CH203 Lecture 24

December 9, 2010

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BOSTON UNIVERSITY

Administrative Announcements 12/09/10

- *Final Exam: Thursday December 16th (12:30 – 2:30 pm)*

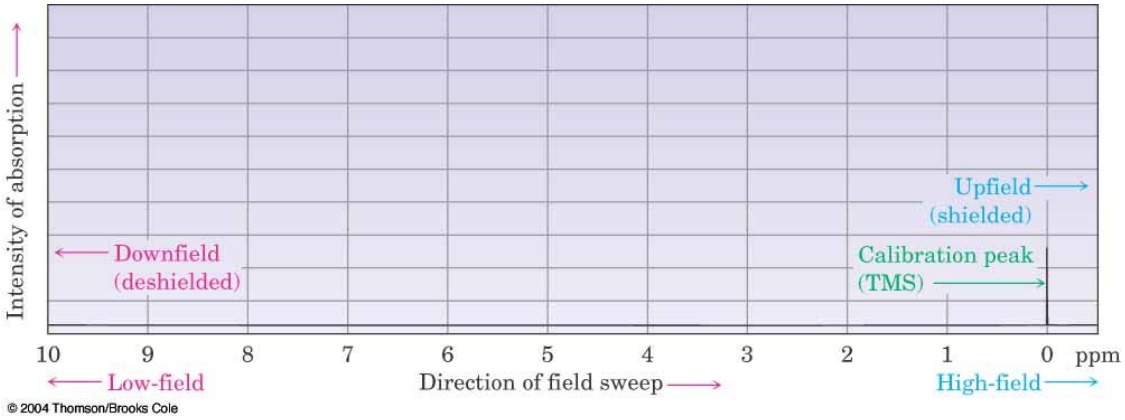
A-S STO B50

T-Z **CAS B 27**

- *NMR problems (Chapter 13) are posted on the course website. Suggested answers will be posted by Friday 12/10/10*
- *Office hours: Monday Dec. 13th from 1-2 pm and Weds. Dec. 15th 4-5 pm in LSEB 804*

What have we learned so far about proton NMR

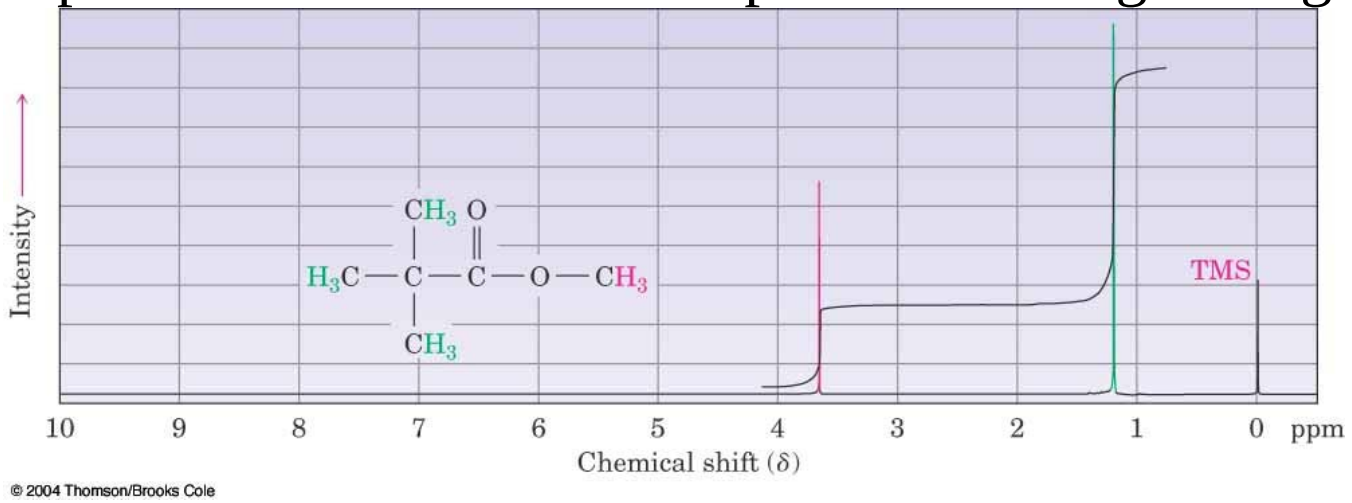
1) Chemical Shift (δ): Differences caused by small local magnetic fields of electrons surrounding different nuclei



