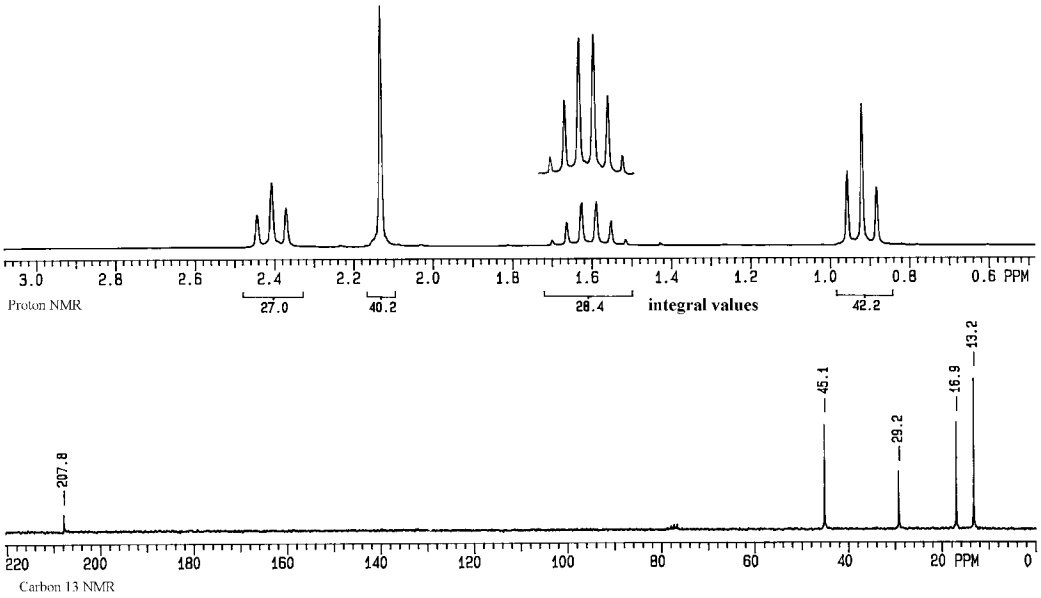
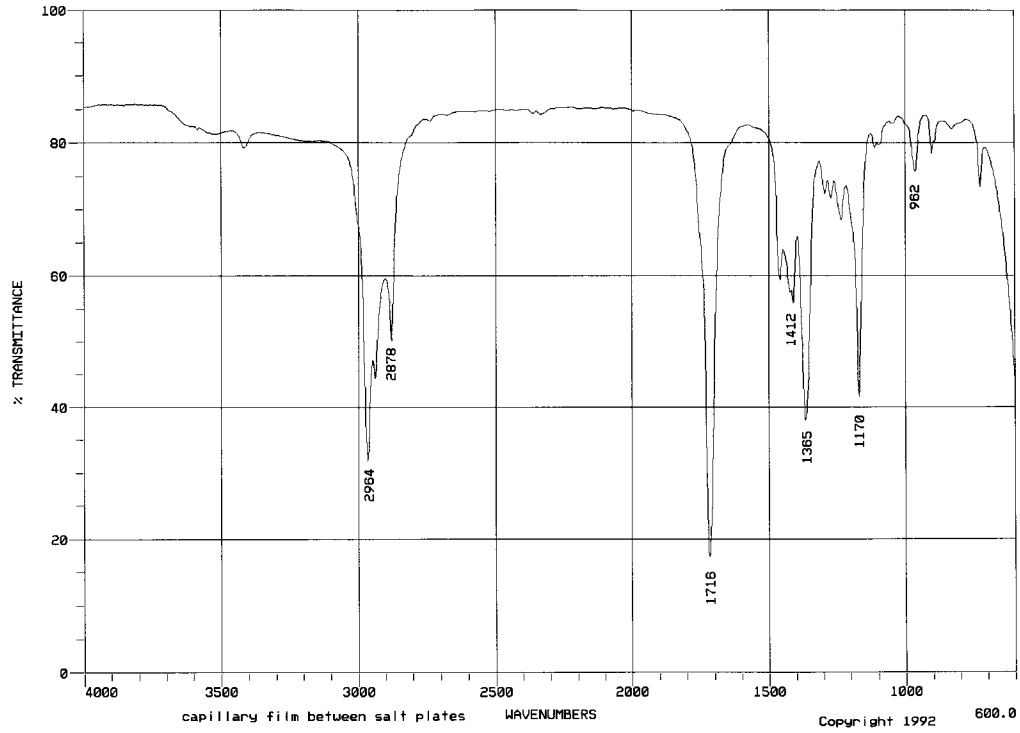
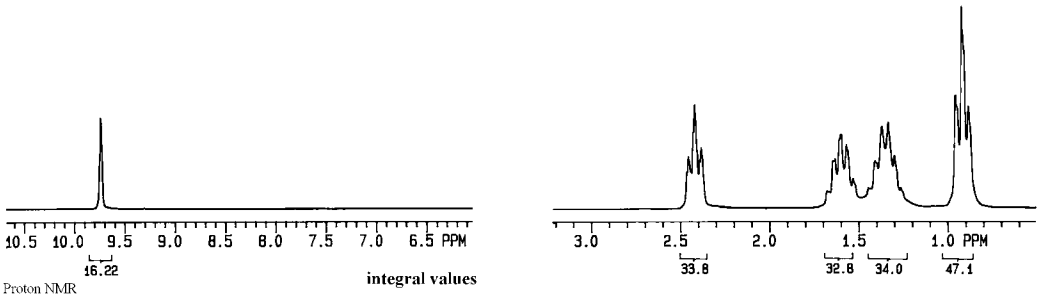
Spectroscopy Problem 1: $C_5H_{10}O$



