Spectroscopy

nuclear magnetic resonance

The nmr spectra included in this presentation have been taken from the SDBS database with permission.

National Institute of Advanced Industrial Science and Technology

(http://www.aist.go.jp/RIODB/SDBS/menu-e.html)

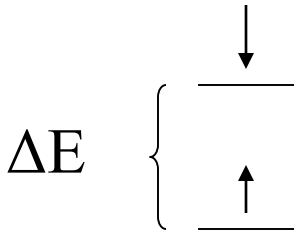
Nuclear Magnetic Resonance (nmr)

-the nuclei of some atoms spin: ^{1}H, ^{13}C, ^{19}F, …

-the nuclei of many atoms do not spin: ^{2}H, ^{12}C, ^{16}O, …

-moving charged particles generate a magnetic field (↗)

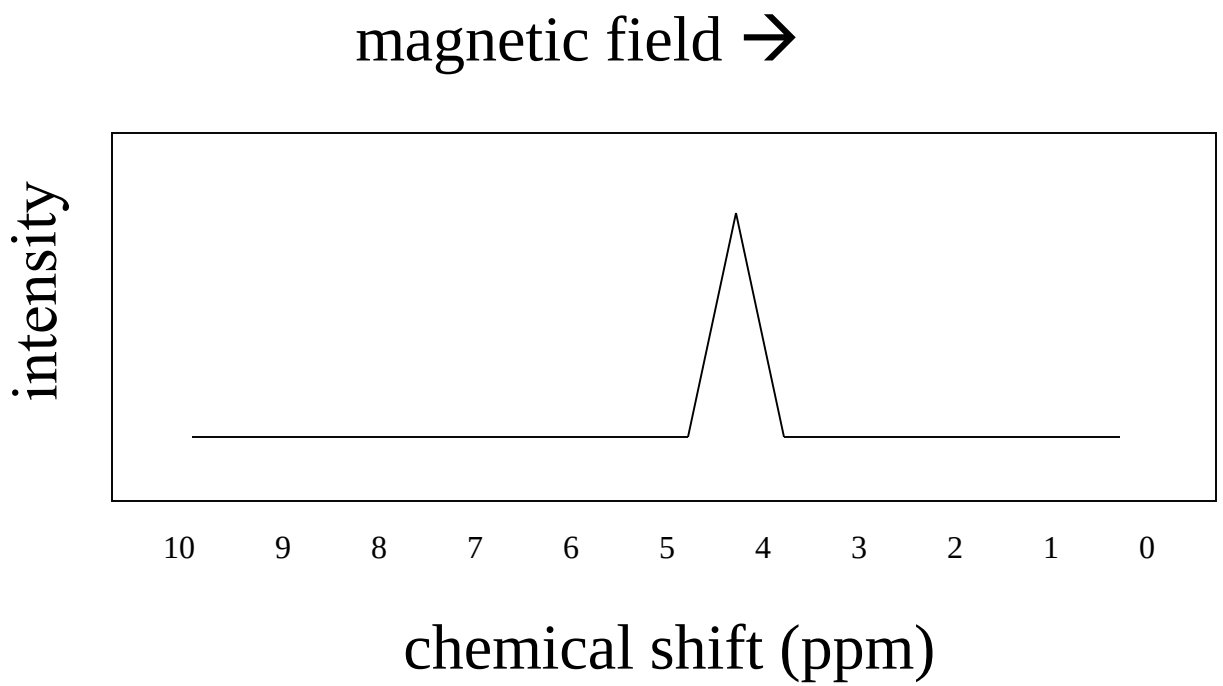
-when placed between the poles of a powerful magnet, spinning nuclei will align with or against the applied field creating an energy difference. Using a fixed radio frequency, the magnetic field is changed until the $\Delta E = E_{EM}$. When the energies match, the nuclei can change spin states (resonate) and give off a magnetic signal.



magnetic field = 14,092 gauss

for ^{1}H v = 60,000,000 Hz (60 MHz)

nmr spectrum



^{1}H nuclei are **shielded** by the magnetic field produced by the surrounding electrons. The higher the electron density around the nucleus, the higher the magnetic field required to cause resonance.

CH_3Cl	versus	CH_4
lower electron density		higher electron density
resonate at lower applied field		resonate at higher applied field

$CHCCl_3$??

Information from ^{1}H-nmr spectra:

1. **Number of signals: How many different types of hydrogens in the molecule.**
2. **Position of signals (chemical shift): What types of hydrogens.**
3. **Relative areas under signals (integration): How many hydrogens of each type.**
4. **Splitting pattern: How many neighboring hydrogens.**

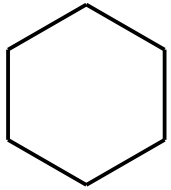
1. **Number of signals: How many different types of hydrogens in the molecule.**

Magnetically equivalent hydrogens resonate at the same applied field.

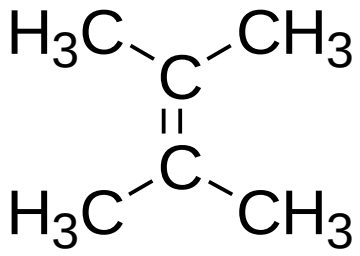
Magnetically equivalent hydrogens are also chemically equivalent.

# of signals? CH_4 CH_3CH_3

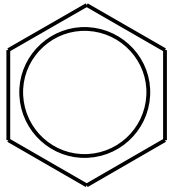
number of signals?



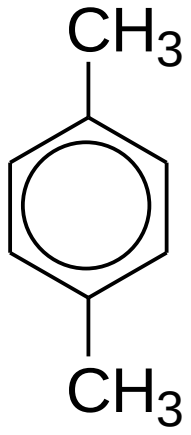
one



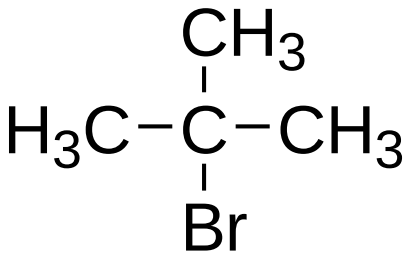
one



one



two



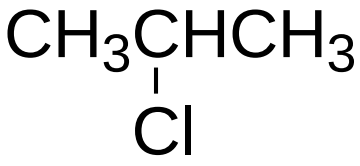
one

CH_3CH_2-Br

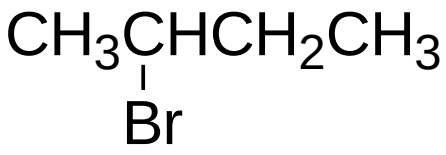
two

$CH_3CH_2CH_2$-Br

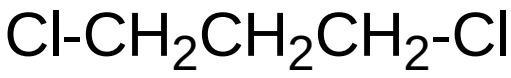
three



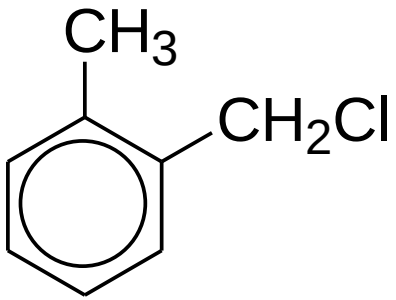
two



four



two



three

2. Position of signals (chemical shift): what types of hydrogens.

primary	0.9 ppm	
secondary	1.3	
tertiary	1.5	
aromatic	6-8.5	
allyl	1.7	
benzyl	2.2-3	
chlorides	3-4	H-C-Cl
bromides	2.5-4	H-C-Br
iodides	2-4	H-C-I
alcohols	3.4-4	H-C-O
alcohols	1-5.5	H-O- (variable)

Note: combinations may greatly influence chemical shifts. For example, the benzyl hydrogens in benzyl chloride are shifted to lower field by the chlorine and resonate at 4.5 ppm.

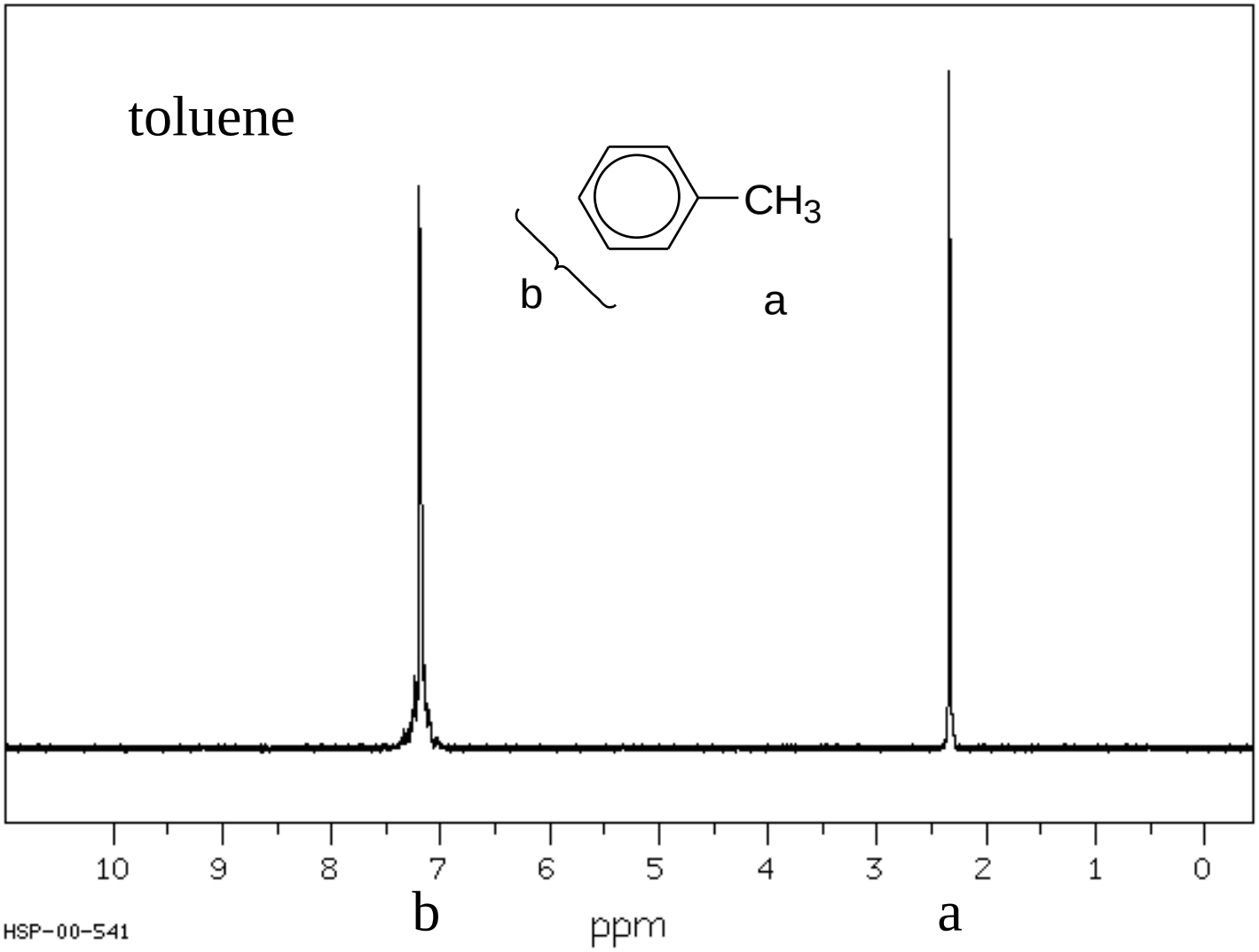
reference compound = tetramethylsilane $(CH_3)_4Si$ @ 0.0 ppm

remember: **magnetic field →**

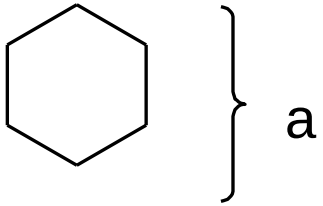
← chemical shift

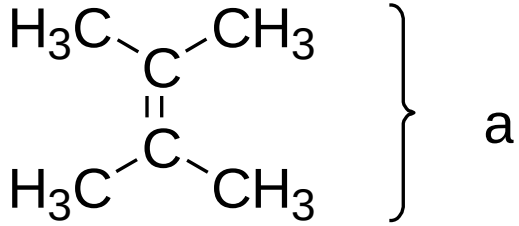
convention: let most upfield signal = a, next most upfield = b, etc.

