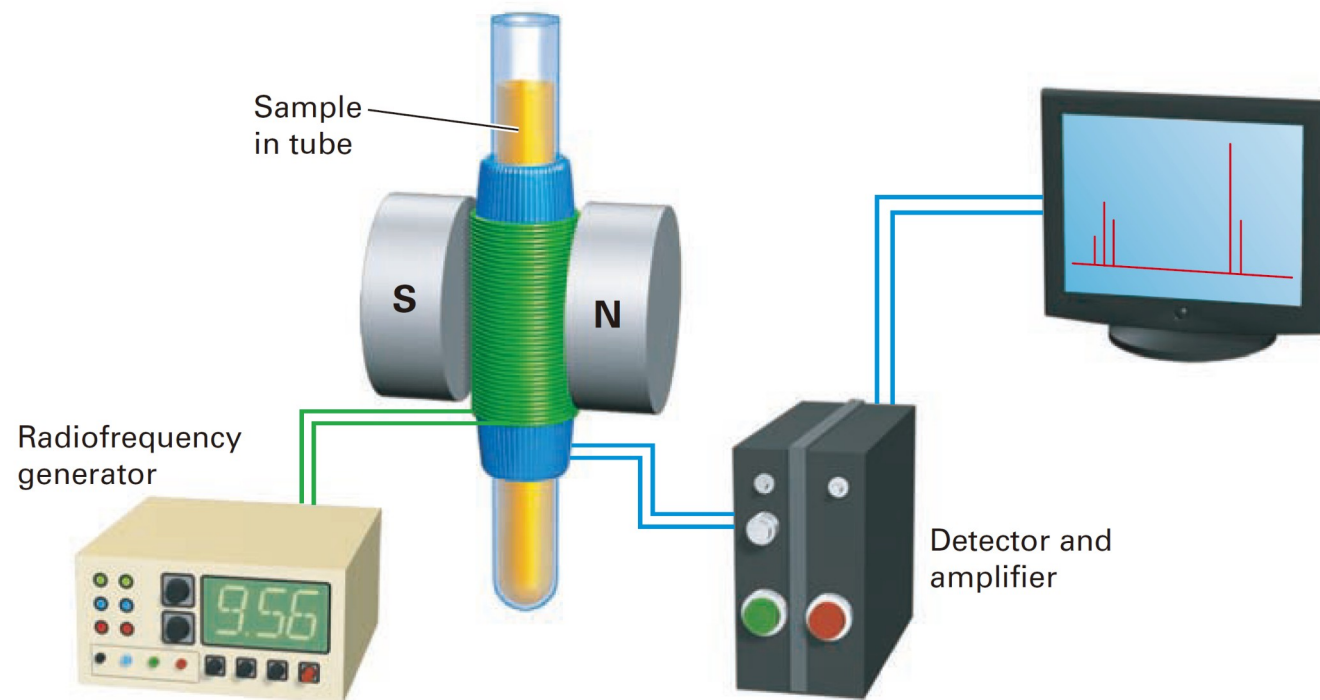




13

结构鉴定：核磁共振谱

13.1 原理

- 原子核的自旋运动在外磁场下呈正向和逆向排列。正向排列的核能量较低，逆向排列的核能量较高。它们之间的能量差为 ΔE 。一个核要从低能态跃迁到高能态，必须吸收 ΔE 的能量。让处于外磁场中的自旋核接受一定频率的电磁波辐射，当辐射的能量恰好等于自旋核两种不同取向的能量差时，处于低能态的自旋核吸收电磁辐射能跃迁到高能态。这种现象称为核磁共振，简称 NMR。

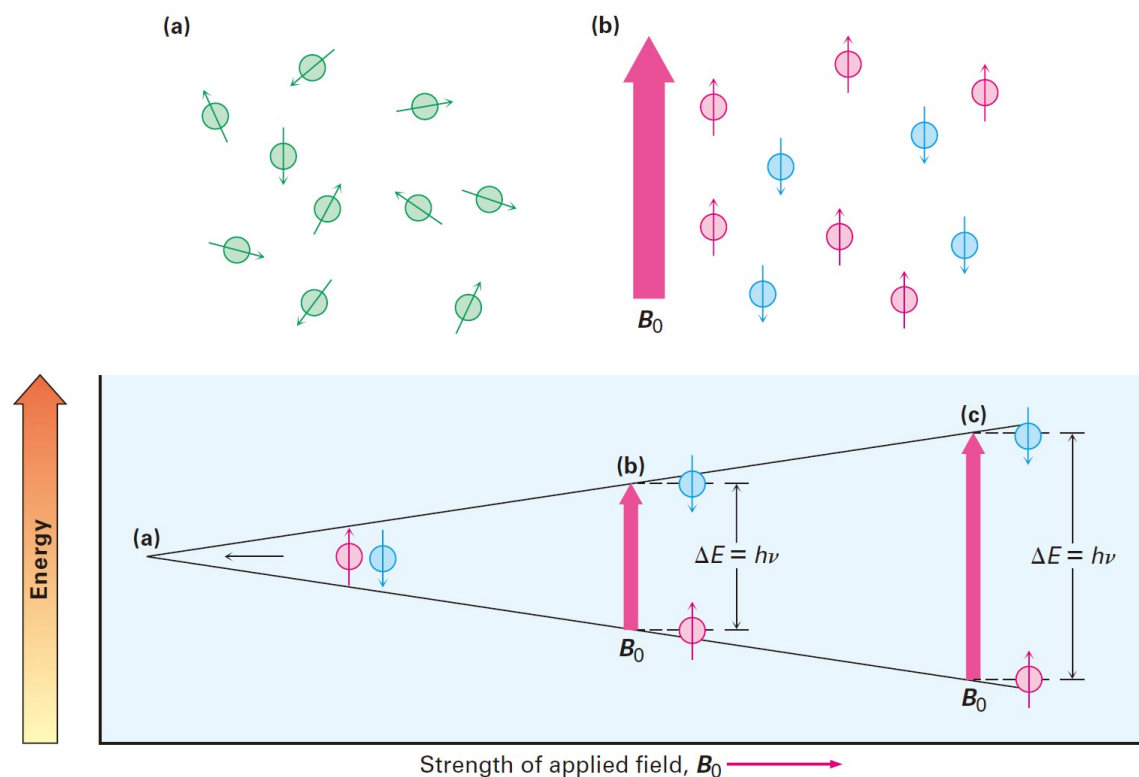


Table 13.1 The NMR Behavior of Some Common Nuclei

Magnetic nuclei	Nonmagnetic nuclei
^1H	^{12}C
^{13}C	^{16}O
^2H	^{32}S
^{14}N	
^{19}F	
^{31}P	



13.2 化学位移

- 在有机化合物中，处在不同结构和位置上的各种氢核周围的电子云密度不同，导致共振频率有差异，即产生共振吸收峰的位移，称为化学位移。
- 氢谱和碳谱的化学位移一般以四甲基硅烷的吸收峰为参照。