-downfield shifts associated with protons next to electron withdrawing groups

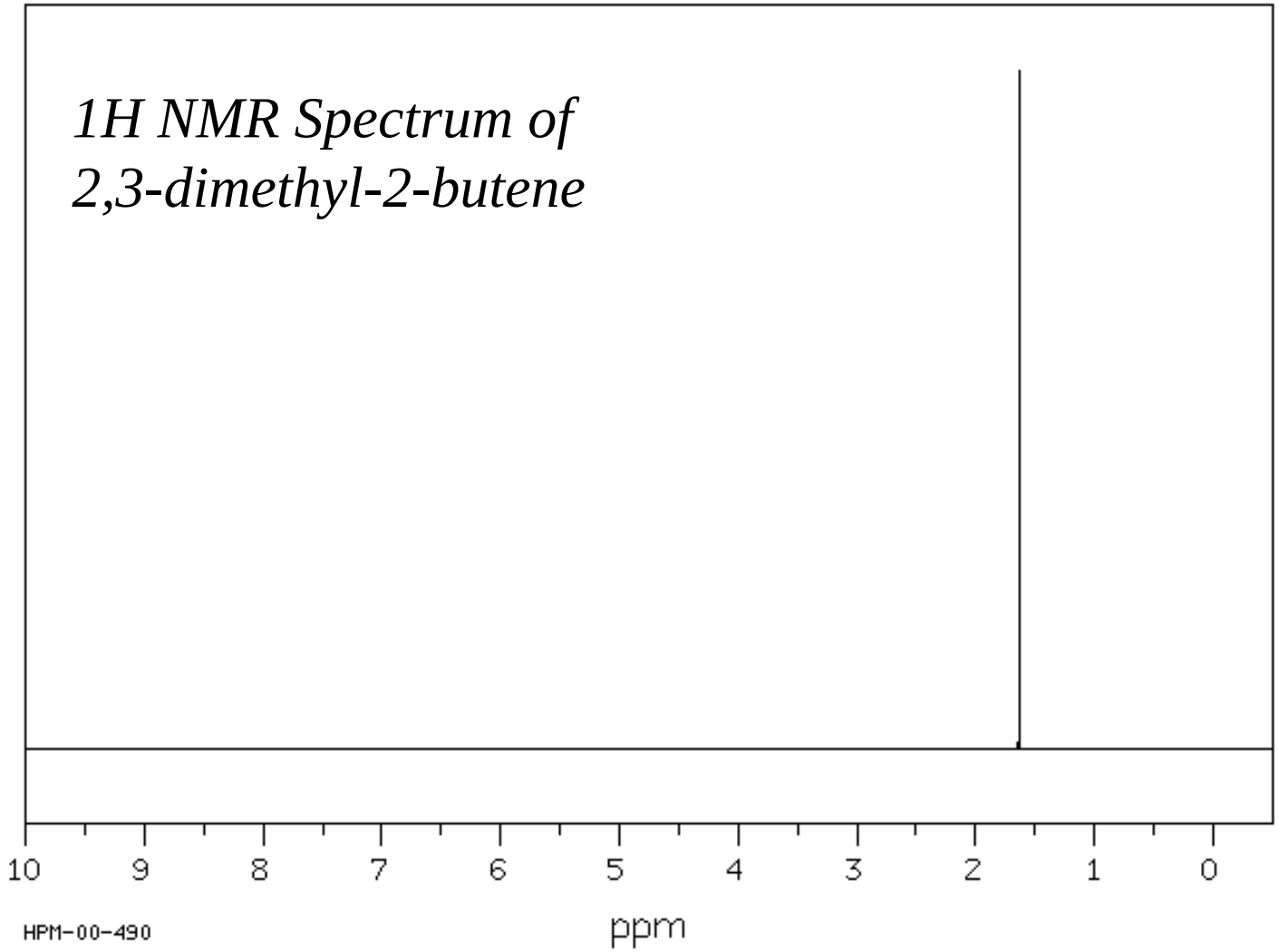
2) Integration of ^1H NMR : Proton Counting

The relative intensity of a signal (integrated area) is proportional to the number of protons causing the signal

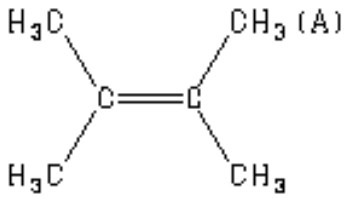


Type of hydrogen	**Chemical shift (ppm)**
H–R	0.8–1.6
H–NR_2 variable,	1.5–4
H–$CH_2C{=}C$	1.6
H–OR variable,	2–5
H– ≡ —	2–3
H–$CH_2C(=O)R$	2.0–2.2
H–CH_2NR	2.2–2.8
H–CH_2X	2.2–4.2
H–CH_2Ph	2.2
H–CH_2OR	3.2–3.8
H–C=C	4–7
H–Ph	7.2
H–C(=O)R	9–10
H–OC(=O)R variable,	10–12