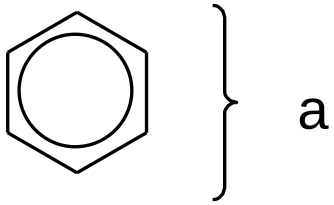
… c b a tms

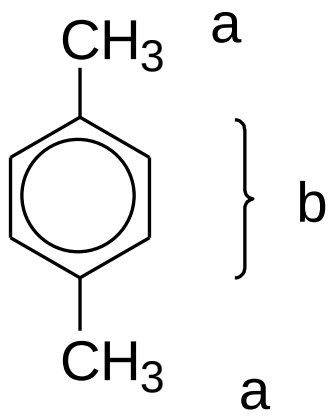

toluene
CH3
b
a
10
9
8
7
6
5
4
3
2
1
0
b
ppm
a
HSP-00-541

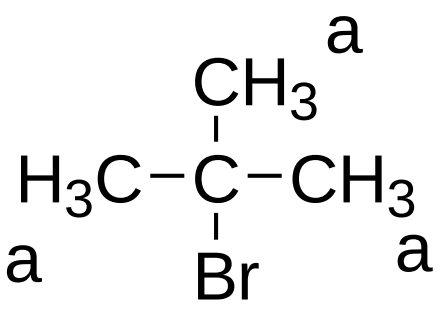
chemical shifts

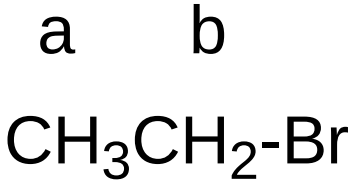


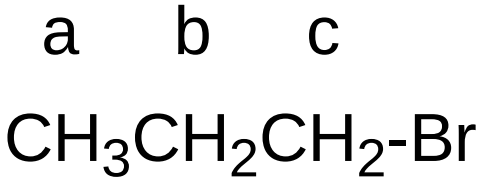


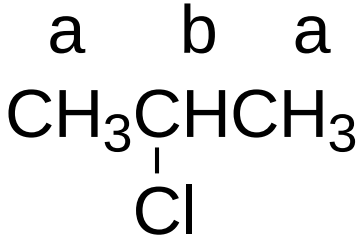


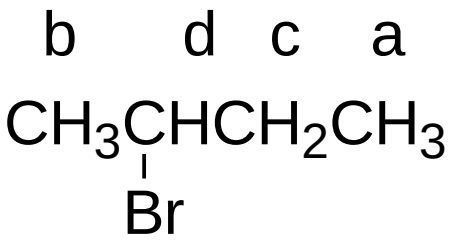


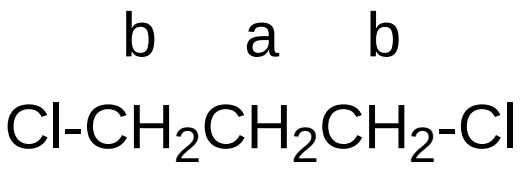

a
CH3
H3C
C
CH3
a
Br
a

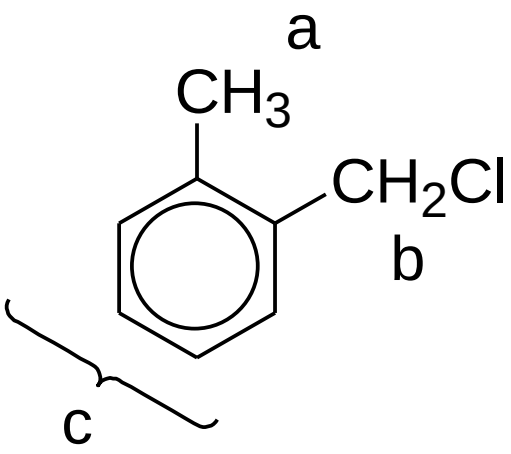

a b
CH3CH2-Br


a b c
CH3CH2CH2-Br


a b a
CH3CHCH3
Cl


b d c a
CH3CHCH2CH3
Br


b a b
Cl-CH2CH2CH2-Cl


a
CH3
CH2Cl
b
c

3. Integration (relative areas under each signal): how many hydrogens of each type.

a b c

$CH_3CH_2CH_2Br$

a 3H

b 2H

c 2H

a : b : c = 3 : 2 : 2

a b a

CH_3CHCH_3

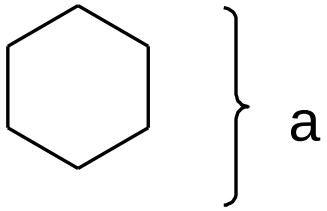
Cl

a 6H

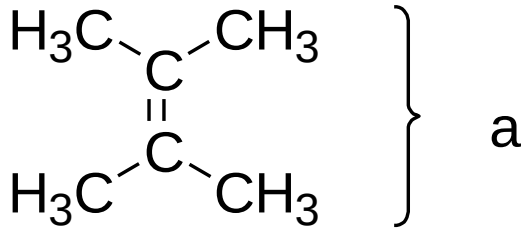
b 1H

a : b = 6 : 1

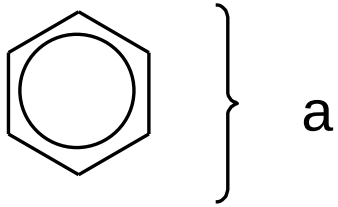
integration



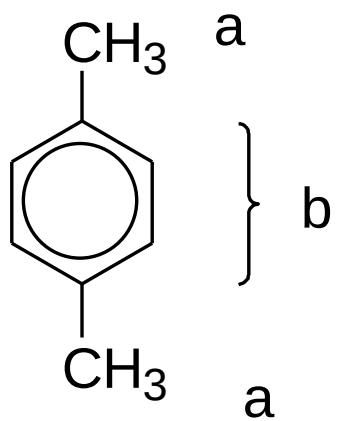
a 12 H



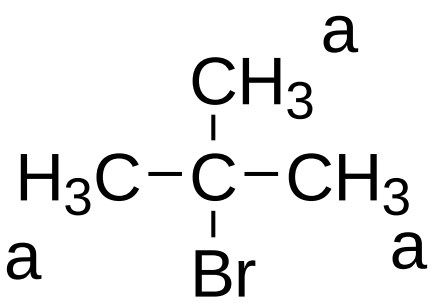
a 12 H



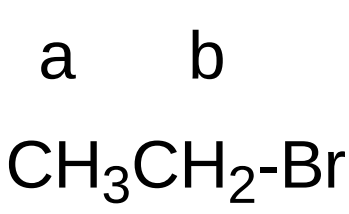
a 6 H



a 6 H
b 4 H



a 9 H

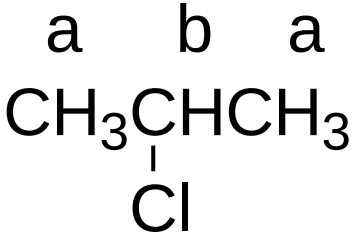


a 3 H
b 2 H

a b c

CH3CH2CH2-Br

a 3 H
b 2 H
c 2 H



a 6 H
b 1 H

b d c a

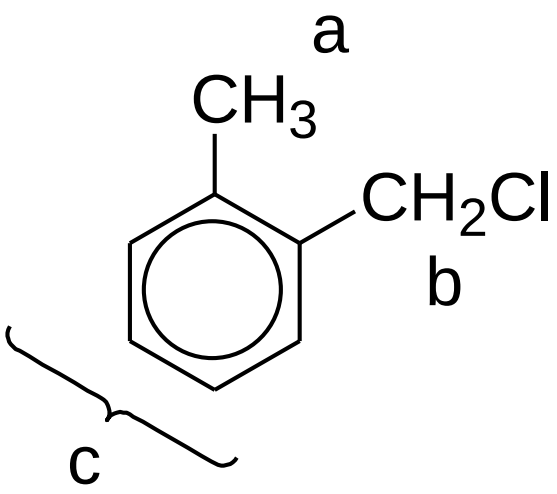
$CH_3\underset{\underset{Br}{|}}{C}HCH_2CH_3$

a 3 H
b 3 H
c 2 H
d 1 H

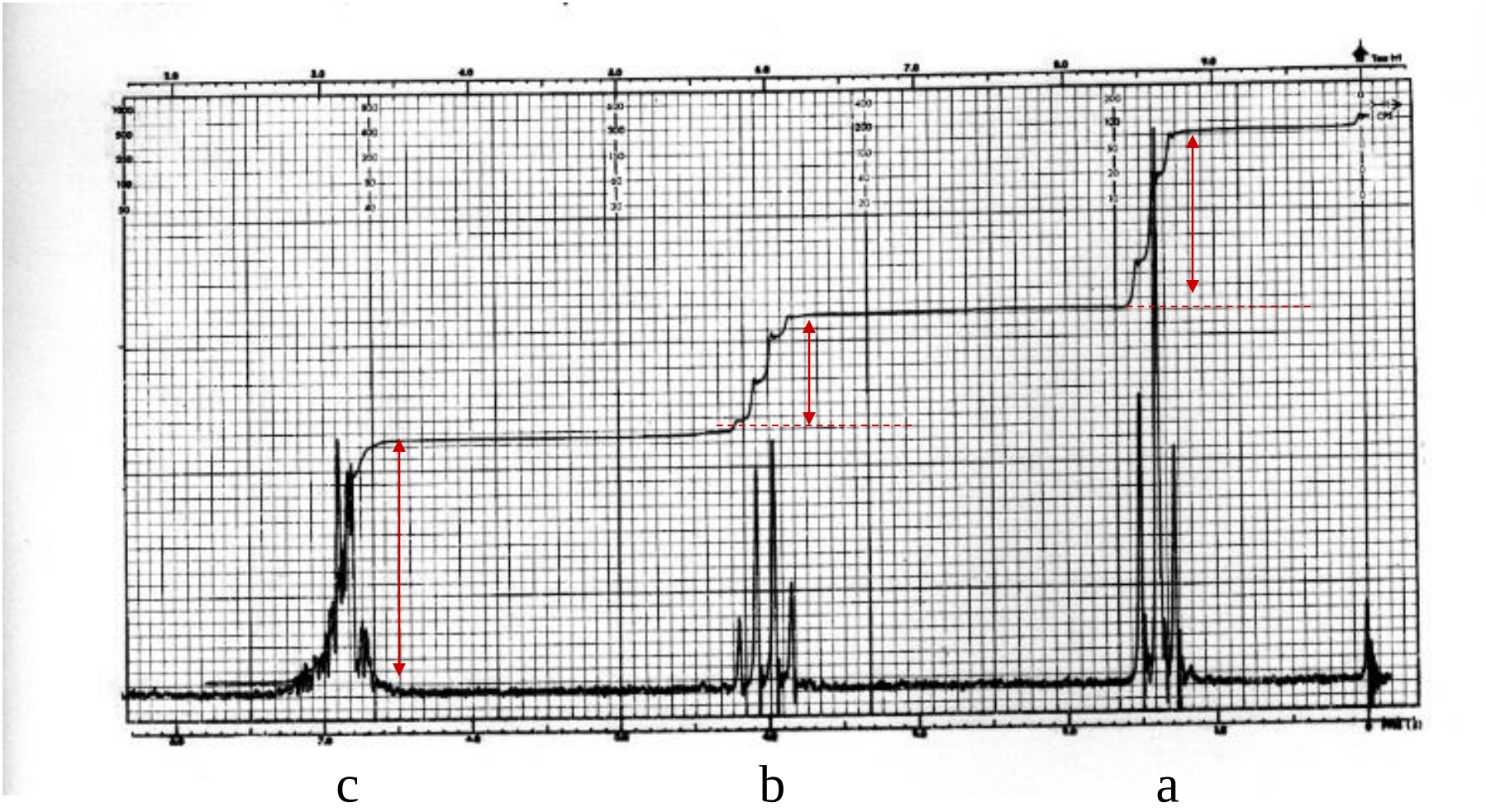
b a b

Cl-$CH_2CH_2CH_2$-Cl

a 2 H
b 4 H

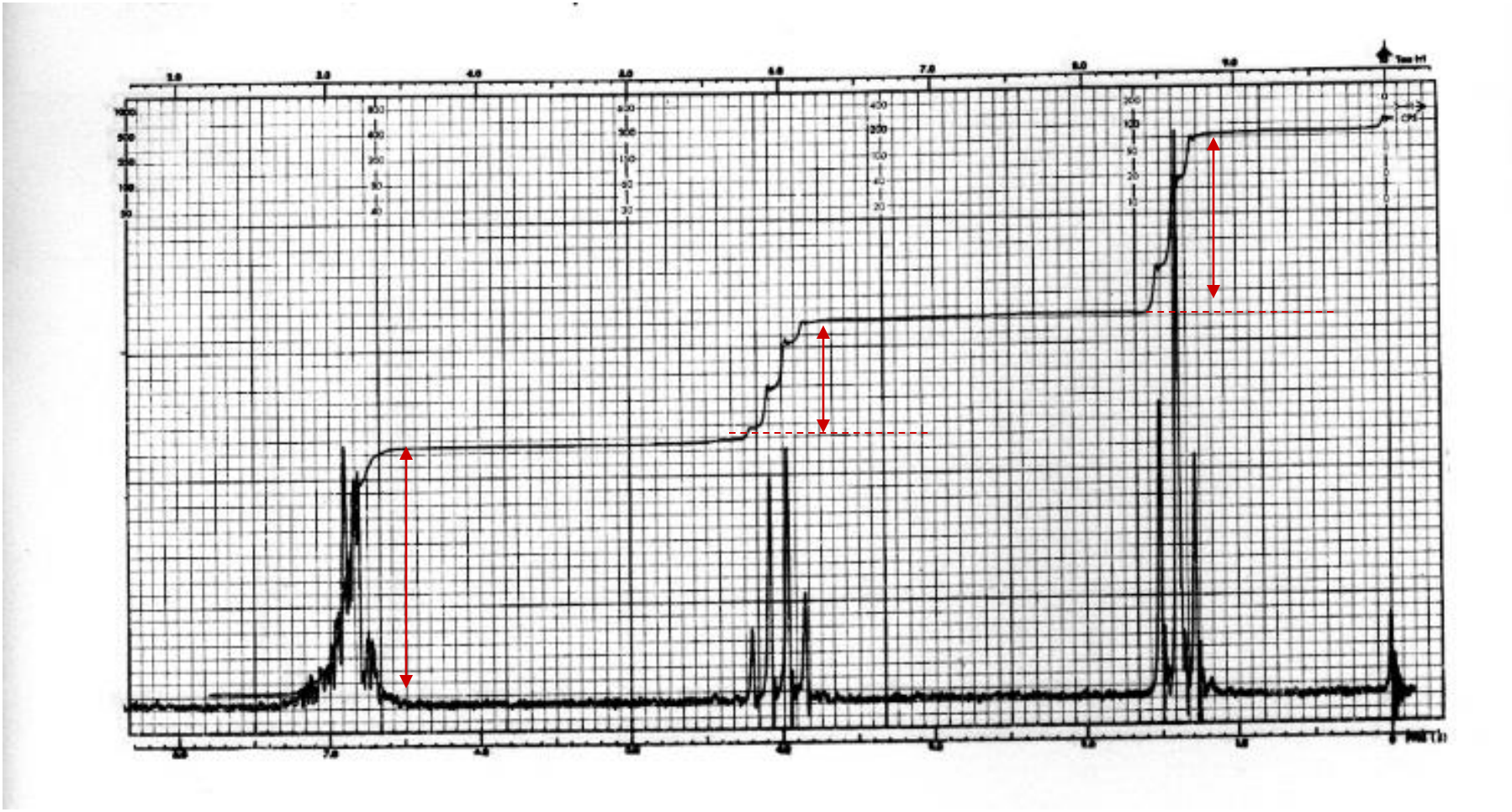


a 3 H
b 2 H
c 4 H



c b a

Integration: measure the height of each “step” in the integration and then calculate the lowest whole number ratio: a:b:c = 24 mm : 16 mm : 32 mm = 1.5 : 1.0 : 2.0 → 3H : 2H : 4H



If the formula is known (C_8H_9OF), add up all of the “steps” and divide by the number of hydrogens = (24 + 16 + 32 mm) / 9H = 8.0 mm / Hydrogen.
a = 24 mm / 8.0 mm/H → 3 H; b = 16 mm/8.0 mm/H → 2H;
c = 32 mm/8.0 mm/H → 4H.

4. Splitting pattern: how many neighboring hydrogens.

In general, n-equivalent neighboring hydrogens will split a ^{1}H signal into an (n + 1) Pascal pattern.

