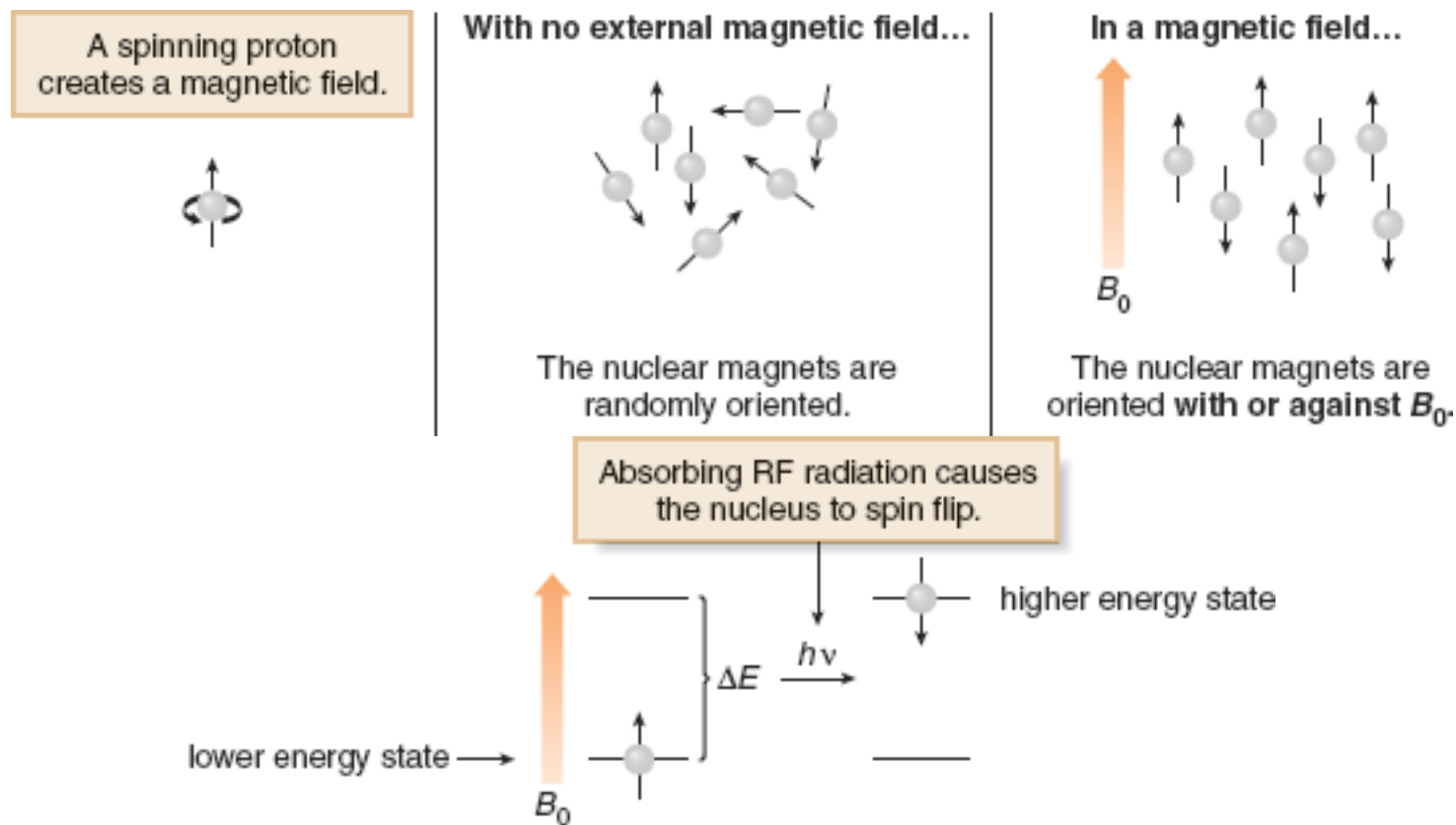# 14.1 An Introduction to NMR Spectroscopy

A. The Basics of Nuclear Magnetic Resonance (NMR) Spectroscopy
• **nuclei with odd atomic number have a S = ½ with two spin states (+1/2 and -1/2)**

^{1}H NMR (proton NMR): determines number and type of H atoms
^{13}C NMR (proton NMR): determines number and type of C atoms

A spinning proton creates a magnetic field.

With no external magnetic field...

The nuclear magnets are randomly oriented.

In a magnetic field...

B_0

The nuclear magnets are oriented **with or against B_0**.

Absorbing RF radiation causes the nucleus to spin flip.

higher energy state

ΔE $\xrightarrow{h\nu}$
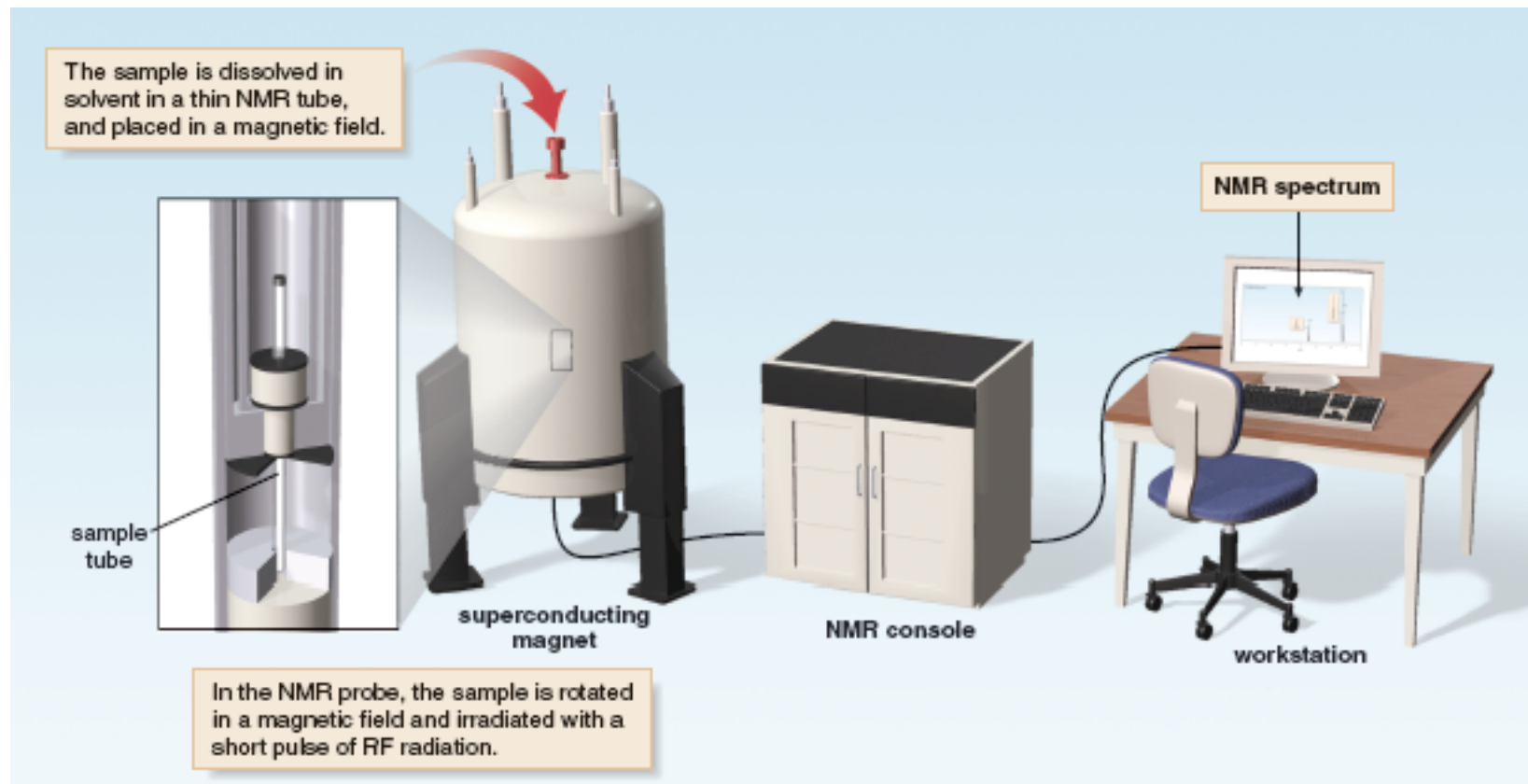
lower energy state →

B_0

B_0 = applied magnetic field, measured in tesla (T)
ν = frequency used for resonance (to induce a spin flip), measured in hertz (Hz) and megahertz (MHz)

14.1 An Introduction to NMR Spectroscopy

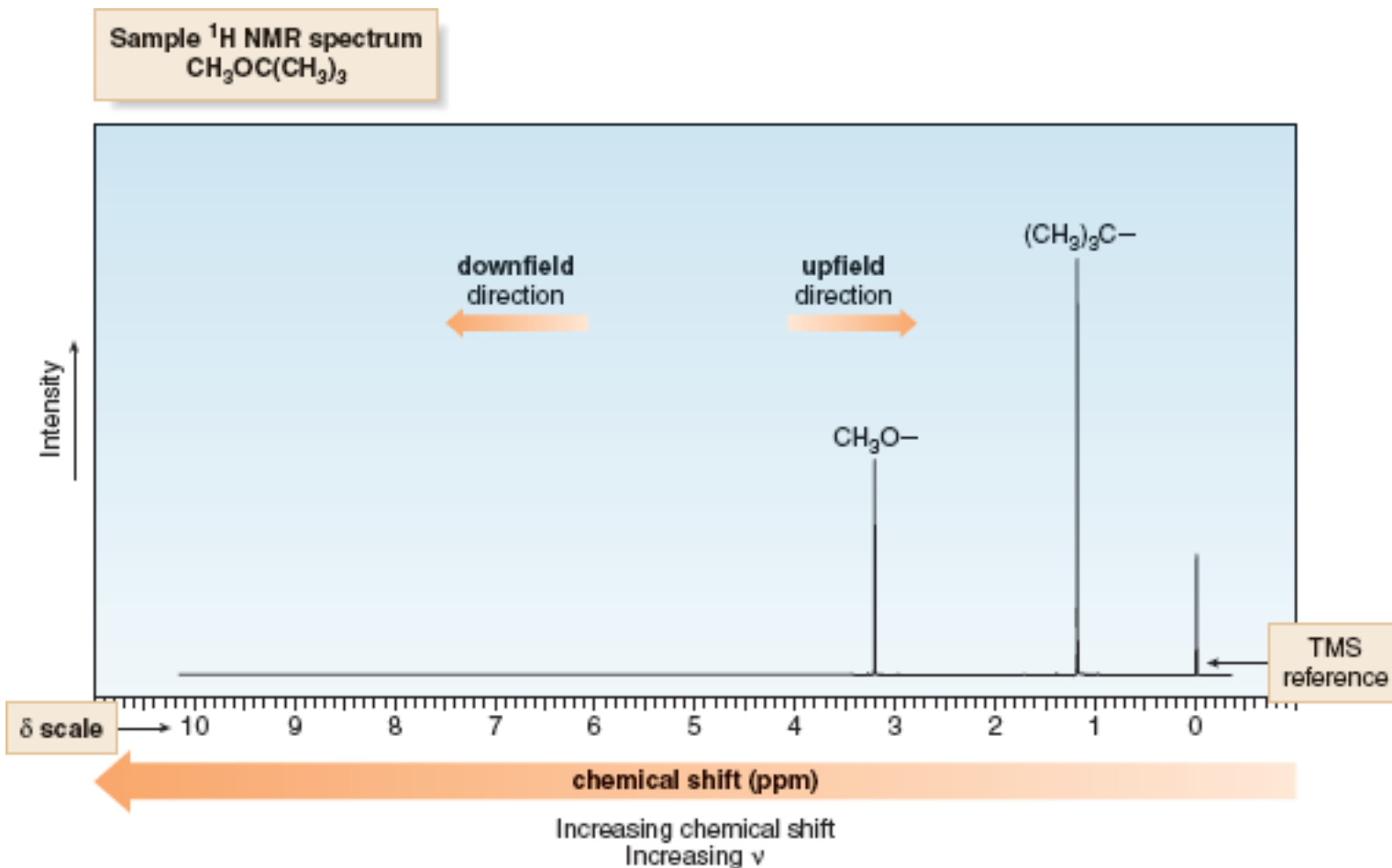**A. The Basics of NMR Spectroscopy**

- **SMU has a 400 MHz (9.4 T) and a 500 MHz (11.7 T) instrument**

The sample is dissolved in solvent in a thin NMR tube, and placed in a magnetic field.

sample tube

superconducting magnet

In the NMR probe, the sample is rotated in a magnetic field and irradiated with a short pulse of RF radiation.

NMR console

NMR spectrum

workstation

14.1 An Introduction to NMR Spectroscopy

B. Example ^{1}H NMR Spectrum

Sample ^{1}H NMR spectrum
$CH_3OC(CH_3)_3$

downfield direction

upfield direction

$(CH_3)_3C-$

CH_3O-

TMS reference

Intensity

δ scale → 10 9 8 7 6 5 4 3 2 1 0

chemical shift (ppm)

Increasing chemical shift
Increasing ν

*
$$\text{chemical shift (in ppm on the δ scale)} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\text{ν of the NMR spectrometer (in MHz)}}$$

14.1 An Introduction to NMR Spectroscopy

C. Outline for interpreting ¹H NMR Spectrum

1. Number of signals (14.2)
2. Chemical shift of signals (14.3–14.4)
3. Intensity of signals (14.5)
4. Spin-spin splitting of signals (14.6–14.8)

14.2 ¹H NMR: Number of signals

A. General Principles

• Each chemically (magnetically) unique proton gives a unique signal
• Usually the 3H of a $-CH_3$ and 2H of a $-CH_2-$ are identical (exceptions are rings and chiral molecules)
• Different $-CH_3$ groups may be identical or different

CH_3-O-CH_3

H_a H_a
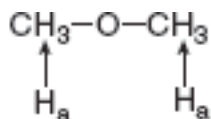
All equivalent H's
1 NMR signal

CH_3CH_2-Cl

H_a H_b
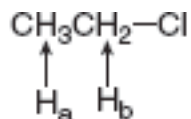
2 types of H's
2 NMR signals

$CH_3-O-CH_2CH_3$

H_a H_b H_c
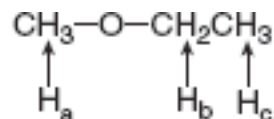
3 types of H's
3 NMR signals

Example: How many magnetically unique H atoms does
$CH_3CH_2CH_2CH_2CH_3$ contain?