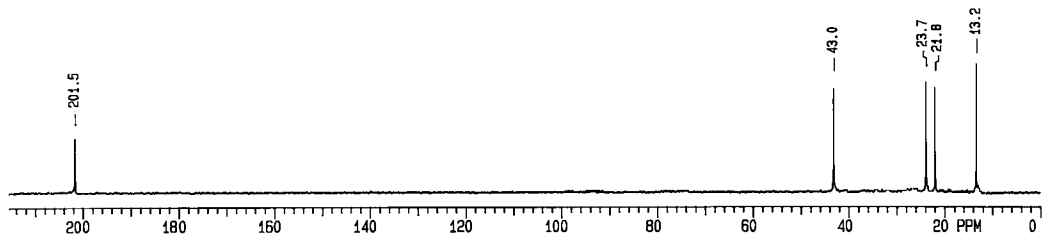


Spectra from *A Spectrum of Spectra, CD Version* by Richard A Tomasi.

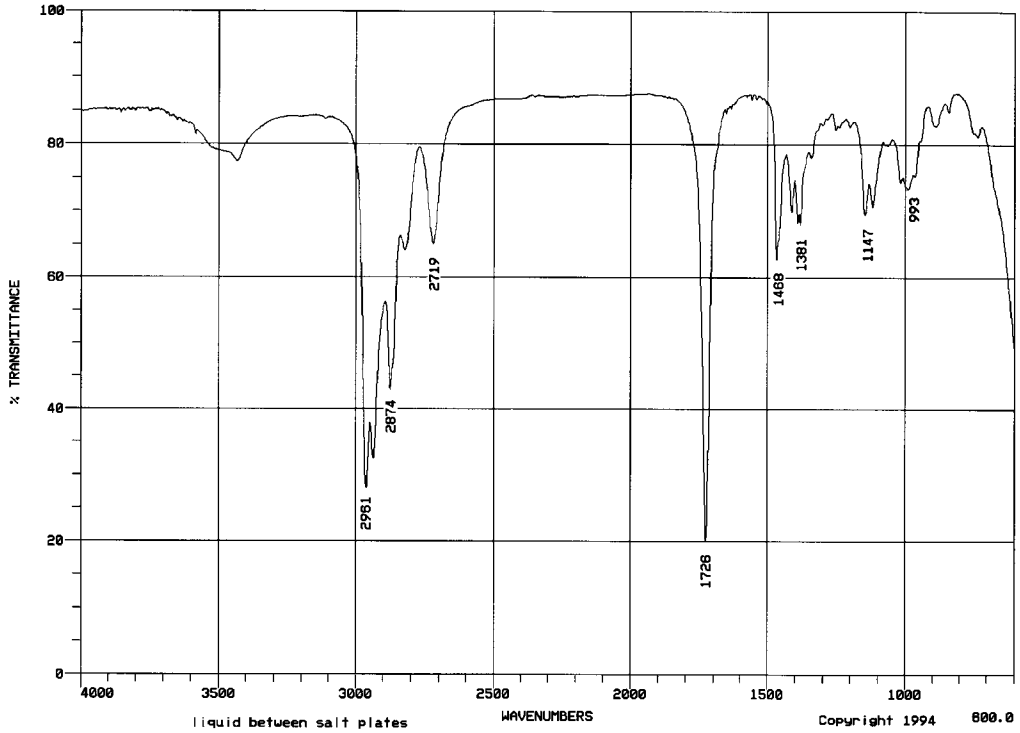
Spectroscopy Problem 2: $C_5H_{10}O$



Proton NMR

