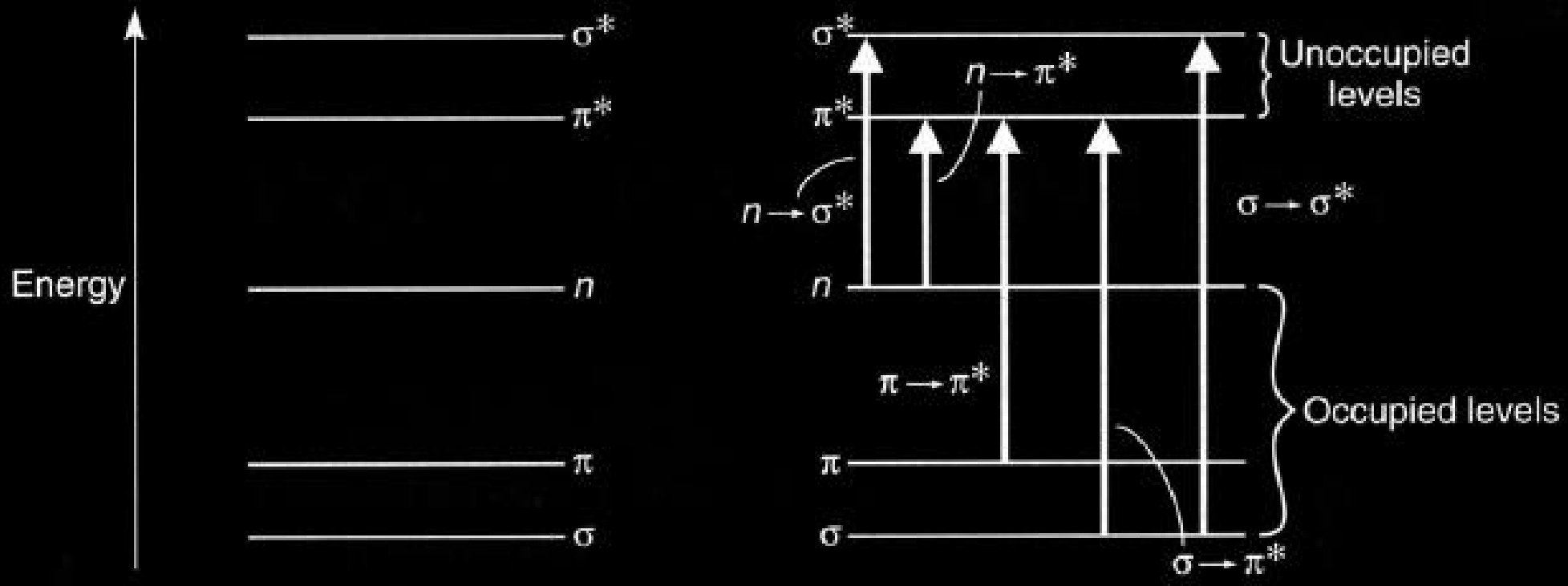
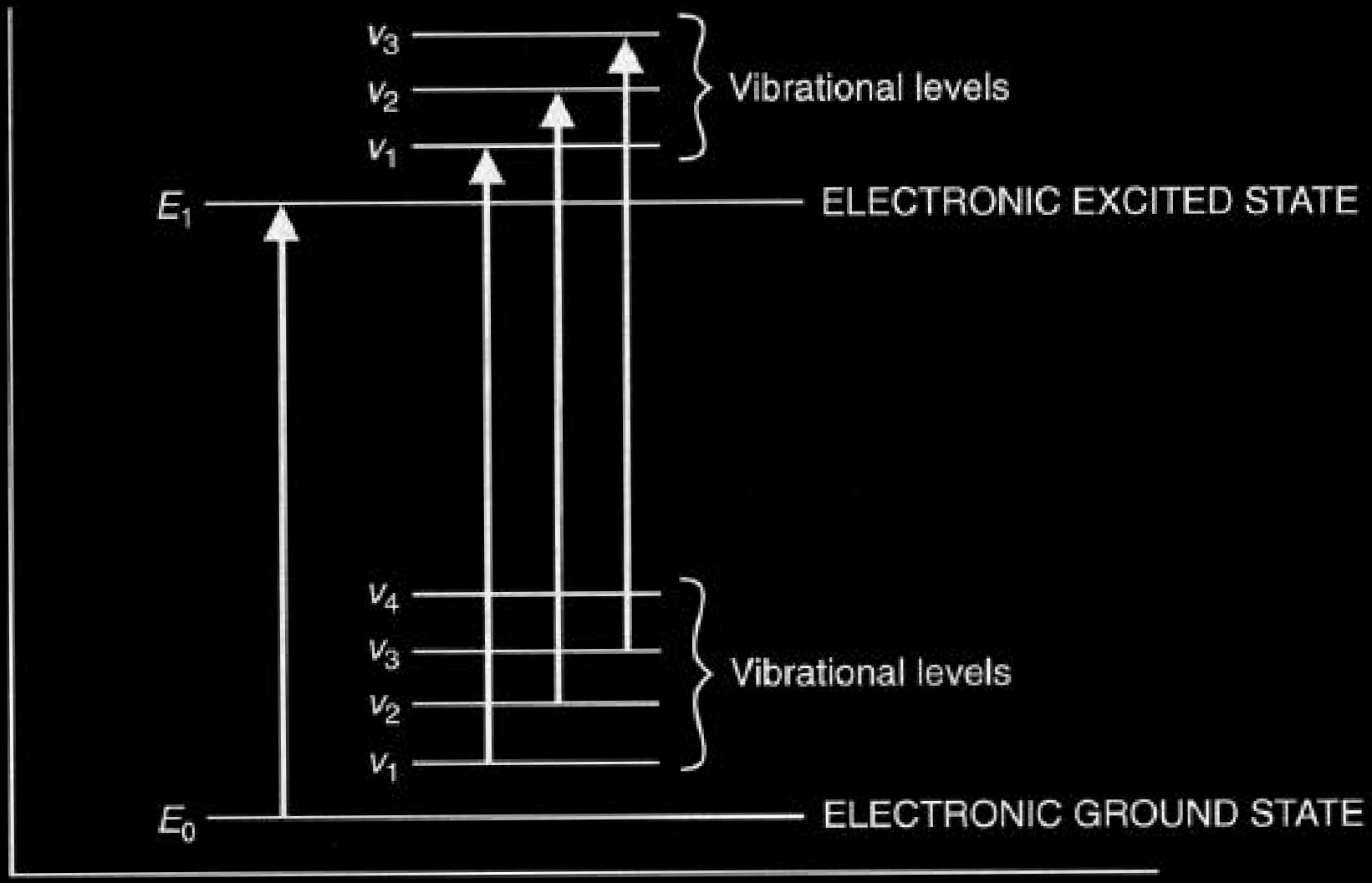
UV / Visible Spectroscopy

- UV wavelengths range from 200-400 nm
- Visible wavelengths range from 400-800 nm
- Energy absorbed causes electronic excitation