^1H NMR Spectroscopy and Proton Equivalence

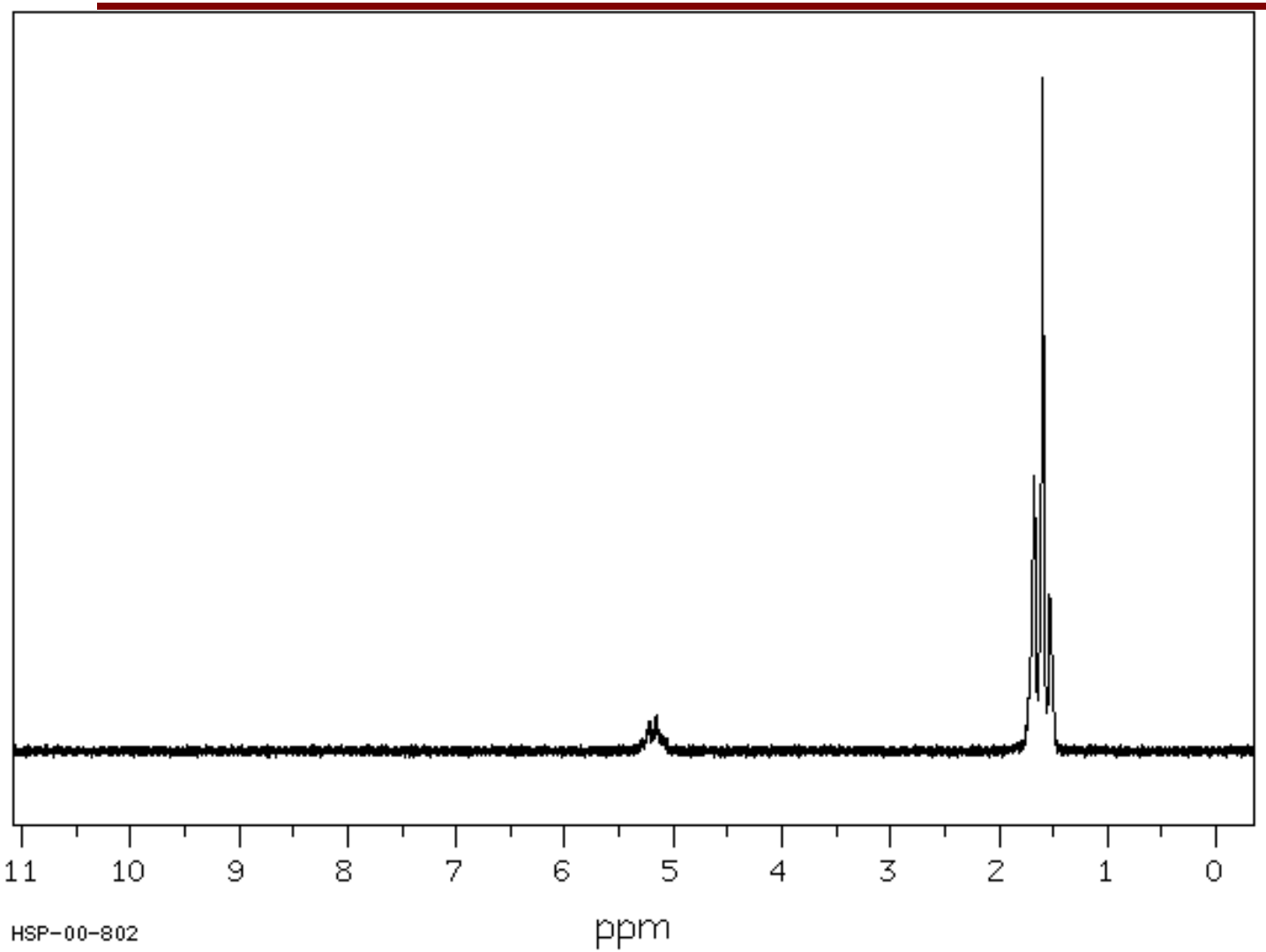


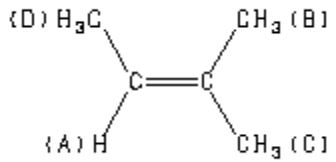
Equivalent H's have the same signal



δ= 1.64 ppm

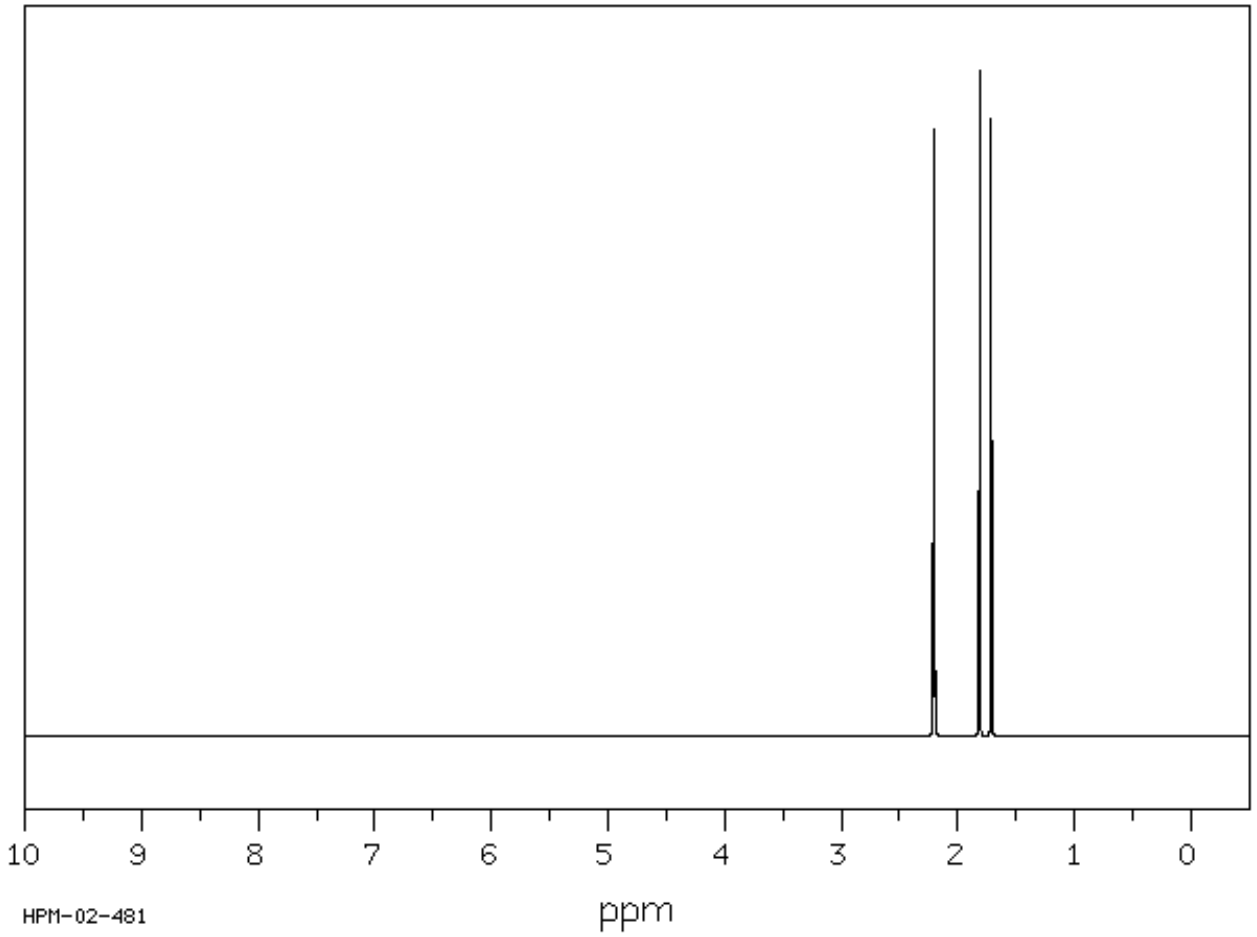
^{1}H NMR Spectrum of 2-Methyl-2-butene

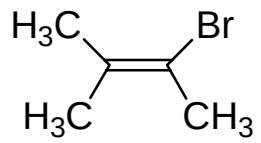




Shift (ppm)	
A	**5.19**
B	**1.68**
C	**1.60**
D	**1.56**

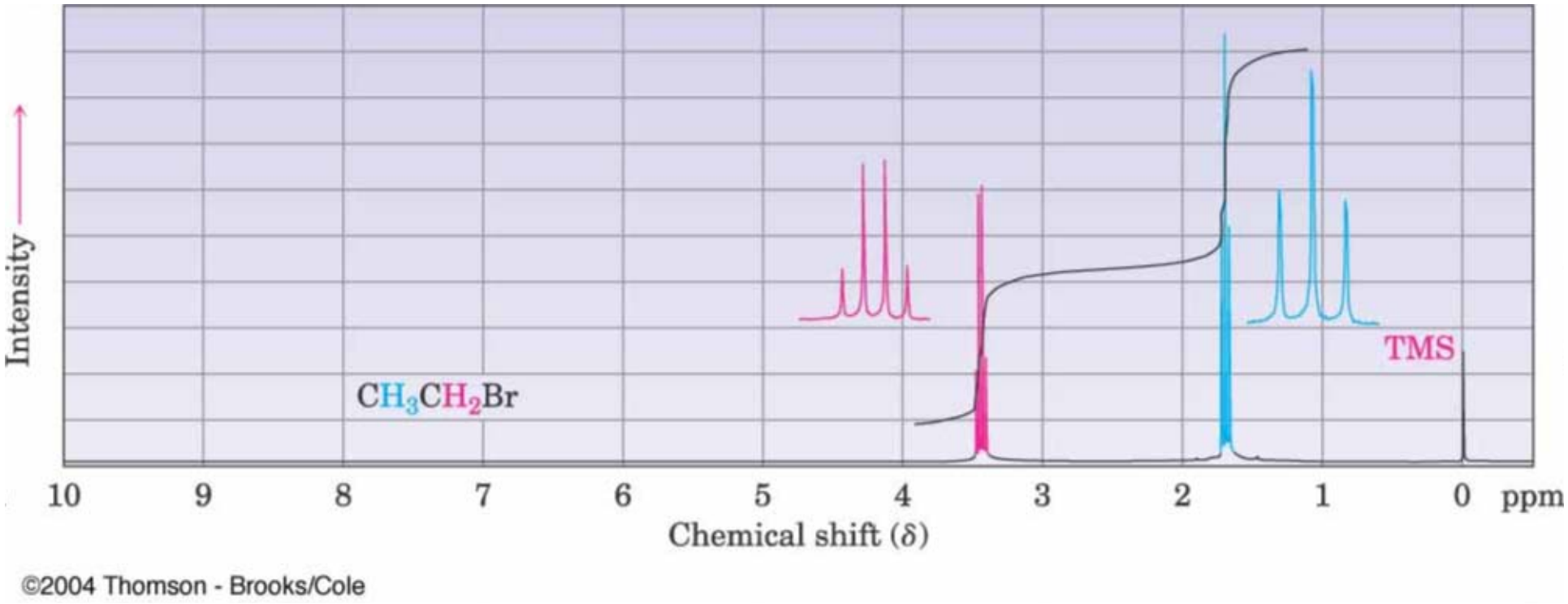
An Additional Example





2-bromo-3-methyl-2-butene

^{1}H NMR Spectrum of Bromoethane

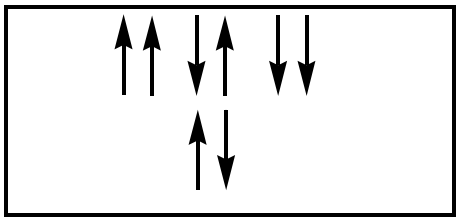


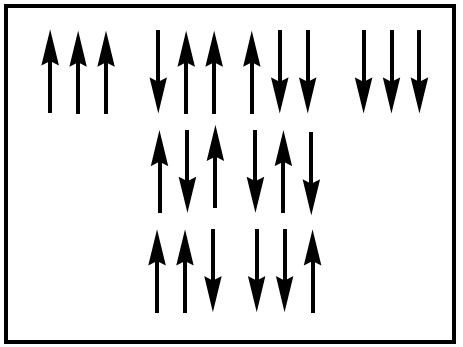
Spin-Spin Splitting in ^1H NMR Spectra

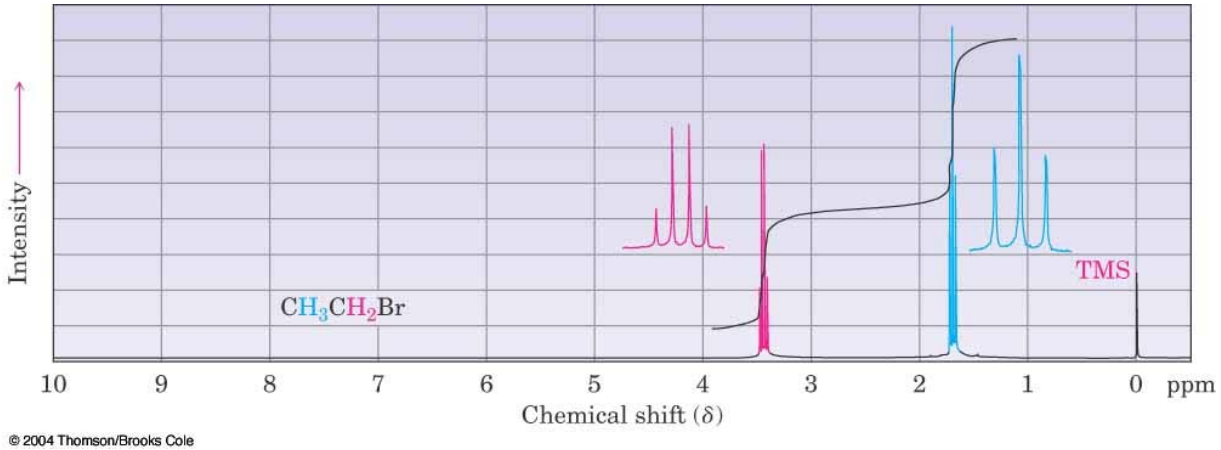