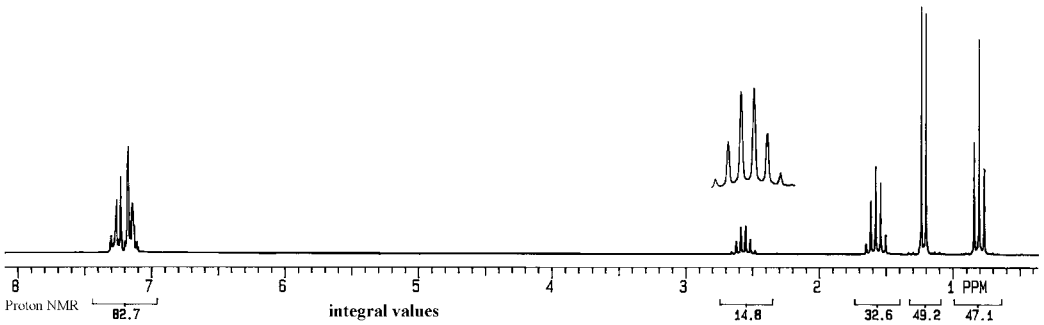


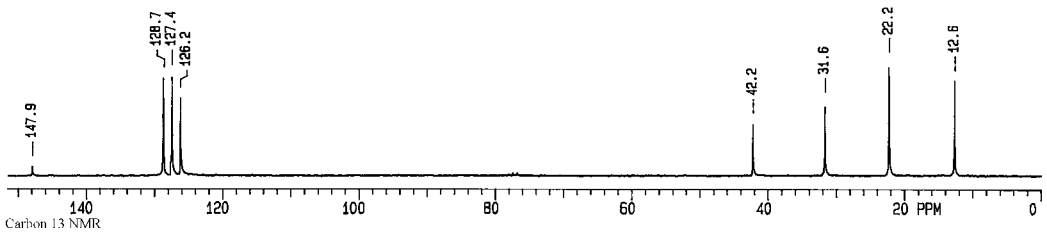
Carbon 13 NMR

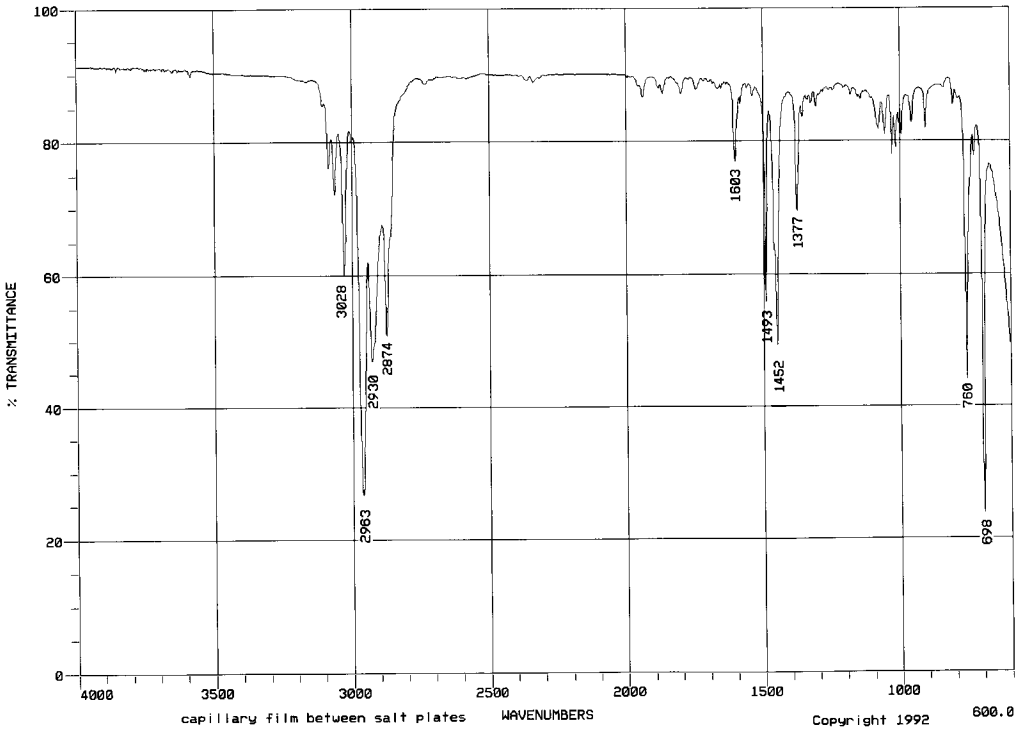


Spectra from *A Spectrum of Spectra, CD Version* by Richard A Tomasi.