MO's Involved in Transition

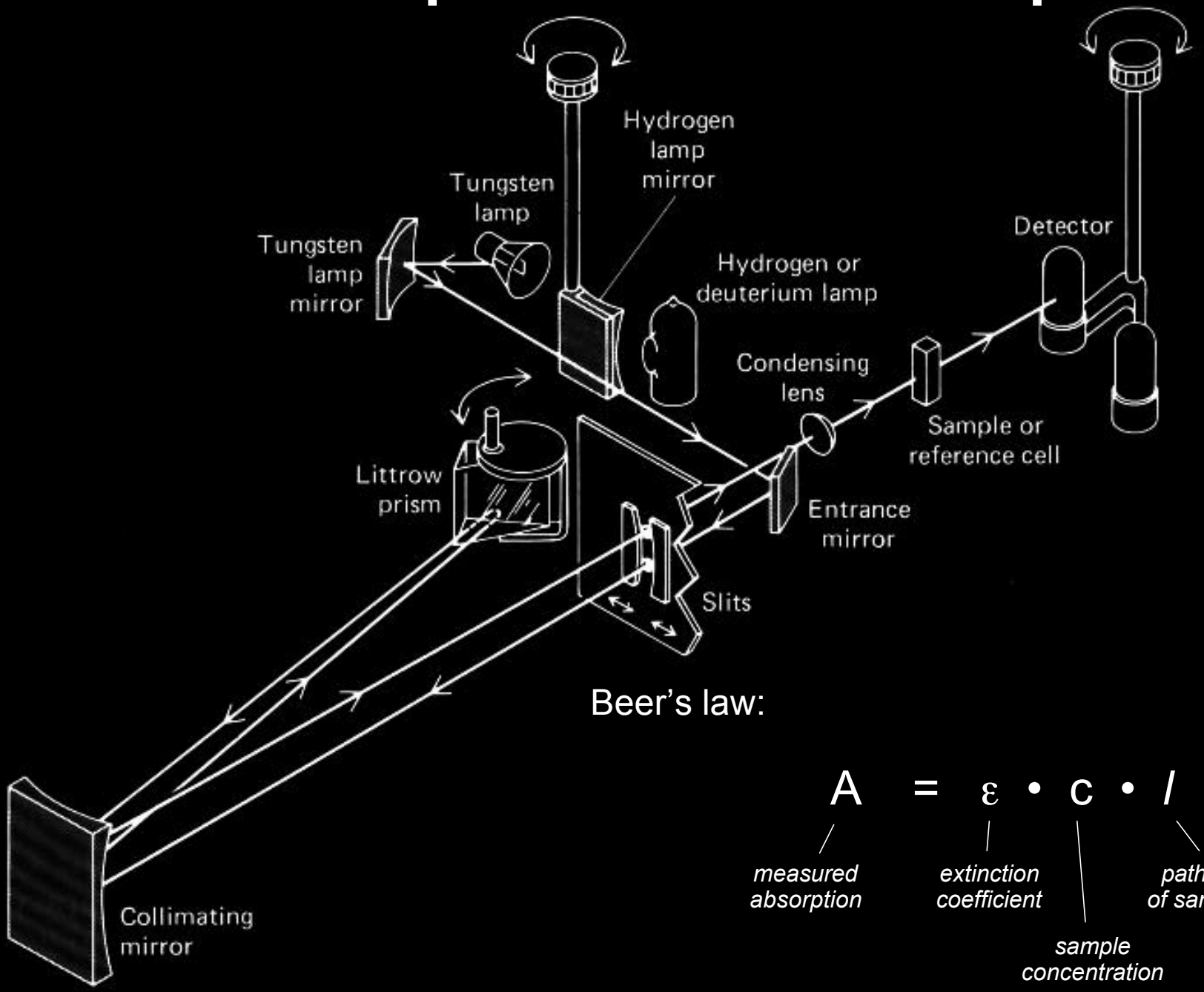


- *σ, π*, and *n* correspond to single bond, multiple bond, and nonbonded electrons, respectively
- absorptions correspond to transitions to antibonding orbitals.
- Energy absorbed causes electronic excitation



- A multitude of associated vibrational states lead to broad observed peaks, usually without fine structure.

Experimental Setup

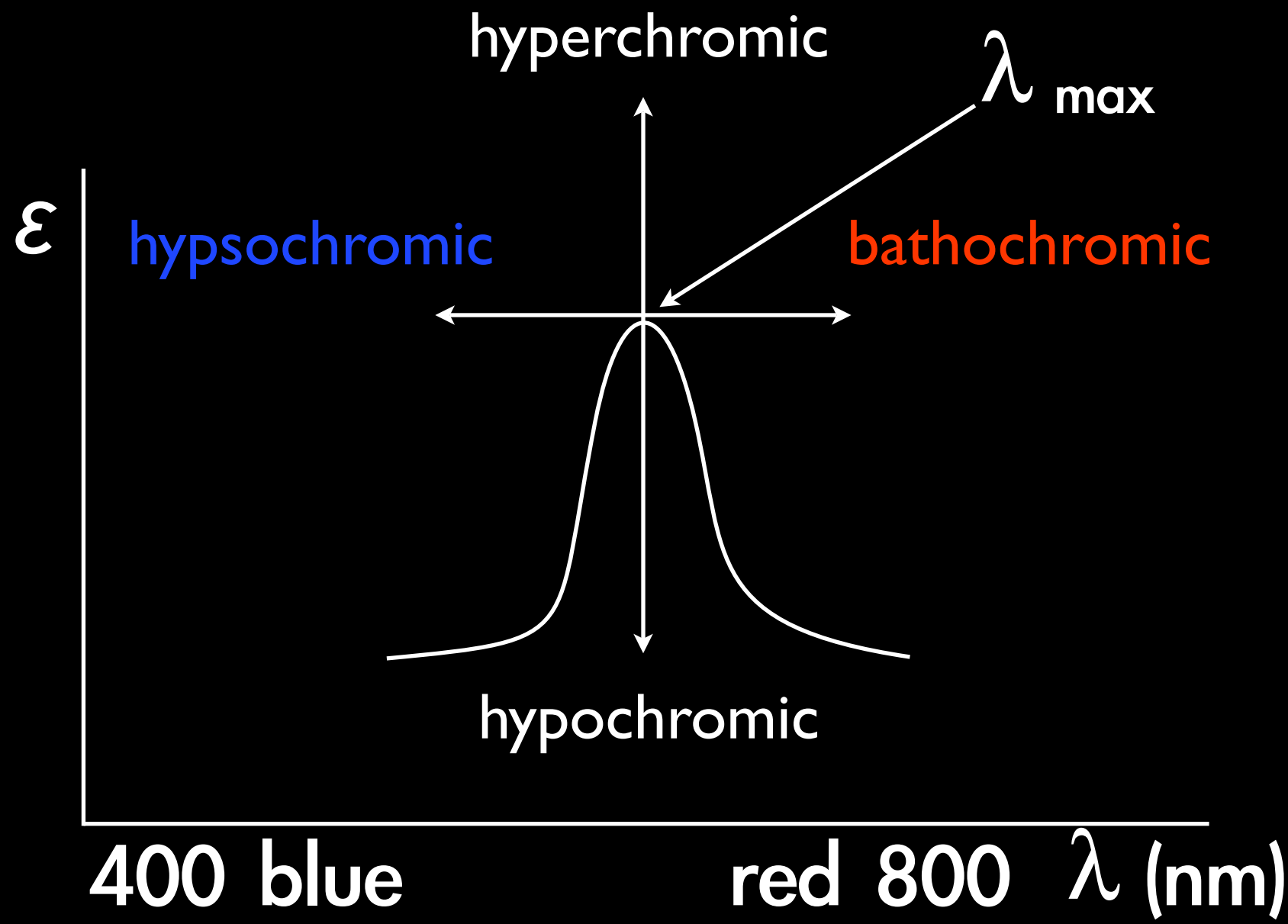


Beer's law:

$$A = \varepsilon \cdot c \cdot l$$

- A — *measured absorption*
- ε — *extinction coefficient*
- c — *sample concentration*
- l — *path length of sample cell*

UV/Vis Spectrum

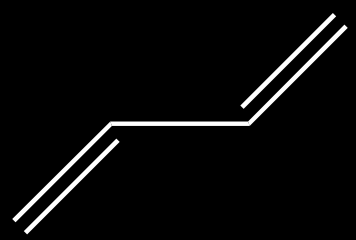


Potential Compound Classes

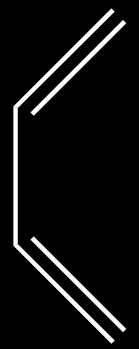
- Polyenes
- Aromatic Compounds
- Compounds containing heteroatoms with non-bonded electrons.

