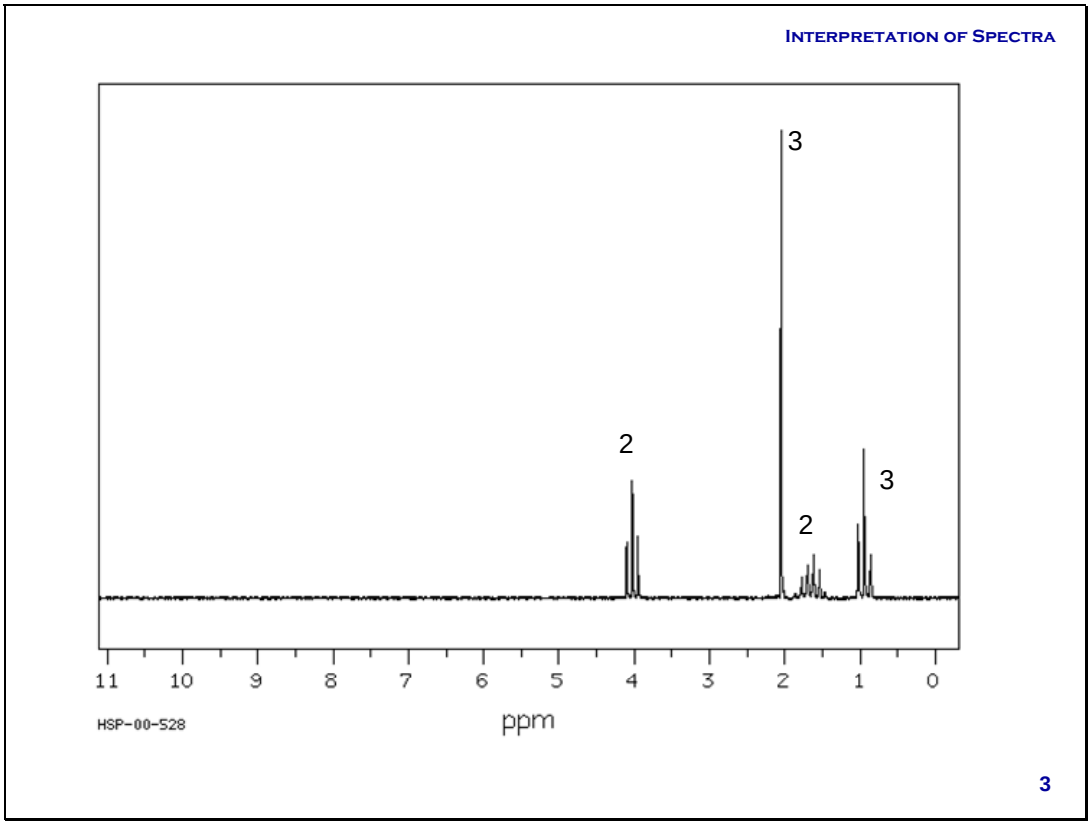
MF: $C_5H_{10}O_2$



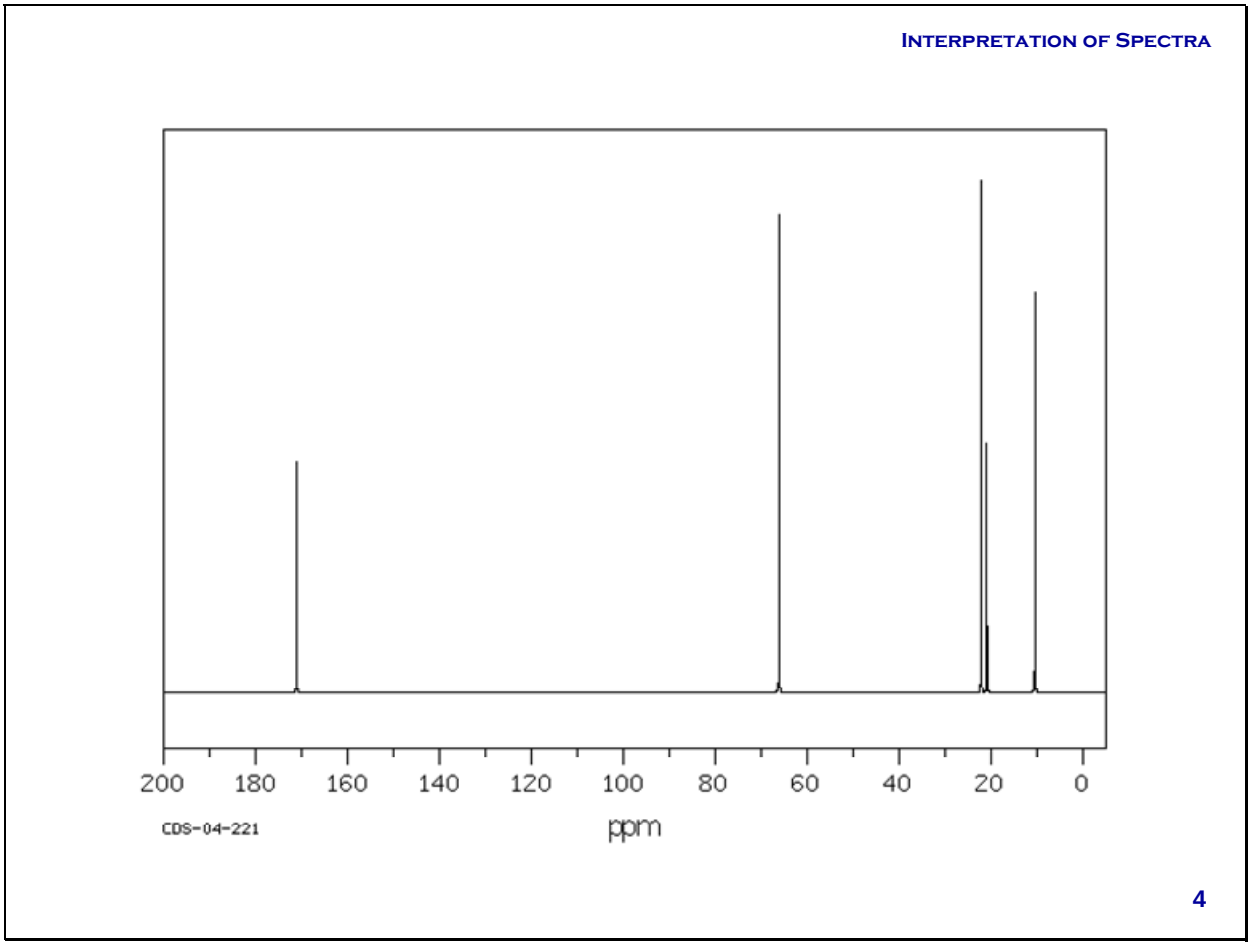
Unknown 16: IR



Unknown 16: NMR

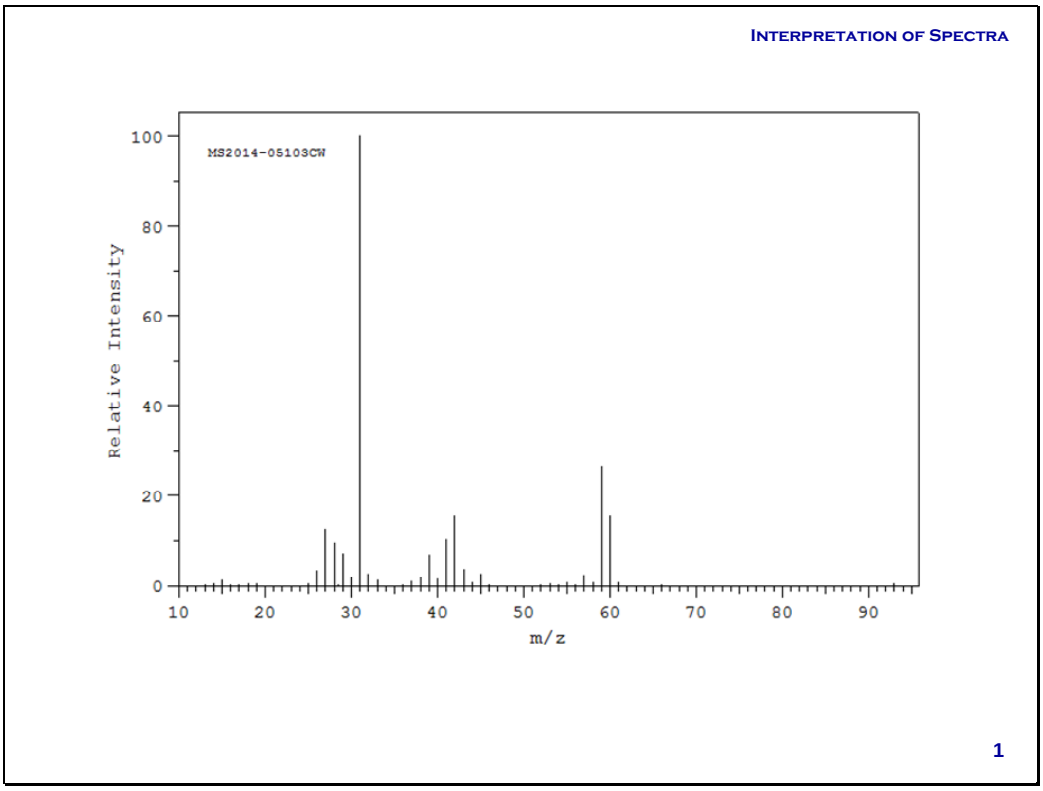


Unknown 16: CNMR

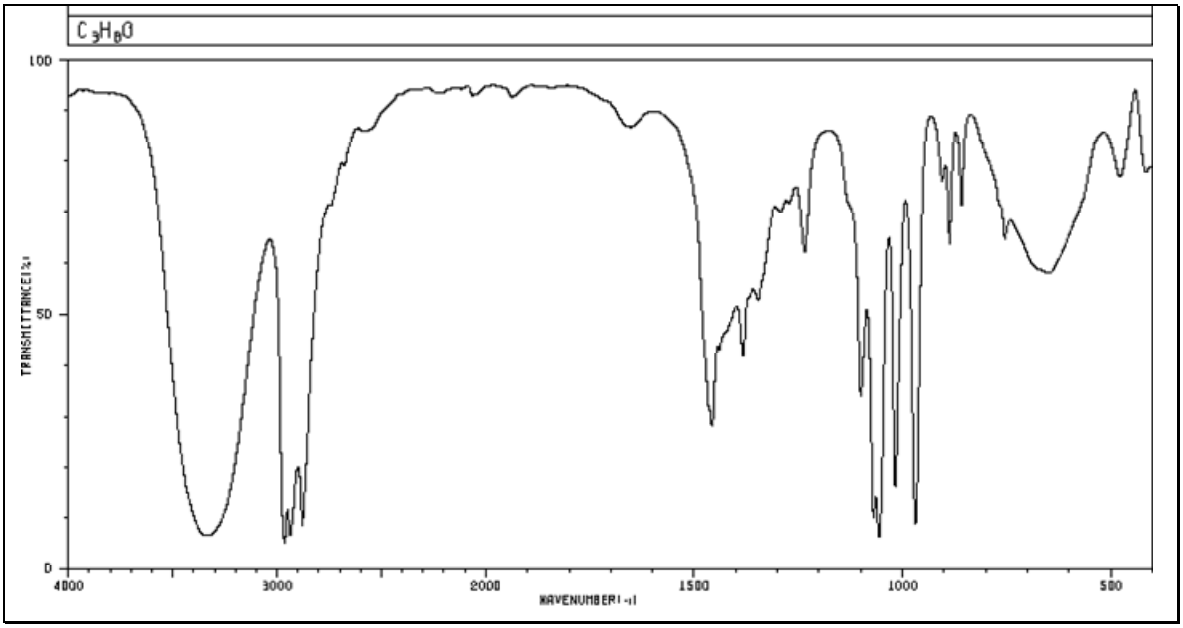


Unknown 17: MS

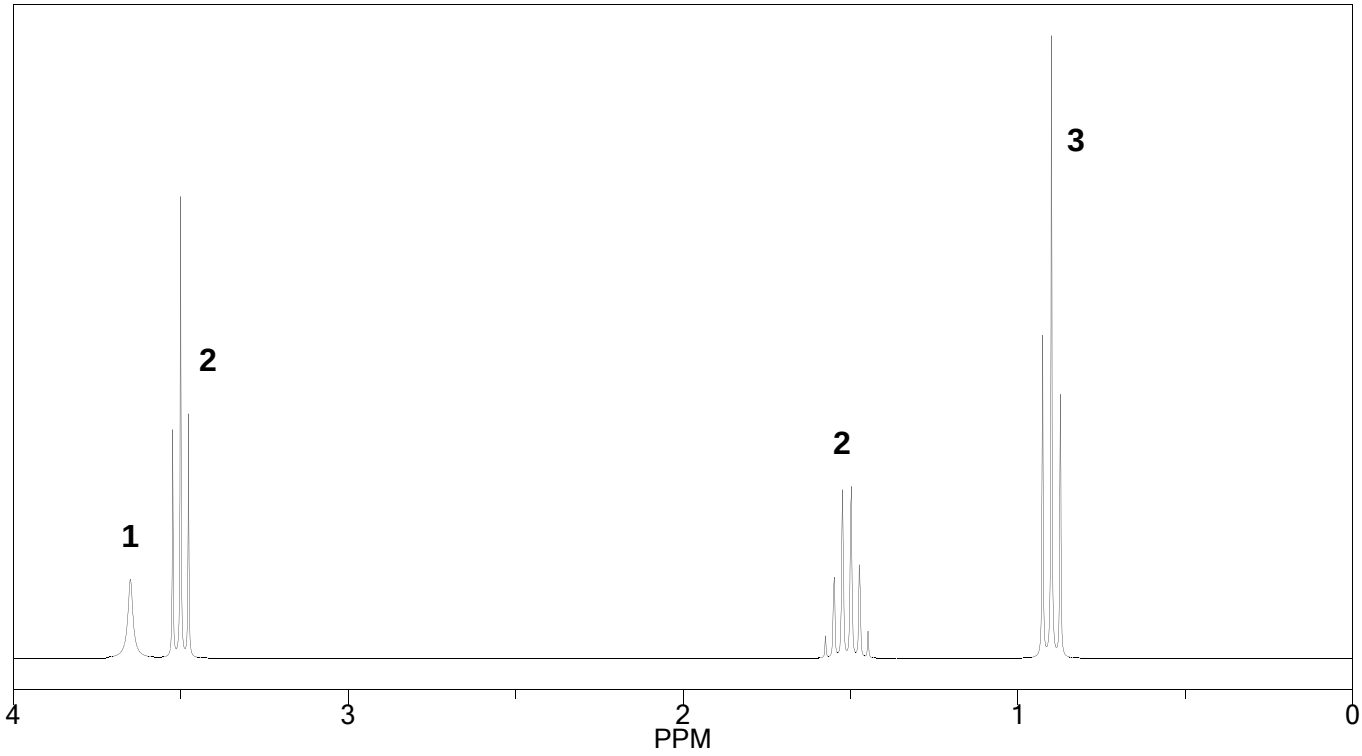
MF: $C_3H_8O_2$



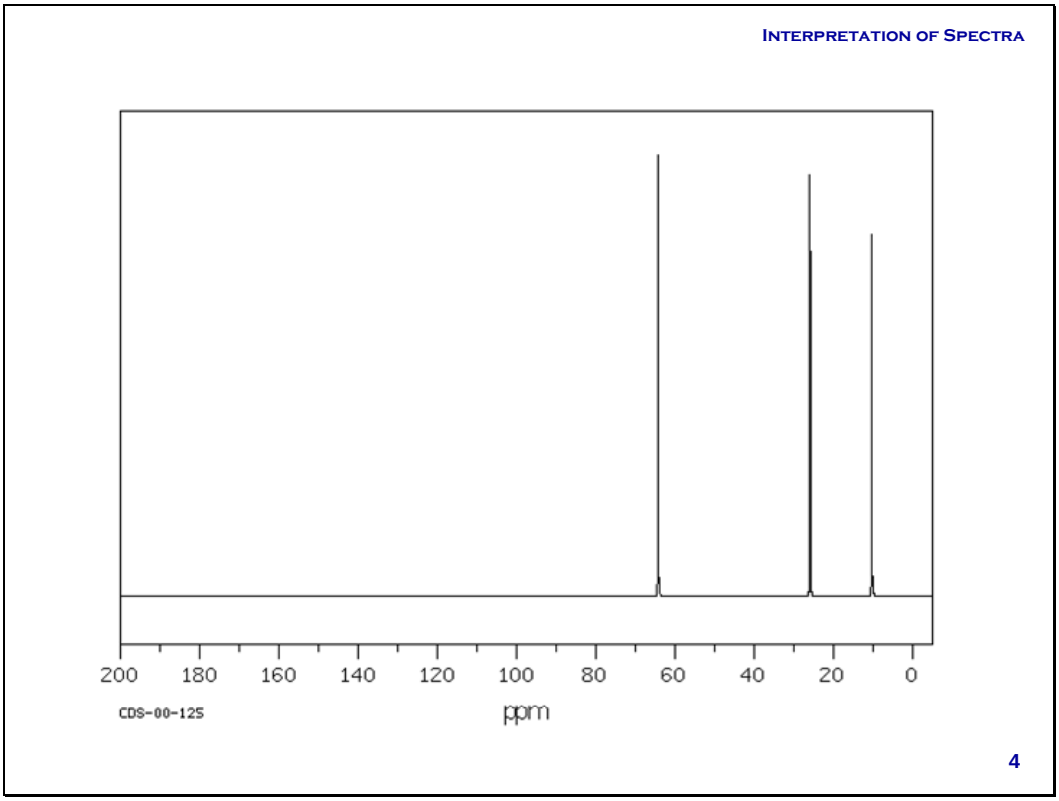
Unknown 17: IR



Unknown 17: NMR

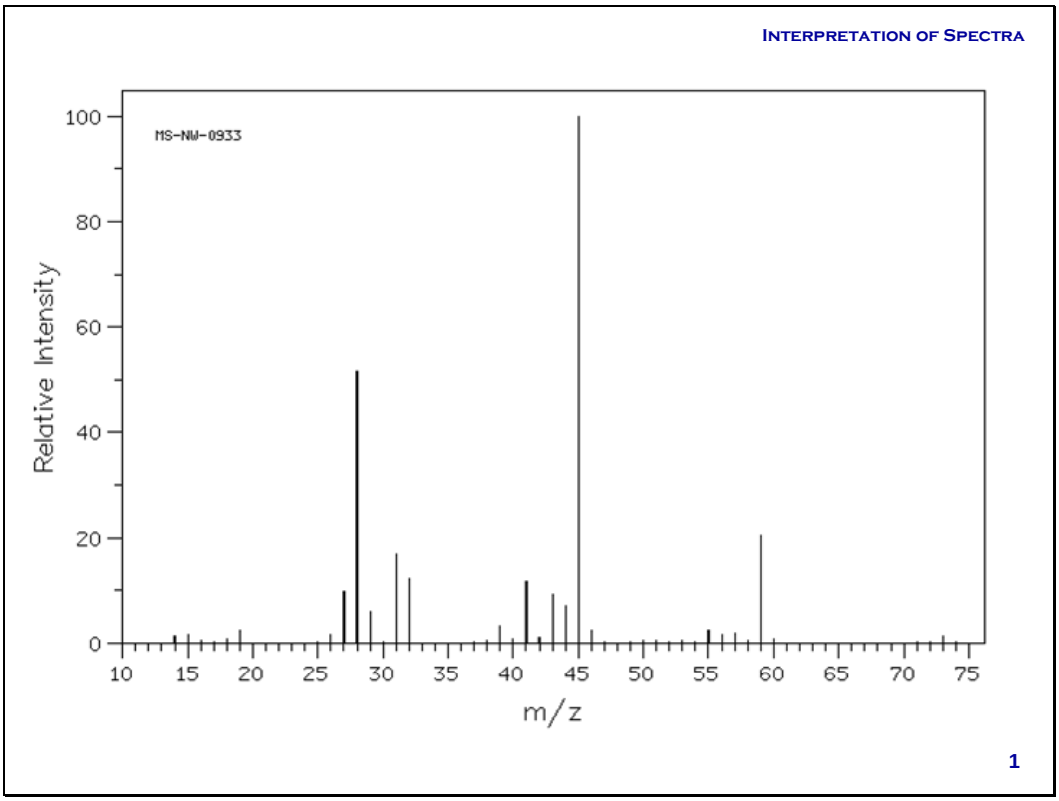


Unknown 17: CNMR

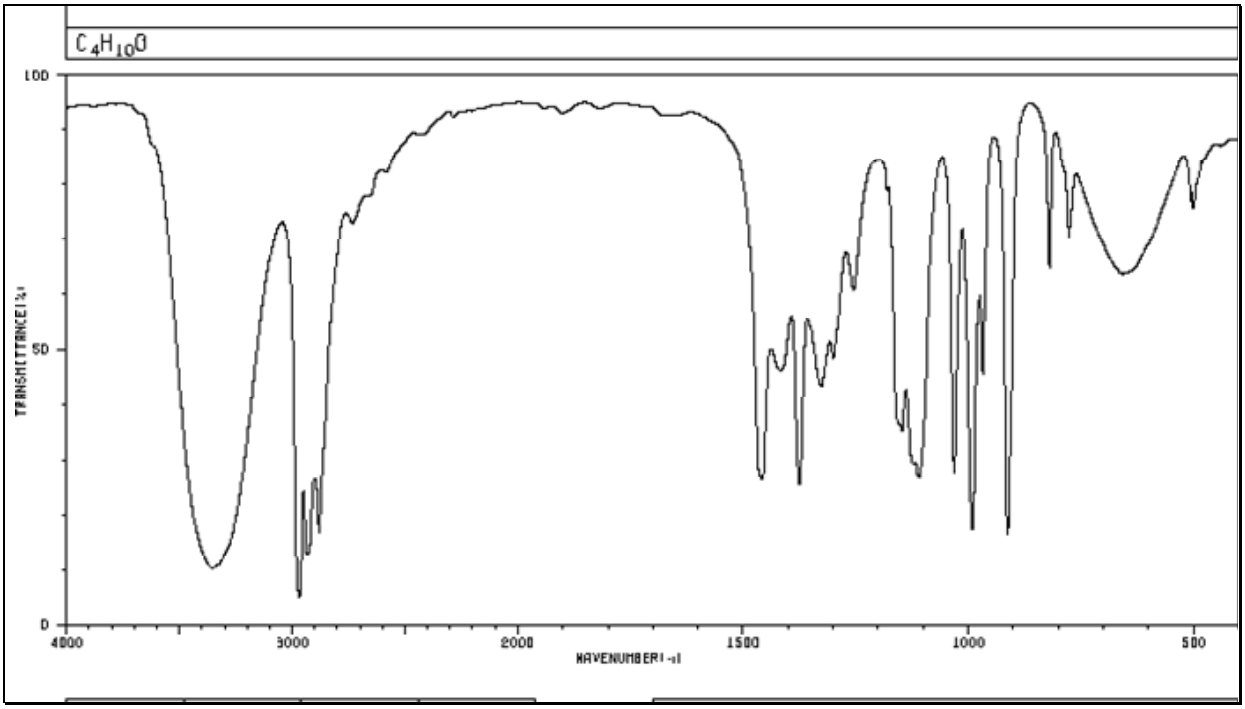


Unknown 18: MS

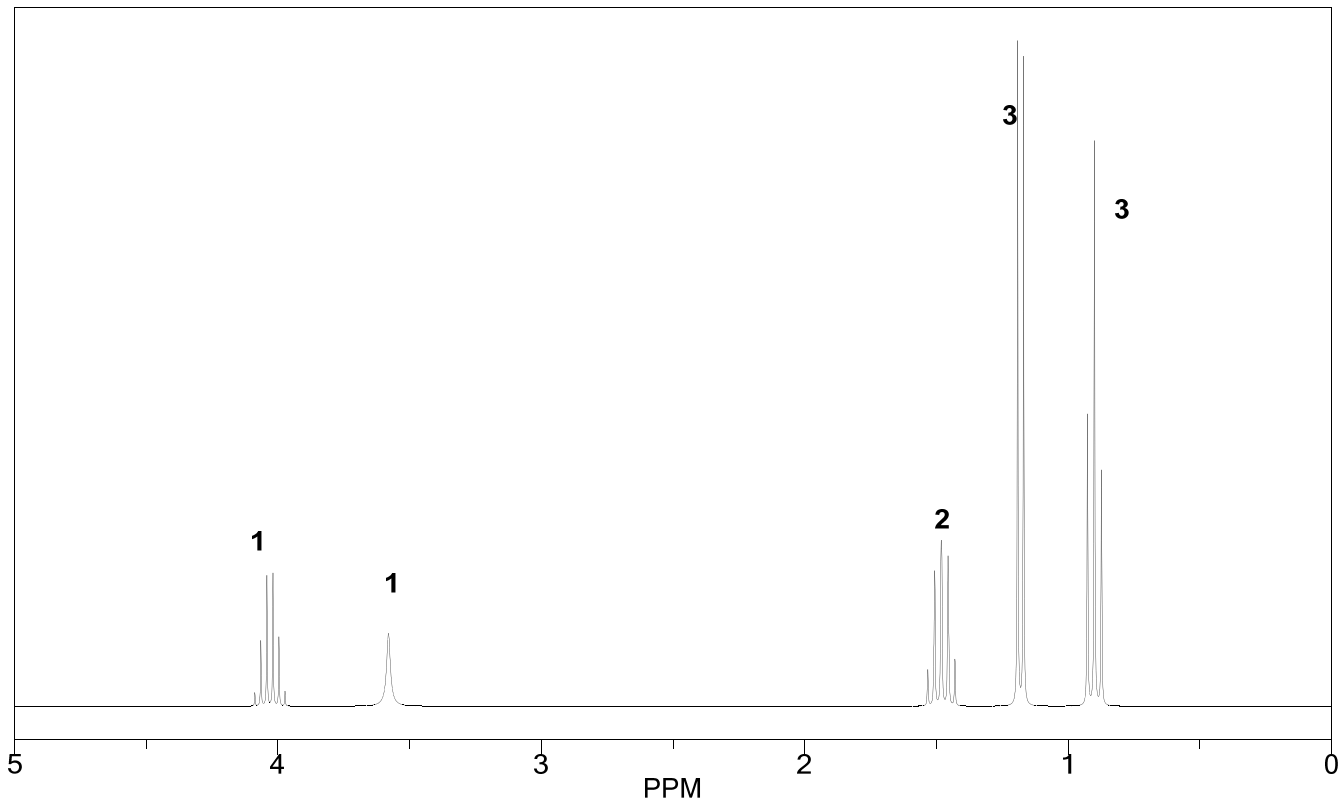
MF: $C_4H_{10}O$



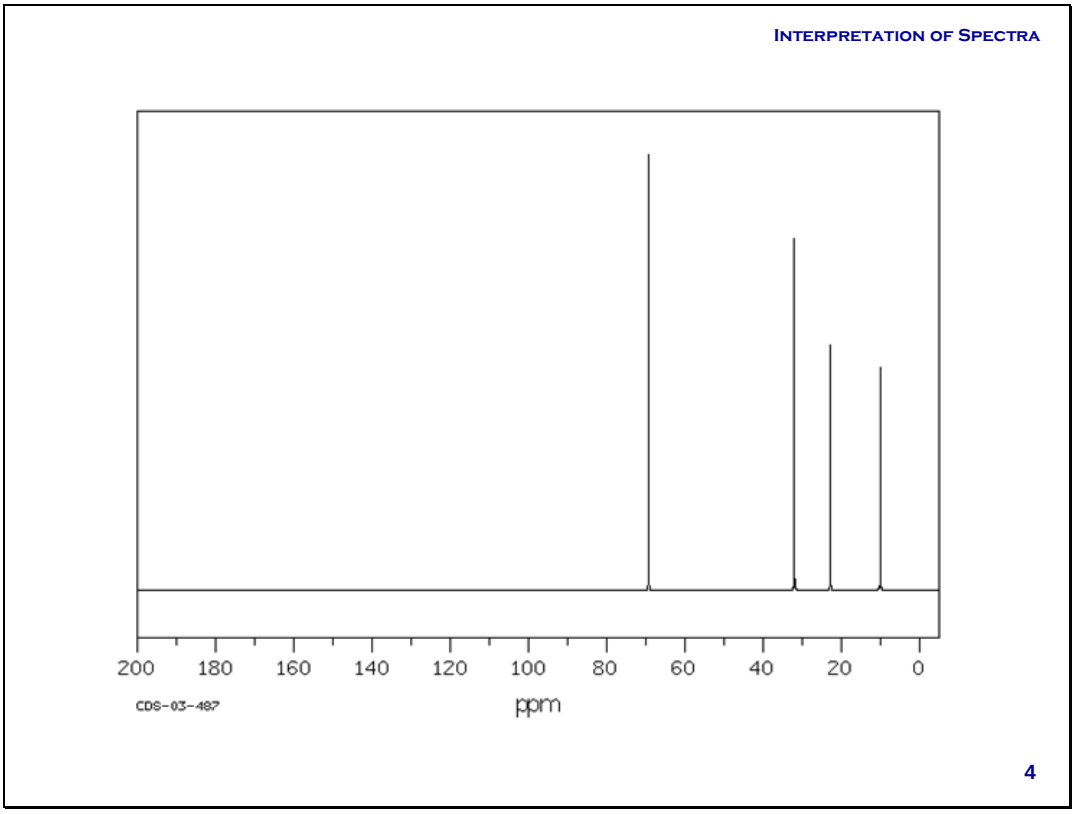
Unknown 18: IR



Unknown 18: NMR

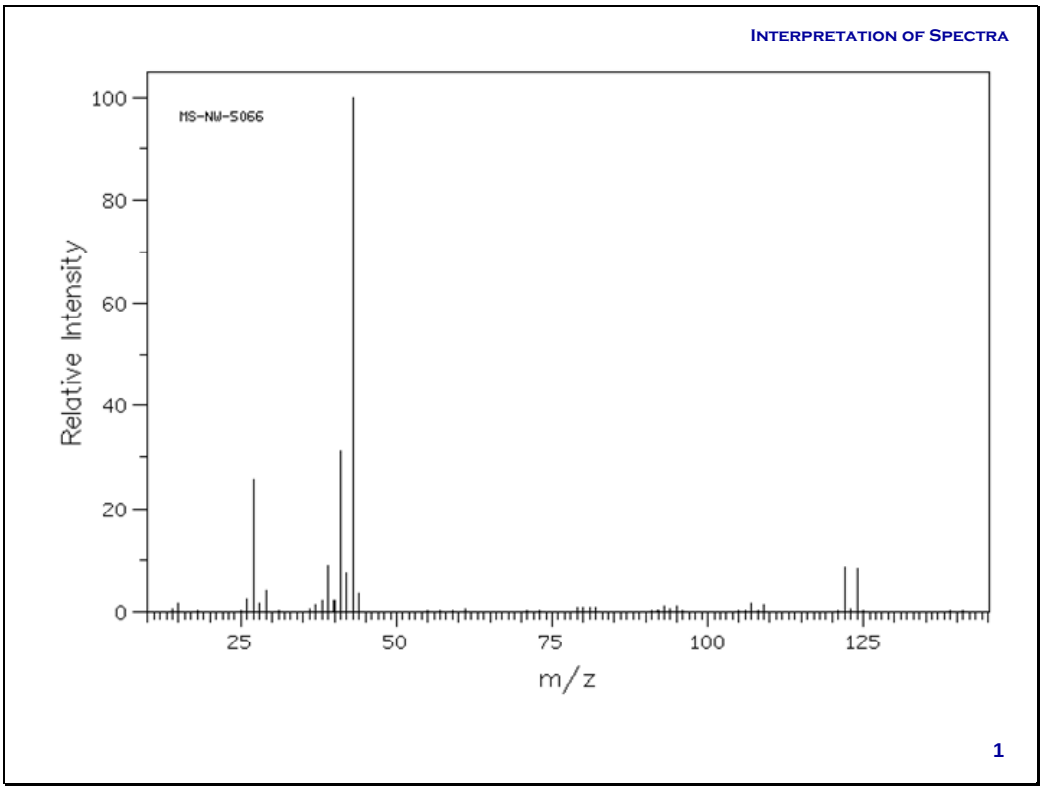


Unknown 18: CNMR

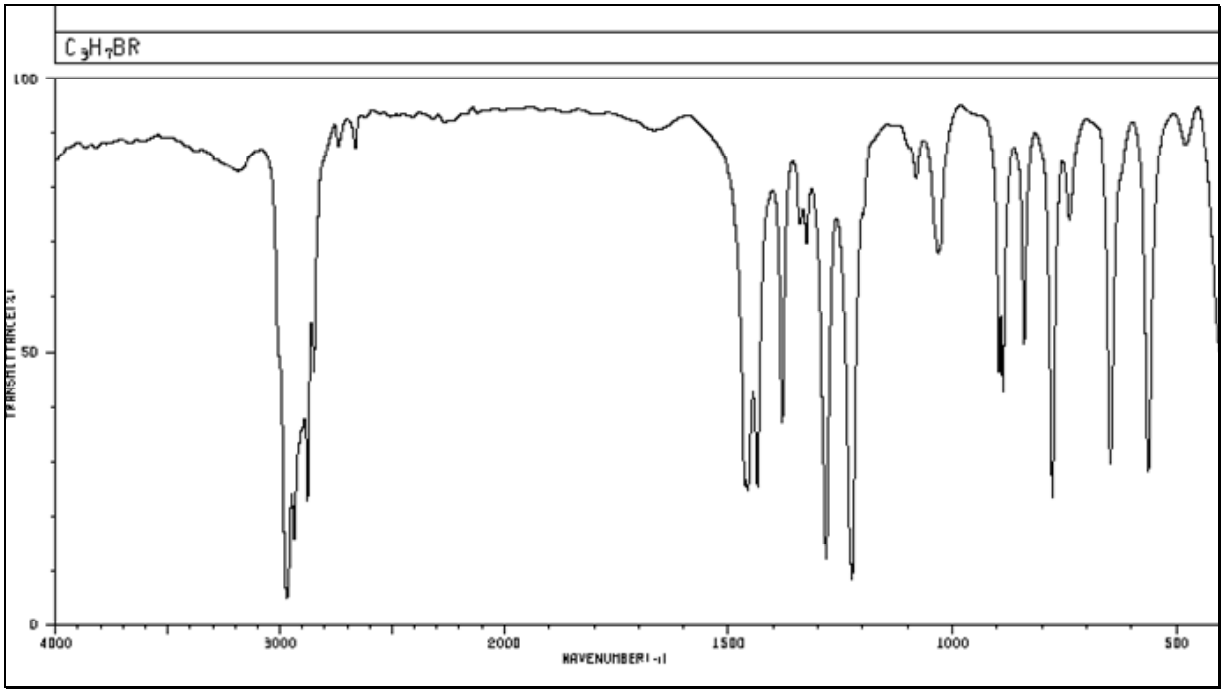


Unknown 19: MS

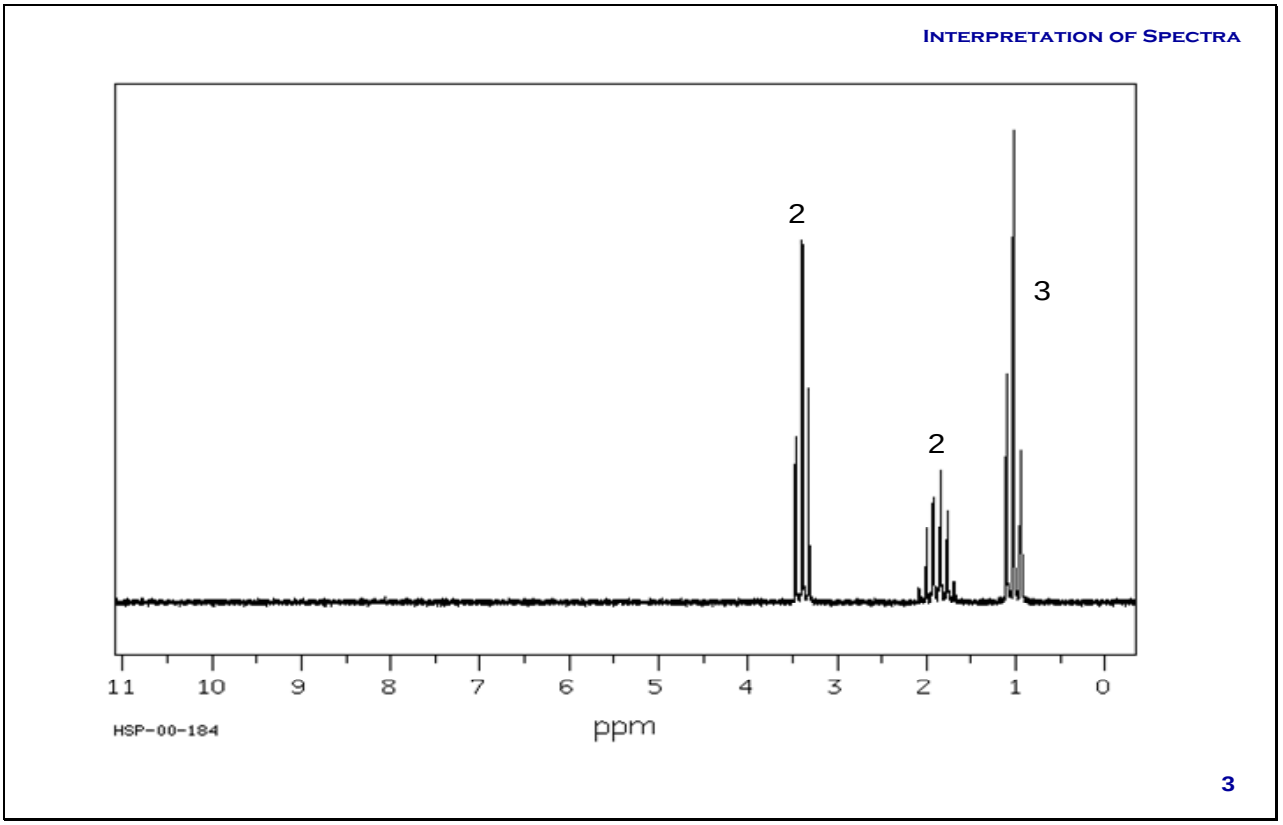
MF: C_3H_7Br



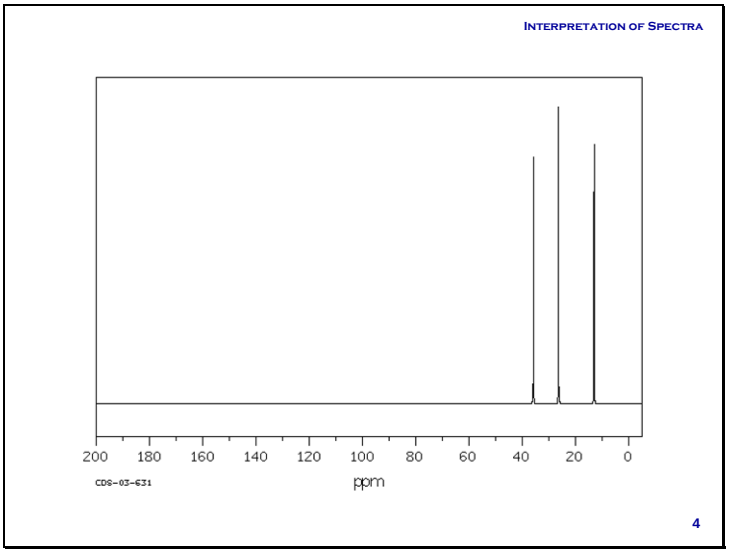
Unknown 19: IR



Unknown 19: NMR

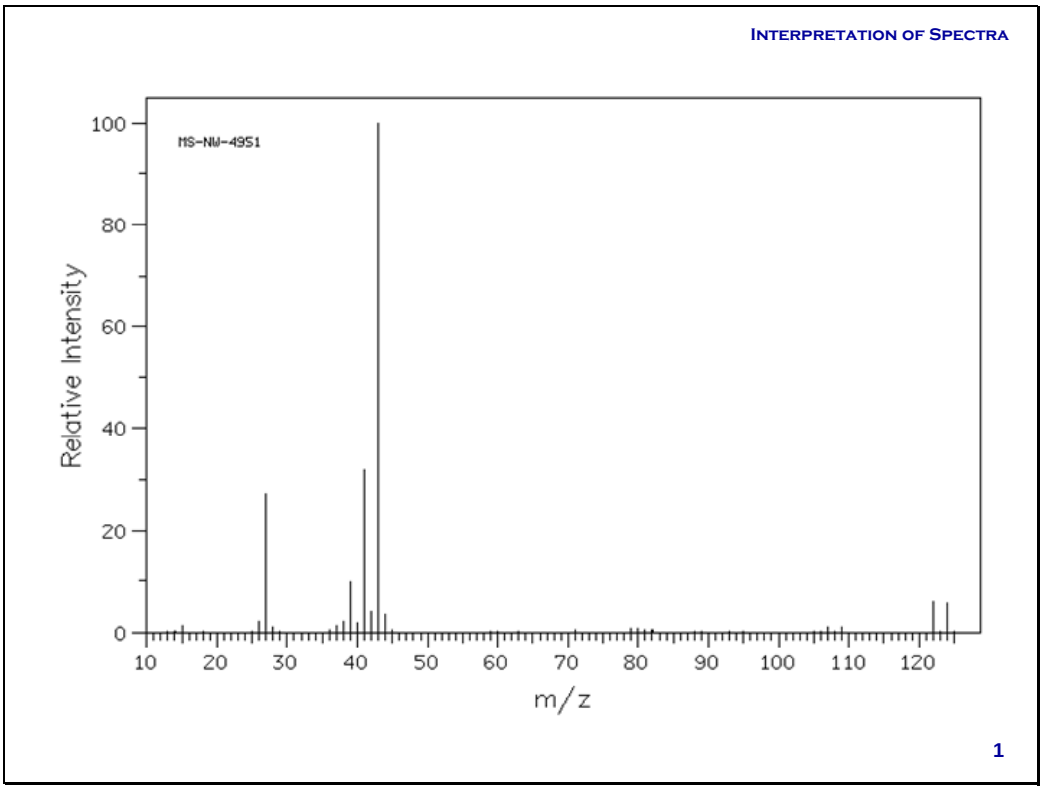


Unknown 19: CNMR



Unknown 20: MS

MF: C_3H_7Br



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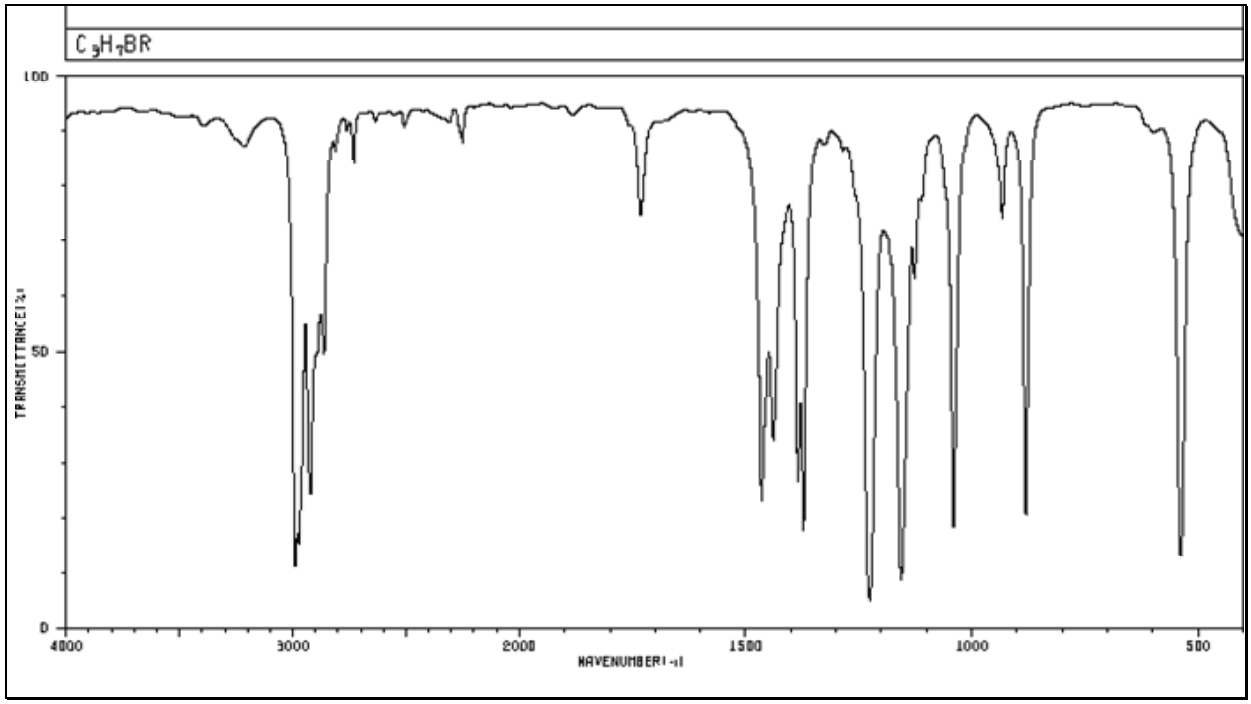
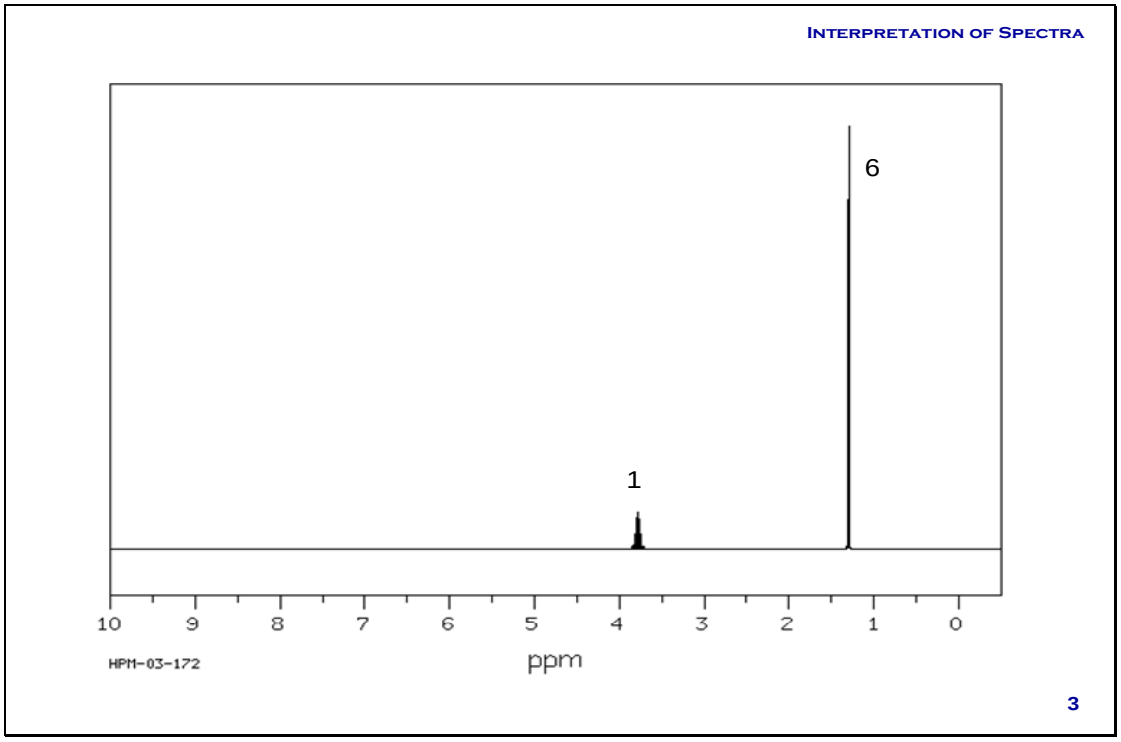
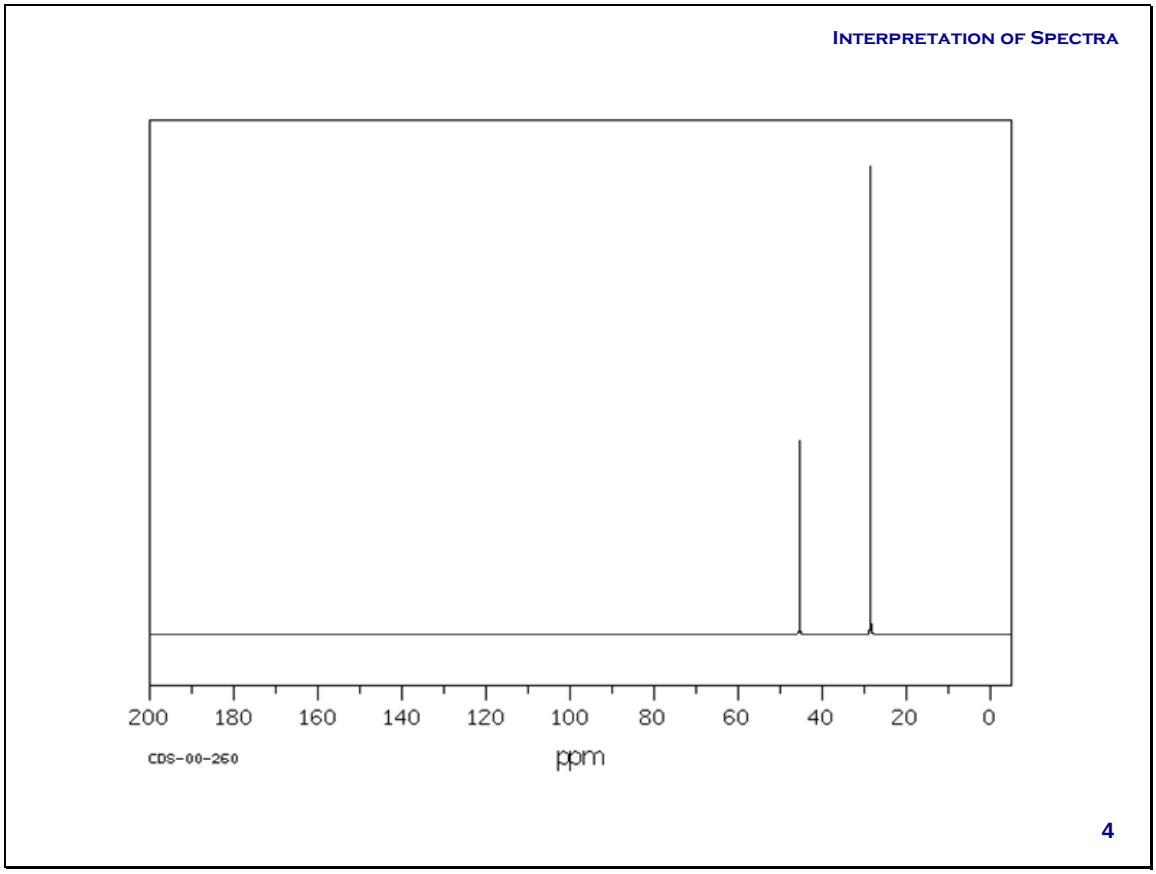


