13.14

^{13}C NMR Spectroscopy

^{1}H and ^{13}C NMR compared:

both give us information about the number of chemically nonequivalent nuclei (nonequivalent hydrogens or nonequivalent carbons)

both give us information about the environment of the nuclei (hybridization state, attached atoms, etc.)

it is convenient to use FT-NMR techniques for ^{1}H; it is standard practice for ^{13}C NMR

^{1}H and ^{13}C NMR compared:

^{13}C requires FT-NMR because the signal for a carbon atom is 10^{-4} times weaker than the signal for a hydrogen atom

a signal for a ^{13}C nucleus is only about 1% as intense as that for ^{1}H because of the magnetic properties of the nuclei, and

at the "natural abundance" level only 1.1% of all the C atoms in a sample are ^{13}C (most are ^{12}C)

^{1}H and ^{13}C NMR compared:

^{13}C signals are spread over a much wider range than ^{1}H signals making it easier to identify and count individual nuclei

Figure 13.20 (a) shows the ^{1}H NMR spectrum of 1-chloropentane; Figure 13.20 (b) shows the ^{13}C spectrum. It is much easier to identify the compound as 1-chloropentane by its ^{13}C spectrum than by its ^{1}H spectrum.

Figure 13.20(a) (page 511)

^1H

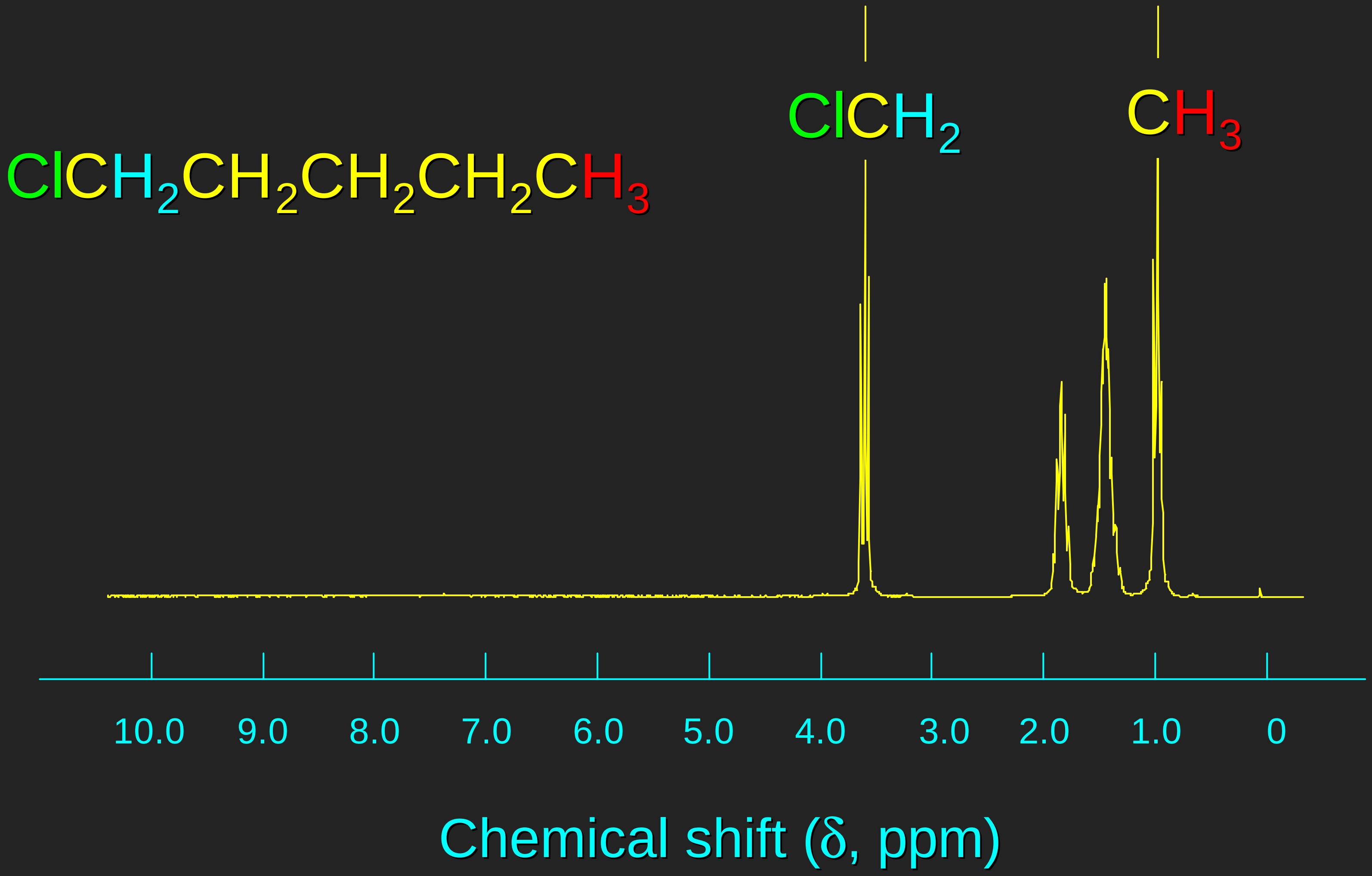
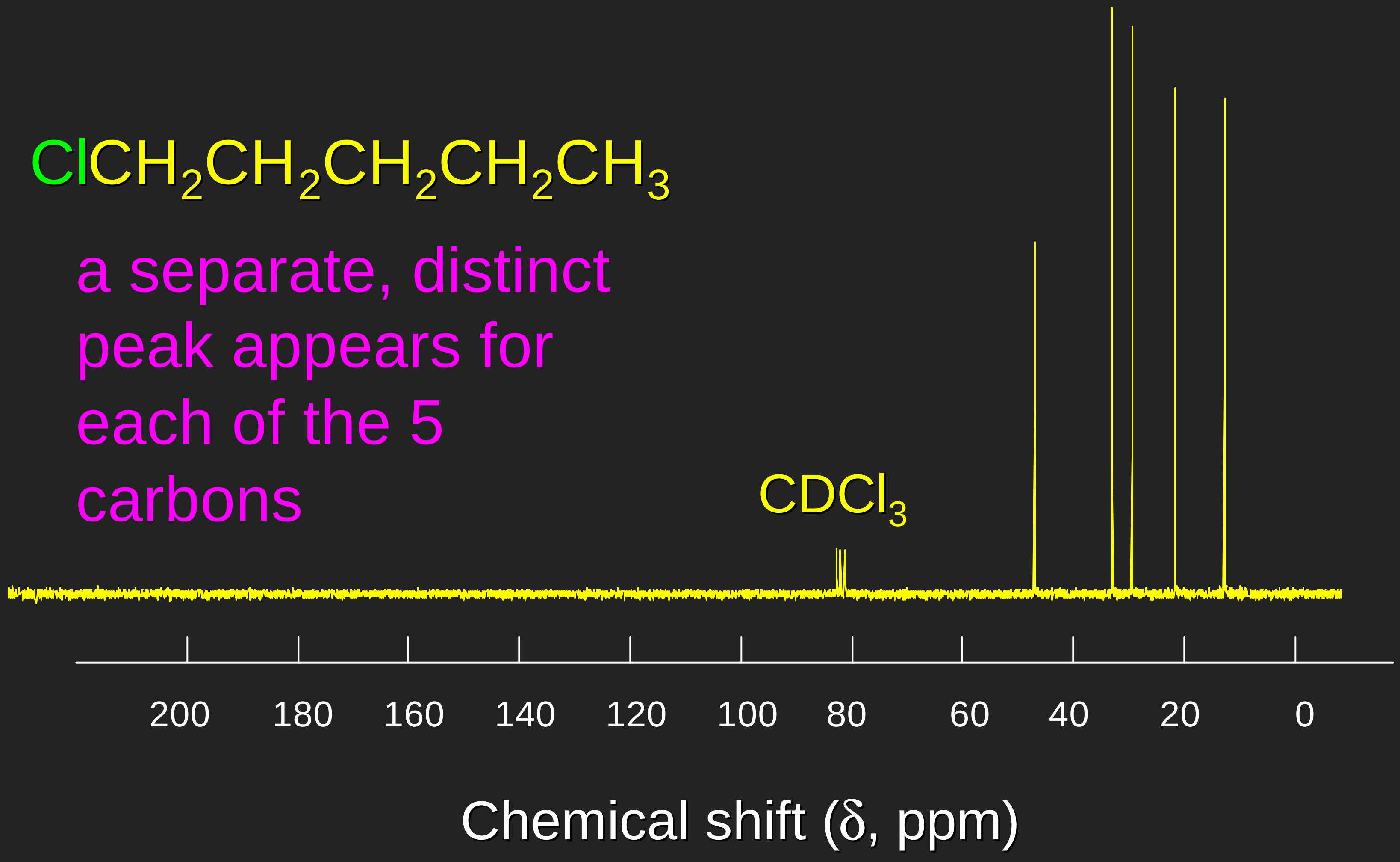