Polyenes

- *s-trans vs. s-cis*
- substituent effects

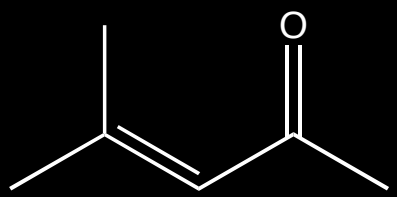


217 nm

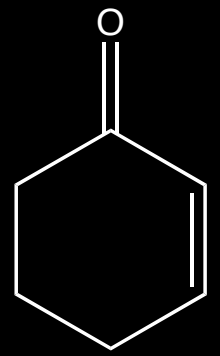


253 nm

Polyenones



227 nm



215 nm

- Exhibit both π π* and n π* transitions
- Solvent effects

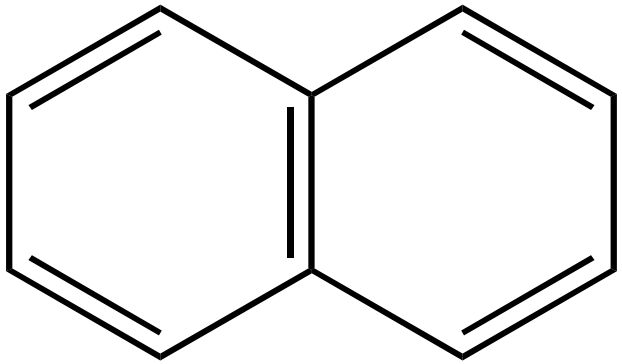
Aromatics

- Some exhibit fine structure unlike polyenes
- Substituent effects often not large enough to distinguish functional groups or substitution patterns

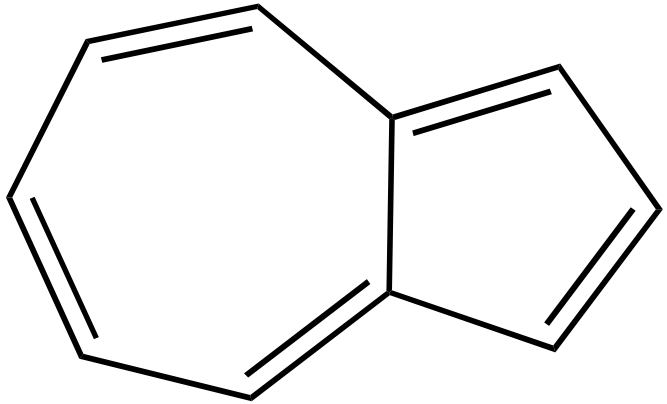
UV Spectroscopy

- Utilize the tables in Crews and Pretsch to confirm the presence of certain functional groups by UV/Vis
- Useful as a detector for liquid-phase separation techniques
- This technique can be used to a limited extent to identify functional groups.

Problem #1



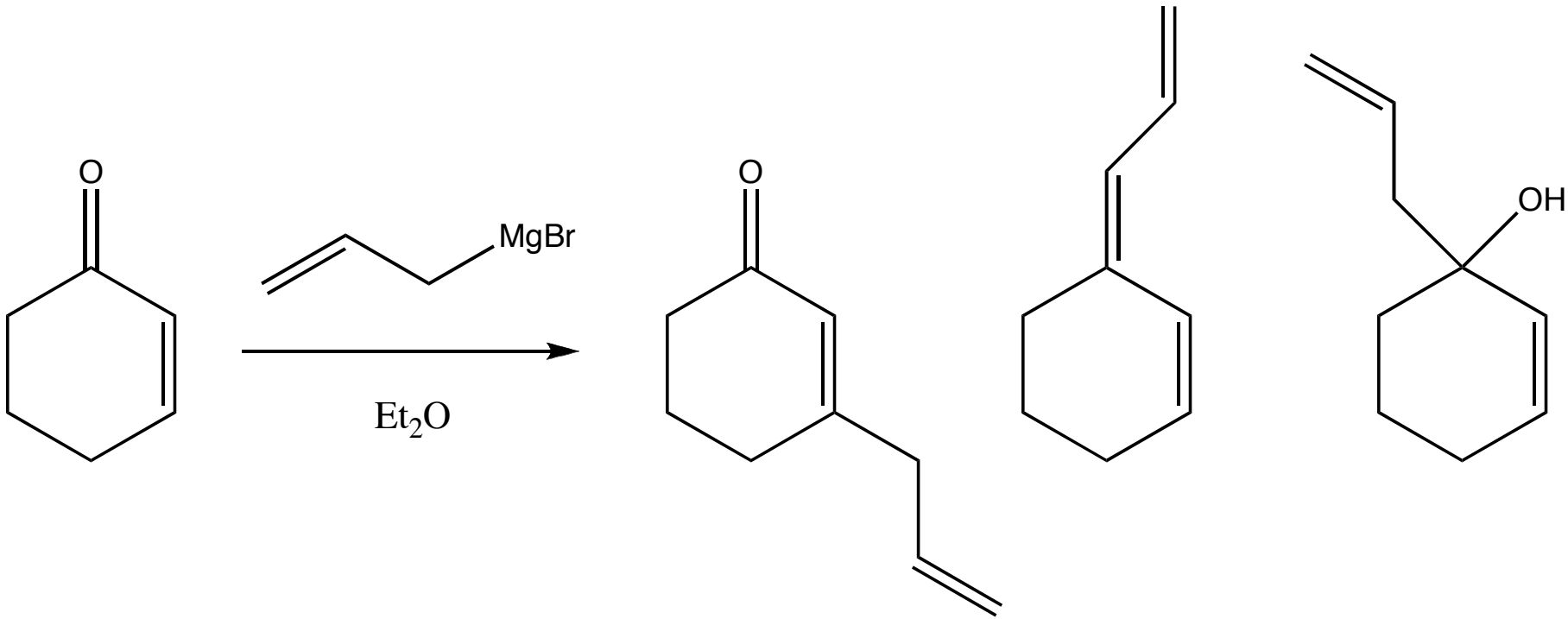
Naphthalene



Azulene

- Azulene is blue and naphthalene is colorless.
- Which compound has the largest λ_{max}?
- Which compound has the smallest HOMO-LUMO gap?