Unknown 20: NMR

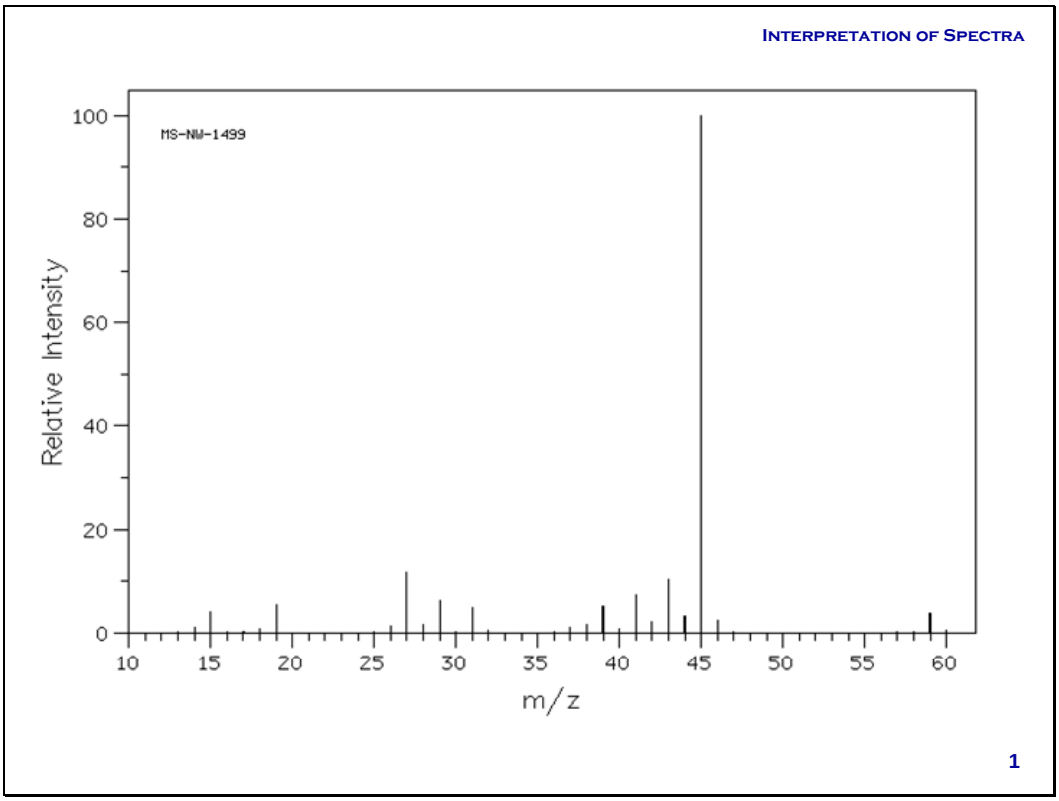


Unknown 20: CNMR



Unknown 21: MS

MF: C_3H_8O



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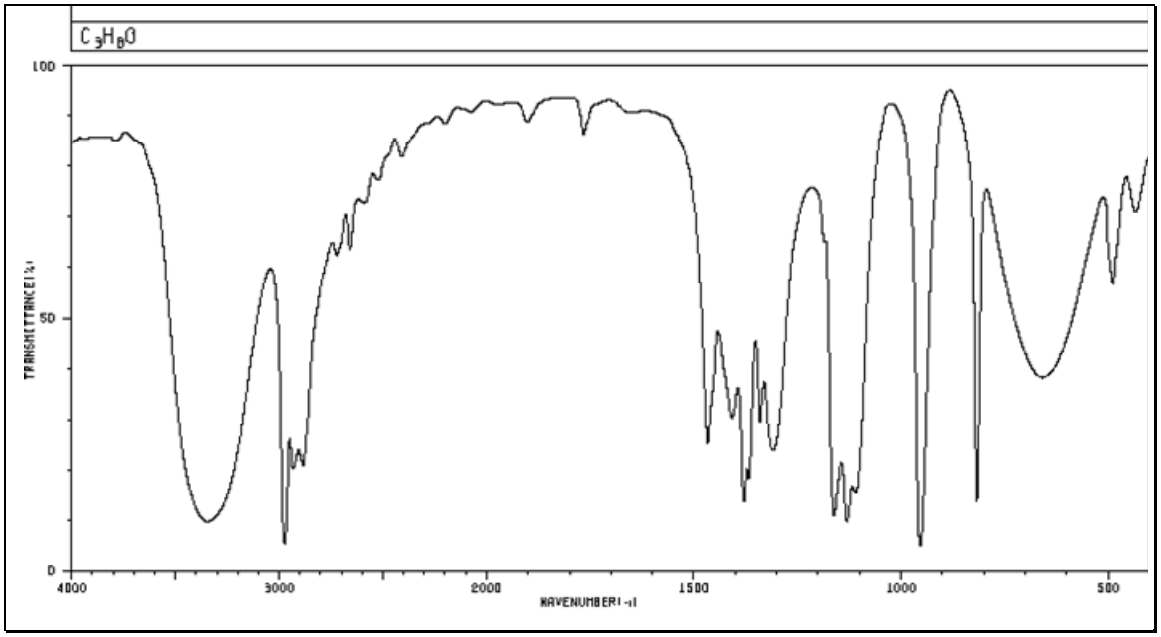
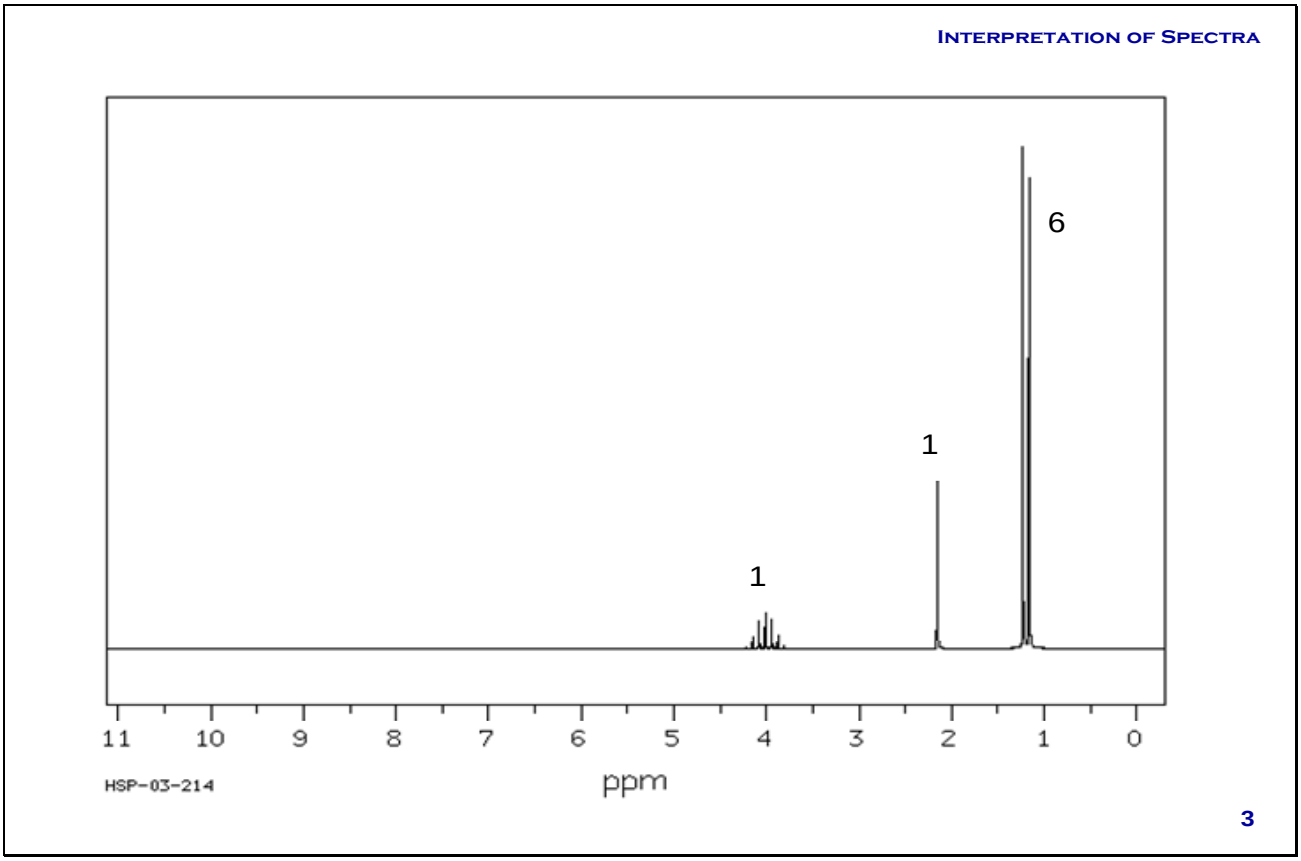
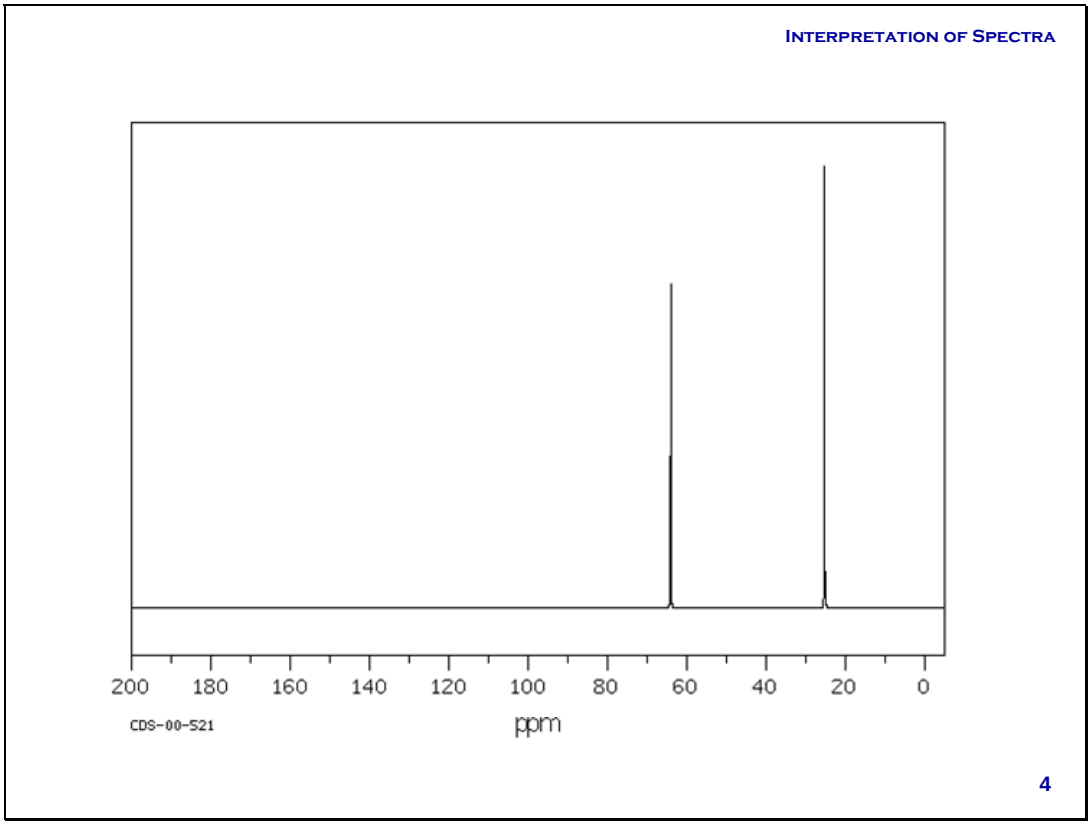


Unknown 21: NMR

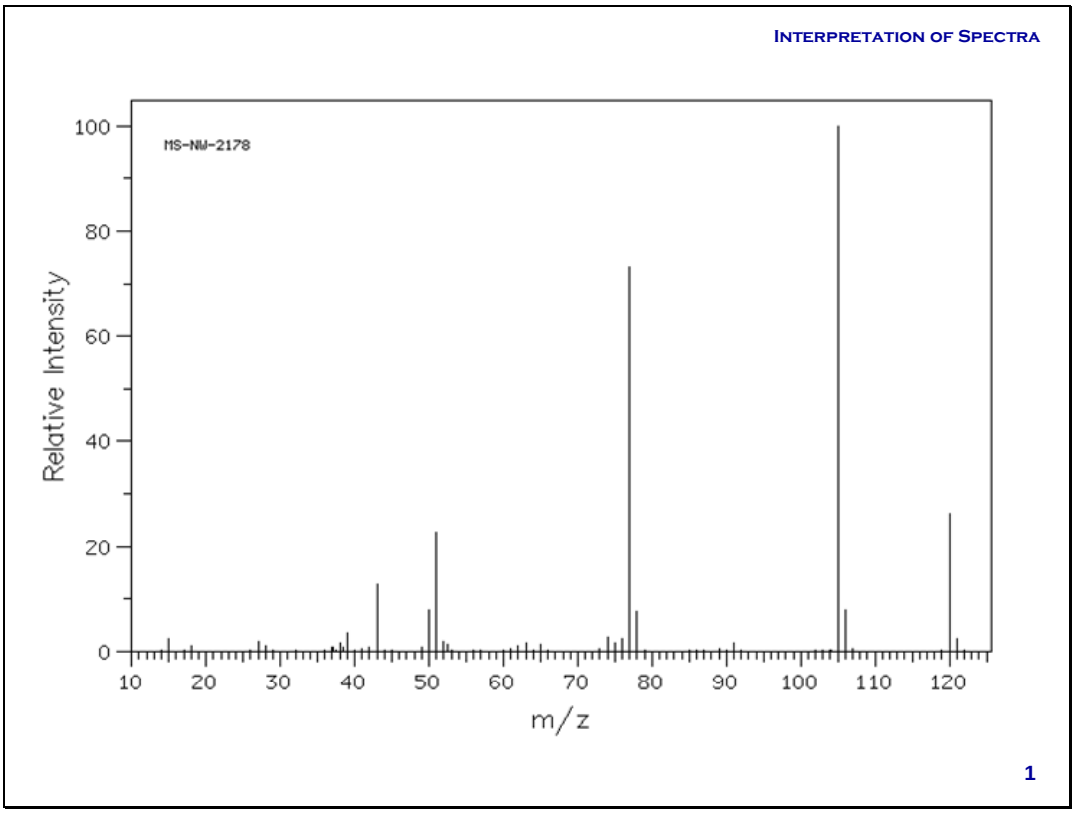


Unknown 21: CNMR

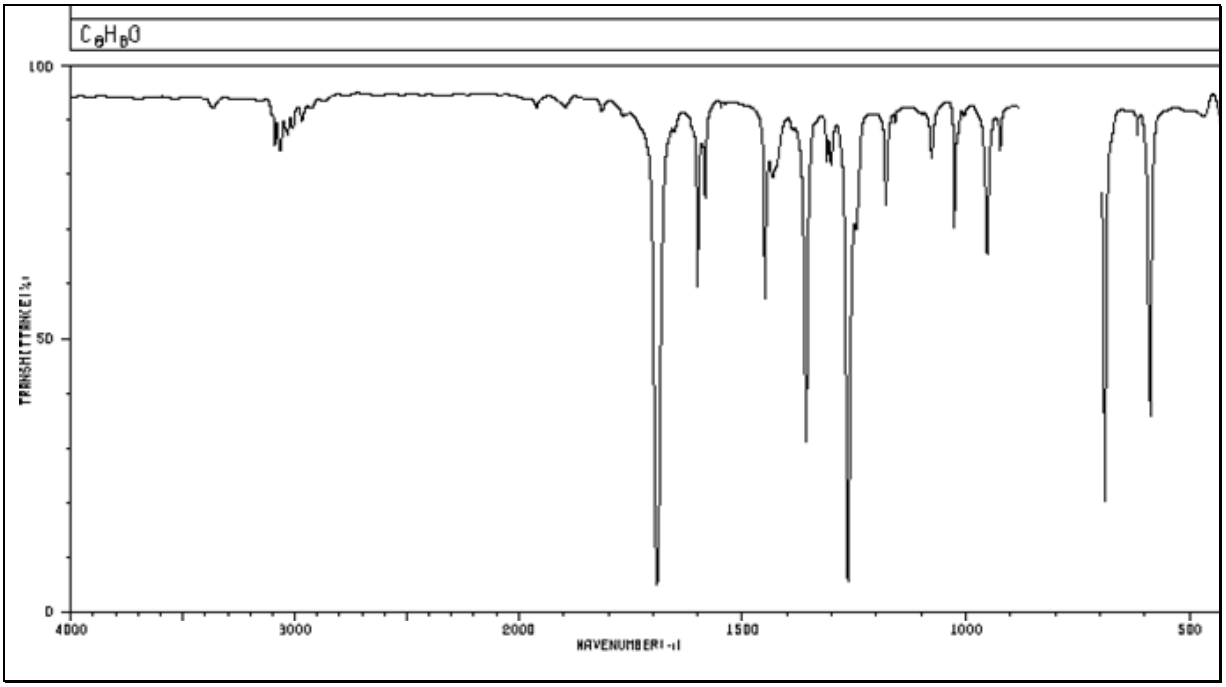


Unknown 22: MS

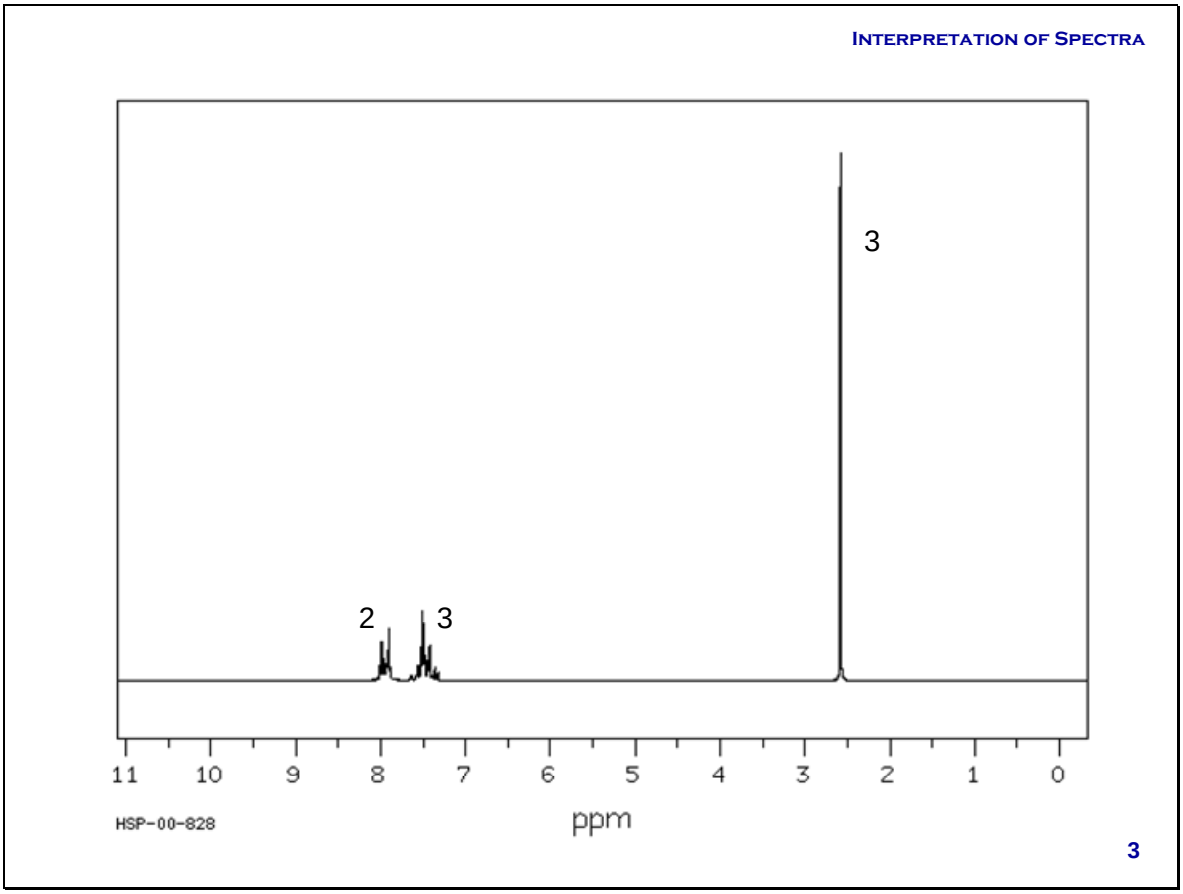
MF: C_8H_8O



Unknown 22: IR



Unknown 22: NMR



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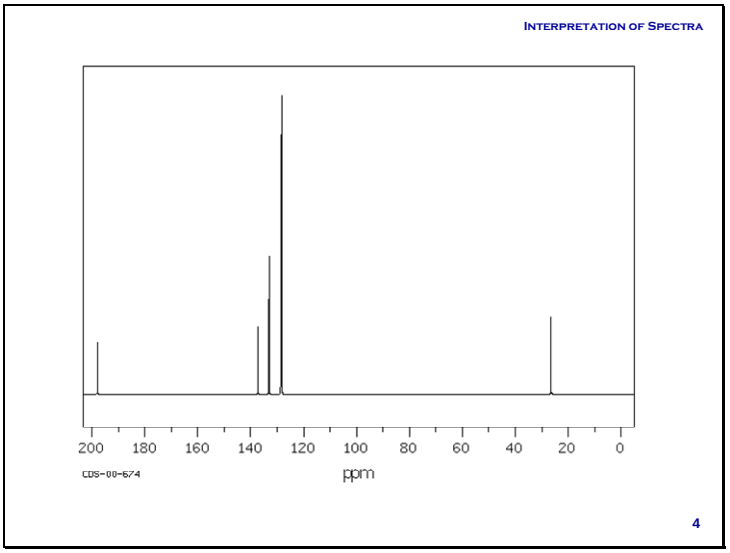
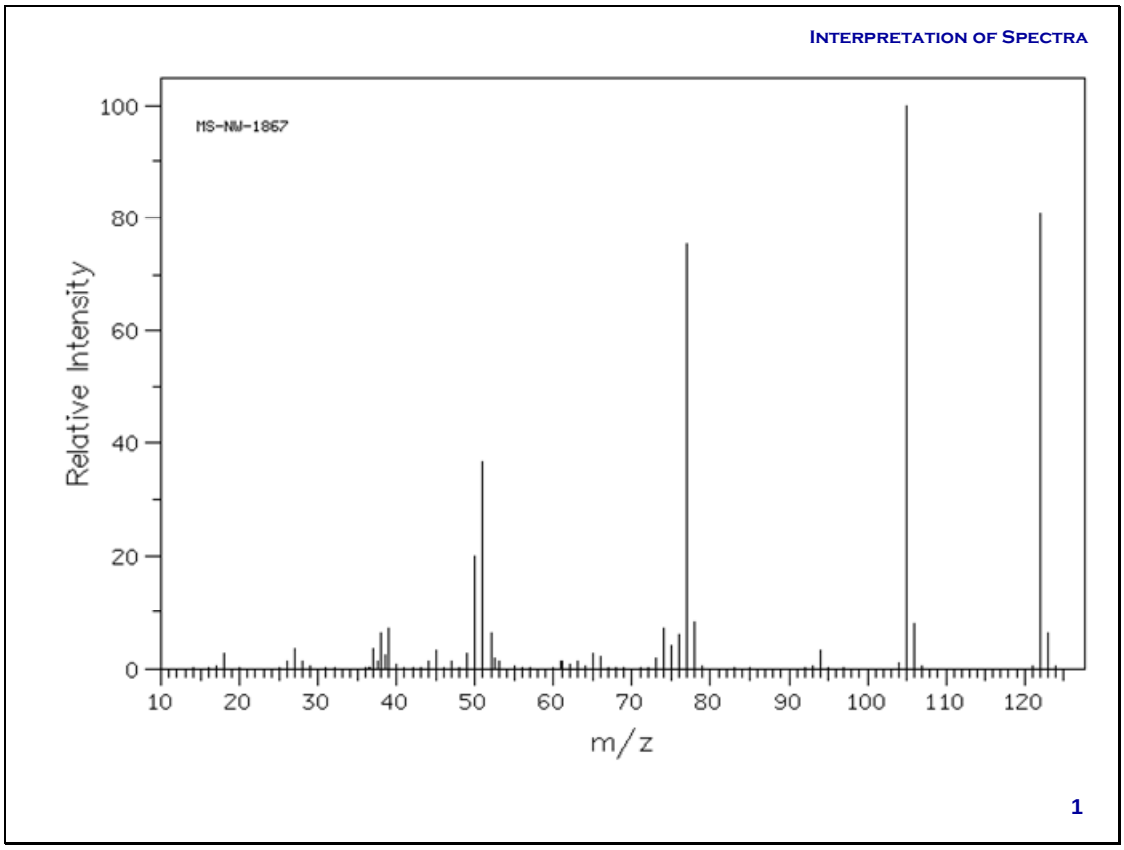


Unknown 23: MS

MF: $C_7H_8O_2$



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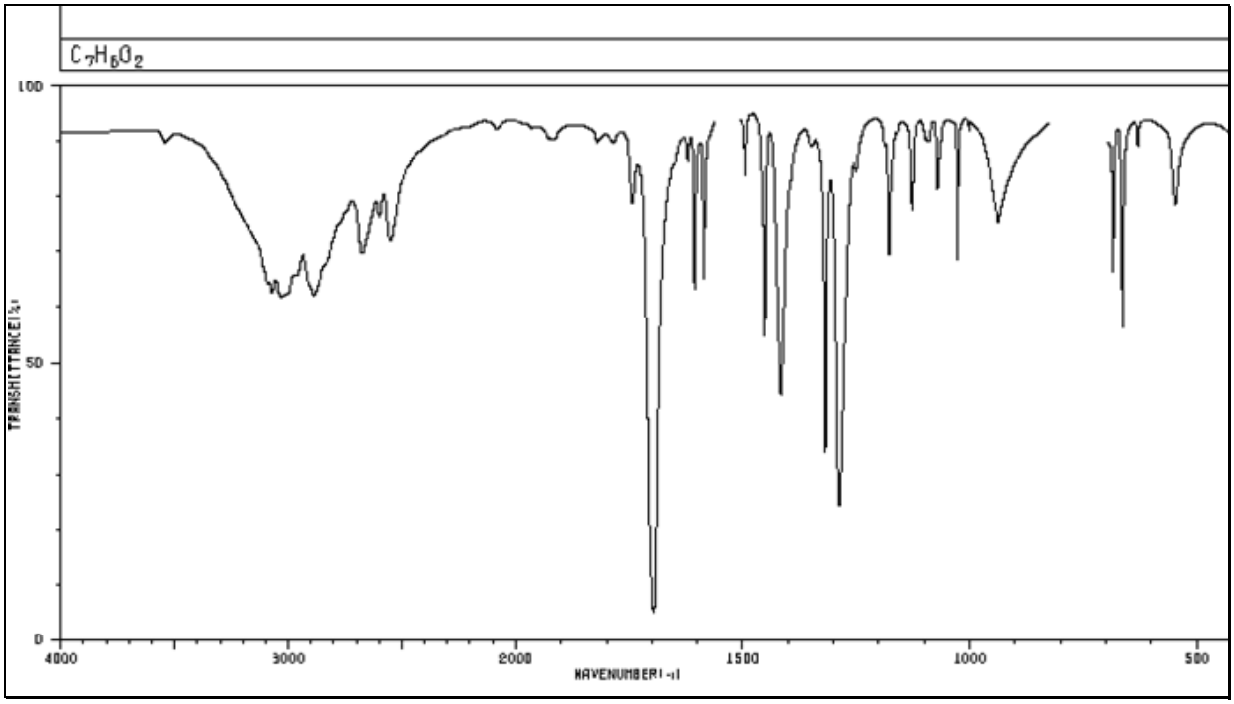
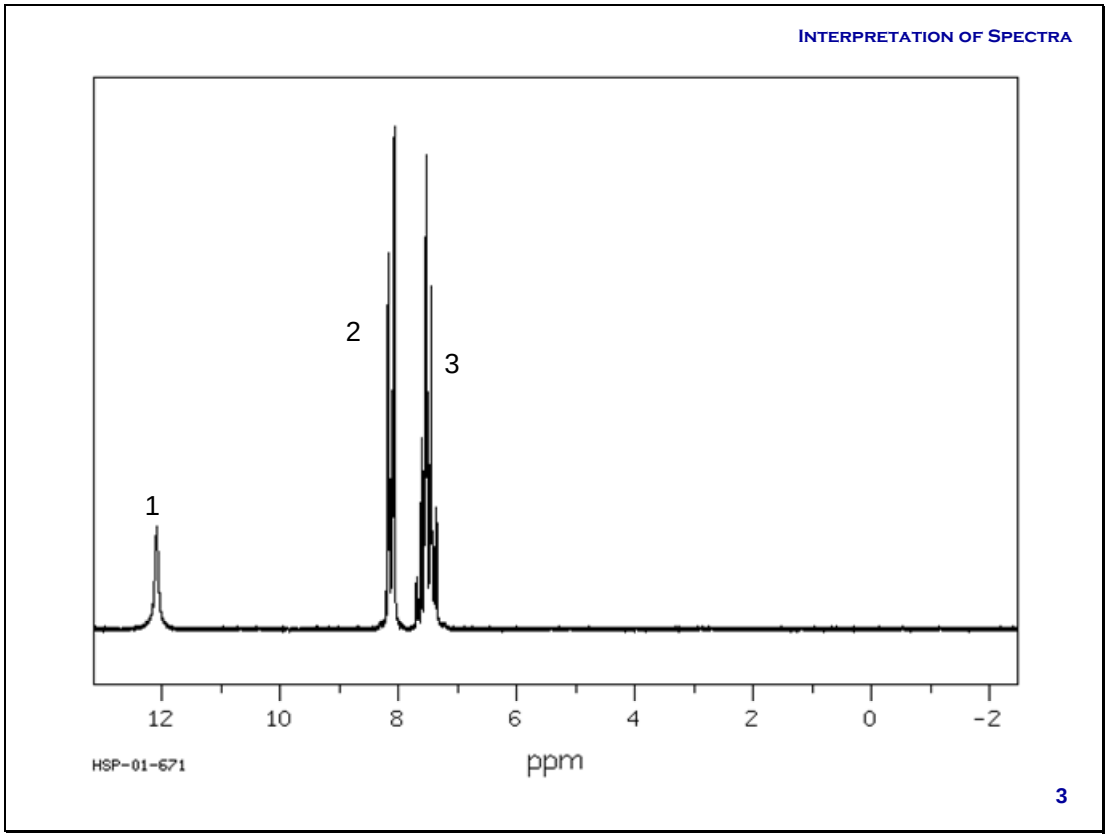
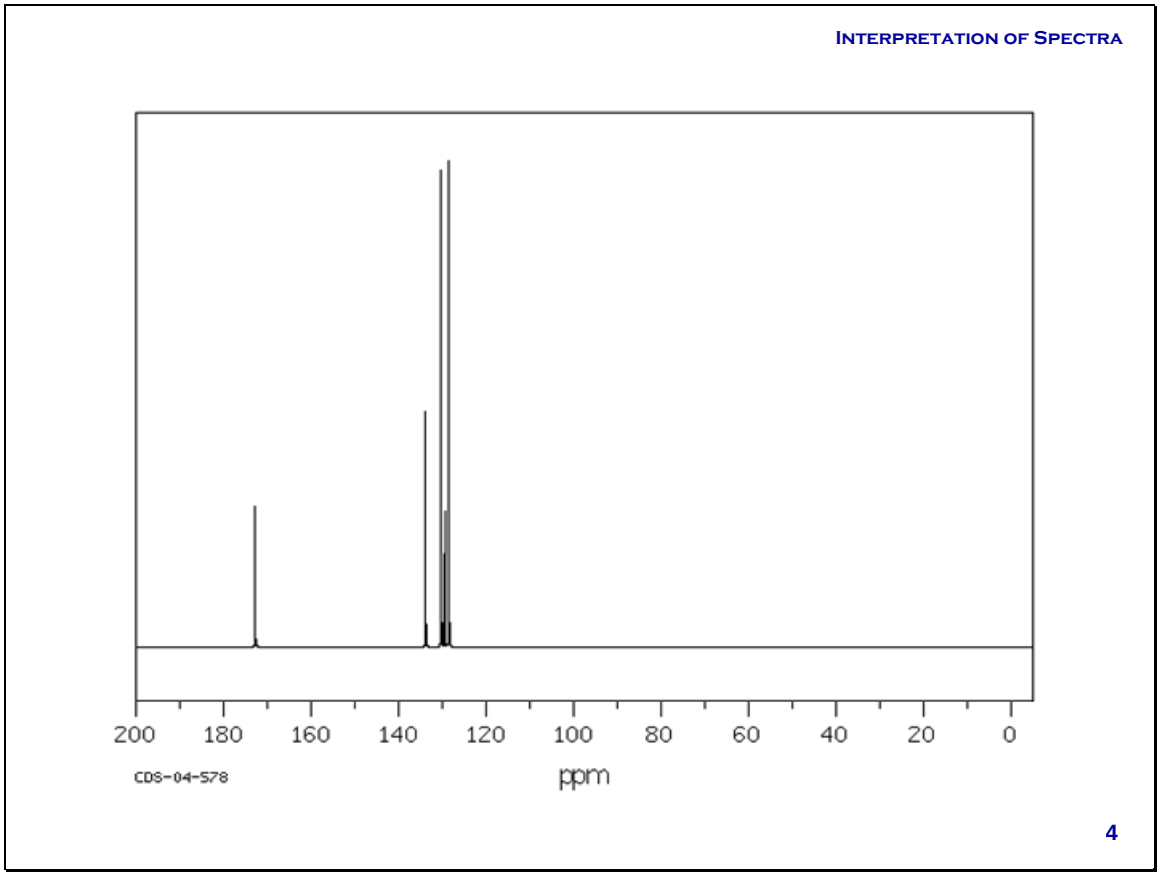


Unknown 23: NMR

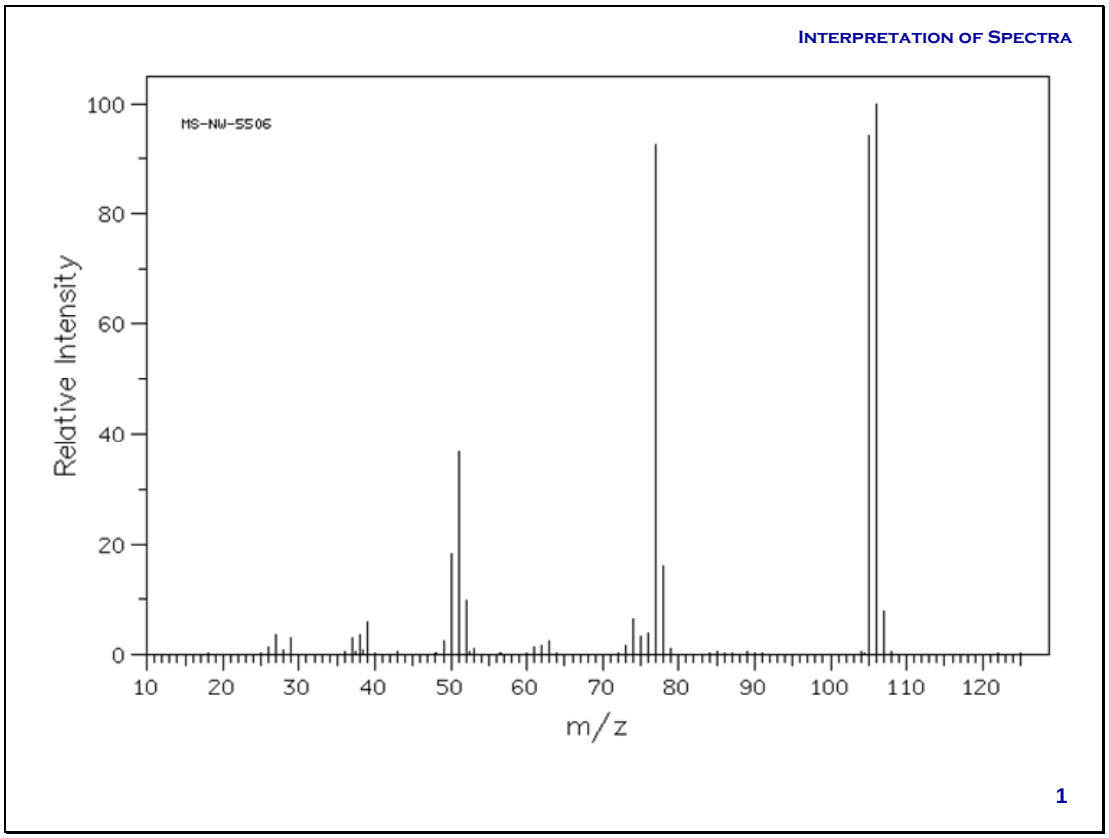


Unknown 23: CNMR



Unknown 24: MS

MF: C_7H_6O



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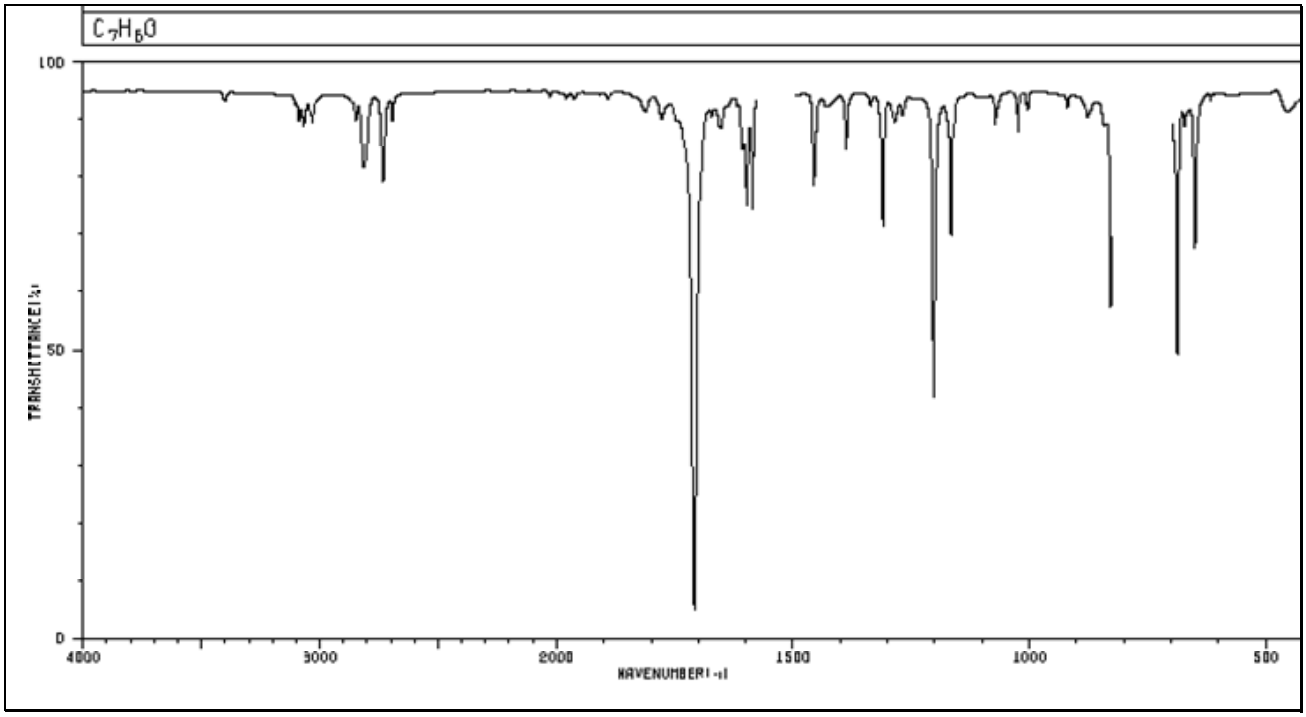
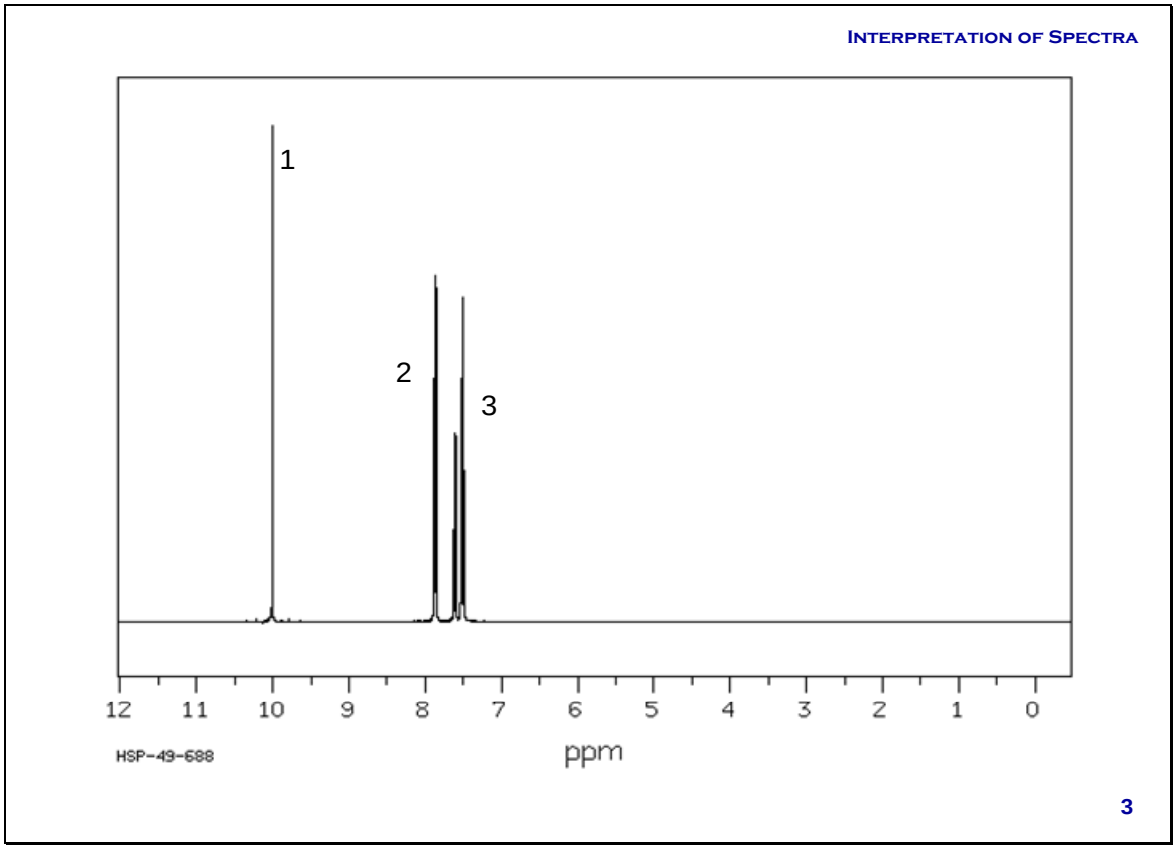
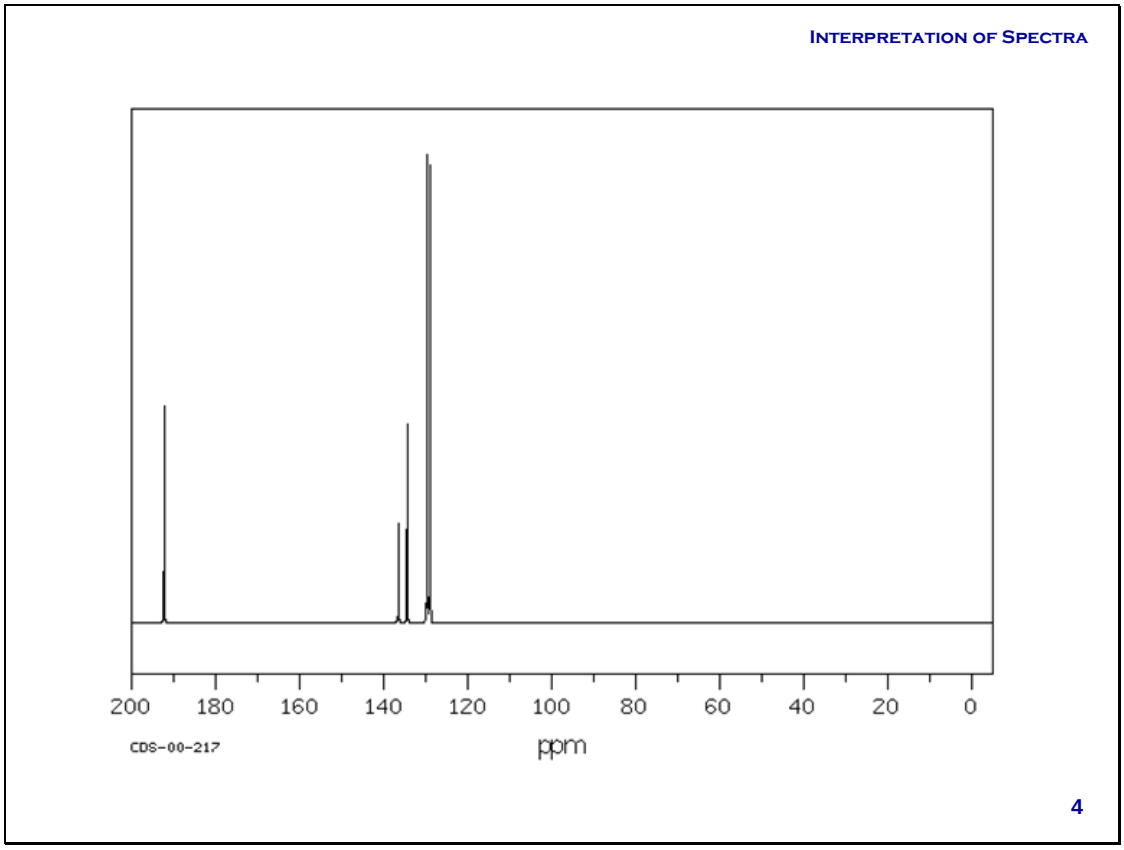