$CH_3CH_2CH_2CH_2CH_3$

different H's

$CH_3CHCH_2CH_2CH_3$
      |
     Cl

2-chloropentane

$CH_3CH_2CHCH_2CH_3$
        |
       Cl

3-chloropentane

different products

H_b H_b

$CH_3CH_2CH_2CH_2CH_3$

H_a H_c H_a
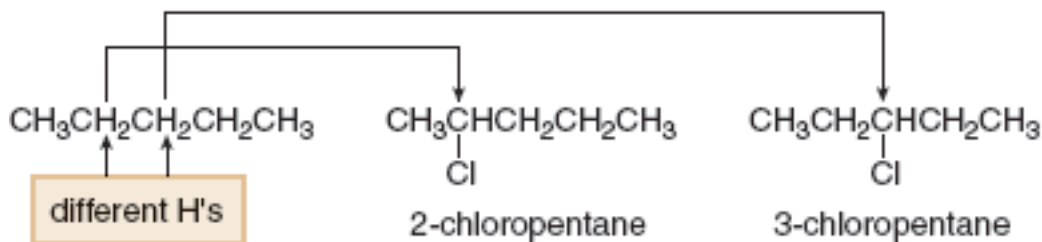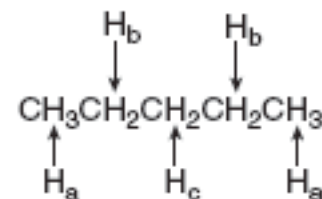
14.2 ¹H NMR: Number of signals

A. General Principles

More Examples: How many ¹H NMR signals for the following?

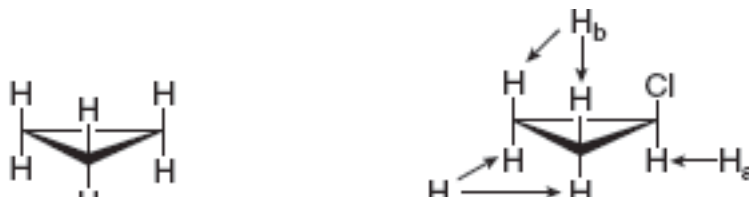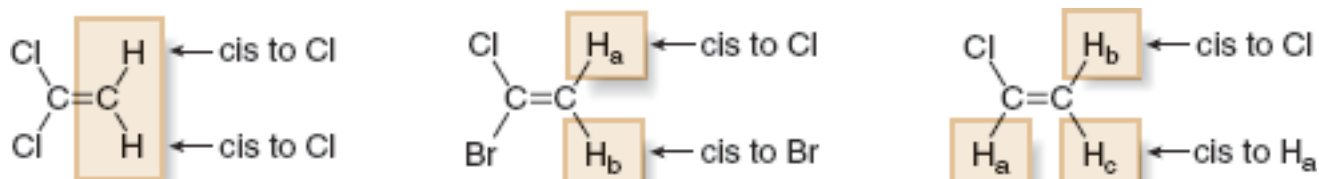$ClCH_2CH_2Cl$ $ClCH_2CH_2CH_2Br$

CH_3CH_2OH
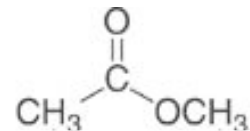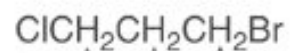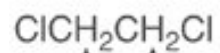
14.2 ¹H NMR: Number of signals

B. Determining Equivalent Protons in Alkenes and Cycloalkanes (Practice Problem 14.4)
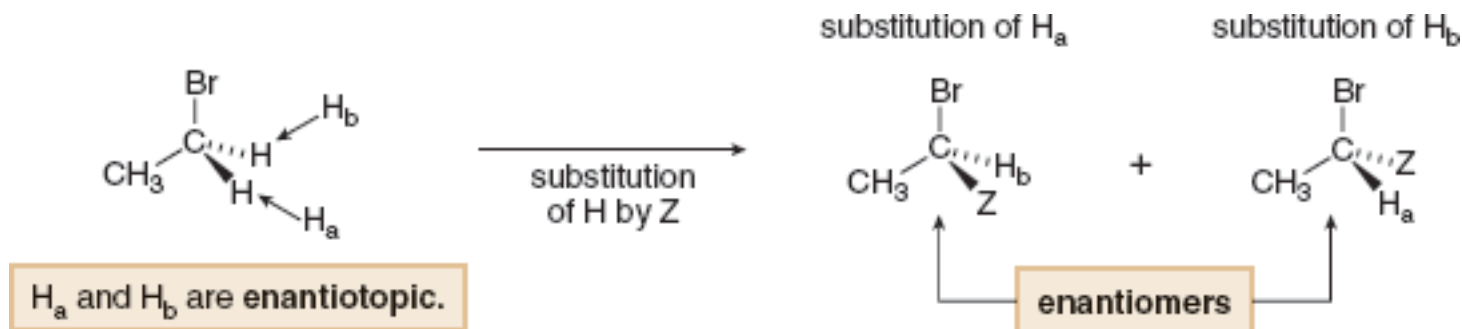
1. Draw all bonds to H

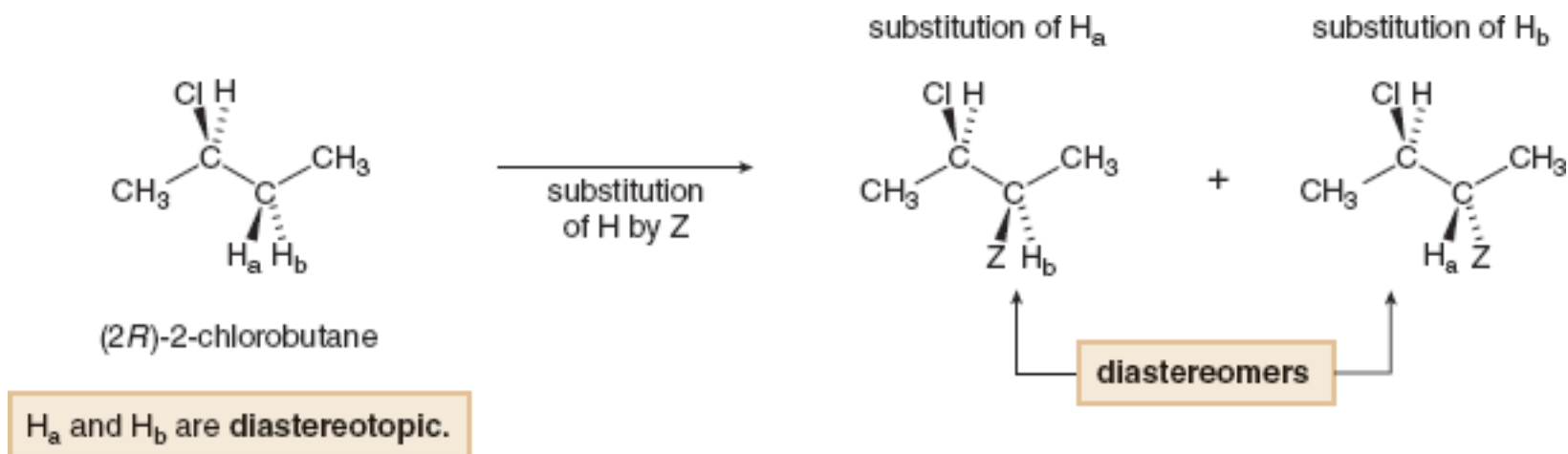### 2. H only equivalent if cis (or trans) to the same groups

14.2 ¹H NMR: Number of signals

C. Enantiotopic and Diastereotopic Protons (Practice Problem 14.5)

1. Enantiotopic protons give a single NMR signal

2. Diastereotopic protons give a two NMR signals

14.2 ¹H NMR: Number of signals

D. Examples (Problem 14.35 c,f)

14.3 ¹H NMR: Position of Signals (Chemical Shift)
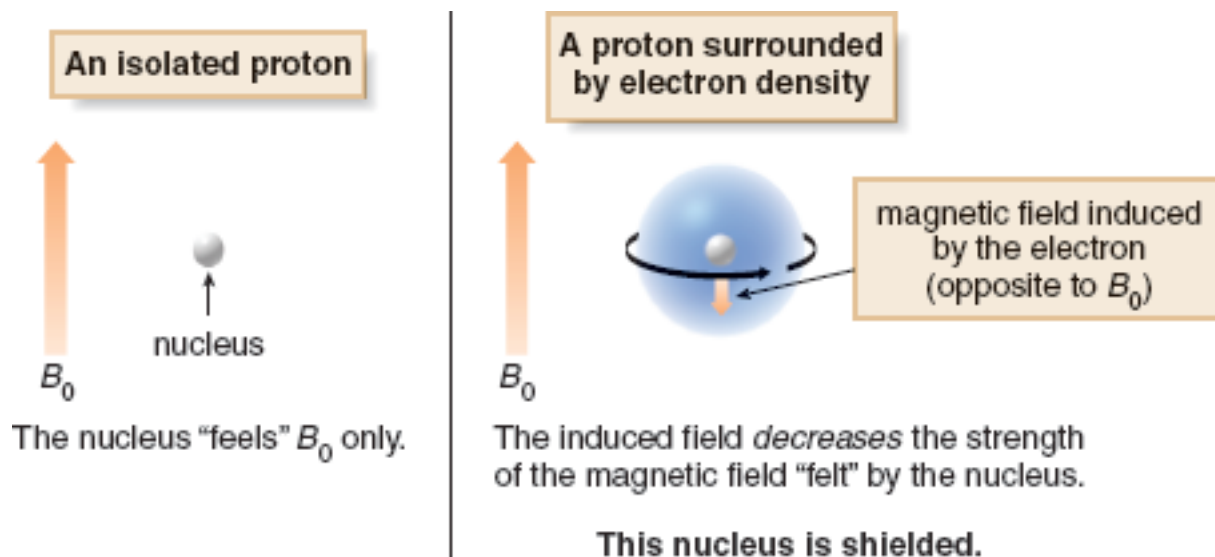
A. Shielding and Deshielding Effects

An isolated proton

nucleus

B_0

The nucleus "feels" B_0 only.

A proton surrounded by electron density

magnetic field induced by the electron (opposite to B_0)

B_0

The induced field *decreases* the strength of the magnetic field "felt" by the nucleus.

This nucleus is shielded.

1. Shielded = more e⁻ density = peak shifts *upfield* = lower ppm
2. **D**eshielded = **d**ecreased e⁻ density = peak shifts ***d**ownfield* = higher ppm

# 14.3 ¹H NMR: Position of Signals (Chemical Shift)

A. Shielding and Deshielding Effects

a. Shielding effects
- An electron shields the nucleus.
- The absorption shifts *upfield*.
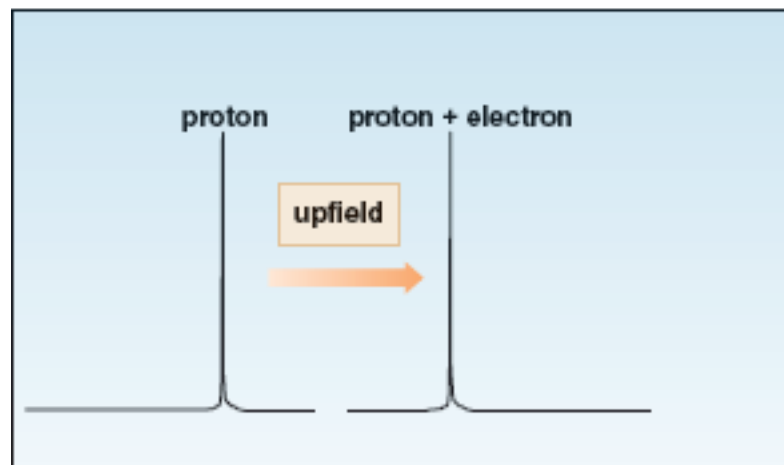
b. Deshielding effects
- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield*.
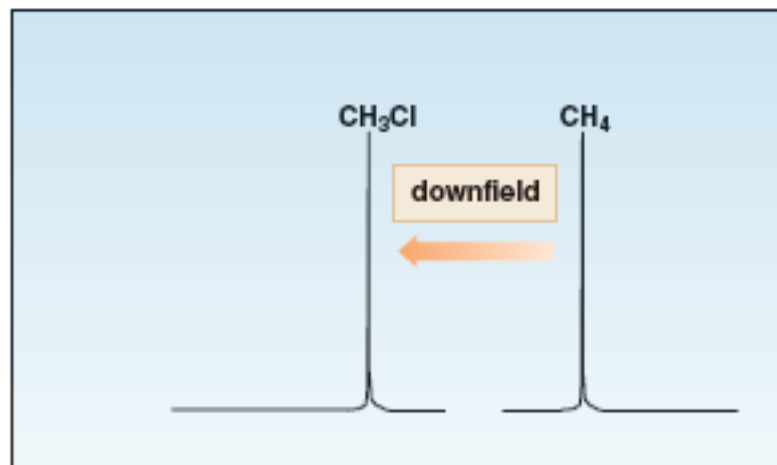
proton   proton + electron

upfield

CH₂Cl   CH₄

downfield

Increasing chemical shift
Increasing ν

Increasing chemical shift
Increasing ν

1. Shielded = more e⁻ density = peak shifts *upfield* = lower ppm
2. **D**eshielded = **d**ecreased e⁻ density = peak shifts ***d**ownfield* = higher ppm

14.3 ¹H NMR: Position of Signals (Chemical Shift)

A. Shielding and Deshielding Effects

A shielded nucleus

The nucleus "feels" **a smaller resultant field.**

—a larger induced magnetic field

B_0

A deshielded nucleus

The nucleus "feels" **a larger resultant field.**

—a smaller induced magnetic field

B_0

1. Shielded = more e⁻ density = peak shifts *upfield* = lower ppm
2. **D**eshielded = **d**ecreased e⁻ density = peak shifts *downfield* = higher ppm

14.3 ^{1}H NMR: Position of Signals (Chemical Shift)

A. Shielding and Deshielding Effects

CH_3CH_2Cl
H_a H_b
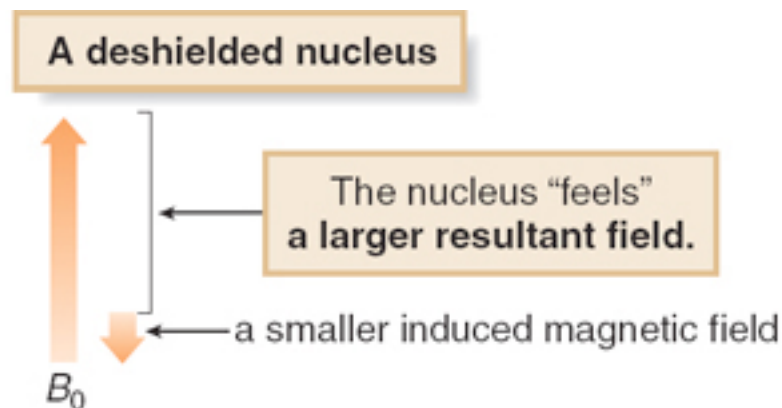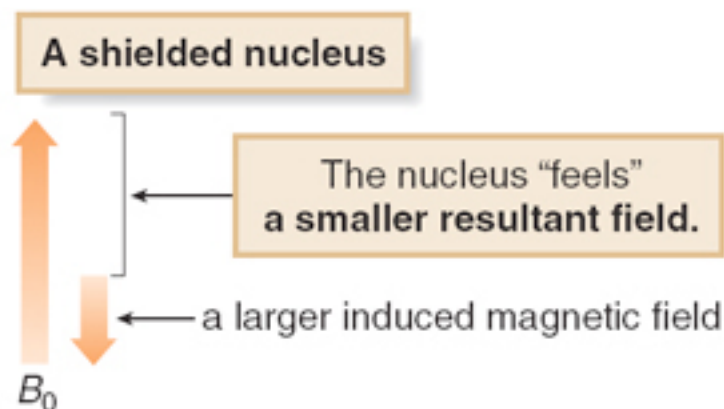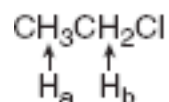
- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.