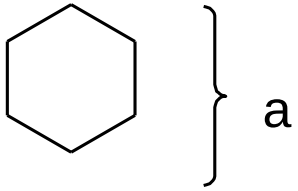
"neighboring" – no more than three bonds away

n	n + 1	Pascal pattern:	
0	1	1	singlet
1	2	1 1	doublet
2	3	1 2 1	triplet
3	4	1 3 3 1	quartet
4	5	1 4 6 4 1	quintet

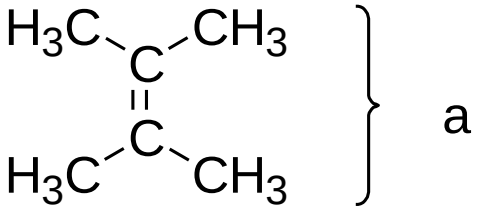
note: n must be equivalent neighboring hydrogens to give rise to a Pascal splitting pattern. If the neighbors are not equivalent, then you will see a complex pattern (aka complex multiplet).

note: the alcohol hydrogen –OH usually does not split neighboring hydrogen signals nor is it split. Normally a singlet of integration 1 between 1 – 5.5 ppm (variable).

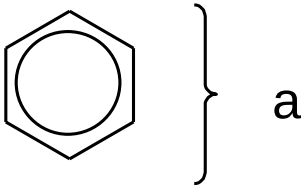
splitting pattern?



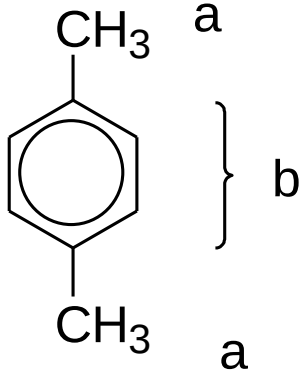
a 12 H singlet



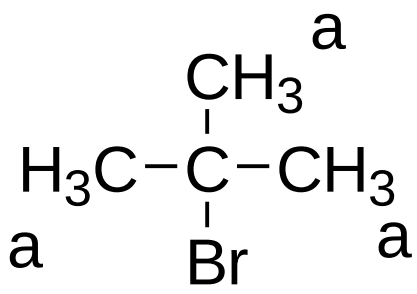
a 12 H singlet



a 6 H singlet



a 6 H singlet
b 4 H singlet



a 9 H singlet

a b

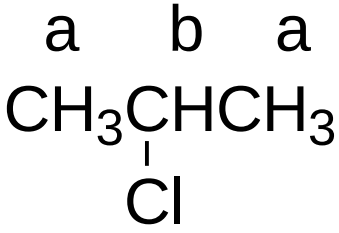
CH_3CH_2-Br

a 3 H triplet
b 2 H quartet

a b c

$CH_3CH_2CH_2$-Br

a 3 H triplet
b 2 H complex
c 2 H triplet



a 6 H doublet
b 1 H septet

b d c a

$CH_3CHCH_2CH_3$

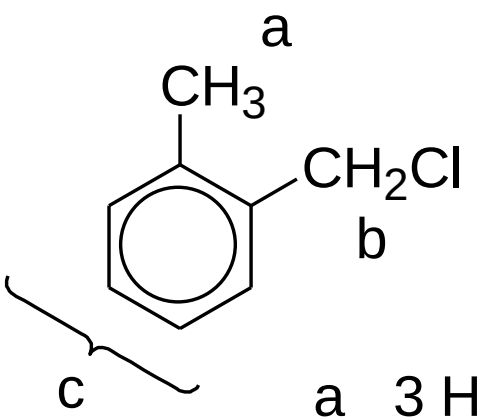
Br

a 3 H triplet
b 3 H doublet
c 2 H complex
d 1 H complex

b a b

Cl-$CH_2CH_2CH_2$-Cl

a 2 H quintet
b 4 H triplet



a 3 H singlet
b 2 H singlet
c 4 H ~singlet

a b c

CH_3CH_2-OH

a 3 H triplet
b 2 H quartet
c 1 H singlet

Information from ^{1}H-nmr spectra:

1. **Number of signals: How many different types of hydrogens in the molecule.**
2. **Position of signals (chemical shift): What types of hydrogens.**
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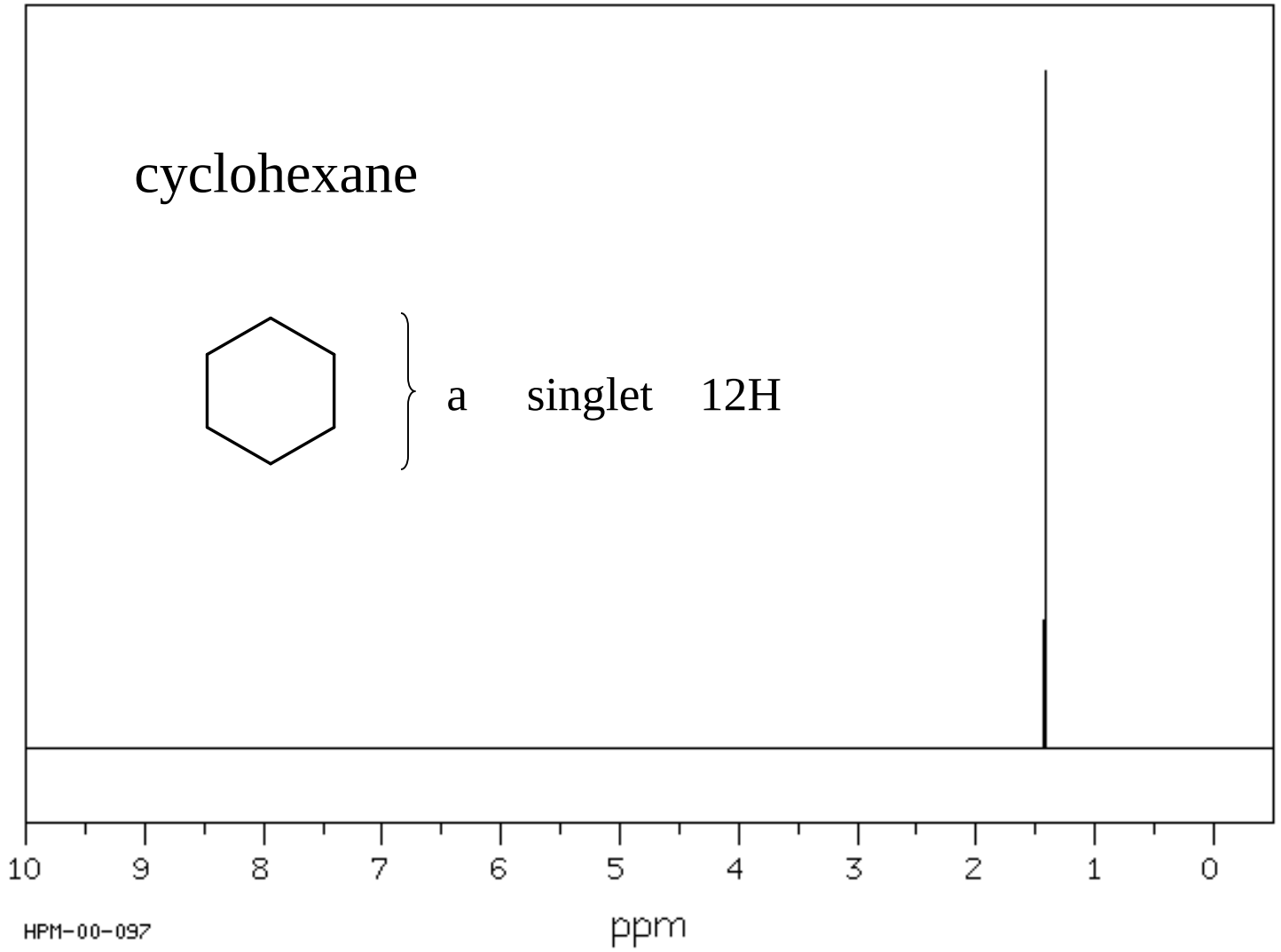
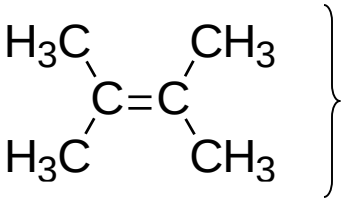
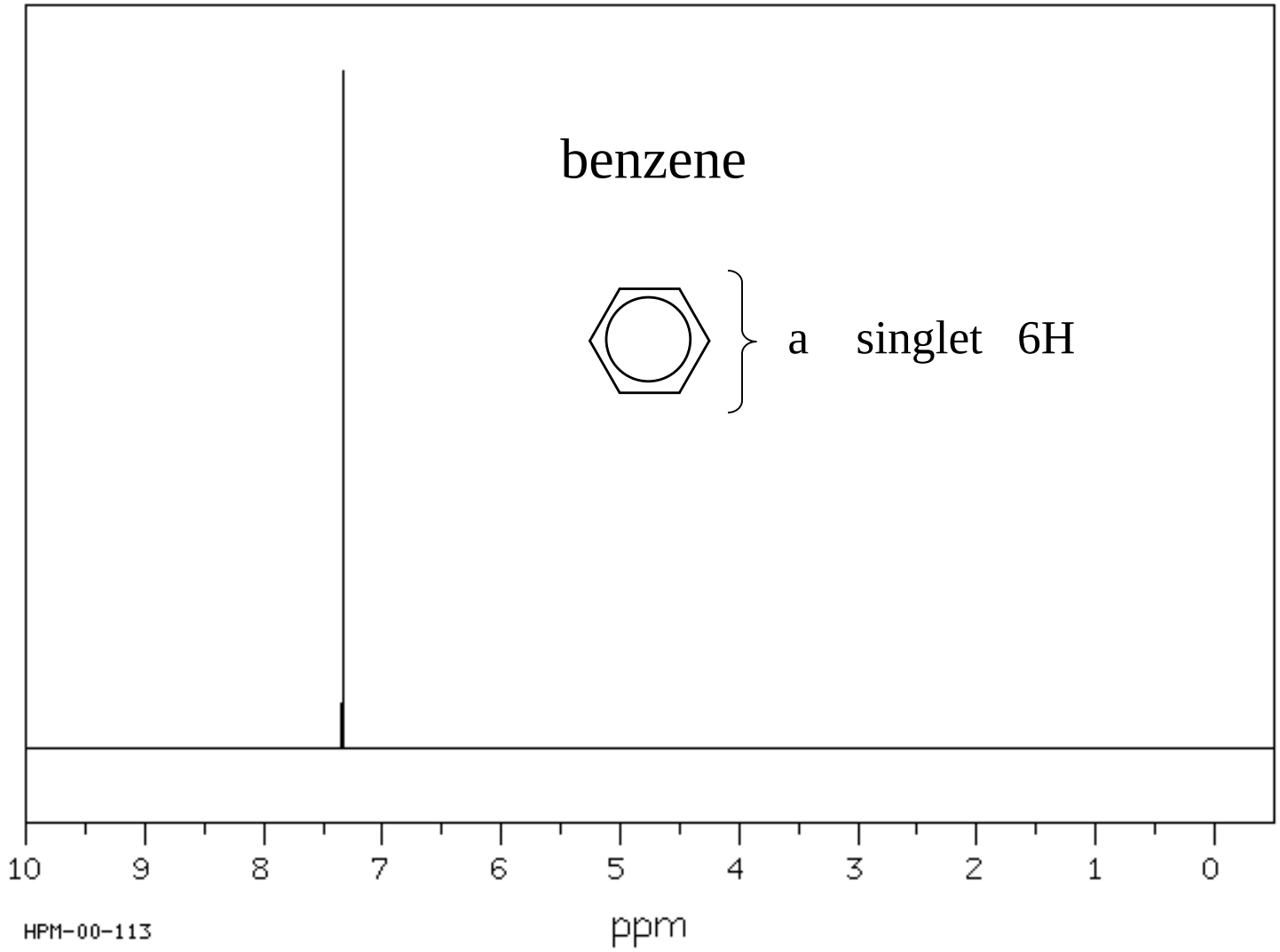
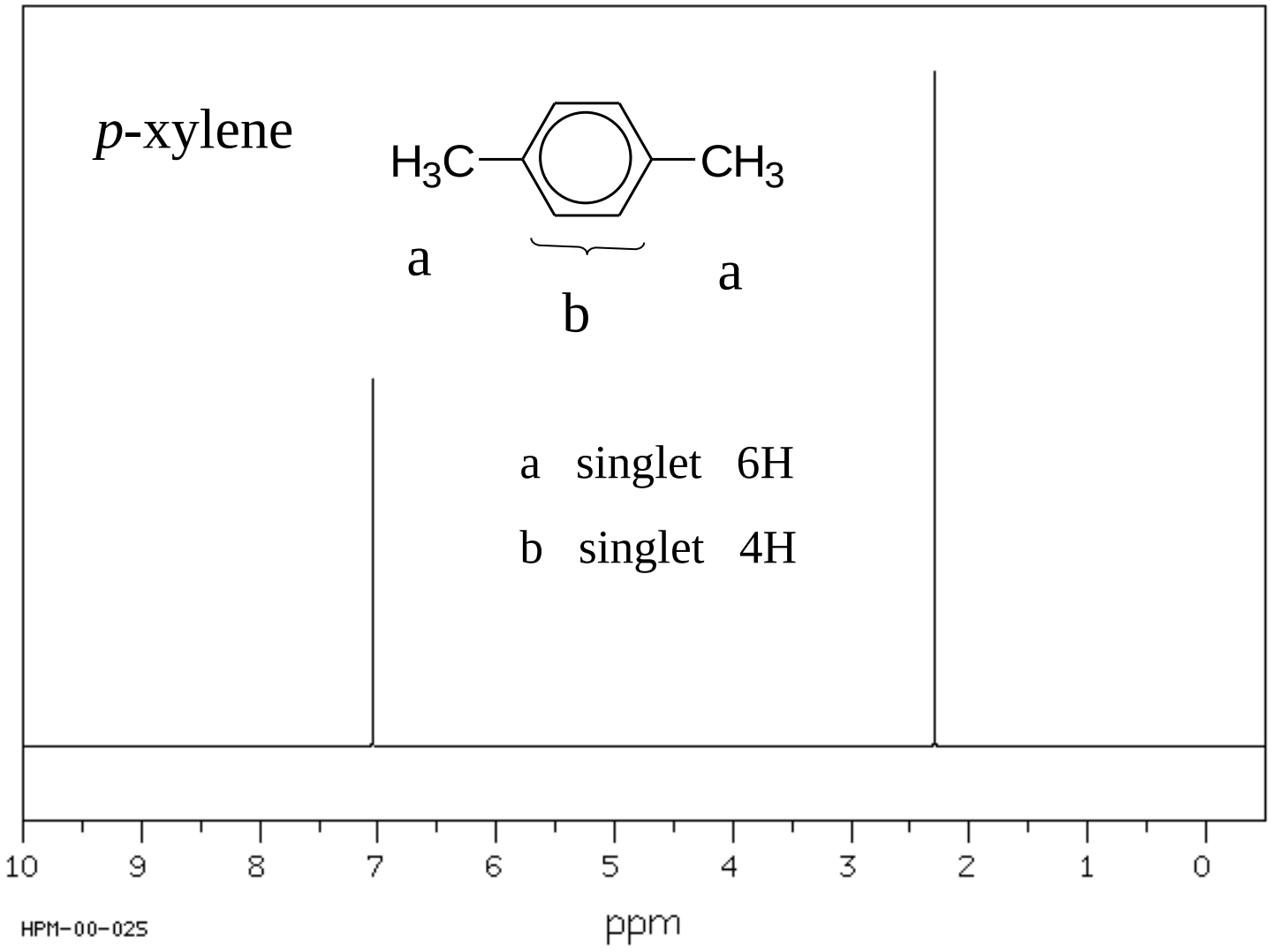