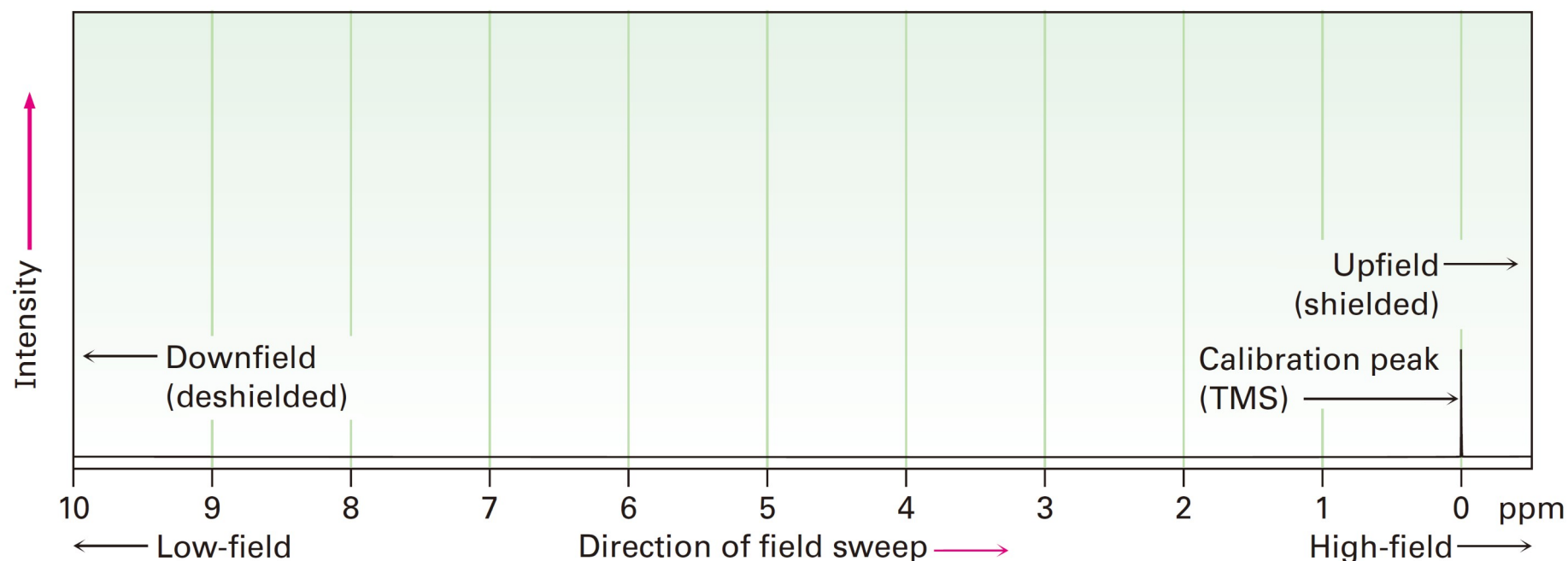
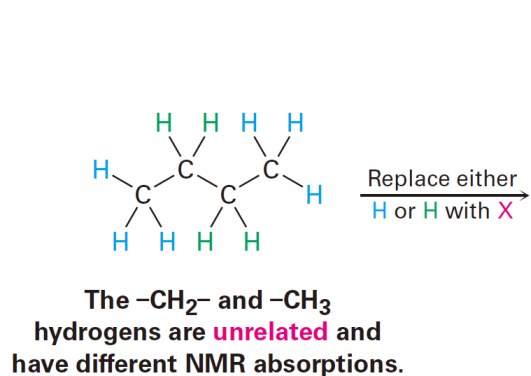
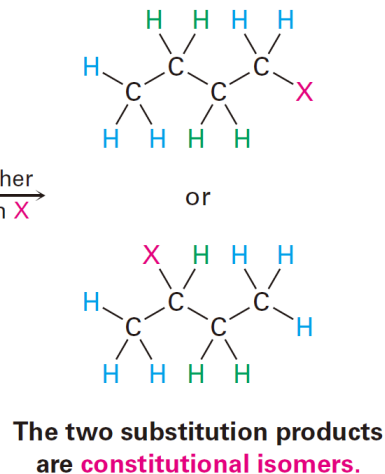
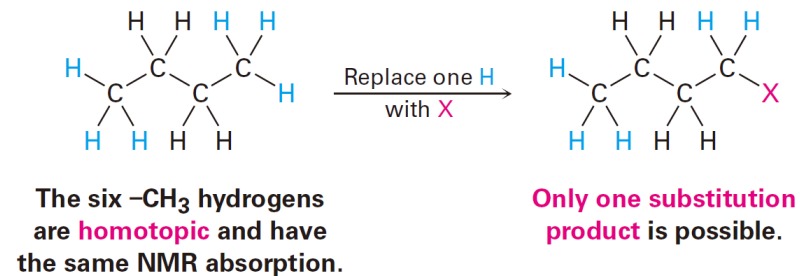
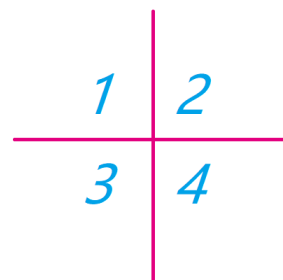
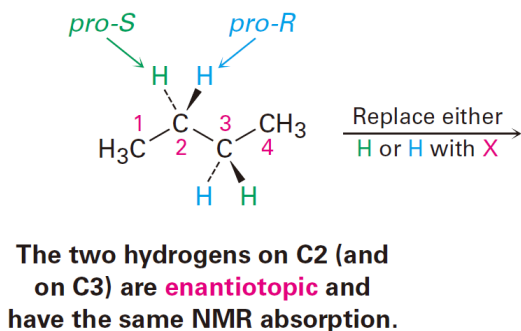
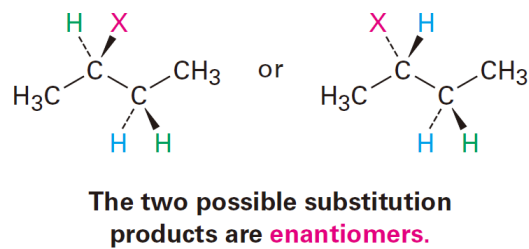
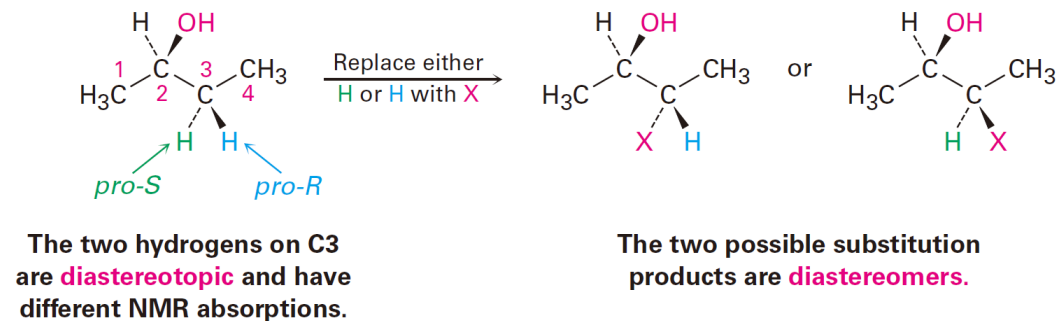


Figure 13.5 The NMR chart. The downfield, deshielded side is on the left, and the upfield, shielded side is on the right. The tetramethylsilane (TMS) absorption is used as reference point.