$BrCH_2CH_2F$
H_a H_b
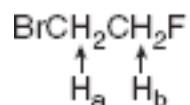
- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**

$ClCH_2CHCl_2$
H_a H_b
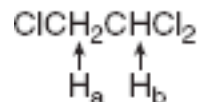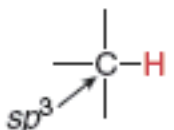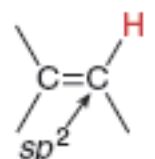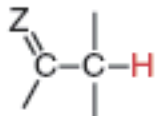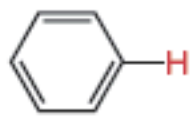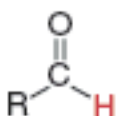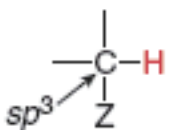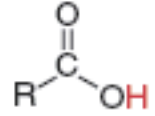
- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.

14.3 ¹H NMR: Position of Signals (Chemical Shift)
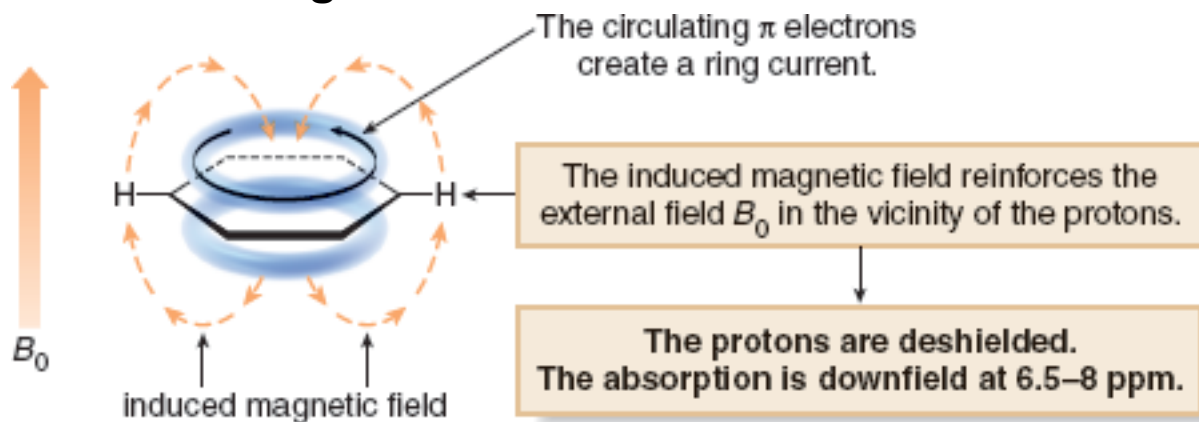
B. Chemical Shift Values

Table 14.1 Characteristic Chemical Shifts of Common Types of Protons

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
sp^3 $-\overset{\mid}{\underset{\mid}{C}}-H$	0.9–2	sp^2 C=C (with H)	4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7	(benzene ring)—H	6.5–8
$\overset{Z}{\underset{}{\parallel}}C-\overset{\mid}{\underset{\mid}{C}}-H$ Z = C, O, N	1.5–2.5	$\underset{R}{}\overset{O}{\underset{H}{\parallel C}}$	9–10
$-C{\equiv}C-H$	~2.5	$\underset{R\quad OH}{}\overset{O}{\parallel C}$	10–12
sp^3 $-\overset{\mid}{\underset{Z}{C}}-H$ Z = N, O, X	2.5–4	RO—H or R—N—H	1–5

14.4 Chemical Shift of Protons on sp² and sp Hybridized Carbons

7.3 ppm   4.5–6 ppm   2.5 ppm
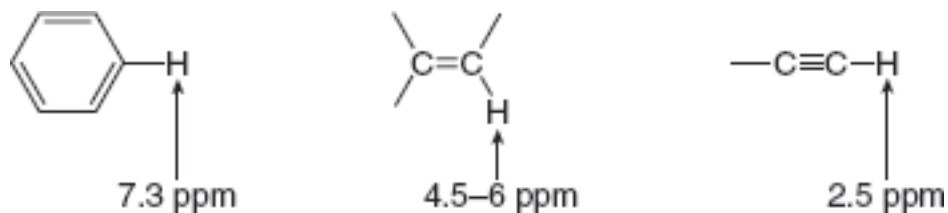
A. Protons on Benzene Rings

The circulating π electrons create a ring current.

The induced magnetic field reinforces the external field B_0 in the vicinity of the protons.

The protons are deshielded. The absorption is downfield at 6.5–8 ppm.

B_0

induced magnetic field

14.4 Chemical Shift of Protons on sp² and sp Hybridized Carbons

B. Protons on Carbon-Carbon Double Bonds

The induced magnetic field reinforces the external field B_0 in the vicinity of the protons.

The protons are deshielded. The absorption is downfield at 4.5–6 ppm.
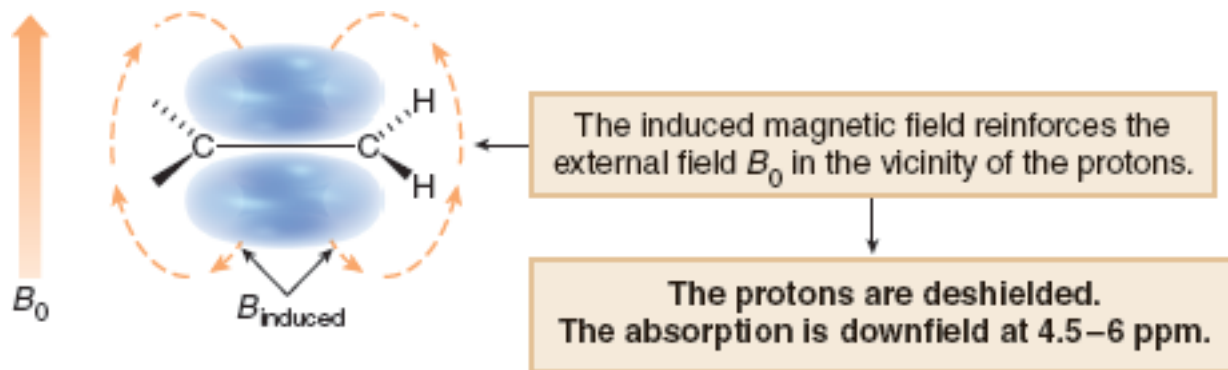
C. Protons on Carbon-Carbon Triple Bonds

The induced magnetic field opposes the external field B_0 in the vicinity of the proton.

The proton is shielded. The absorption is upfield at ~2.5 ppm.
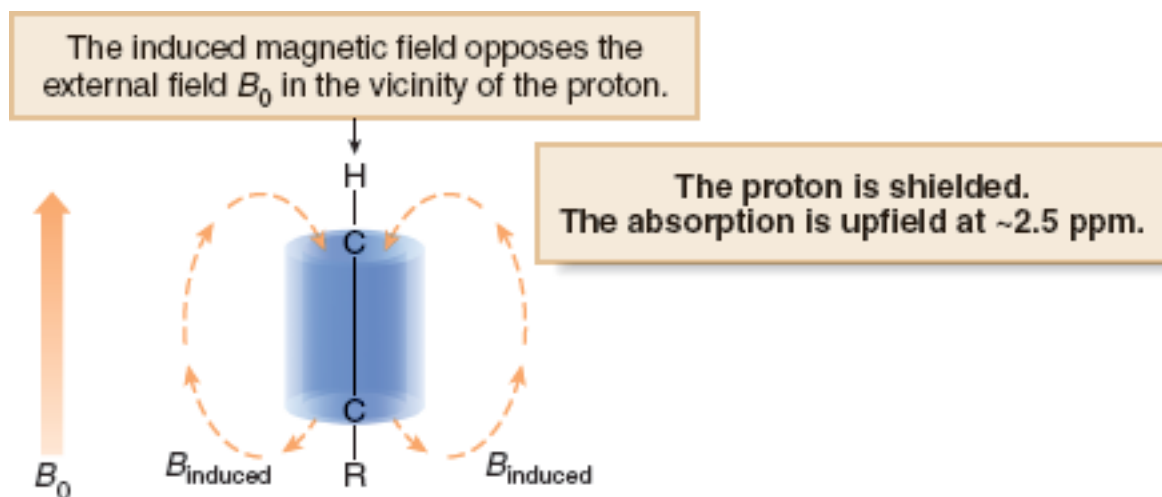
14.4 Chemical Shift of Protons on sp² and sp Hybridized Carbons

D. Regions of ¹H NMR Spectra
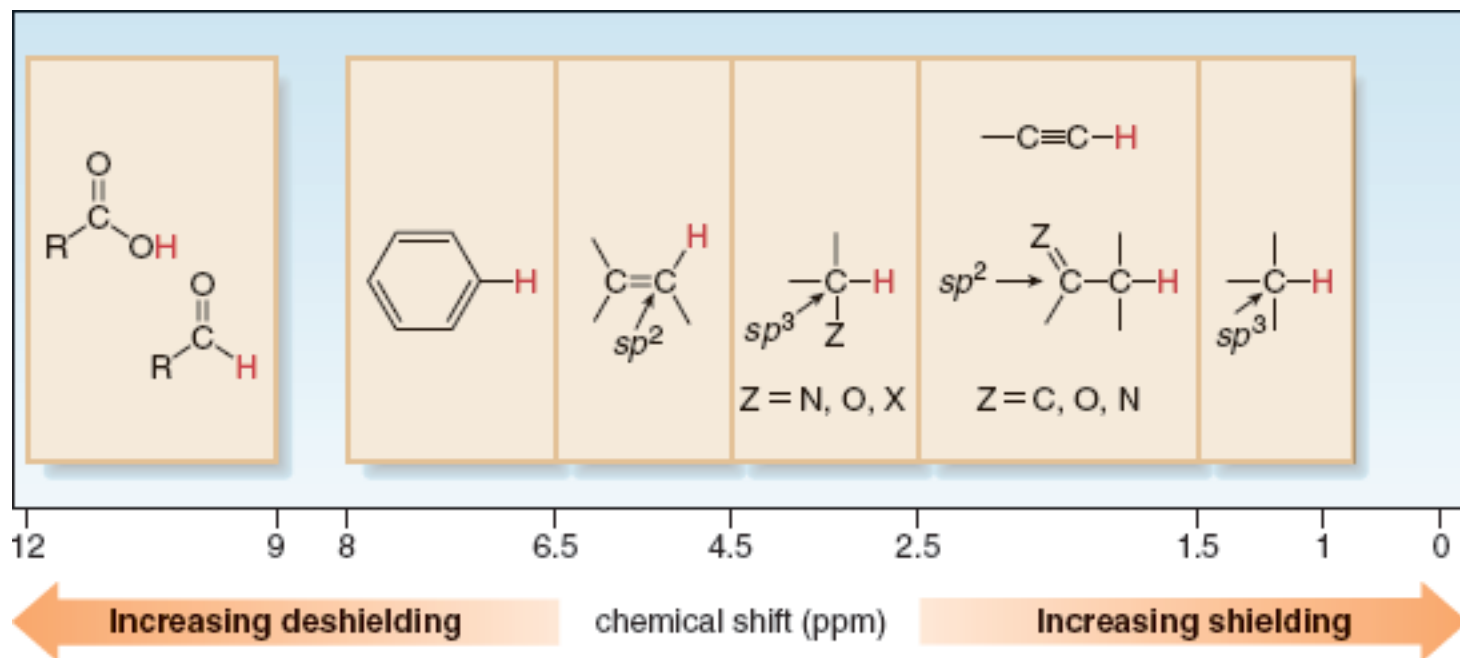
14.4 Chemical Shift of Protons on sp^2 and sp Hybridized Carbons