Unknown 24: NMR

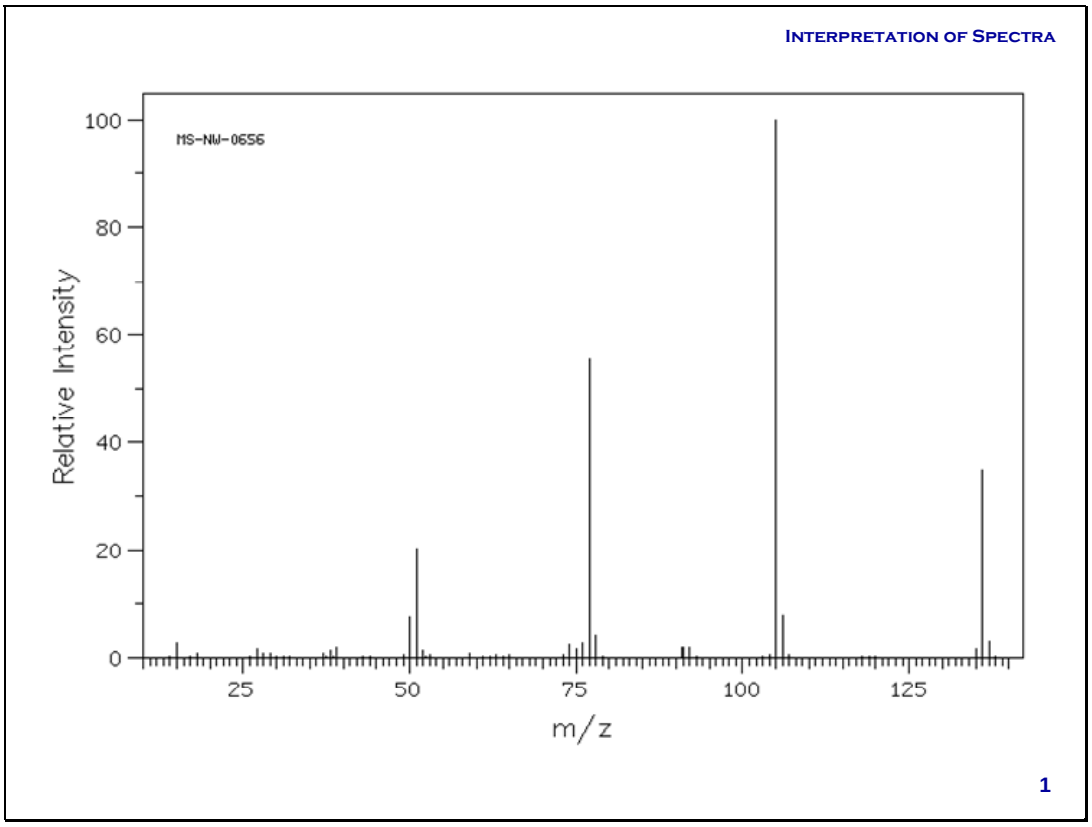


Unknown 24: CNMR



Unknown 25: MS

MF: $C_8H_8O_2$



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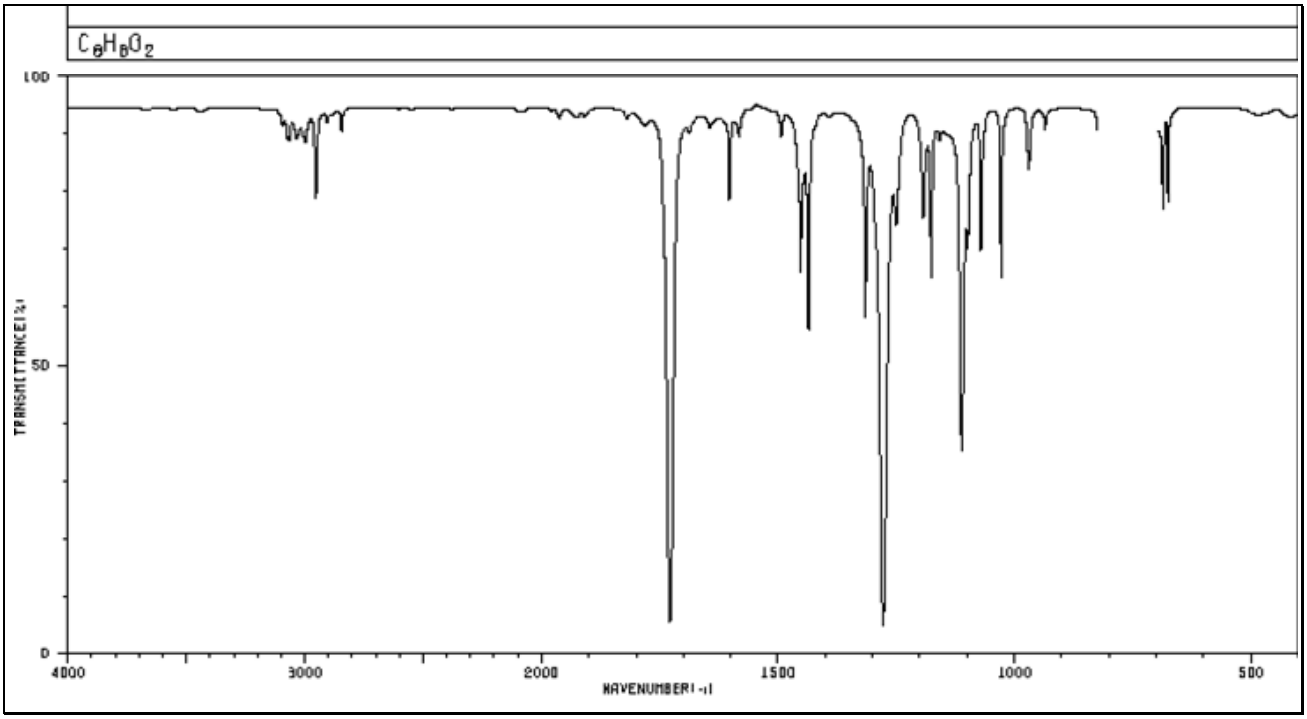
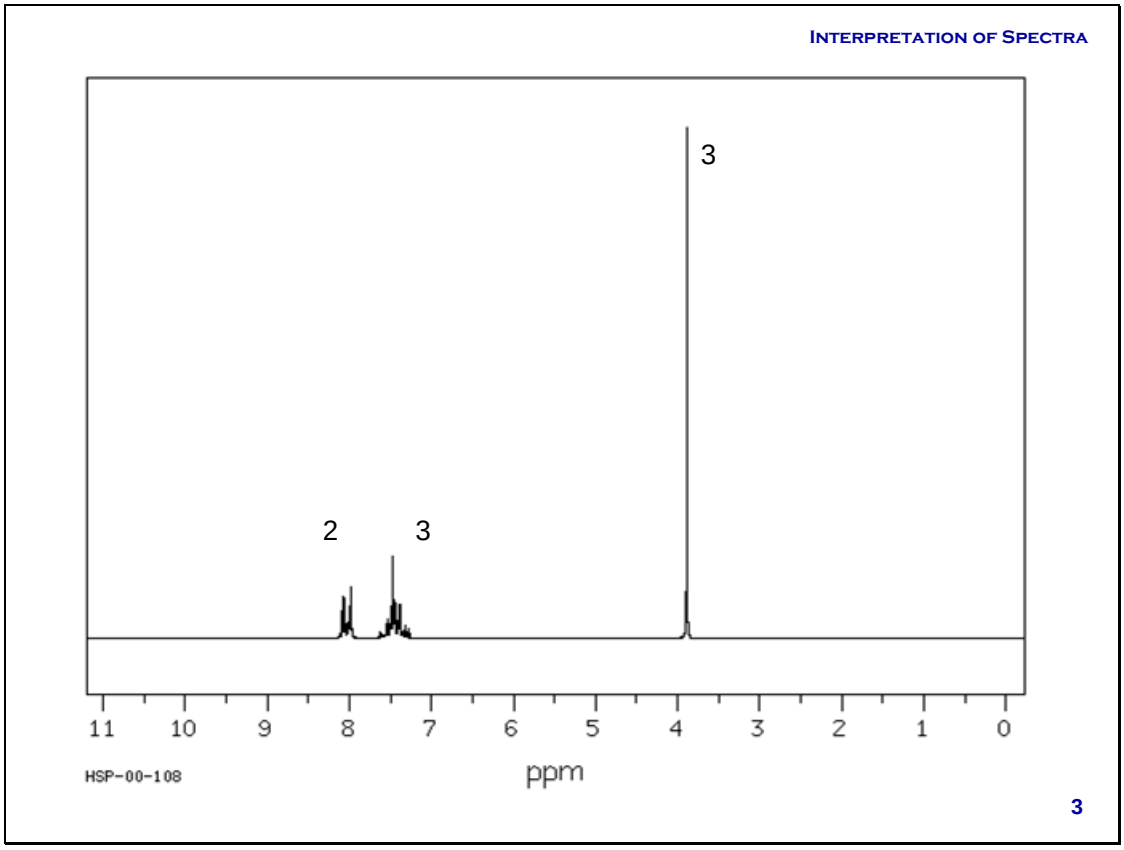
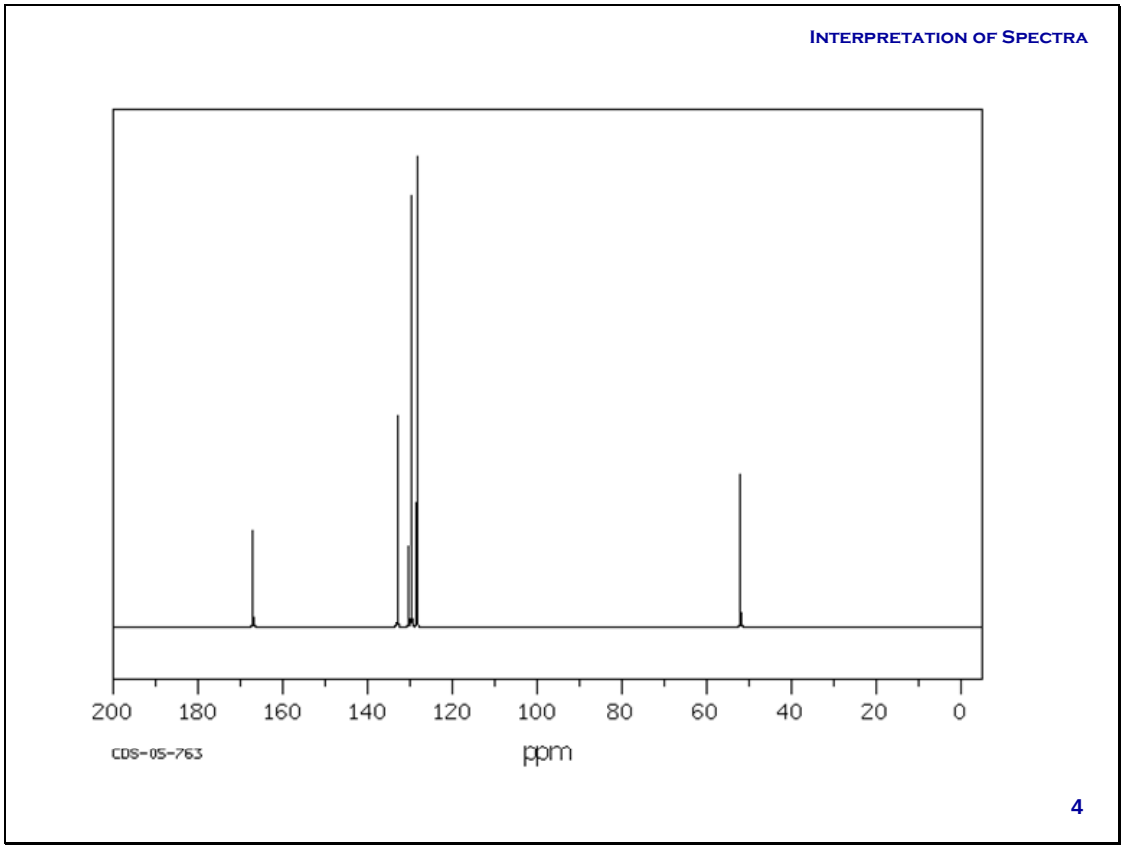


Unknown 25: NMR

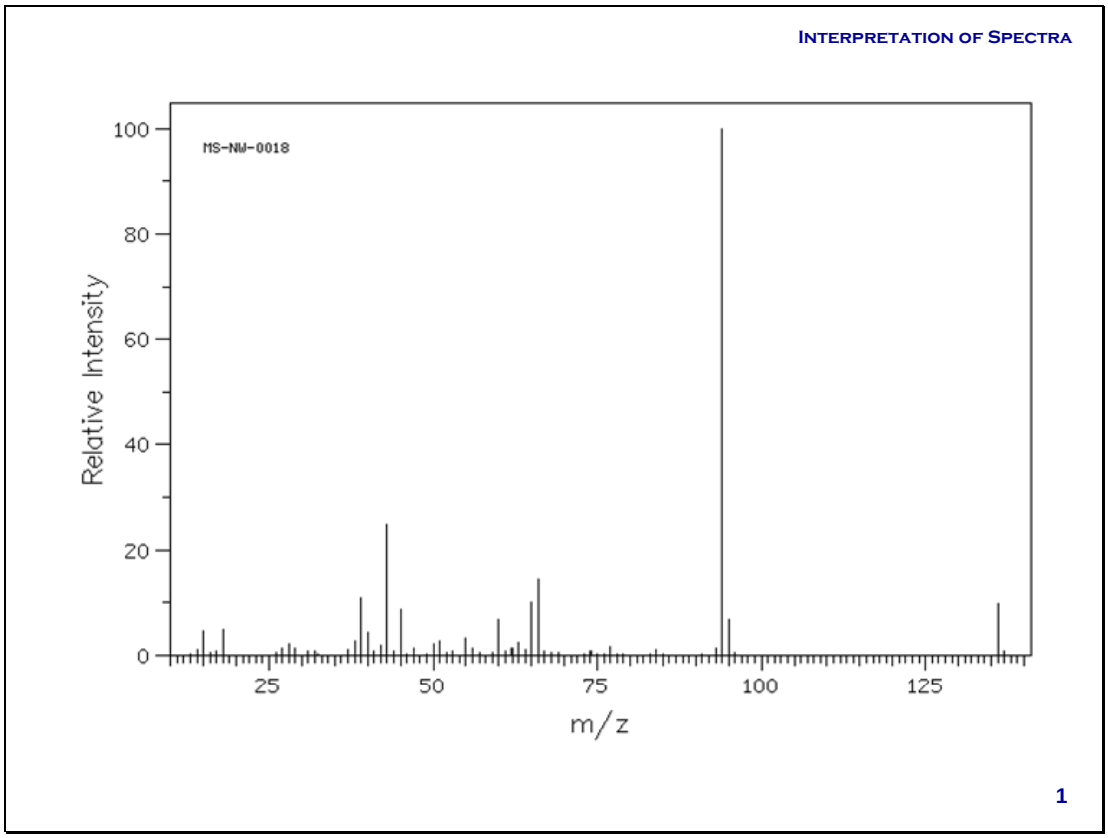


Unknown 25: CNMR

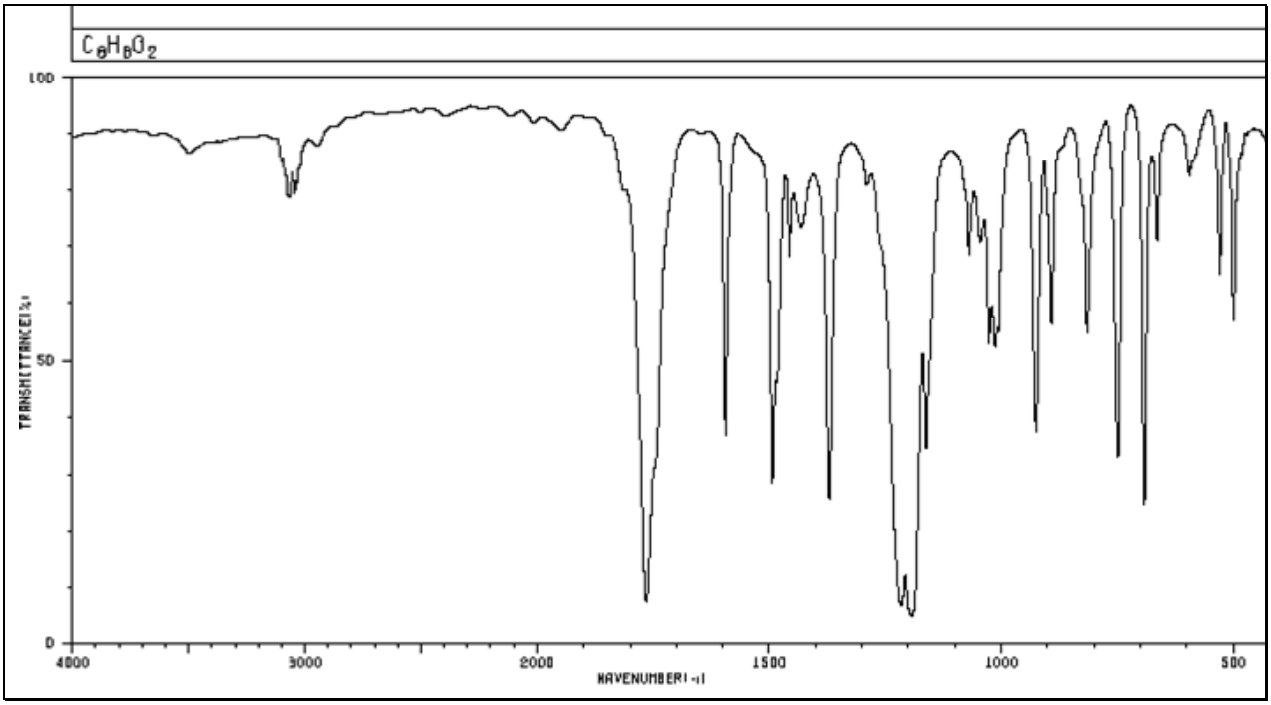


Unknown 26: MS

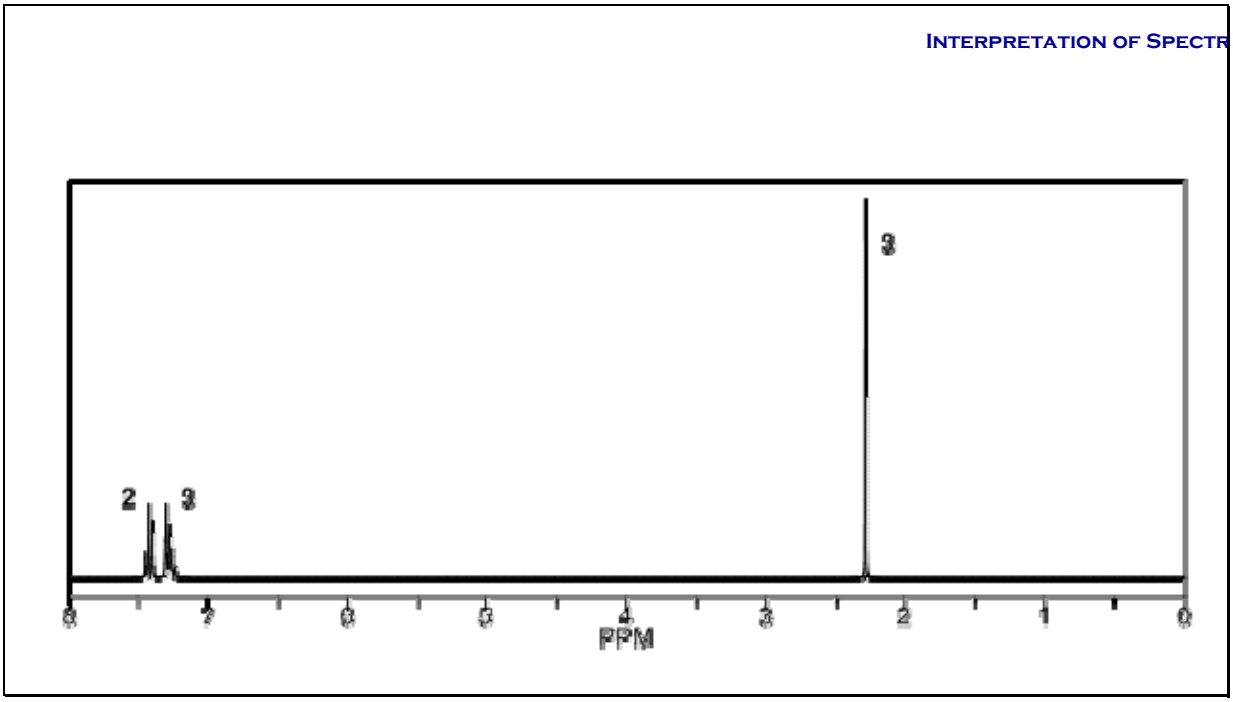
MF: $C_8H_8O_2$



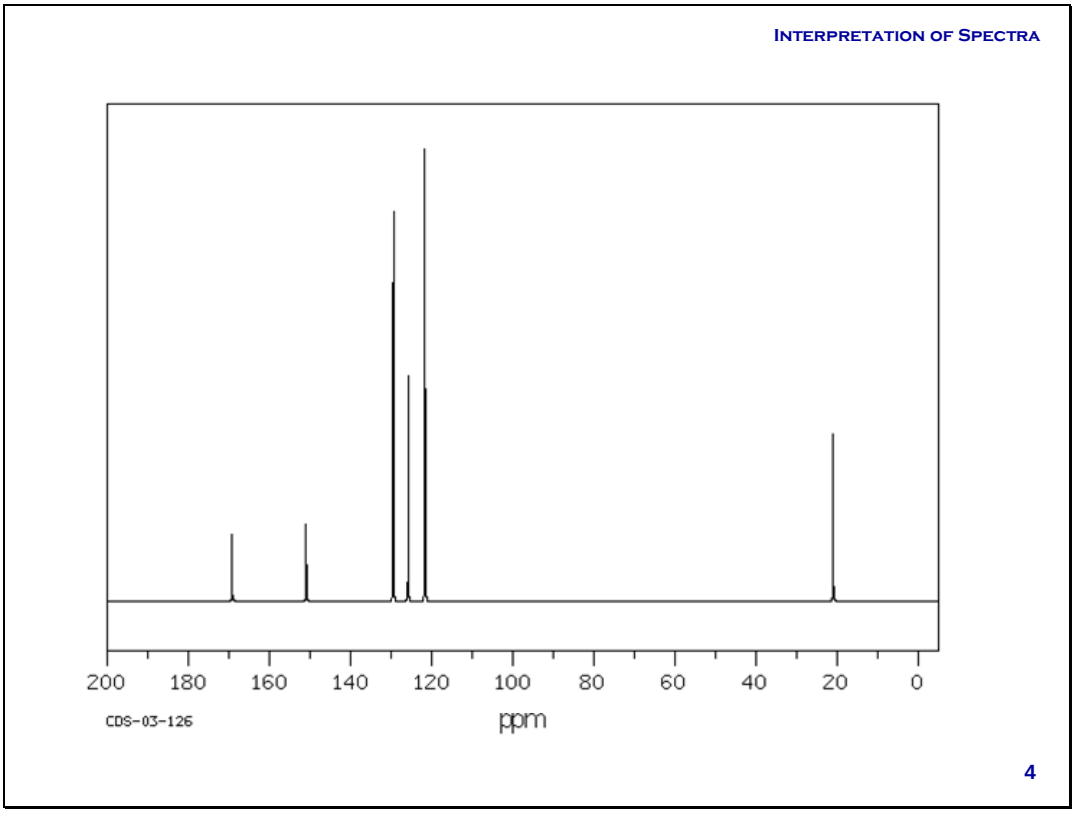
Unknown 26: IR



Unknown 26: NMR

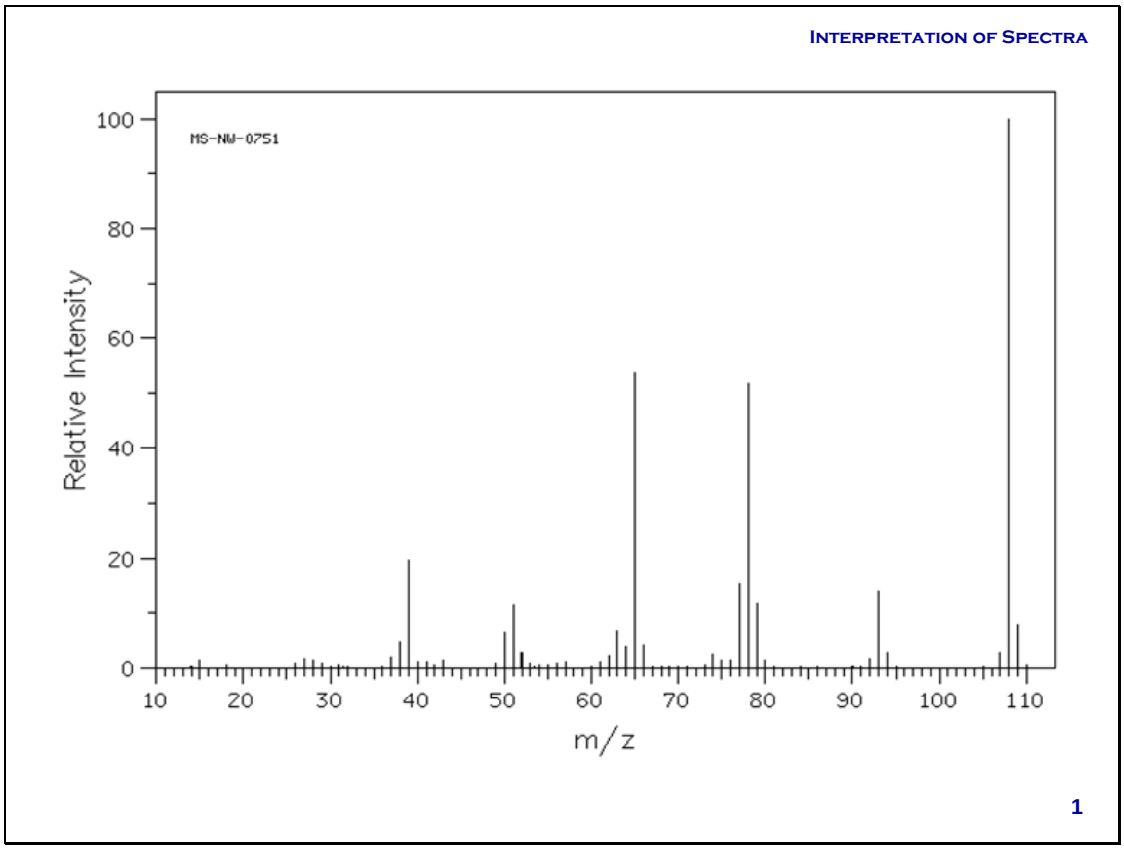


Unknown 26: CNMR



Unknown 27: MS

MF: C_7H_8O



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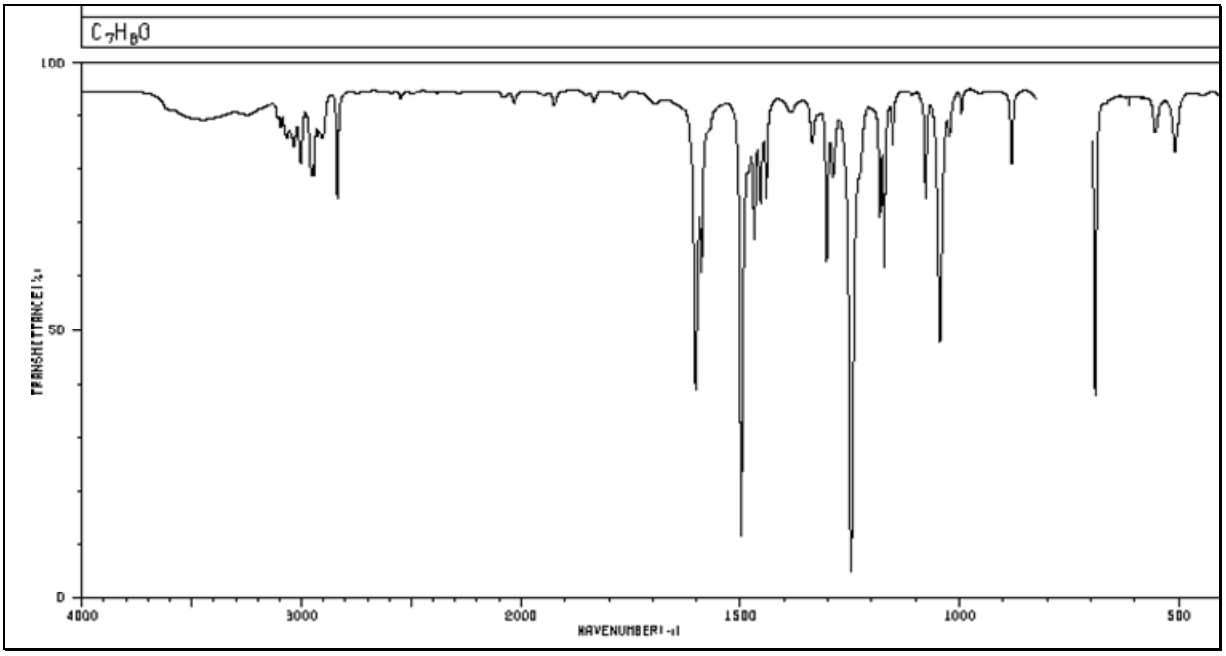
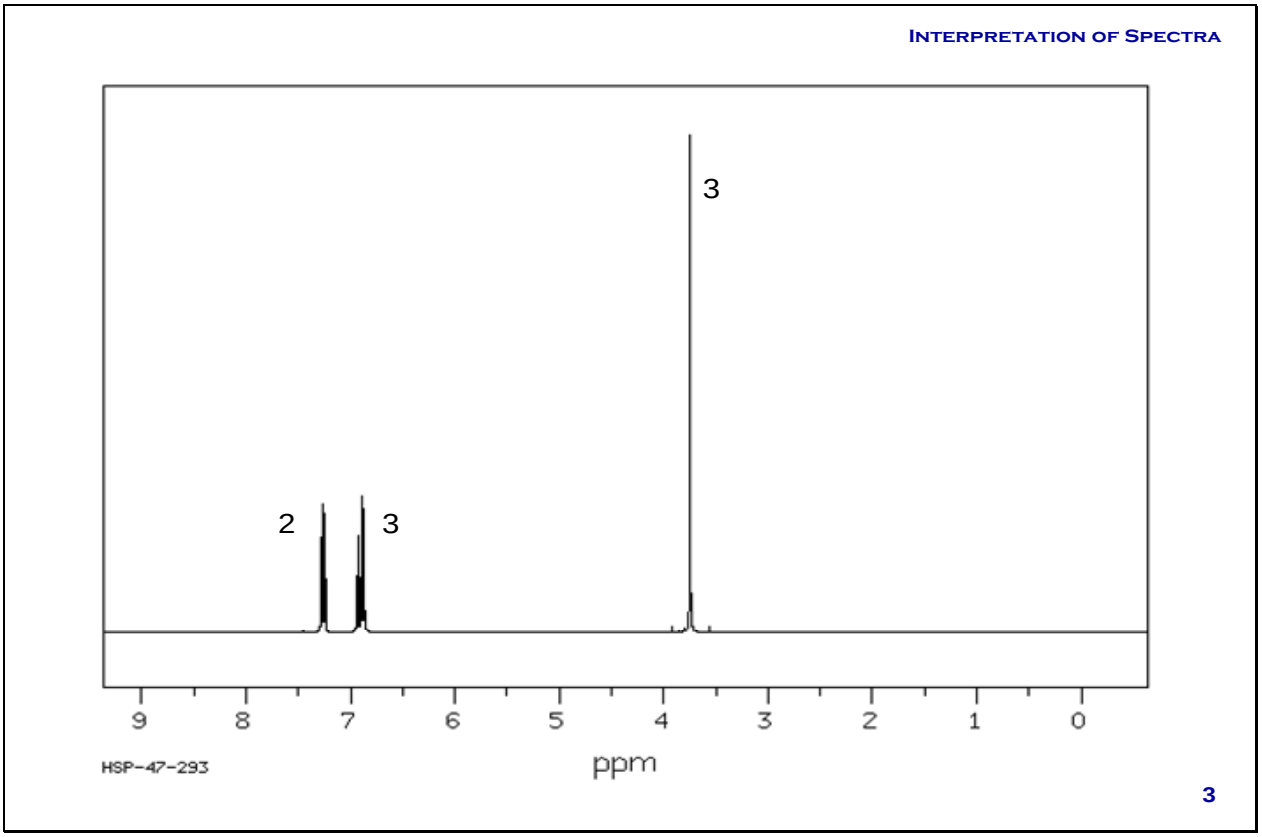
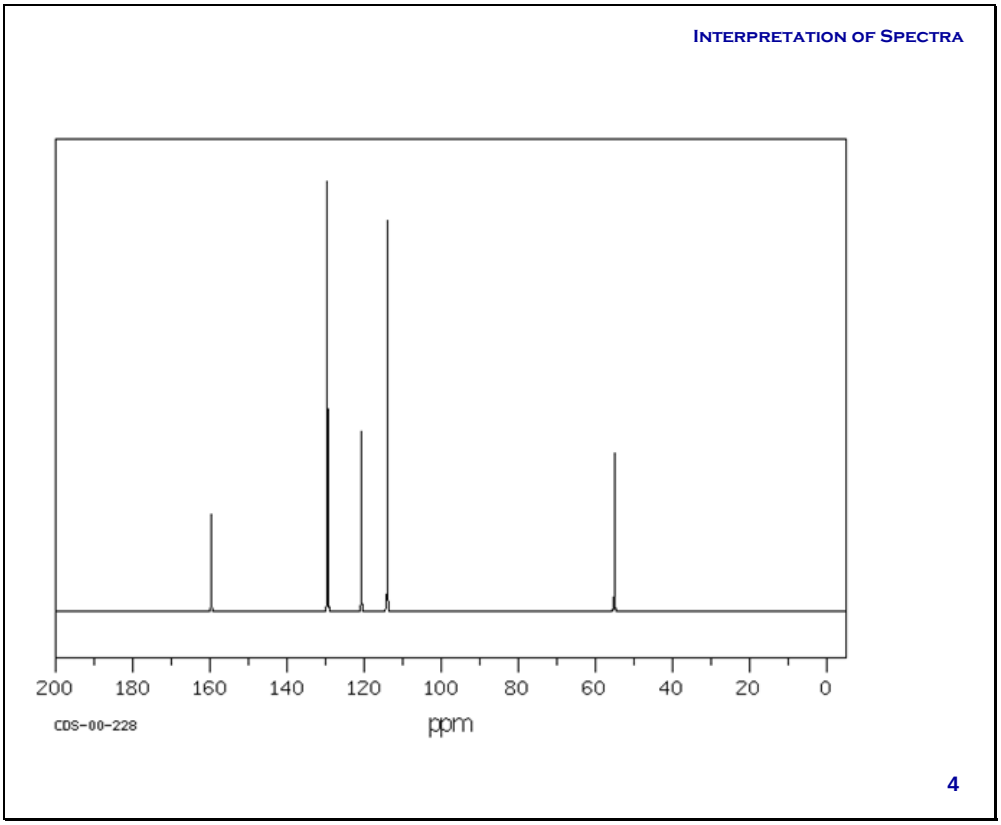