cyclohexane
a singlet 12H
10
9
8
7
6
5
4
3
2
1
0
ppm
HPM-00-097

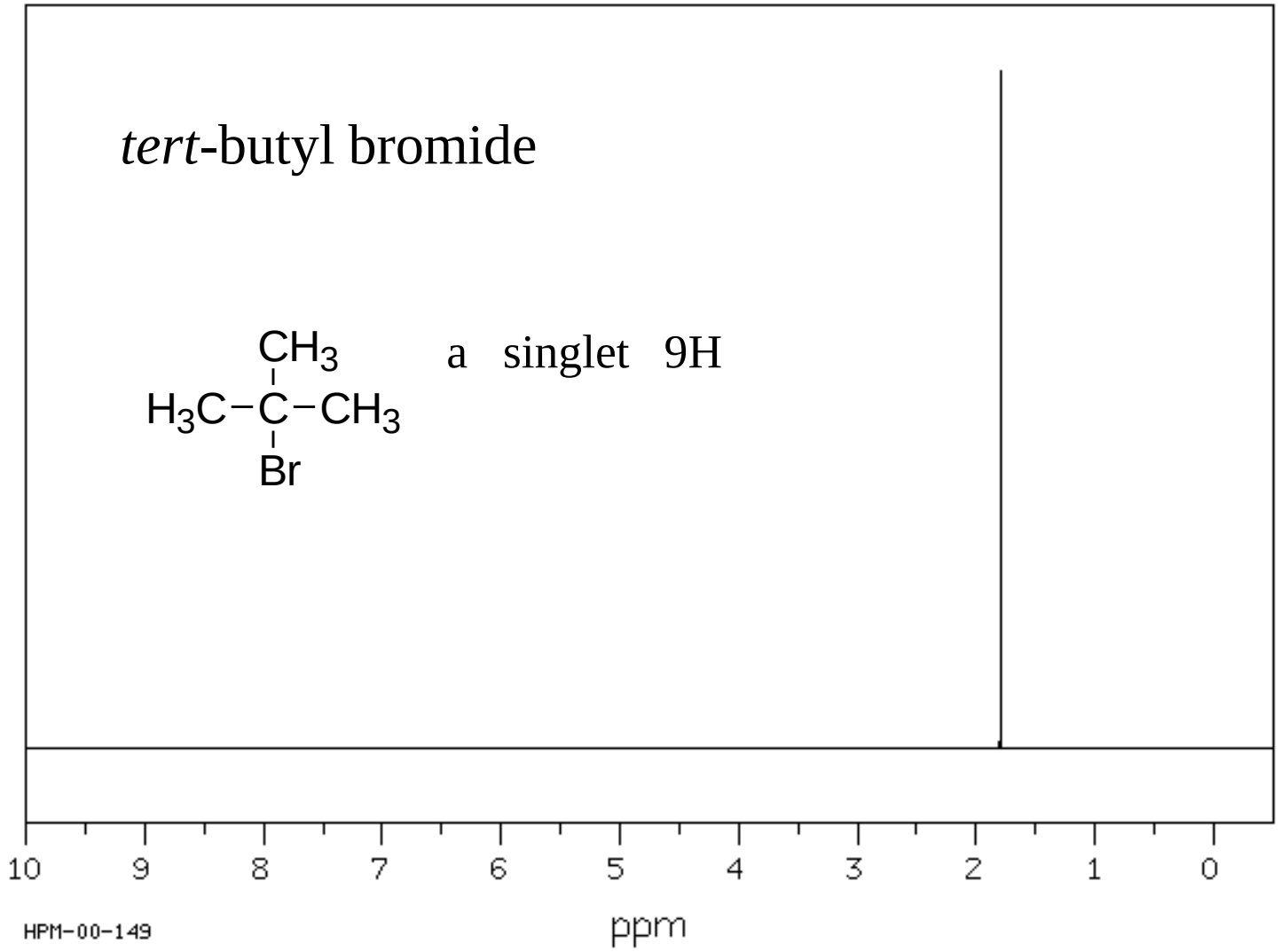
2,3-dimethyl-2-butene



a singlet 12H


benzene
a singlet 6H
10
9
8
7
6
5
4
3
2
1
0
HPM-00-113
ppm


p-xylene
H_3C
CH_3
a
a
b
a singlet 6H
b singlet 4H
10
9
8
7
6
5
4
3
2
1
0
HPM-00-025
ppm


tert-butyl bromide
CH3
H3C−C−CH3
Br
a singlet 9H
10
9
8
7
6
5
4
3
2
1
0
HPM-00-149
ppm