13.3 核磁氢谱

- 化学环境等价的几种情况

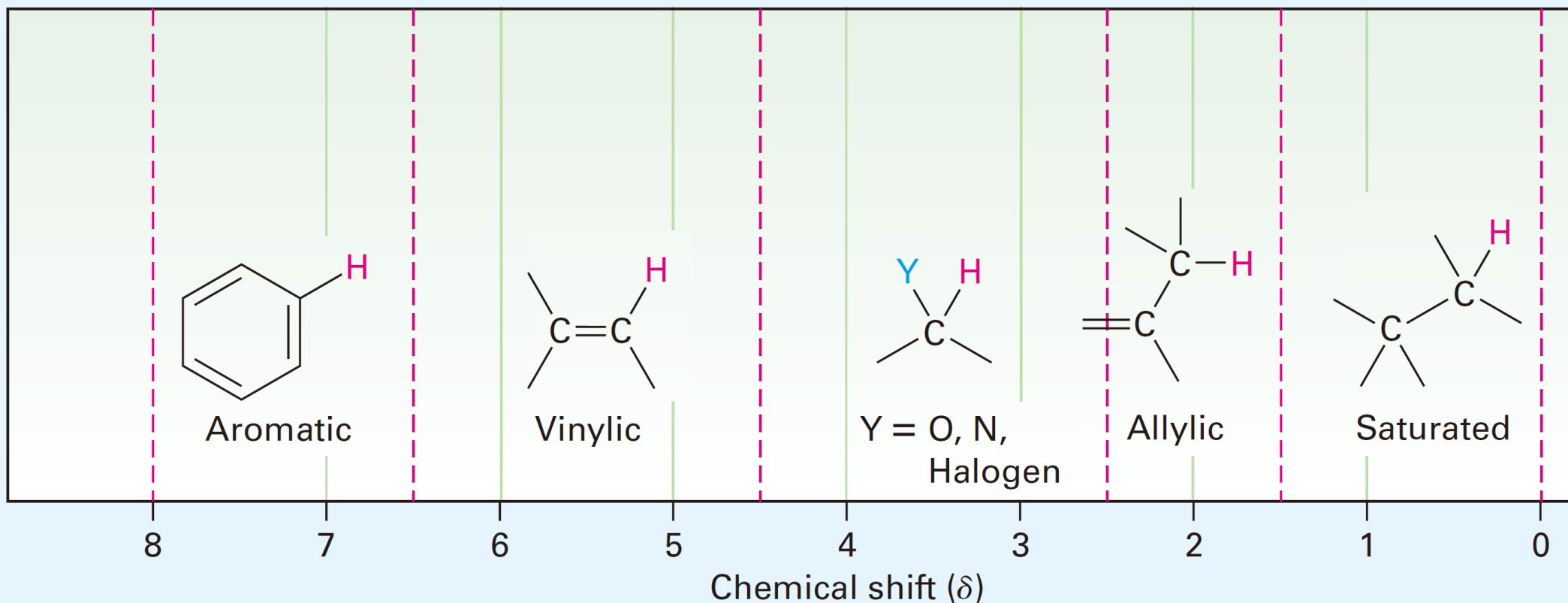


The two possible substitution products are **diastereomers**.



13.3 核磁氢谱

Table 13.2 Regions of the ^1H NMR Spectrum



13.3 核磁氢谱

Table 13.3 Correlation of ^1H Chemical Shift with Environment

Type of hydrogen		Chemical shift (δ)	Type of hydrogen		Chemical shift (δ)
Reference	$\text{Si}(\text{CH}_3)_4$	0	Alcohol	$\begin{array}{c} \\ -\text{C}-\text{O}-\text{H} \\ \end{array}$	2.5–5.0
Alkyl (primary)	$-\text{CH}_3$	0.7–1.3			
Alkyl (secondary)	$-\text{CH}_2-$	1.2–1.6			
Alkyl (tertiary)	$\begin{array}{c} \\ -\text{CH}- \\ \end{array}$	1.4–1.8	Alcohol, ether	$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{O}- \\ \end{array}$	3.3–4.5
Allylic	$\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C}-\text{C}- \\ \end{array}$	1.6–2.2			
Methyl ketone	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{CH}_3 \end{array}$	2.0–2.4	Vinylic	$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \end{array}$	4.5–6.5
Aromatic methyl	$\text{Ar}-\text{CH}_3$	2.4–2.7	Aryl	$\text{Ar}-\text{H}$	6.5–8.0
Alkynyl	$-\text{C}\equiv\text{C}-\text{H}$	2.5–3.0	Aldehyde	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$	9.7–10.0
Alkyl halide	$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{Hal} \\ \end{array}$	2.5–4.0	Carboxylic acid	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{H} \end{array}$	11.0–12.0



13.3 核磁氢谱

- 氢谱峰面积的积分与氢的数目成比例

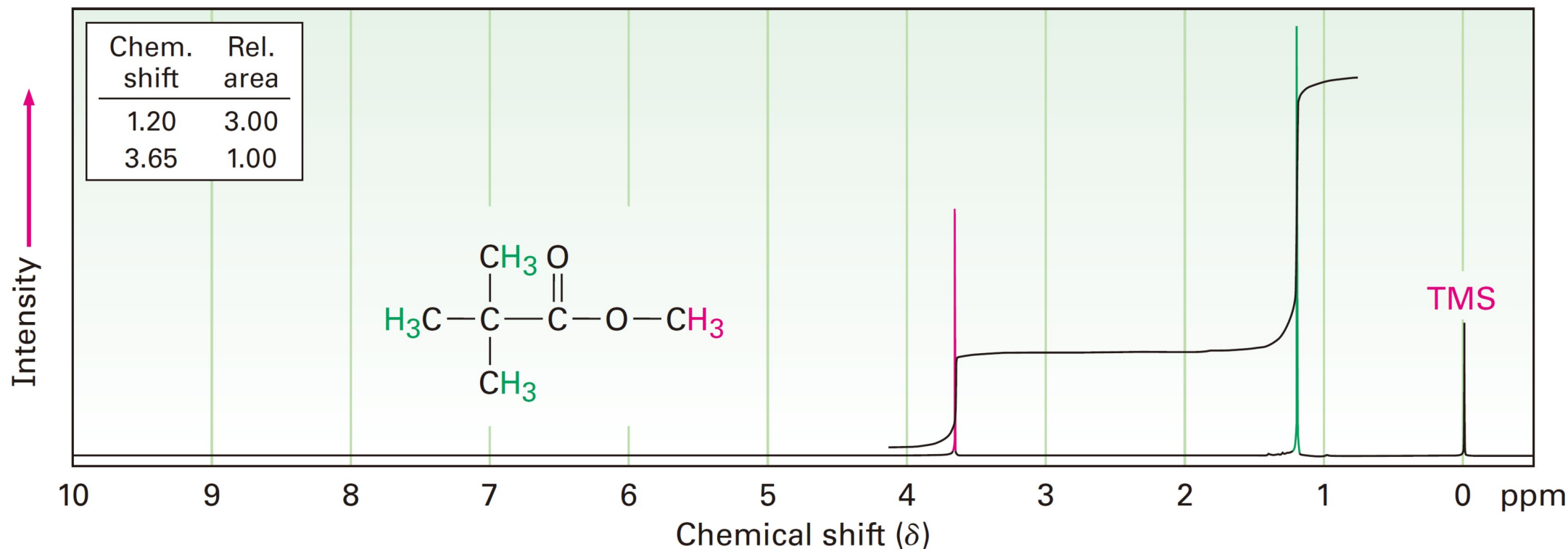


Figure 13.12 The ^1H NMR spectrum of methyl 2,2-dimethylpropanoate. Integrating the peaks in a stair-step manner shows that they have a 1:3 ratio, corresponding to the ratio of the numbers of protons (3:9) responsible for each peak. Modern instruments give a direct digital readout of relative peak areas.