Spectroscopy Problem 3: $C_{10}H_{14}$

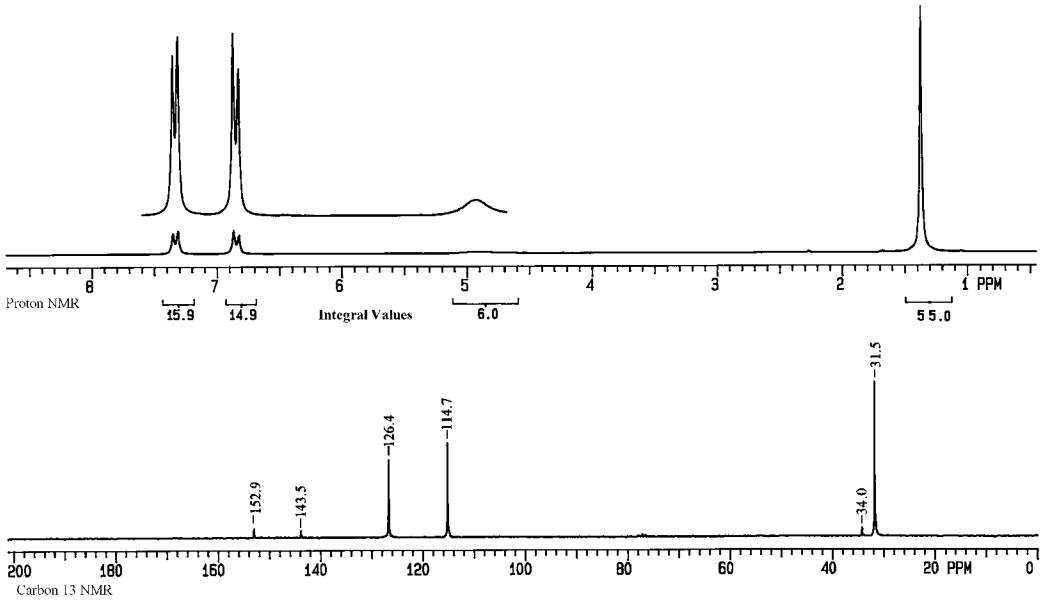


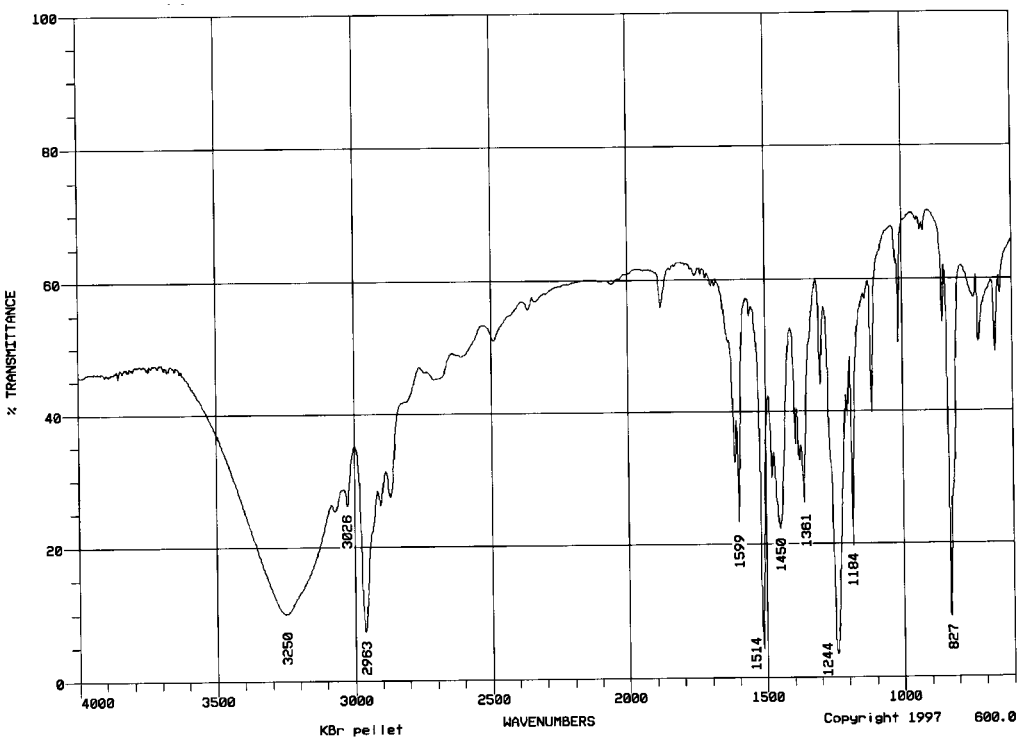




Spectra from *A Spectrum of Spectra, CD Version* by Richard A Tomasi.