- Peaks are often split into multiple peaks due to interactions between nonequivalent protons on adjacent carbons, called **spin-spin splitting**
- The splitting is into one more peak than the number of H's on the adjacent carbon ("n+1 rule")
- The relative intensities are in proportion of a binomial distribution and are due to interactions between nuclear spins that can have two possible alignments with respect to the magnetic field
- The set of peaks is a multiplet (2 = doublet, 3 = triplet, 4 = quartet)

Simple Spin-Spin Splitting

- An adjacent CH_2 has three different spin alignments in a ratio of 1:2:1
- This leads to peaks in the same ratio for the adjacent H signal
- An adjacent CH_3 group can have four different spin alignments as 1:3:3:1
- The separation of peaks in a multiplet is measured is a constant, in Hz
  - ***J*** (coupling constant)

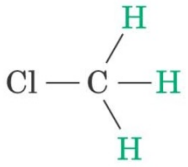




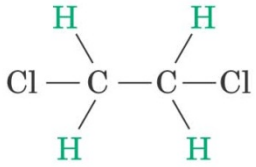


Rules for Spin-Spin Splitting

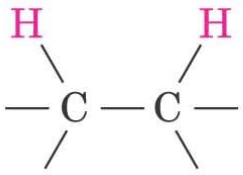
- Equivalent protons do not split each other
- The signal of a proton with ***n*** equivalent neighboring H's is split into ***n*** + 1 peaks
- Protons that are farther than two carbon atoms apart do not split each other



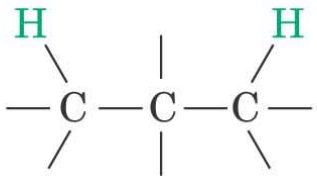
Three C–H protons are chemically equivalent; no splitting occurs.