Figure 13.20(b) (page 511)

^{13}C

$ClCH_2CH_2CH_2CH_2CH_3$

a separate, distinct peak appears for each of the 5 carbons



13.15

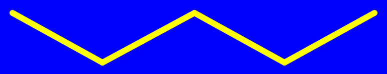
^{13}C Chemical Shifts

are measured in ppm (δ)
from the carbons of TMS

^{13}C Chemical shifts are most affected by:

- hybridization state of carbon
- electronegativity of groups attached to carbon

Examples (chemical shifts in ppm from TMS)



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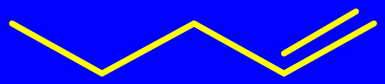

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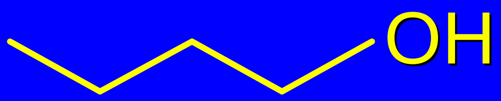
sp^3 hybridized carbon is more shielded than sp^2

Examples (chemical shifts in ppm from TMS)



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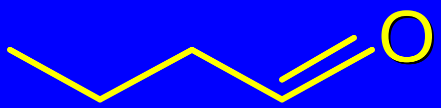
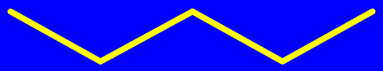


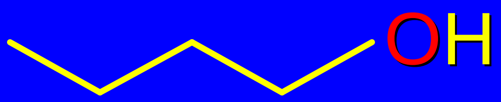
202

sp^3 hybridized carbon is more shielded than *sp*^{2}

Examples (chemical shifts in ppm from TMS)



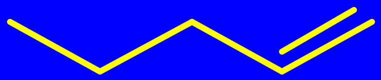
23



61

an electronegative atom deshields the carbon to which it is attached

Examples (chemical shifts in ppm from TMS)



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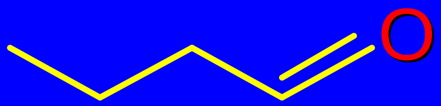


202

an electronegative atom deshields the carbon to which it is attached

Table 13.3 (p 513)

Type of carbon	Chemical shift (δ), ppm
RCH_3	0-35
R_2CH_2	15-40
R_3CH	25-50
R_4C	30-40

Table 13.3 (p 513)

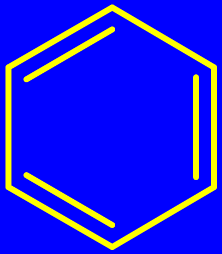
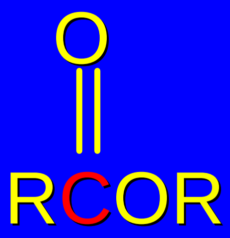
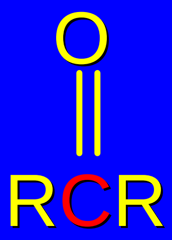
Type of carbon	Chemical shift (δ), ppm	Type of carbon	Chemical shift (δ), ppm
RCH_3	0-35	$RC\equiv CR$	65-90
R_2CH_2	15-40	$R_2C=CR_2$	100-150
R_3CH	25-50		110-175
R_4C	30-40		

Table 13.3 (p 513)

Type of carbon	Chemical shift (δ), ppm
RCH_2Br	20-40
RCH_2Cl	25-50
RCH_2NH_2	35-50
RCH_2OH	50-65
RCH_2OR	50-65

Table 13.3 (p 513)