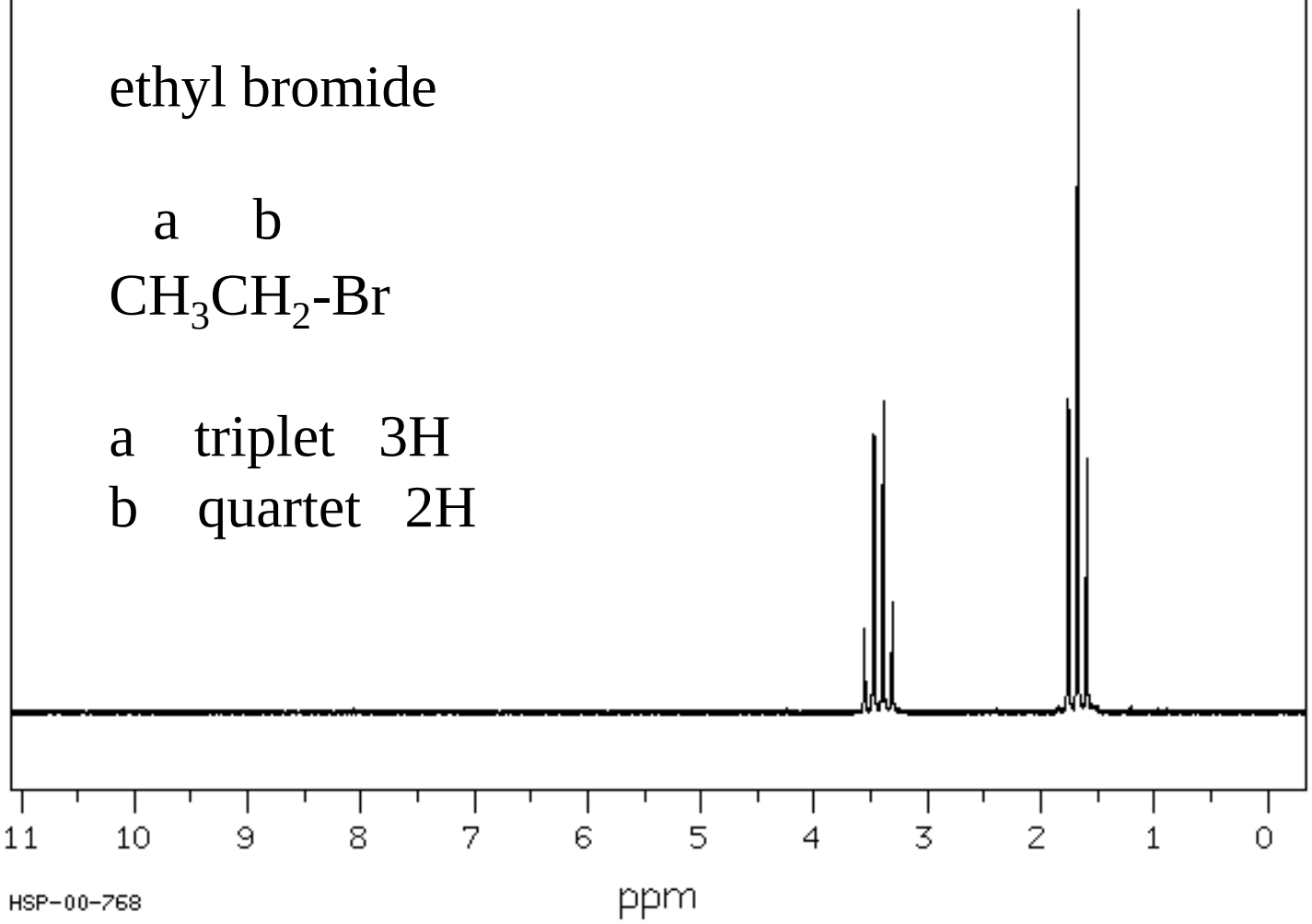
ethyl bromide

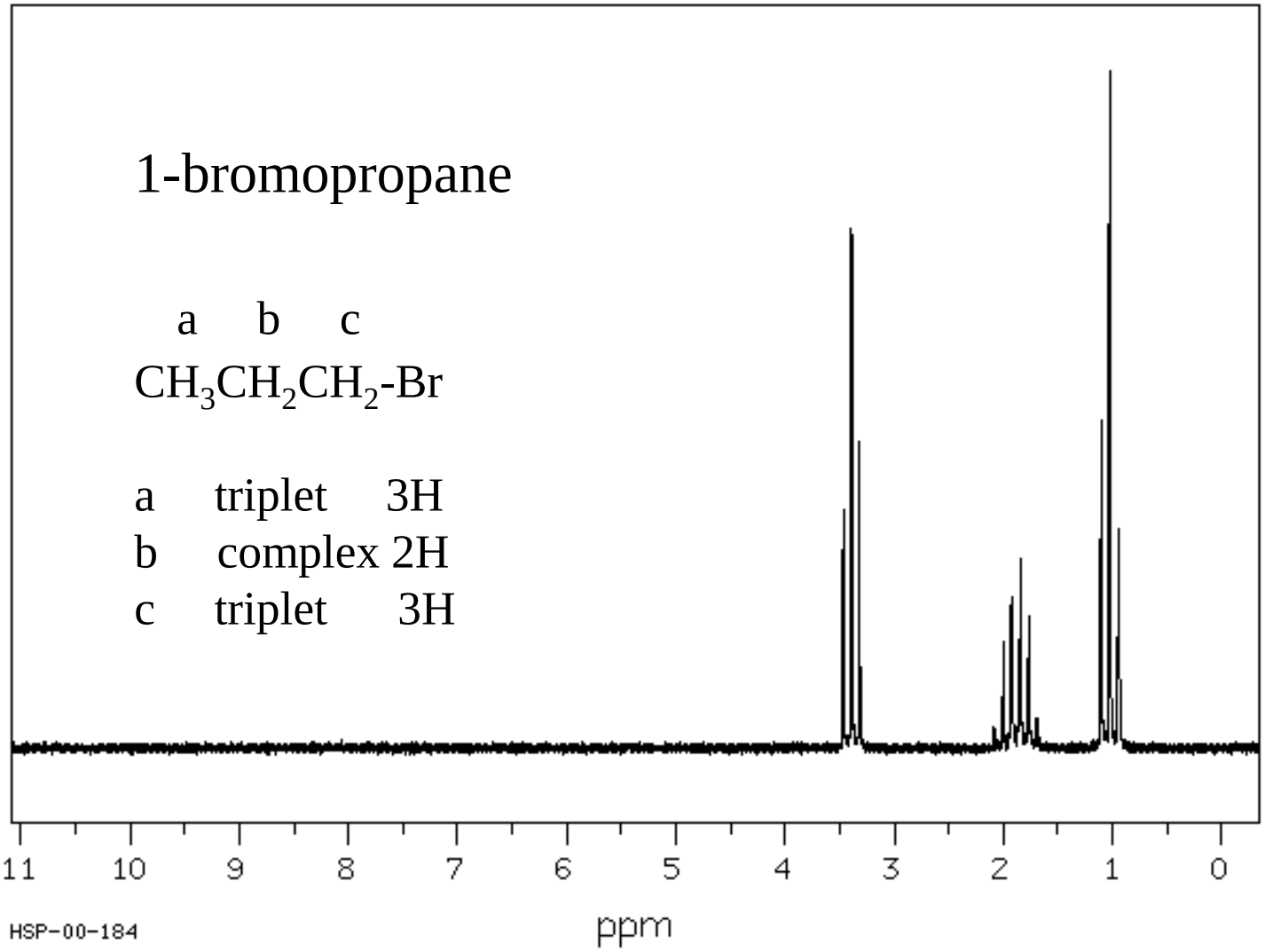
a b

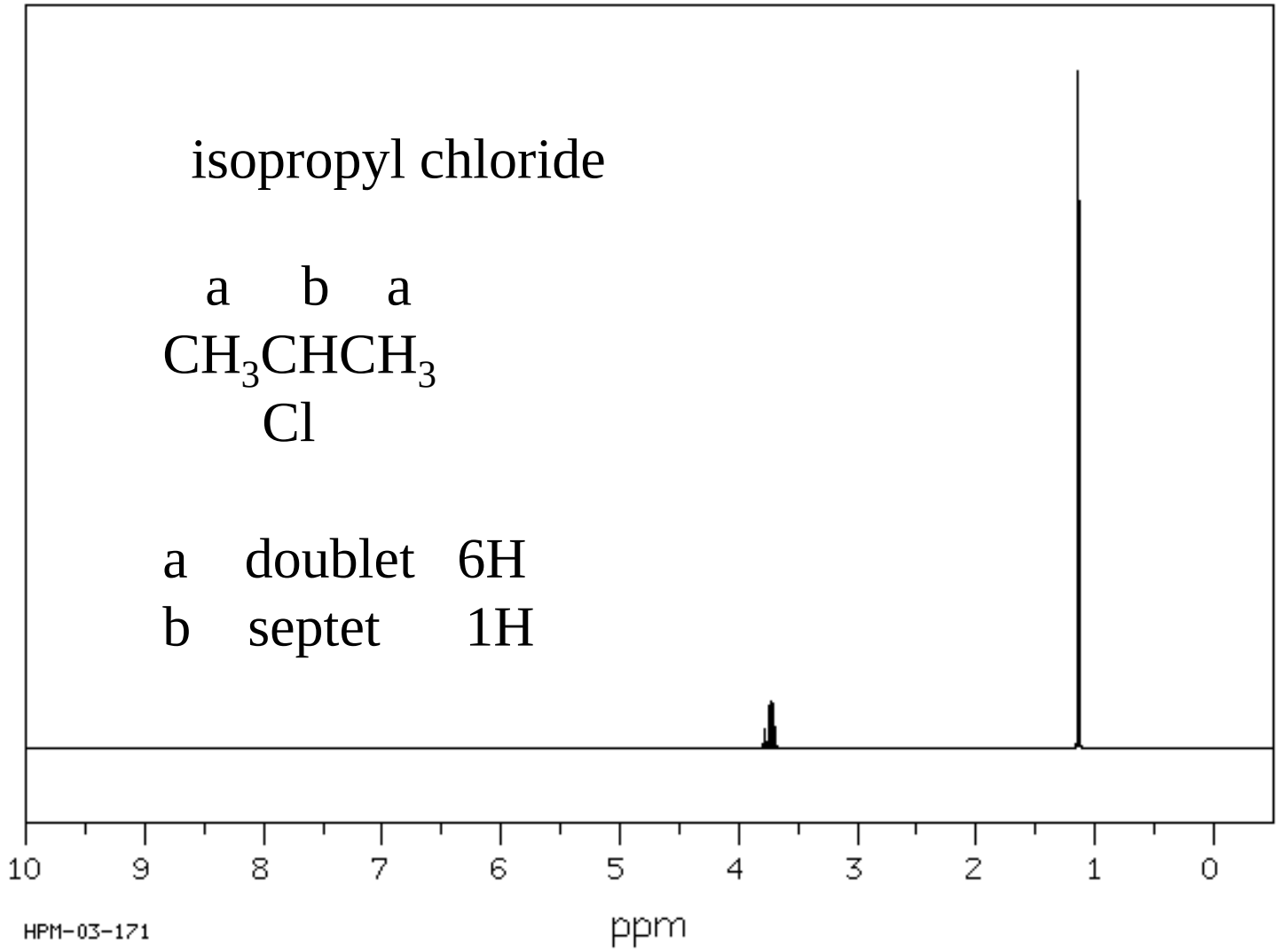
CH_3CH_2-Br

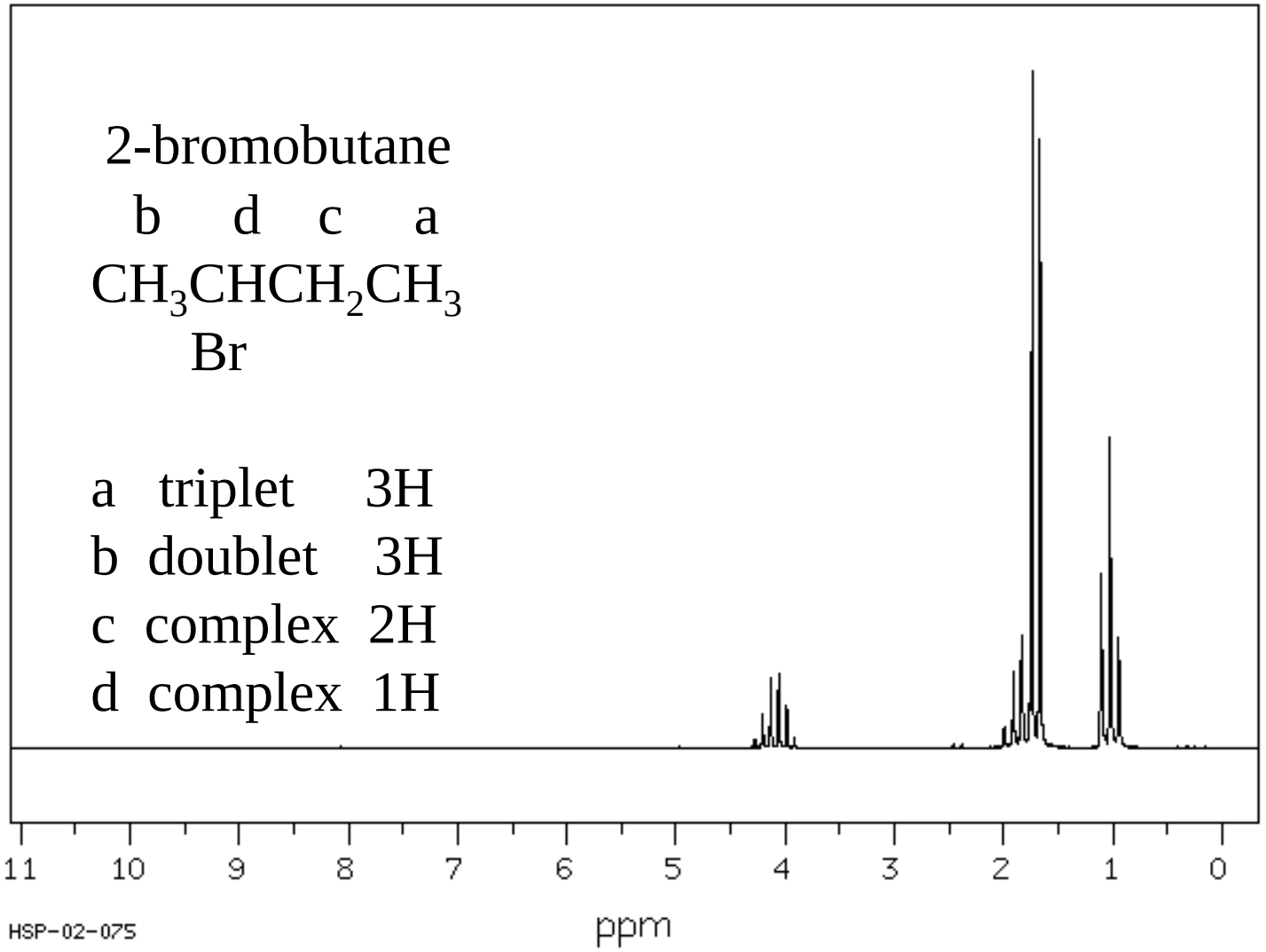
a triplet 3H

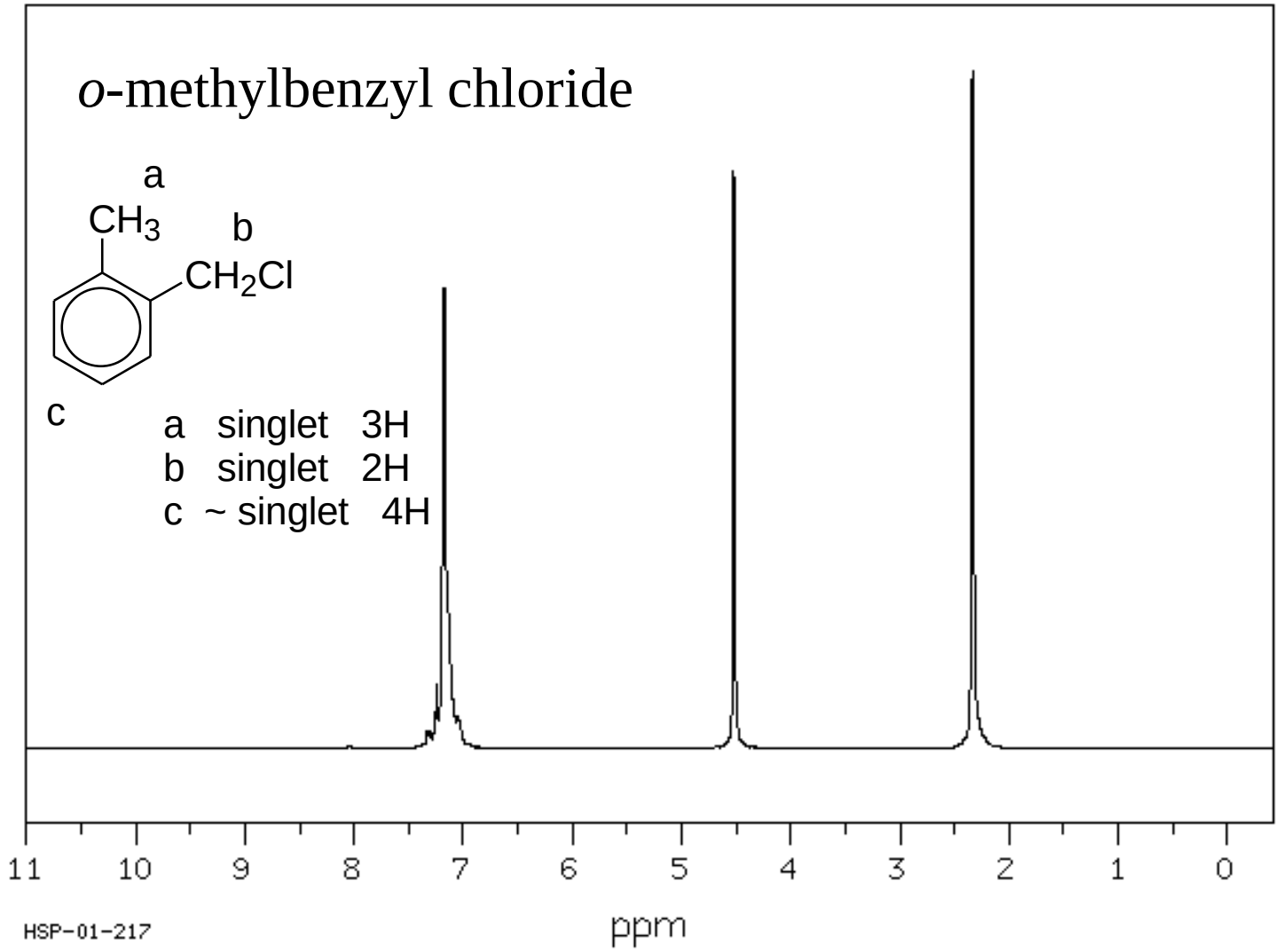
b quartet 2H

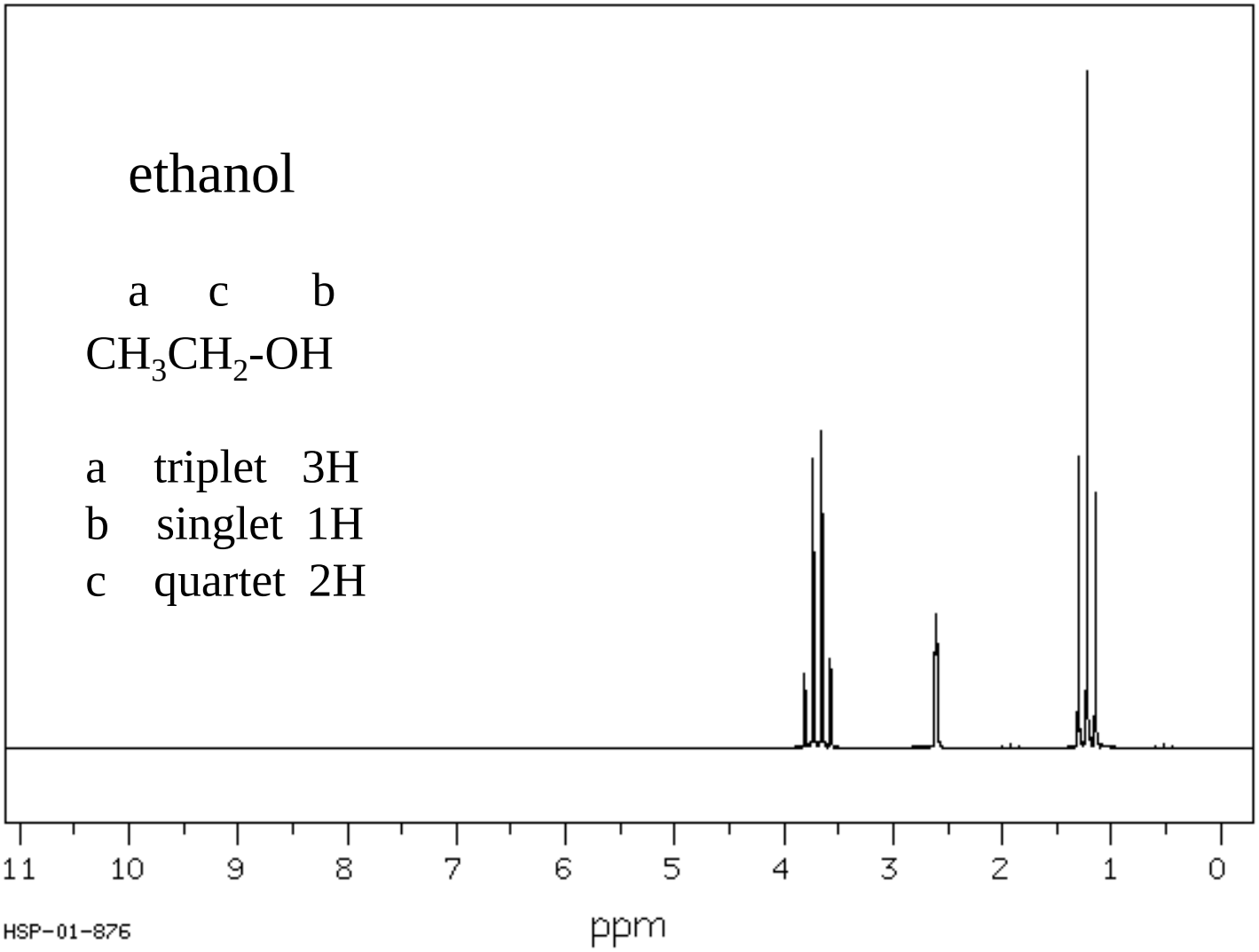


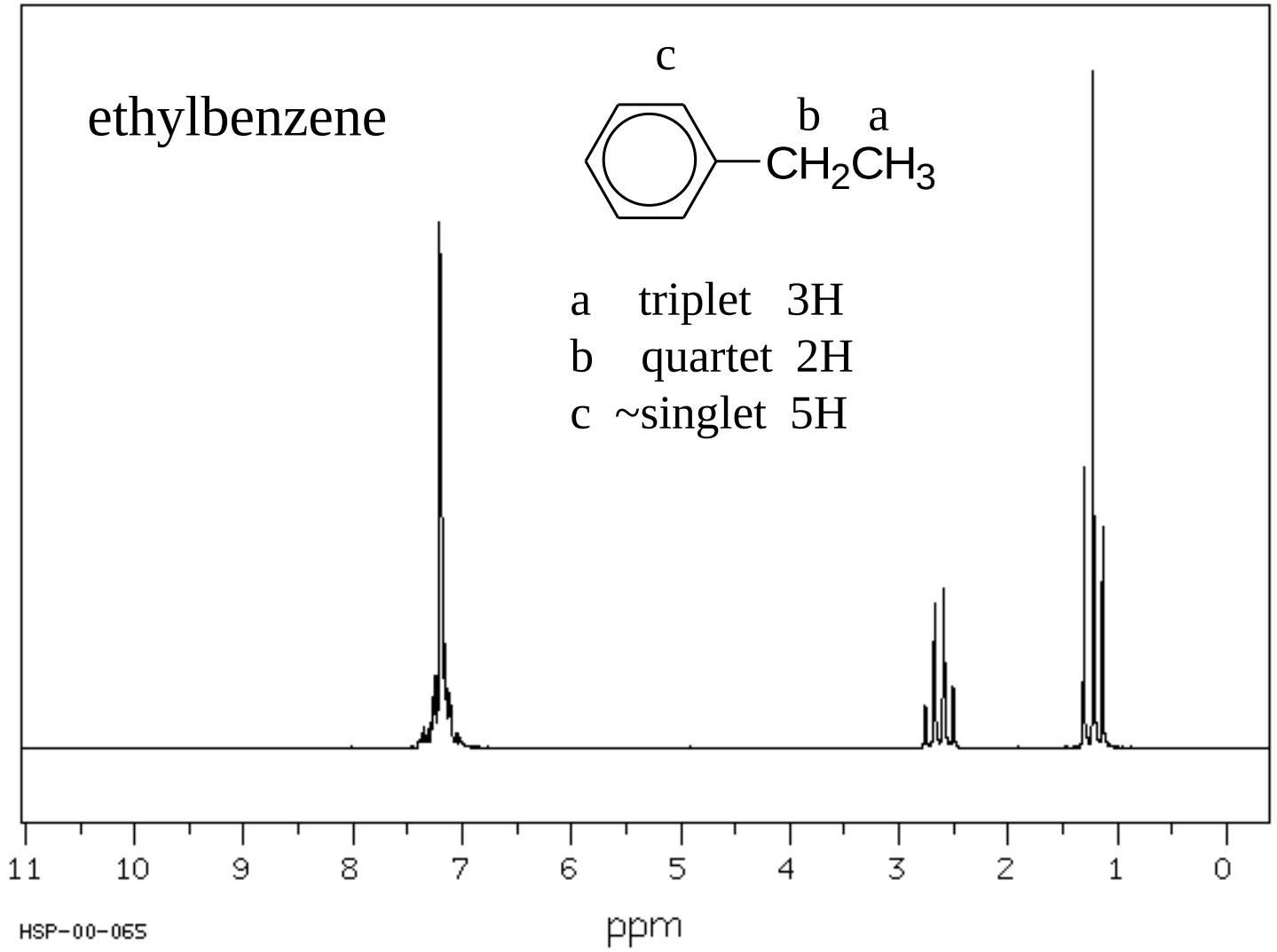

1-bromopropane
a b c
CH3CH2CH2-Br
a triplet 3H
b complex 2H
c triplet 3H
11 10 9 8 7 6 5 4 3 2 1 0
HSP-00-184
ppm