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



Splitting observed



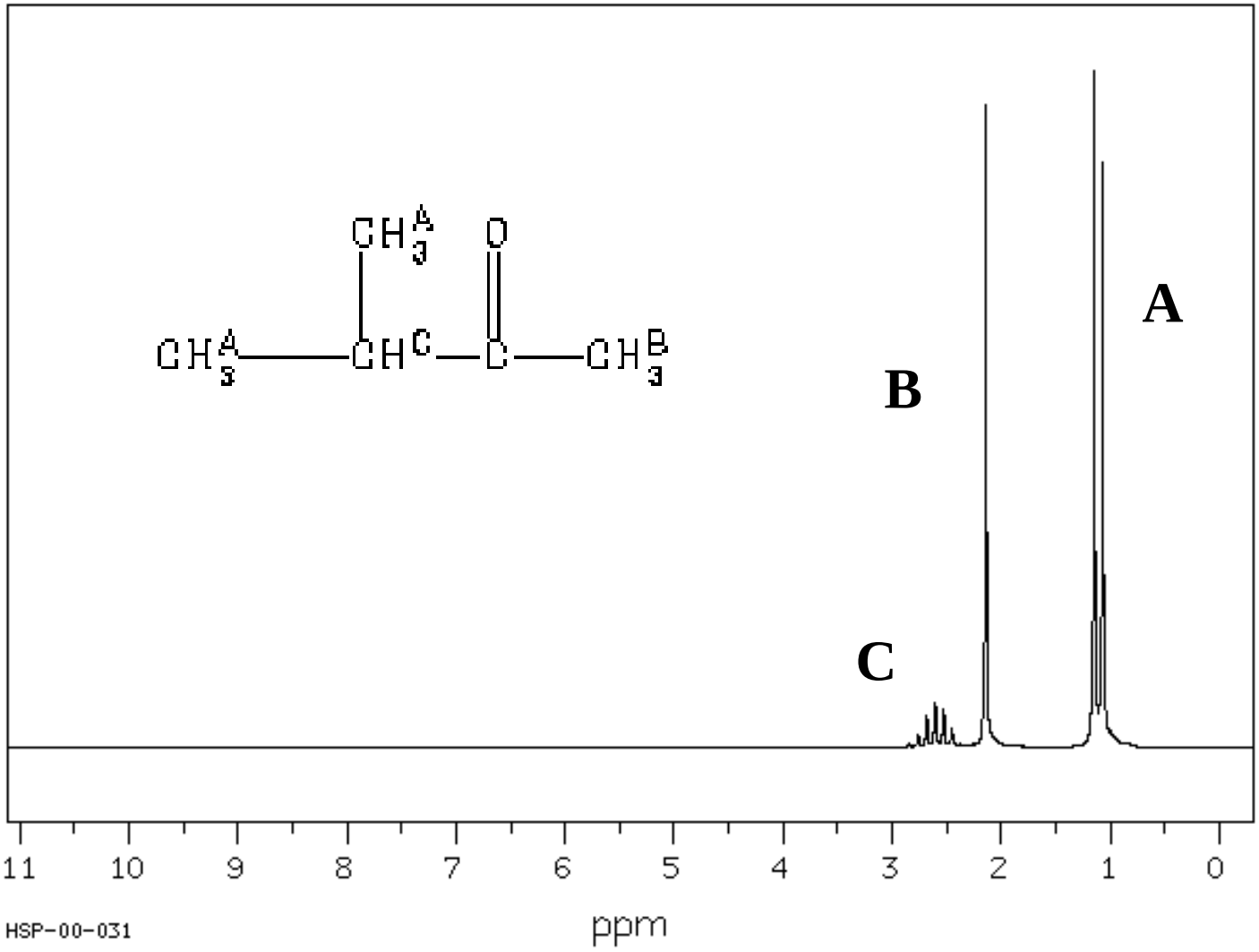
Splitting not usually observed

Common Spin Multiplicities

Figure 19. Pascal's Triangle.

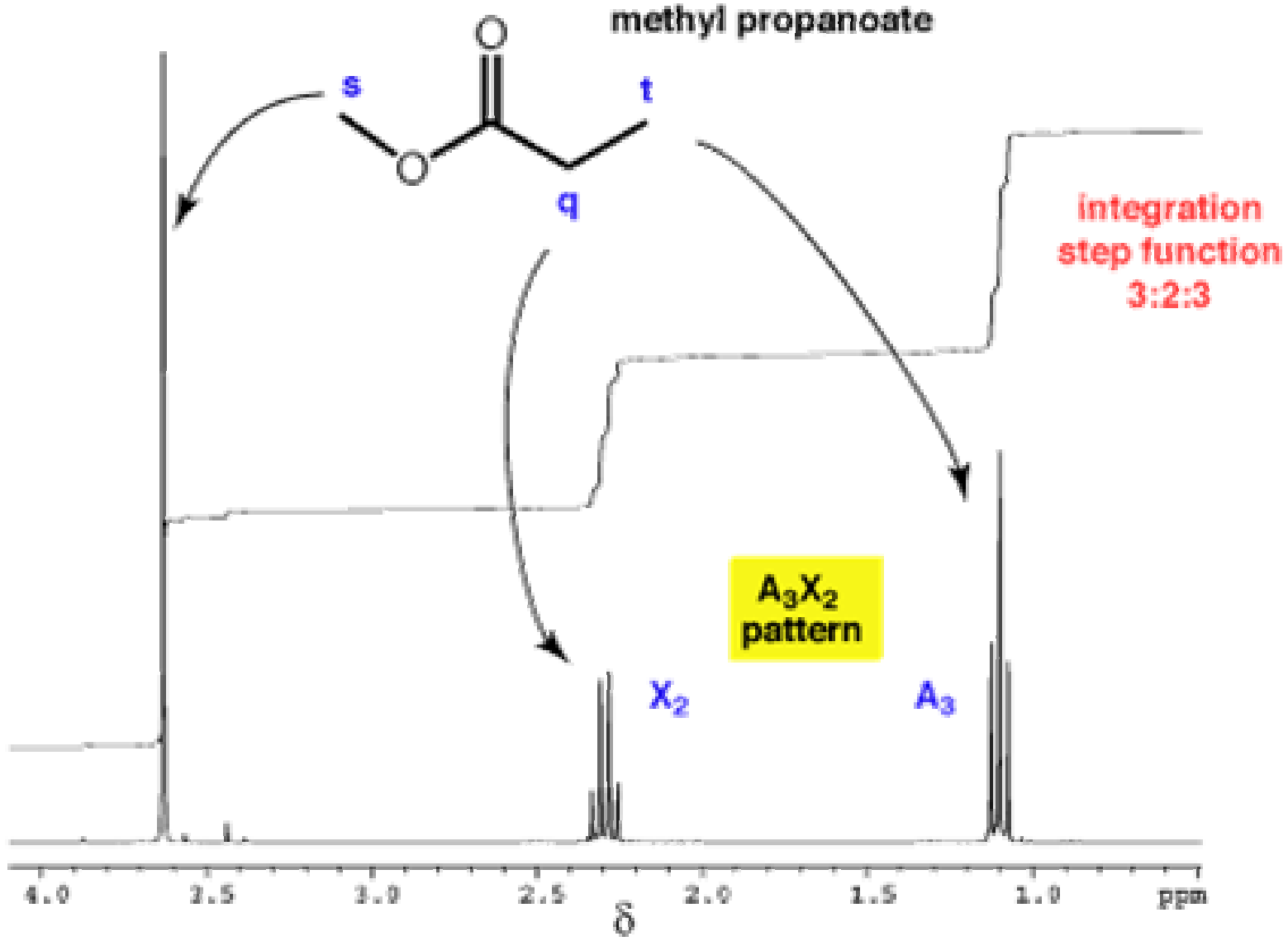
no. of neighbors	relative intensities	pattern	example
0	1	singlet (s)	
1	1 1	doublet (d)	
2	1 2 1	triplet (t)	
3	1 3 3 1	quartet (q)	
4	1 4 6 4 1	pentet	RCH_2-CHR'-CH_2R
5	1 5 10 10 5 1	sextet	CH_3-CH_2-CH_2R' (equal J's)
6	1 6 15 20 15 6 1	septet	CH_3-CHR-CH_3