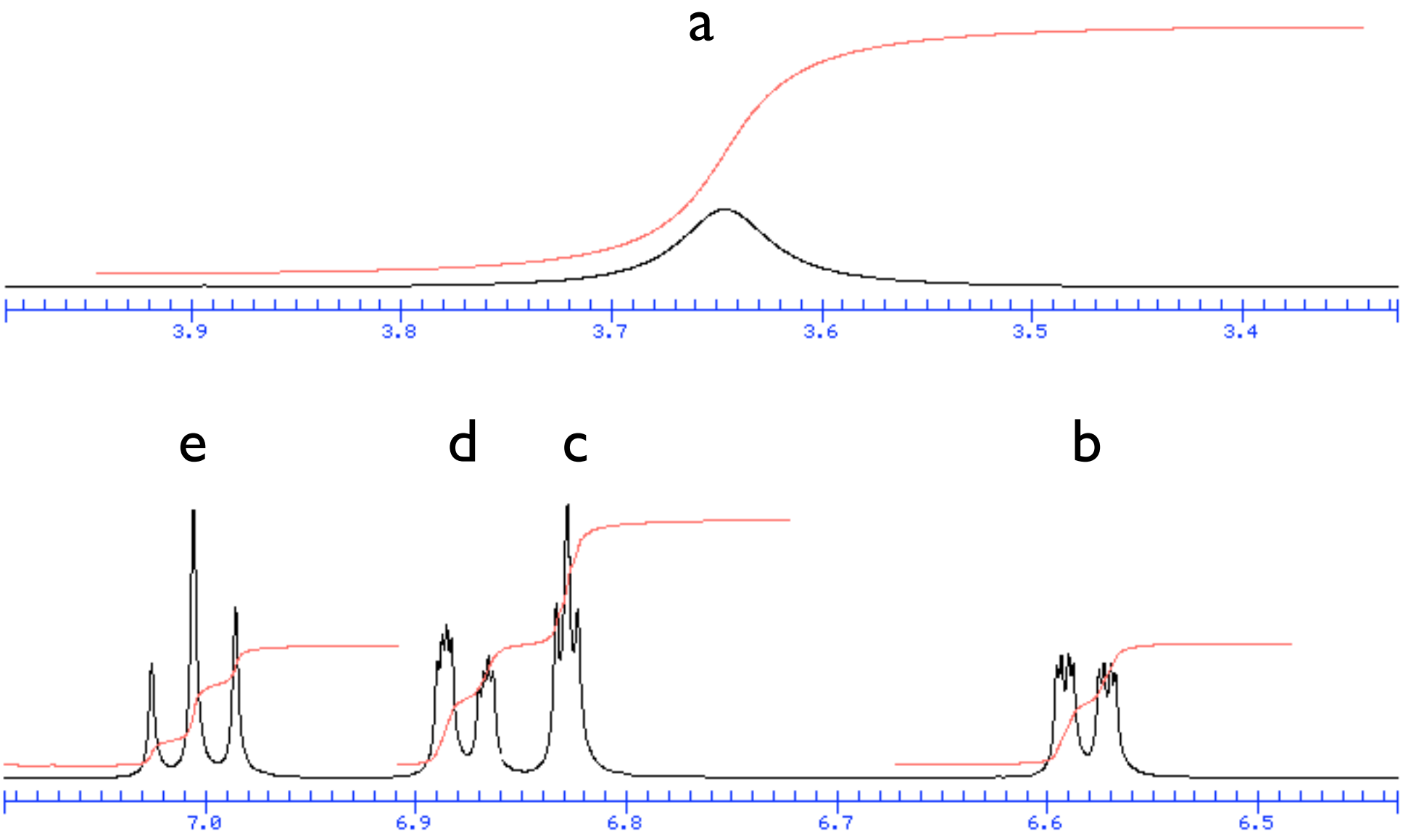
Problem #2



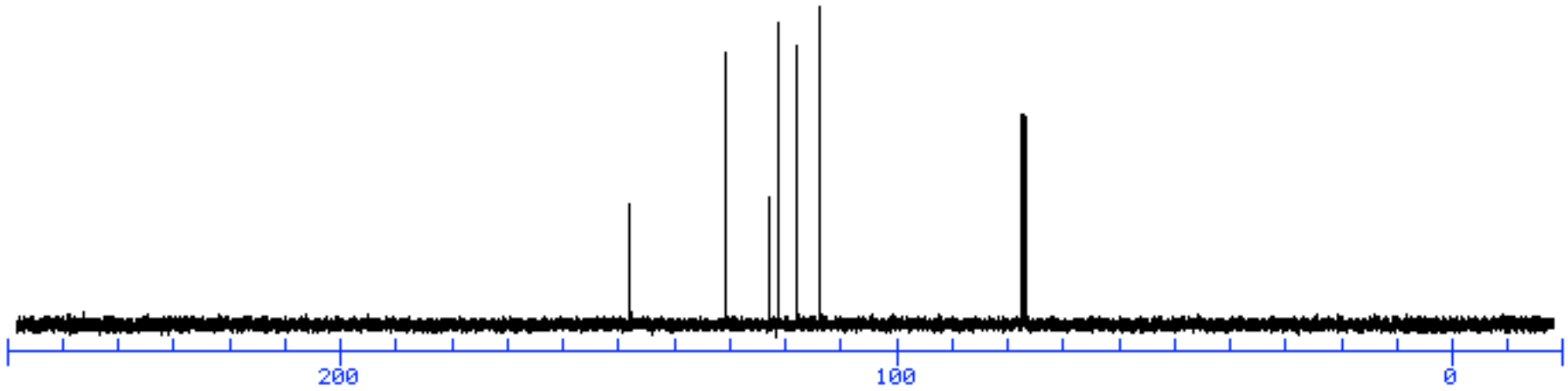
Which compound(s) in this incomplete reaction will be invisible to an HPLC equipped with a UV detector operating at 254 nm?