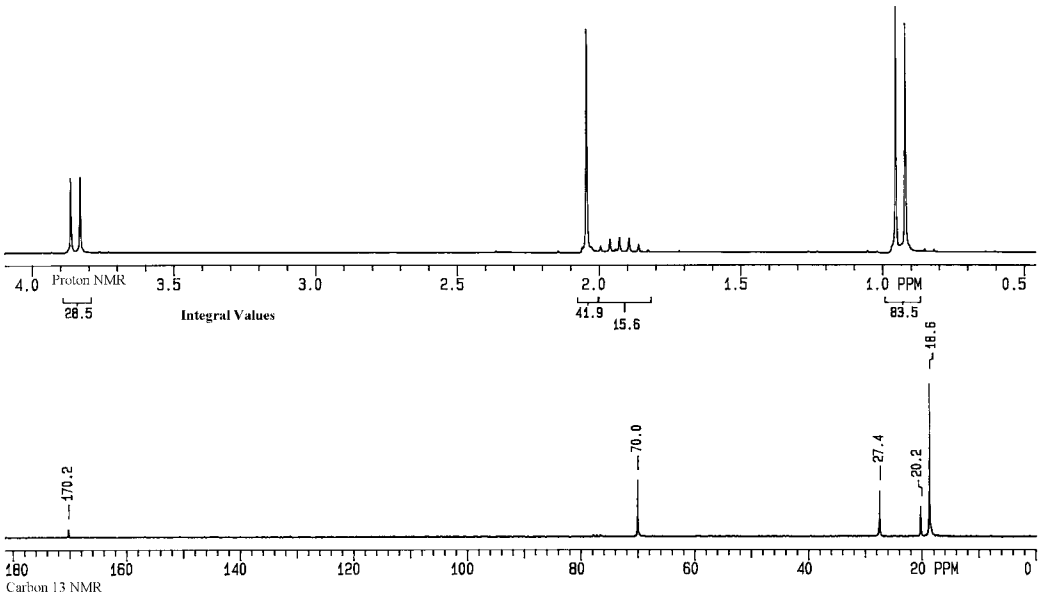
Spectroscopy Problem 4: $C_{10}H_{14}O$

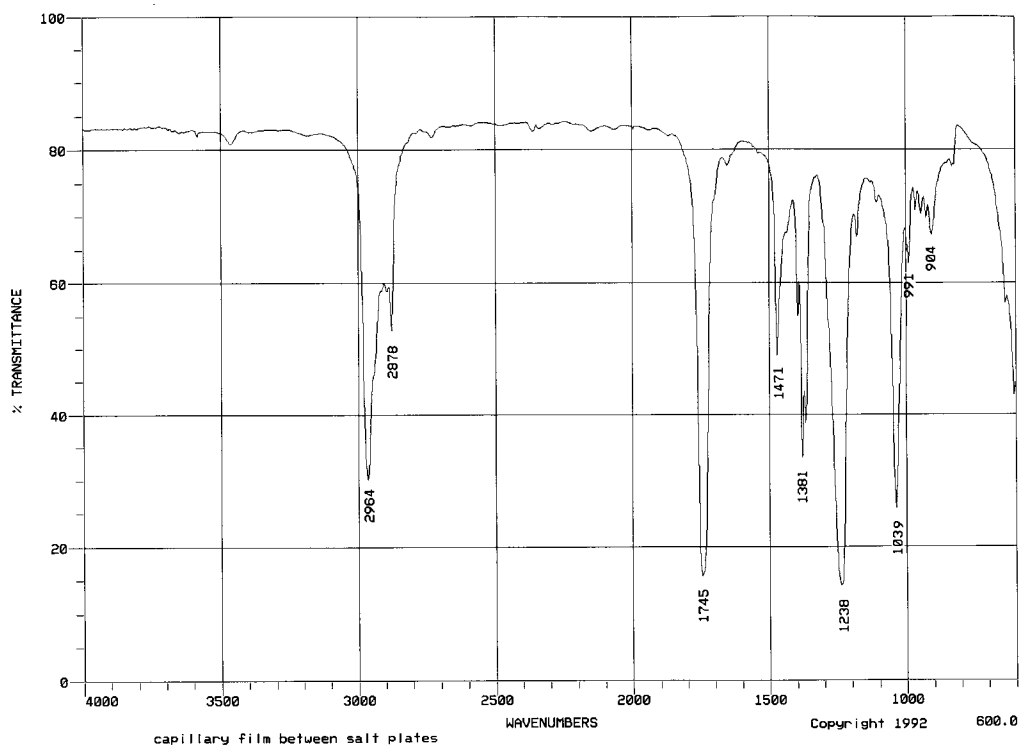




Spectra from *A Spectrum of Spectra, CD Version* by Richard A Tomasi.