^{1}H NMR Spectrum of 3-methyl-2-butanone



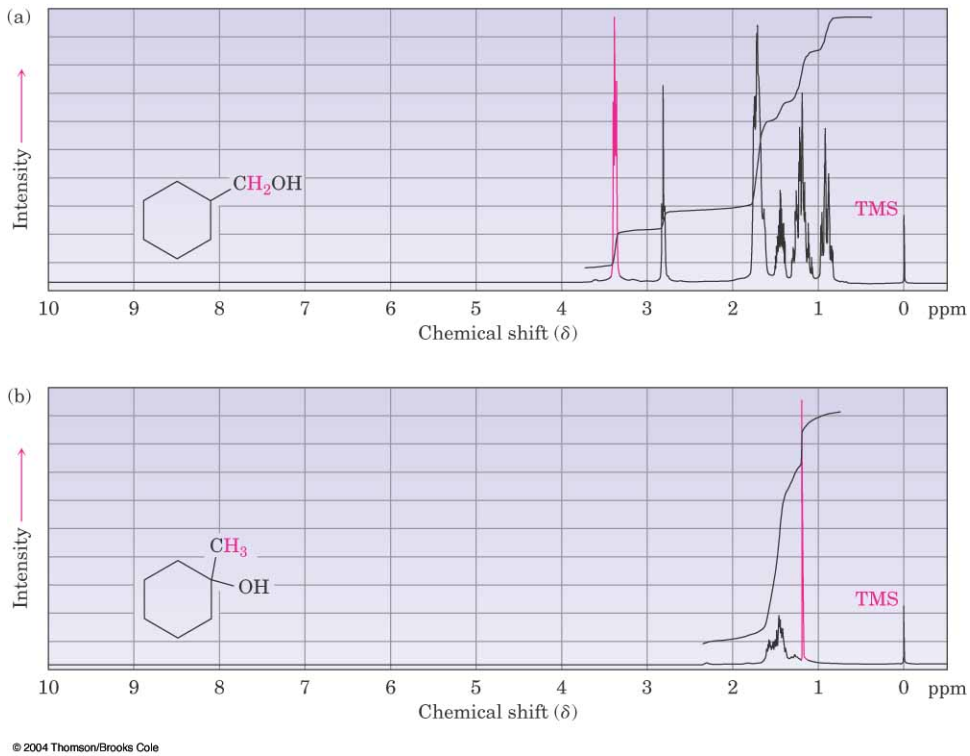
A 1.10 ppm
d, J = 7 Hz
B s, 2.14 ppm
C 2.5 ppm
septet, J = 7 Hz

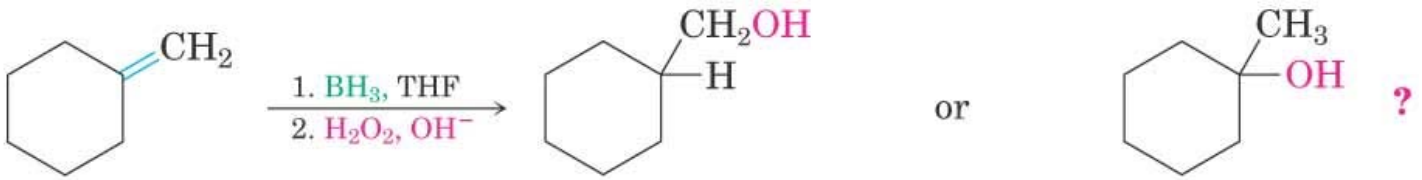
Figure 22. ^{1}H NMR spectrum of methyl propanoate.



Uses of ^{1}H NMR Spectroscopy

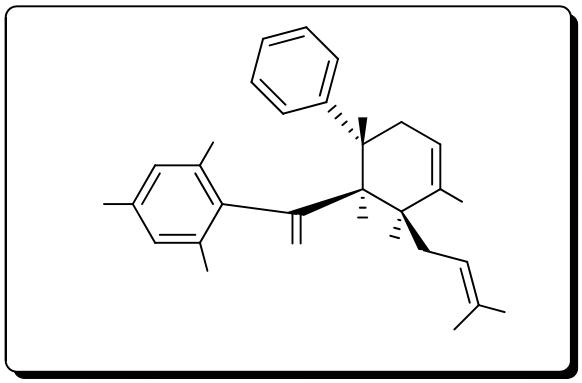
- The technique is used to identify likely products in the laboratory quickly and easily
- Example: regiochemistry of hydroboration/oxidation of methylenecyclohexane
- Only peaks for cyclohexylmethanol is observed