E. Examples (Problem 14.40a)

14.5 ¹H NMR: Intensity of Signals

A. The peak integration is proportional to the number of protons
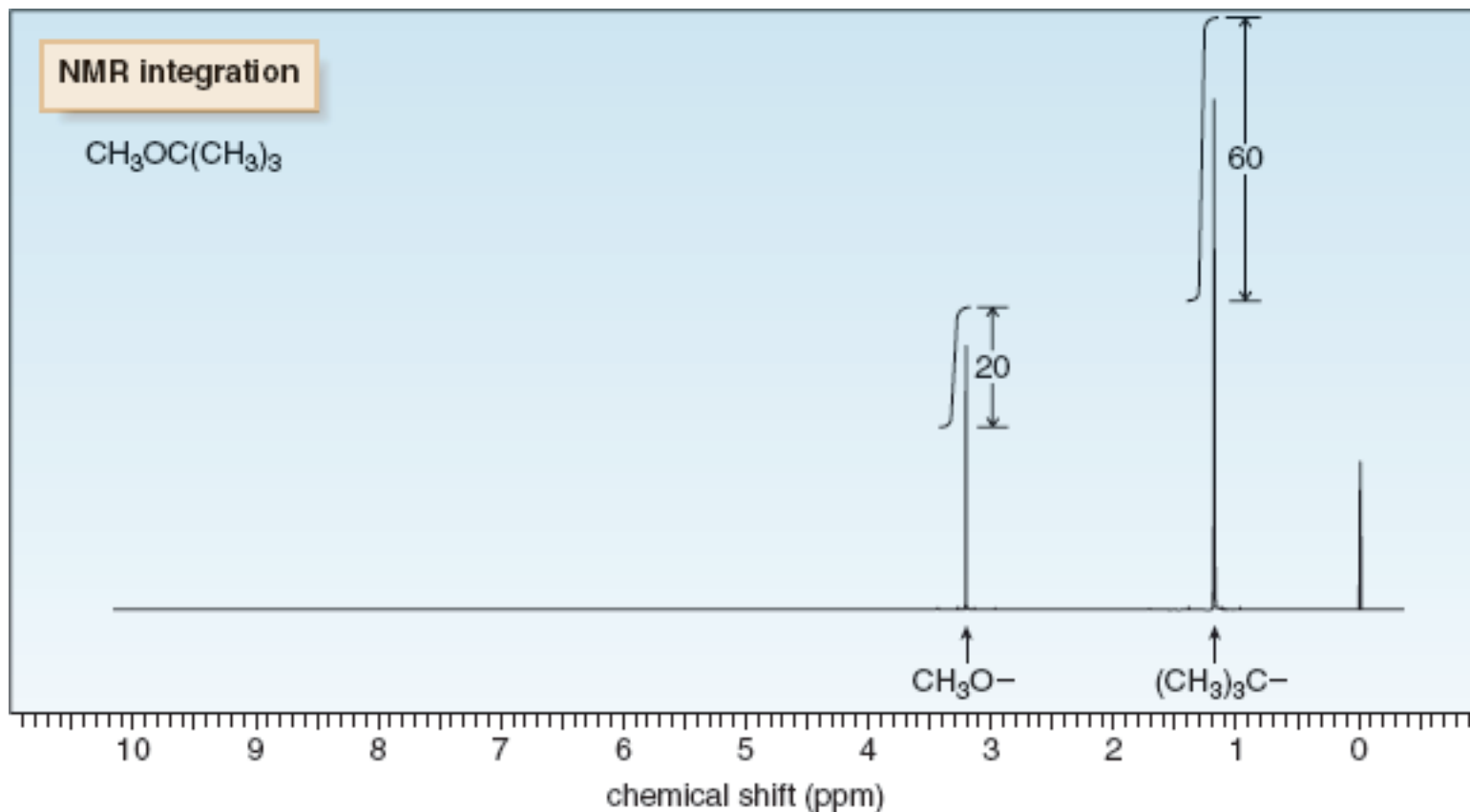
14.5 ¹H NMR: Intensity of Signals

B. A compound with molecular formula $C_9H_{10}O_2$ has the following spectrum. How many protons for each signal?
• add all integrations
• divide by #H
• Int/H = sum(integrations)/total H

signal [A]   54

signal [B]   23

signal [C]   33

ppm
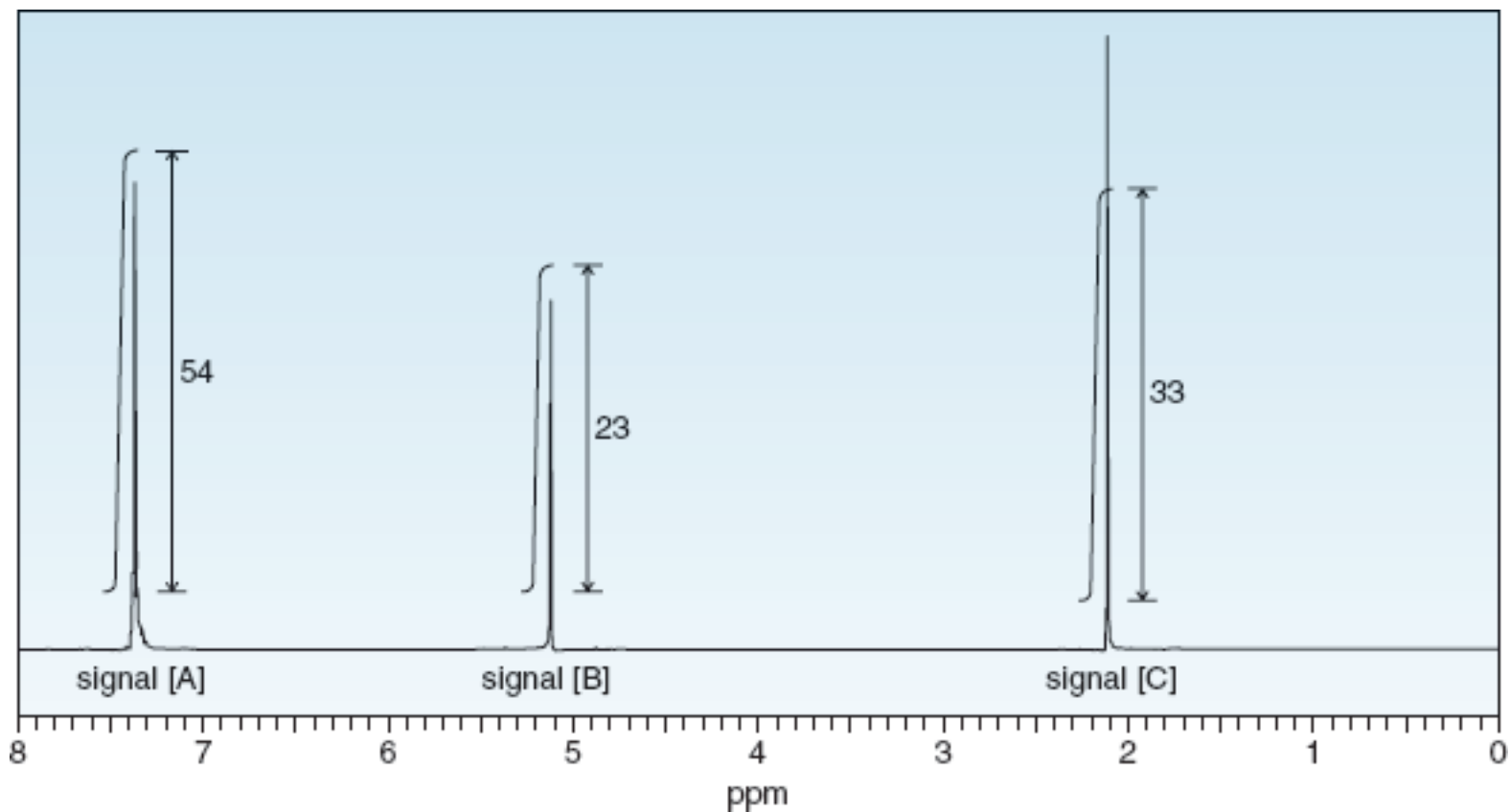
14.5 ^{1}H NMR: Intensity of Signals

C. Practice Problem 14.11:

A compound of molecular formula $C_8H_{14}O_2$ gives three NMR signals having the indicated integration values: signal [A] 14 units, signal [B] 12 units, signal [C] 44 units. How many protons give rise to each signal?

Sum of integration = 14+12+44 = 70
Total H = 14

Int/H = 5

[A] = 14/5 ~ 3
[B] = 12/5 ~ 2
[C] = 44/5 ~ 9

14.6 ¹H NMR: Spin-Spin Splitting
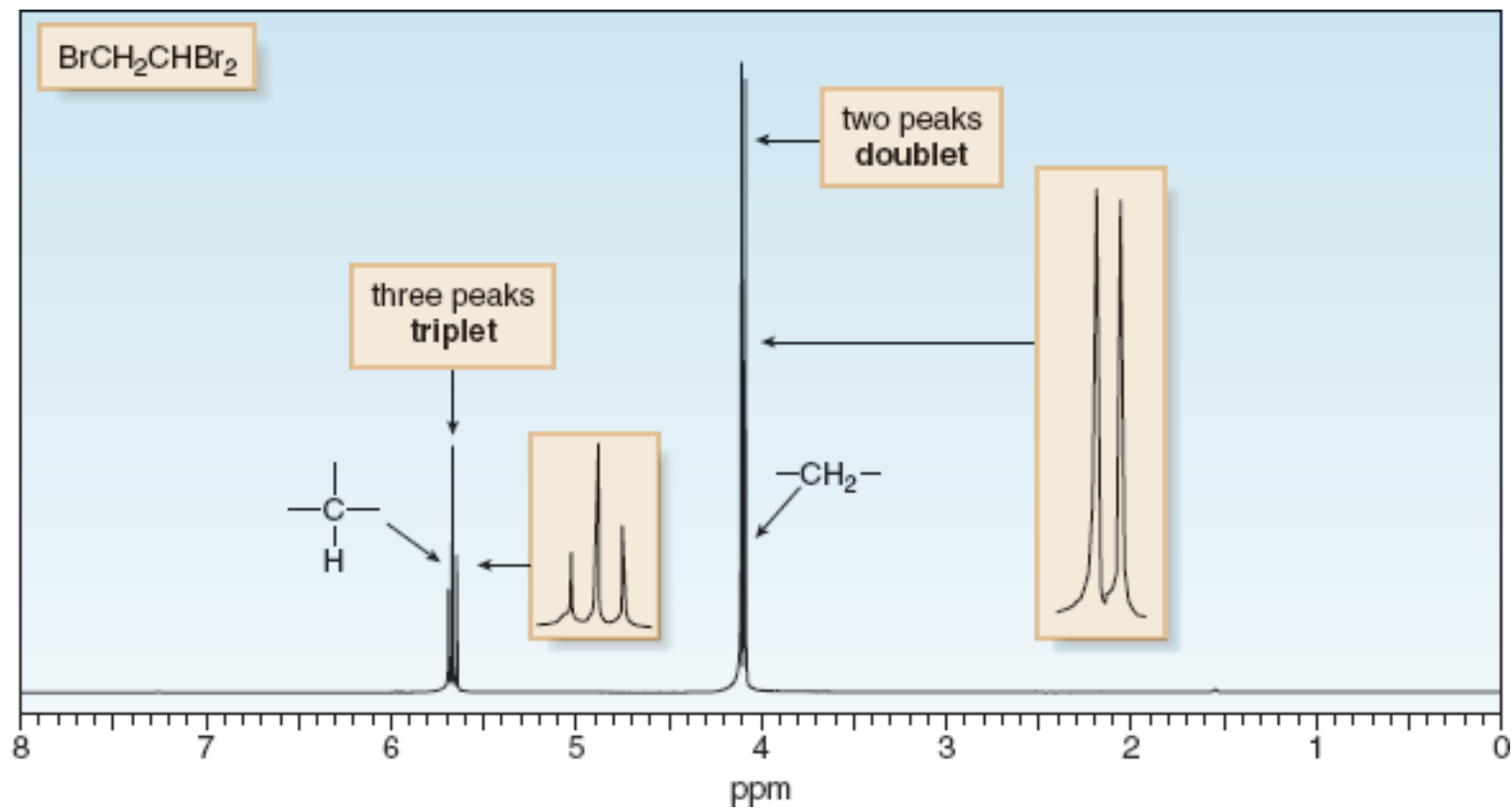
14.6 ¹H NMR: Spin-Spin Splitting

NMR signals are often split into multiple peaks.
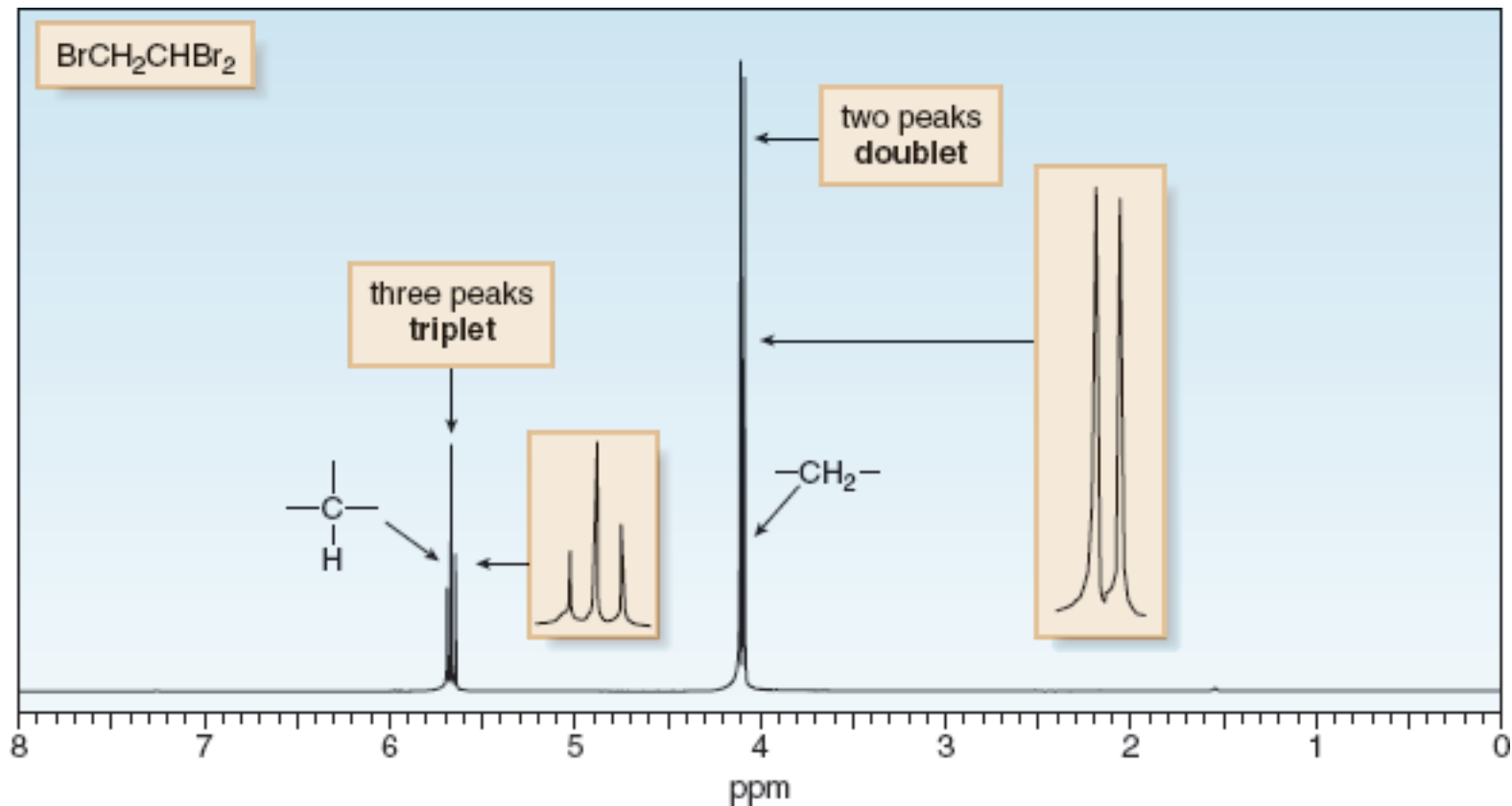
14.6 ¹H NMR: Spin-Spin Splitting

A. Splitting: How a Doublet Arises

Absorbing protons: give rise to NMR signal
Adjacent protons: cause signal to split

absorbing H's

$BrCH_2-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-Br$ ← 1 adjacent H ← This H can be aligned with (↑) or against (↓) B_0.
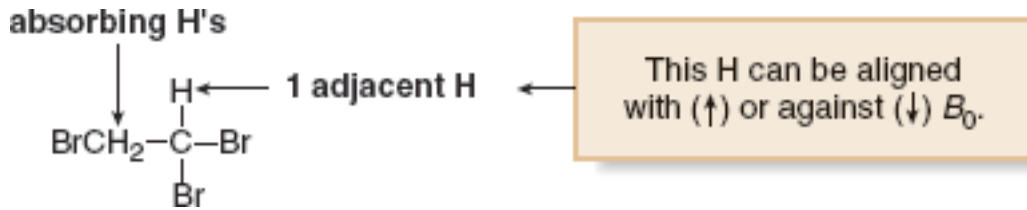
How a doublet arises

With no adjacent H's:
The absorbing H's feel only one magnetic field. → The NMR signal is a single peak.