Unknown 27: NMR

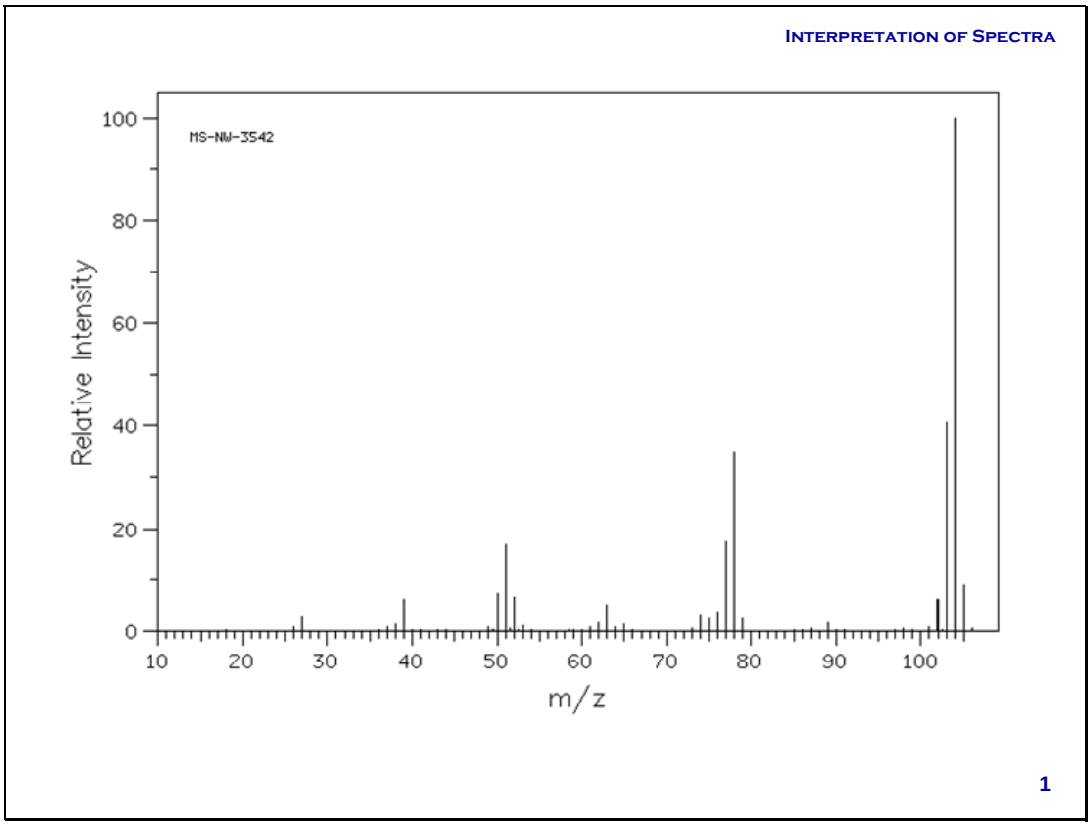


Unknown 27: CNMR

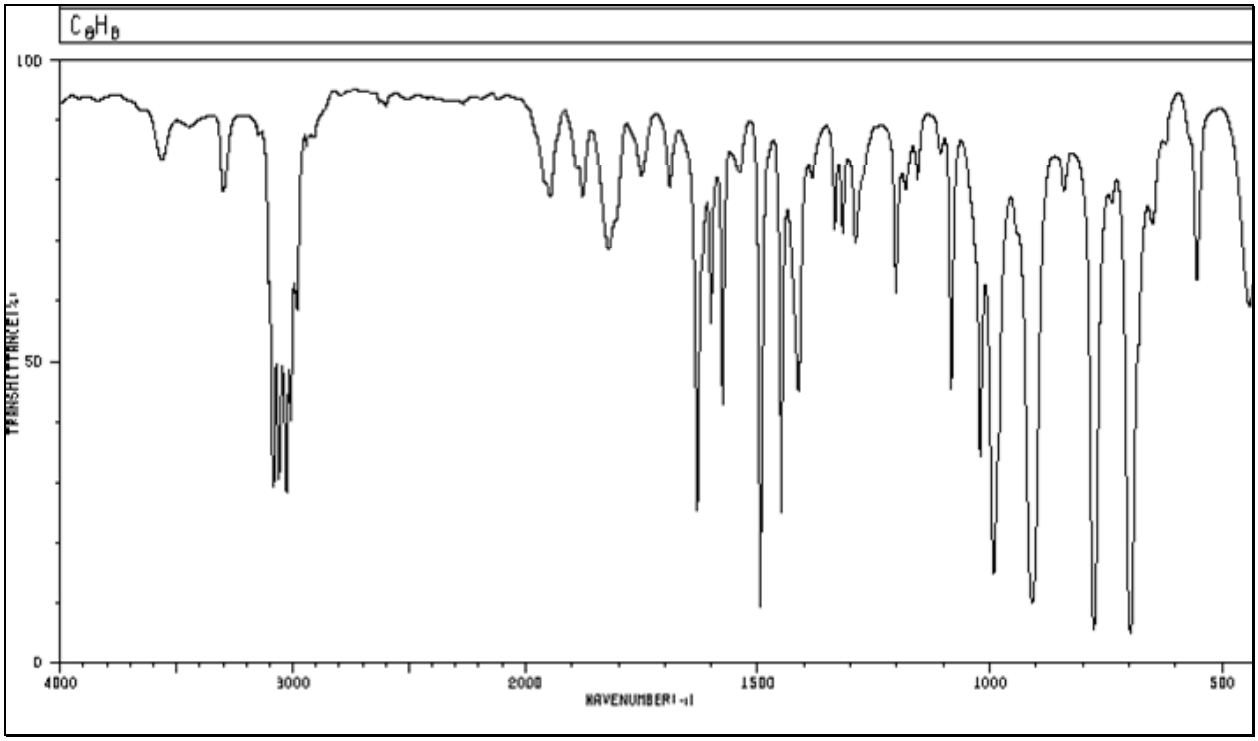


Unknown 28: MS

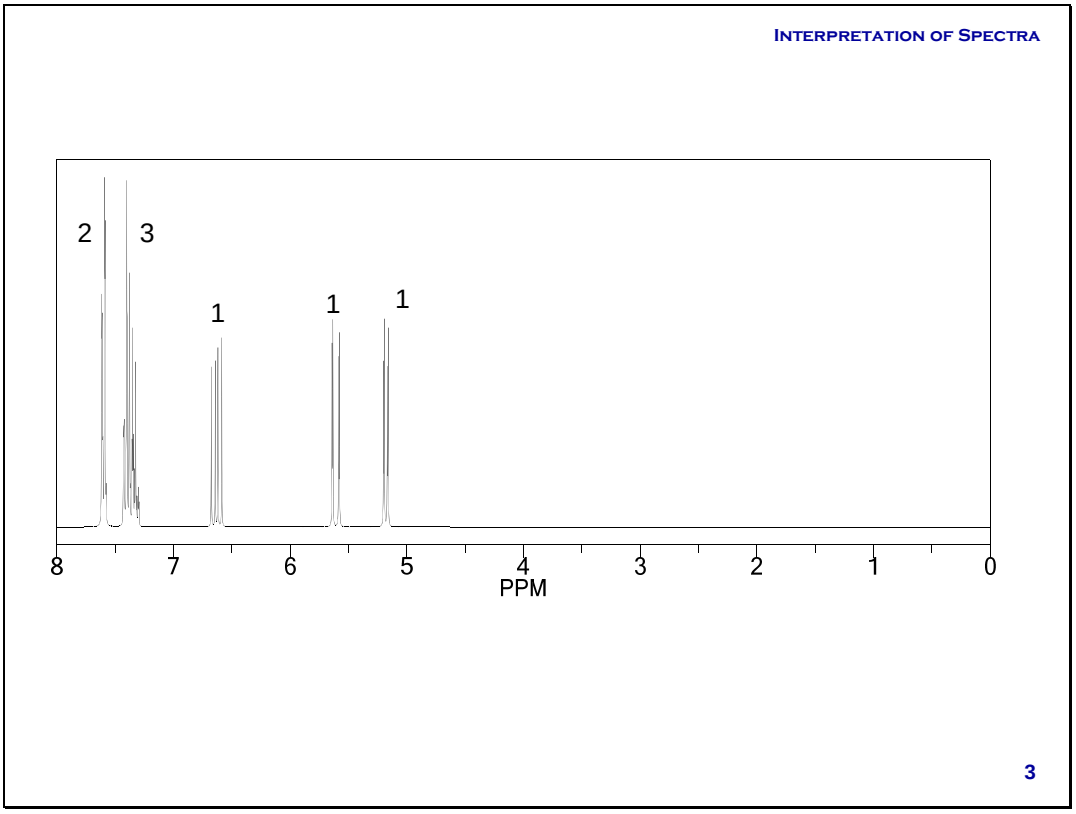
MF: C_8H_8



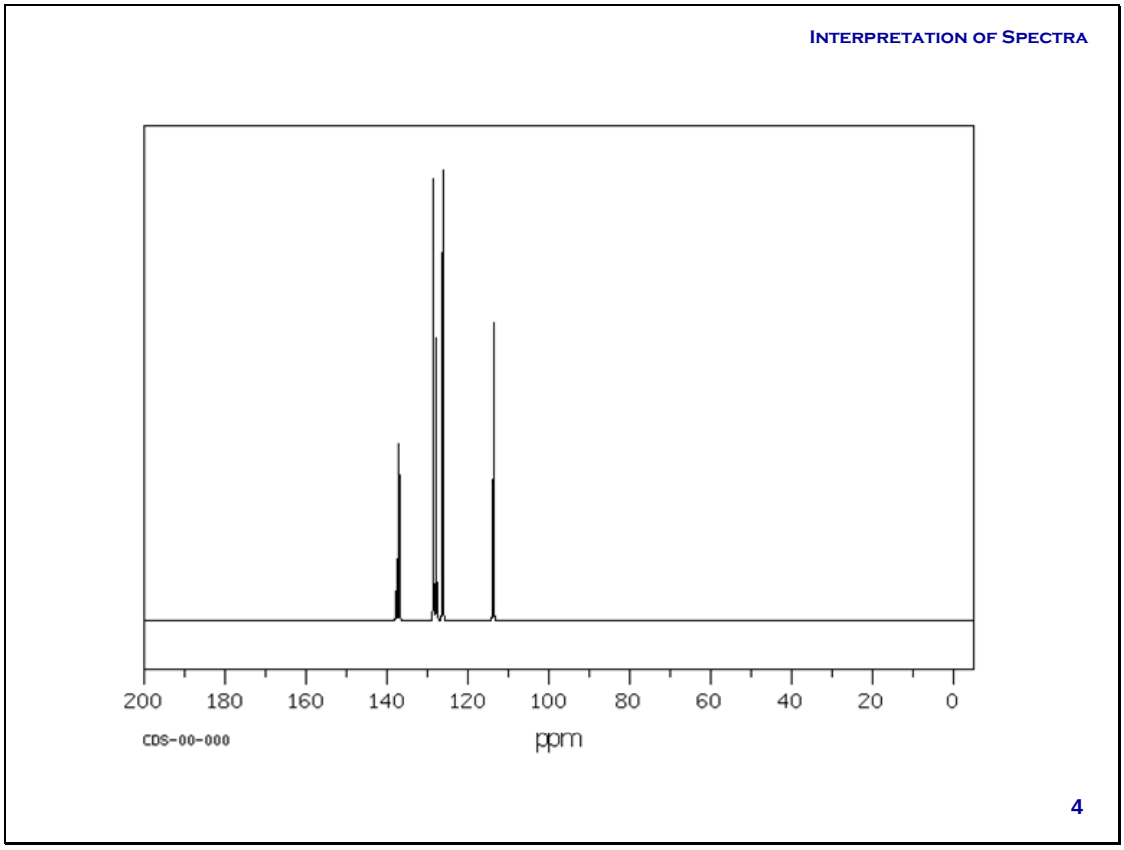
Unknown 28: IR



Unknown 28: NMR

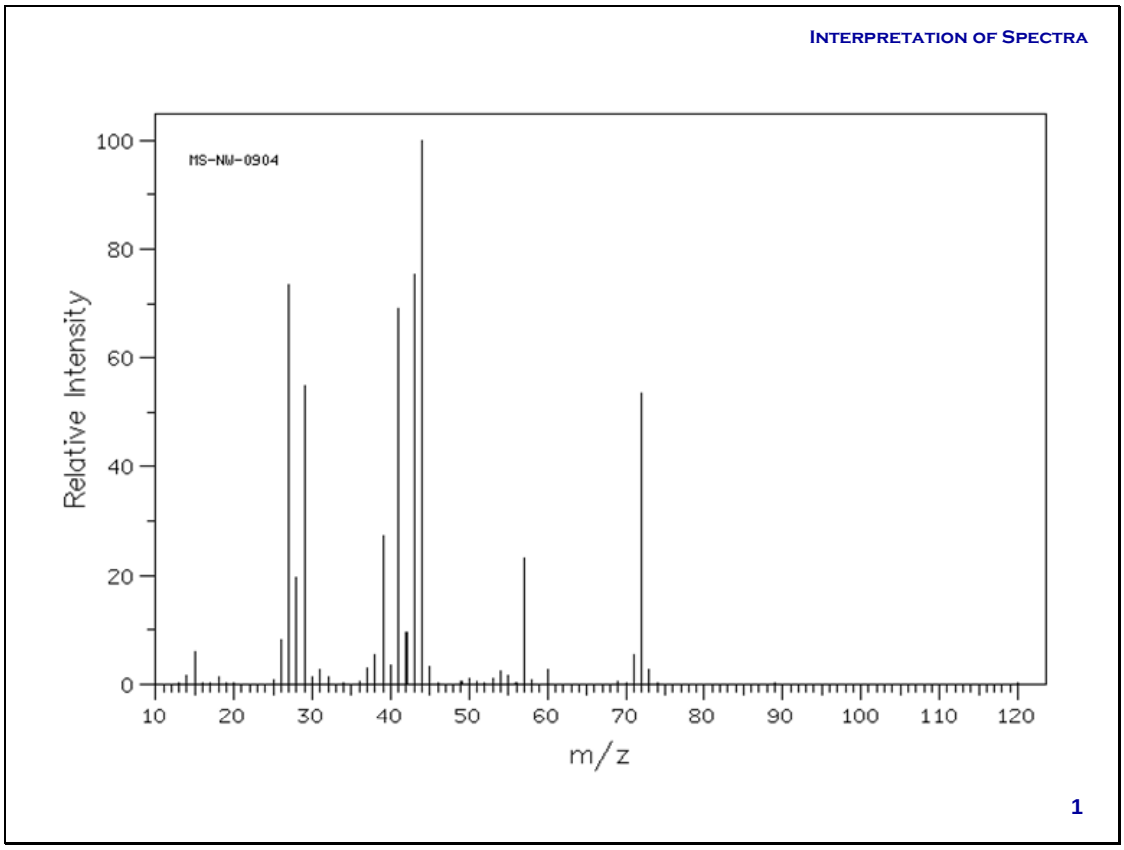


Unknown 28: CNMR

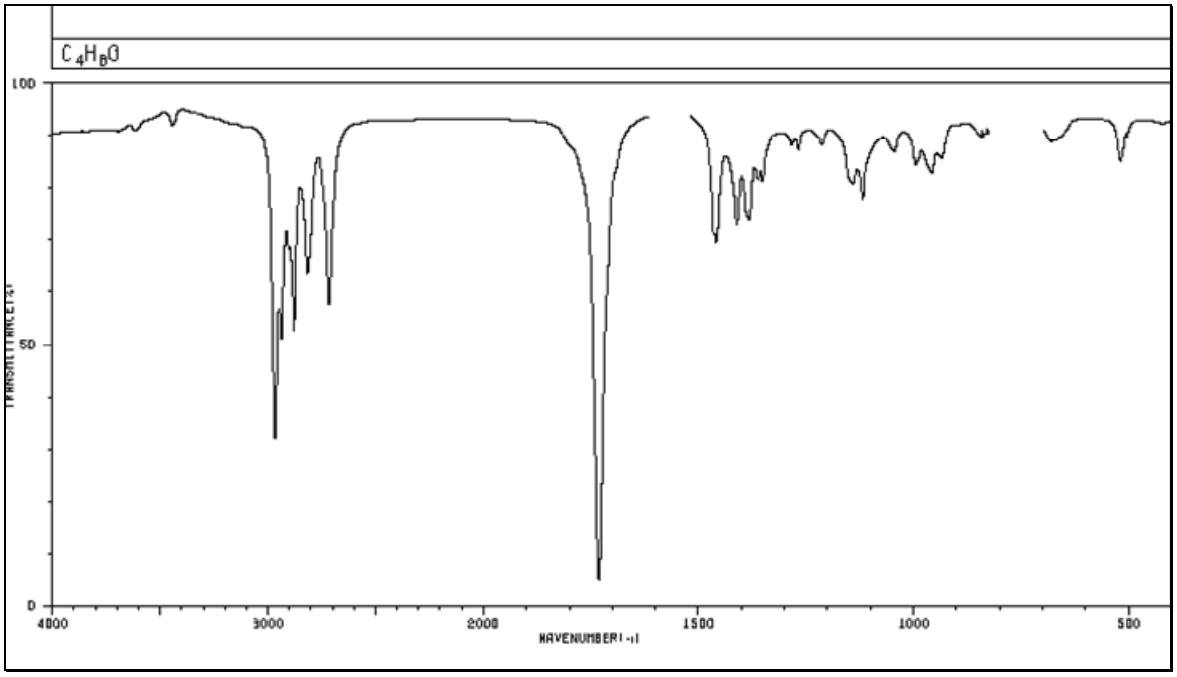


Unknown 29: MS

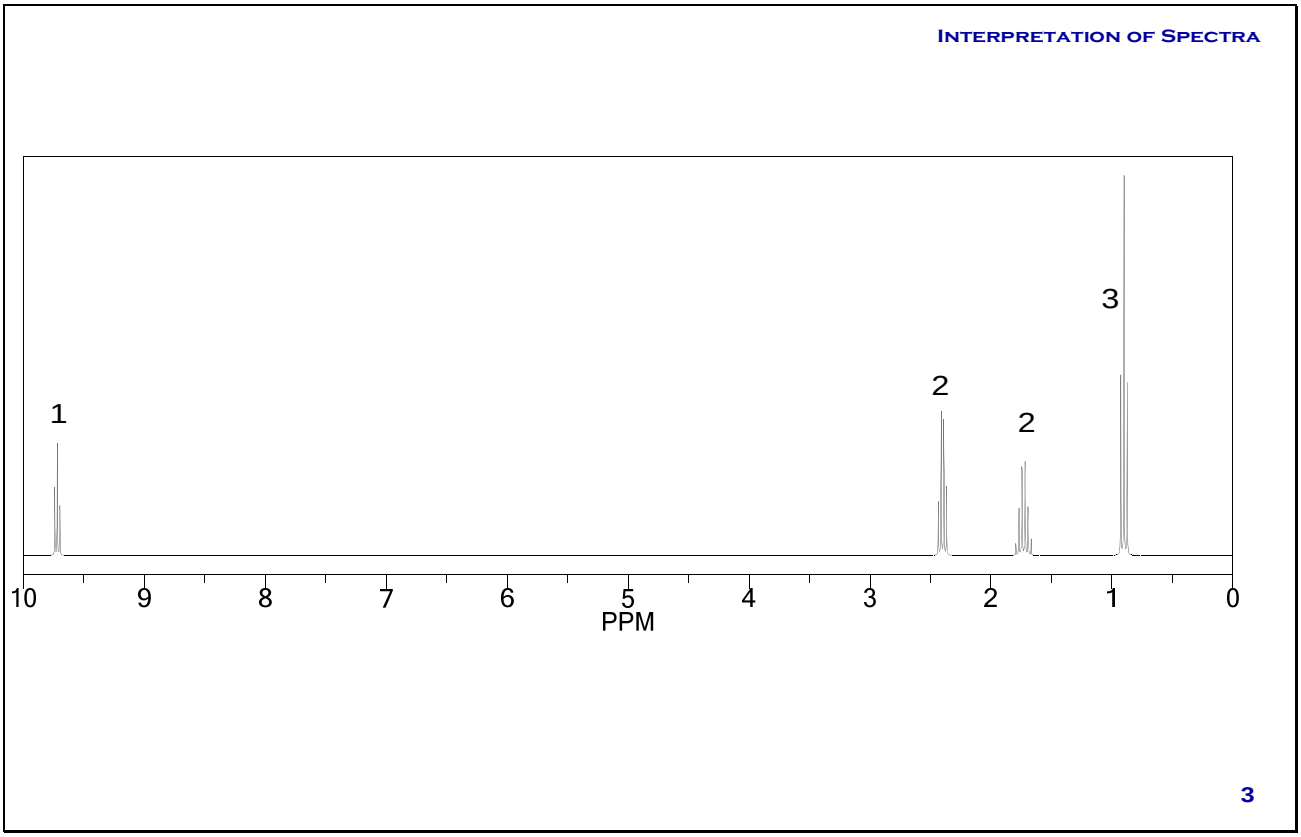
MF: C_4H_8O



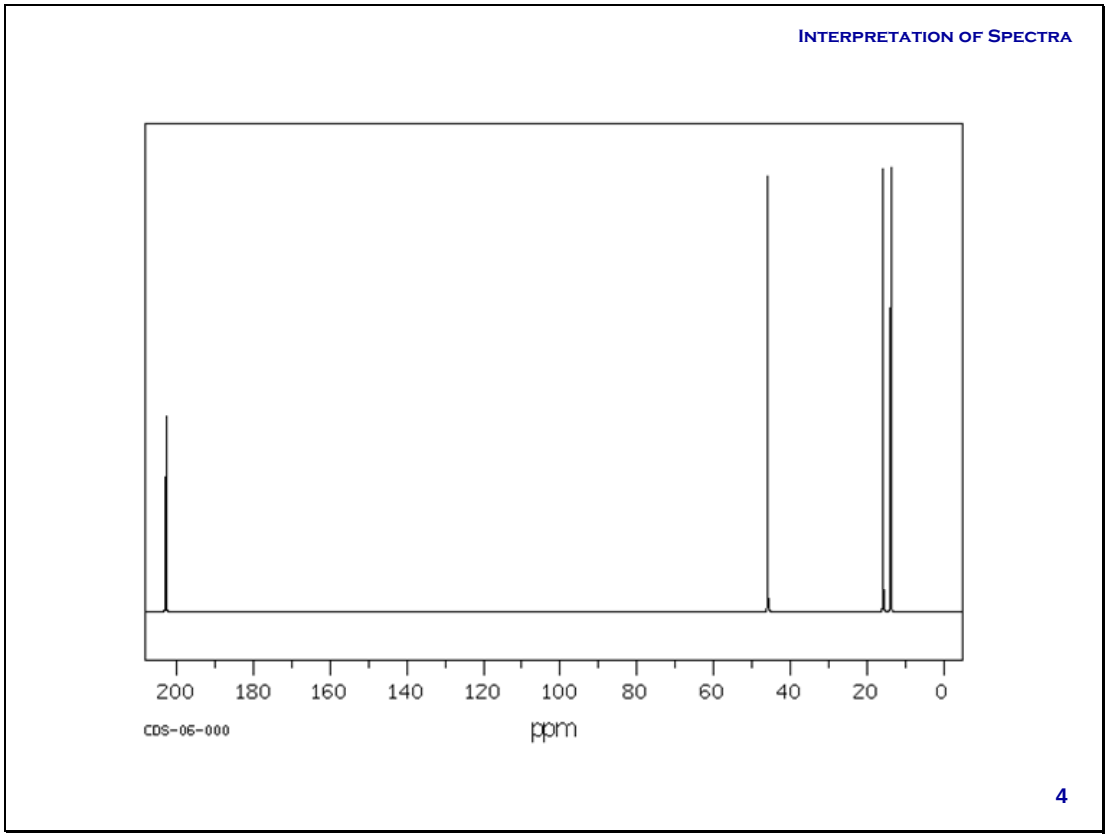
Unknown 29: IR



Unknown 29: NMR

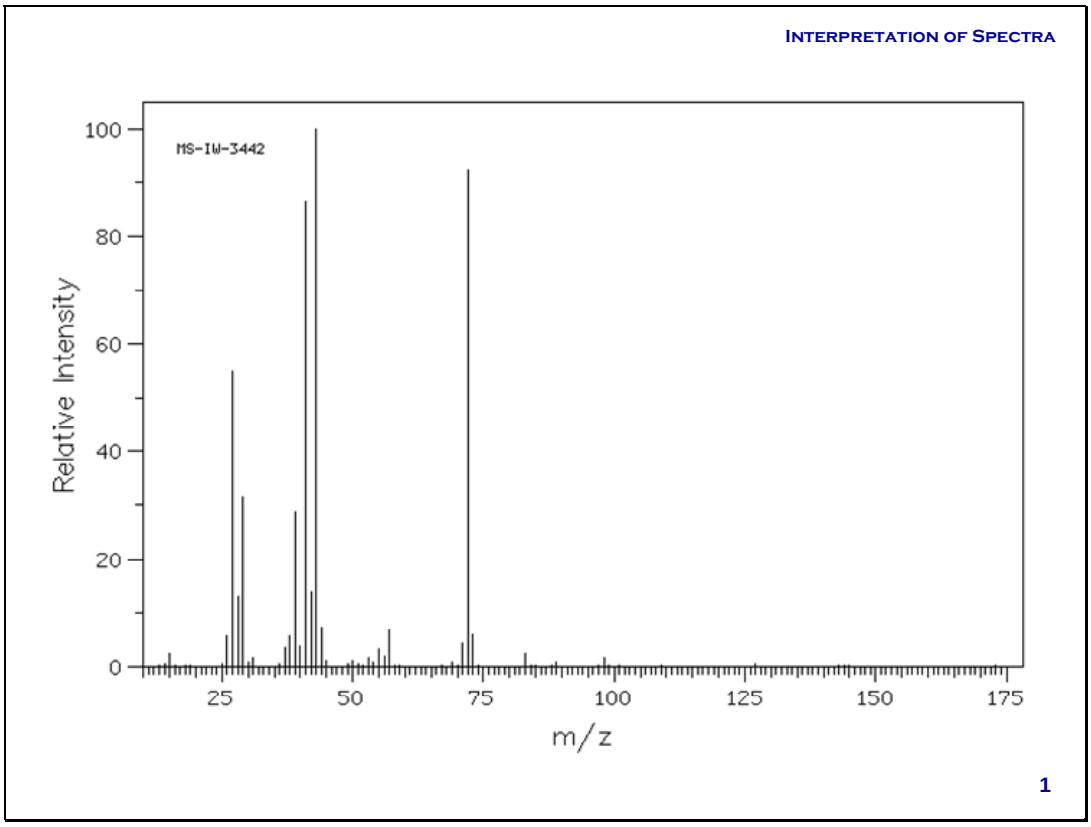


Unknown 29: CNMR

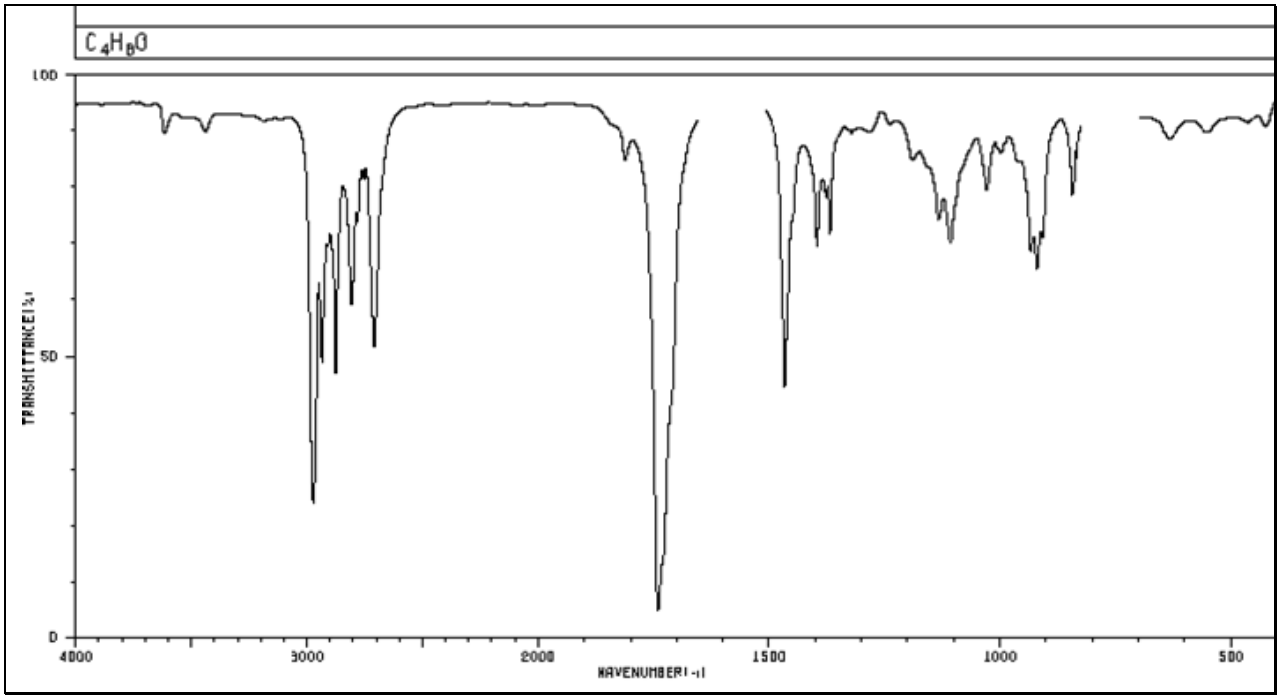


Unknown 30: MS

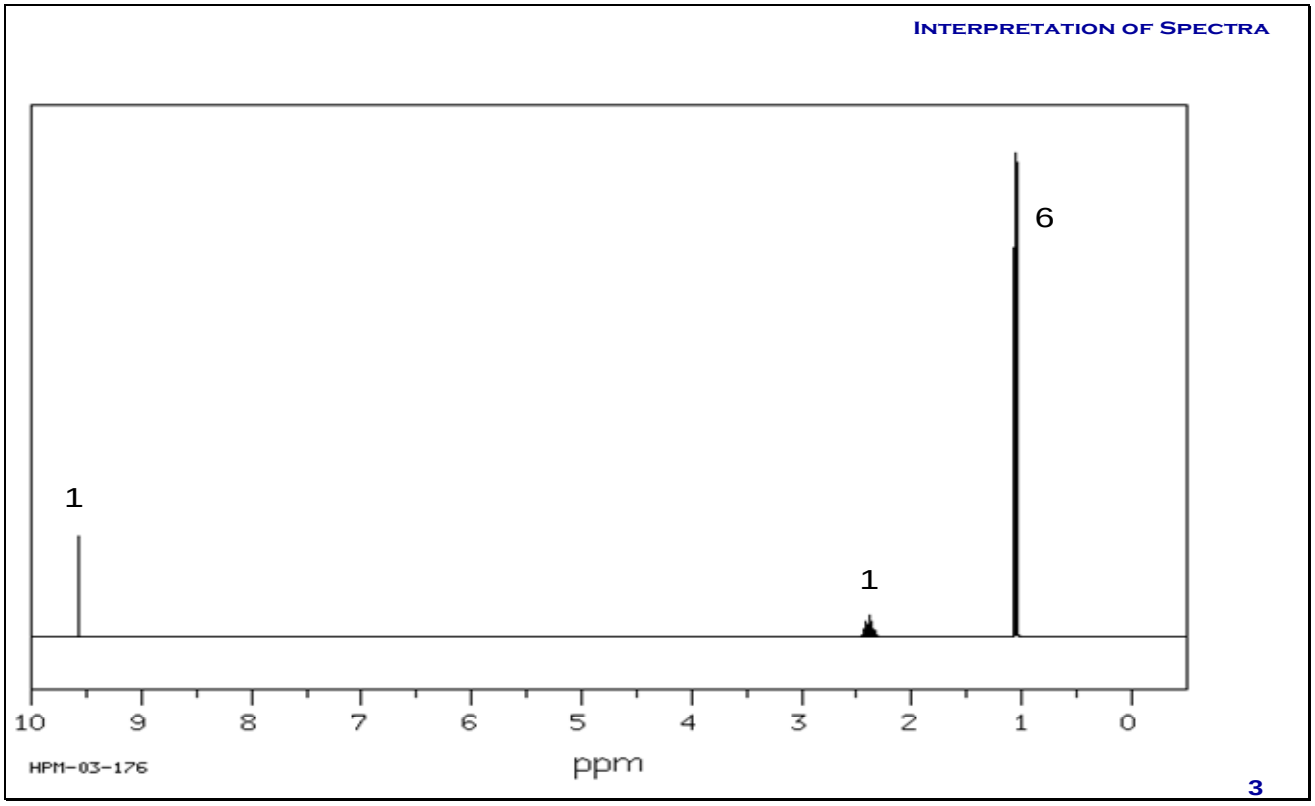
MF: C_4H_8O



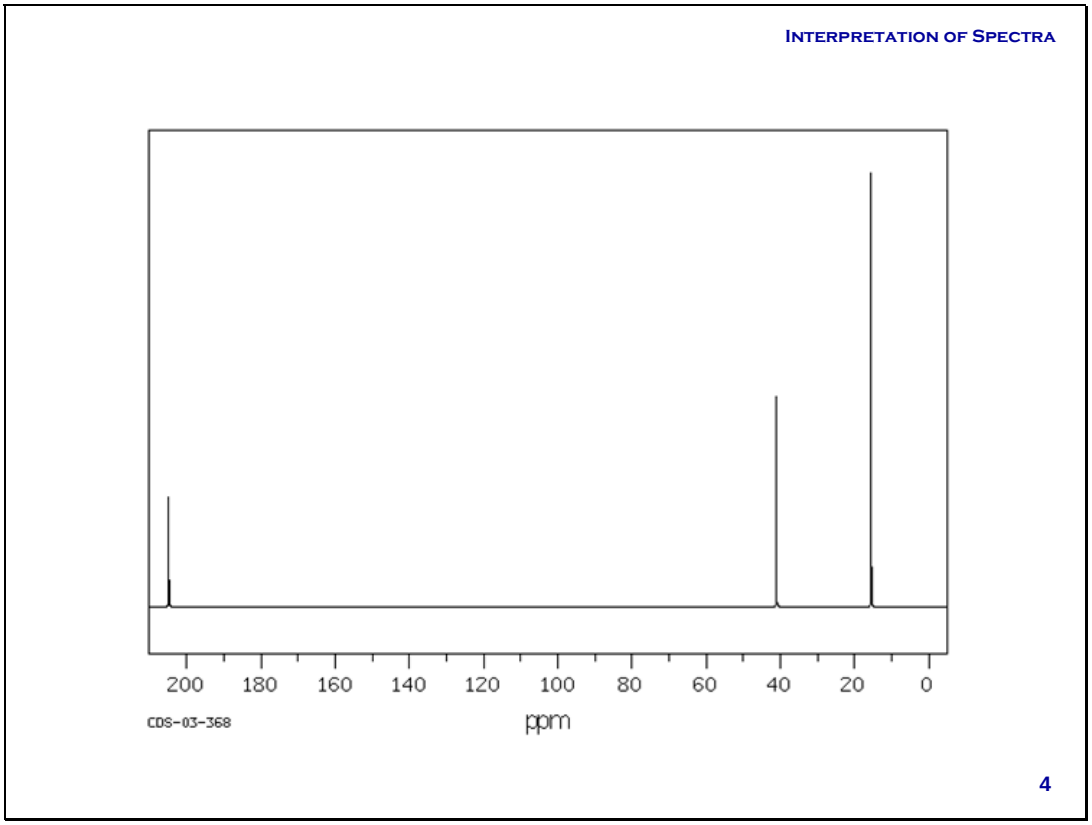
Unknown 30: IR



Unknown 30: NMR

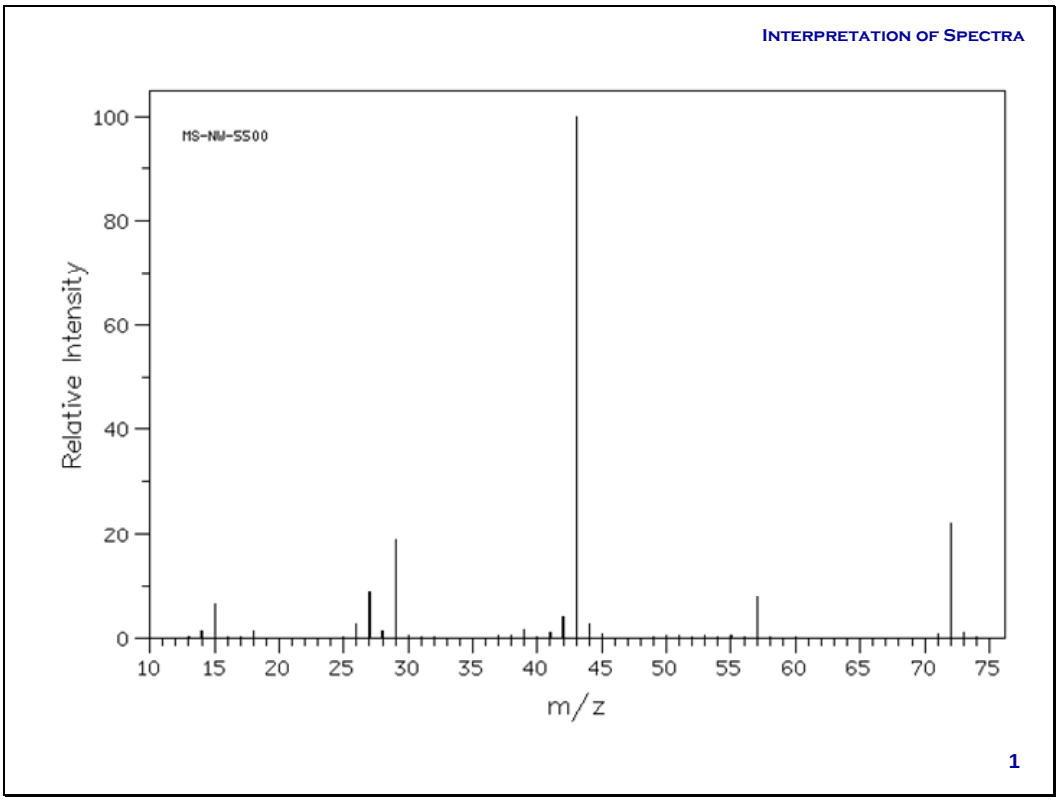


Unknown 30: CNMR

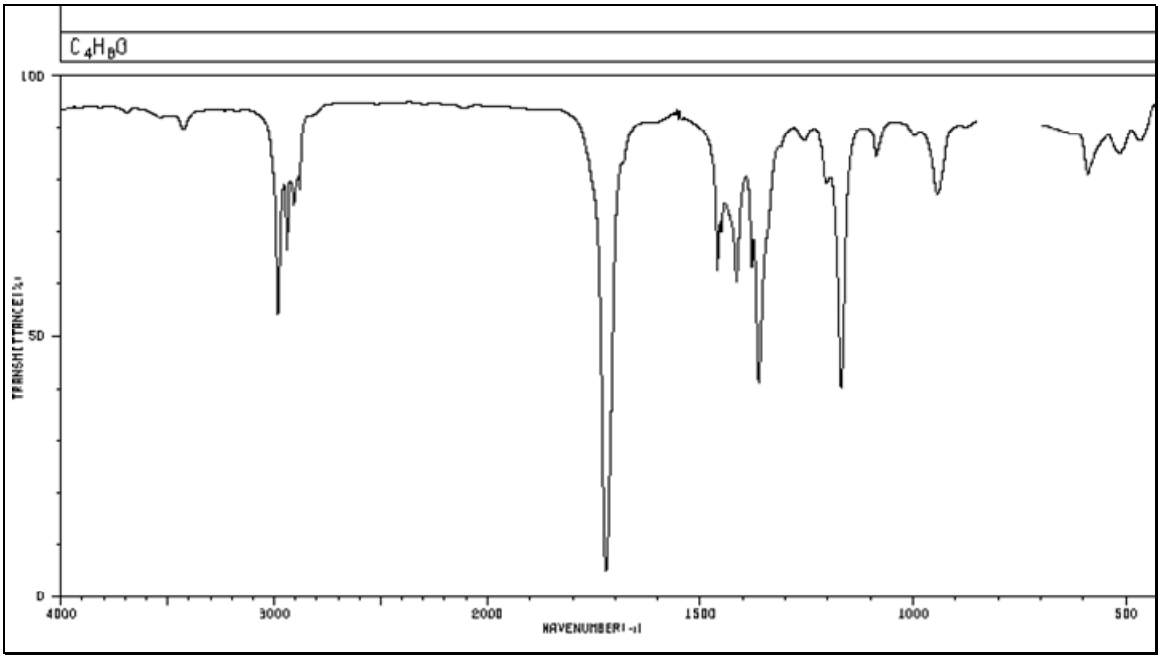


Unknown 31: MS

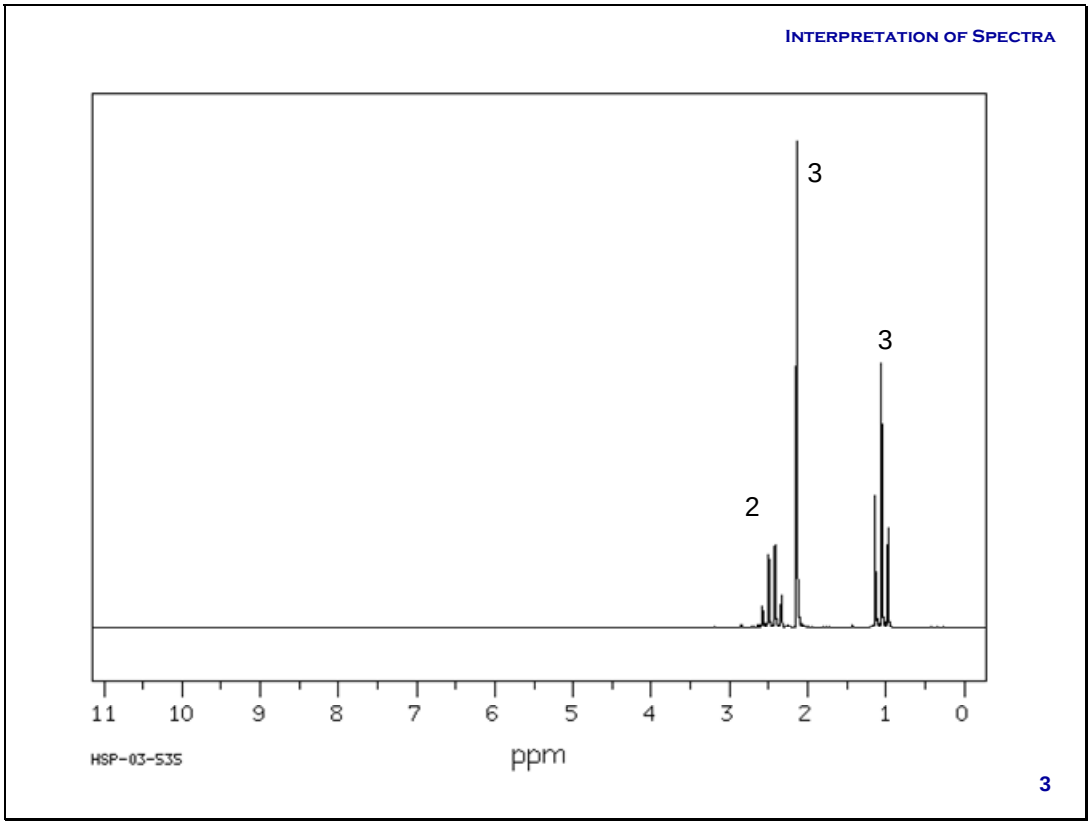
MF: C_4H_8O



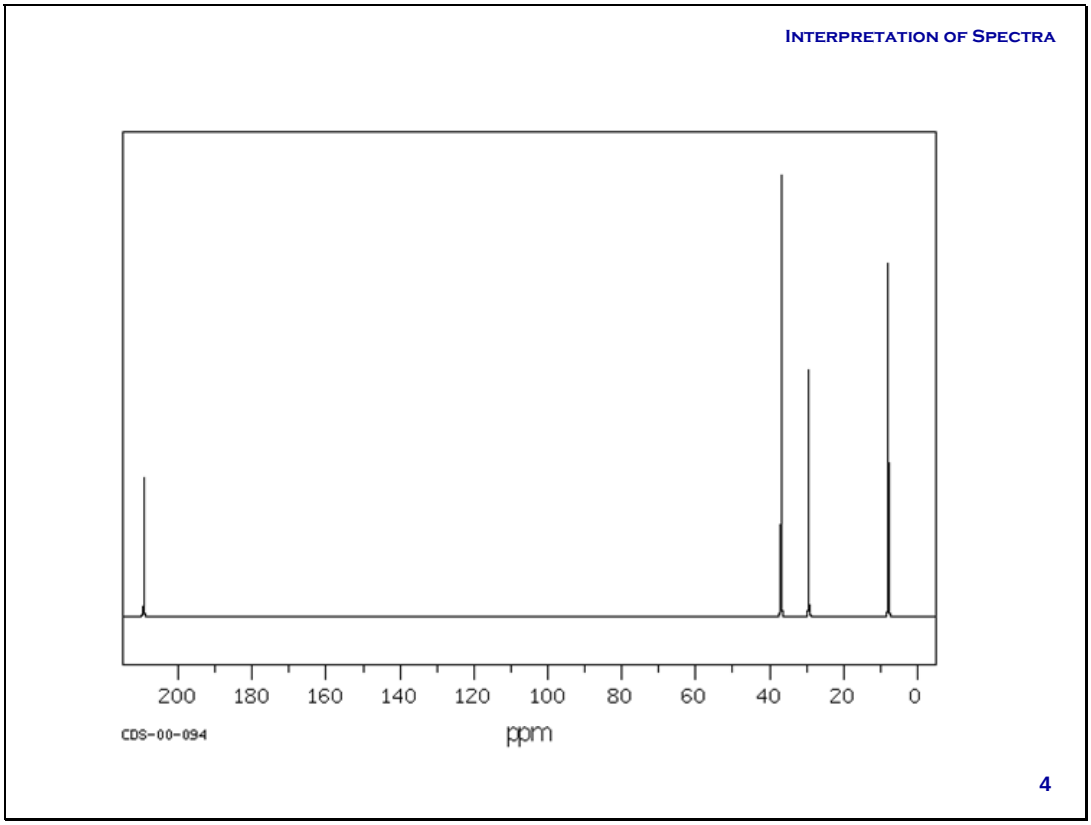
Unknown 31: IR



Unknown 31: NMR

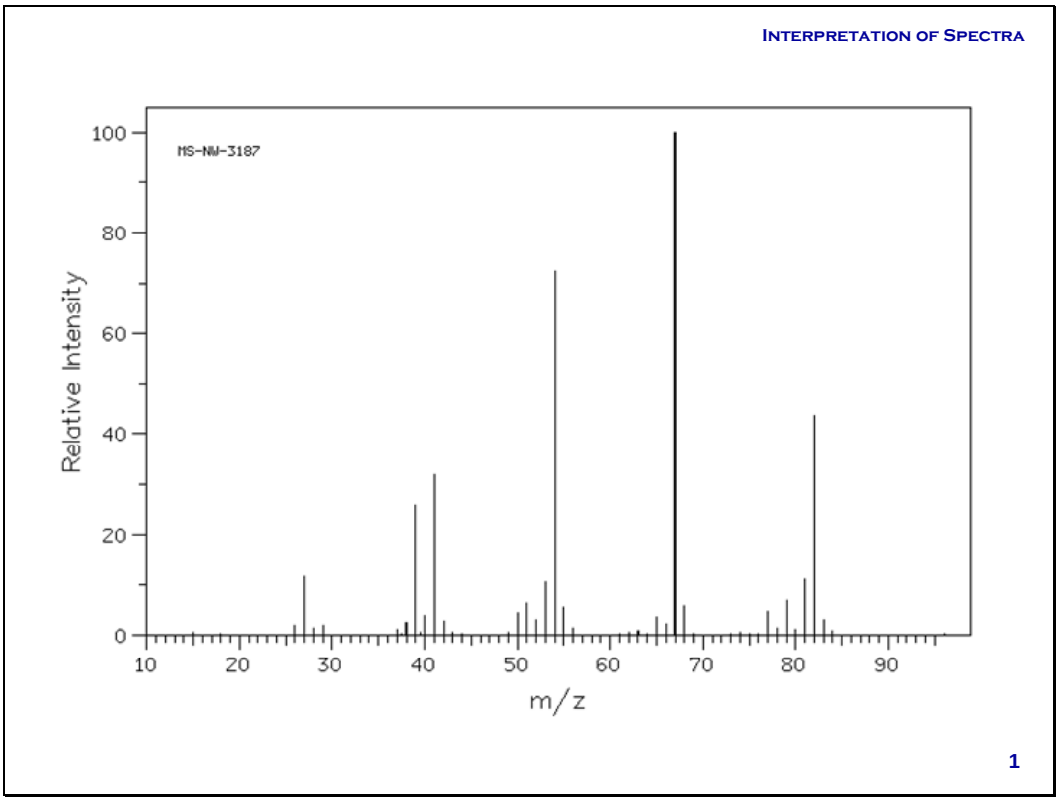


Unknown 31: CNMR

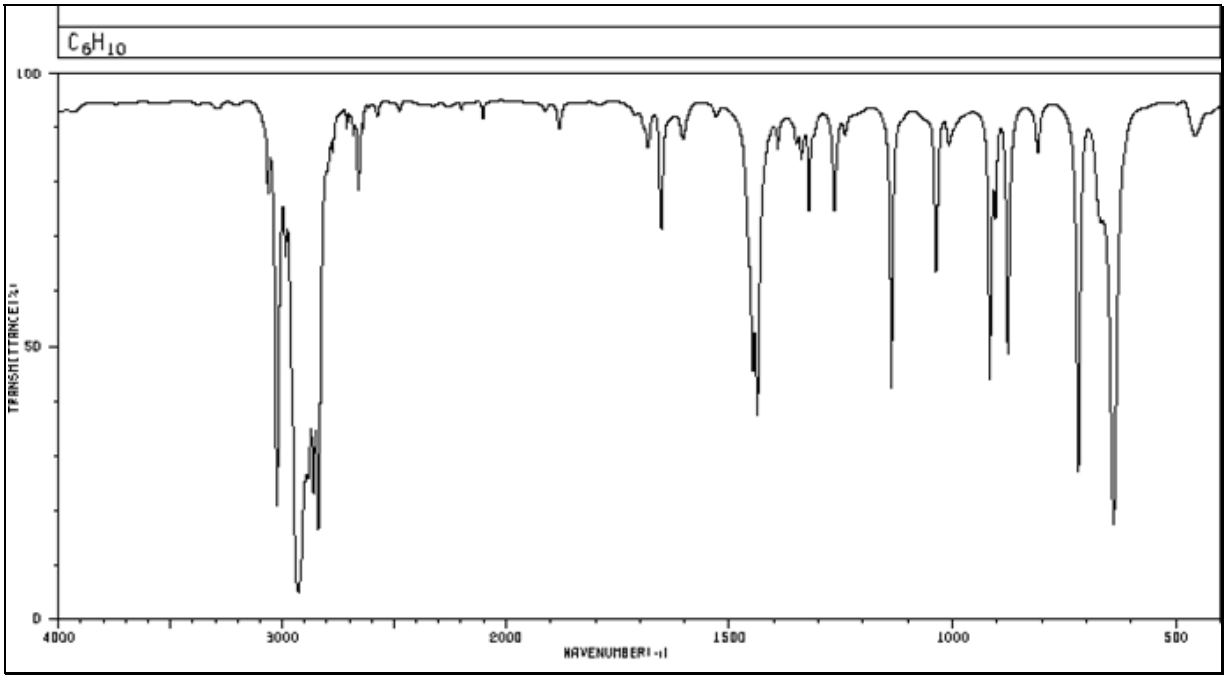


Unknown 32: MS

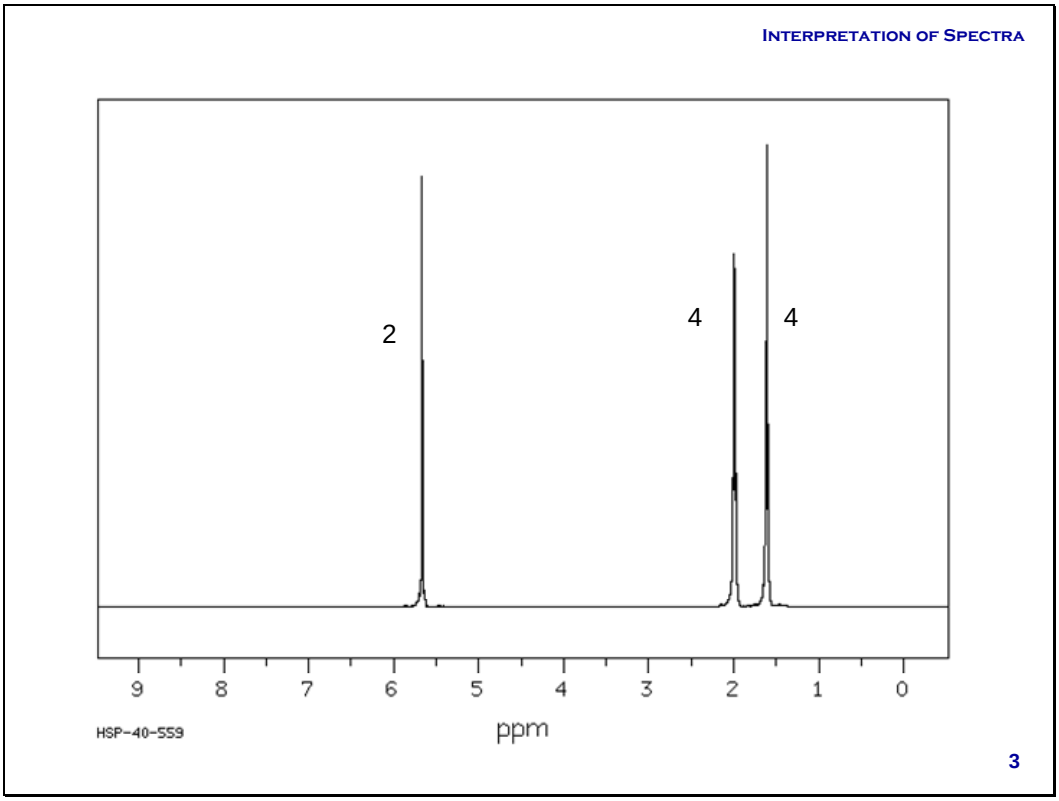
MF: C_6H_{10}



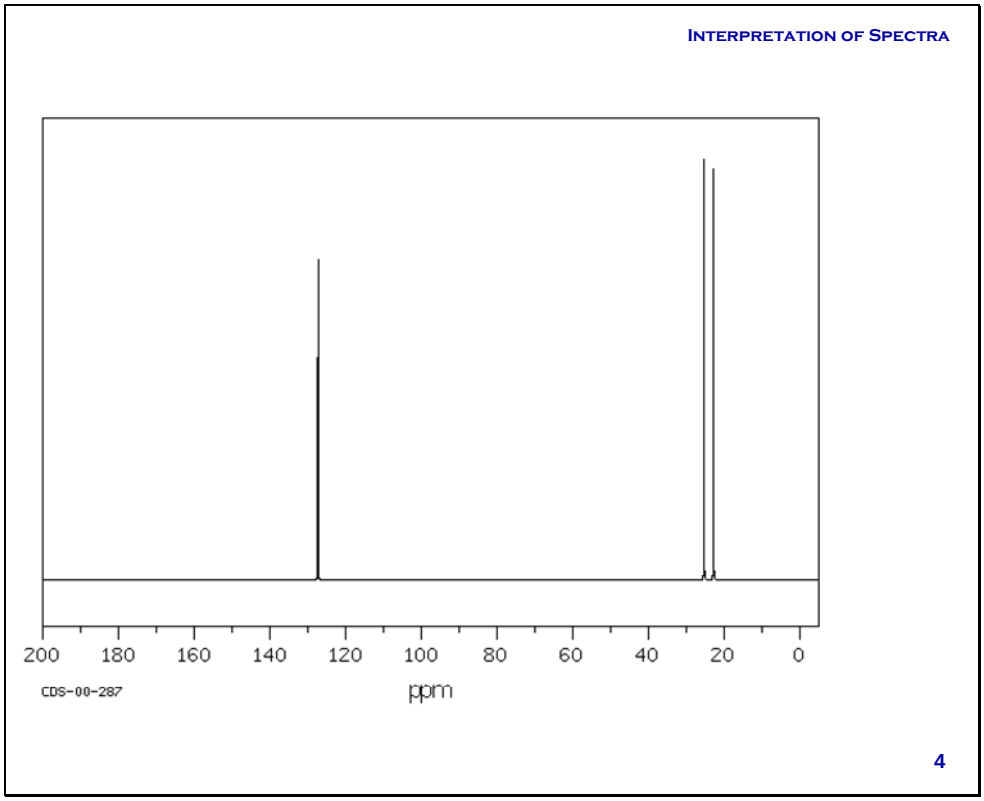
Unknown 32: IR



Unknown 32: NMR

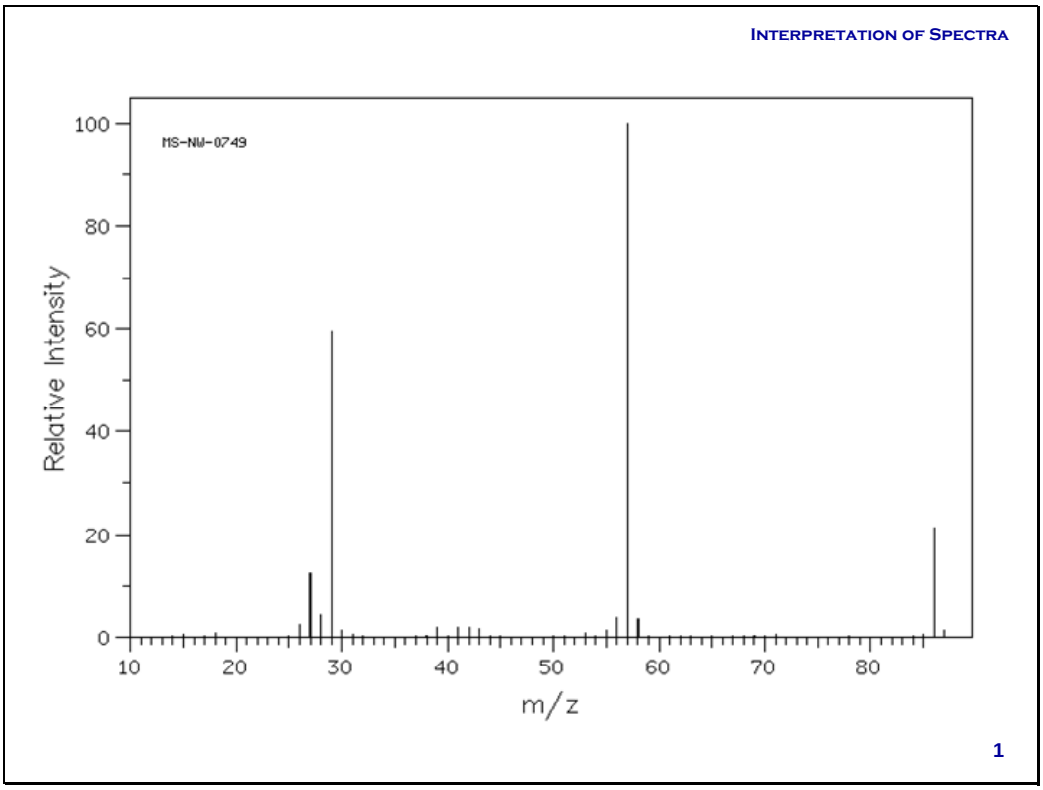


Unknown 32: CNMR

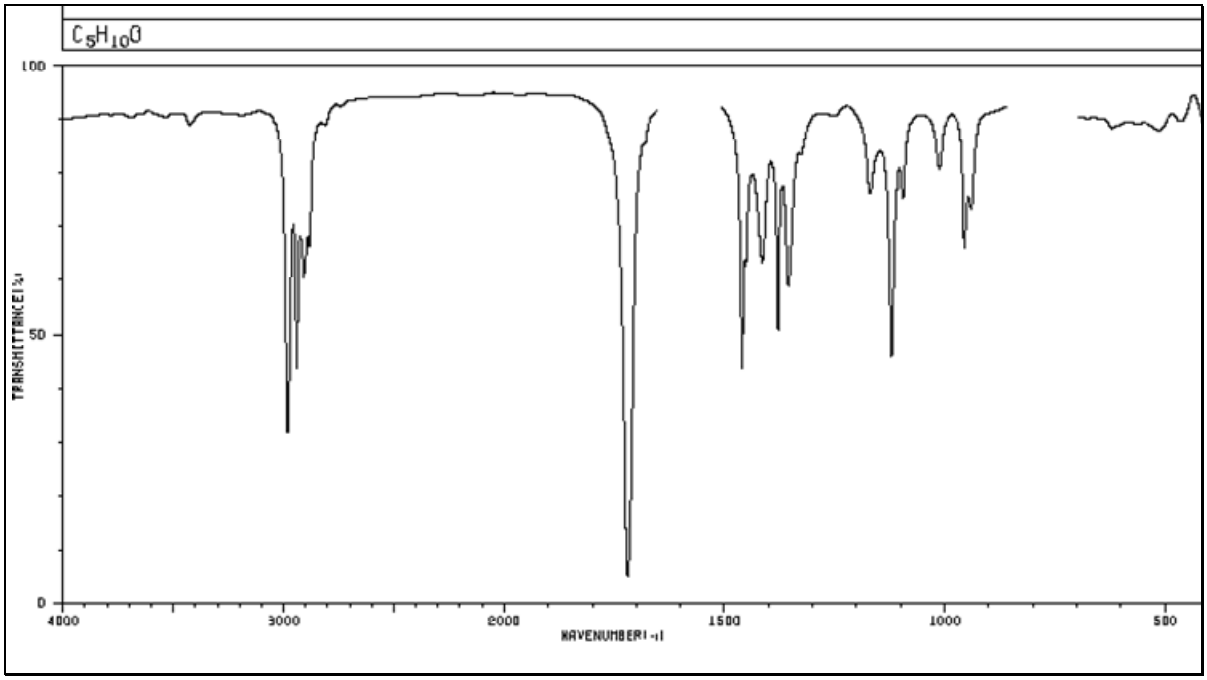


Unknown 33: MS

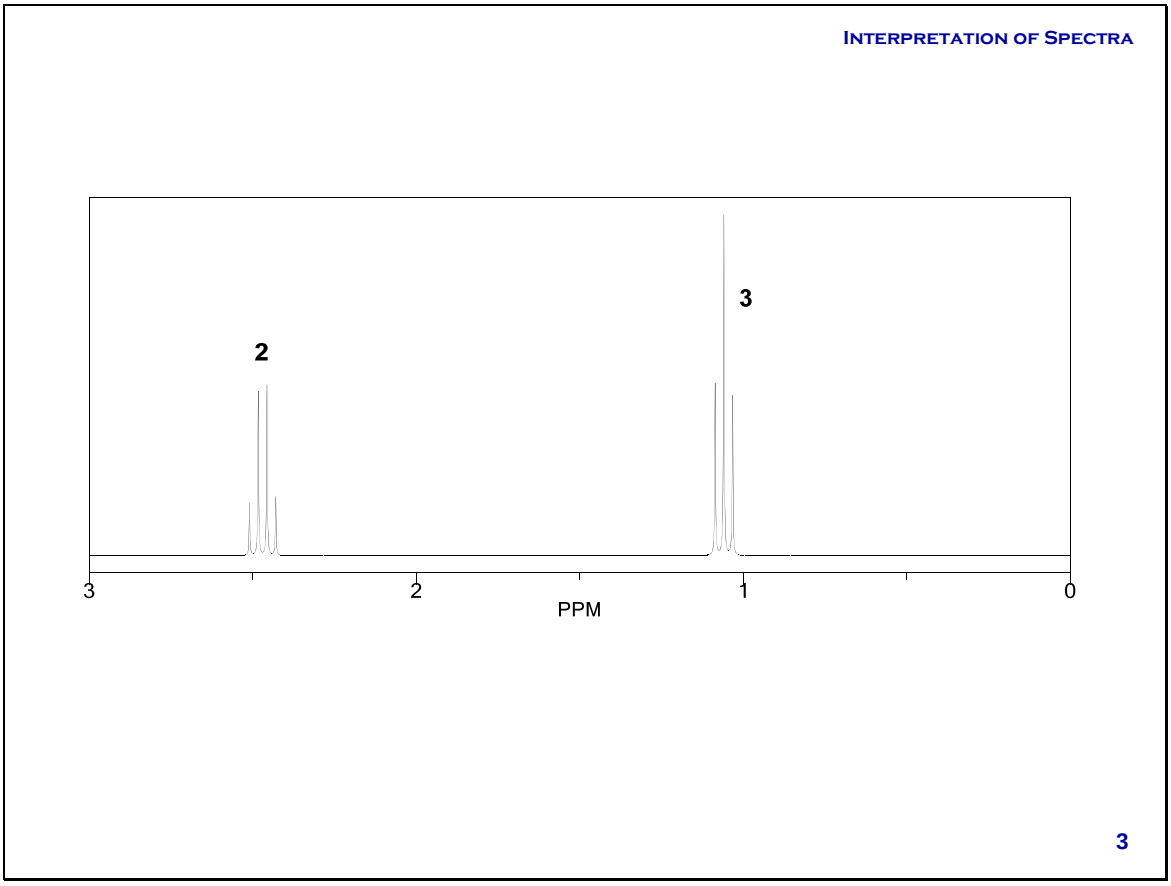
MF: $C_5H_{10}O$



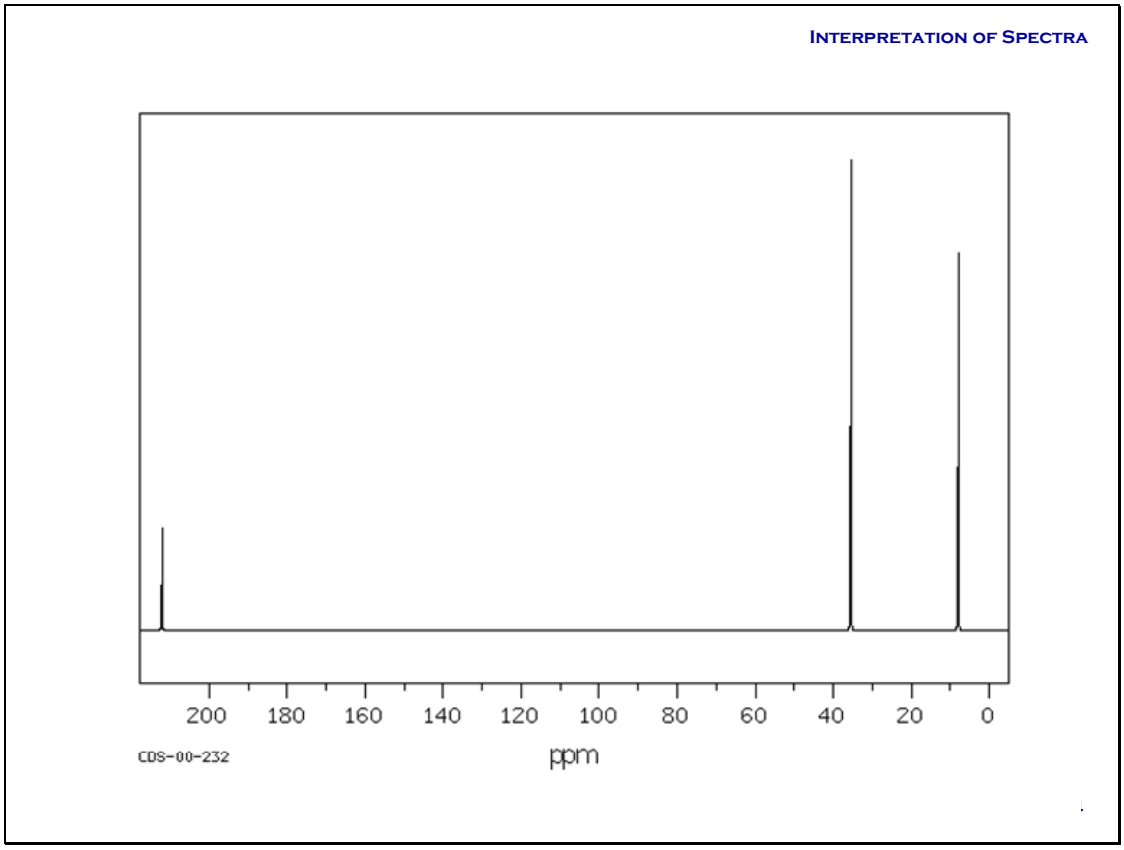
Unknown 33: IR



Unknown 33: NMR

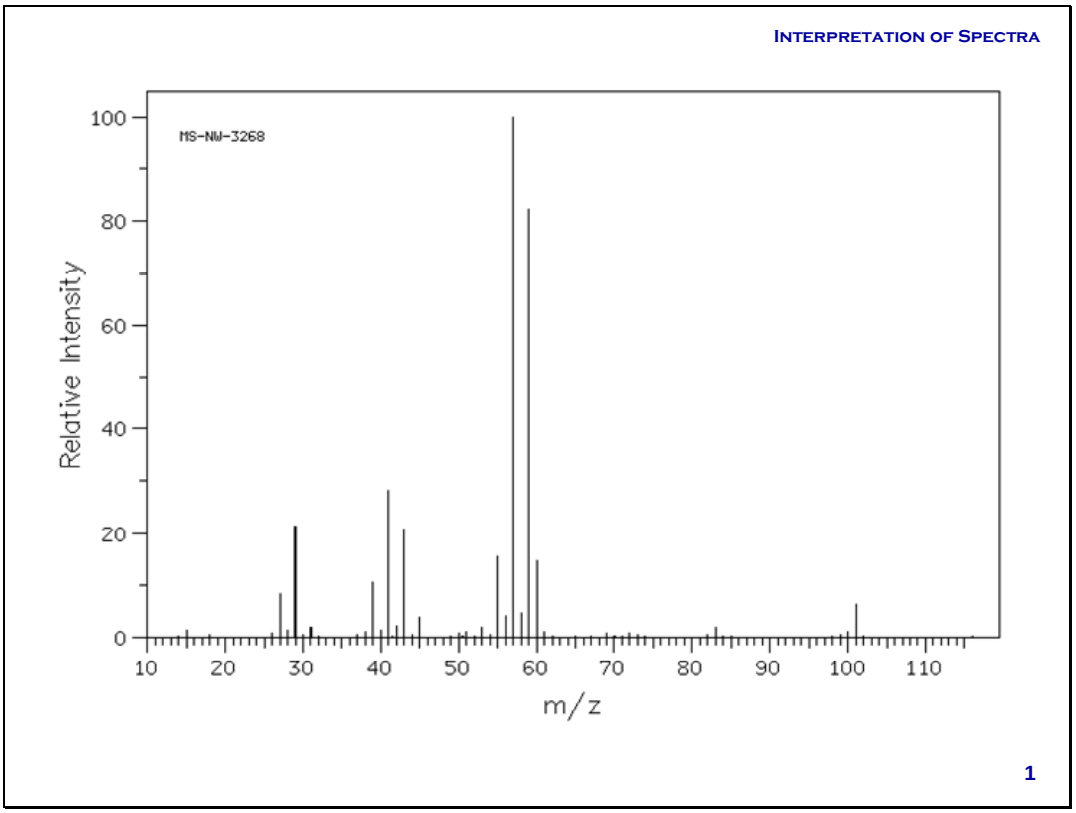


Unknown 33: CNMR

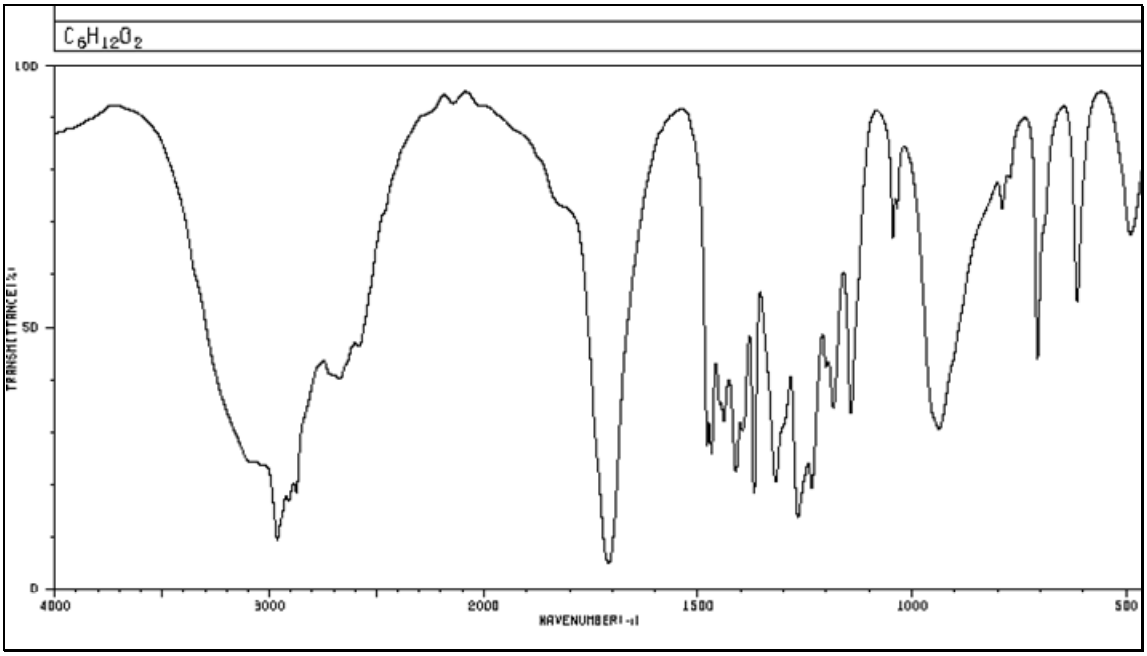


Unknown 34: MS

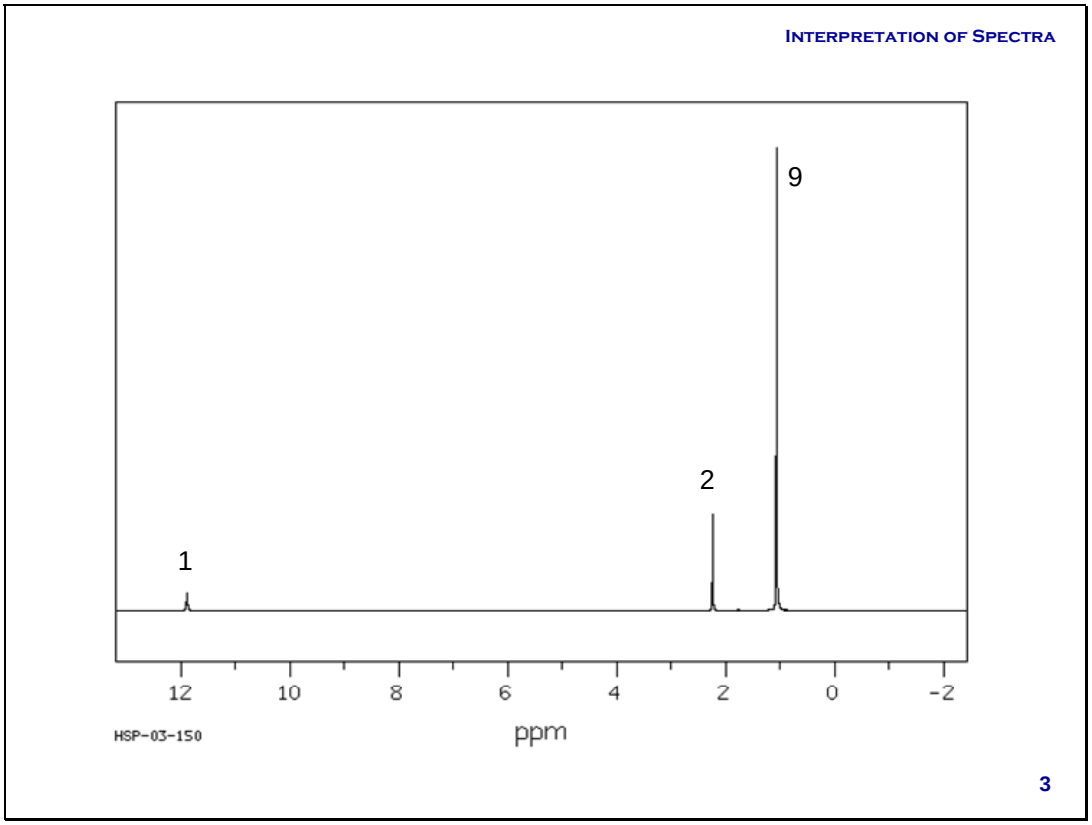
MF: $C_6H_{12}O_2$



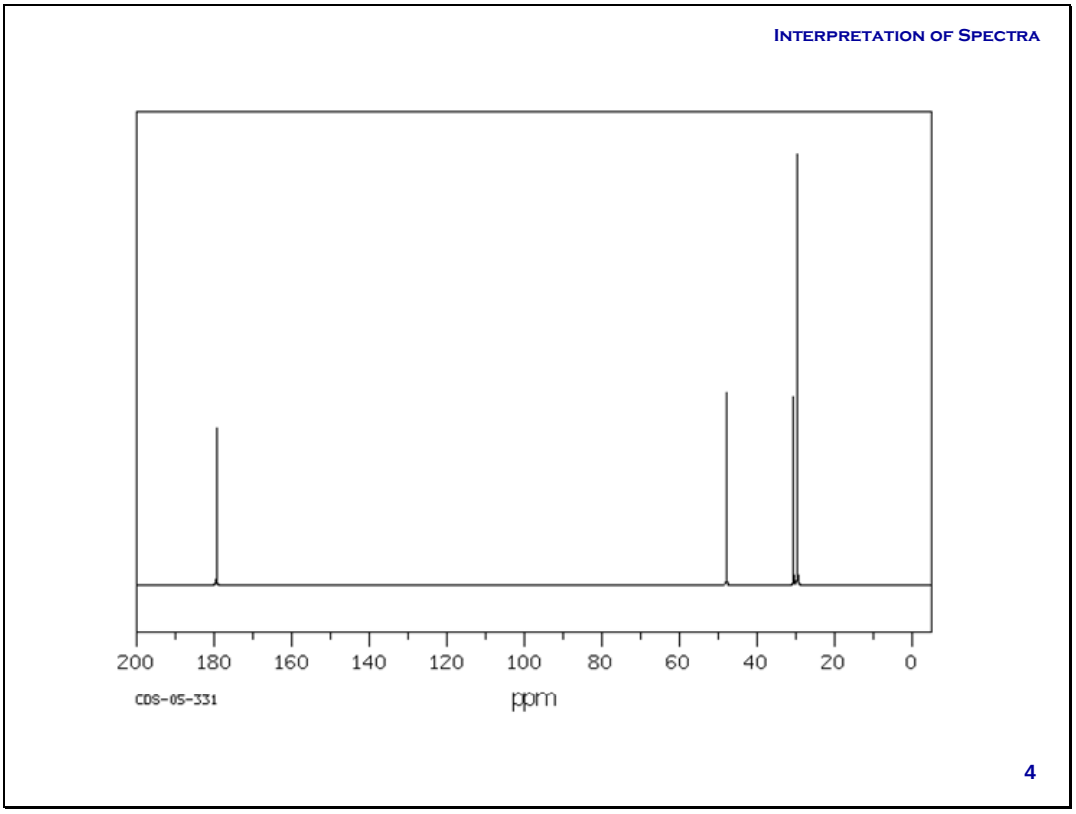
Unknown 34: IR



Unknown 34: NMR