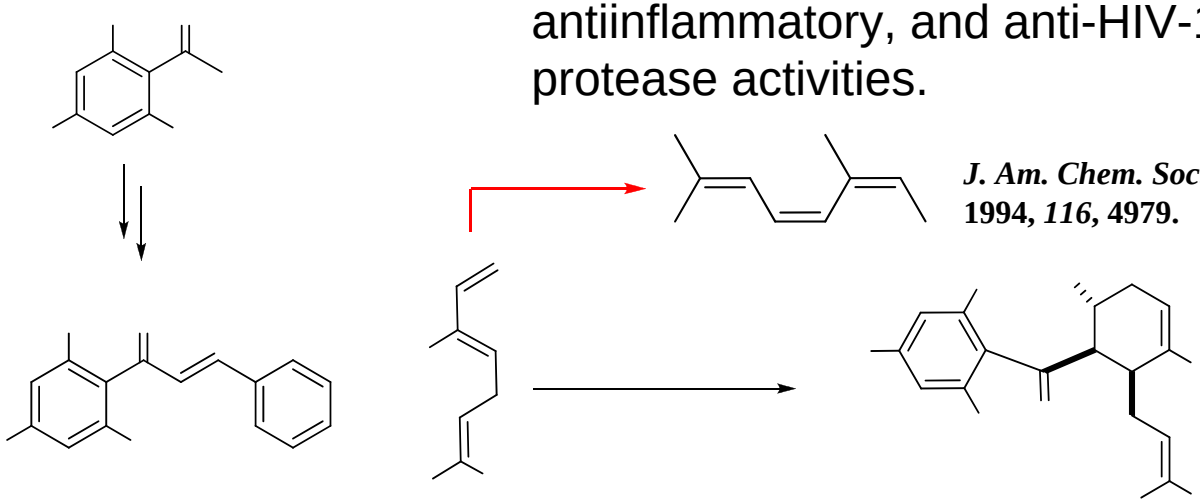


Methylenecyclohexane **Cyclohexylmethanol** **1-Methylcyclohexanol**

Total Synthesis of Panduratin A



- Isolated from Fingerroot (*Boesenbergia pandurata)* as a racemic compound
- Rhizome is used as folk medicine and food flavor.
- Panduratin A exhibits anticancer, antiinflammatory, and anti-HIV-1 protease activities.

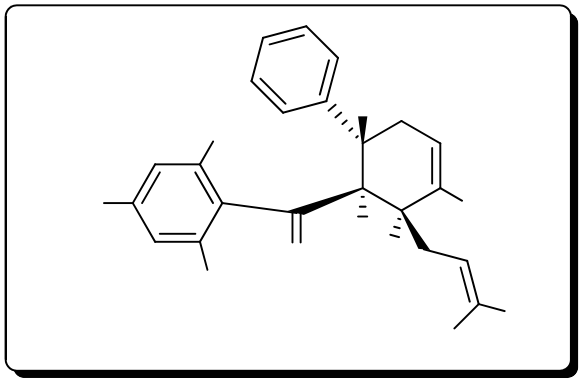


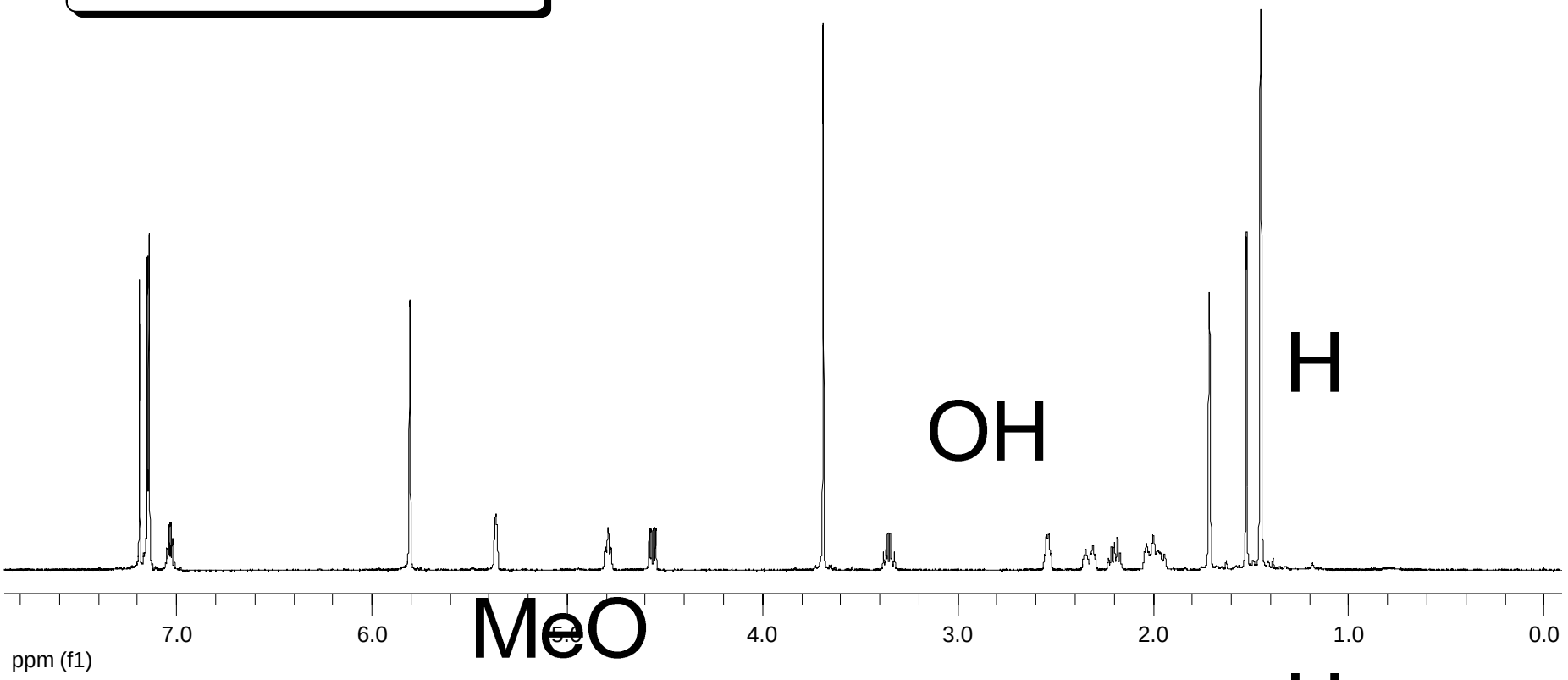
J. Am. Chem. Soc. **1994, *116*, 4979.**

6 steps, 55% overall yield

(a) silica gel-supported AgNP (0.5 mol% AgNP loading), CH_2Cl_2, 50°C, 48 h, 85%, approx. 5% *exo*-cycloadduct. Major isomer is shown; (b) aq. $NaHCO_3$, MeOH, 40°C, 6 h, 87% (98% based on recovered starting material).

MeC




7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

H
OH
MeO
Me
H
H
O
OH