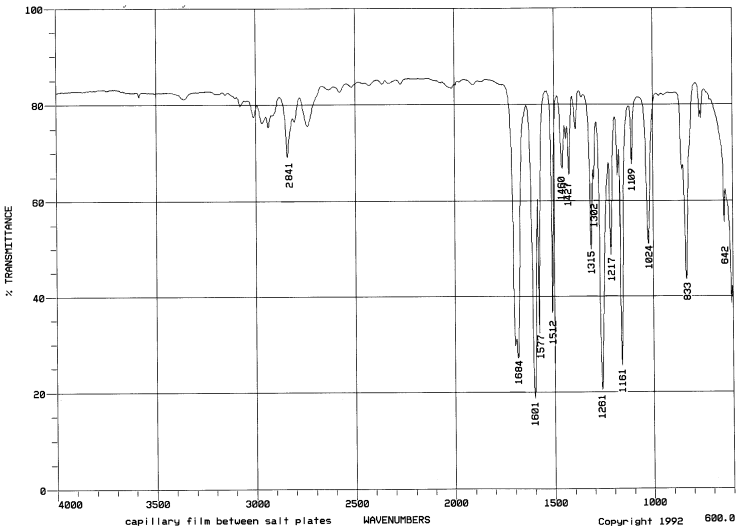
Spectroscopy Problem 5: $C_6H_{12}O_2$

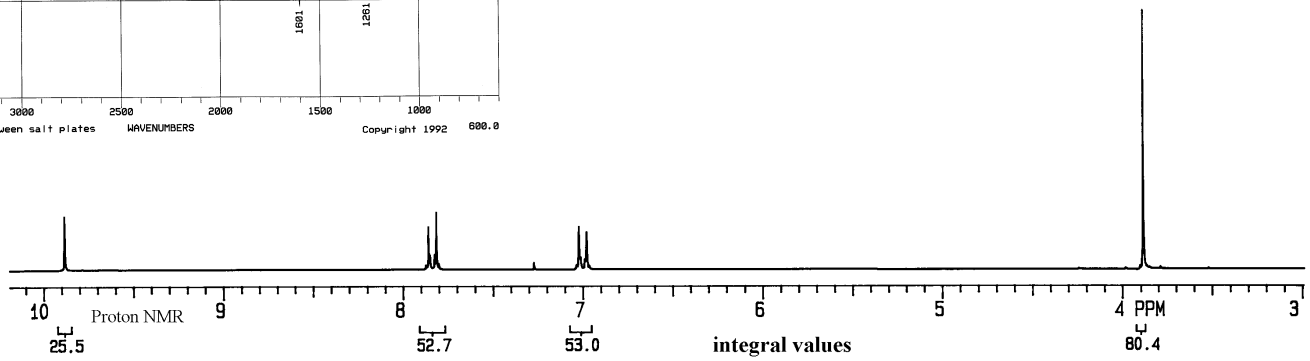




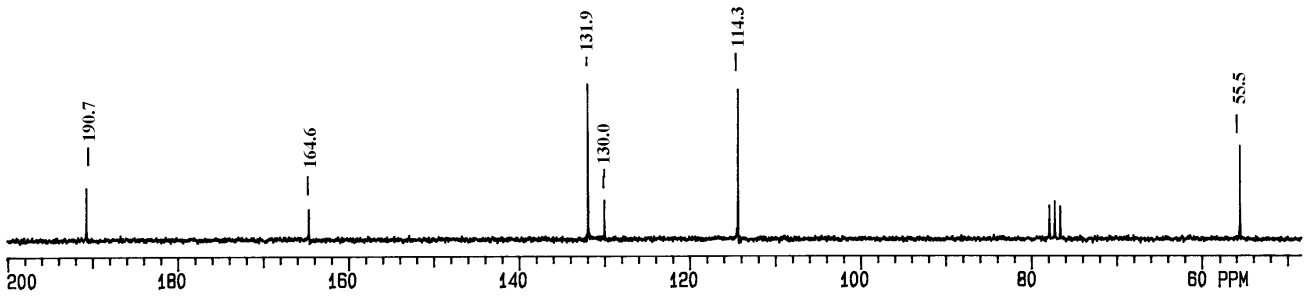
Spectra from *A Spectrum of Spectra, CD Version* by Richard A Tomasi.