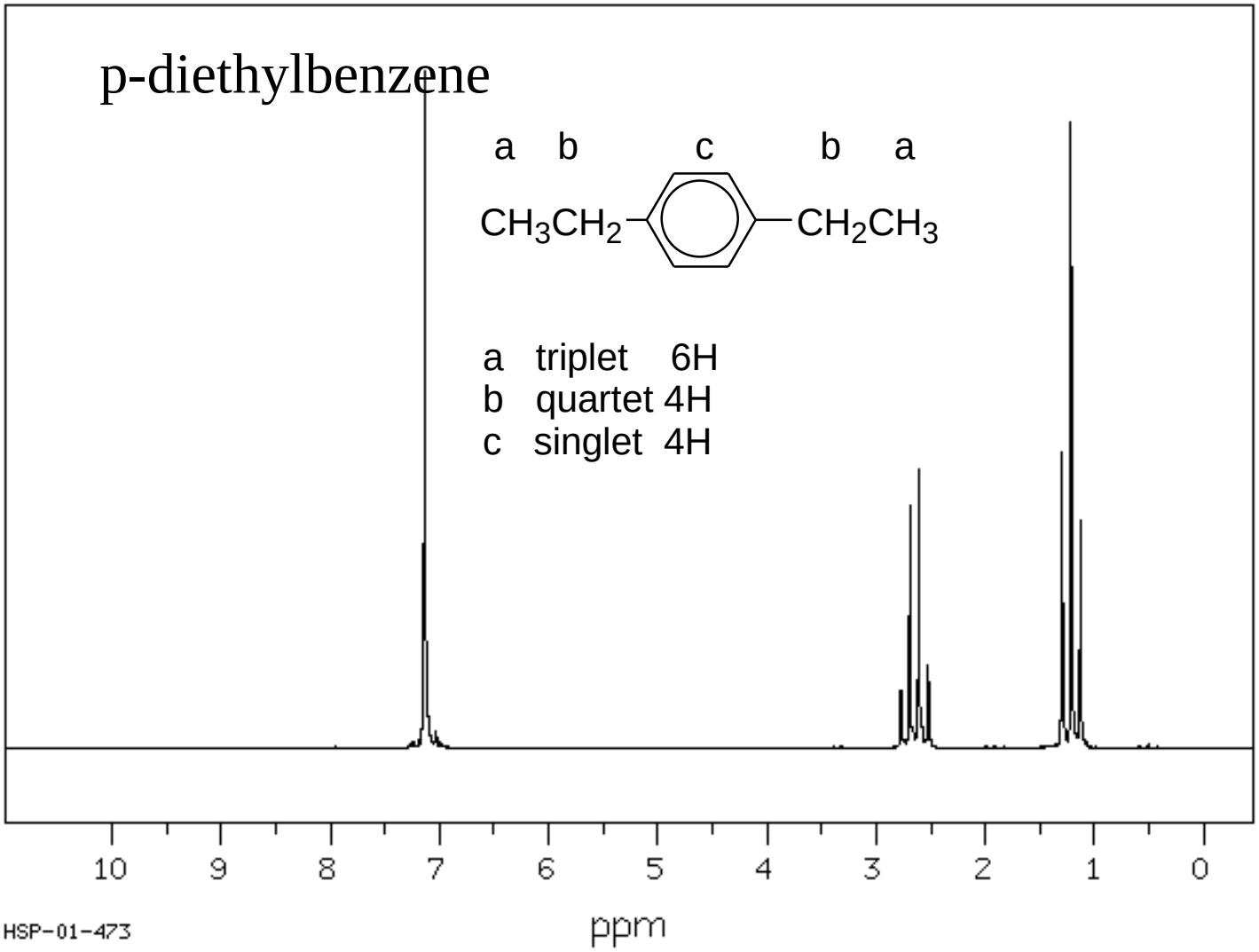

isopropyl chloride
a b a
CH3CHCH3
Cl
a doublet 6H
b septet 1H
10 9 8 7 6 5 4 3 2 1 0
ppm
HPM-03-171

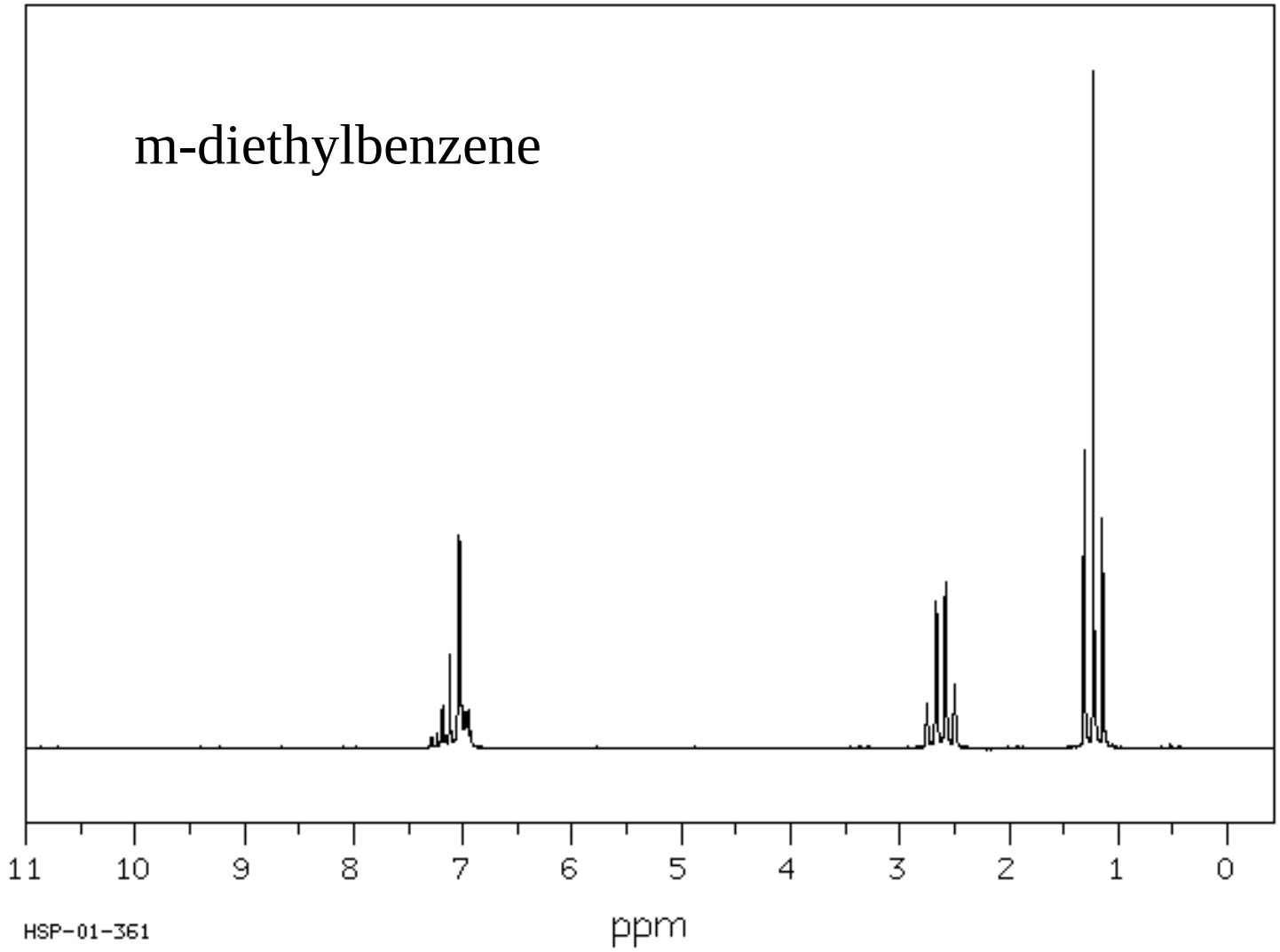

2-bromobutane
b d c a
CH3CHCH2CH3
Br
a triplet 3H
b doublet 3H
c complex 2H
d complex 1H
11 10 9 8 7 6 5 4 3 2 1 0
HSP-02-075
ppm

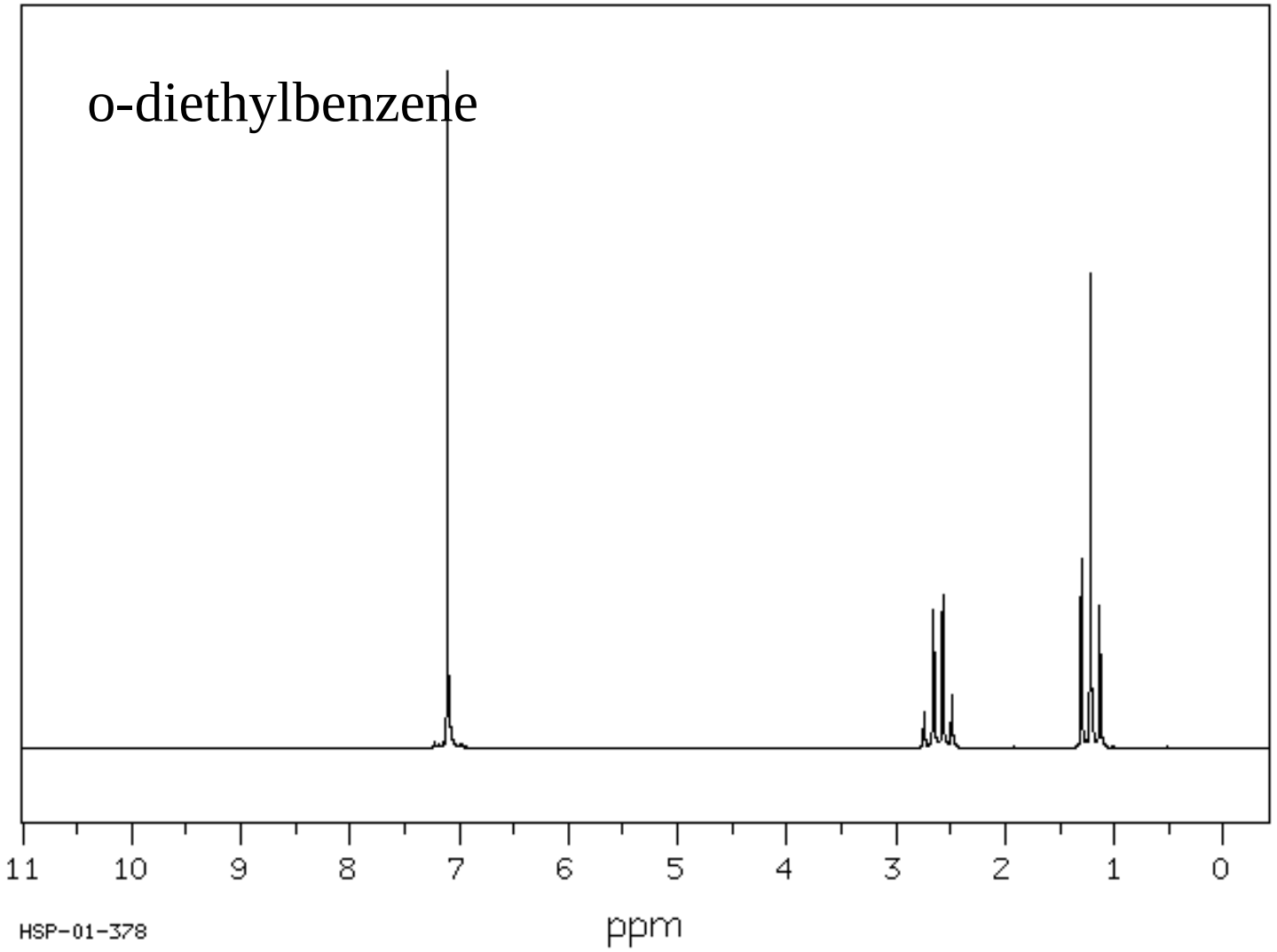

o-methylbenzyl chloride
a
CH3
b
CH2Cl
c
a singlet 3H
b singlet 2H
c ~ singlet 4H
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-01-217