13.3 核磁氢谱

- 彼此裂分：n+1 规则

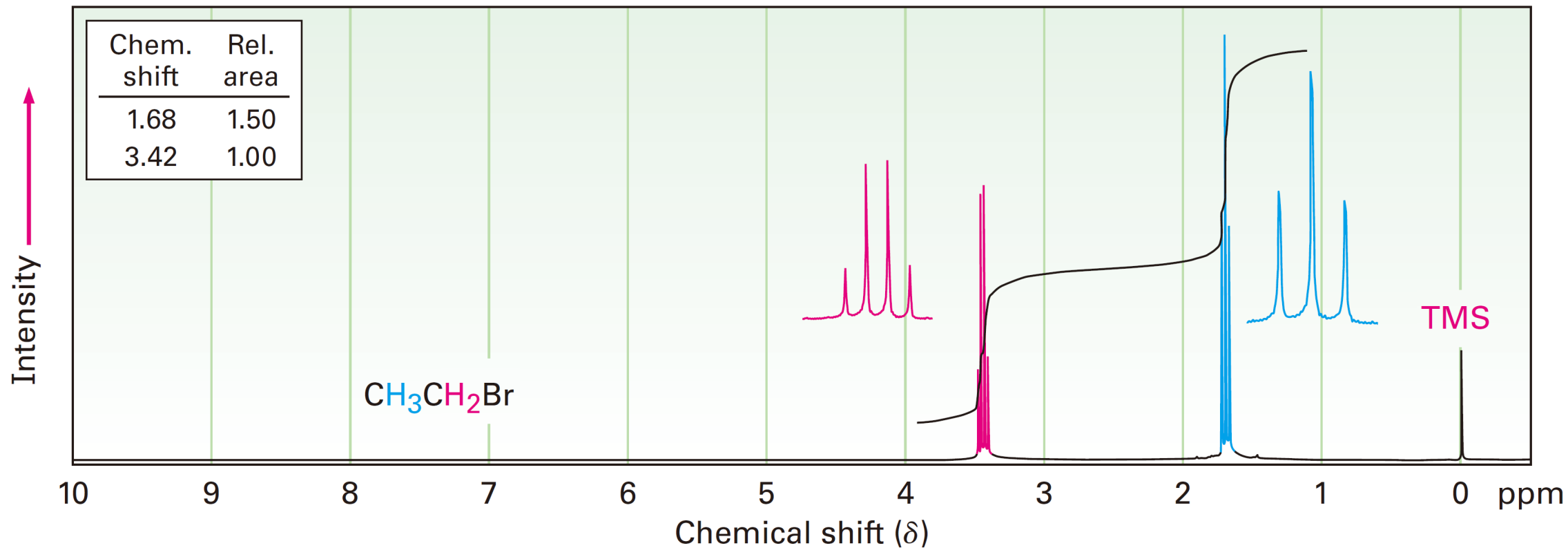


Figure 13.13 The ^1H NMR spectrum of bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$. The $-\text{CH}_2\text{Br}$ protons appear as a quartet at $3.42\ \delta$, and the $-\text{CH}_3$ protons appear as a triplet at $1.68\ \delta$.

13.3 核磁氢谱

- 彼此裂分：n+1 规则

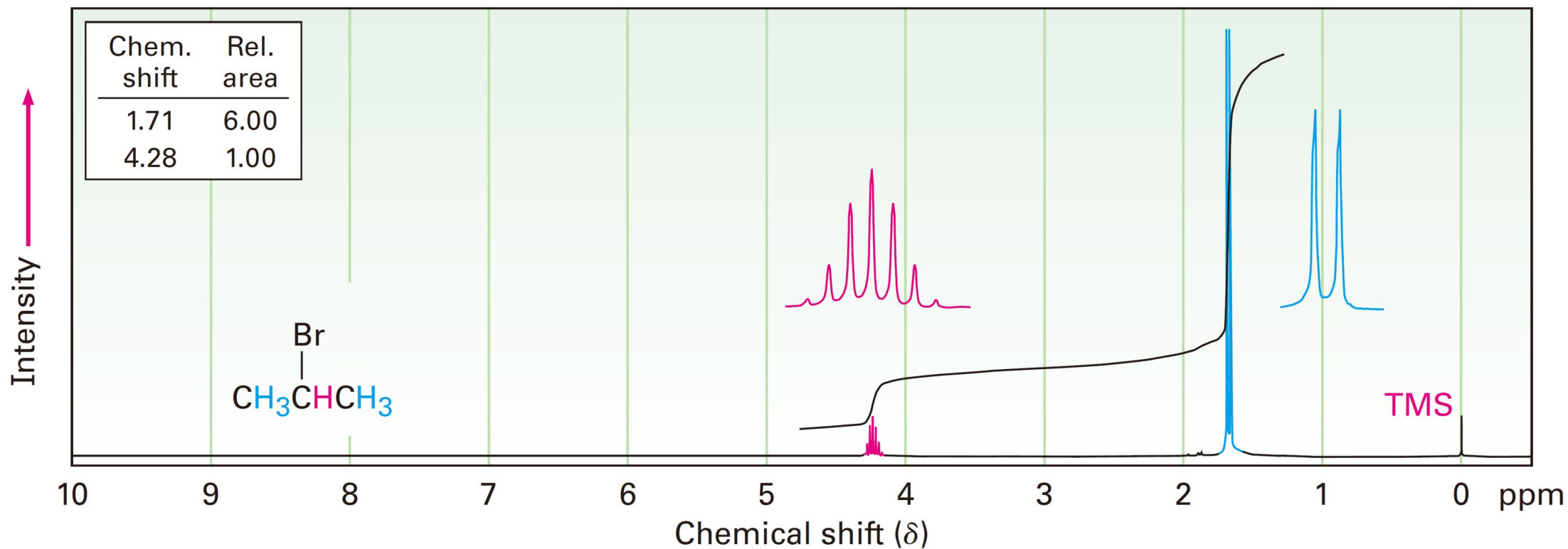


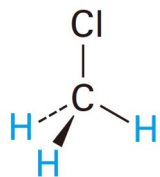
Figure 13.15 The ^1H NMR spectrum of 2-bromopropane. The $-\text{CH}_3$ proton signal at 1.71 δ is split into a doublet, and the $-\text{CHBr}-$ proton signal at 4.28 δ is split into a septet. Note that the distance between peaks—the *coupling constant*—is the same in both multiplets. Note also that the outer two peaks of the septet are so small as to be nearly lost.

13.3 核磁氢谱

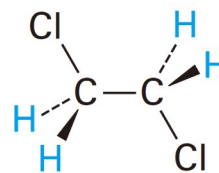
- 耦合规律

RULE 1

Chemically equivalent protons don't show spin-spin splitting. The equivalent protons may be on the same carbon or on different carbons, but their signals don't split.



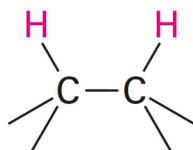
Three C-H protons are chemically equivalent; no splitting occurs.



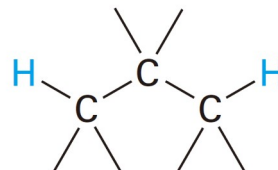
Four C-H protons are chemically equivalent; no splitting occurs.

RULE 2

The signal of a proton with n equivalent neighboring protons is split into a multiplet of $n + 1$ peaks with coupling constant J . Protons that are farther than two carbon atoms apart don't usually couple, although they sometimes show small coupling when they are separated by a π bond.