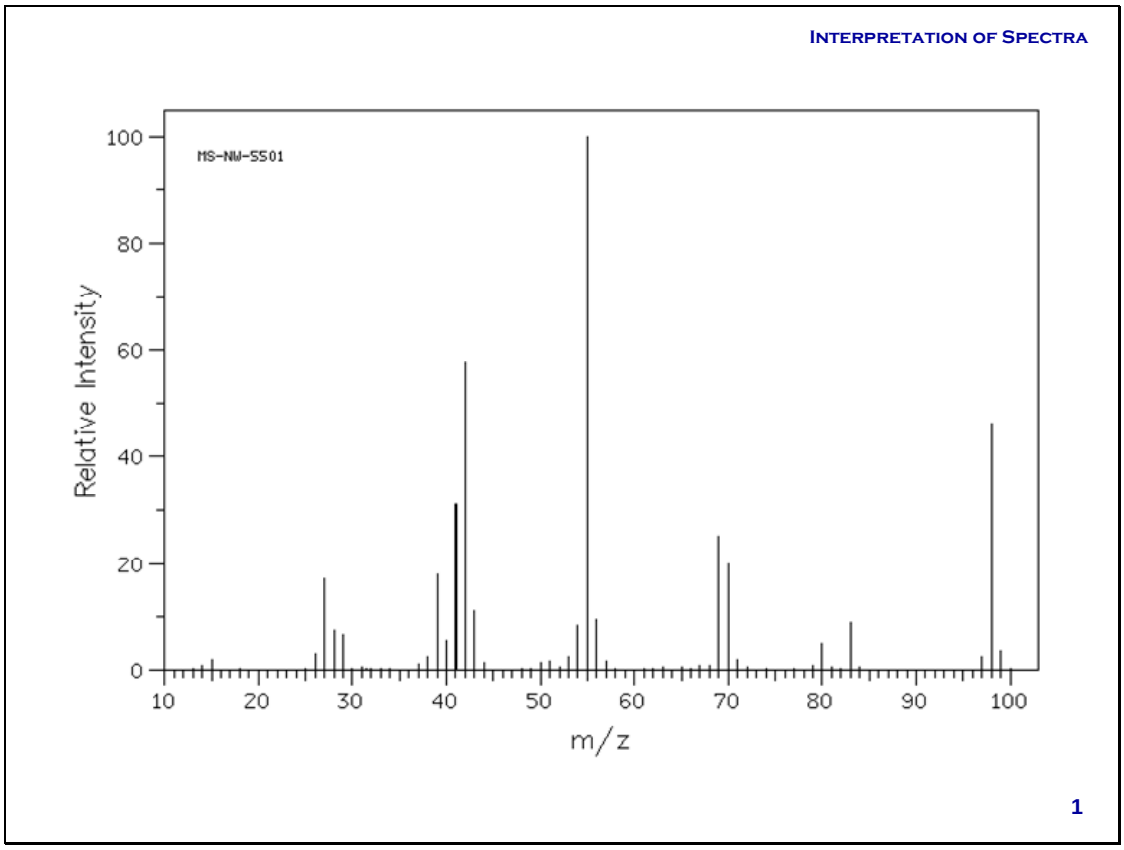


Unknown 34: CNMR

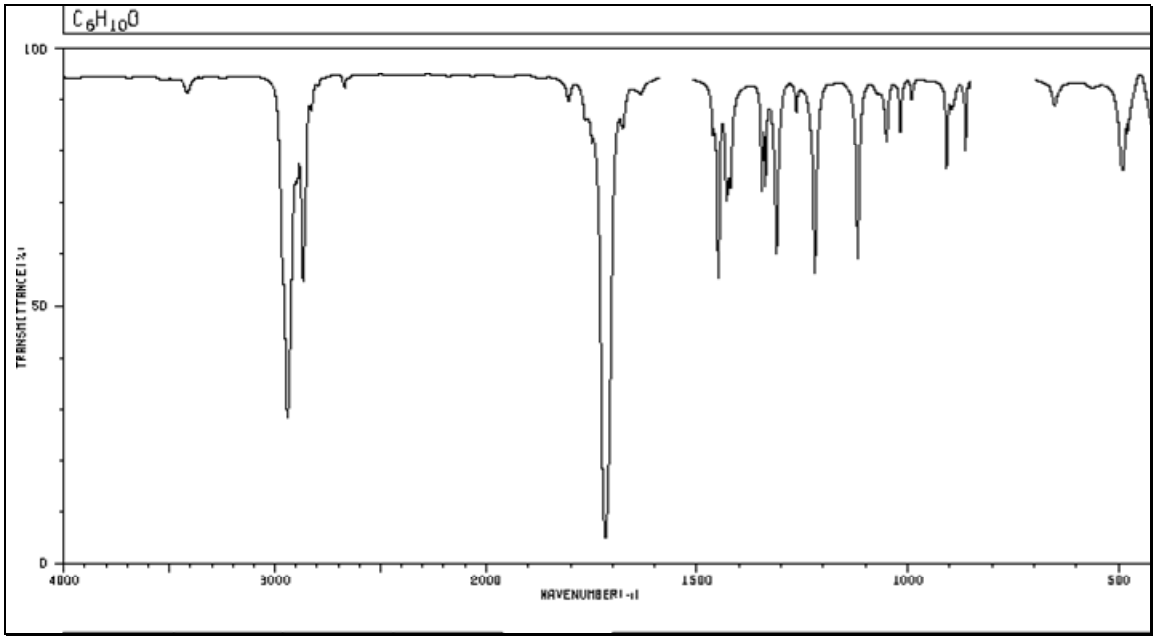


Unknown 35: MS

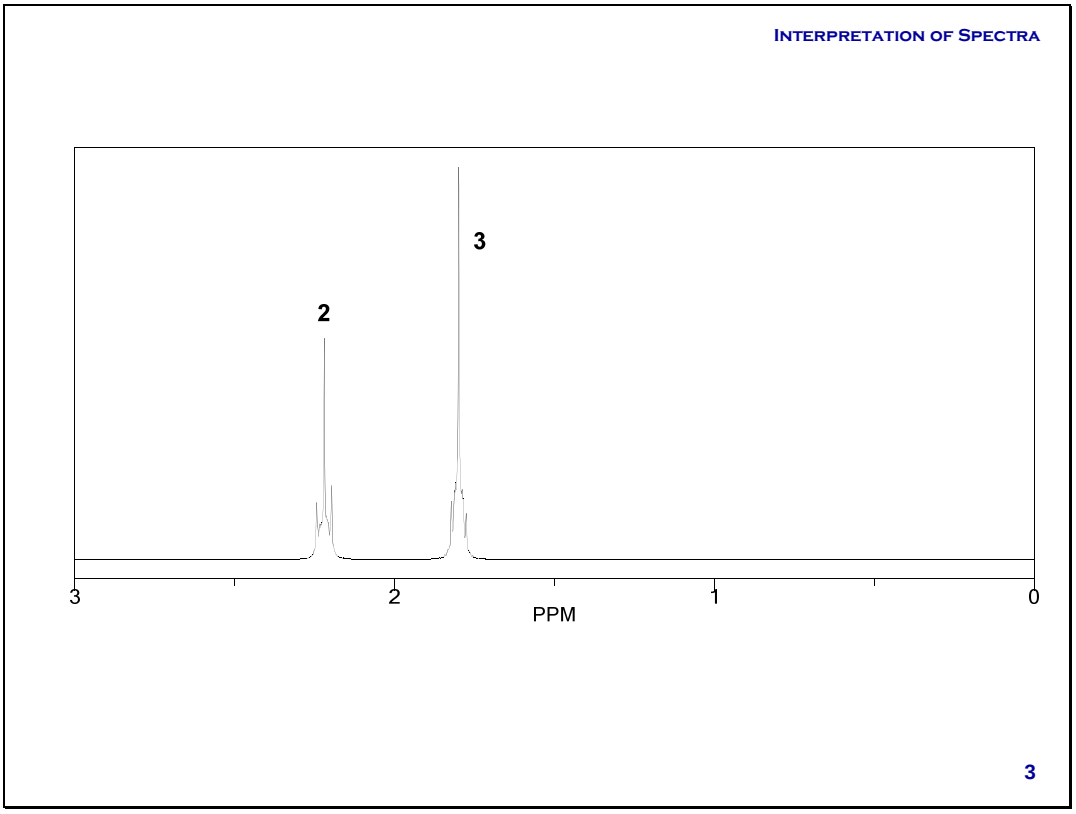
MF: $C_6H_{10}O$



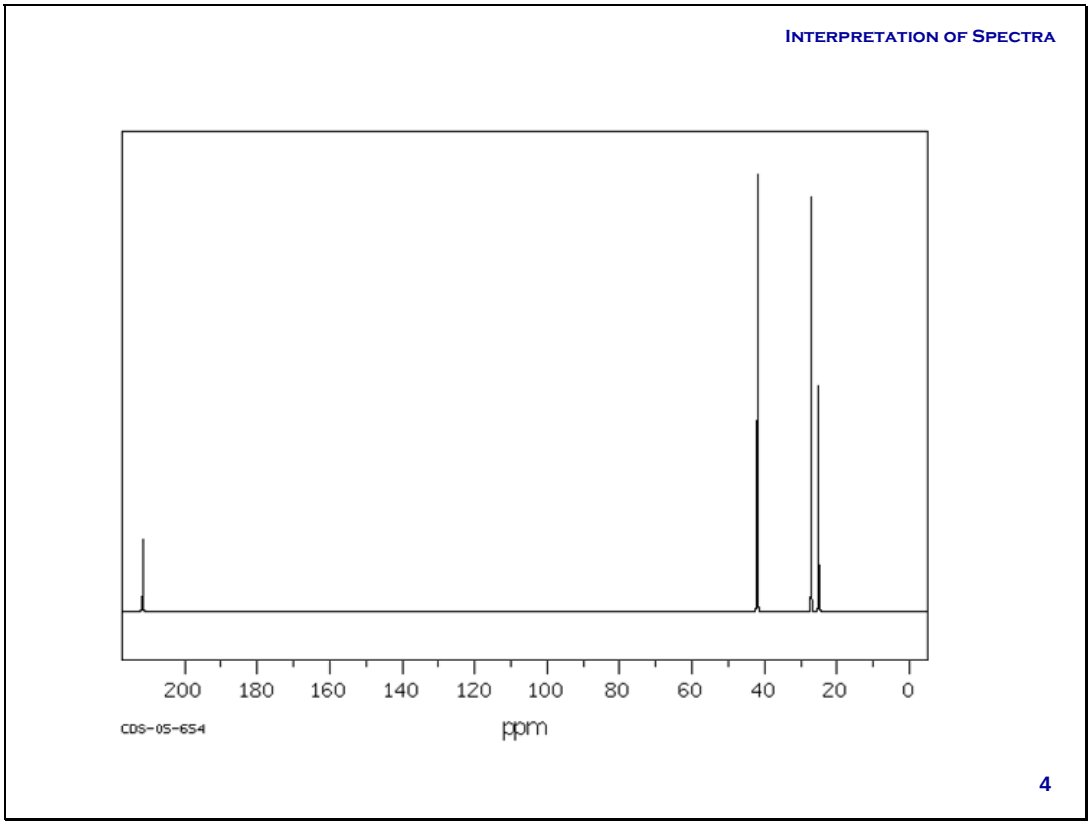
Unknown 35: IR



Unknown 35: NMR

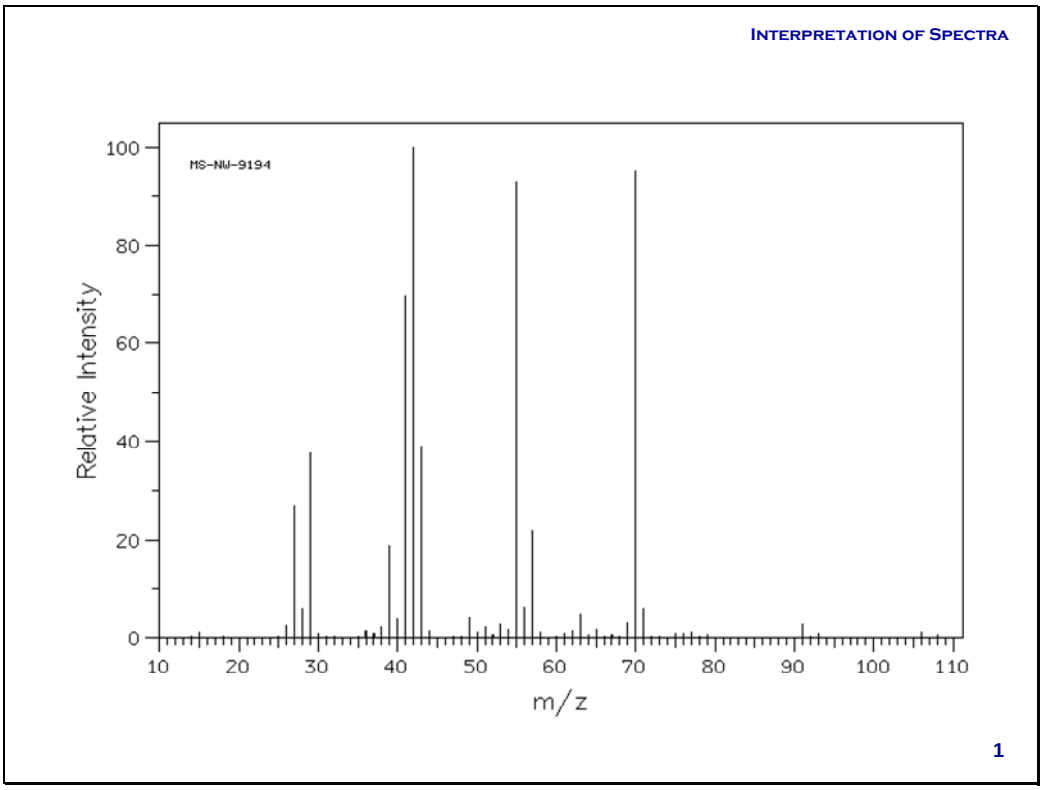


Unknown 35: CNMR

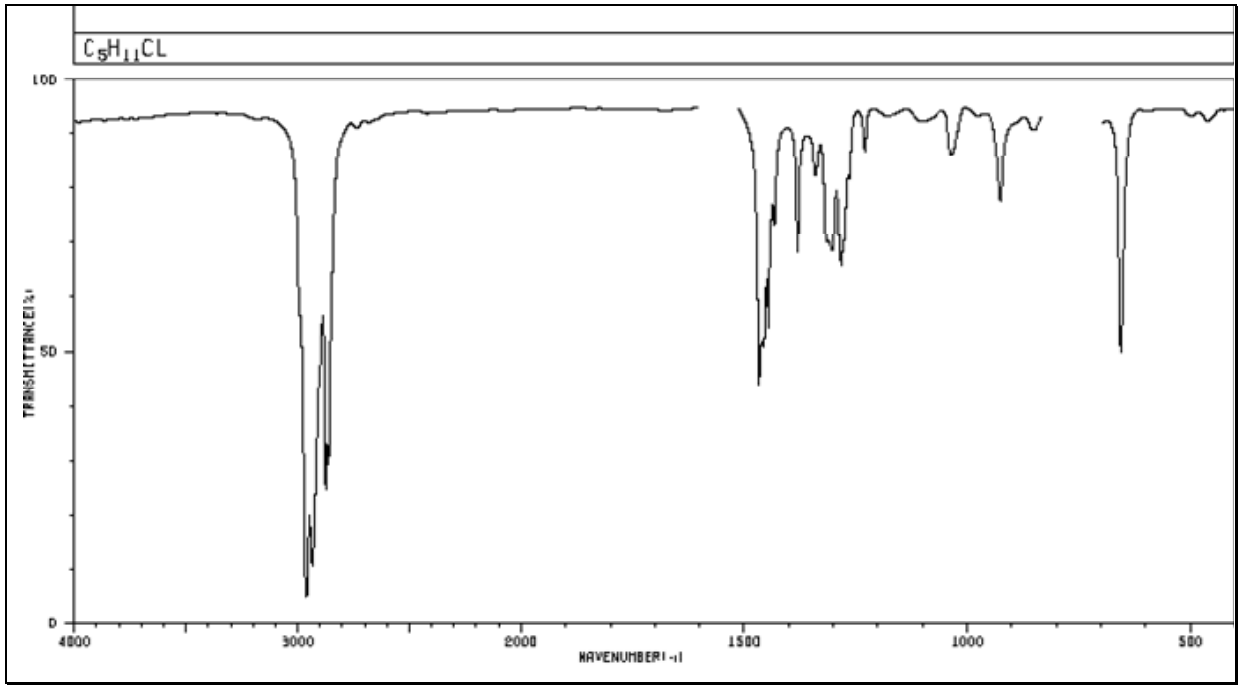


Unknown 36: MS

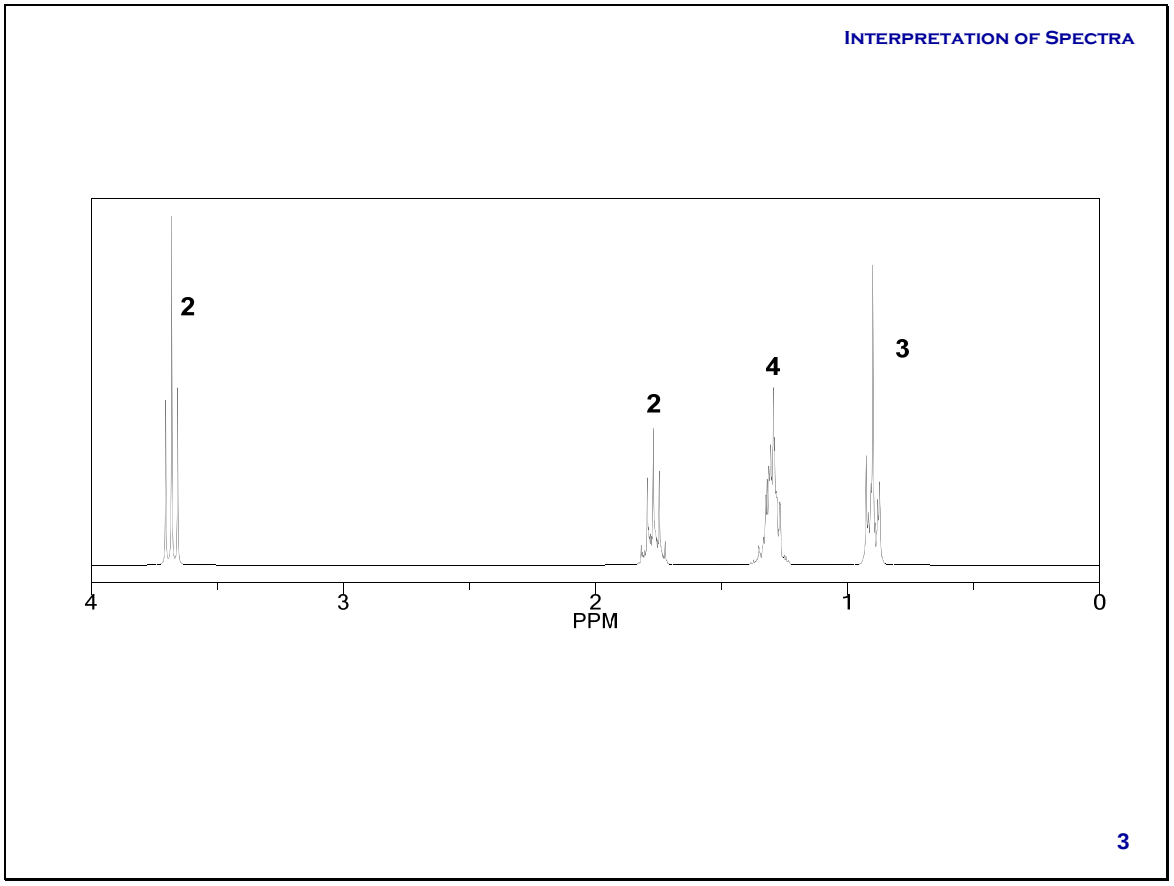
MF: $C_5H_{11}Cl$



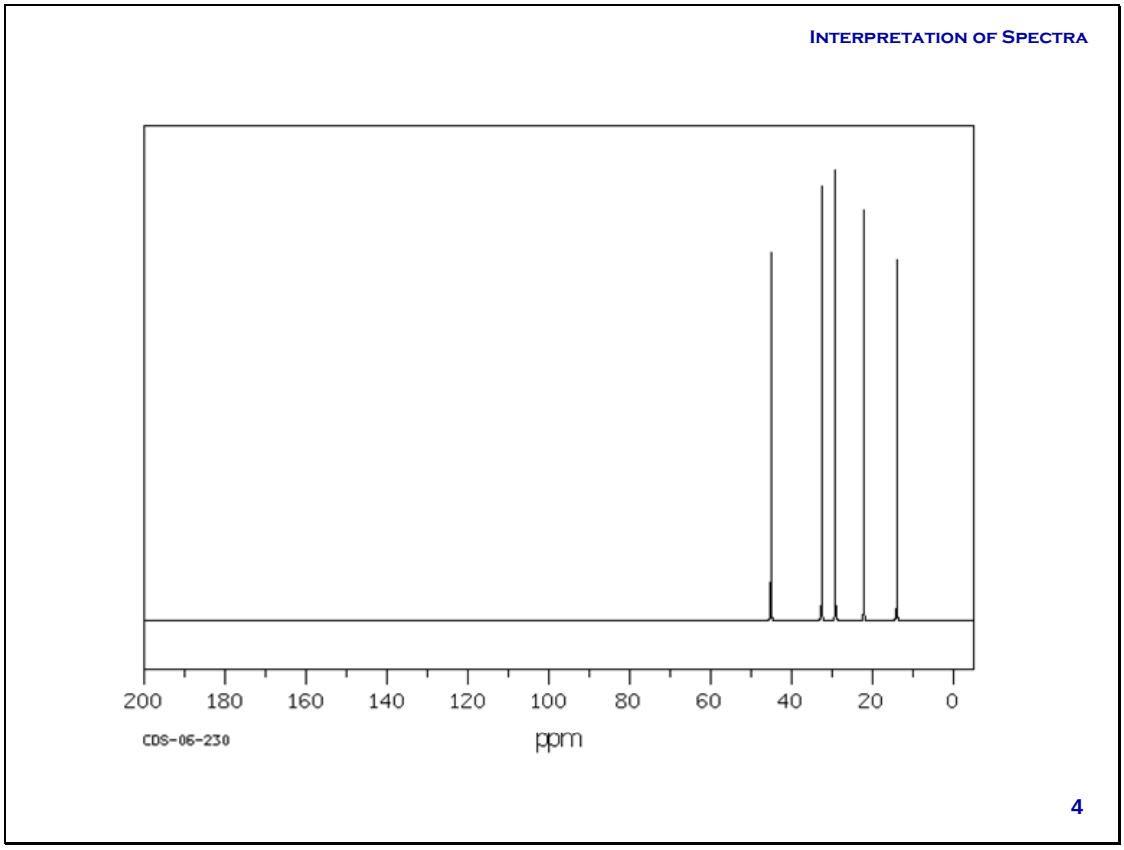
Unknown 36: IR



Unknown 36: NMR

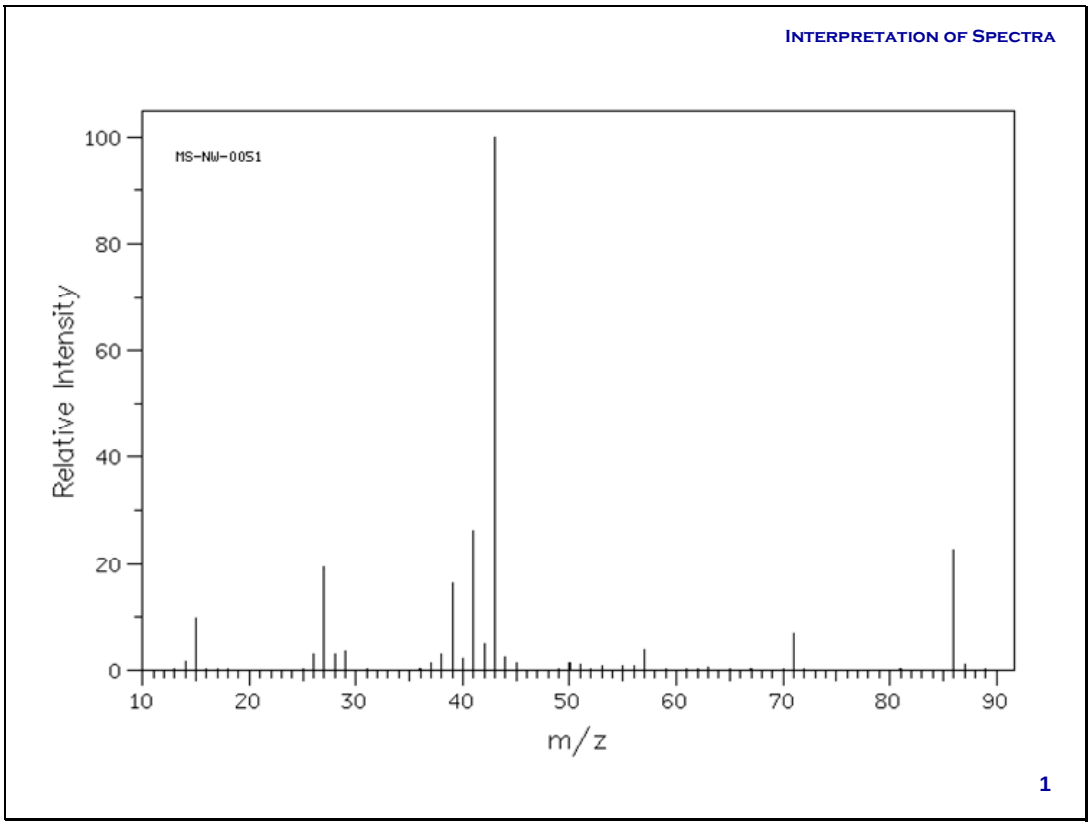


Unknown 36: CNMR

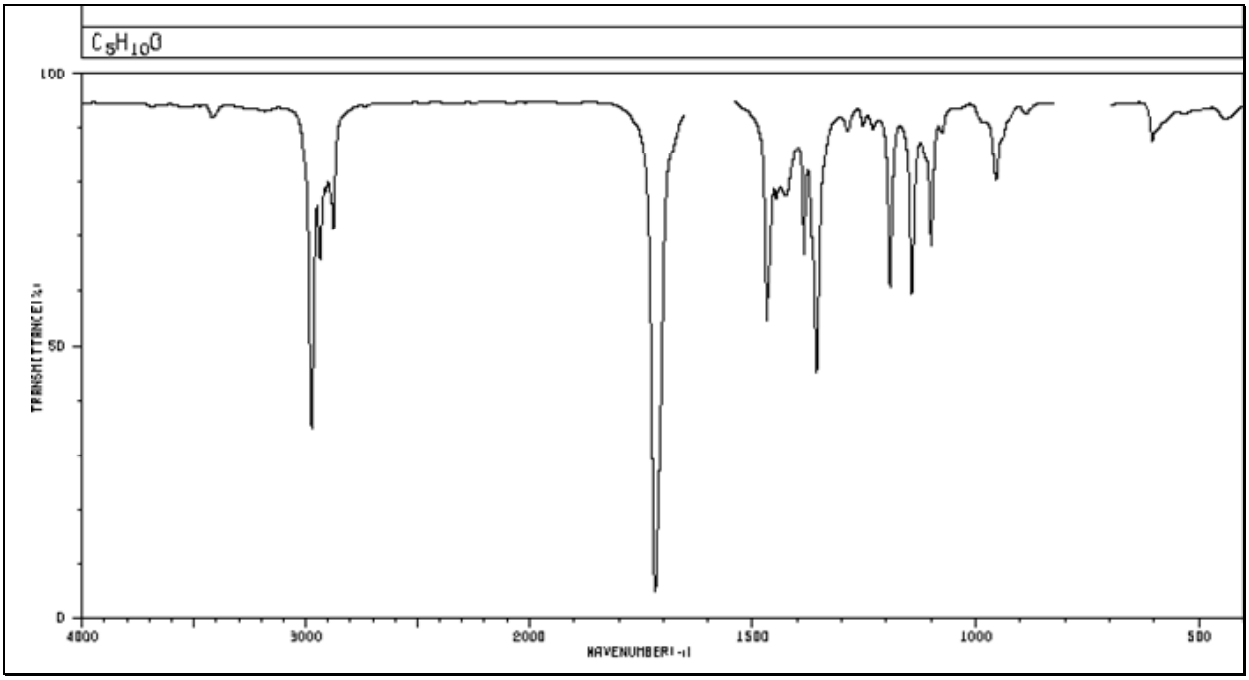


Unknown 37: MS

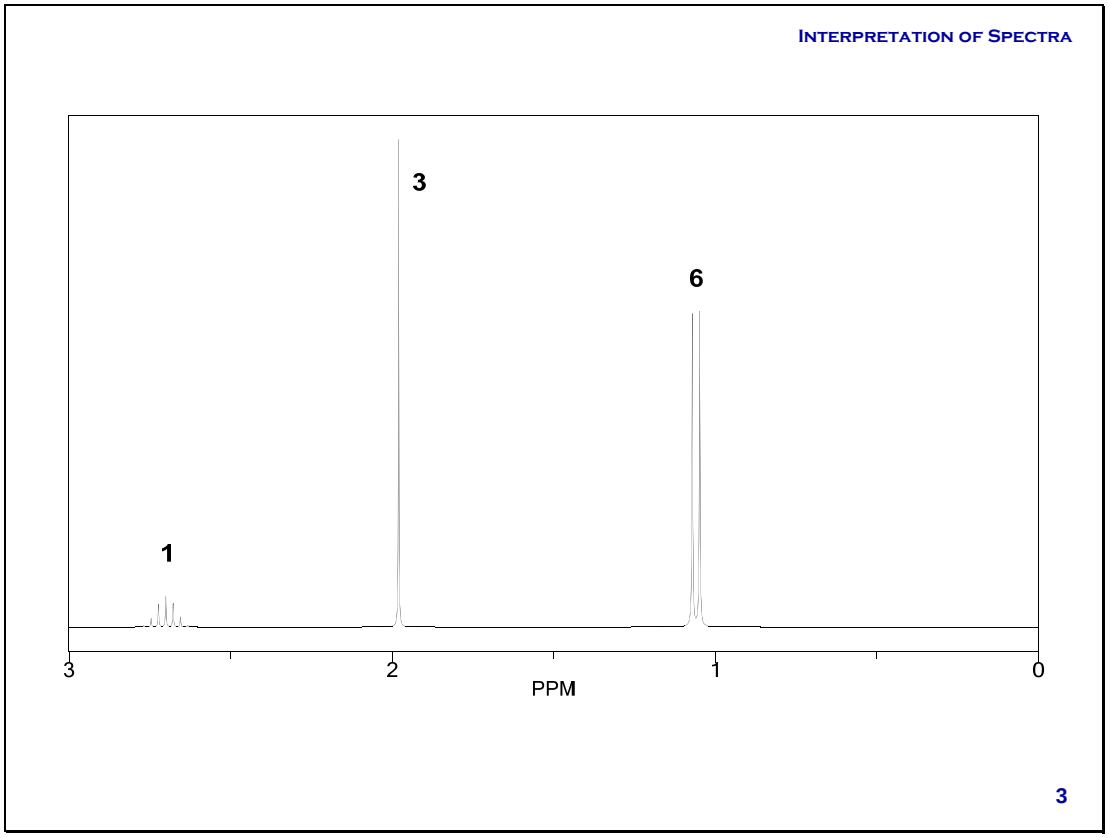
MF: $C_5H_{10}O$



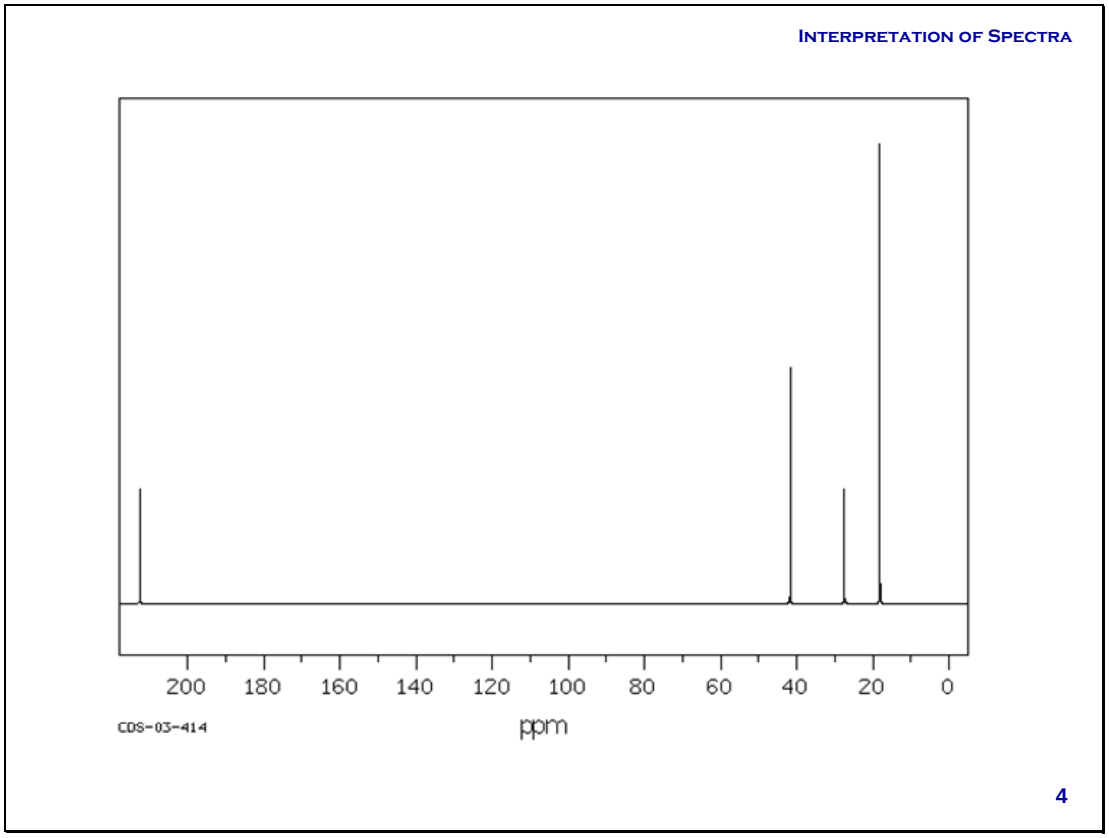
Unknown 37: IR



Unknown 37: NMR

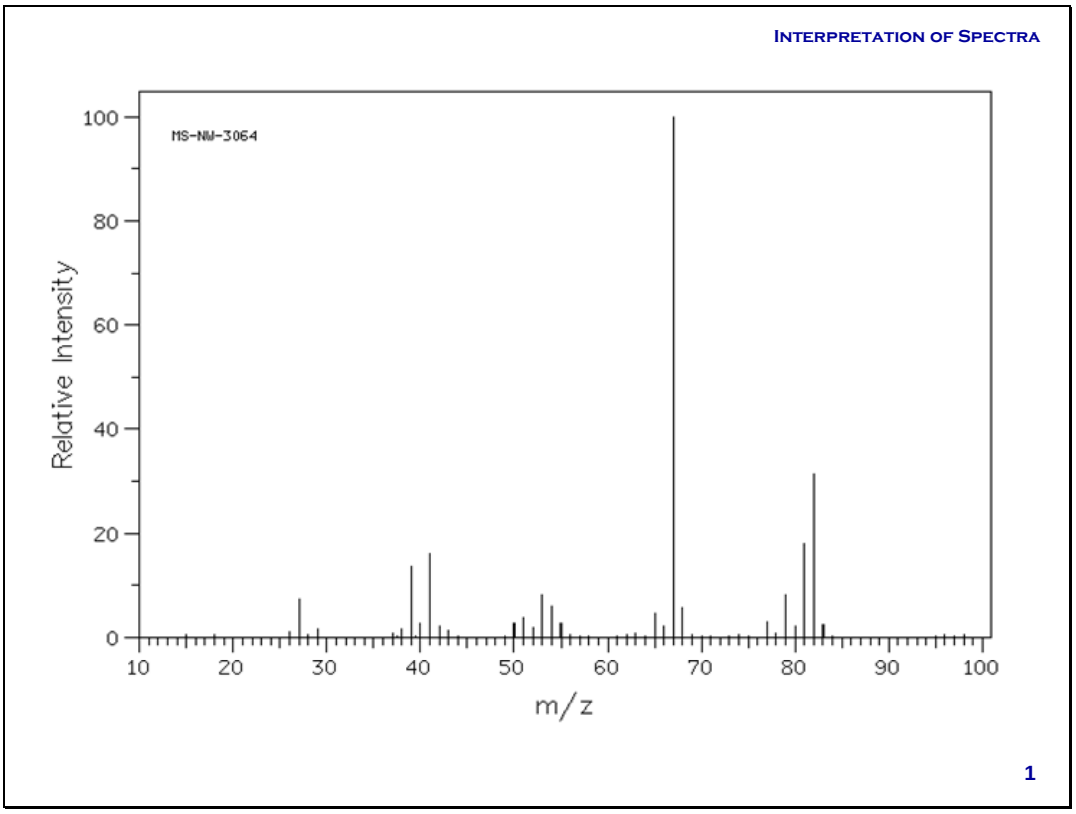


Unknown 37: CNMR

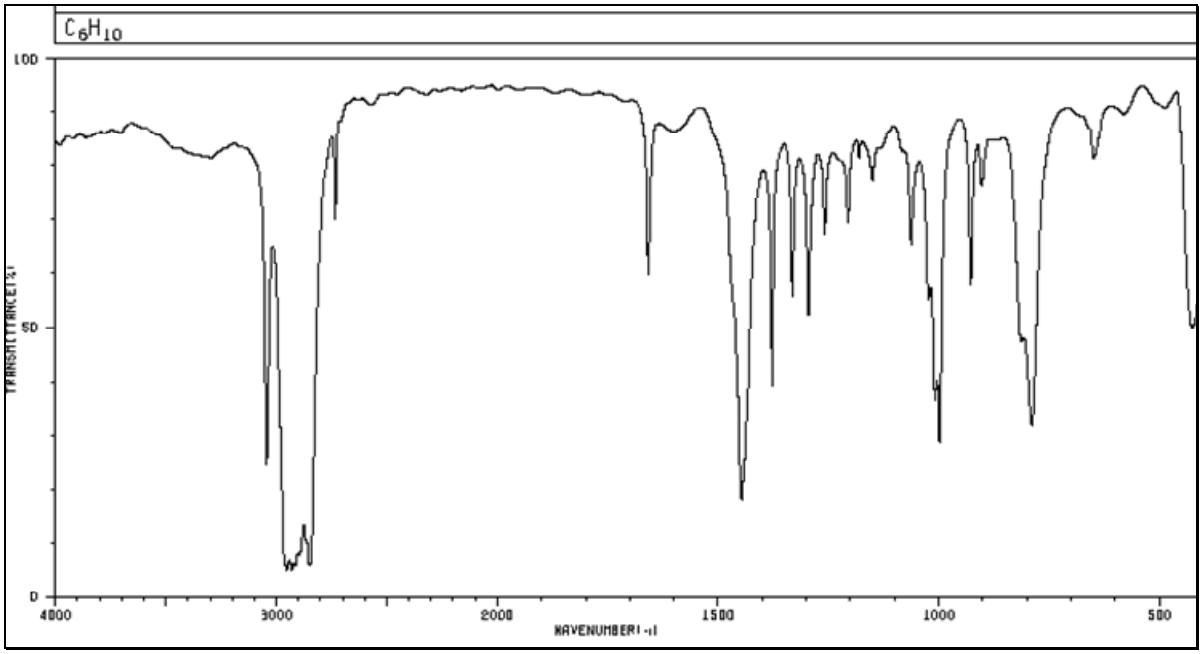


Unknown 38: MS

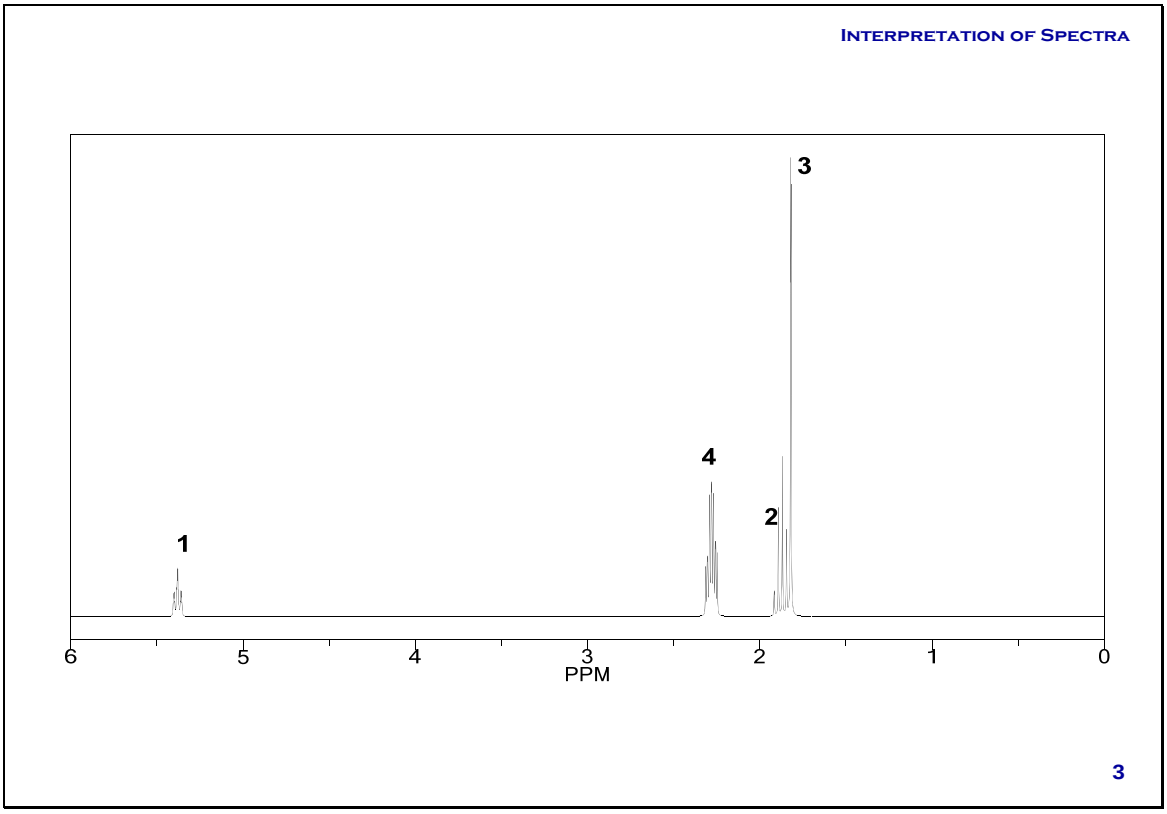
MF: C_6H_{10}



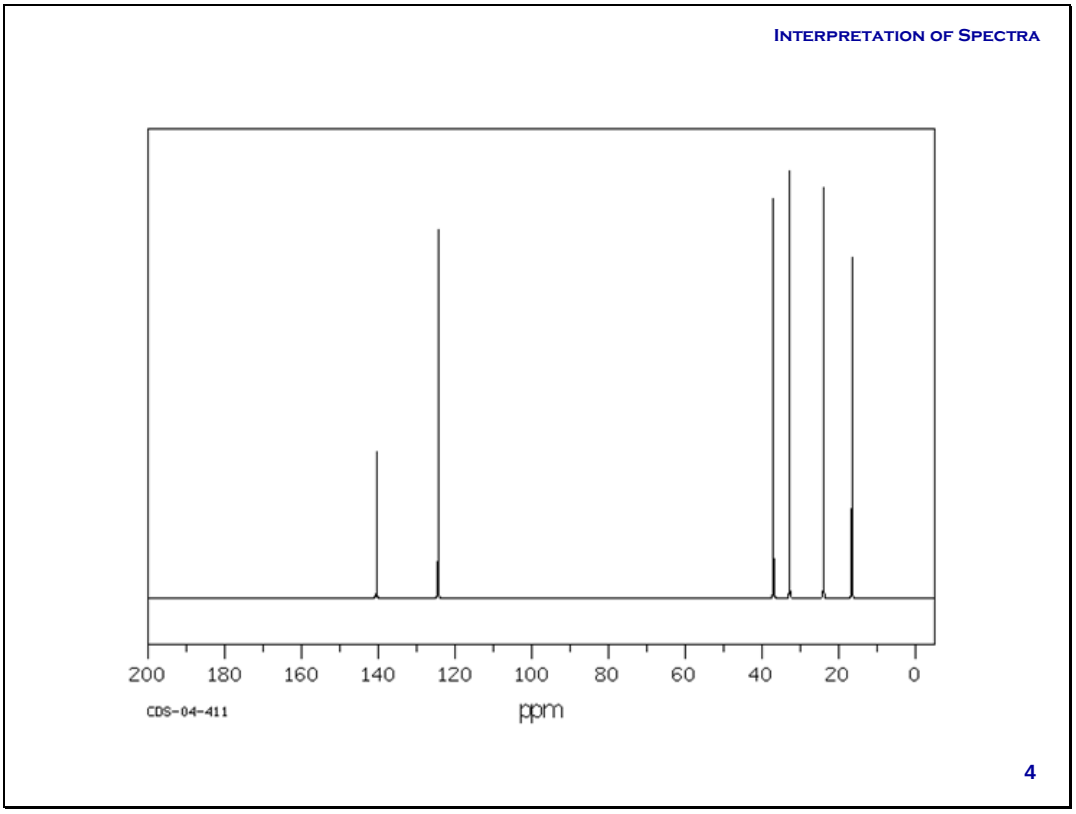
Unknown 38: IR



Unknown 38: NMR

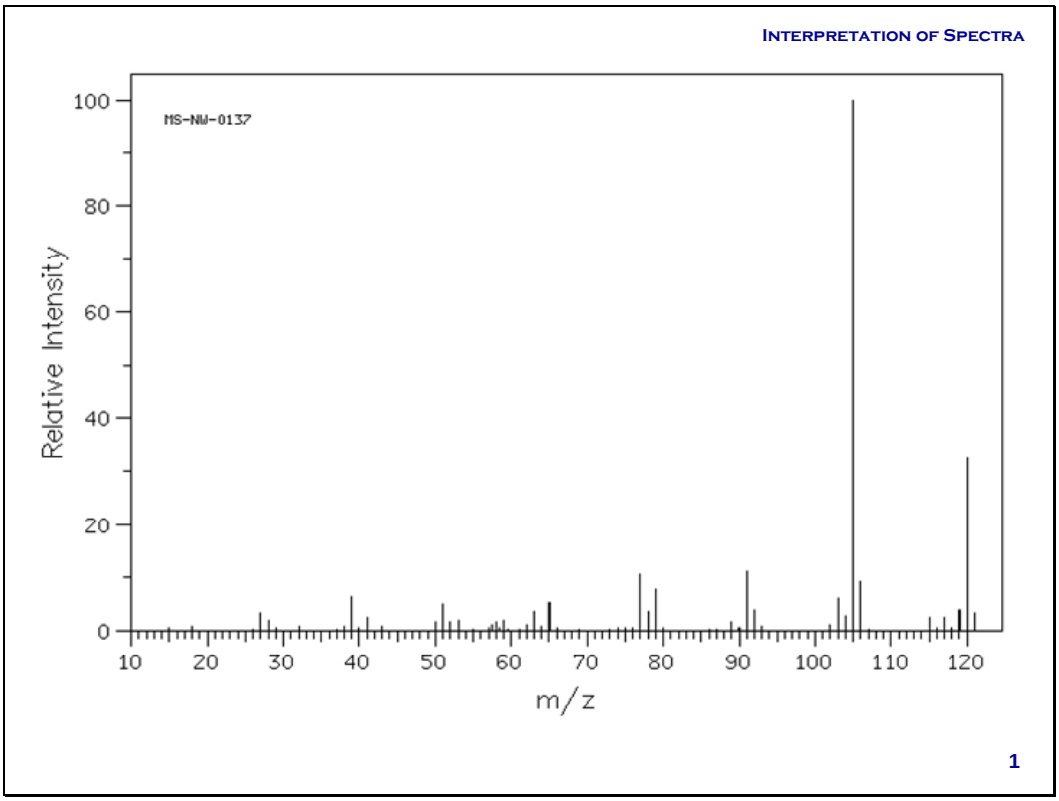


Unknown 38: CNMR

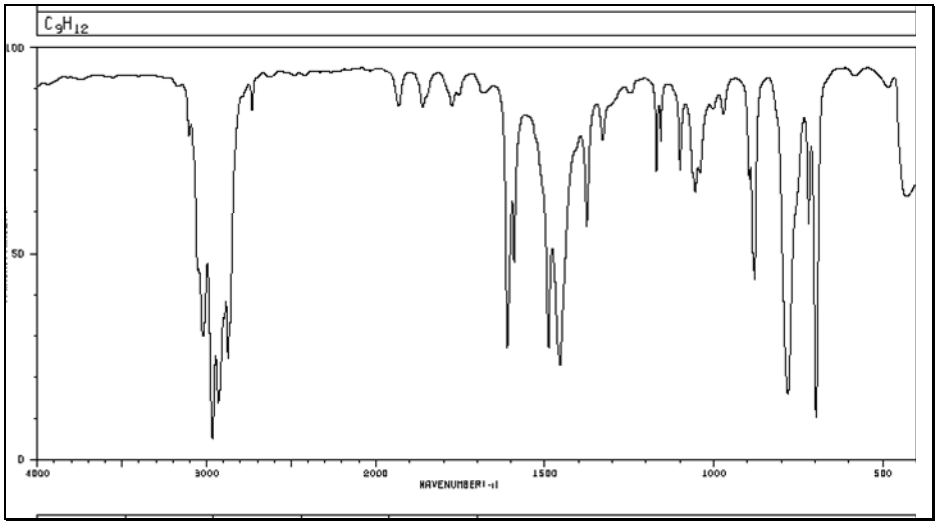


Unknown 39: MS

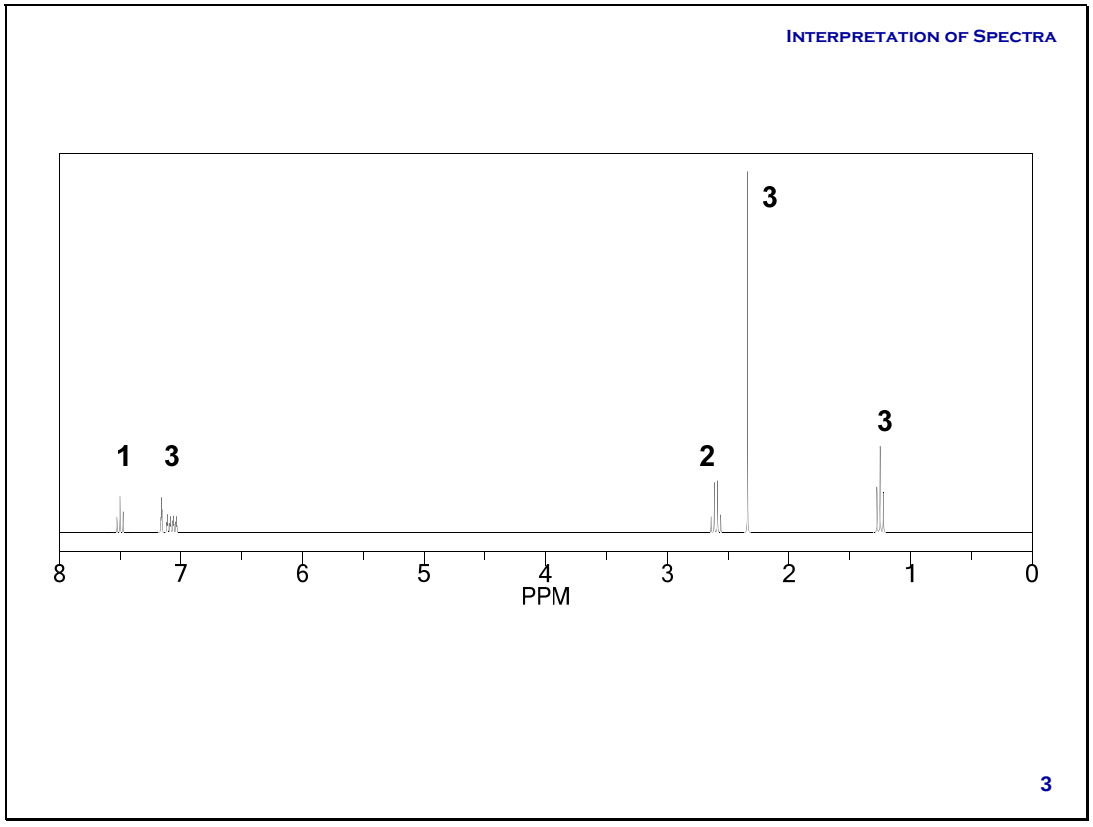
MF: C_9H_{12}



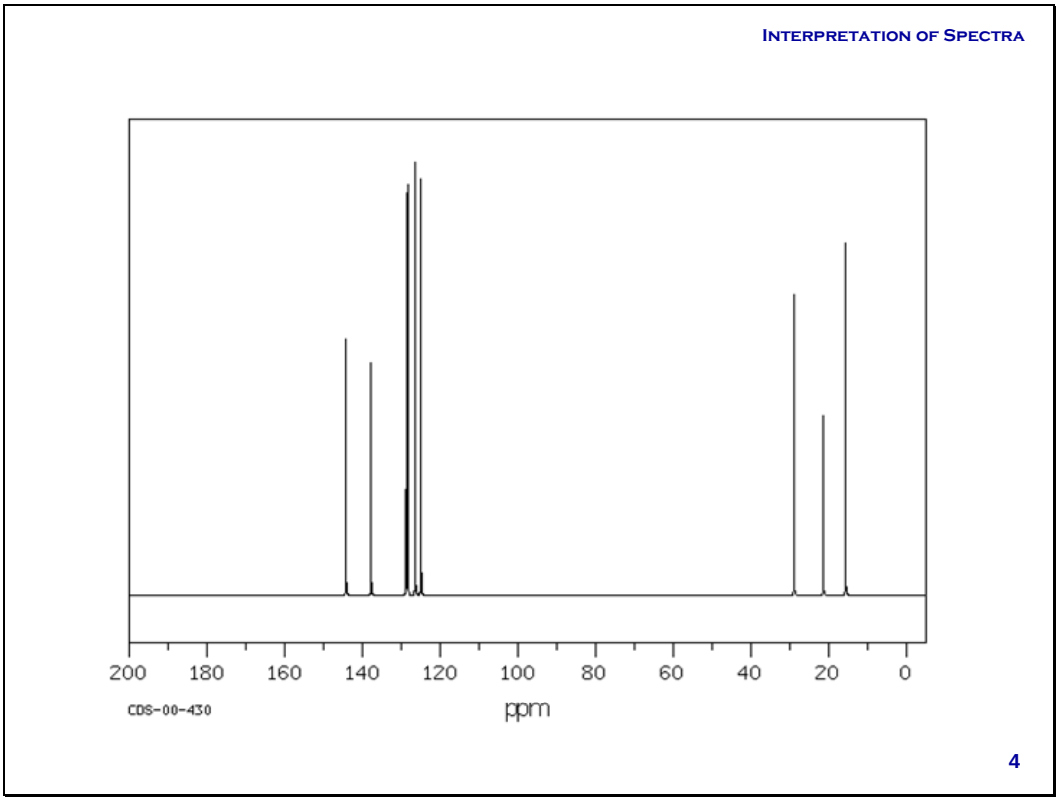
Unknown 39: IR



Unknown 39: NMR

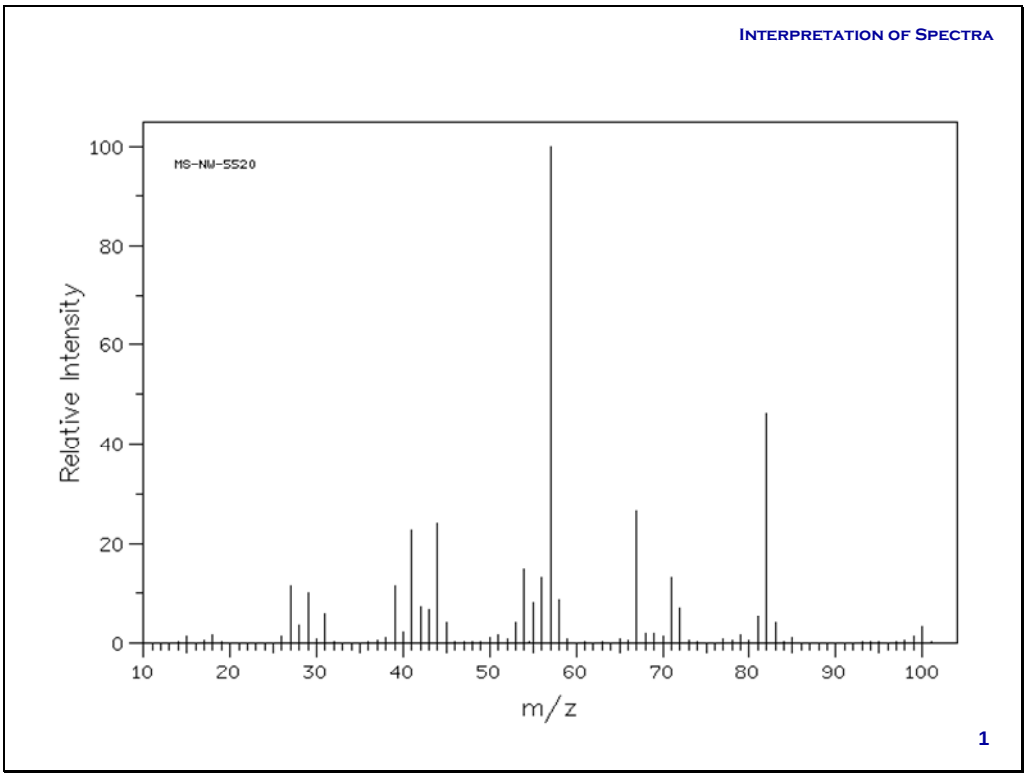


Unknown 39: CNMR

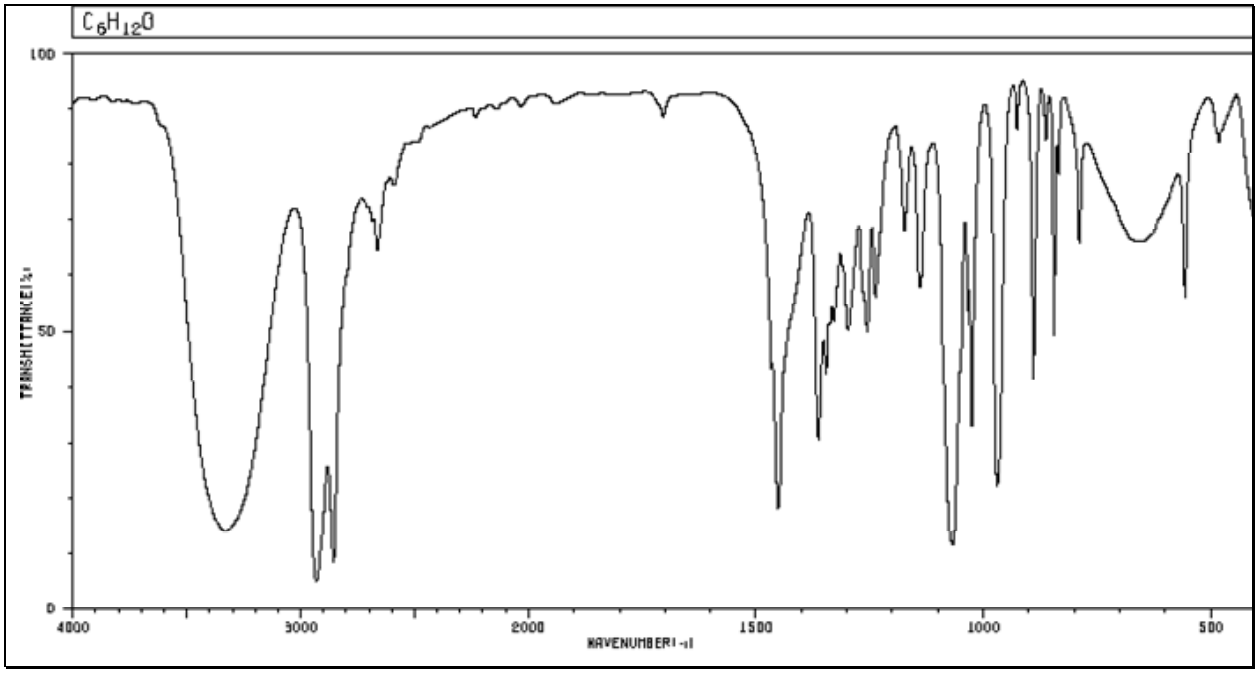


Unknown 40: MS

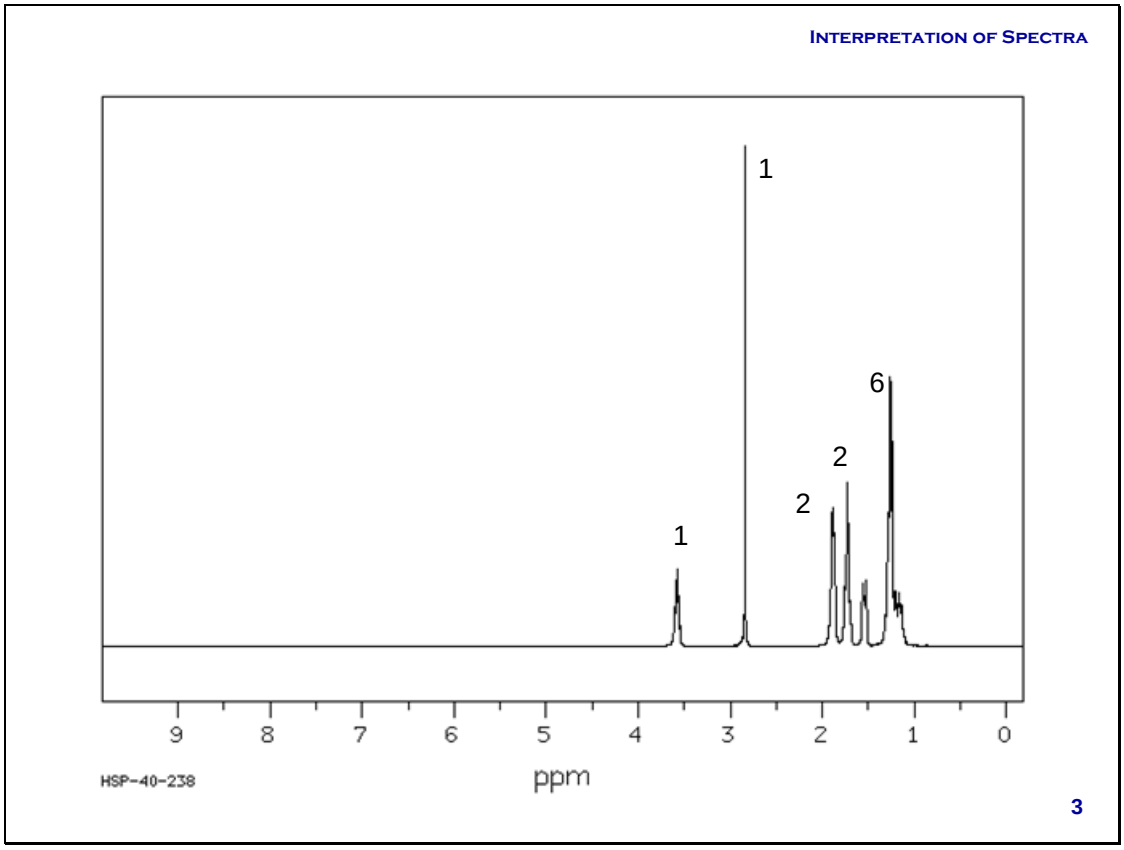
MF: $C_6H_{12}O$



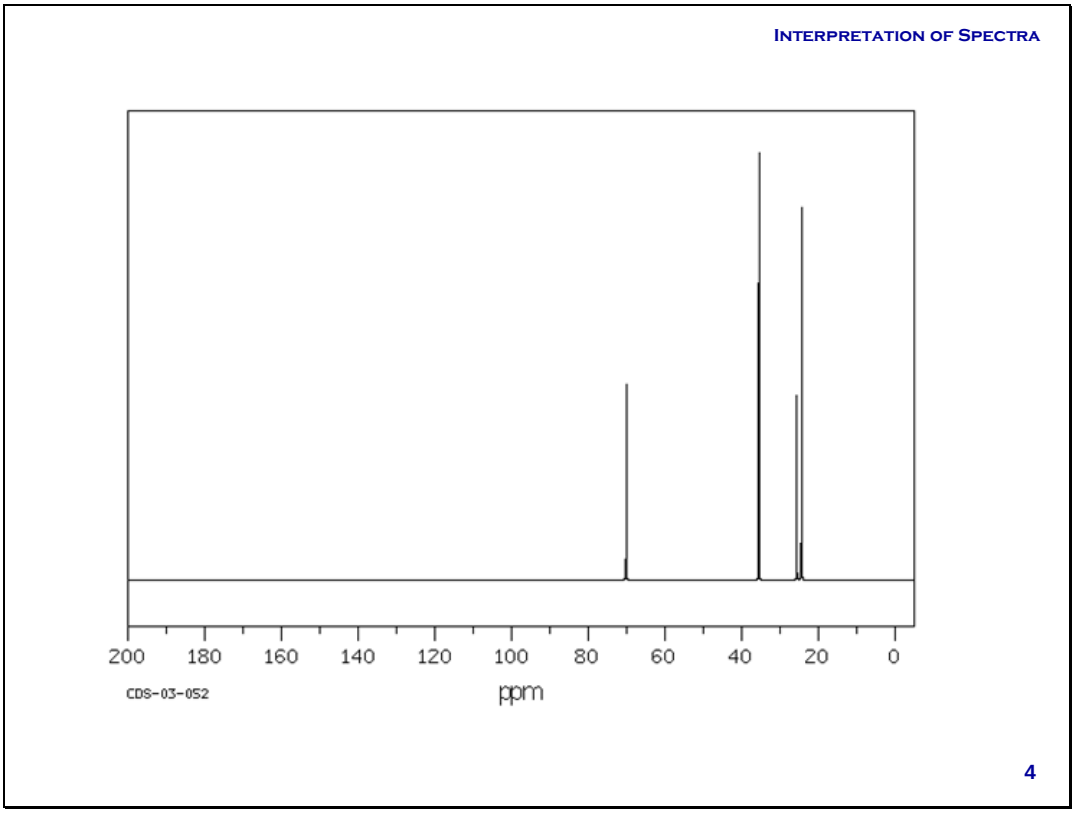
Unknown 40: IR



Unknown 40: NMR

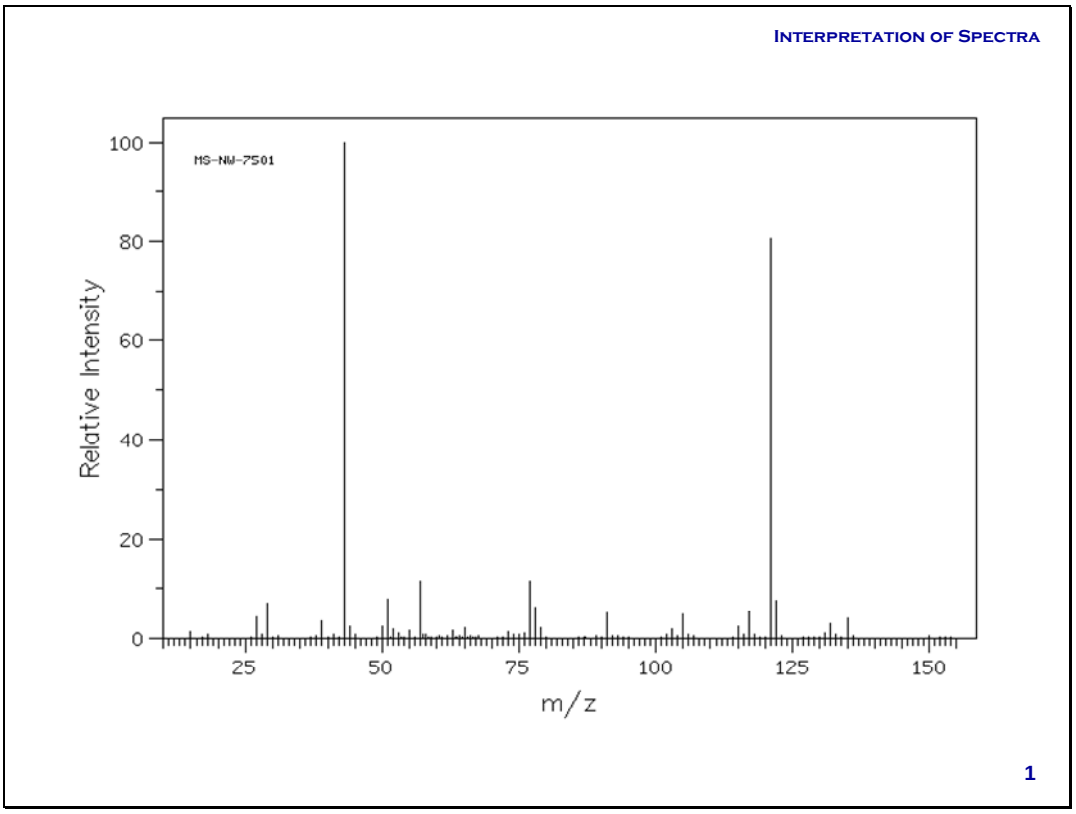


Unknown 40: CNMR

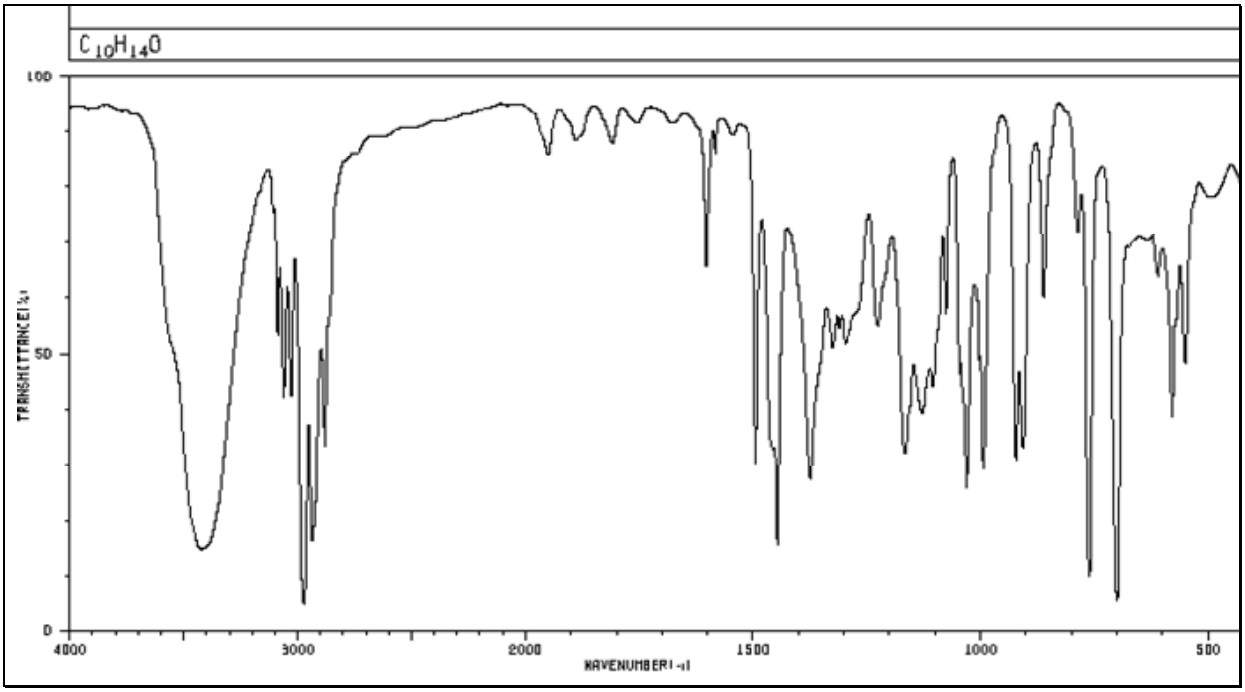


Unknown 41: MS

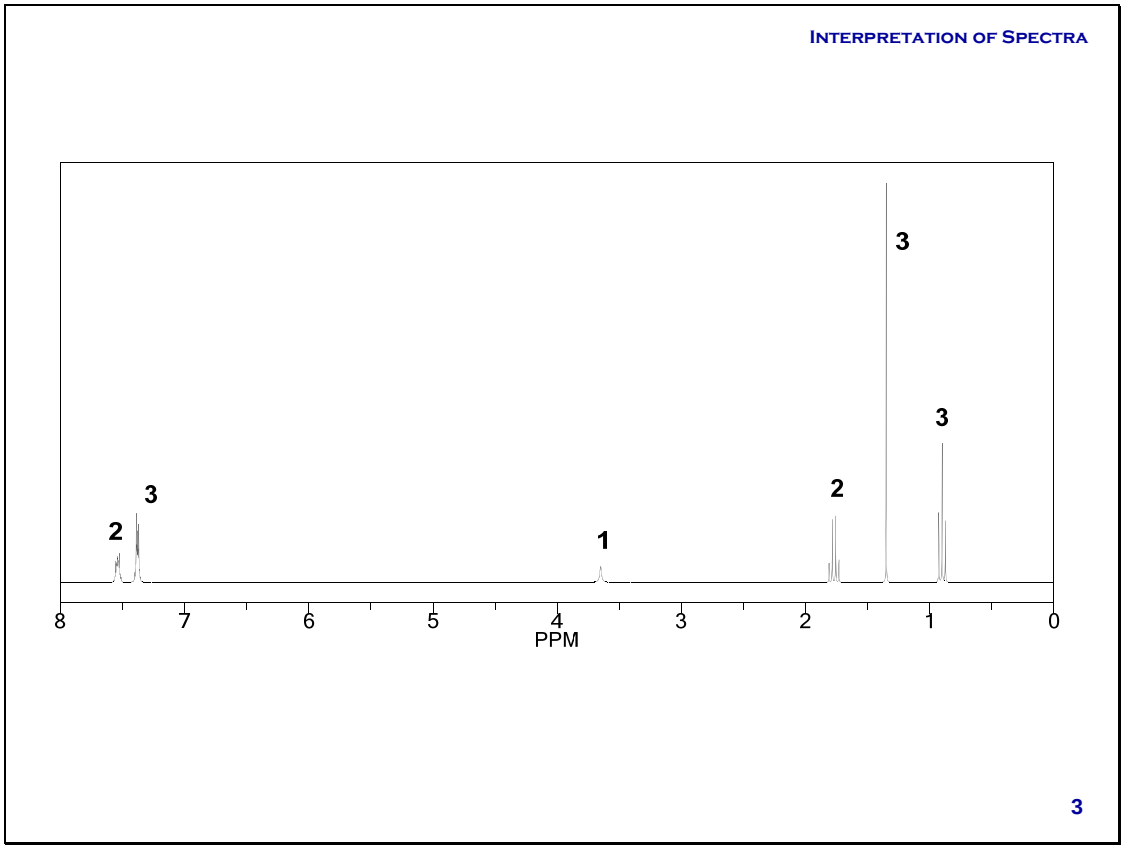
MF: $C_{10}H_{14}O$



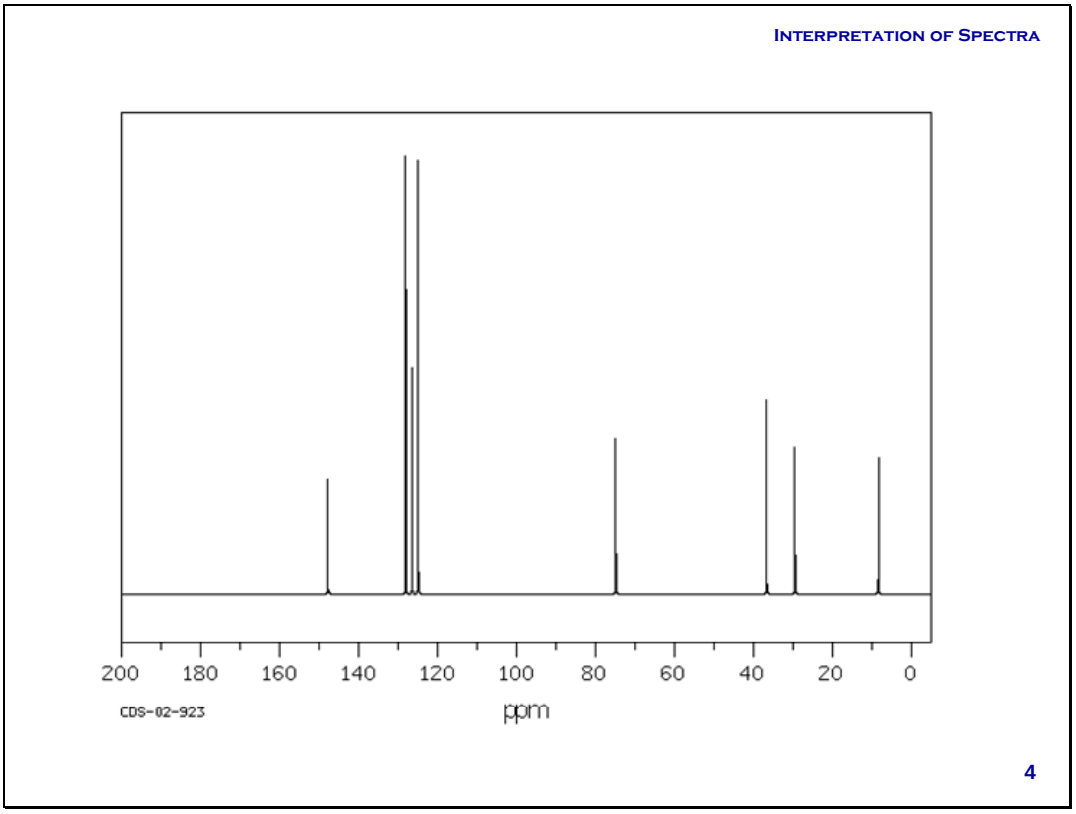
Unknown 41: IR



Unknown 41: NMR