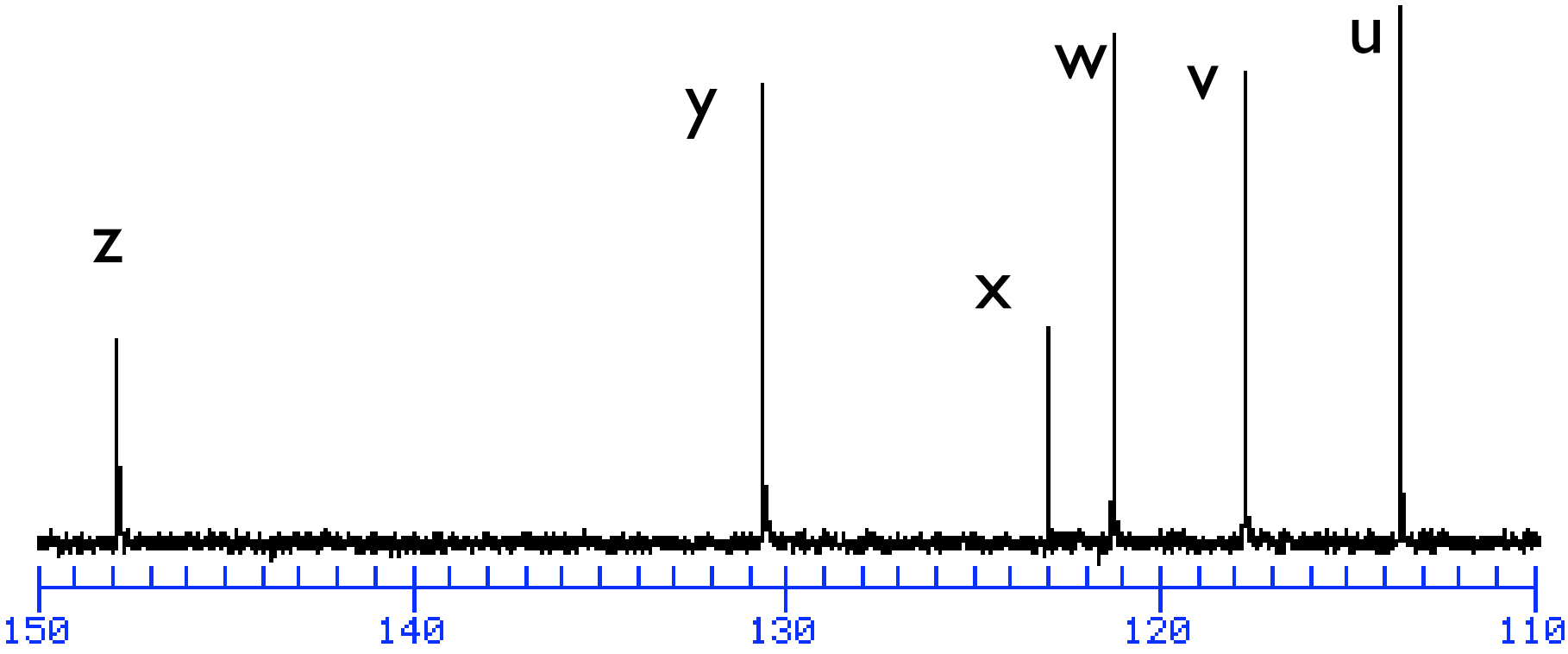
Problem #3

^{1}H NMR Spectrum

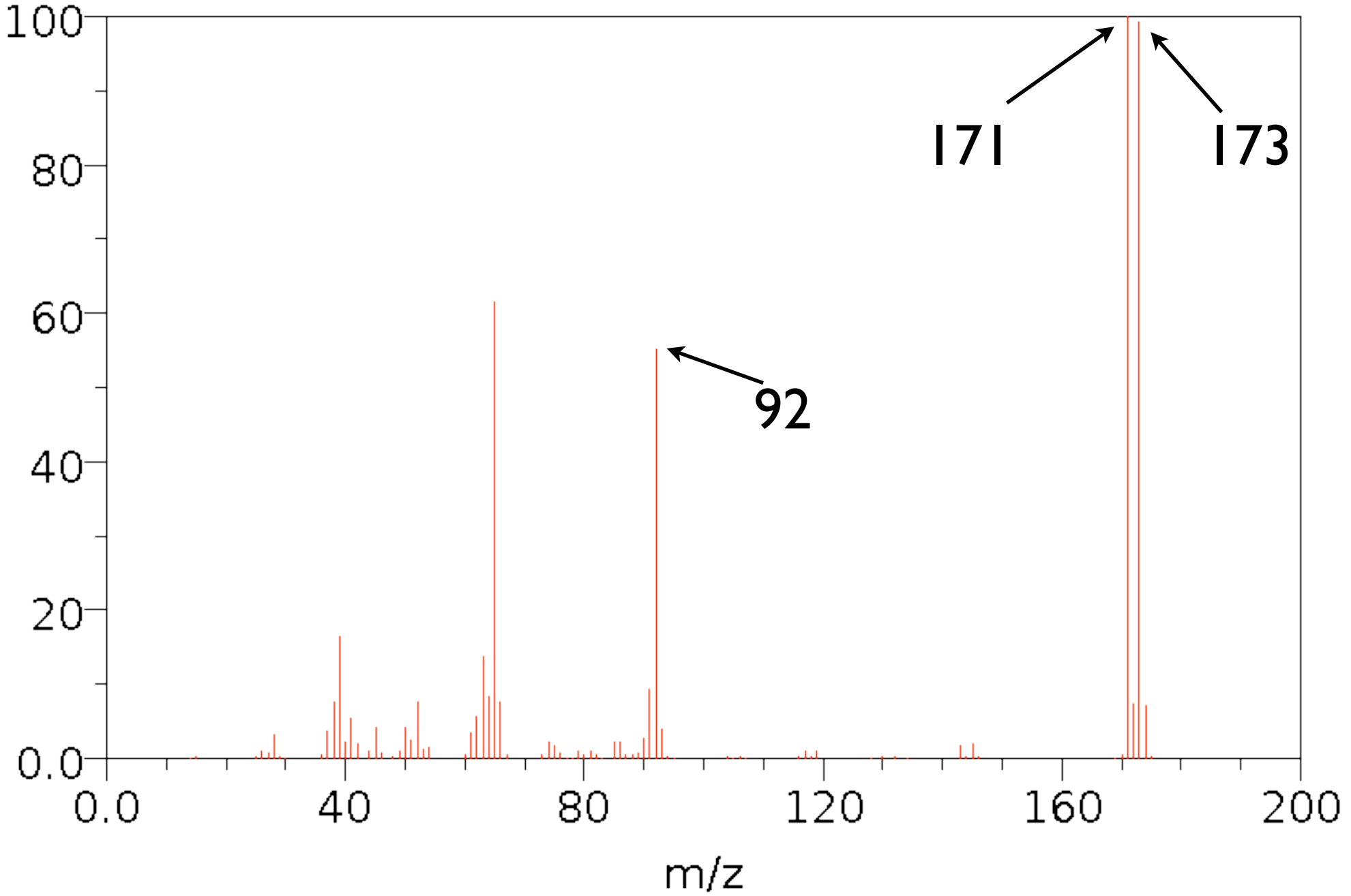


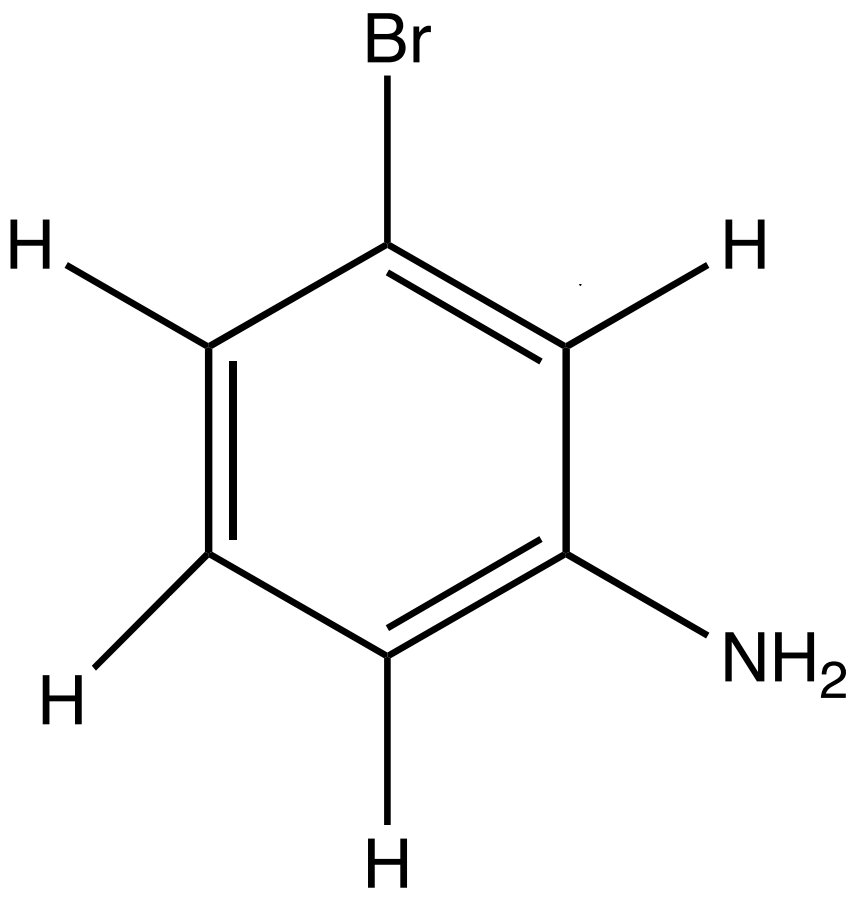
^{13}C NMR Spectrum

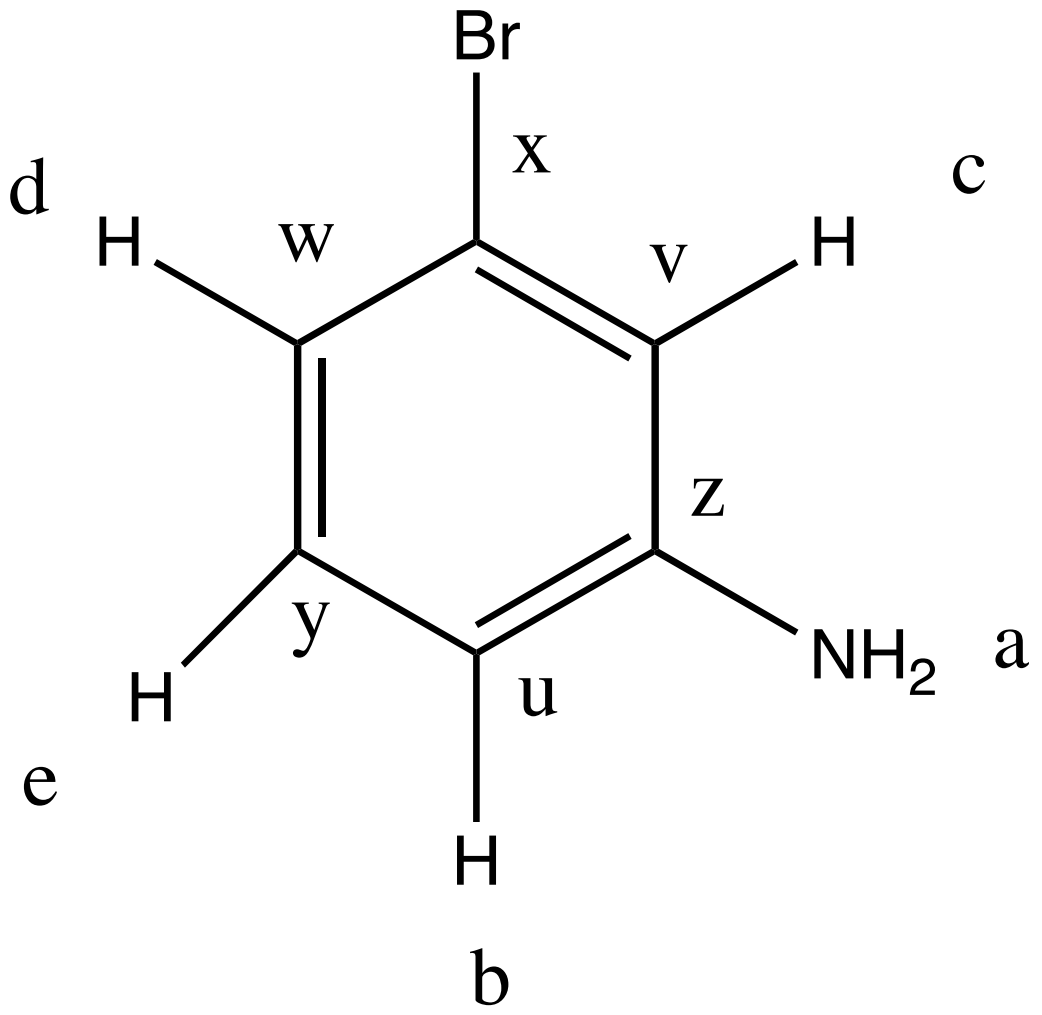




70 eV EI Mass Spectrum

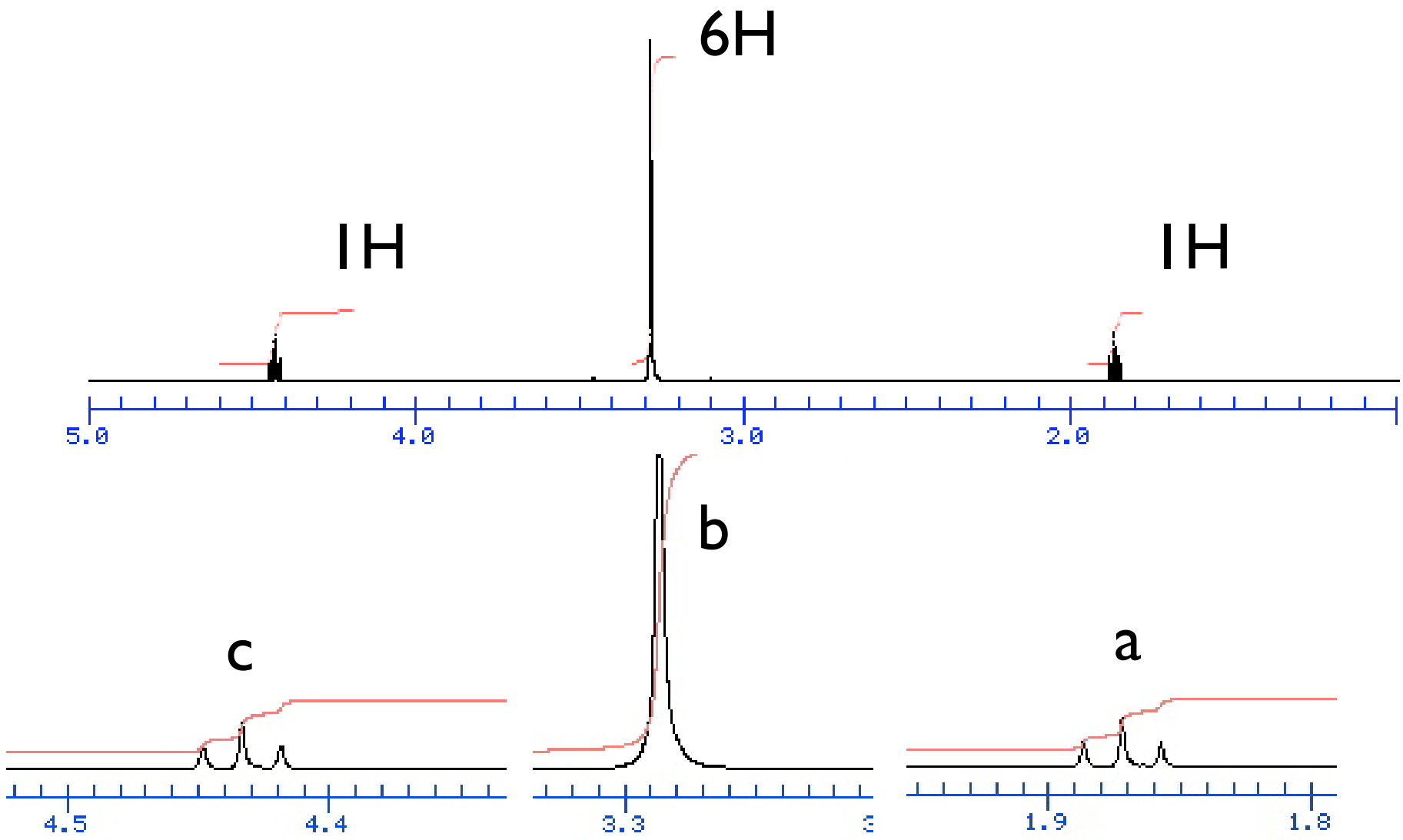



Br
H
H
H
NH2
H

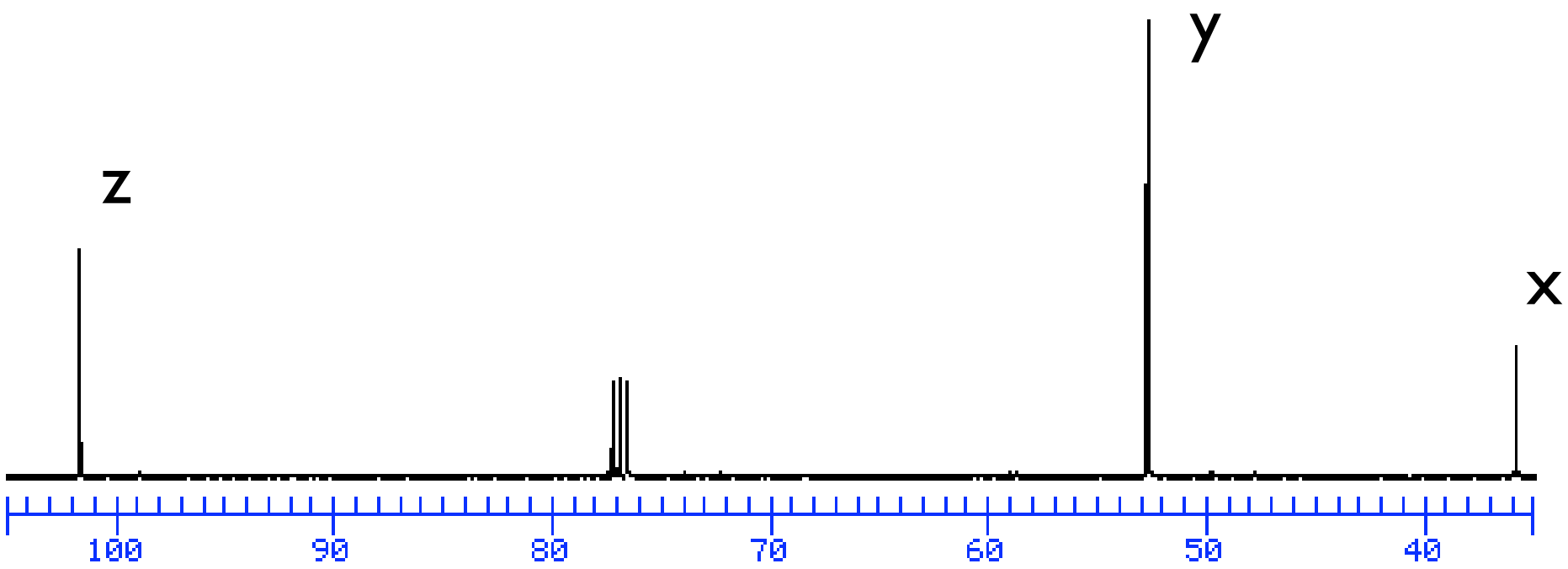

Br
x
c
d
H
w
v
H
z
y
NH2
a
H
u
e
H
b

Problem #4

^{1}H NMR Spectrum



^{13}C NMR Spectrum



LR CI Mass Spectrometry

Measured M+H 165.1±.05 by Chemical Ionization

H20 C3 N O4 P
H25 N2 O S3
H17 C7 O4
H17 N6 O2 S
H28 C P3 S
H13 C8 N4
H16 C4 N5 P
H18 C N4 O3 P
H19 N6 P2
H15 C5 N3 O3
H19 C2 N3 O3 S
H26 C O2 P S2
H15 C10 N O
H18 C6 N2 O P
H22 O7 P
H21 C2 N3 O P2
H13 C3 N6 O2
H21 C4 O4 S
H24 N O4 P S
H21 C3 N2 O S2
H27 N P4
H24 C4 P3
H23 C4 O2 P2
H17 C2 N2 O6
H11 C N9 O
H17 C5 N4 S
H26 N O2 P3
H20 C N5 P S
H19 C N5 S2
H25 N O2 P2 S
H22 C4 O2 P S
H21 O9
H15 N5 O5