Splitting observed



Splitting not usually observed

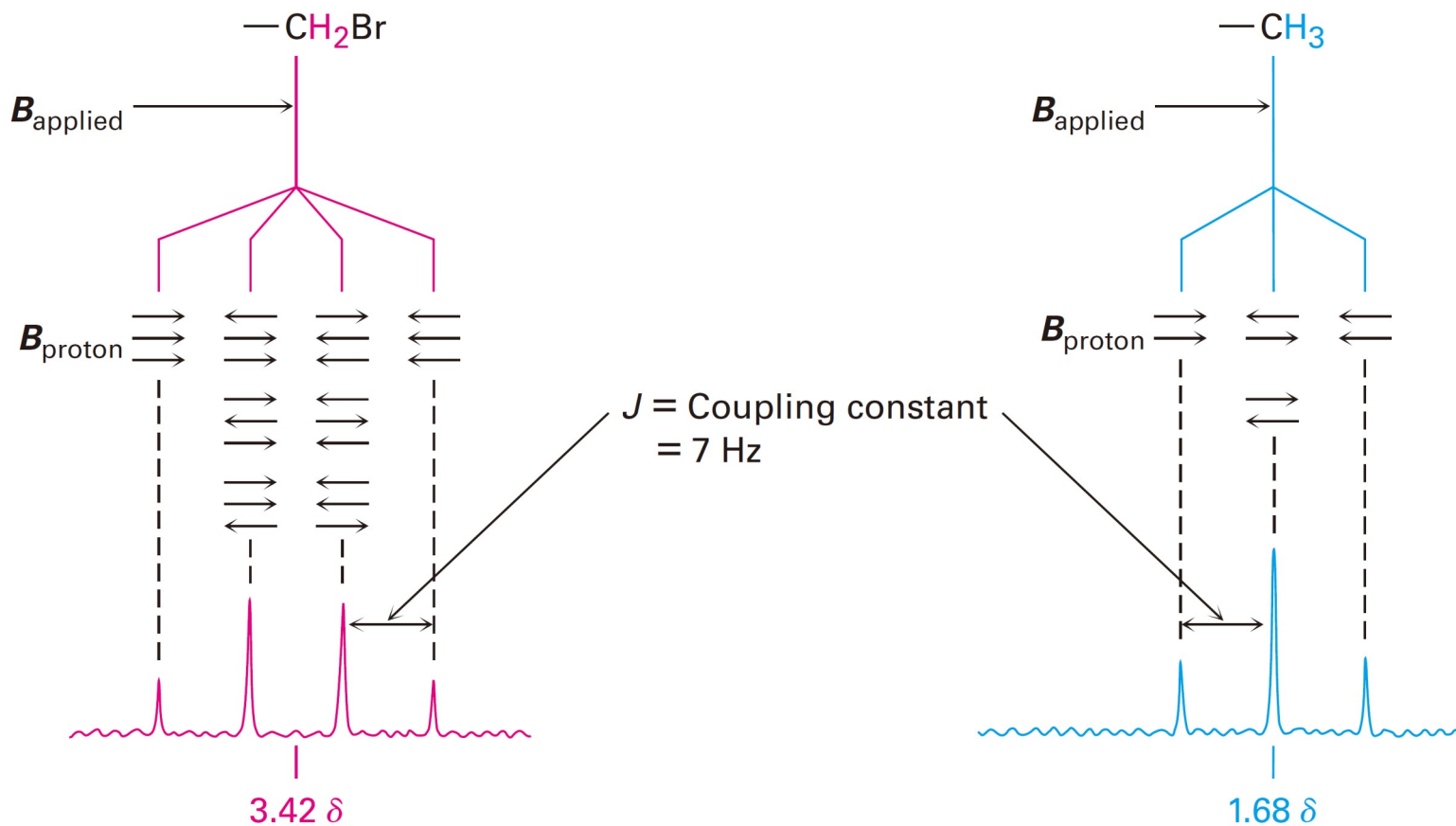


13.3 核磁氢谱

- 耦合规律

RULE 3

Two groups of protons coupled to each other have the same coupling constant, J .



13.3 核磁氢谱

• 实例一

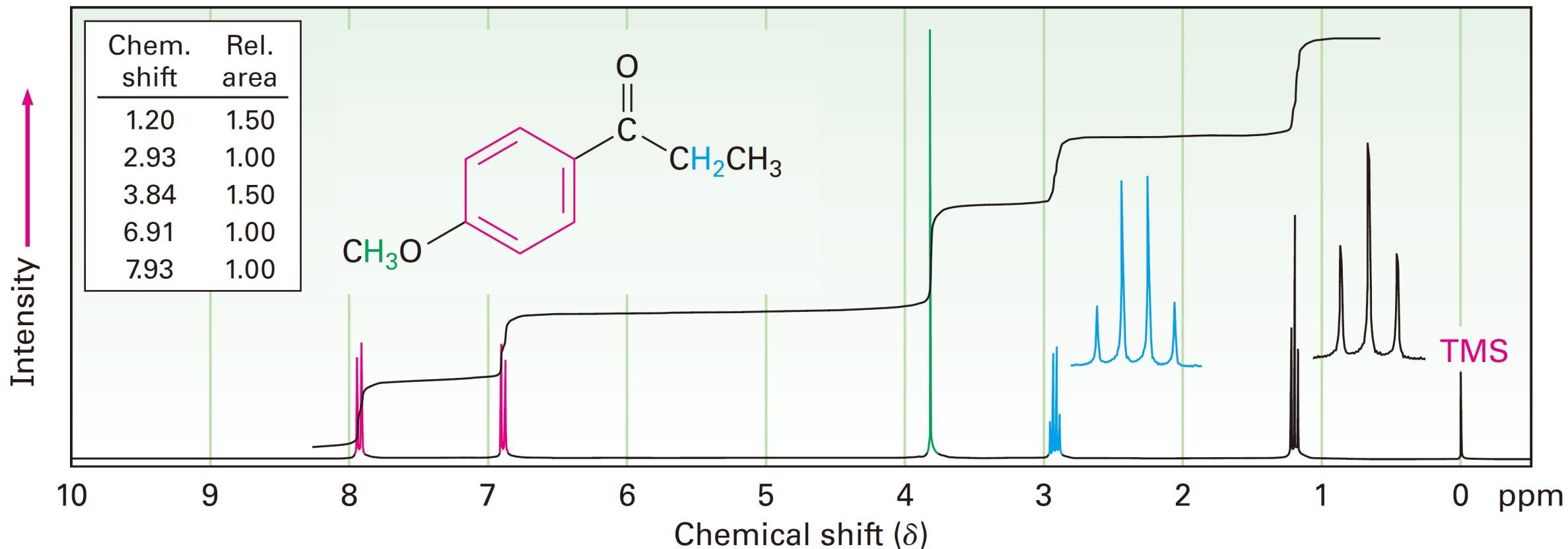


Figure 13.16 The ^1H NMR spectrum of *para*-methoxypropiophenone.

13.3 核磁氢谱

- 课堂练习

Problem 13.21

The integrated ^1H NMR spectrum of a compound of formula $\text{C}_4\text{H}_{10}\text{O}$ is shown in **Figure 13.17**. Propose a structure.