B_0

With one adjacent H:
The absorbing H's feel two different fields, so they absorb at two different frequencies. → The NMR signal is split into a doublet.
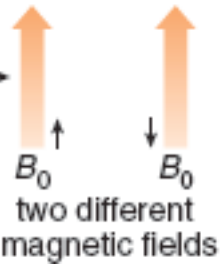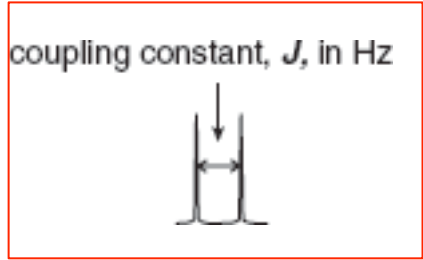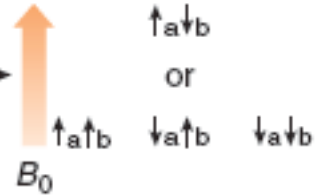
B_0 B_0
two different magnetic fields

1:1

coupling constant, J, in Hz
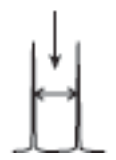
NMR signal: entire absorption due to a particular kind of proton
NMR peak: lines within a signal
A doublet is 1 signal with 2 peaks.

14.6 ¹H NMR: Spin-Spin Splitting

B. Splitting: How a Triplet Arises

NMR signal: entire absorption due to a particular kind of proton
NMR peak: lines within a signal
A doublet is 1 signal with 2 peaks.

14.6 ¹H NMR: Spin-Spin Splitting

C. Splitting: Rules and Examples

Rule 1: Equivalent protons don't split each other's signals.
Rule 2: n adjacent protons split nearby protons into n + 1 peaks

Table 14.3 Names for a Given Number of Peaks in an NMR Signal

Number of peaks	Name	Number of peaks	Name
1	singlet	5	quintet
2	doublet	6	sextet
3	triplet	7	septet
4	quartet	>7	multiplet

Rule 3: Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons

If H_a and H_b are not equivalent, splitting is observed when:
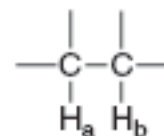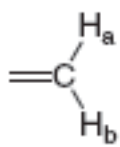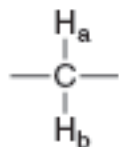
H_a and H_b are on the **same** carbon.

H_a and H_b are on **adjacent** carbons.

Rule 4: Splitting is not generally observed between protons separated by more than three sigma bonds

14.6 ¹H NMR: Spin-Spin Splitting

C. Splitting: Rules and Examples

Rule 4: Splitting is not generally observed between protons separated by more than three sigma bonds
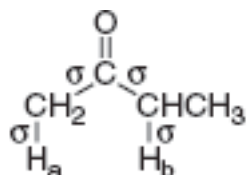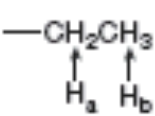

2-butanone
Ha and Hb are separated by four σ bonds.

no splitting between Ha and Hb
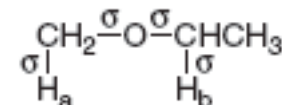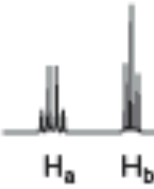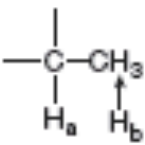
ethyl methyl ether
Ha and Hb are separated by four σ bonds.
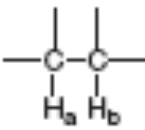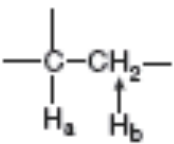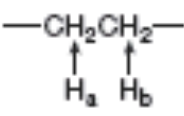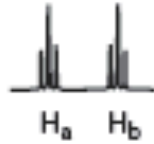
no splitting between Ha and Hb

14.6 ¹H NMR: Spin-Spin Splitting

C. Splitting: Rules and Examples

Table 14.4 Common Splitting Patterns Observed in ¹H NMR

Example	Pattern	Analysis (H_a and H_b are not equivalent.)				
[1]		• H_a: one adjacent H_b proton	----→	two peaks	----→	a doublet
		• H_b: one adjacent H_a proton	----→	two peaks	----→	a doublet
[2]		• H_a: two adjacent H_b protons	----→	three peaks	----→	a triplet
		• H_b: one adjacent H_a proton	----→	two peaks	----→	a doublet
[3]		• H_a: two adjacent H_b protons	----→	three peaks	----→	a triplet
		• H_b: two adjacent H_a protons	----→	three peaks	----→	a triplet
[4]		• H_a: three adjacent H_b protons	----→	four peaks	----→	a quartet*
		• H_b: two adjacent H_a protons	----→	three peaks	----→	a triplet
[5]		• H_a: three adjacent H_b protons	----→	four peaks	----→	a quartet*
		• H_b: one adjacent H_a proton	----→	two peaks	----→	a doublet

14.6 ¹H NMR: Spin-Spin Splitting

C. Splitting: Rules and Examples

Cl—CH₂CH₂—Cl

H$_a$

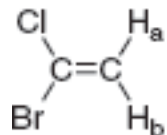Cl—CH₂CH₂—Br

H$_a$ H$_b$

CH₃—C(=O)—OCH₂CH₃

H$_a$ H$_b$ H$_c$

Cl, Br—C=C—H$_a$, H$_b$
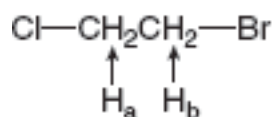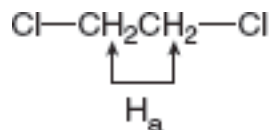
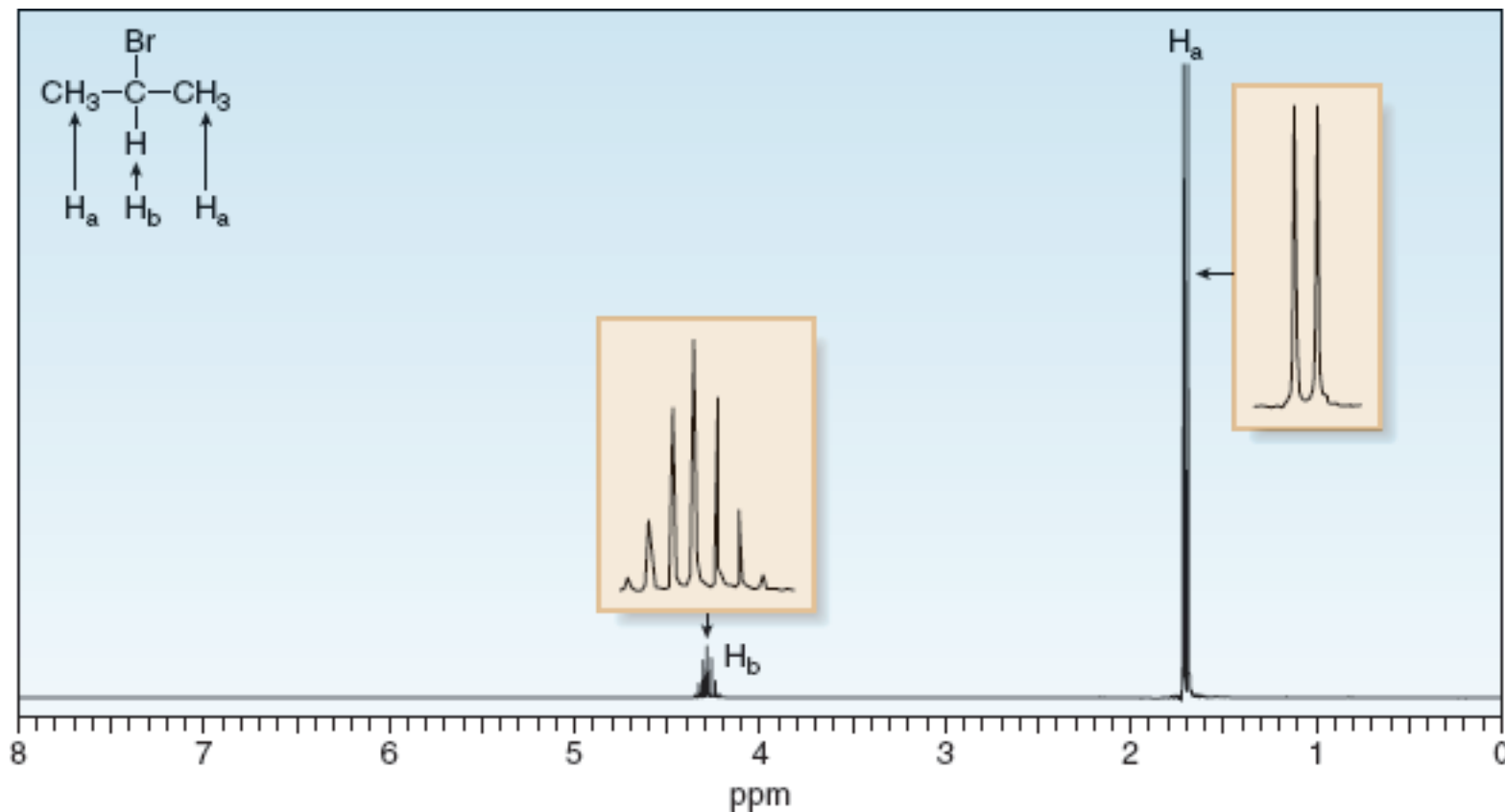Step 1: Determine if protons are equivalent or different
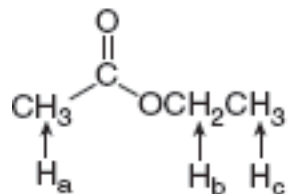
Step 2: Determine if nonequivalent protons are close enough to split each others signals
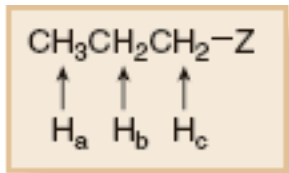
14.7 More Complex Examples of Splitting

A. Equivalent Protons on Two Adjacent Carbons

- both $-CH_3$ are equivalent
- H_b sees 6 H_a protons
- n + 1 rule gives a septet

14.7 More Complex Examples of Splitting

B. Nonequivalent Protons on Two Adjacent Carbons

$CH_3CH_2CH_2-Z$

H_a H_b H_c

Three H_a protons split the H_b signal into $3 + 1 = 4$ peaks.

Two H_c protons further split the H_b signal into $2 + 1 = 3$ peaks.

H_b

J_{ab}

J_{ab} = the coupling constant between H_a and H_b

a quartet of triplets

J_{bc} = the coupling constant between H_b and H_c

Total = 12 peaks
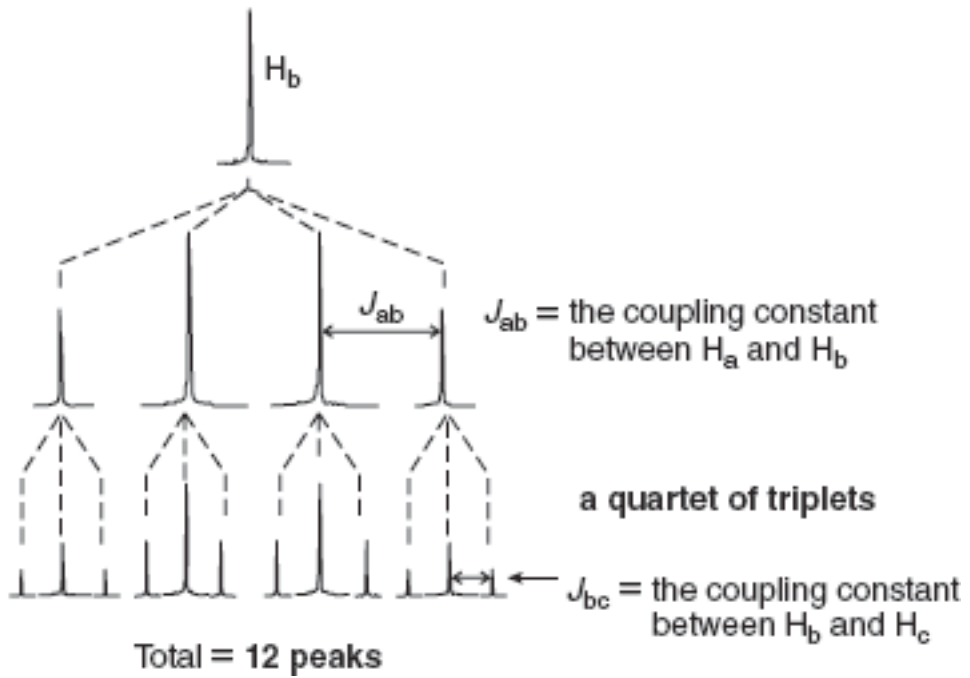
- if $J_{ab} \neq J_{bc}$, signal is split into 12 peaks
- in linear chains $J_{ab} \sim J_{bc}$ and a sextet is observed, (n + 1 rule)