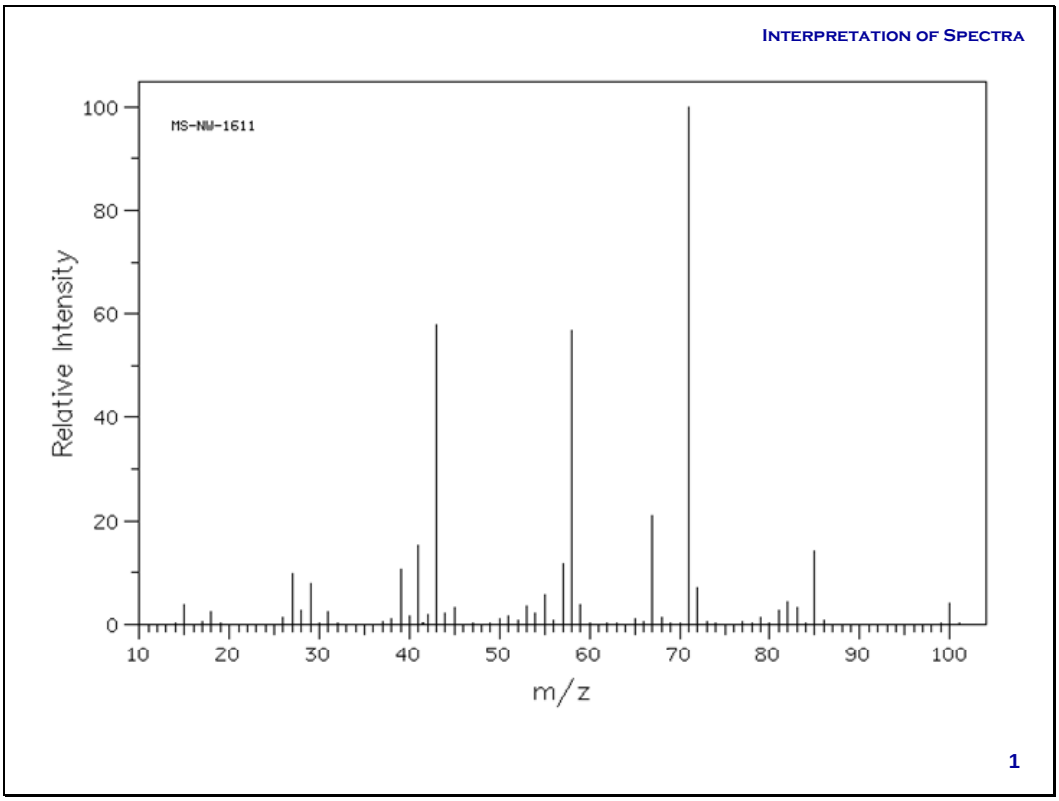


Unknown 41: CNMR

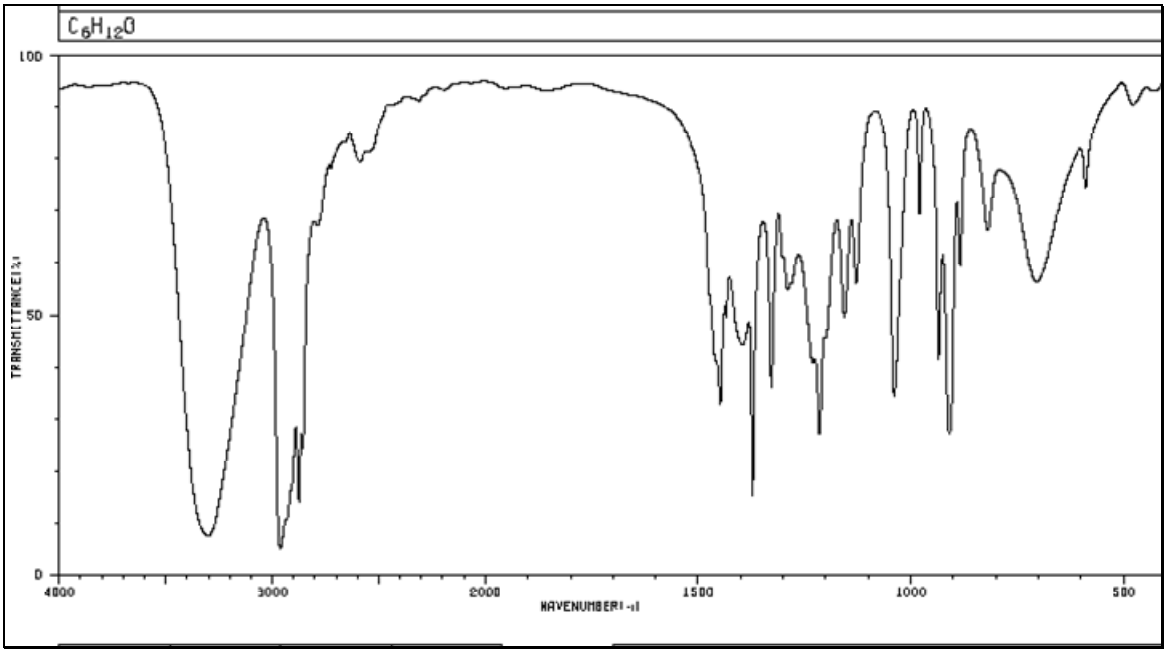


Unknown 42: MS

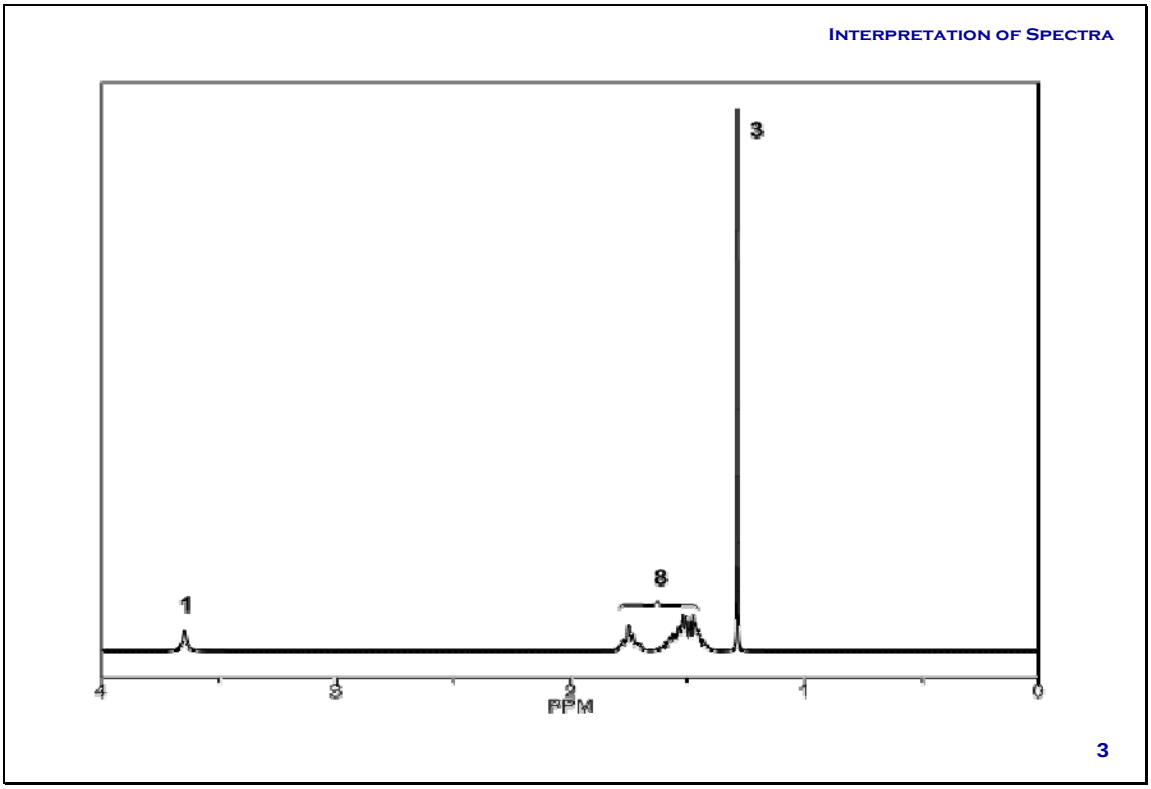
MF: $C_6H_{12}O$



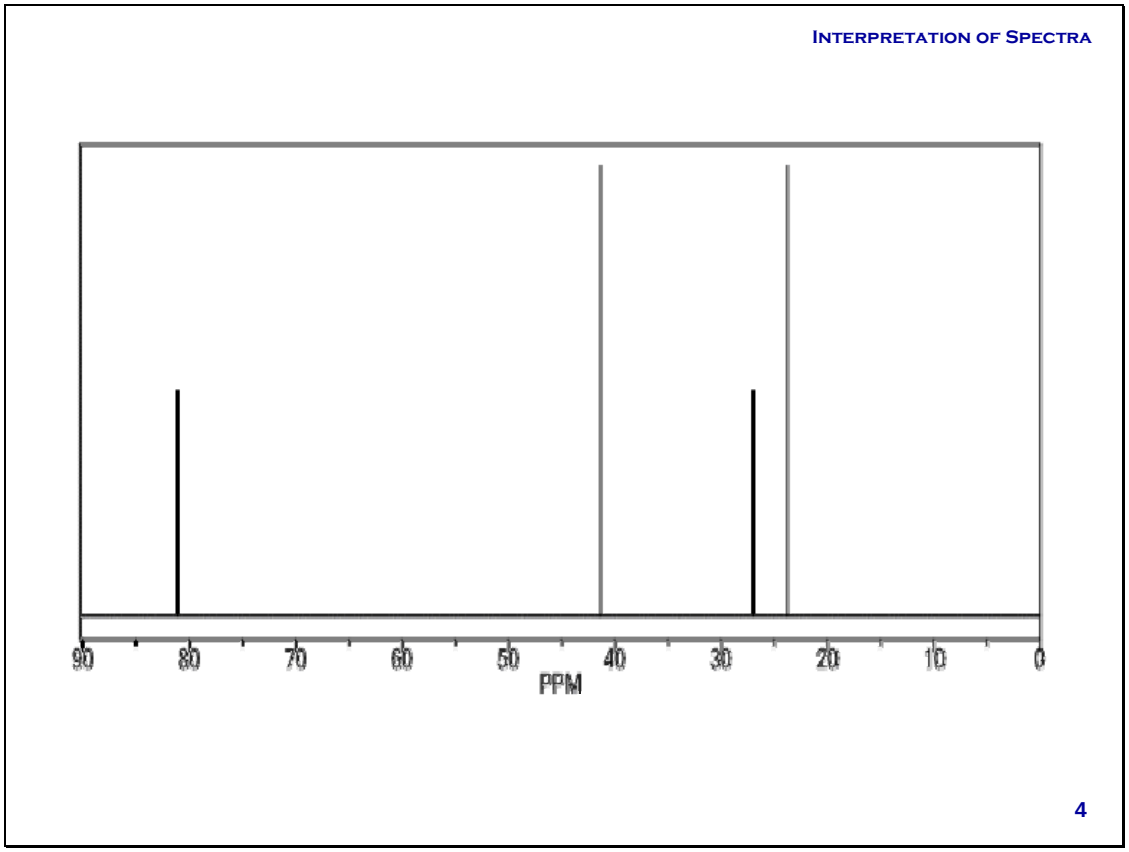
Unknown 42: IR



Unknown 42: NMR

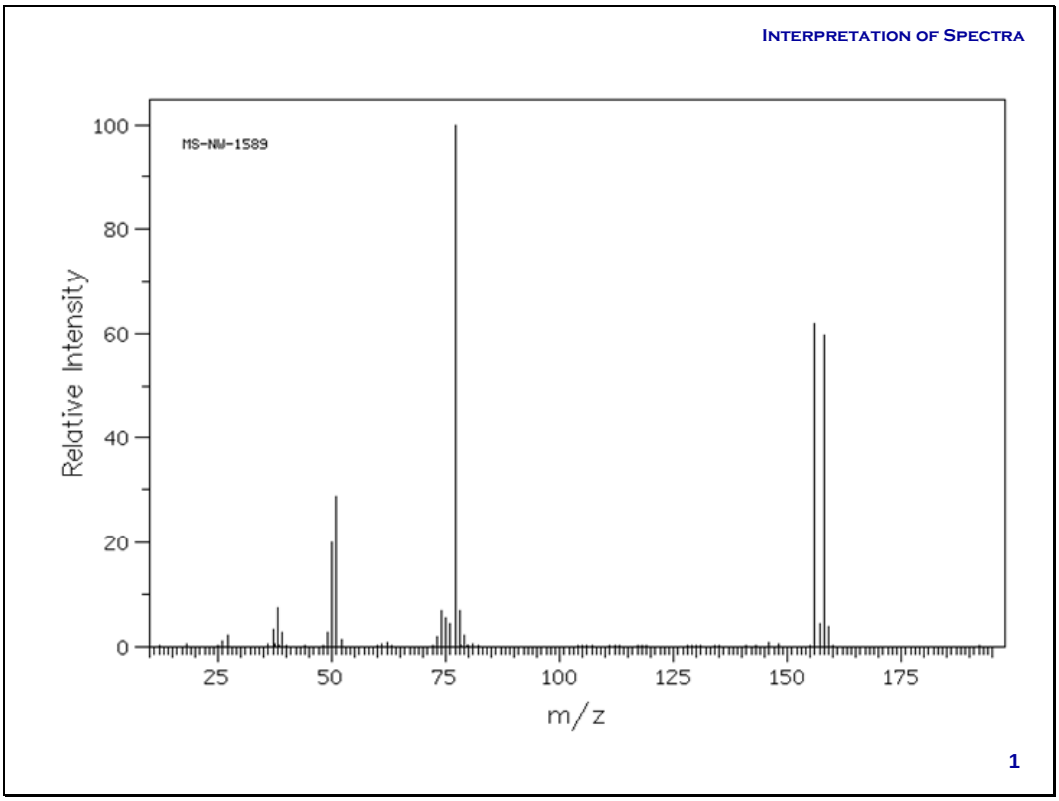


Unknown 42: CNMR

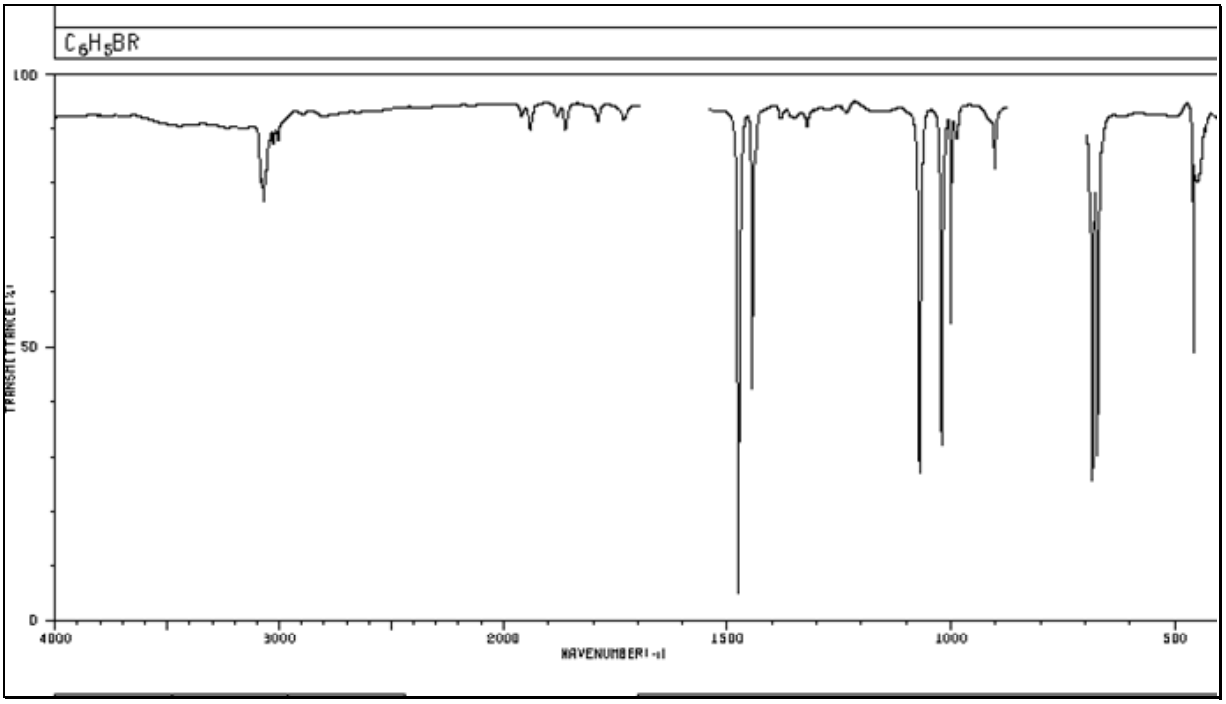


Unknown 43: MS

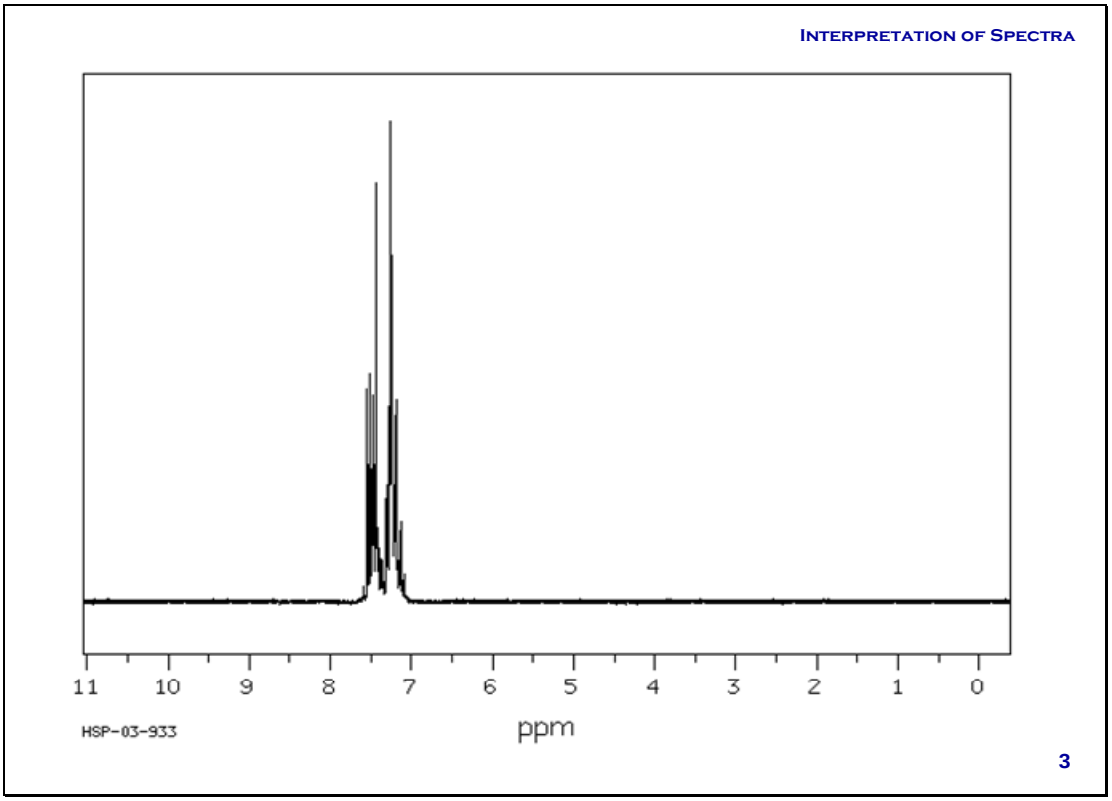
MF: C_6H_5Br



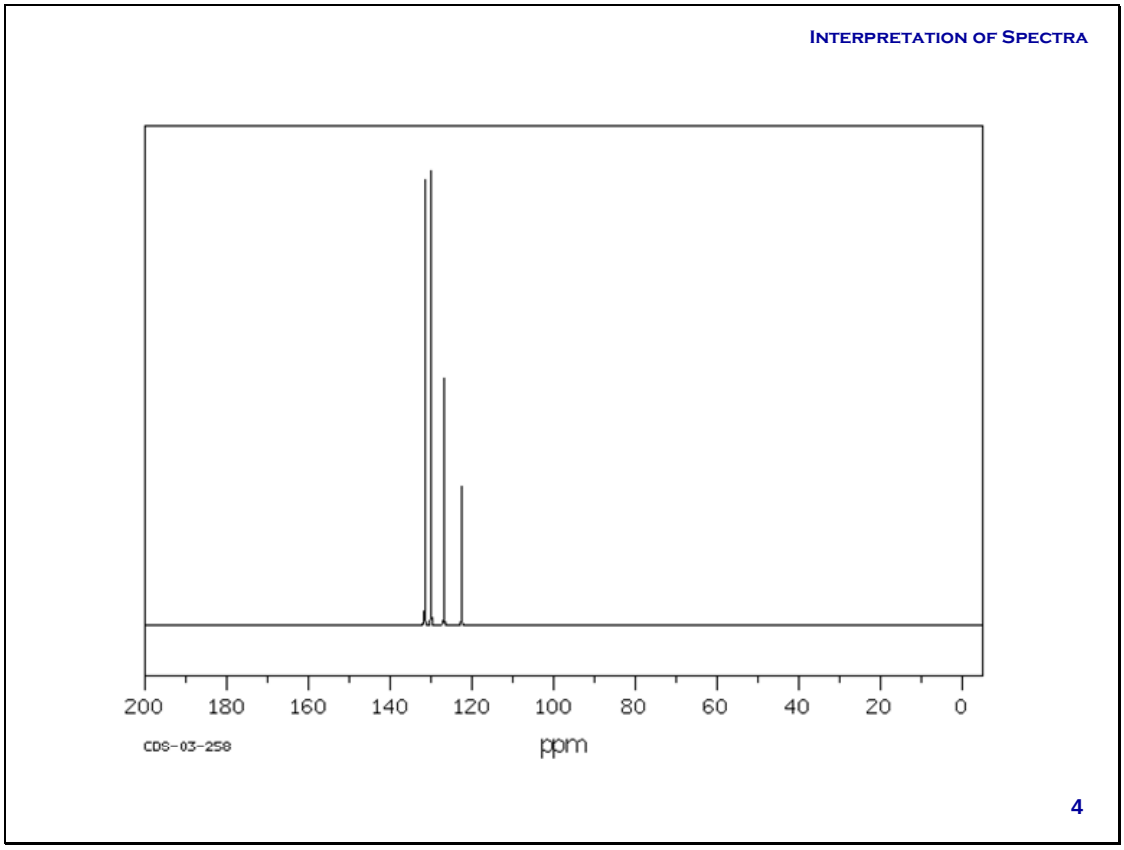
Unknown 43: IR



Unknown 43: NMR

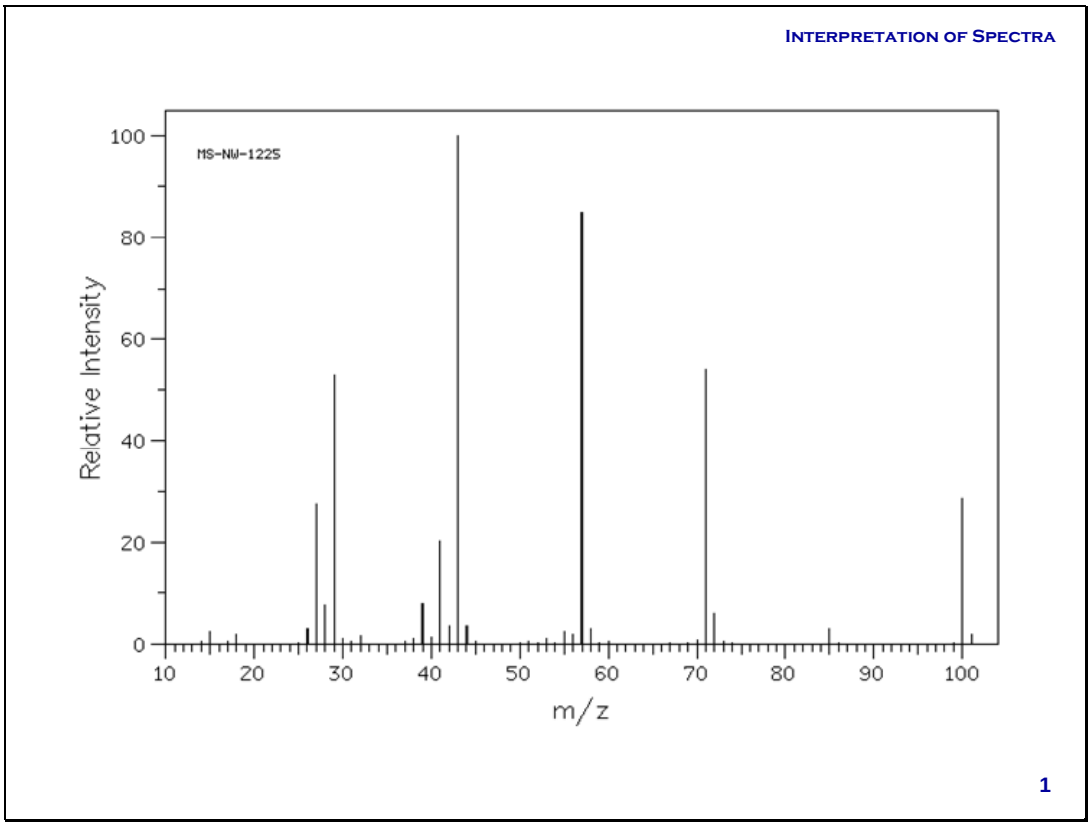


Unknown 43: CNMR

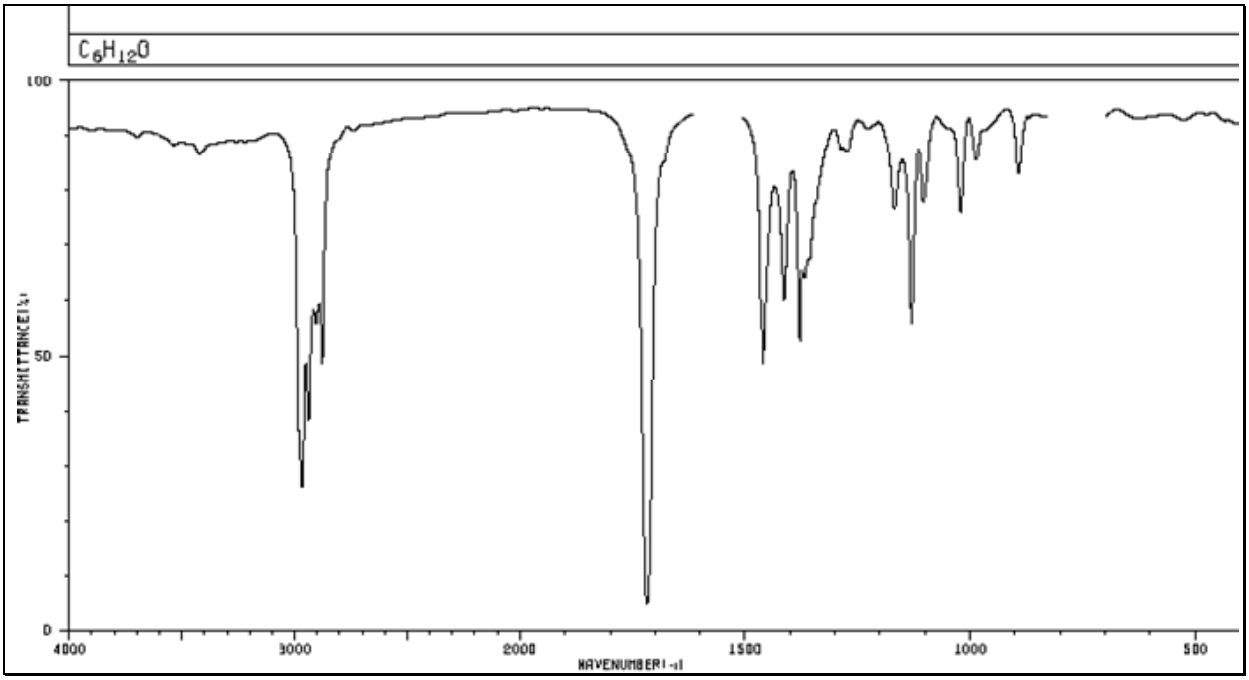


Unknown 44: MS

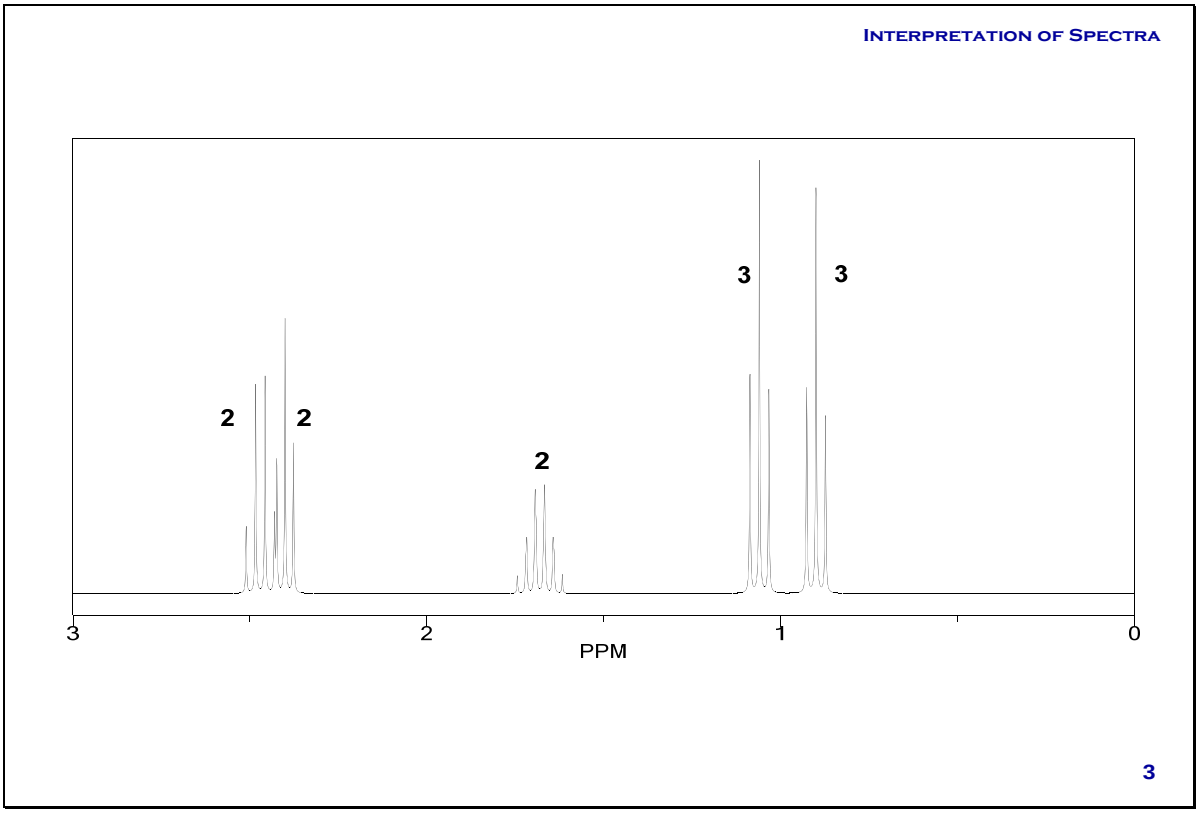
MF: $C_6H_{12}O$



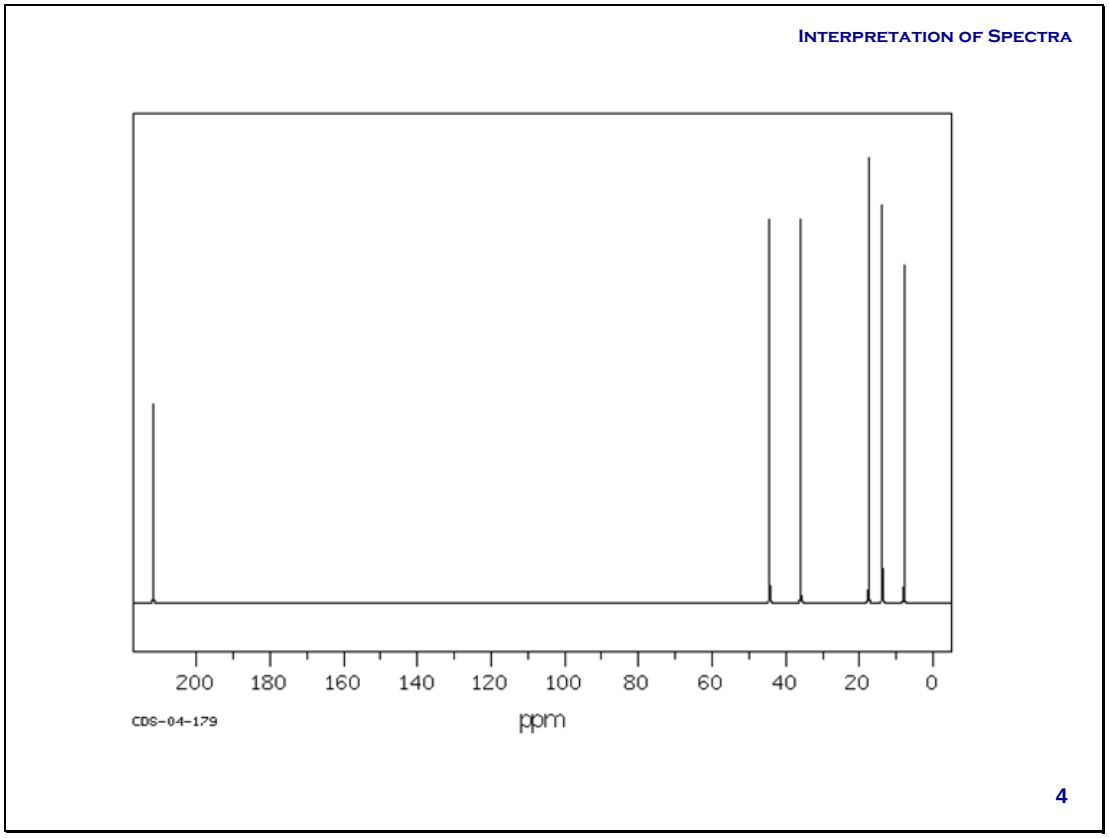
Unknown 44: IR



Unknown 44: NMR

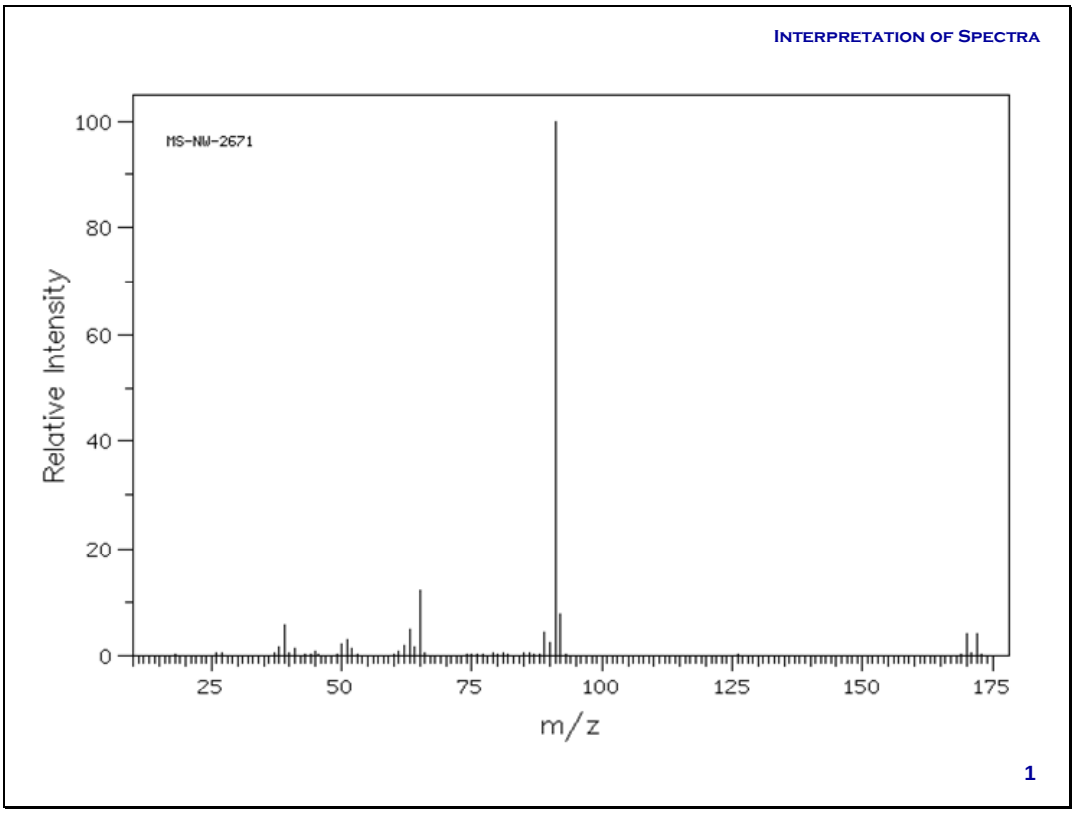


Unknown 44: CNMR

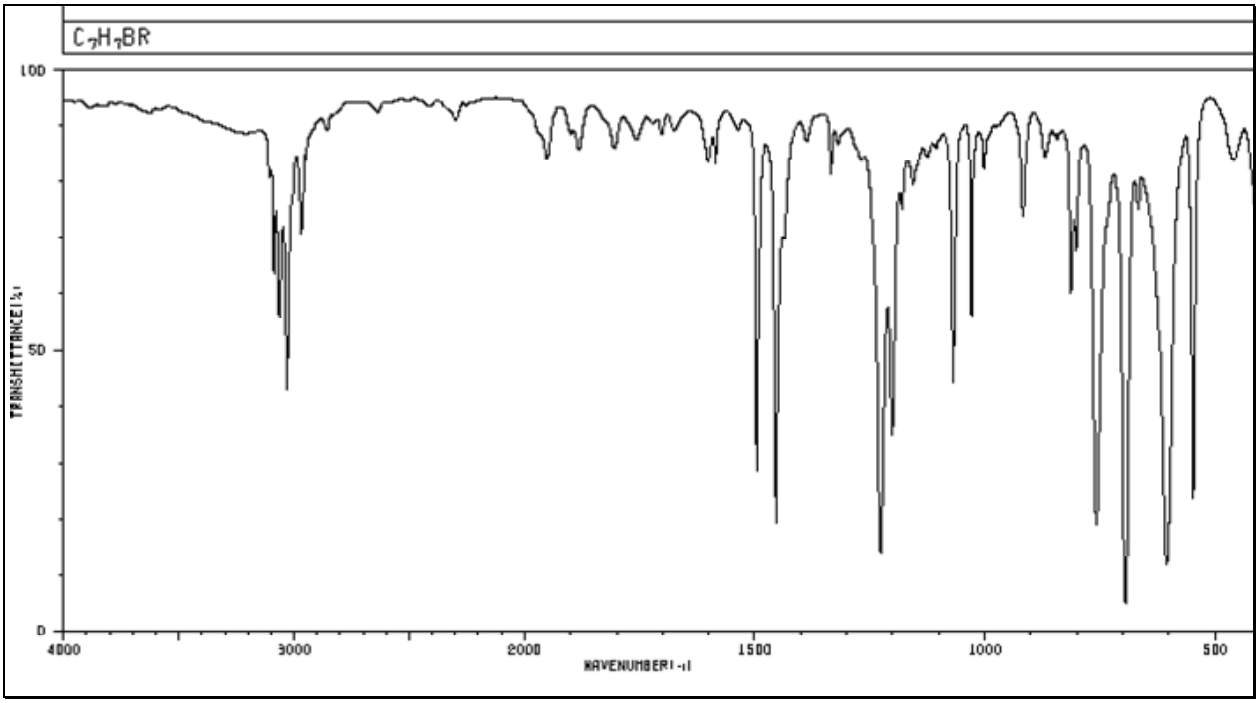


Unknown 45: MS

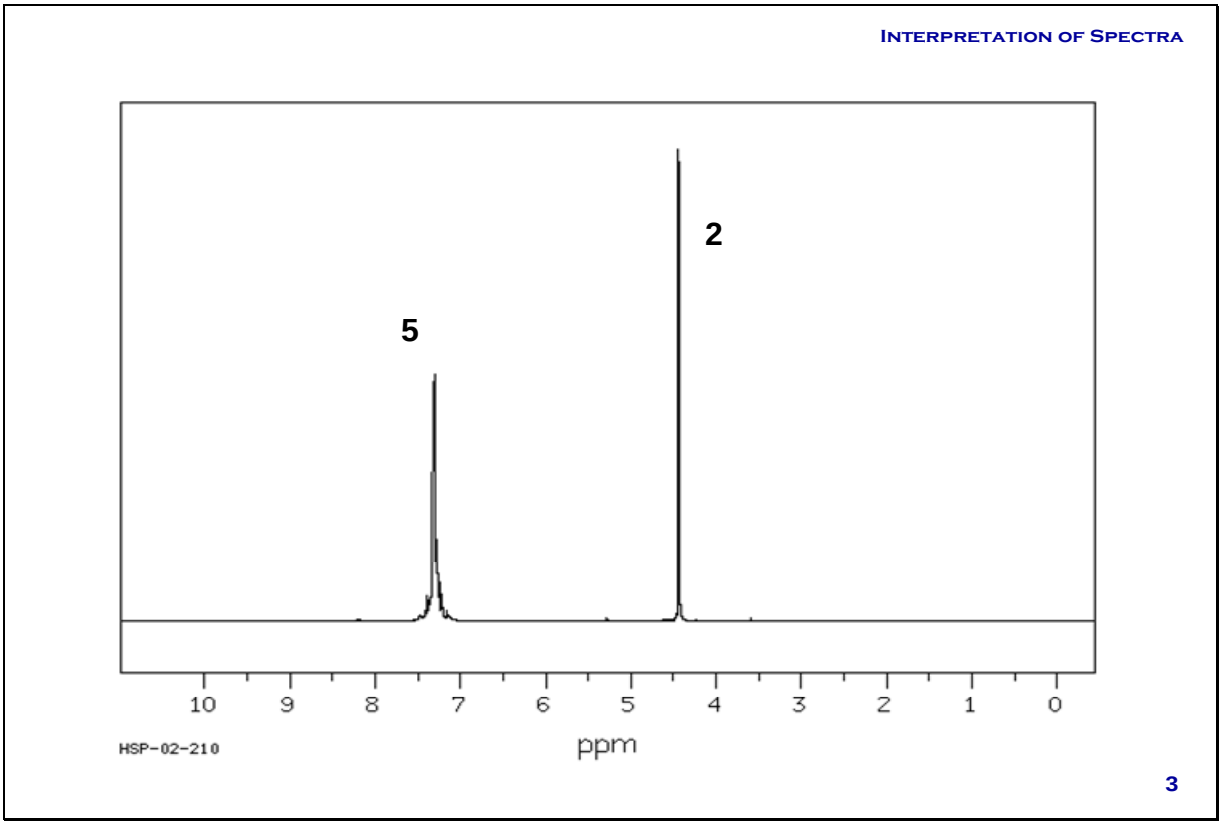
MF: C_7H_7Br



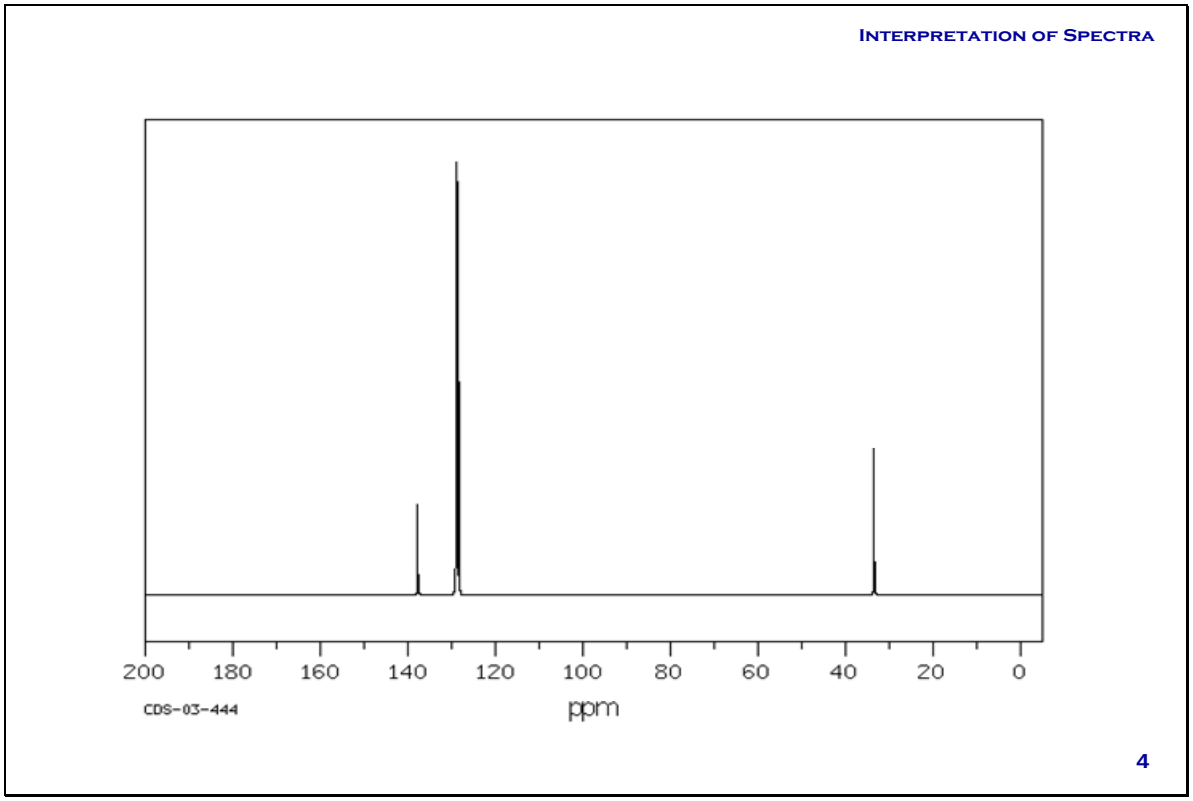
Unknown 45: IR



Unknown 45: NMR

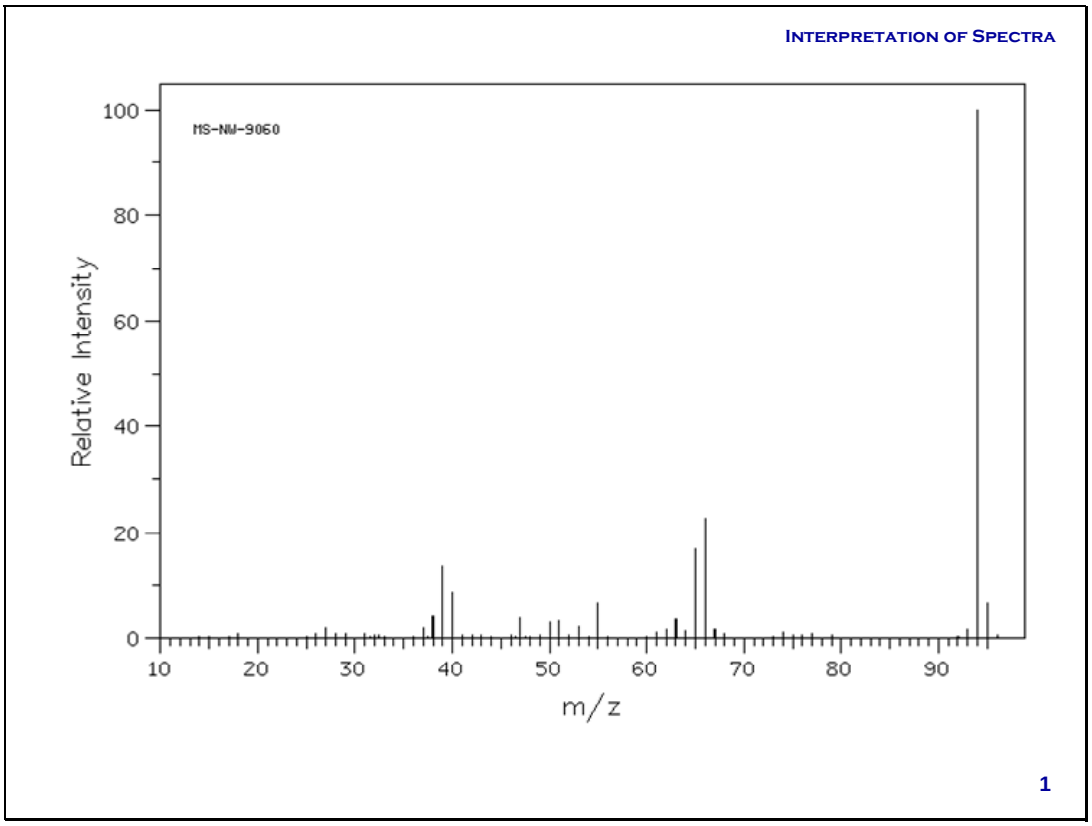


Unknown 45: CNMR

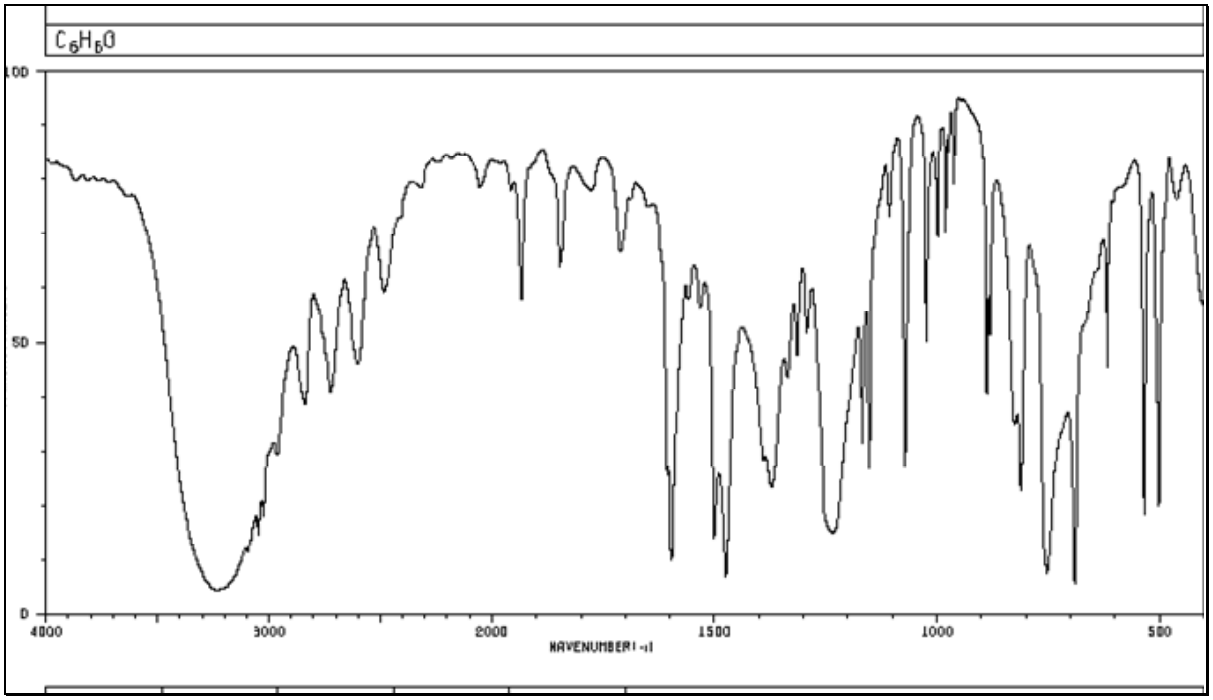


Unknown 46: MS

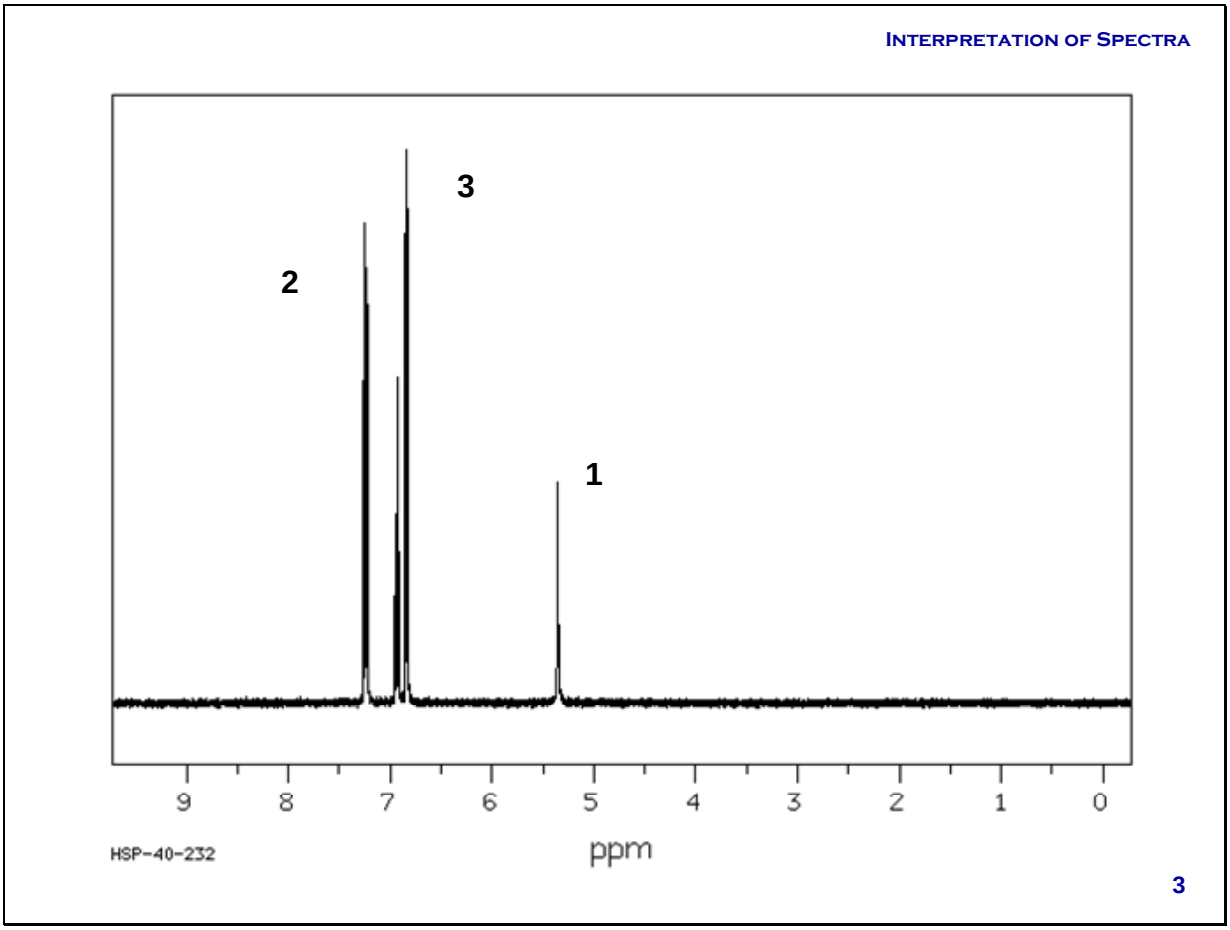
MF: C_6H_6O



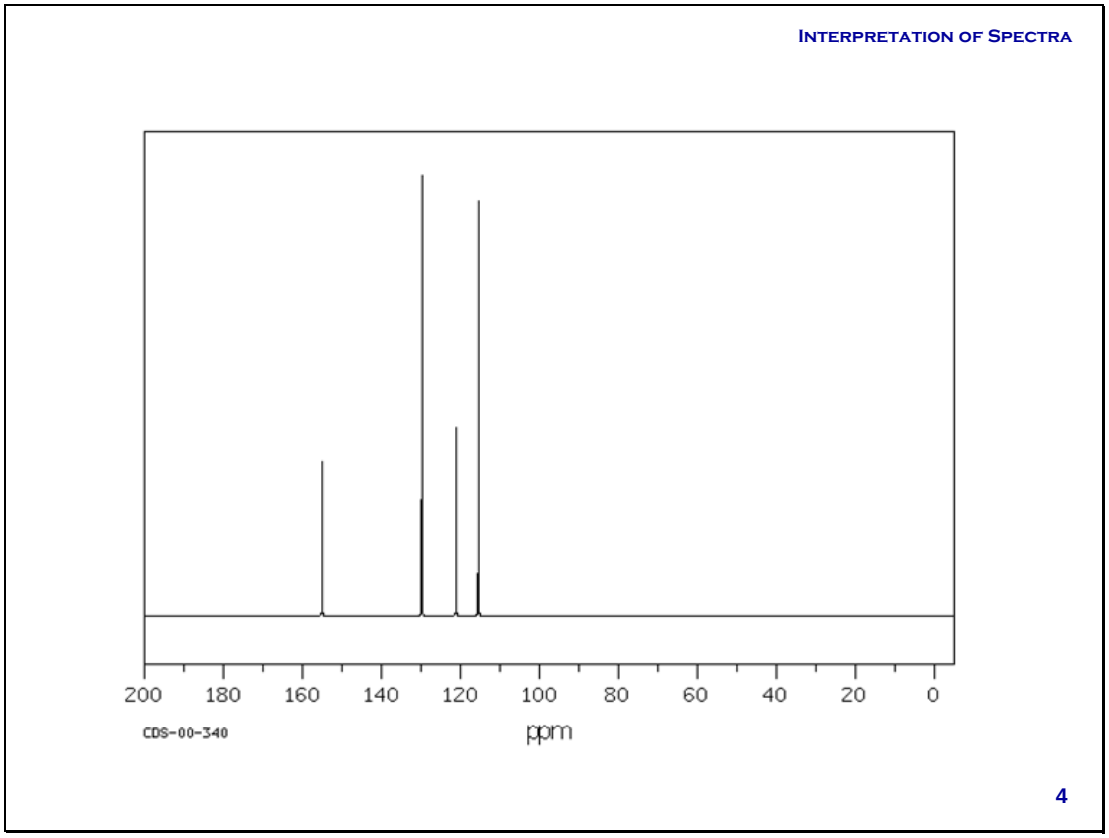
Unknown 46: IR



Unknown 46: NMR

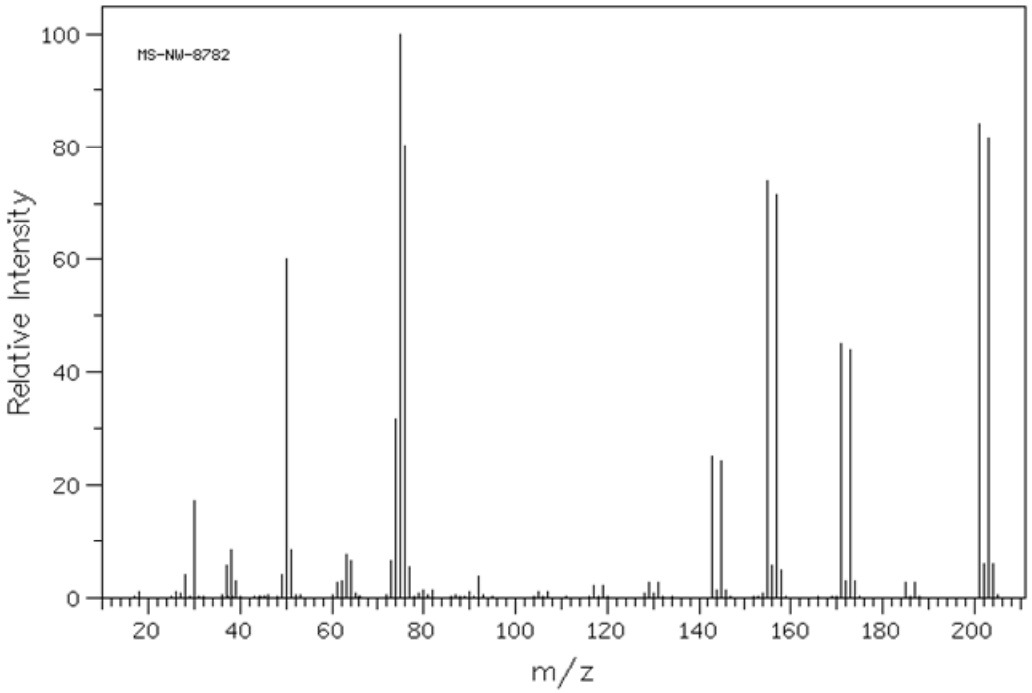


Unknown 46: CNMR



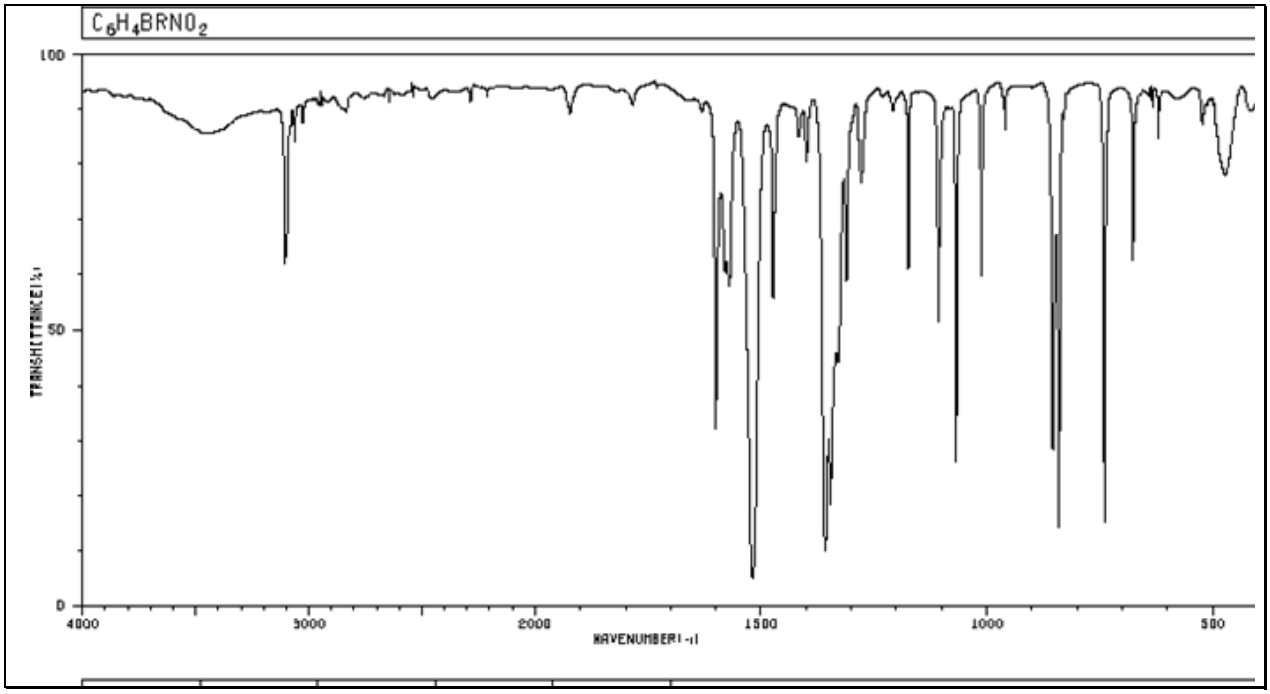
Unknown 47: MS

MF: $C_6H_4BrNO_2$

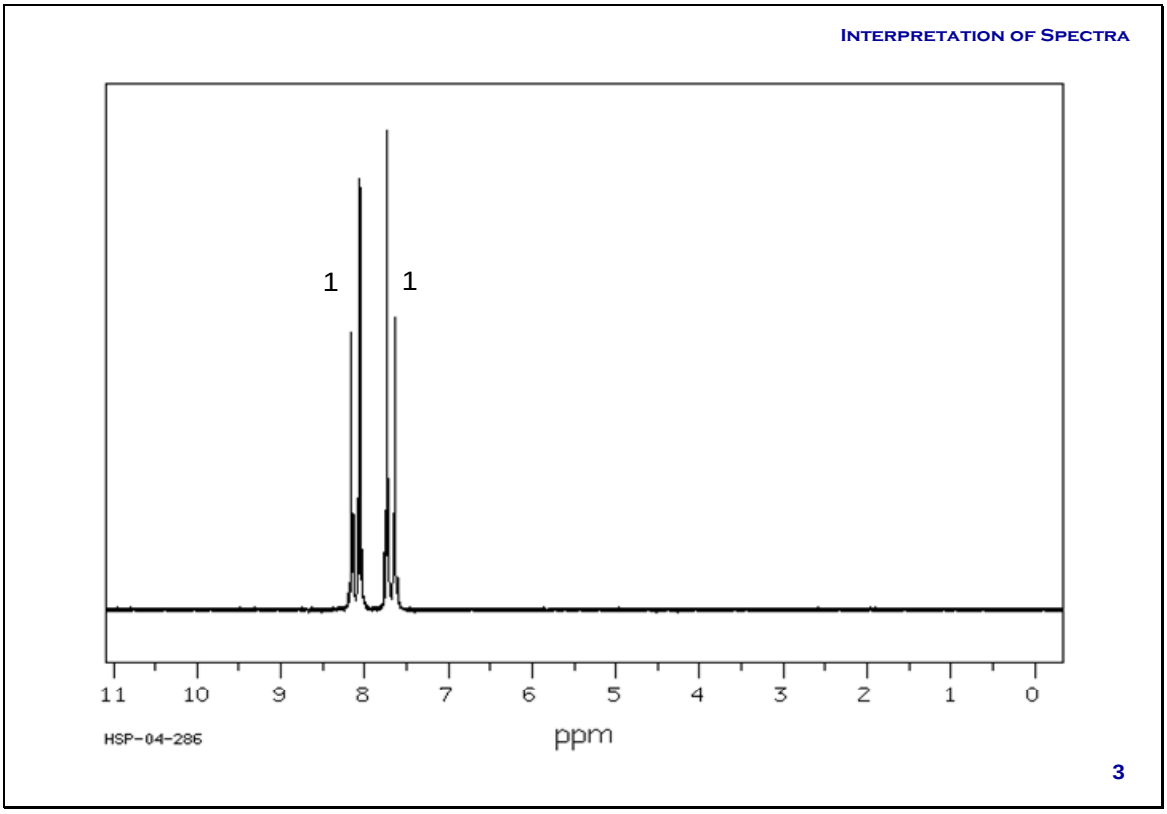


1

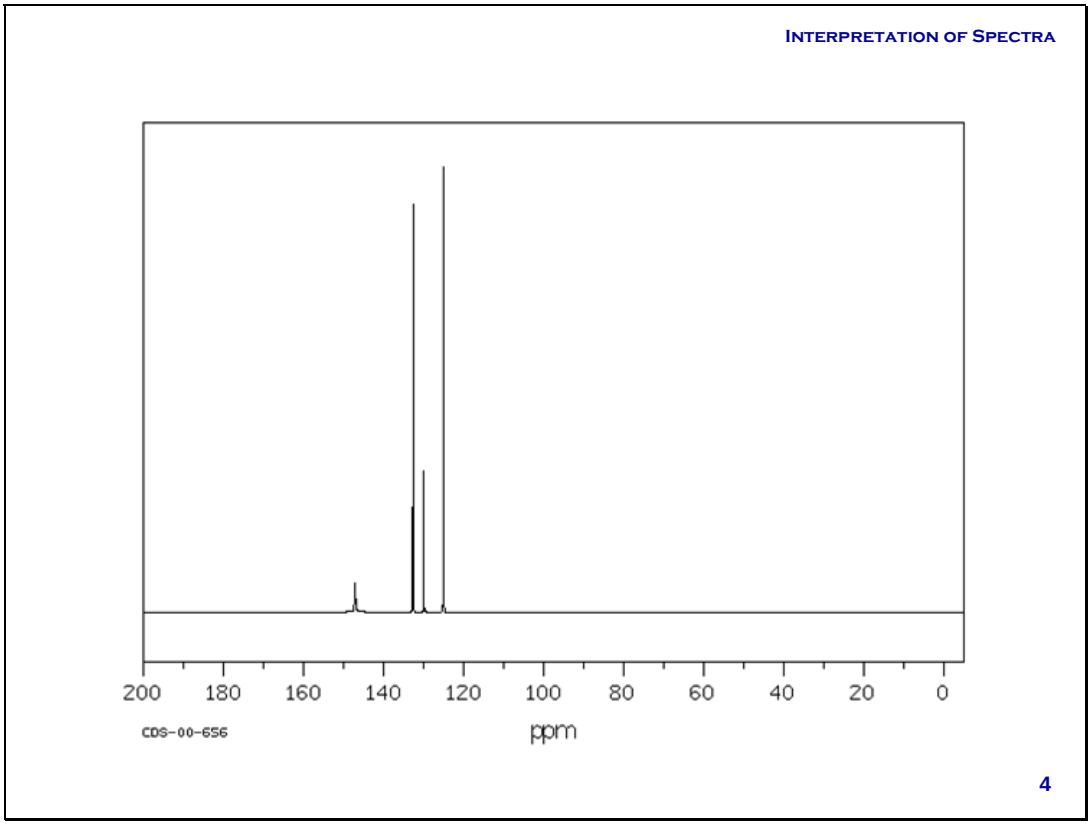
Unknown 47: IR



Unknown 47: NMR

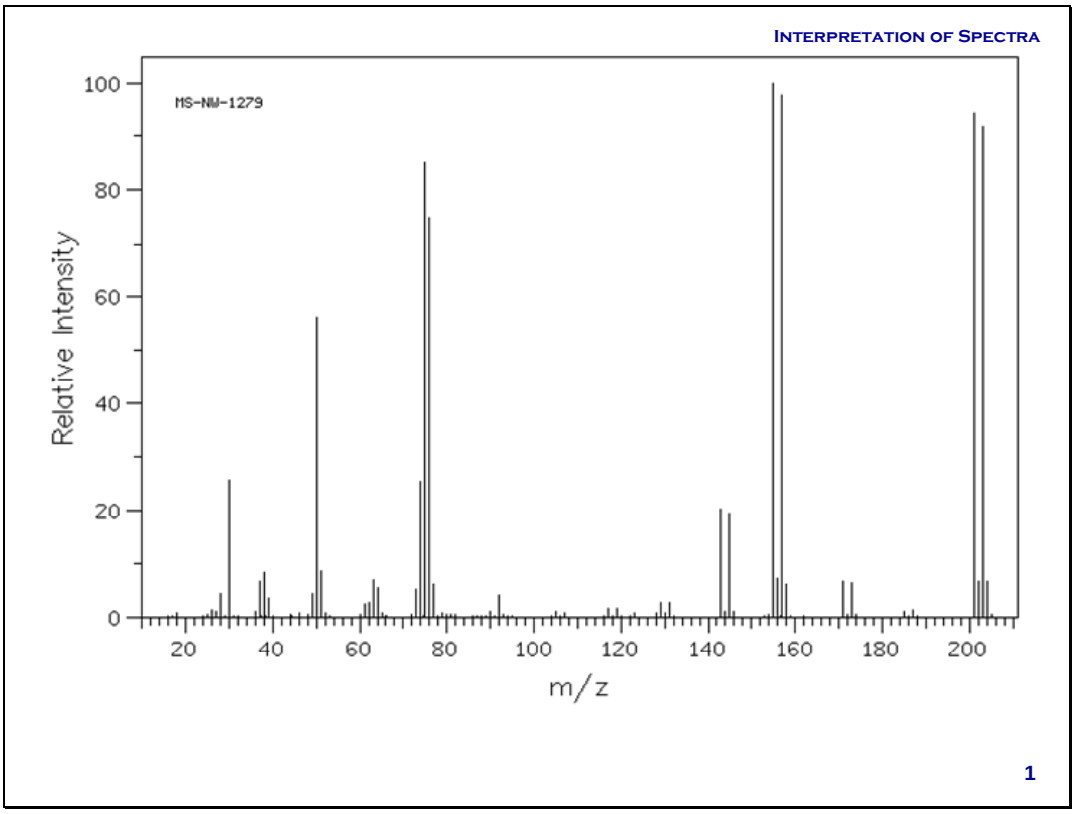


Unknown 47: CNMR

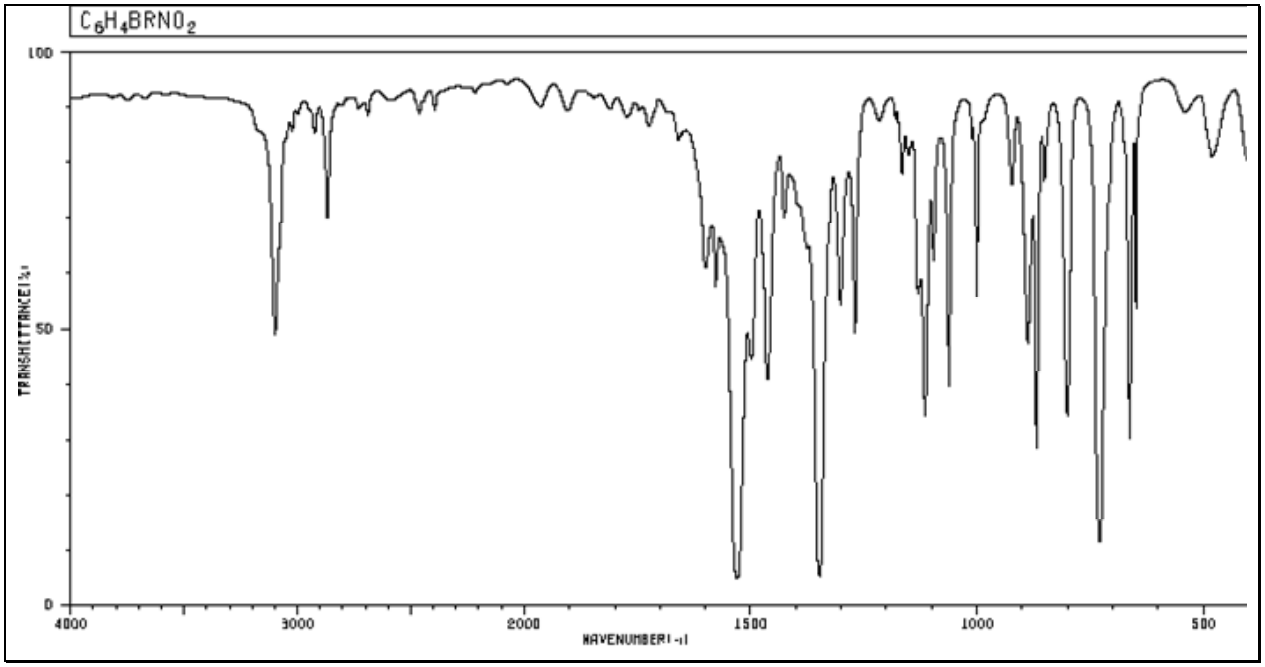


Unknown 48: MS

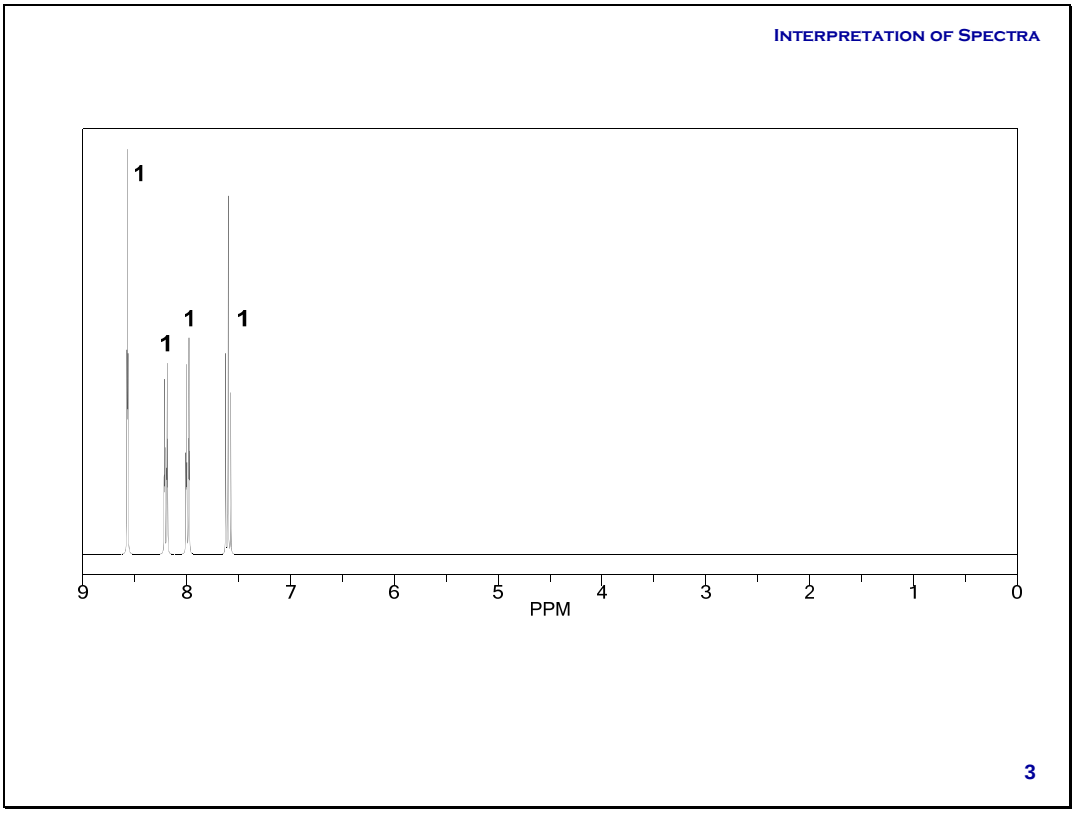
MF: $C_6H_4BrNO_2$



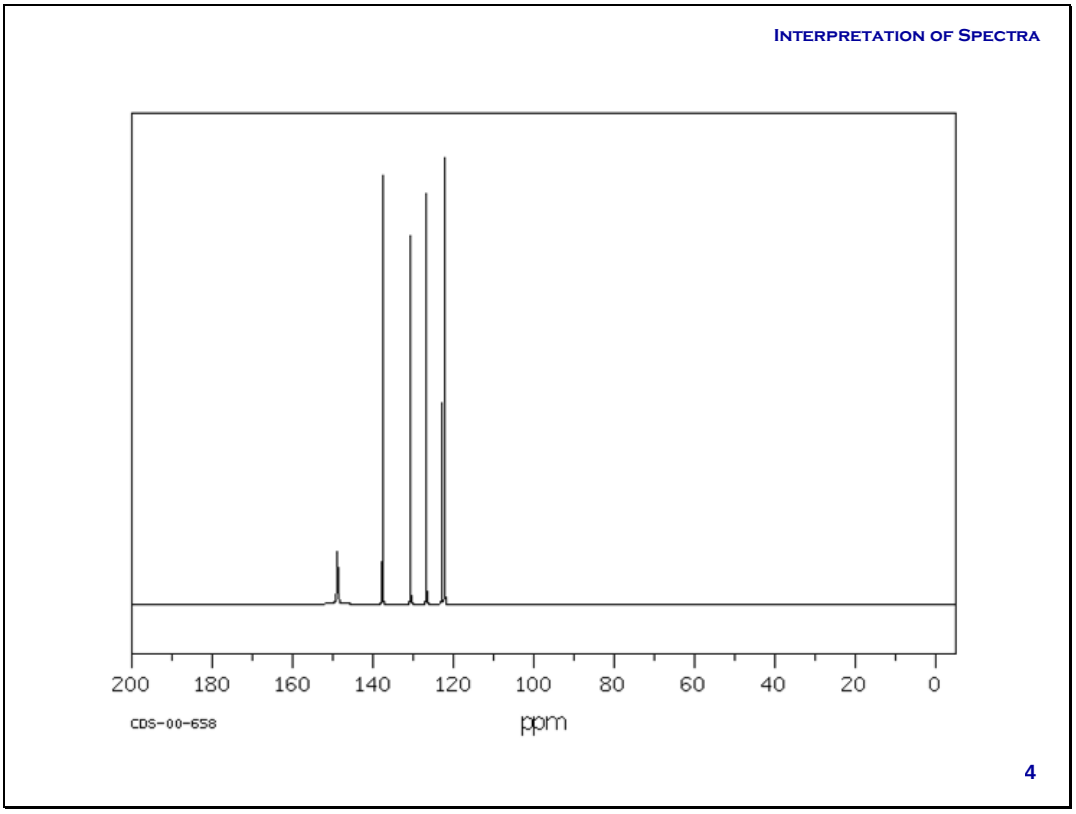
Unknown 48: IR



Unknown 48: NMR