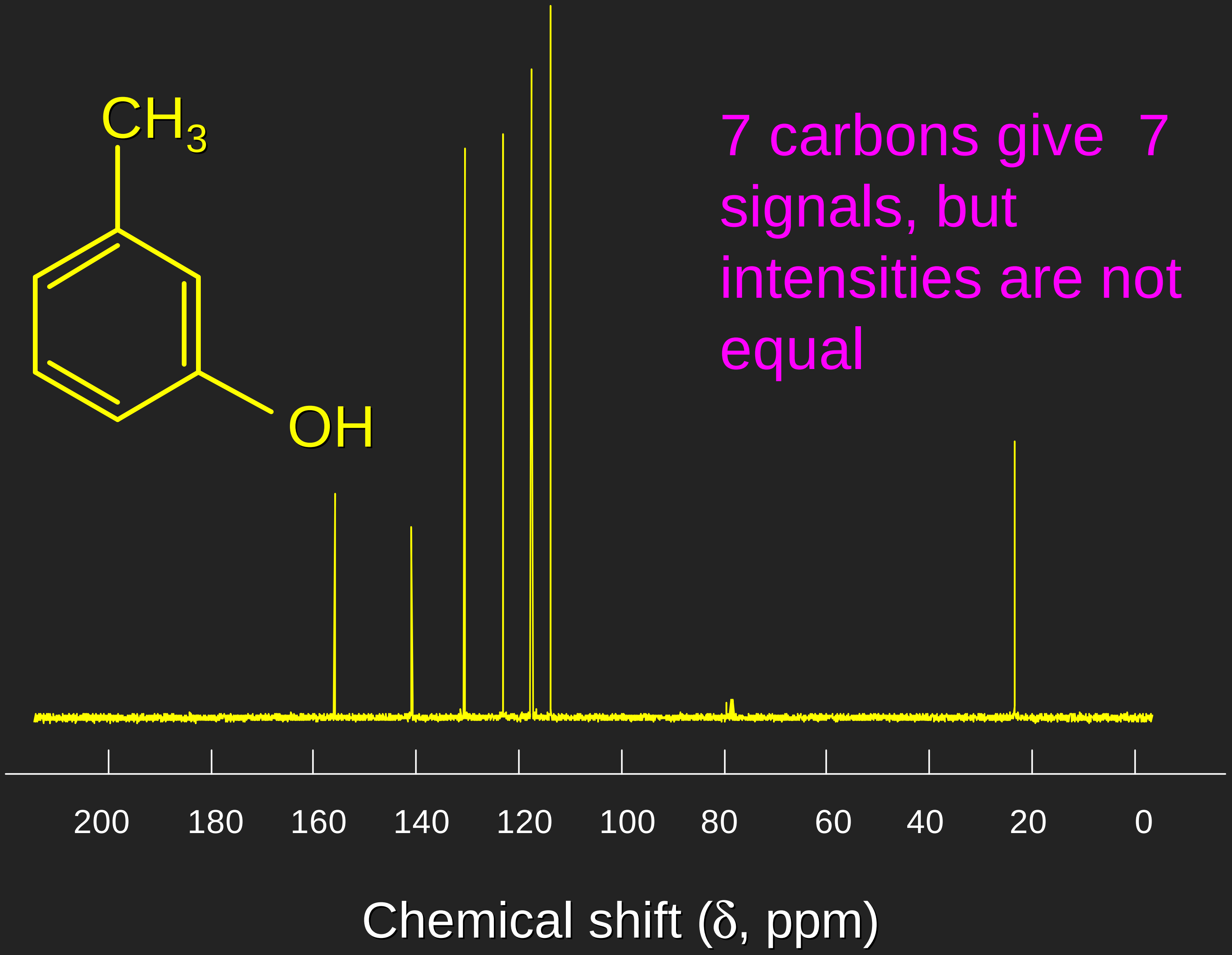
Type of carbon	Chemical shift (δ), ppm	Type of carbon	Chemical shift (δ), ppm
RCH_2Br	20-40		
RCH_2Cl	25-50	 $R\overset{\overset{O}{\|}}{C}OR$	160-185
RCH_2NH_2	35-50		
RCH_2OH	50-65	 $R\overset{\overset{O}{\|}}{C}R$	190-220
RCH_2OR	50-65		

13.16

^{13}C NMR and Peak Intensities

Pulse-FT NMR distorts intensities of signals. Therefore, peak heights and areas can be deceptive.

Figure 13.21 (page 514)



7 carbons give 7 signals, but intensities are not equal

13.17

^{13}C—H Coupling

Peaks in a ^{13}C NMR spectrum are typically singlets

^{13}C—^{13}C splitting is not seen because the probability of two ^{13}C nuclei being in the same molecule is very small.