H19 C7 N O S
H22 C3 N2 O P S
H23 N O4 S2
H25 C O4 S2
H20 C2 N3 O P S
H17 C6 N2 O S
H11 N11
H17 C N4 O5
H27 C O2 P2 S
H21 C2 N4 S2
H18 N6 P S
H15 C4 N5 S
H13 C2 N8 O
H19 C3 N O6
H21 C3 N O2 P2
H18 C7 O2 P
H29 C P4
H23 C4 N O S2
H26 N2 O P S2
H19 C3 N O4 S
H15 C4 N5 O2
H19 C N4 O P2
H18 N6 O2 P
H16 C5 N3 O P
H27 C P2 S2
H13 C9 N2 O
H17 C N4 O3 S
H17 C6 N2 O3
H23 O5 P2
H20 C2 N3 O3 P
H14 C3 N6 P
H25 C O2 S3
H11 C7 N5
H23 N O6 S

H21 O7 S
H27 C N O S3
H22 C4 O4 P
H18 C2 N2 O4 P
H25 N O4 P2
H15 C6 N O4
H19 C N5 O2 S
H26 N P3 S
H23 C4 P2 S
H15 C9 N3
H18 C5 N4 P
H16 N5 O3 P
H21 C N5 P2
H13 C4 N4 O3
H21 C3 N2 O3 S
H24 N O2 P S2
H21 C4 O2 S2
H17 C11 O
H20 C7 N O P
H23 C3 N2 O P2
H17 C3 O7
H11 C2 N7 O2
H26 C O4 P S
H19 C2 N3 O S2
H22 C3 N P3
H19 C7 P2
H15 C N3 O6
H9 N10 O
H19 C6 N3 S
H28 C O2 P3
H22 C2 N4 P S
H17 N6 S2
H140 C2
H25 N2 O3 S2

H20 C3 N O2 P S
H17 C7 O2 S
H17 N6 O4
H21 C8 O S
H24 C4 N O P S
H27 N2 O P2 S
H18 C N4 O P S
H24 O3 P3
H15 C5 N3 O S
H13 C N10
H19 C2 N3 O5
H26 C P S3
H23 C3 N3 S2
H22 O5 P S
H13 C3 N6 S
H15 C3 N7 O
H21 C4 O6
H19 C2 N2 O2 P2
H24 N O6 P
H16 C6 N O2 P
H13 C10 O2
H25 C5 O S2
H28 C N O P S2
H17 C2 N2 O4 S
H17 C5 N4 O2
H17 N5 O P2
H20 C N5 O2 P
H14 C4 N4 O P
H25 N P2 S2
H11 C8 N3 O
H22 C4 P S2
H15 N5 O3 S
H19 C7 N O3
H27 N3 S3

H22 C3 N2 O3 P
H18 C3 O5 P
H12 C2 N7 P
H23 N O2 S3
H9 C6 N6
H19 N7 O S
H25 C O6 S
H29 C2 O S3
H16 C N3 O4 P
H27 C O4 P2
H13 C5 N2 O4
H21 C2 N4 O2 S
H21 C3 N P2 S
H17 C10 N2
H18 C7 P S
H20 C6 N3 P
H23 C2 N4 P2
H11 C3 N5 O3
H23 C4 N O3 S
H26 N2 O3 P S
H19 C3 N O2 S2
H25 O P4
H22 C8 O P
H25 C4 N O P2
H15 C2 N O7
H9 C N8 O2
H28 N2 O P3
H17 C N4 O S2
H23 O3 P2 S
H20 C2 N2 P3
H25 C S4
H23 N O8
H17 C6 N P2
H13 N4 O6

H21 C7 N2 S
H14 C10 P
H24 C3 N3 P S
H21 O5 S2
H138 C N
H27 C N O3 S2
H18 C2 N2 O2 P S
H15 C6 N O2 S
H19 C N5 O4
H26 C5 O P S
H29 C N O P2 S
H16 N5 O P S
H13 C4 N4 O S
H15 C2 N9
H21 C3 N2 O5
H19 C3 O3 P2
H24 N P S3
H21 C4 S3
H25 C4 N2 S2
H28 N3 P S2
H17 C3 O5 S
H11 C2 N7 S
H17 C4 N6 O
H17 C N3 O2 P2
H20 N7 O P
H26 C O6 P
H14 C5 N2 O2 P
H17 C N4 O S2
H11 C9 N O2
H30 C2 O P S2
H15 C N3 O4 S
H19 C6 N3 O2
H22 C2 N4 O2 P
H12 C3 N5 O P
H9 C7 N4 O

H25 N2 O5 S
H20 C3 N P S2
H17 C7 S2
H21 C8 O3
H29 C N2 S3
H24 C4 N O3 P
H18 C2 N2 O2 P S
H10 C N8 P
H27 N2 O3 P2
H13 C6 O5
H7 C5 N7
H21 C N6 O S
H24 O P3 S
H14 N4 O4 P
H11 C4 N3 O4
H23 C3 N3 O2 S
H22 O3 P S2
H19 C2 N2 P2 S
H19 C11 N
H16 C6 N P S
H22 C7 N2 P
H13 C10 S
H25 C3 N3 P2
H9 C2 N6 O3
H25 C5 O3 S
H28 C N O3 P S
H17 C2 N2 O2 S2
H148 O
H20 C3 O P3
H27 C5 O P2
H13 C N2 O7
H7 N9 O2
H30 C N O P3
H15 N5 O S2

H27 N3 O2 S2
H18 C3 O3 P S
H18 C N3 P3
H23 N S4
H19 N7 O3
H25 C O8
H15 C5 N2 P2
H23 C8 N S
H12 C9 N P
H26 C4 N2 P S
H9 C13
H136 N2
H29 N3 P2 S
H29 C2 O3 S2
H16 C N3 O2 P S
H13 C5 N2 O2 S
H21 C2 N4 O4
H31 C2 O P2 S
H11 C3 N5 O S
H17 C3 N8
H23 C4 N O5
H17 C2 N O3 P2
H26 N2 O5 P
H14 C6 O3 P
H19 C3 N S3
H27 C5 N S2
H30 C N2 P S2
H15 C2 N O5 S
H9 C N8 S
H19 C5 N5 O
H15 N4 O2 P2
H22 C N6 O P
H12 C4 N3 O2 P
H23 O P2 S2

H9 C8 N2 O2
H13 N4 O4 S
H21 C7 N2 O2
H24 C3 N3 O2 P
H10 C2 N6 O P
H21 O3 S3
H7 C6 N5 O
H21 N8 S
H27 C N O5 S
H18 C2 N2 P S2
H15 C6 N S2
H31 C2 N S3
H26 C5 O3 P
H14 C N2 O5 P
H8 N9 P
H29 C N O3 P2
H11 C5 N O5
H5 C4 N8
H23 C2 N5 O S
H19 C3 O P2 S

HR CI Mass Spectrometry

Measured M+H 165.1130±.002 by Chemical Ionization

Deviation	Mass	Formula
-0.029543	165.112995	H20 C3 N O4 P
-0.602715	165.112900	H25 N2 O S3
-1.913659	165.112684	H17 C7 O4
2.237752	165.113369	H17 N6 O2 S
-3.285386	165.112458	H28 C P3 S
6.186054	165.114021	H13 C8 N4
8.070170	165.114332	H16 C4 N5 P
-8.161453	165.111652	H18 C N4 O3 P
9.954286	165.114644	H19 N6 P2

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8.070170	165.114332	H16 C4 N5 P
-8.161453	165.111652	H18 C N4 O3 P
9.954286	165.114644	H19 N6 P2

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Measured M+H 165.1130±.002 by Chemical Ionization

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~~-0.602715~~	~~165.112900~~	~~H25 N2 O S3~~
-1.913659	165.112684	H17 C7 O4
~~2.237752~~	~~165.113369~~	~~H17 N6 O2 S~~
~~-3.285386~~	~~165.112458~~	~~H28 C P3 S~~
6.186054	165.114021	H13 C8 N4
~~8.070170~~	~~165.114332~~	~~H16 C4 N5 P~~
-8.161453	165.111652	H18 C N4 O3 P
9.954286	165.114644	H19 N6 P2