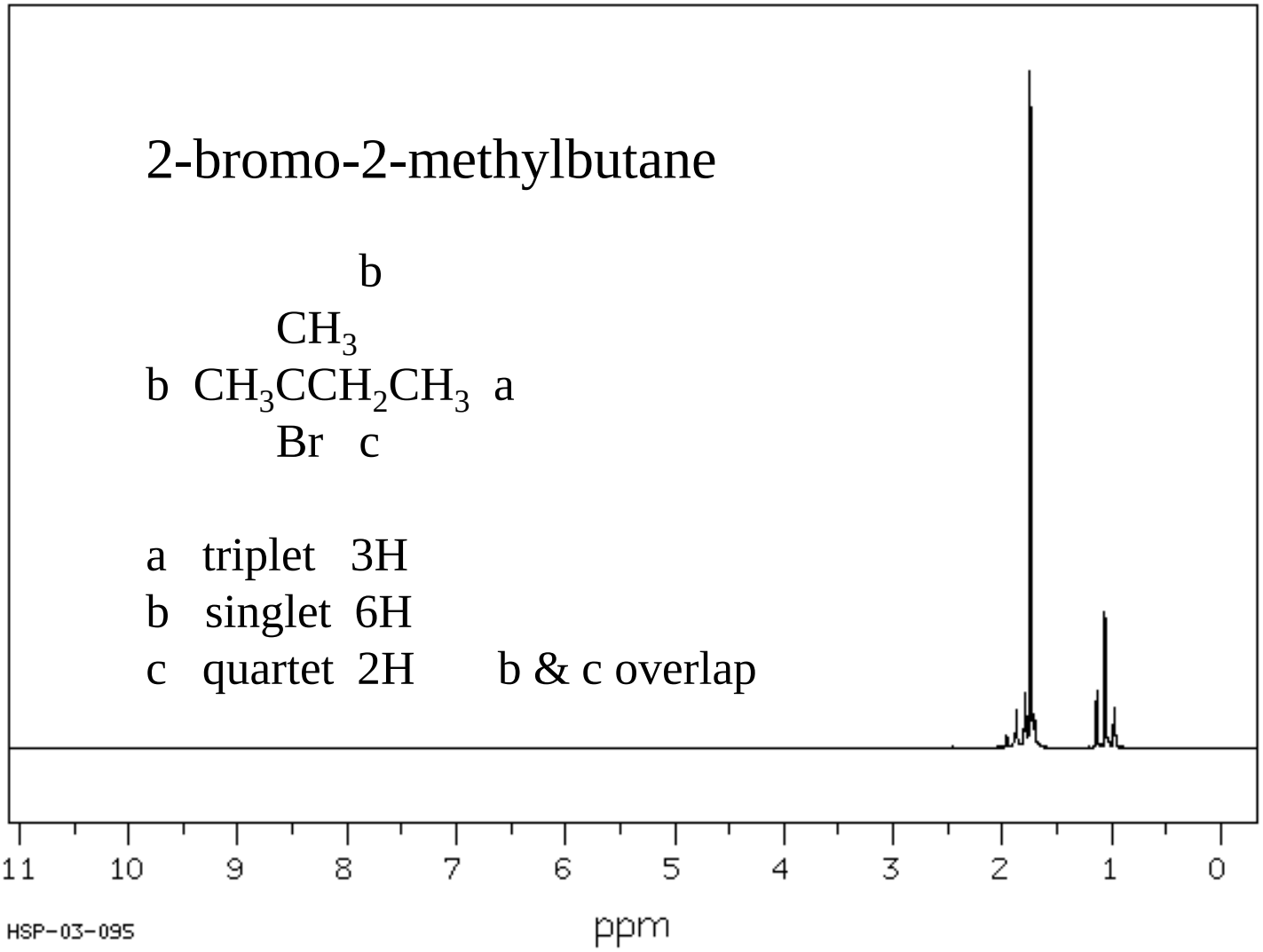

ethanol
a c b
CH3CH2-OH
a triplet 3H
b singlet 1H
c quartet 2H
11 10 9 8 7 6 5 4 3 2 1 0
HSP-01-876
ppm

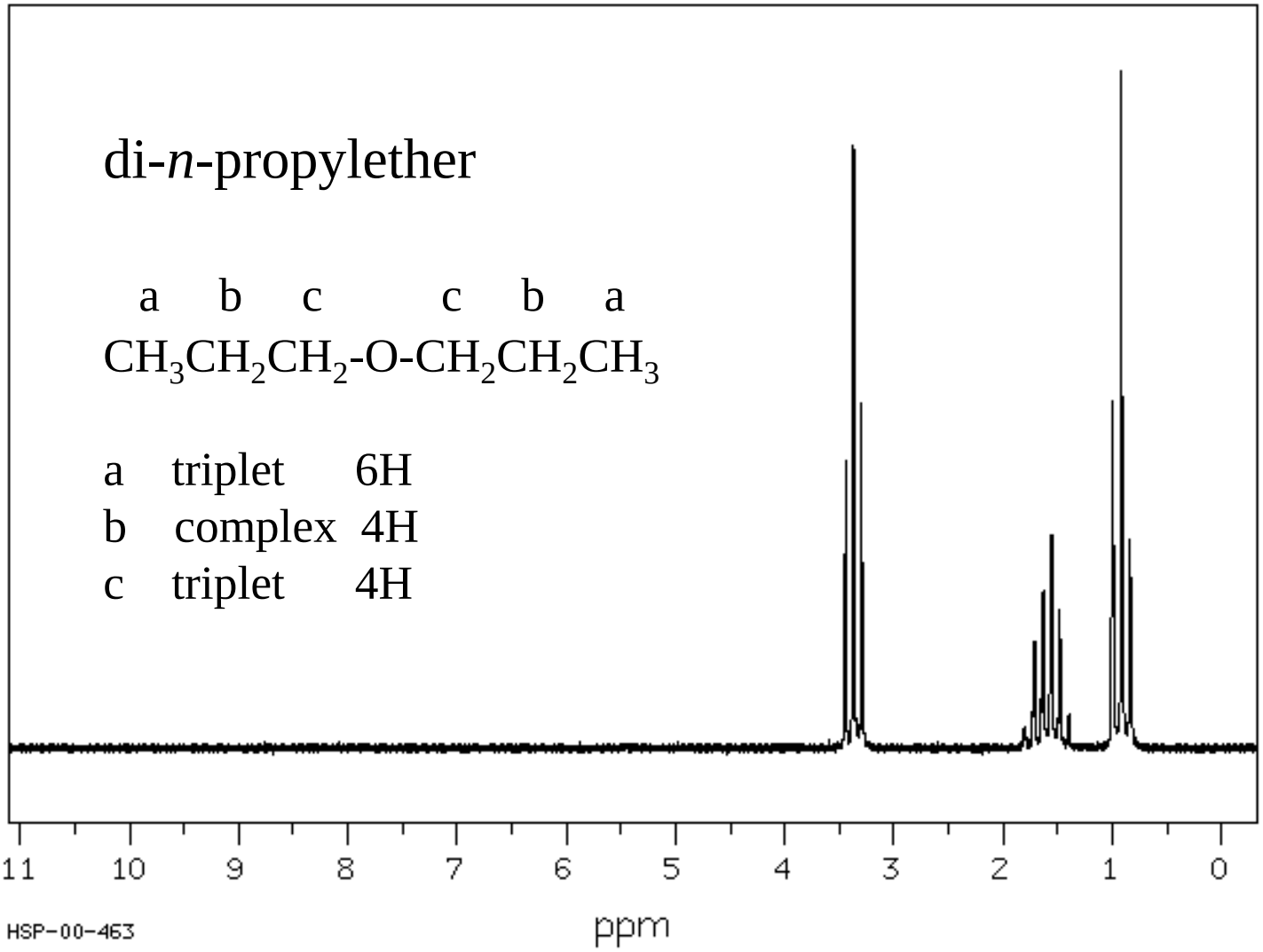

ethylbenzene
c
b a
CH2CH3
a triplet 3H
b quartet 2H
c ~singlet 5H
11
10
9
8
7
6
5
4
3
2
1
0
HSP-00-065
ppm

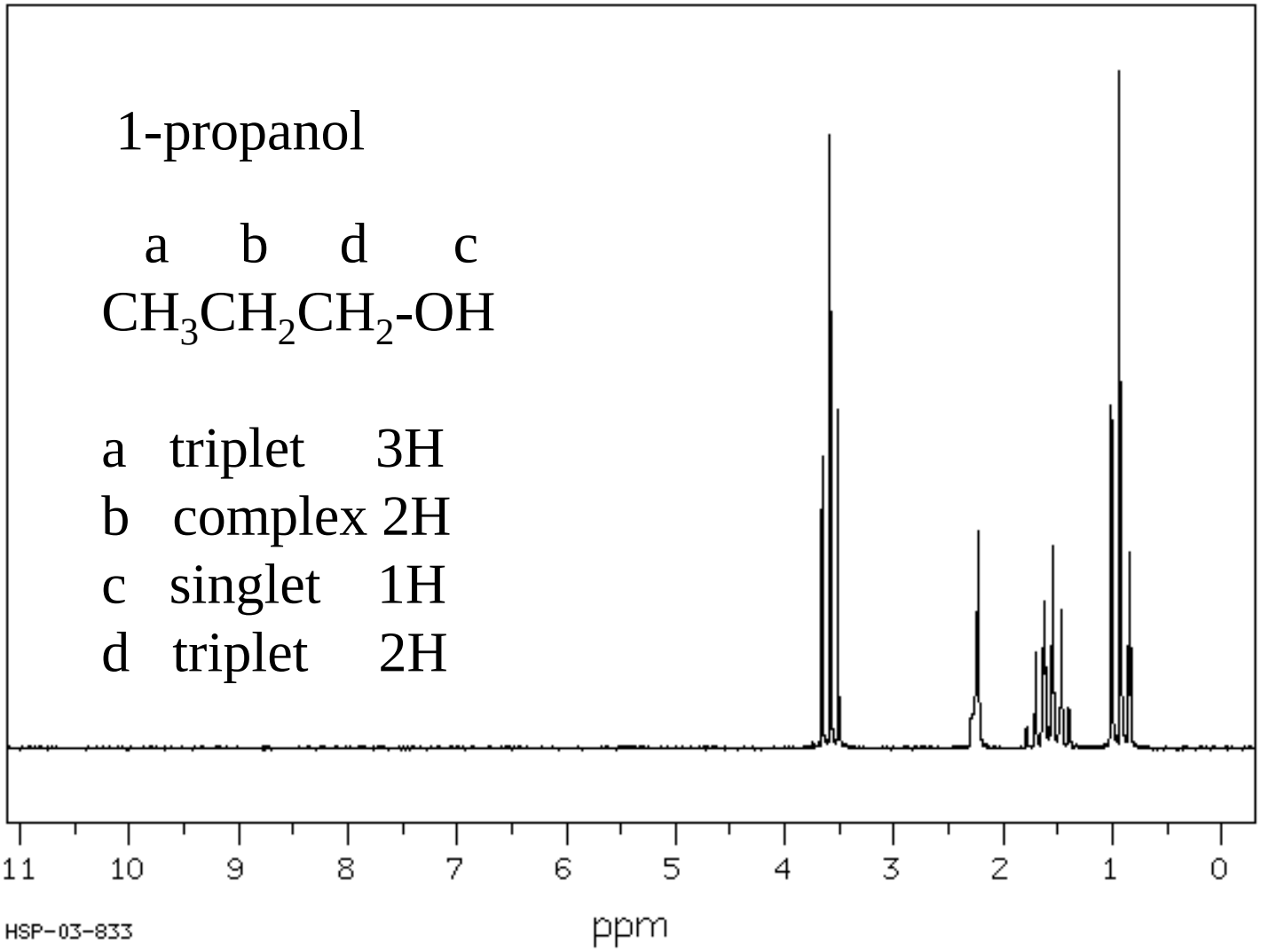

p-diethylbenzene
a b c b a
CH3CH2
CH2CH3
a triplet 6H
b quartet 4H
c singlet 4H
10 9 8 7 6 5 4 3 2 1 0
ppm
HSP-01-473