^{13}C—^{1}H splitting is not seen because spectrum is measured under conditions that suppress this splitting (*broadband decoupling*).

13.18

Using DEPT to Count the Hydrogens Attached to ^{13}C

Distortionless Enhancement of Polarization Transfer

Measuring a ^{13}C NMR spectrum involves

1. Equilibration of the nuclei between the lower and higher spin states under the influence of a magnetic field
2. Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state
3. Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored
4. Mathematical manipulation (Fourier transform) of the data to plot a spectrum

Measuring a ^{13}C NMR spectrum involves

Steps 2 and 3 can be repeated hundreds of times to enhance the signal-noise ratio

2. Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state
3. Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored

Measuring a ^{13}C NMR spectrum involves

In DEPT, a second transmitter irradiates ^{1}H during the sequence, which affects the appearance of the ^{13}C spectrum.

some ^{13}C signals stay the same

some ^{13}C signals disappear

some ^{13}C signals are inverted

Figure 13.23 (a) (page 516)

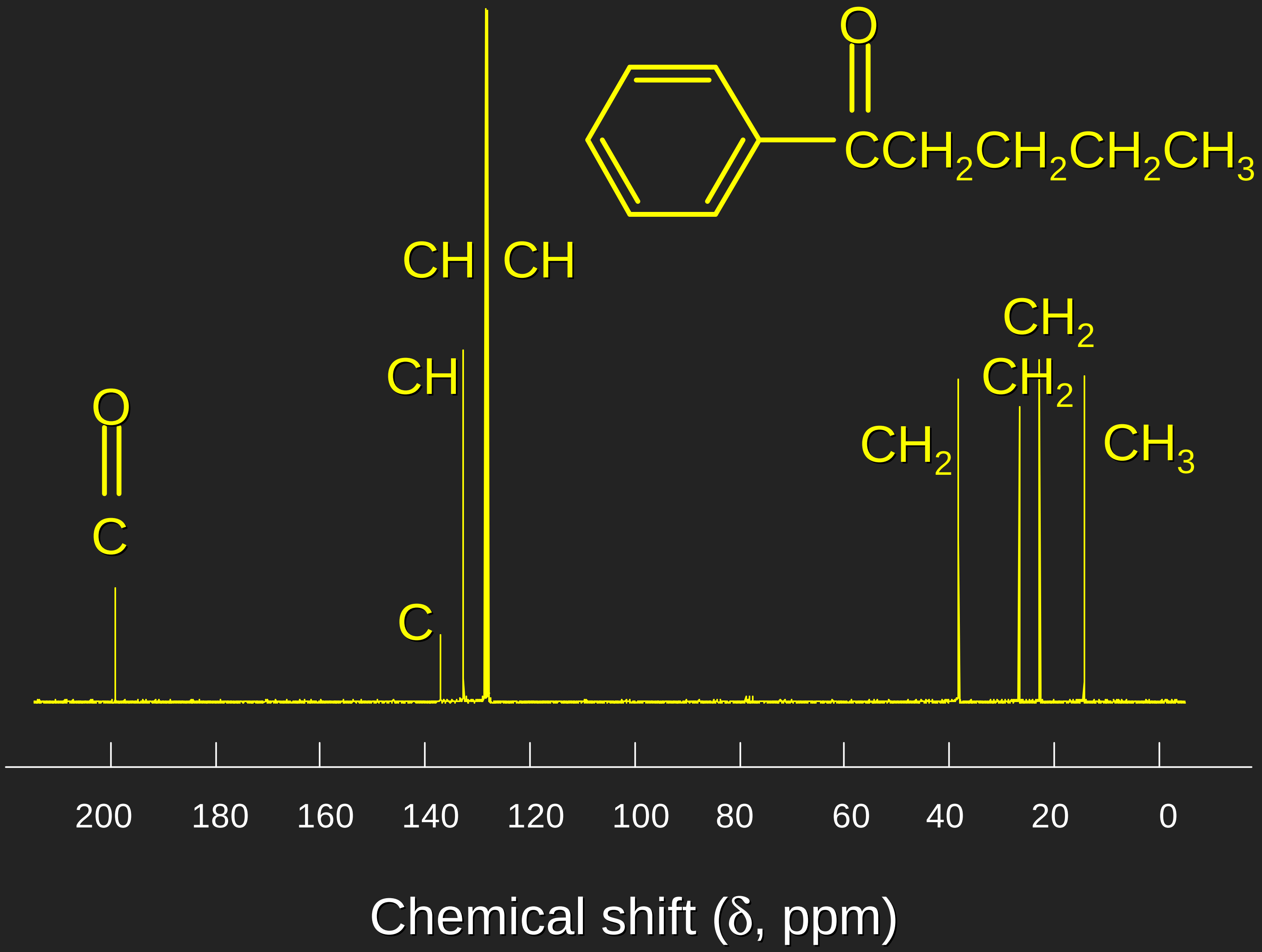


Figure 13.23 (a) (page 516)