14.8 Spin-Spin Splitting in Alkenes

A. Alkenes with 2H

geminal H's $\quad$ cis H's $\quad$ trans H's

$J_{geminal}$ $\quad<\quad$ J_{cis} $\quad<\quad$ J_{trans}

0–3 Hz $\qquad$ 5–10 Hz $\qquad$ 11–18 Hz

characteristic coupling constants for three types of disubstituted alkenes

(E)-3-chloropropenoic acid

(Z)-3-chloropropenoic acid

J_{trans} = 14 Hz $\rightarrow$ $\qquad$ $\leftarrow J_{trans}$ = 14 Hz $\qquad$ J_{cis} = 8 Hz $\rightarrow$ $\qquad$ $\leftarrow J_{cis}$ = 8 Hz

H_a $\qquad$ H_b $\qquad\qquad$ H_a $\qquad$ H_b

14.8 Spin-Spin Splitting in Alkenes

B. Alkenes with 3H

vinyl acetate
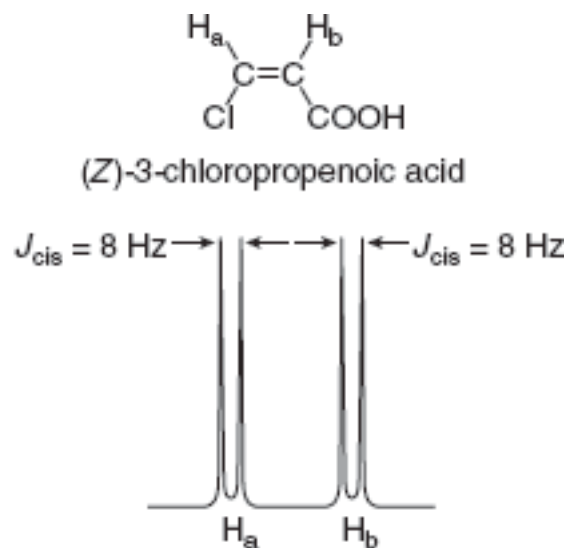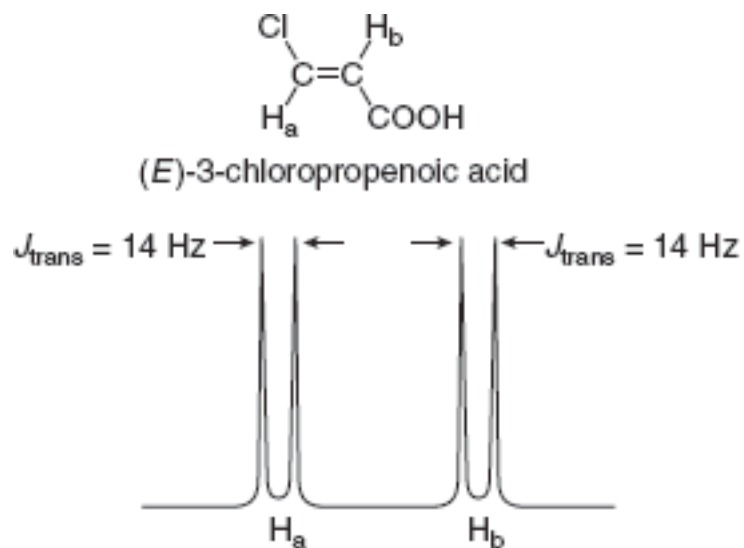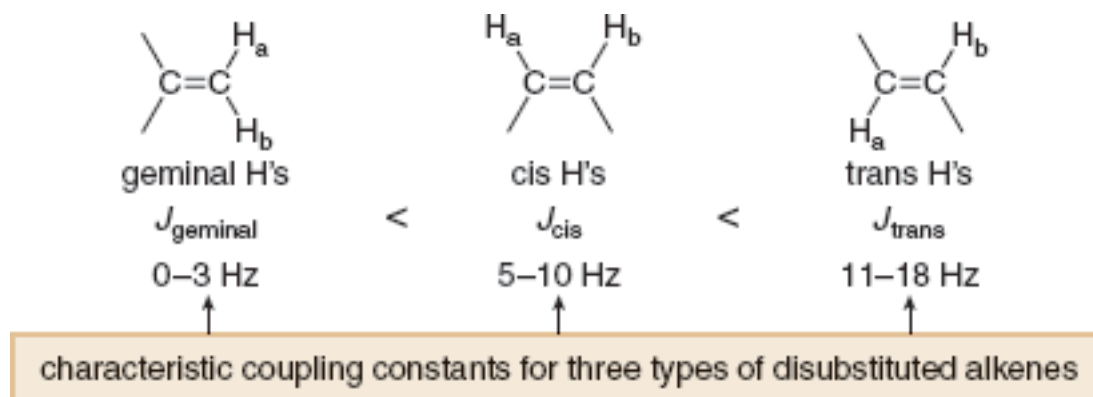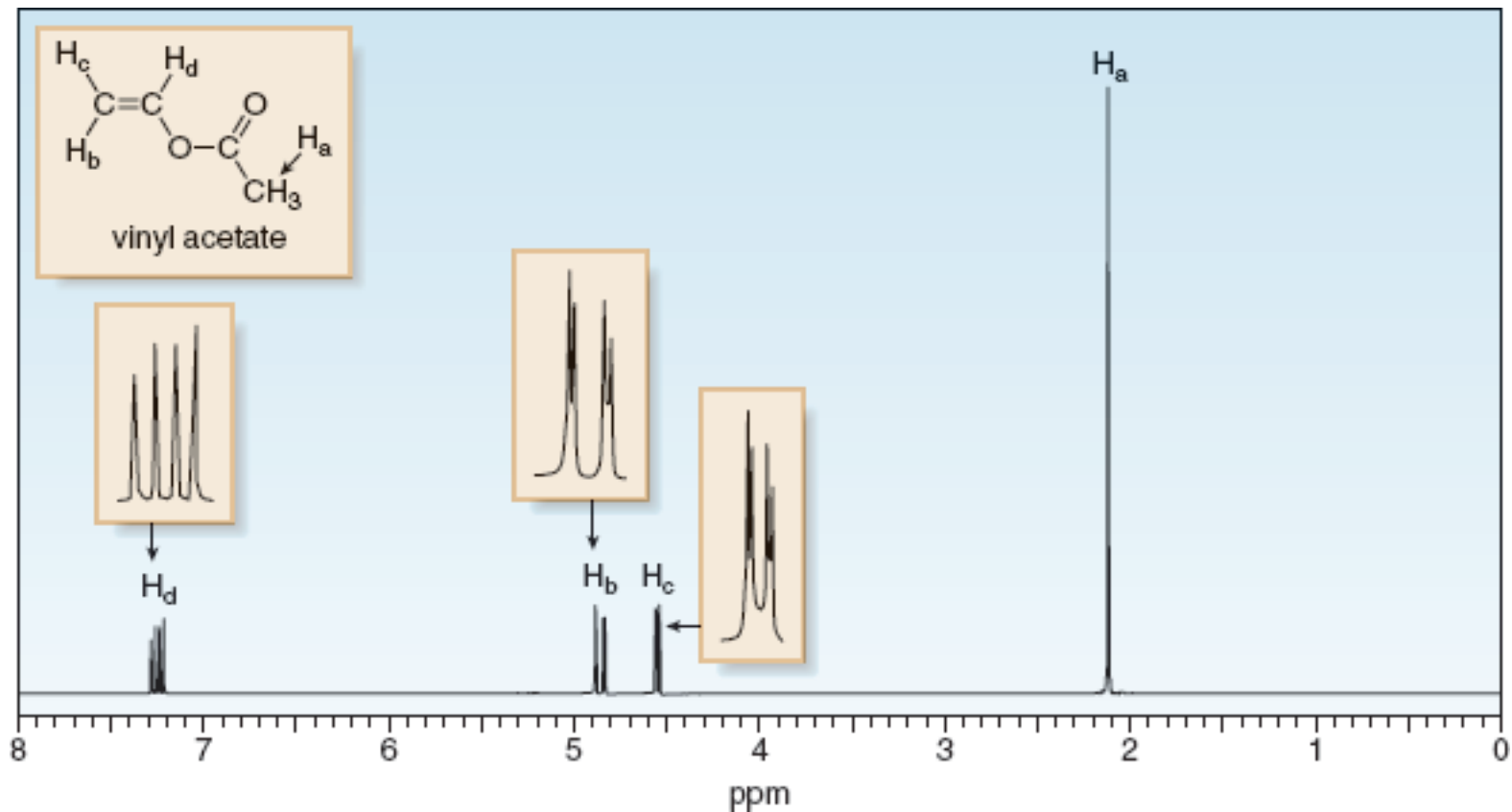
H_a: singlet
H_b: doublet of doublets (J_{trans} , $J_{geminal}$)
H_c: doublet of doublets (J_{cis} , $J_{geminal}$)
H_d: doublet of doublets (J_{trans} , J_{cis})

14.8 Spin-Spin Splitting in Alkenes

B. Alkenes with 3H (Practice Problem 14.18)

Draw splitting diagram for H$_b$

J_{ab} = 13.1 Hz

J_{bc} = 7.2 Hz
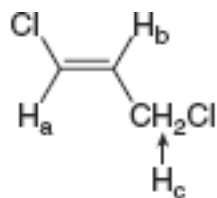
trans-1,3-dichloropropene

14.9 Other Facts About ^1H NMR Spectroscopy

A. OH Protons – Usually aren't split and don't split other protons
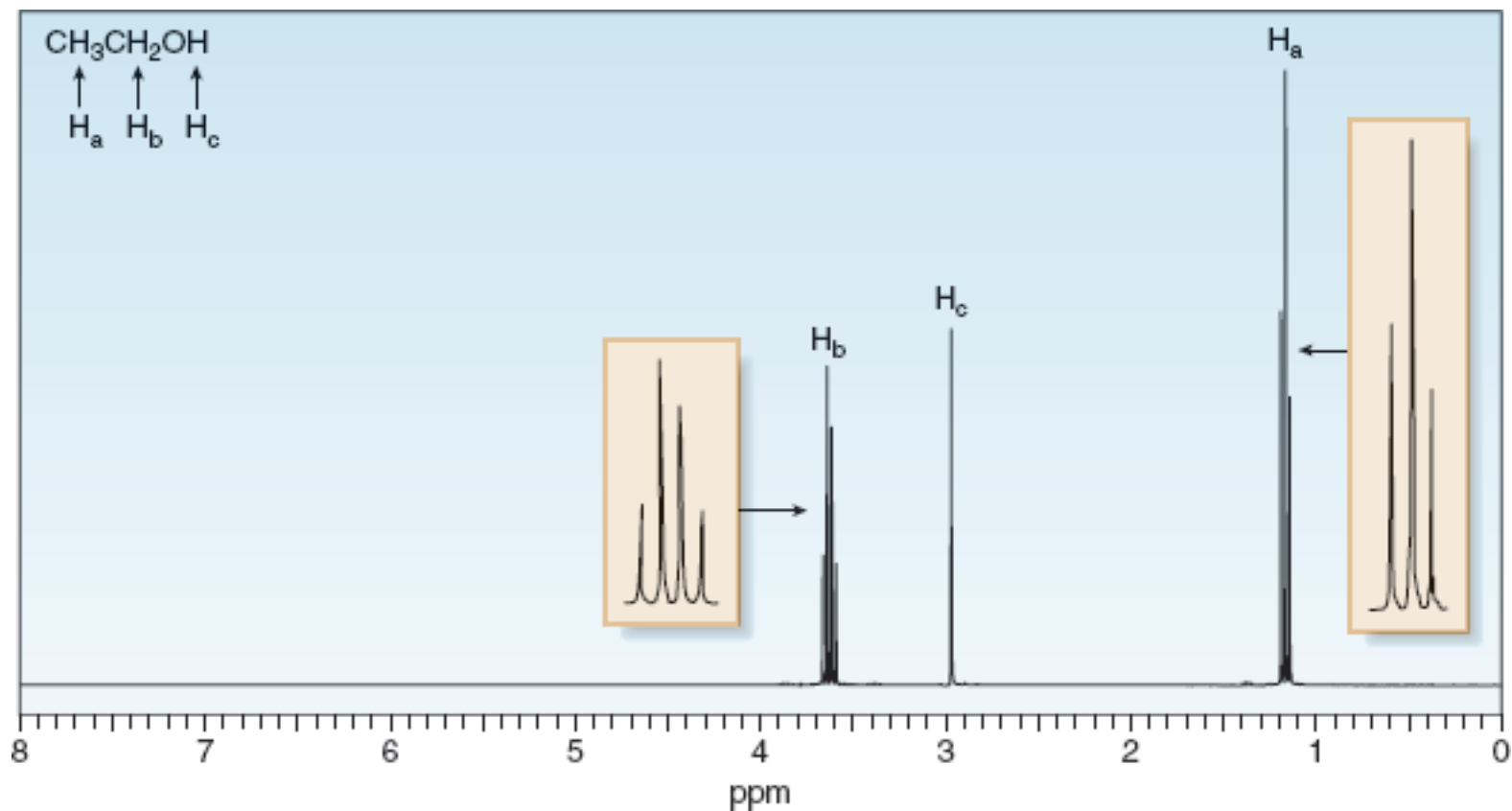
14.9 Other Facts About ^1H NMR Spectroscopy

B. Cyclohexanes

axial → H_a equatorial
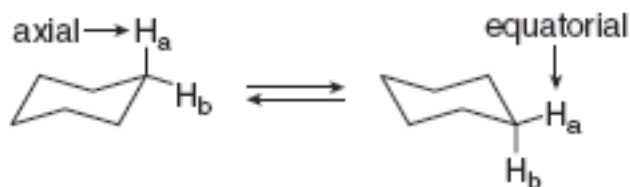
| Axial and equatorial H's rapidly interconvert. NMR sees an average environment and shows one signal. |

C. Benzene Rings (Chapter 17)

| A benzene ring with one substituent Z |
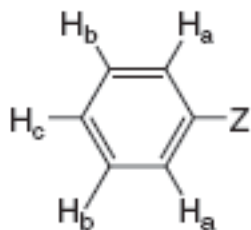
A monosubstituted benzene ring has three different types of H atoms: H_a, H_b, and H_c.