m-diethylbenzene
11
10
9
8
7
6
5
4
3
2
1
0
HSP-01-361
ppm

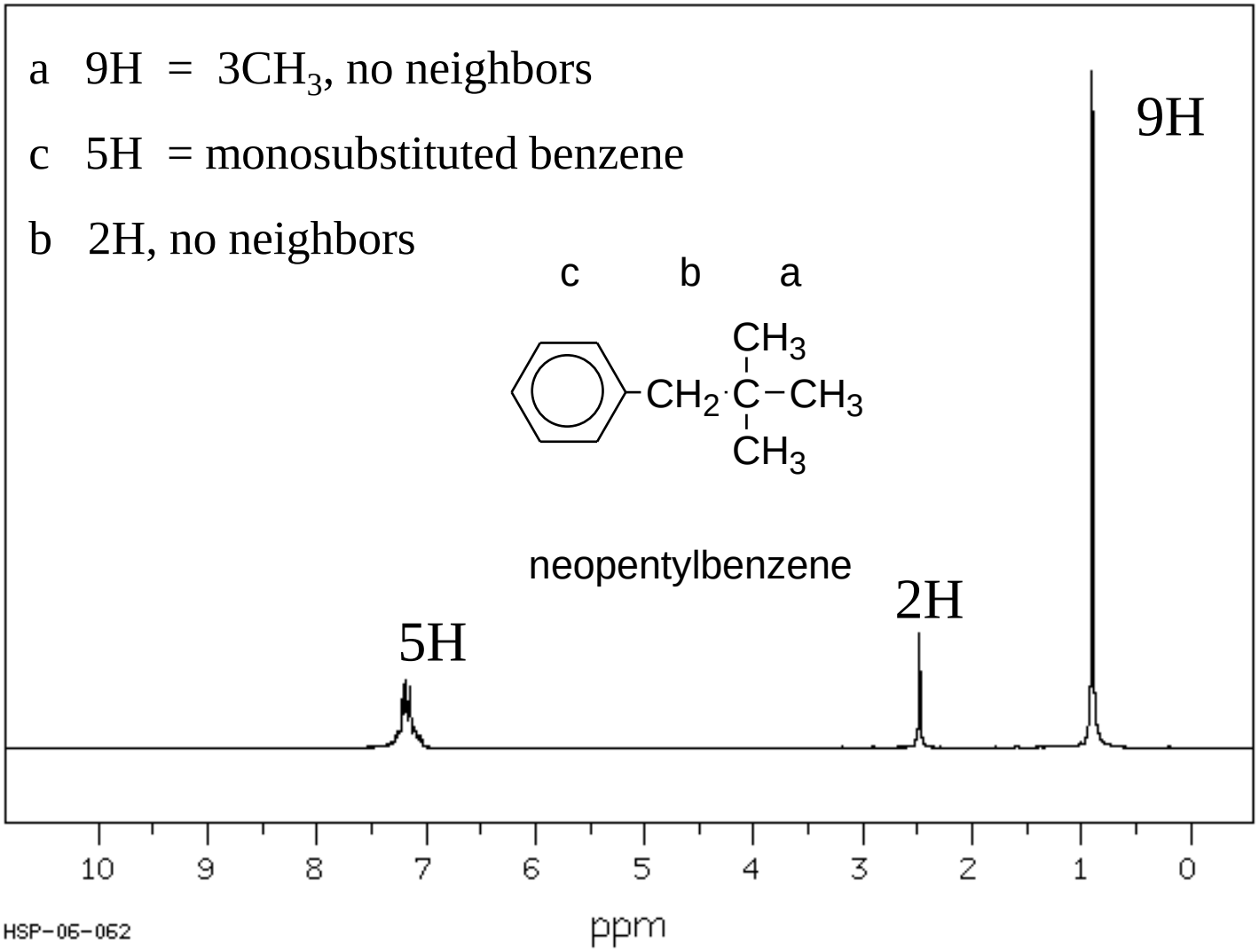

o-diethylbenzene
11
10
9
8
7
6
5
4
3
2
1
0
HSP-01-378
ppm


2-bromo-2-methylbutane
b
CH3
b CH3CCH2CH3 a
Br c
a triplet 3H
b singlet 6H
c quartet 2H b & c overlap
11 10 9 8 7 6 5 4 3 2 1 0
HSP-03-095
ppm


di-*n*-propylether
a b c c b a
$CH_3CH_2CH_2$-O-$CH_2CH_2CH_3$
a triplet 6H
b complex 4H
c triplet 4H
11 10 9 8 7 6 5 4 3 2 1 0
ppm
HSP-00-463


1-propanol
a b d c
CH3CH2CH2-OH
a triplet 3H
b complex 2H
c singlet 1H
d triplet 2H
11
10
9
8
7
6
5
4
3
2
1
0
HSP-03-833
ppm

$C_{11}H_{16}$

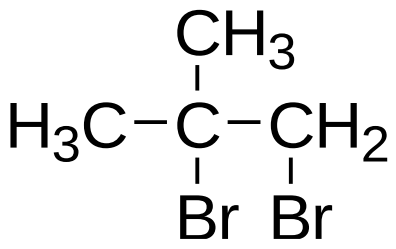

a 9H = 3CH3, no neighbors
c 5H = monosubstituted benzene
b 2H, no neighbors
c b a
CH3
CH2 C CH3
CH3
neopentylbenzene
9H
2H
5H
10 9 8 7 6 5 4 3 2 1 0
ppm
HSP-06-062

$C_4H_8Br_2$

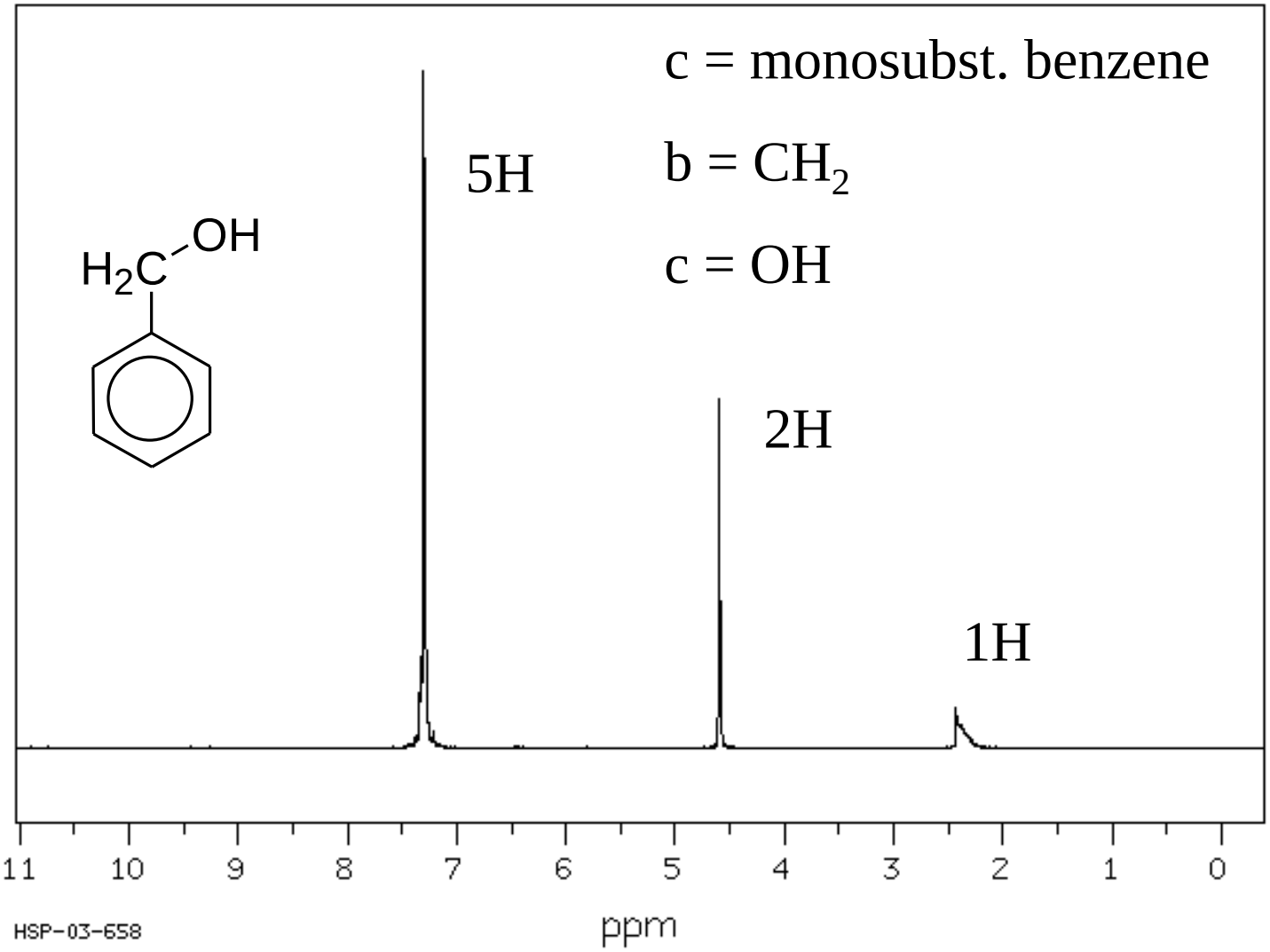
a = 6H, two CH_3 with no neighbors

$(CH_3)_2C$—

b = CH_2, no neighbors & shifted downfield due to Br



C_7H_8O


c = monosubst. benzene
b = CH2
c = OH
5H
2H
1H
H2C
OH
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-03-658

C_4H_9Br

a	doublet	1.04 ppm	6H
b	complex	1.95 ppm	1H
c	doublet	3.33 ppm	2H

a = two equivalent CH_3's with one neighboring H (b?)

c = CH_2 with one neighbor H (also b)

a

CH_3

CH_3CHCH_2Br

a b c

a 6H doublet

b 1H complex

c 2H doublet

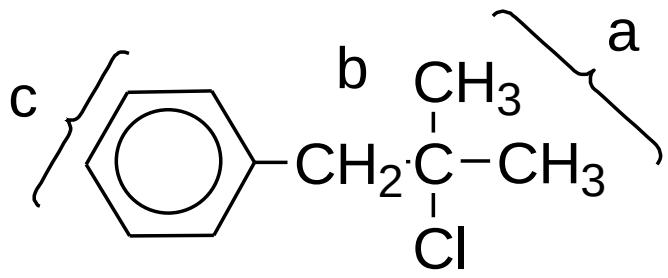
$C_{10}H_{13}Cl$

a singlet 1.57 ppm 6H
b singlet 3.07 ppm 2H
c singlet 7.27 ppm 5H

a = two-equilalent CH_3's with no neighbors

c = monosubstituted benzene ring

b = CH_2



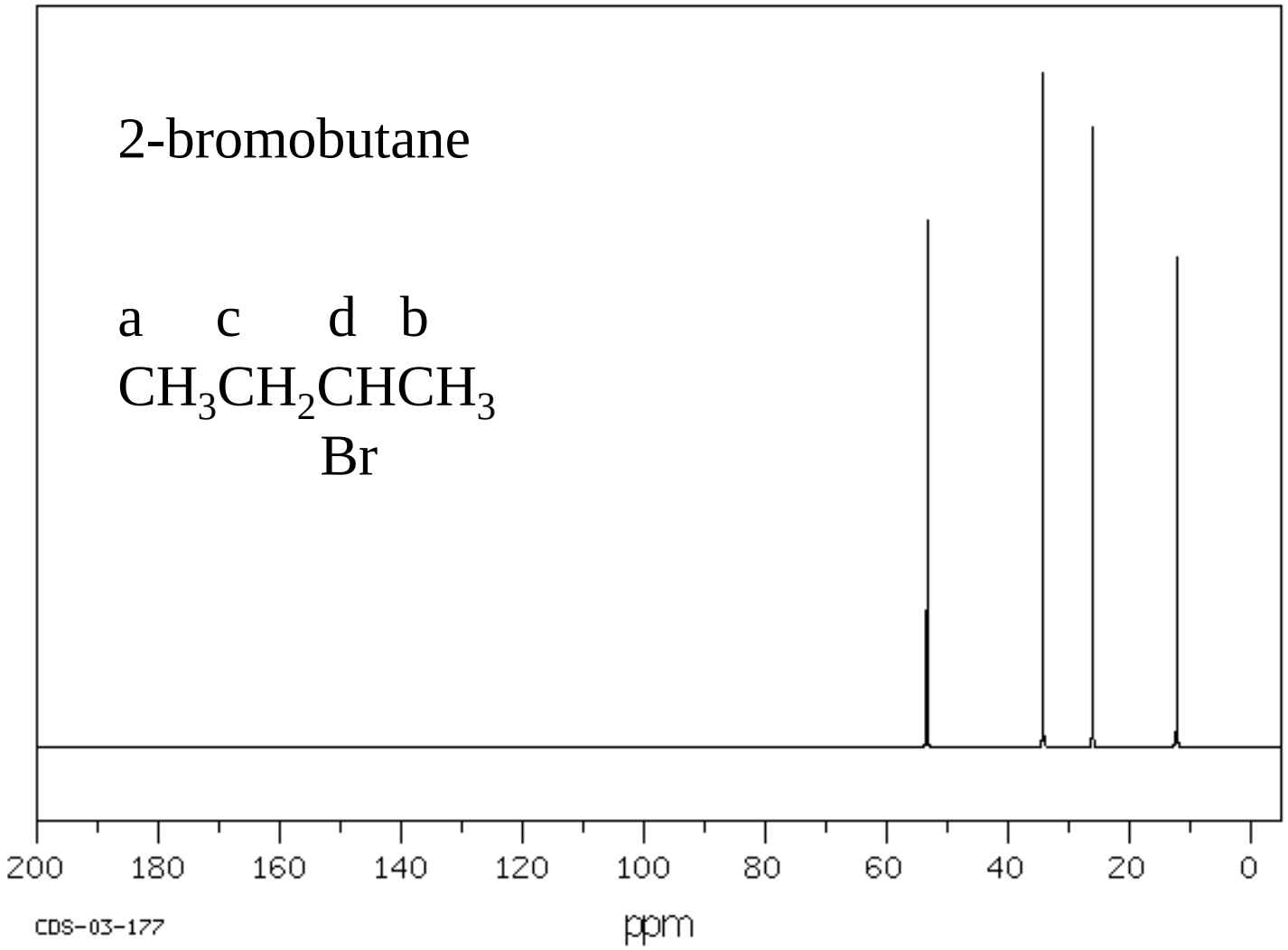
a singlet 6H
b singlet 2H
c singlet 5H

^{13}C – nmr

^{13}C ~ 1.1% of carbons

1) number of signals: how many different types of carbons
2) splitting: number of hydrogens on the carbon
3) chemical shift: hybridization of carbon sp, sp^2, sp^3
4) chemical shift: evironment

^{13}C-nmr


2-bromobutane
a c d b
CH3CH2CHCH3
Br
200
180
160
140
120
100
80
60
40
20
0
CDS-03-177
ppm

mri

magnetic resonance imaging

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http://www.cis.rit.edu/htbooks/mri/