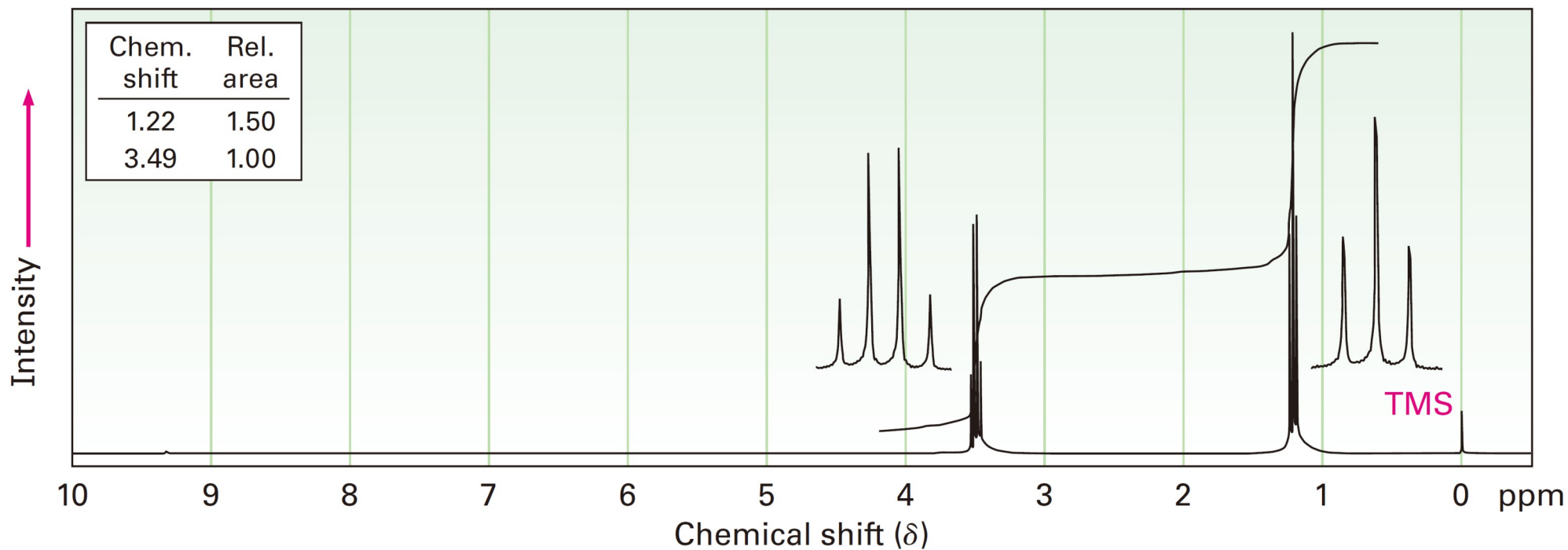


Figure 13.17 An integrated ^1H NMR spectrum for Problem 13.21.

13.4 核磁共振

- 化学位移的大致范围

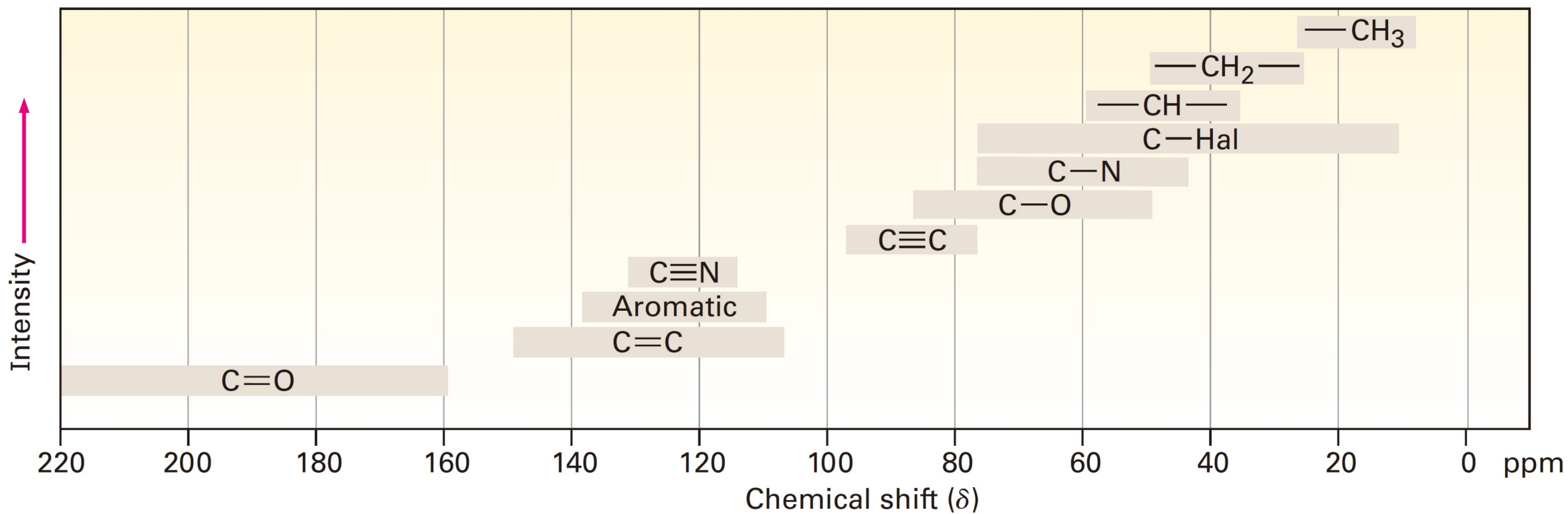
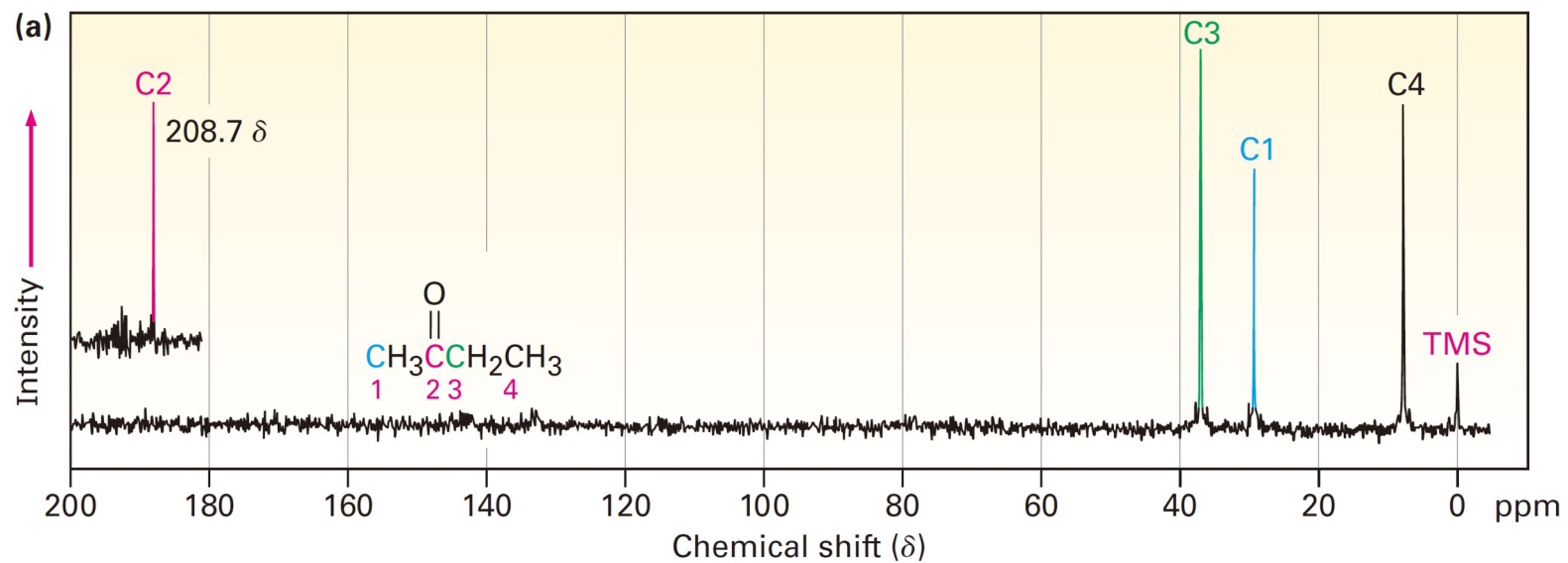
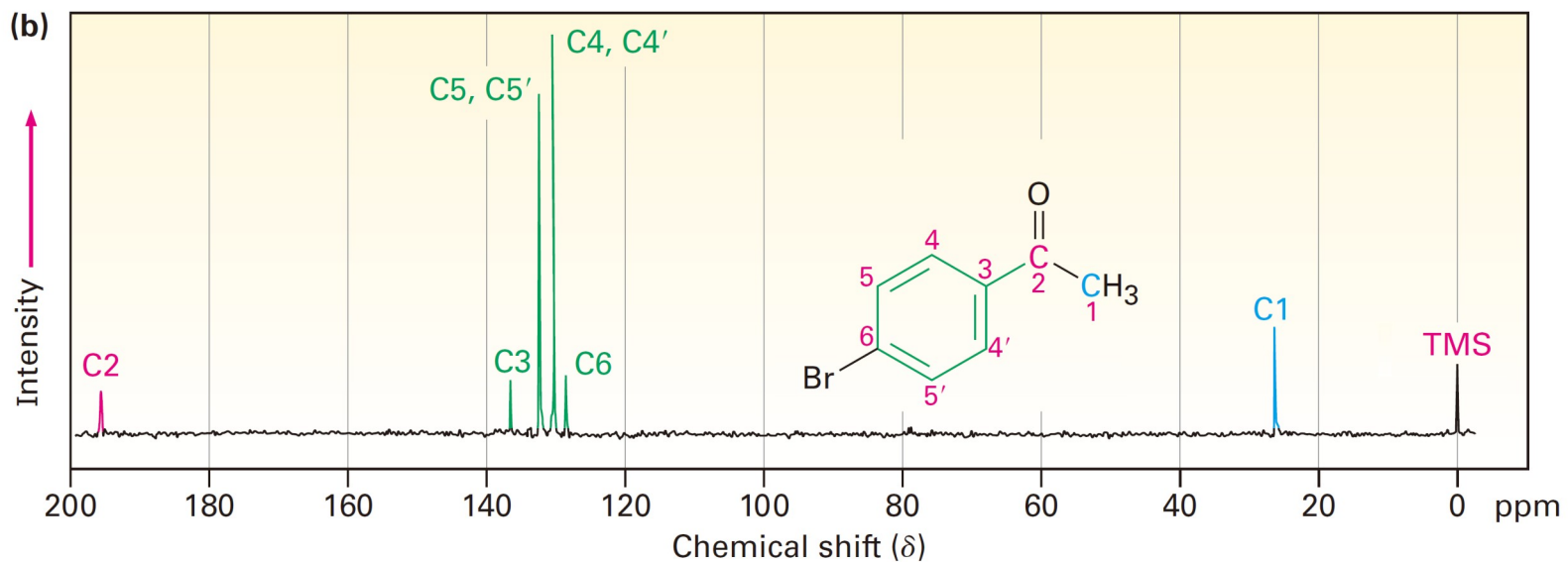