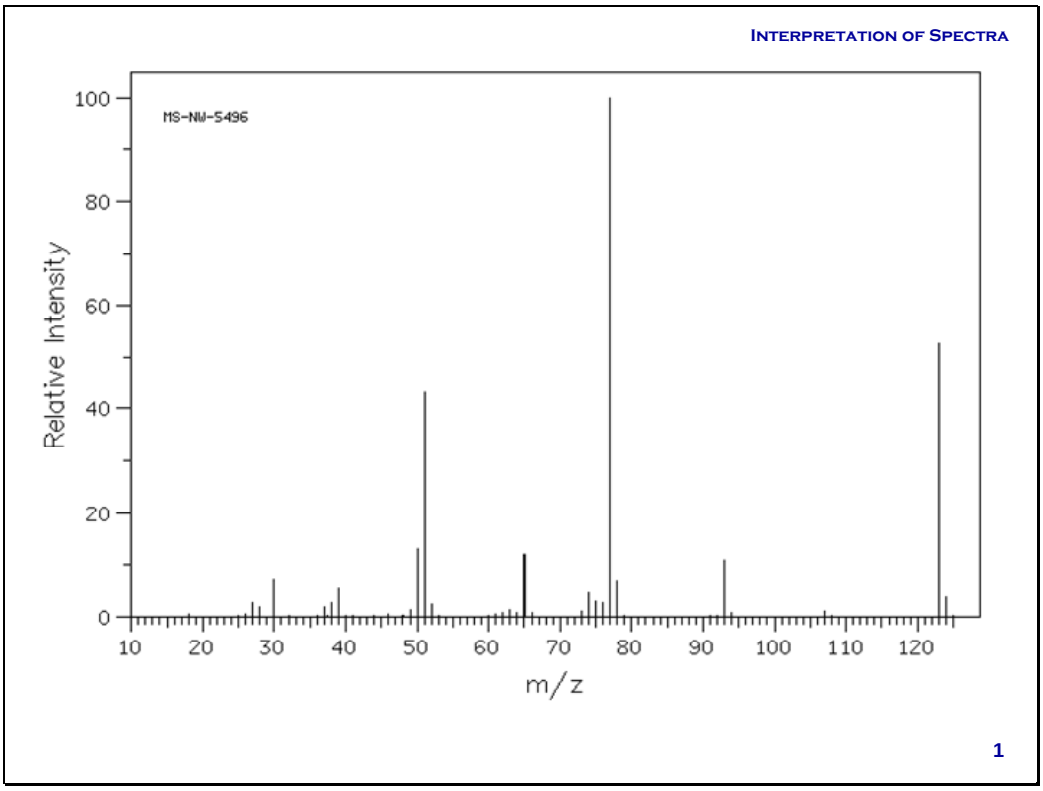


Unknown 48: CNMR

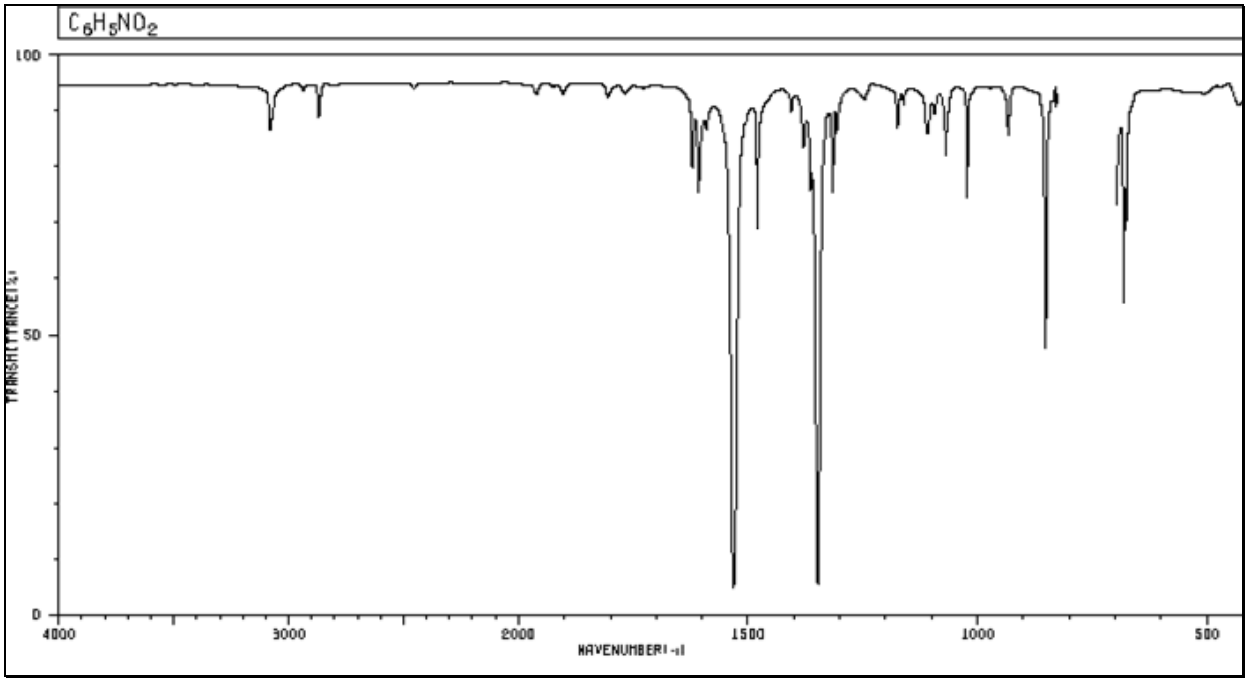


Unknown 49: MS

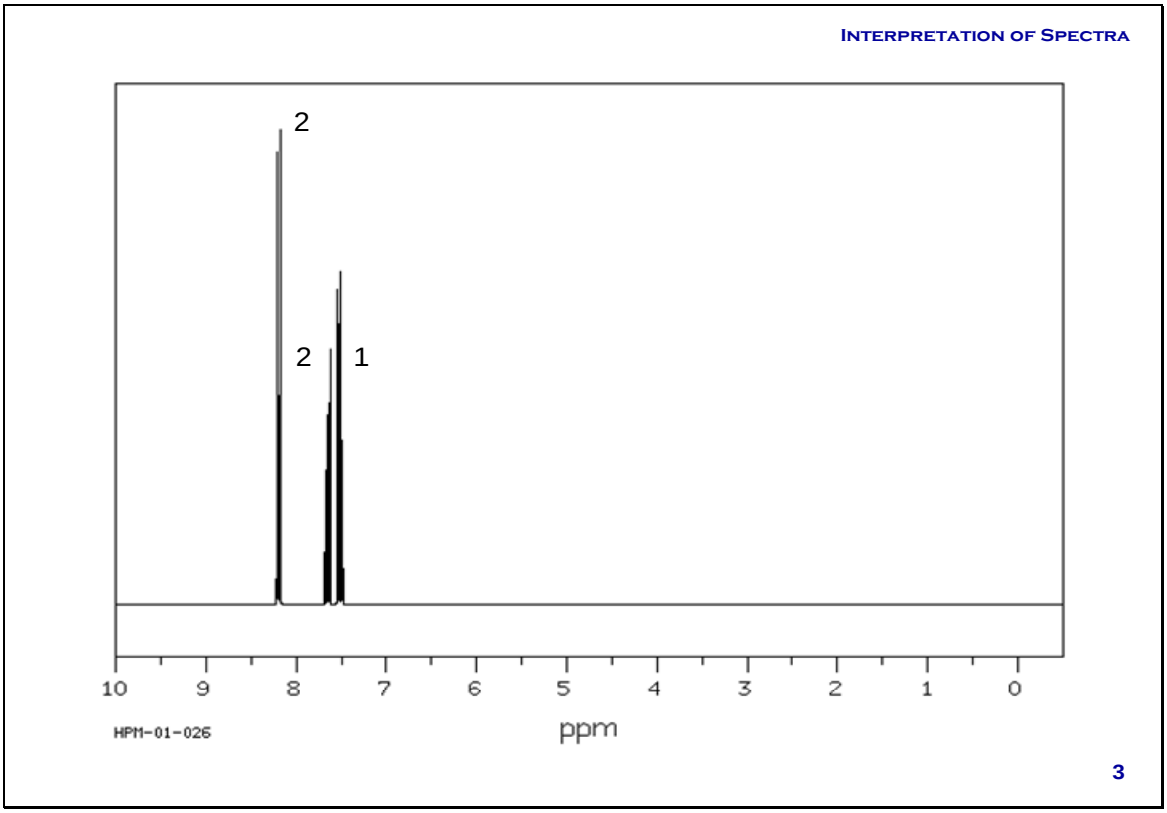
MF: $C_6H_5NO_2$



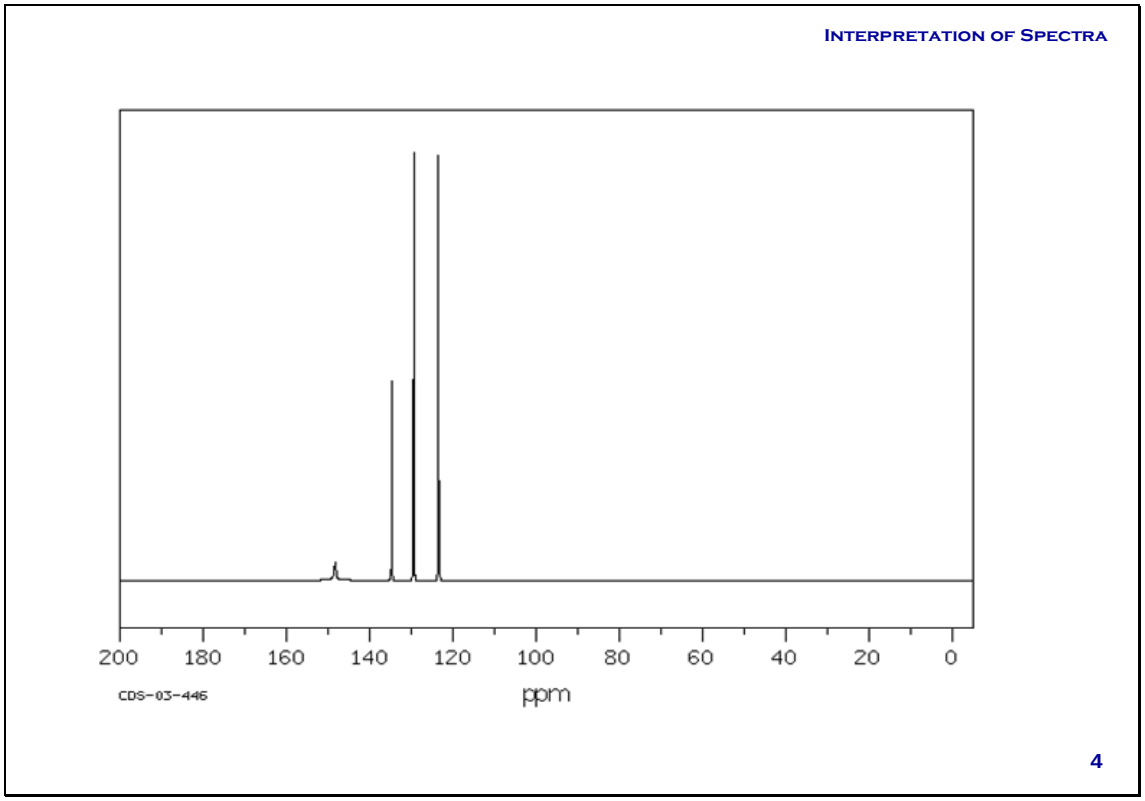
Unknown 49: IR



Unknown 49: NMR

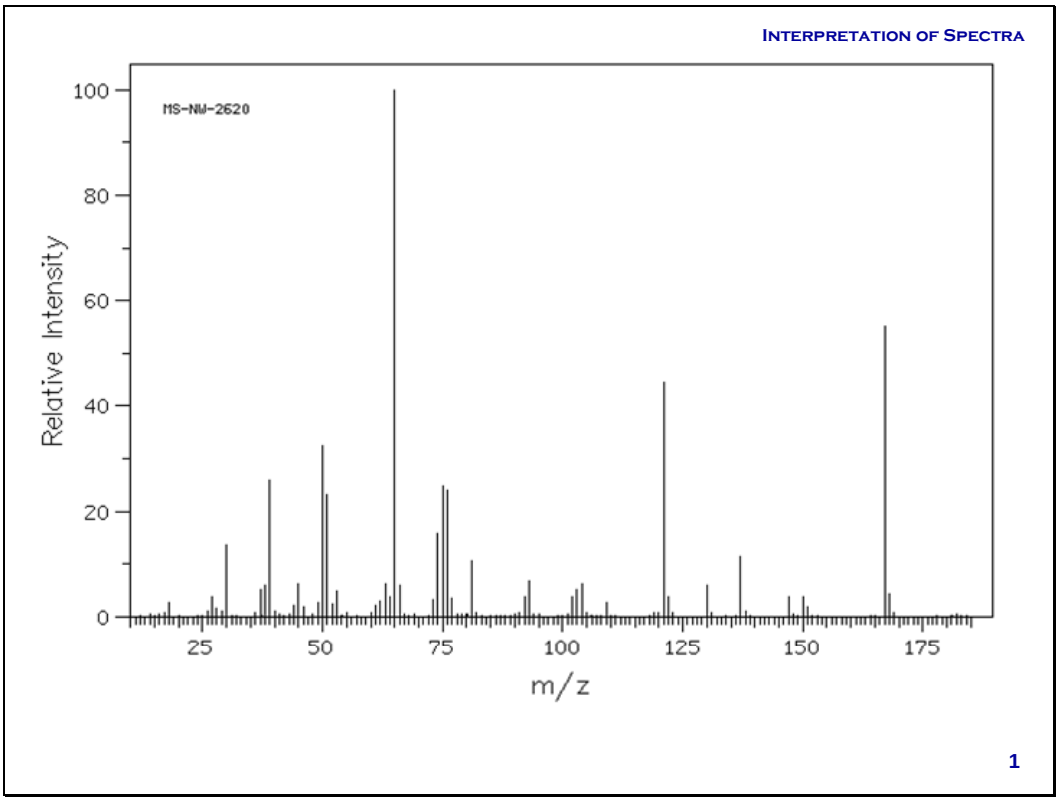


Unknown 49: CNMR

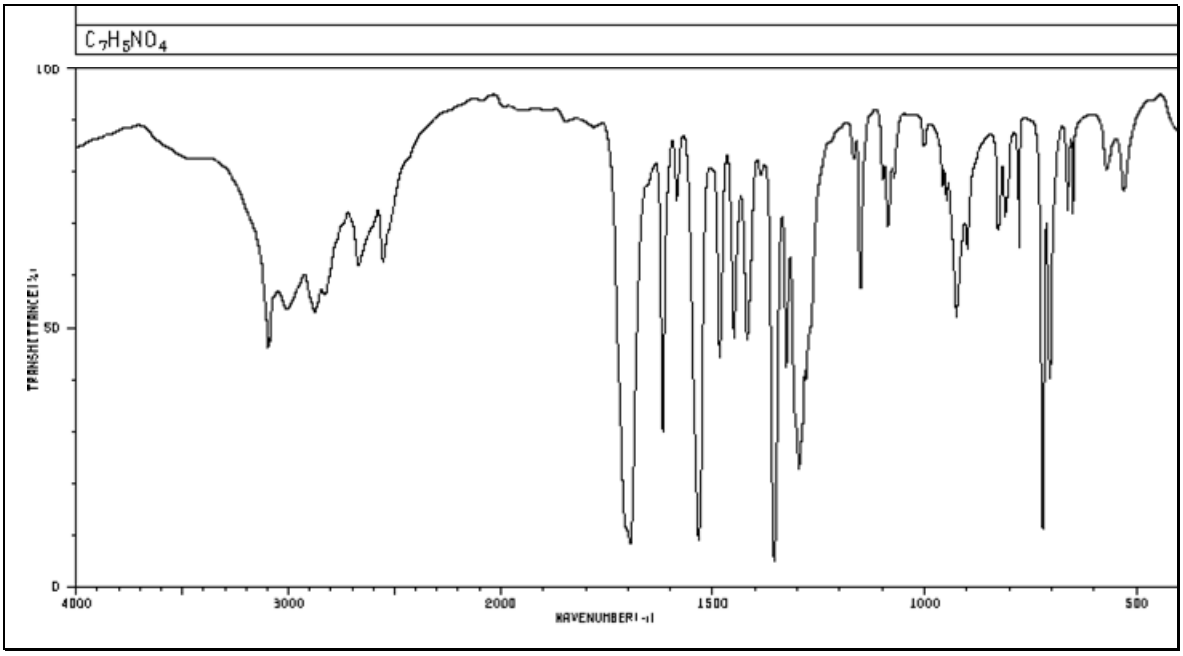


Unknown 50: MS

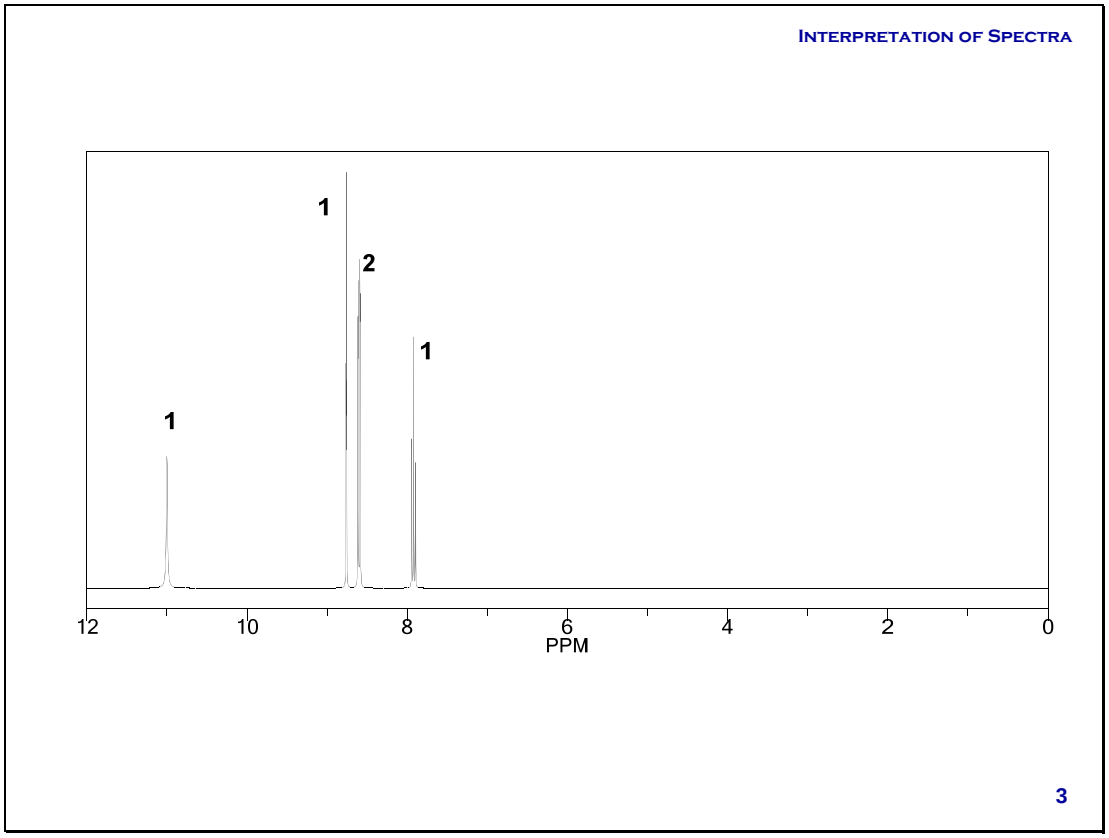
MF: $C_7H_5NO_4$



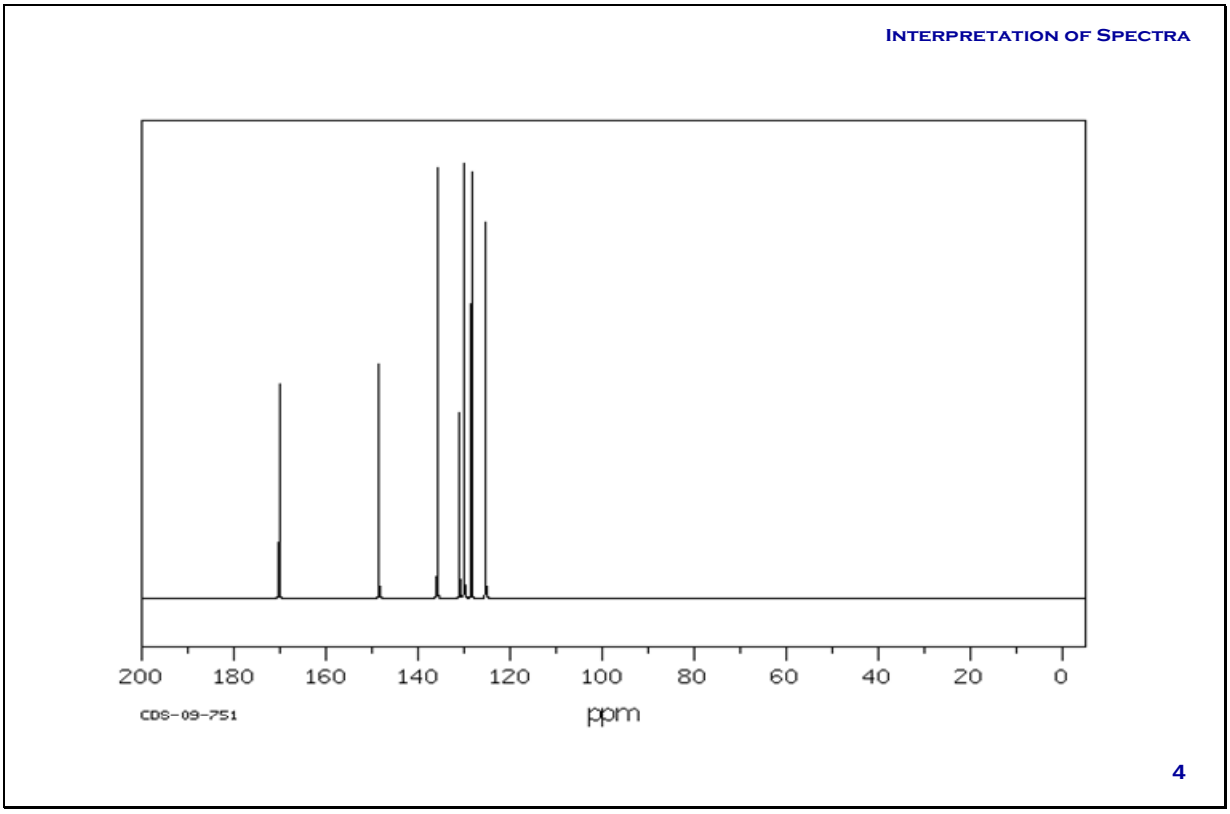
Unknown 50: IR



Unknown 50: NMR



Unknown 50: CNMR



Appendices

A. Natural Abundance of Isotopes for selected Elements

Element	Symbol	Nominal Mass	Exact Mass	Abundance
Hydrogen	H	1	1.00783	99.99
	D or ^{2}H	2	2.0141	0.01
Carbon	^{12}C	12	12	98.91
	^{13}C	13	13.0034	1.09
Nitrogen	^{14}N	14	14.0031	99.6
	^{15}N	15	15.0001	0.37
Oxygen	^{16}O	16	15.9949	99.76
	^{17}O	17	16.9991	0.037
	^{18}O	18	17.9992	0.2
Fluorine	F	19	18.9984	100
Silicon	^{28}Si	28	27.9769	92.28
	^{29}Si	29	28.9765	4.7
	^{30}Si	30	29.9738	3.02
Phosphorus	P	31	30.9738	100
Sulphur	^{32}S	32	31.9721	95.02
	^{33}S	33	32.9715	0.74
	^{34}S	34	33.9679	4.22
Chlorine	^{35}Cl	35	34.9689	75.77
	^{37}Cl	37	36.9659	24.23
Bromine	^{79}Br	79	78.9183	50.5
	^{81}Br	81	80.9163	49.5
Iodine	I	127	126.9045	100

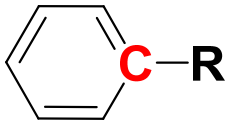
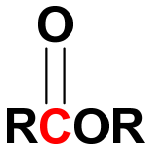
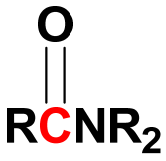
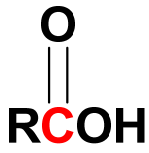
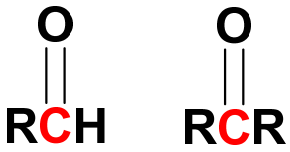
B. Characteristic Absorptions for various Functional Groups in IR Spectra

Functional Group	***Absorption(s) (cm-1)***	***Comments***
Alkyl C-H Stretch	2950 - 2850 (m or s)	Alkane C-H bonds are common and are not usually diagnostic; however, the demarkation of 3000 cm^{-1} should be noted: aliphatic C--H are below this value.