$-CH_2CH_3$

$-CHO$

$-OCH_3$
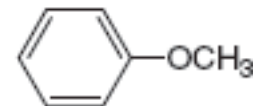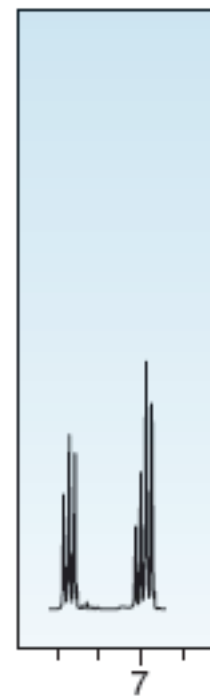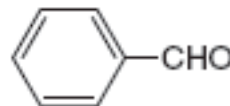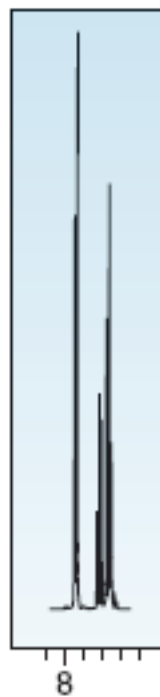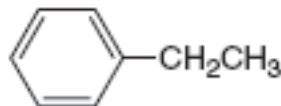
14.10 Using ¹H NMR to Identify an Unknown

Molecular formula: $C_4H_8O_2$
IR shows an absorption for a C=O bond

absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14
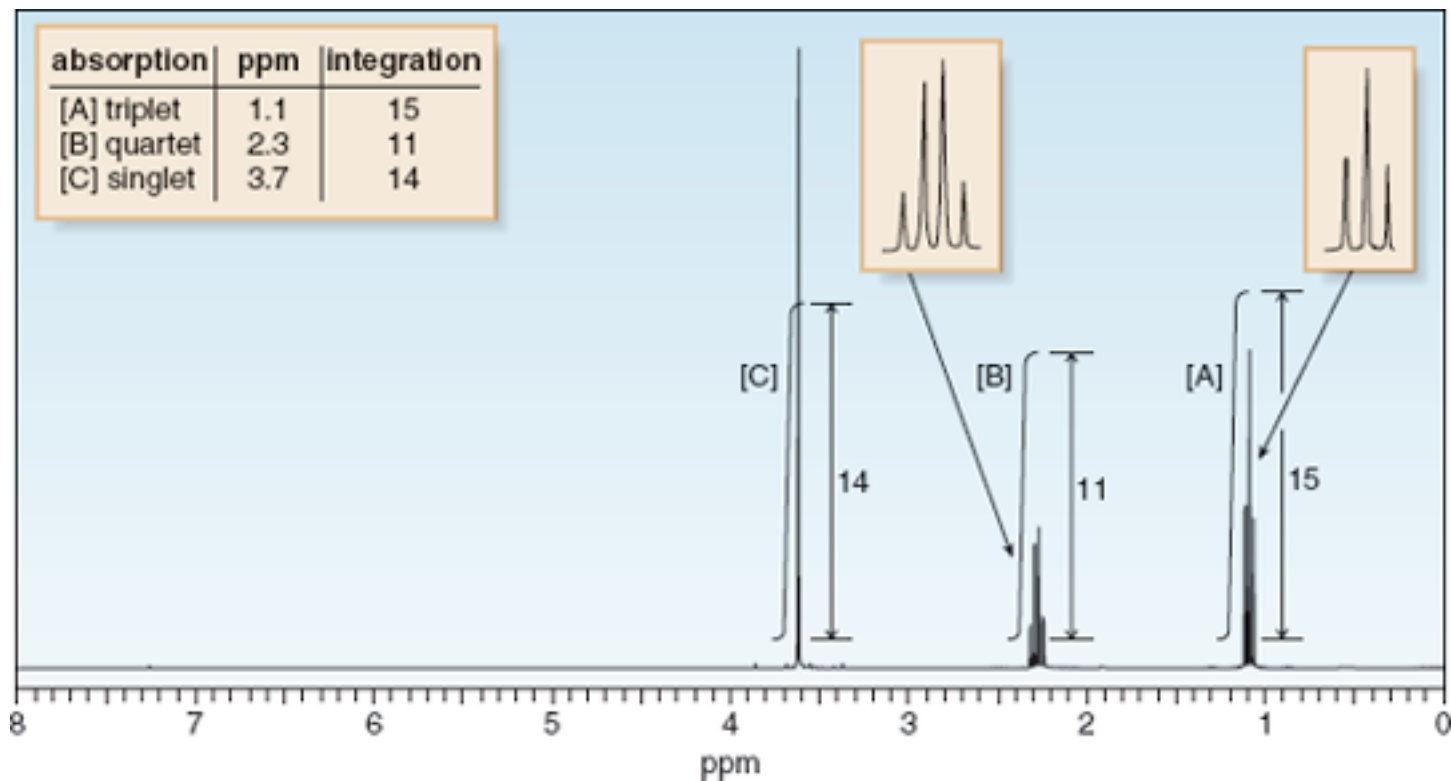
1. Determine # protons
2. Integration: # H atoms per signal
3. Splitting patterns (with integrations) determine connectivity
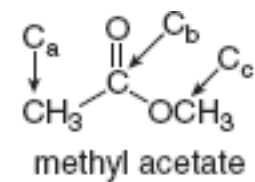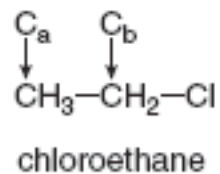4. Chemical shifts to complete structure

14.11 ^{13}C NMR Spectroscopy

A. ^{13}C NMR: Number of Signals

- ^{13}C has only 1.1% natural abundance giving a much weaker signal than ^{1}H
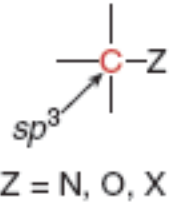- No splitting, every nonequivalent carbon appears as 1 peak
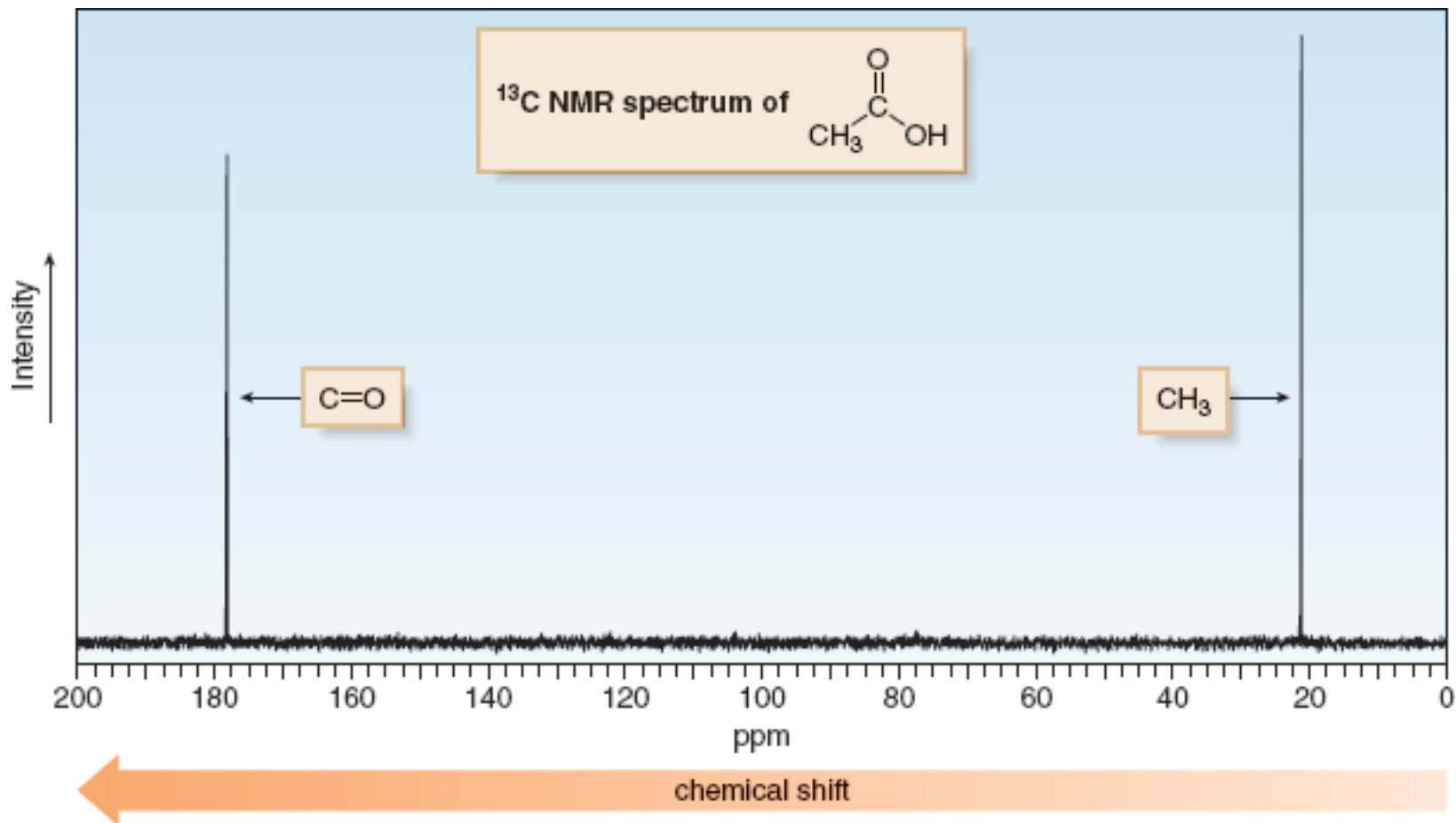
^{13}C NMR spectrum of (CH$_3$C(=O)OH)
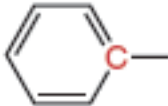
14.11 ^{13}C NMR Spectroscopy

A. ^{13}C NMR: Number of Signals

dimethyl ether

chloroethane

methyl acetate

chrysanthemic acid
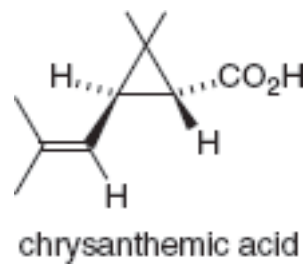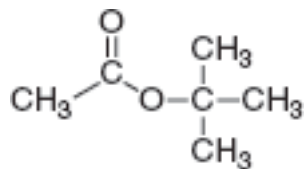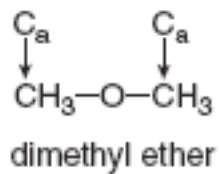
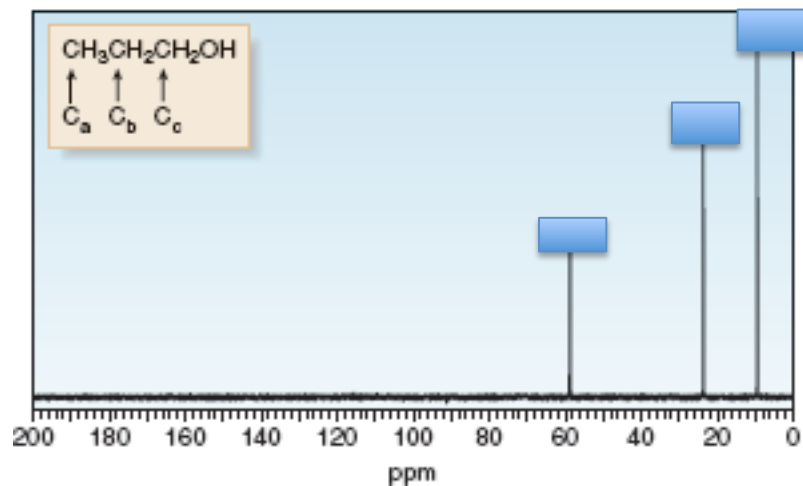# 14.11 ^{13}C NMR Spectroscopy

B. ^{13}C NMR: Chemical Shifts

Table 14.5 Common ^{13}C Chemical Shift Values

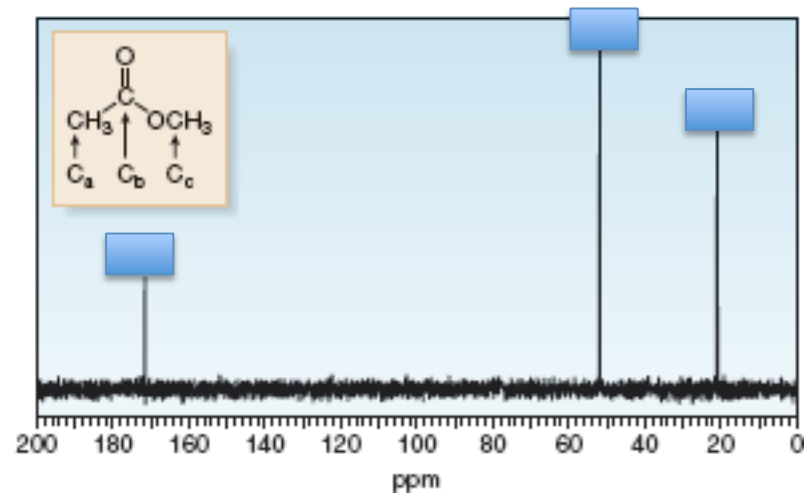| Type of carbon	Chemical shift (ppm)	Type of carbon	Chemical shift (ppm)
sp^3 C—H	5–45	C=C	100–140
sp^3 C—Z Z = N, O, X	30–80	C— (aromatic)	120–150
—C≡C—	65–100	C=O	160–210