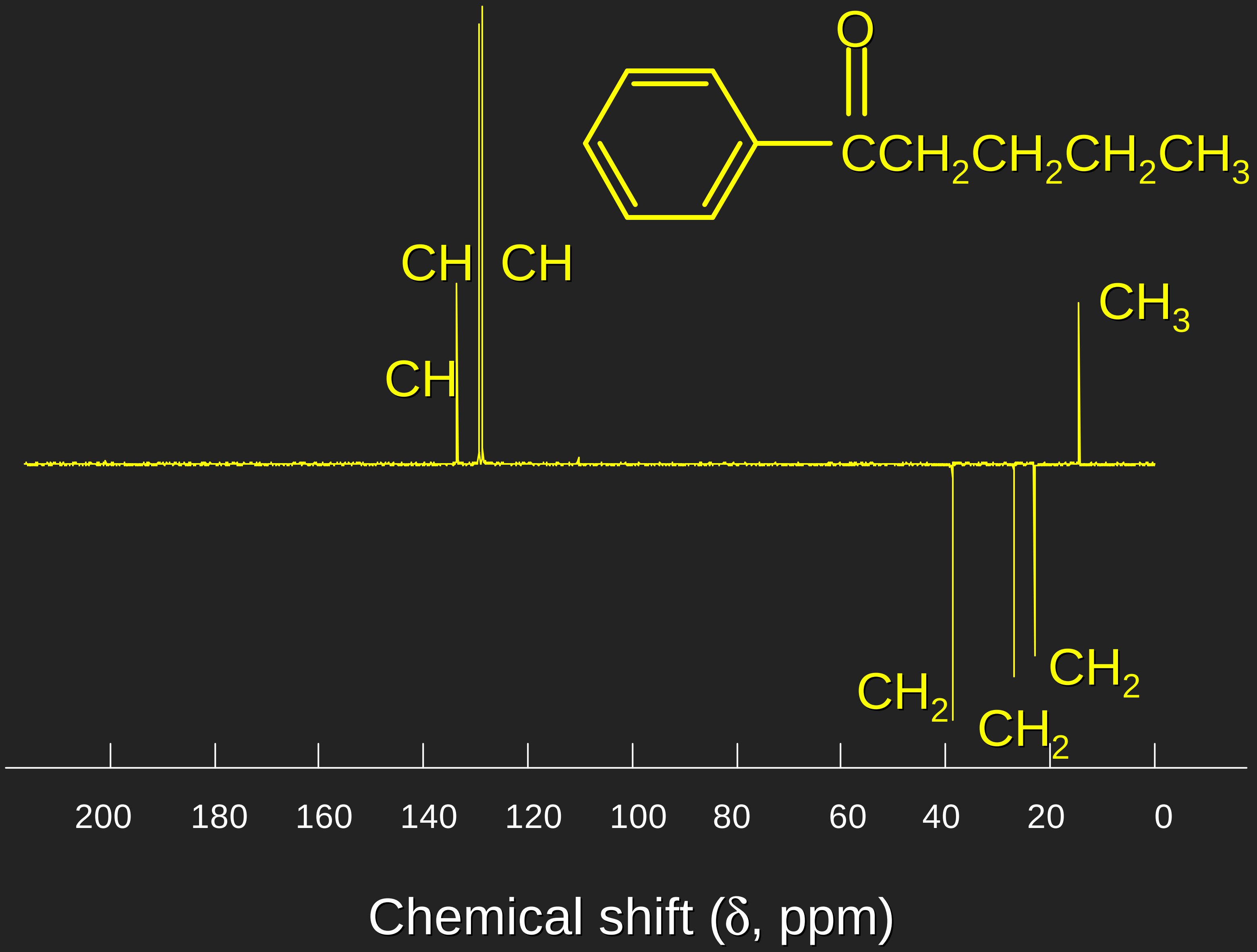
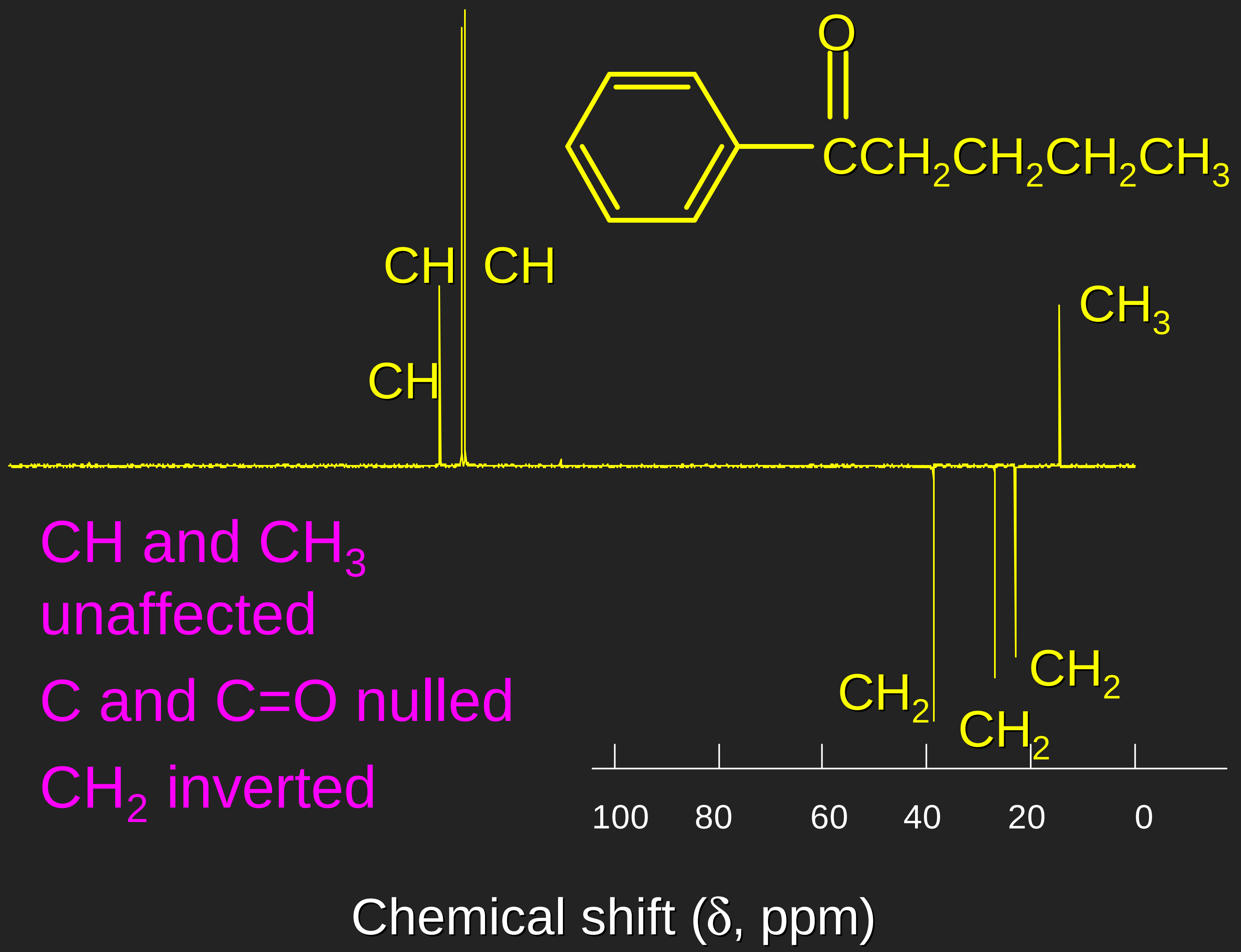


Figure 13.23 (b) (page 516)



CH and CH_3 unaffected

C and C=O nulled

CH_2 inverted