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)	Absorption peaks above 3000 cm^{-1} are frequently diagnostic of unsaturation
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)	
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)	Absorption peaks above 3000 cm^{-1}
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)	Hydrogen-Bonded Hydroxyl display an intese, broad "U" shaped appearance.
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)	This OH stretch paired with a C=O ~ 1780-1710 cm^{-1}
Amine N-H Stretch	3500 - 3300 (m)	Primary amines produce two N-H stretch absorptions, secondary amides only one, and tetriary none.
Nitrile C≡N Stretch	2260 - 2220 (m)	
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)	The carbonyl stretching absorption is usually one of the strongest in the spectrum. It is also one of the most common.
Amide N-H Stretch	3700 - 3500 (m)	As with amines, an amide produces zero to two N-H absorptions depending on its type.

C. Chemical Shifts for ^{1}H NMR

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
$(CH_3)_4Si$	0 (by definition)	$RCOCH_3$	3.7-3.9
RCH_3	0.8-1.0	$RCOCH_2R$	4.1-4.7
RCH_2R	1.2-1.4	RCH_2I	3.1-3.3
R_3CH	1.4-1.7	RCH_2Br	3.4-3.6
$R_2C=CRCHR_2$	1.6-2.6	RCH_2Cl	3.6-3.8
$RC\equiv CH$	2.0-3.0	RCH_2F	4.4-4.5
$ArCH_3$	2.2-2.5	$ArOH$	4.5-4.7
$ArCH_2R$	2.3-2.8	$R_2C=CH_2$	4.6-5.0
ROH	0.5-6.0	$R_2C=CHR$	5.0-5.7
RCH_2OH	3.4-4.0	ArH	6.5-8.5
RCH_2OR	3.3-4.0	RCH	9.5-10.1
R_2NH	0.5-5.0	$RCOH$	10-13
$RCCH_3$	2.1-2.3		
$RCCH_2R$	2.2-2.6		

D. Chemical Shifts for ^{13}C NMR

Carbon Type	Chemical Shift (δ)	Carbon Type	Chemical Shift (δ)
RCH_3	10-40		110-160
RCH_2R	15-55		
R_3CH	20-60		160-180
RCH_2I	10-40		
RCH_2Br	25-65		165-180
RCH_2Cl	35-80		
R_3COH	40-80		165-185
R_3COR	40-80		
$RC\equiv CR$	65-85		180-215
$R_2C=CR_2$	100-150		

D. Index of Unknowns