14.11 ^{13}C NMR Spectroscopy

B. ^{13}C NMR: Chemical Shifts

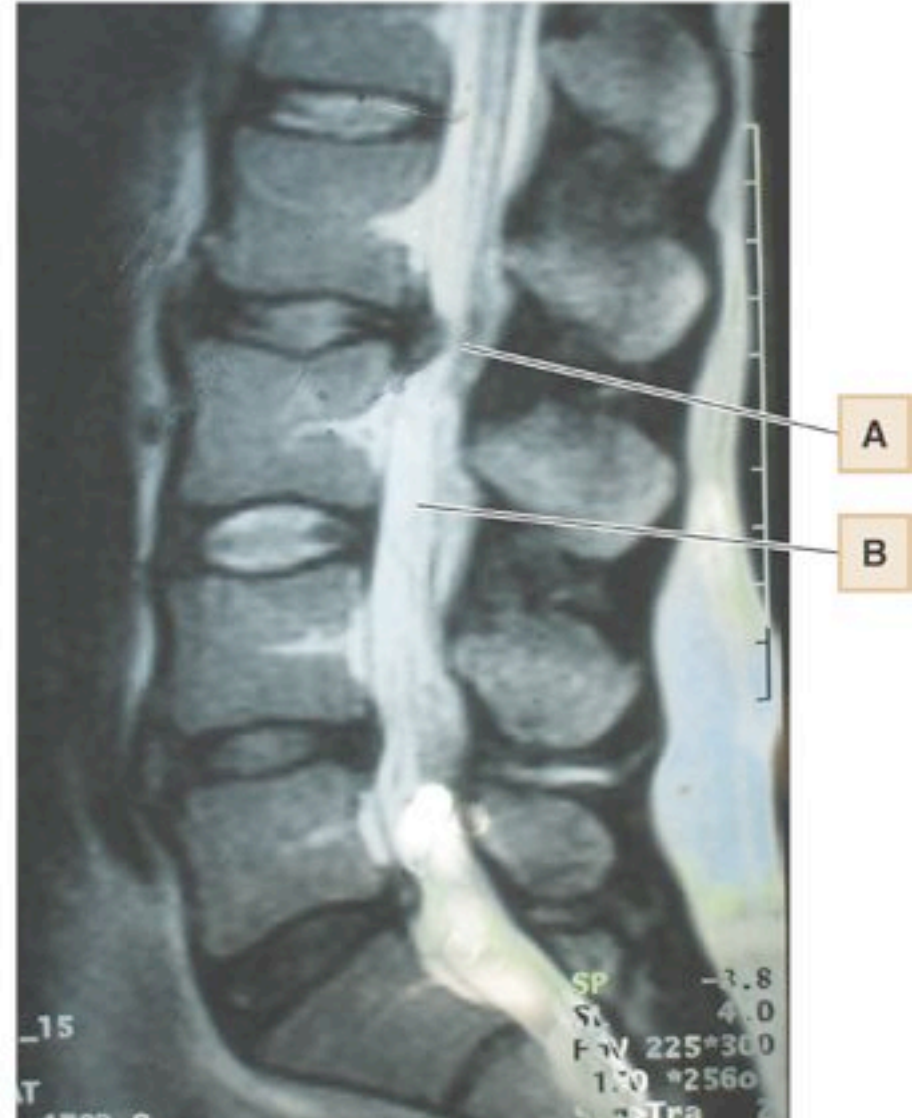a. 1-Propanol

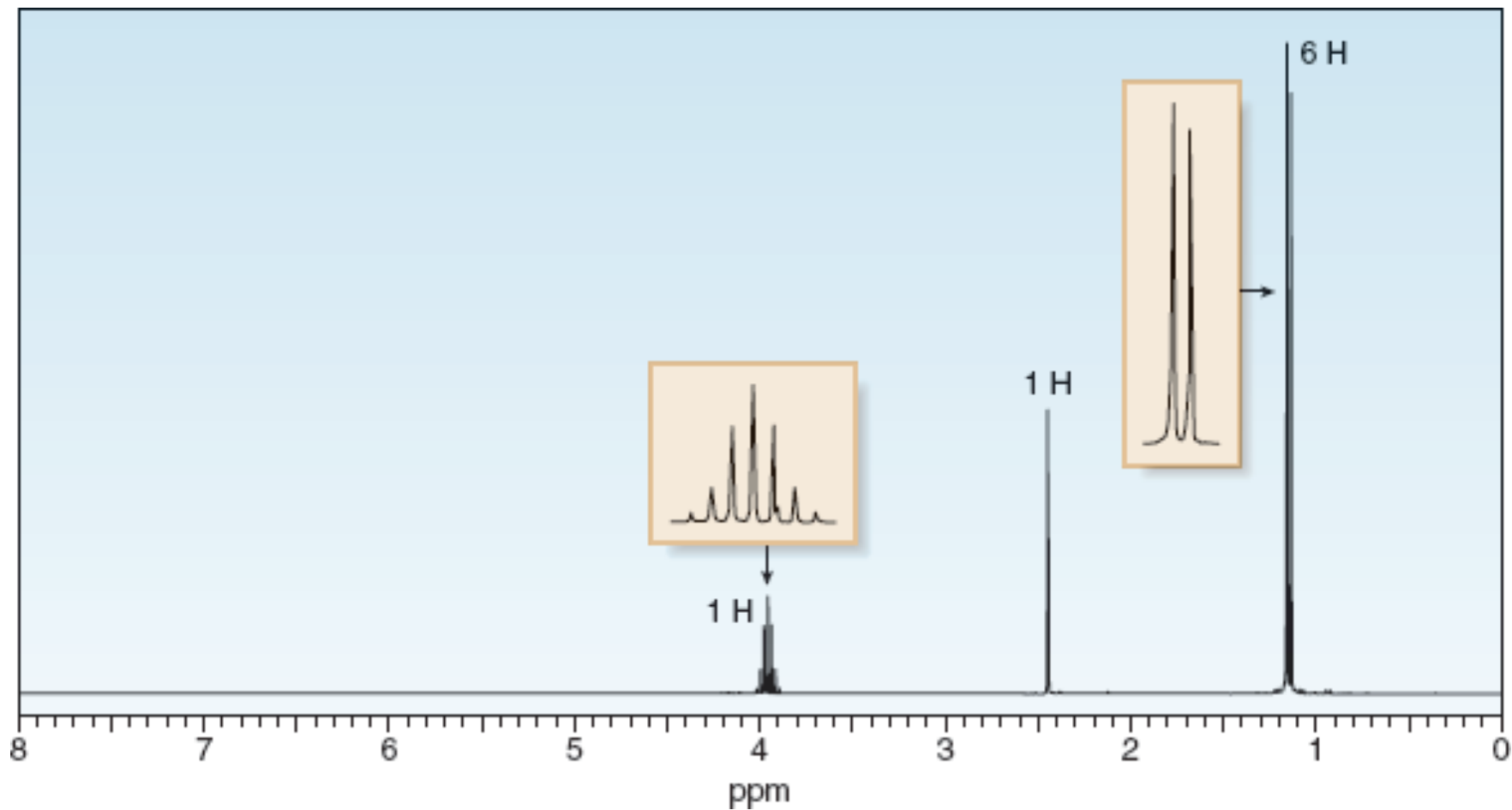b. Methyl acetate

14.12 Magnetic Resonance Imaging
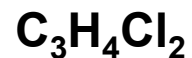
(a)

(b)

A

B

Chapter 14 Sample Problems

14.24

m/z = 60

IR: 3600-3200 cm^{-1}

Chapter 14 Sample Problems

14.19

$C_3H_4Cl_2$

A. ^1H NMR:
1.75 ppm (doublet, 3H, J = 6.9 Hz)
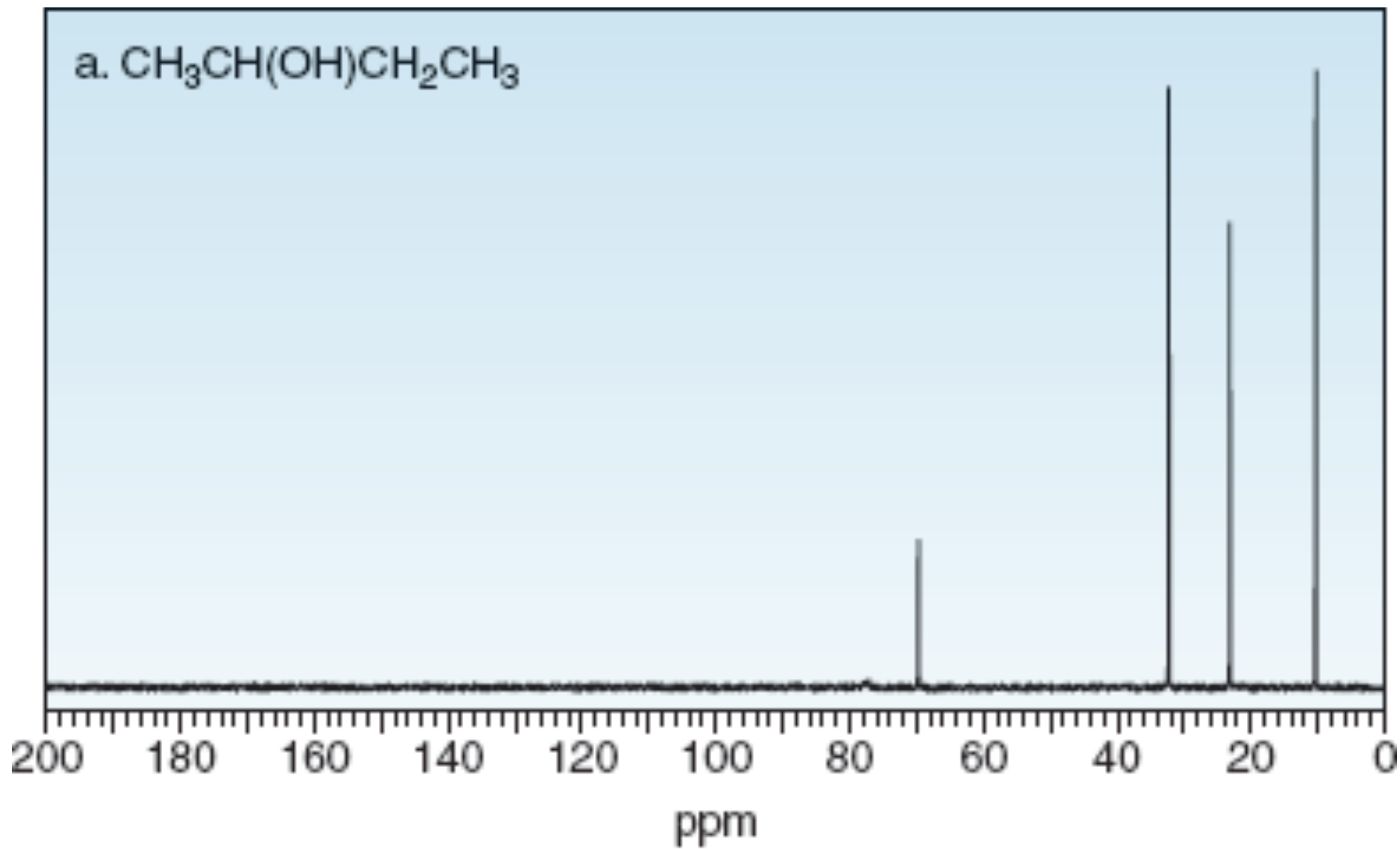5.89 ppm (quartet, 1H, J = 6.9 Hz)

B. ^1H NMR:
4.16 ppm (singlet, 2H)
5.42 ppm (doublet, 1H, J = 1.9 Hz)
5.59 ppm (doublet, 1H, J = 1.9 Hz)
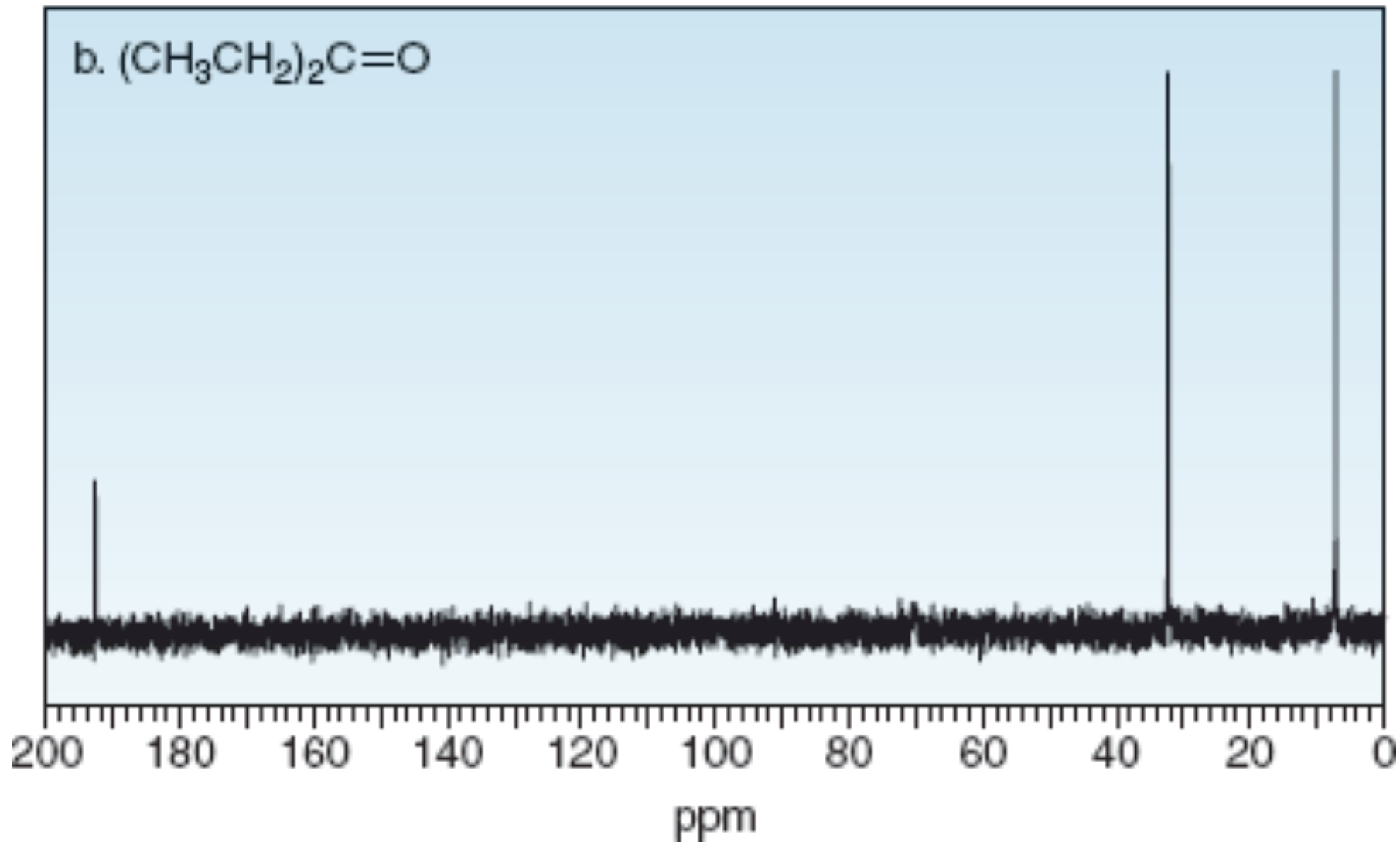
Chapter 14 Sample Problems

a. $CH_3CH(OH)CH_2CH_3$

Chapter 14 Sample Problems

14.30

b. $(CH_3CH_2)_2C=O$

14.70

¹H NMR of Q

3 H

6 H

1 H

IR of Q