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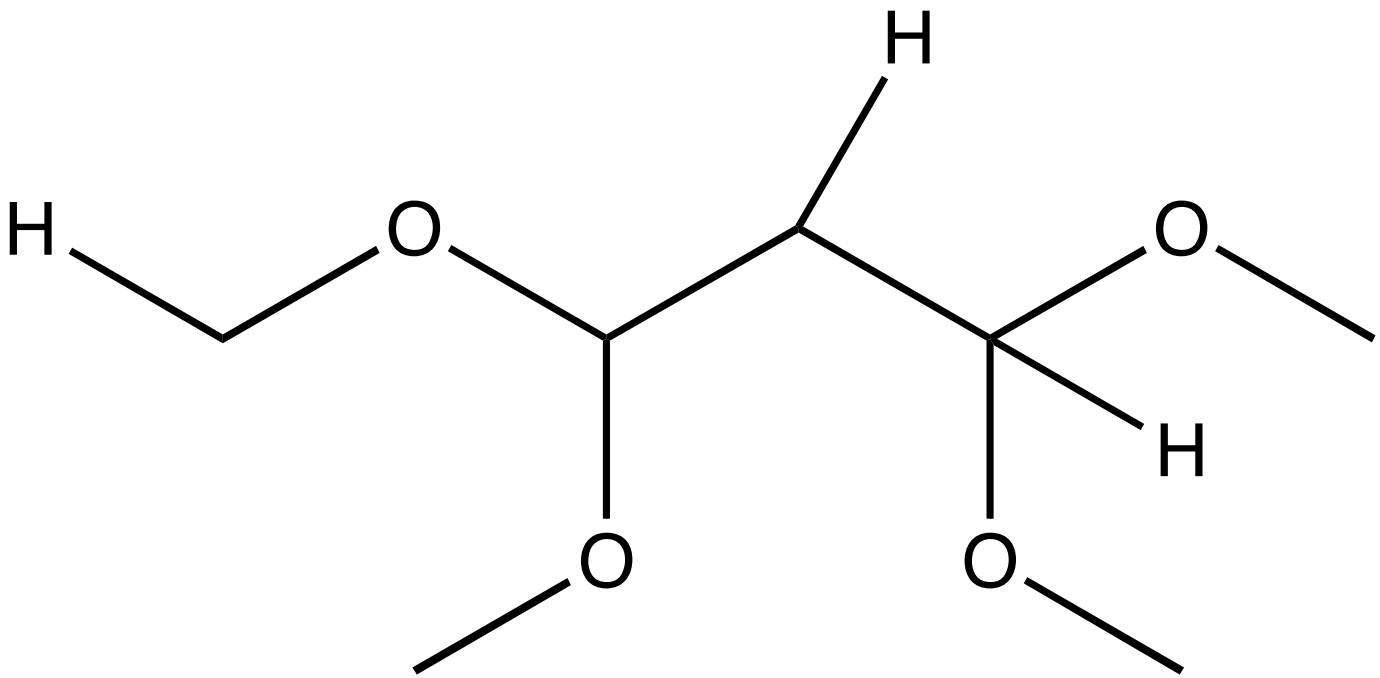
Measured M+H 165.1130±.002 by Chemical Ionization

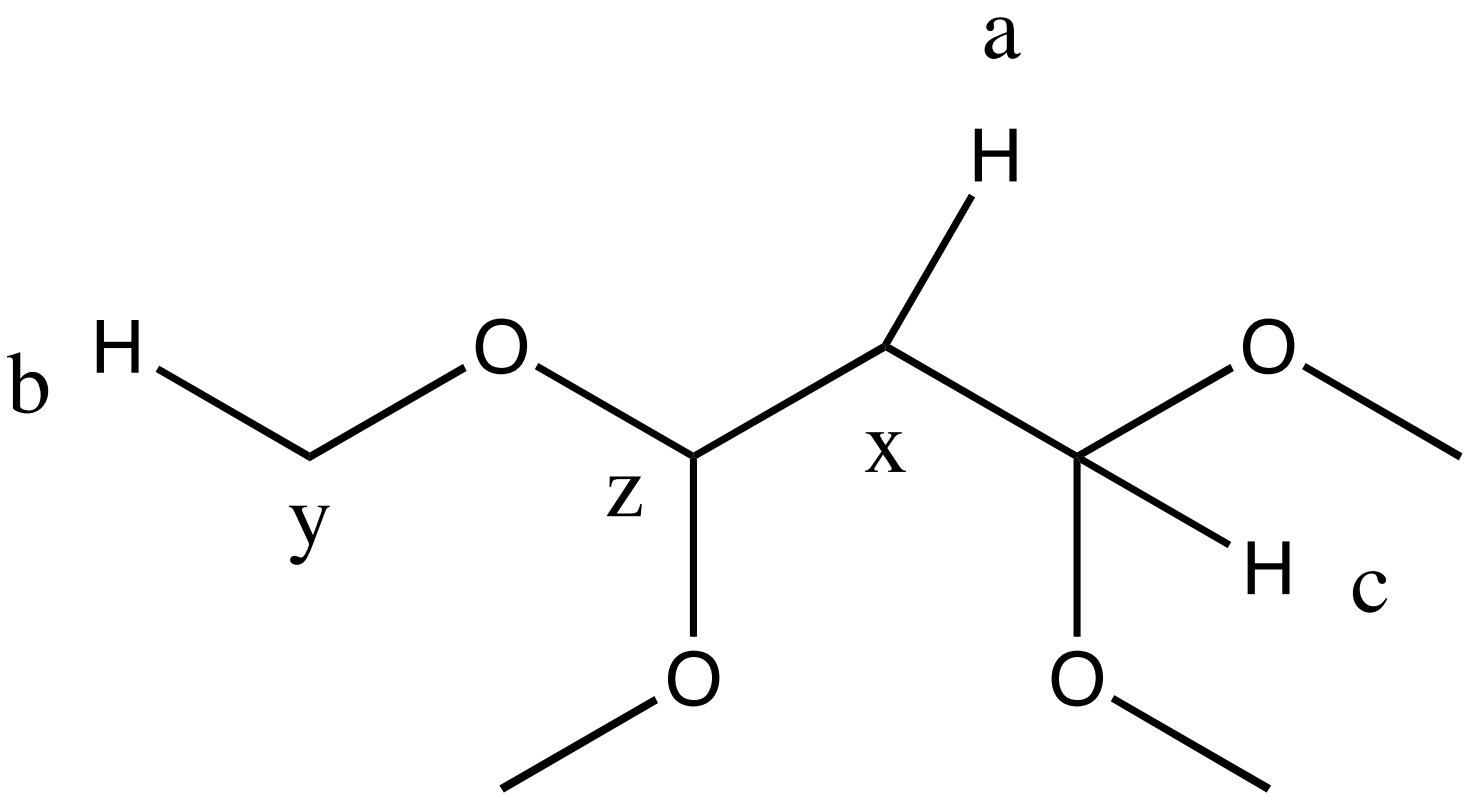
Deviation	Mass	Formula
~~-0.029543~~	~~165.112995~~	~~H20 C3 N O4 P~~
~~-0.602715~~	~~165.112900~~	~~H25 N2 O S3~~
-1.913659	165.112684	H17 C7 O4
~~2.237752~~	~~165.113369~~	~~H17 N6 O2 S~~
~~-3.285386~~	~~165.112458~~	~~H28 C P3 S~~
6.186054	165.114021	H13 C8 N4
~~8.070170~~	~~165.114332~~	~~H16 C4 N5 P~~
~~-8.161453~~	~~165.111652~~	~~H18 C N4 O3 P~~
9.954286	165.114644	H19 N6 P2

HR CI Mass Spectrometry

Measured M+H 165.1130±.002 by Chemical Ionization

Deviation	Mass	Formula
~~-0.029543~~	~~165.112995~~	~~H20 C3 N O4 P~~
~~-0.602715~~	~~165.112900~~	~~H25 N2 O S3~~
-1.913659	165.112684	H17 C7 O4
~~2.237752~~	~~165.113369~~	~~H17 N6 O2 S~~
~~-3.285386~~	~~165.112458~~	~~H28 C P3 S~~
6.186054	165.114021	H13 C8 N4
~~8.070170~~	~~165.114332~~	~~H16 C4 N5 P~~
~~-8.161453~~	~~165.111652~~	~~H18 C N4 O3 P~~
~~9.954286~~	~~165.114644~~	~~H19 N6 P2~~


H
O
H
O
O
O
H


a
H
b
H
O
O
x
z
y
H
c
O
O