Figure 13.7 Chemical shift correlations for ^{13}C NMR.

13.4 核磁共振谱

• 实例



13.4 核磁共振

- 课堂练习

Problem 13.8

Assign the resonances in the ^{13}C NMR spectrum of methyl propanoate, $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ (Figure 13.9).

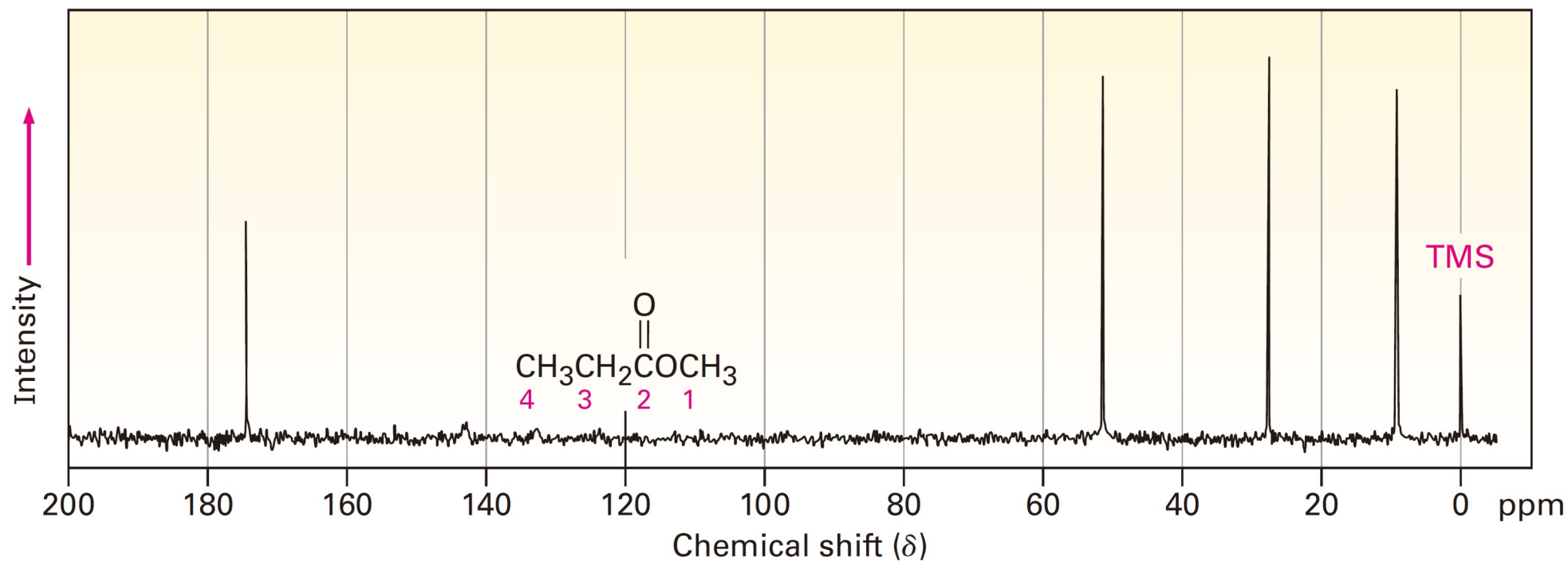


Figure 13.9 ^{13}C NMR spectrum of methyl propanoate, Problem 13.8.

13.4 核磁碳谱

- DEPT-90 for CH carbon;
- DEPT-135 for CH₂ carbon

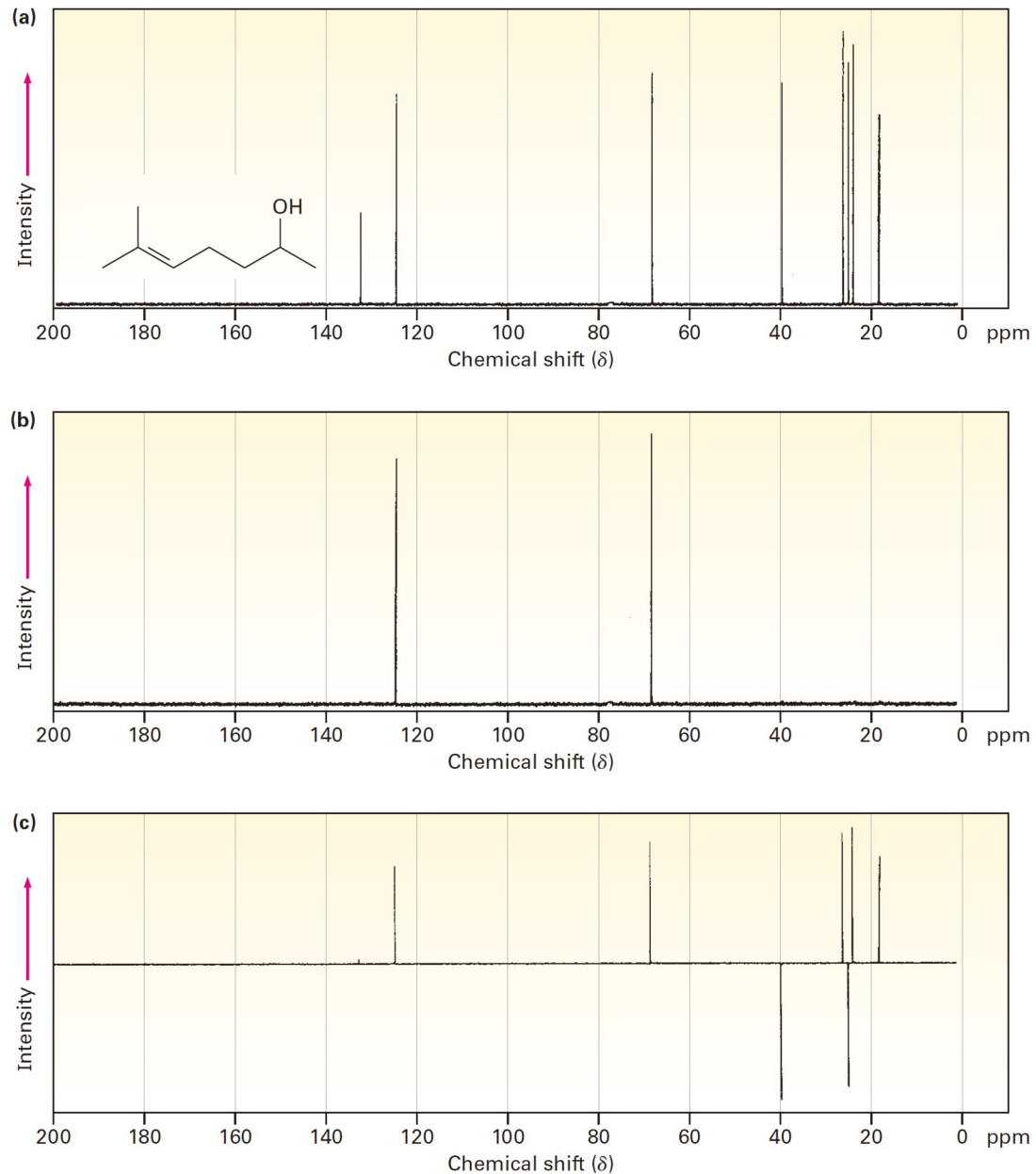
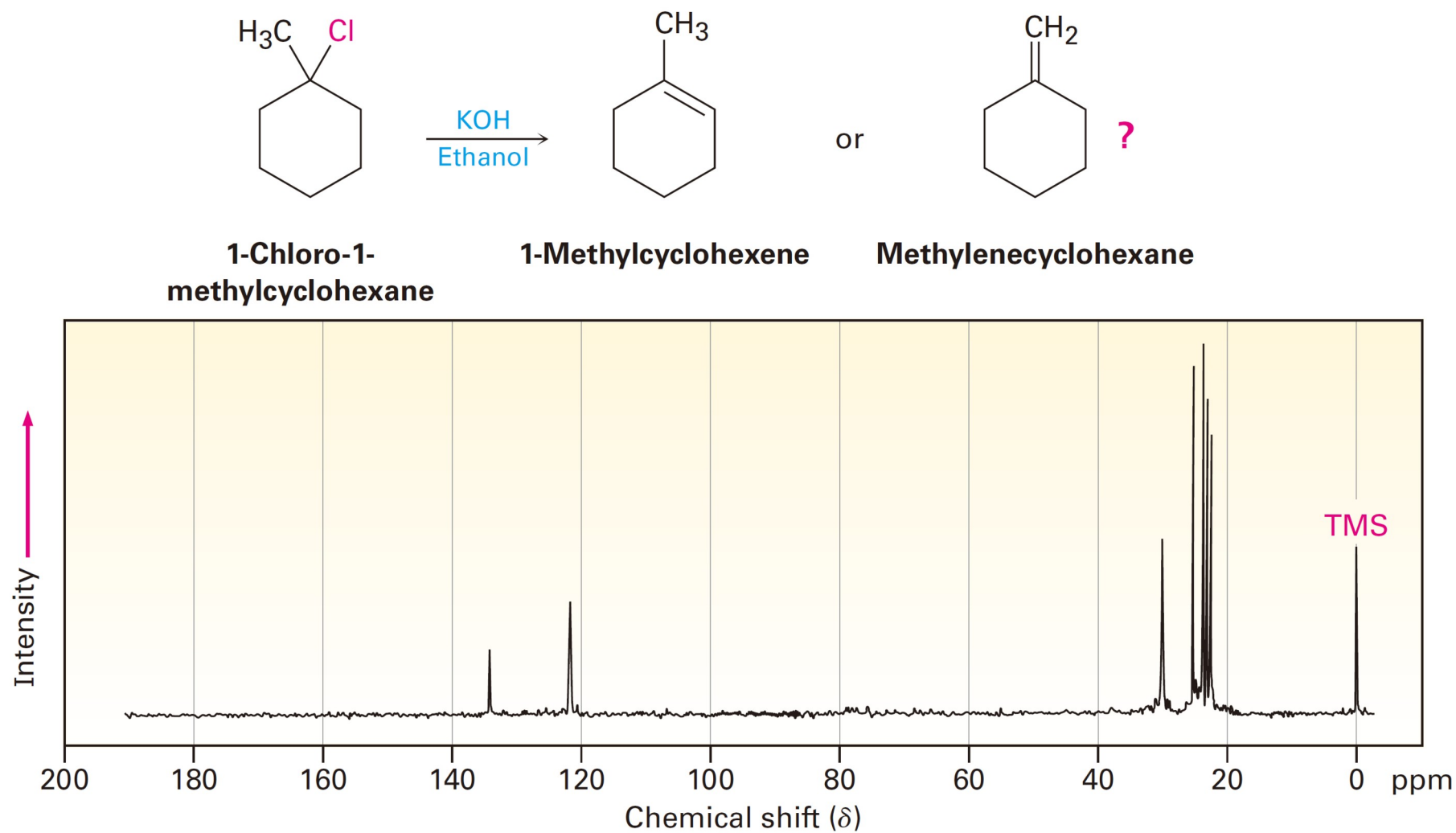


Figure 13.10 DEPT-NMR spectra for 6-methyl-5-hepten-2-ol. Part (a) is an ordinary broadband-decoupled spectrum, which shows signals for all eight carbons. Part (b) is a DEPT-90 spectrum, which shows only signals for the two CH carbons. Part (c) is a DEPT-135 spectrum, which shows positive signals for the two CH and three CH₃ carbons and negative signals for the two CH₂ carbons.

13.4 核磁共振谱

- 用于结构鉴定



作业

- 13.45, 13.51, 13.53, 13.54, 13.57, 13.59