Spectroscopy Problem 6: $C_8H_8O_2$



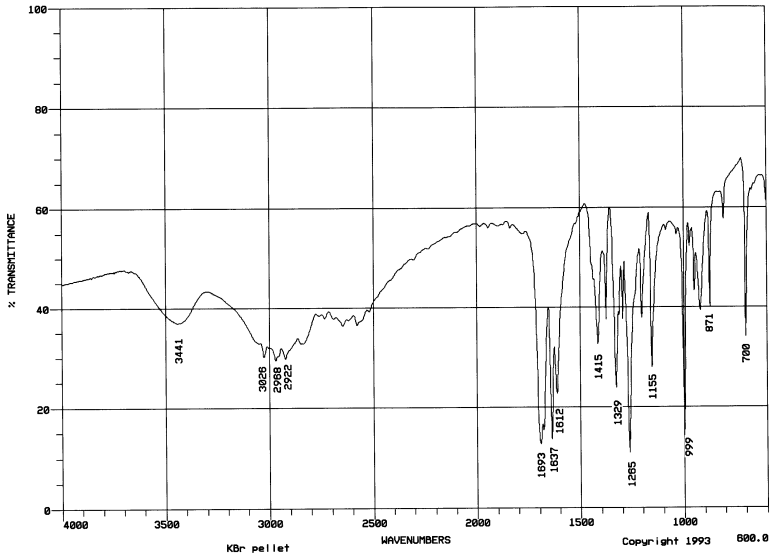


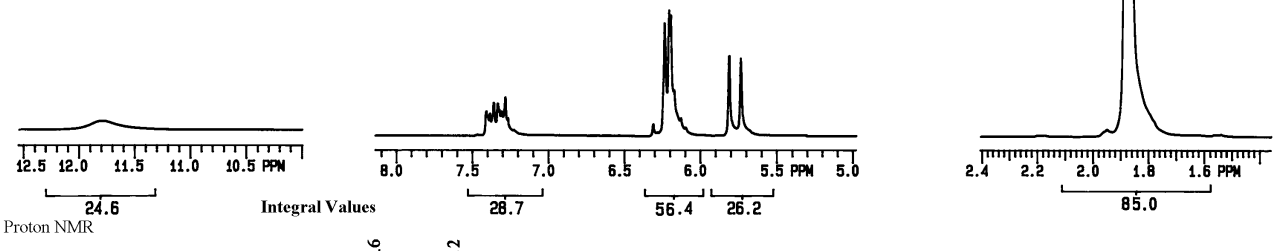
Proton NMR



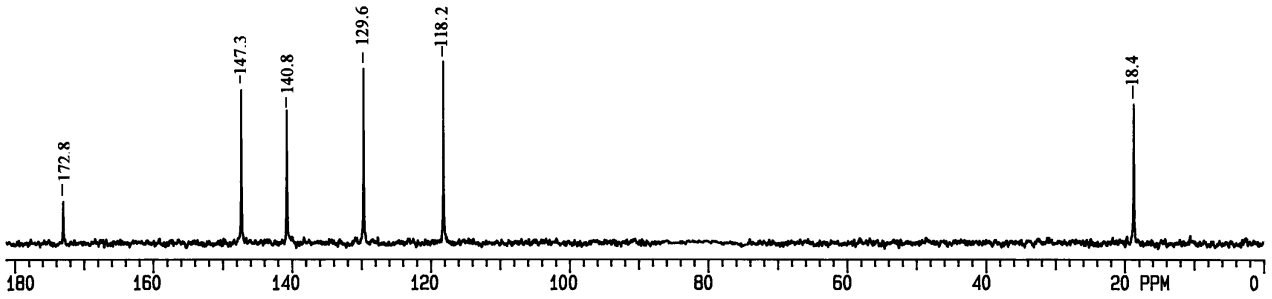
Carbon 13 NMR

Spectroscopy Problem 7: $C_6H_8O_2$



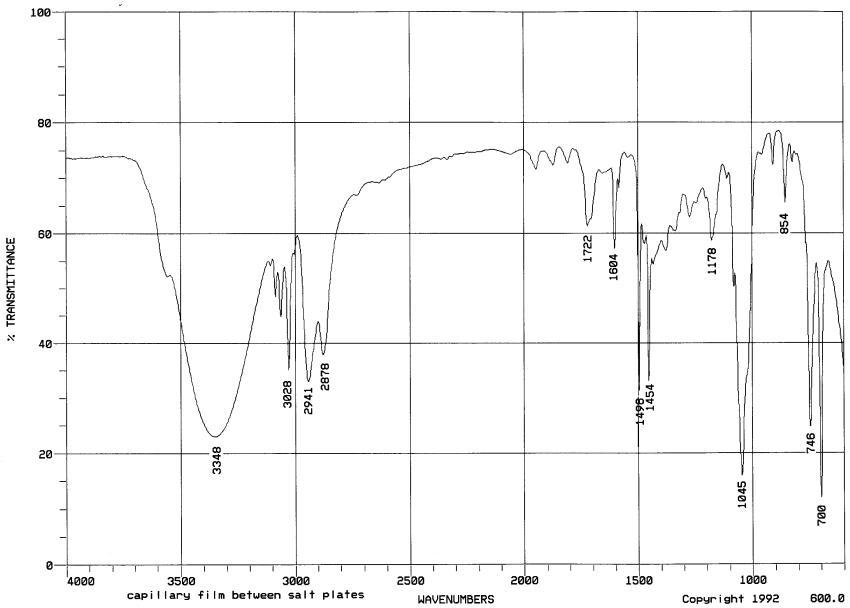


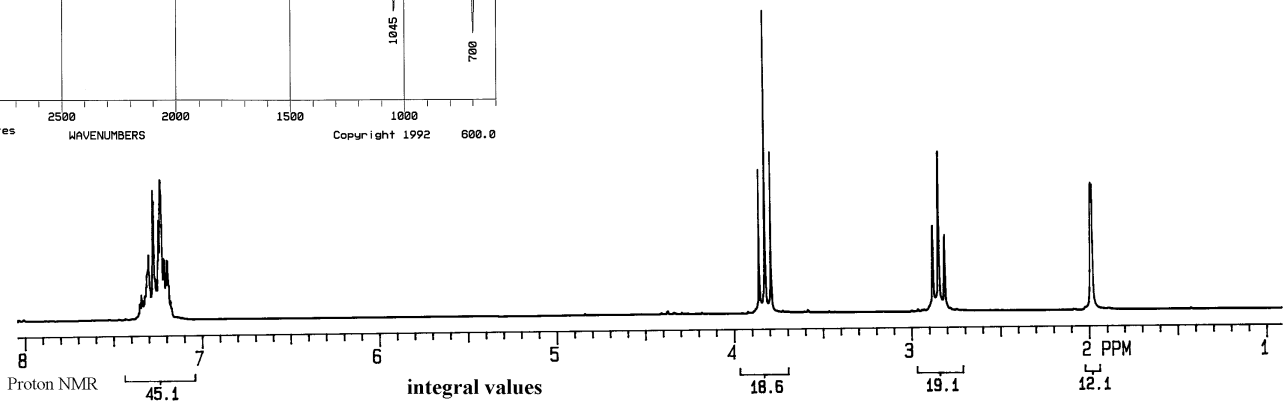
Proton NMR

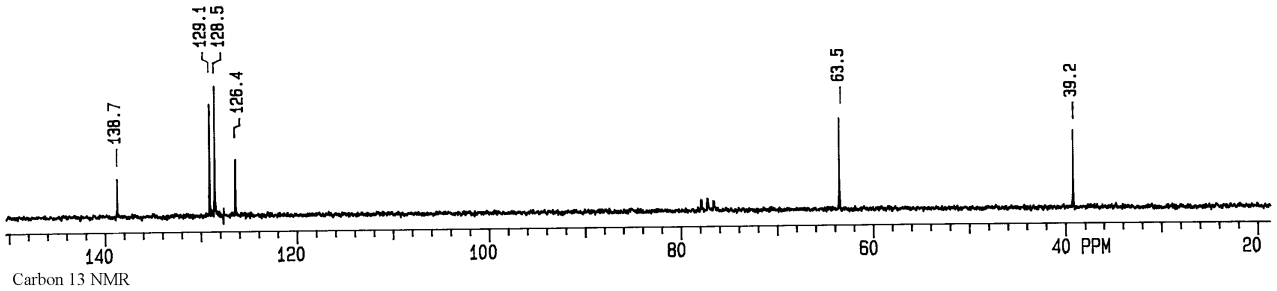


Carbon 13 NMR

Spectroscopy Problem 8: $C_8H_{10}O$







Answers to Spectroscopy Problems

1. $C_5H_{10}O$: 2-pentanone

Step 1: the obvious stuff.

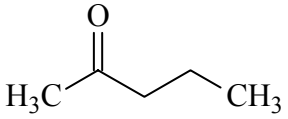
- Four distinct ^{1}H NMR signals, integrating 2:3:2:3, triplet, singlet, multiplet, triplet.
- Five distinct ^{13}C NMR signals, one of which is a carbonyl, either ketone or aldehyde. Other signals all aliphatic.
- IR shows ketone-type carbonyl, but no OH, no alkene.

Step 2: look closer at ^{1}H signals.

- 3H singlet at ~2.12 ppm almost certainly C**H**$_3$C(O)–
- 3H triplet at ~0.95 ppm probably C**H**$_3$CH$_2$–
- 2H triplet at ~2.4 ppm probably –CH$_2$C**H**$_2$C(O)–

Step 3: propose a structure.

- You now have all of the carbons and hydrogens figured out. Structure is therefore:



2. $C_5H_{10}O$: pentanal

Step 1: the obvious stuff.

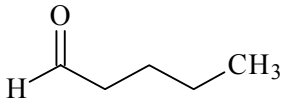
- Five distinct ^{1}H NMR signals, integration 1:2:2:2:3, singlet, triplet, multiplet, multiplet, triplet.
- ^{1}H signal at ~9.75 ppm says aldehyde (sharp singlet).
- Five ^{13}C NMR signals, one definitely ketone or aldehyde carbonyl, four aliphatic.
- IR confirms ketone or aldehyde carbonyl at 1726 cm^{-1}, no OH (slight blob at 3400-3500 cm^{-1} is an overtone of the carbonyl plus a trace of water).

Step 2: look closer at ^{1}H and IR.

- IR bands at 2719 and ~2800 cm^{-1} confirm aldehyde (C(O)–H stretch).
- 2H triplet at ~2.4 ppm consistent with –$CH_2C\mathbf{H}_2CHO$. Note triplet is quite broad due to small coupling to aldehyde H as well as larger coupling to CH_2 neighbor.
- 3H triplet at 0.9 ppm certainly due to –$CH_2C\mathbf{H}_3$.

Step 3: propose a structure.

- There is really only one possibility:



3. *$C_{10}H_{14}$: 2-butylbenzene*

Step 1: the obvious stuff.

- Five distinct ^{1}H NMR signals, integrating 5.6:1:2:3:3, multiplet, multiplet, multiplet, doublet, triplet.
- 5H signal cluster at ~7.2 ppm says aromatic, probably monosubstituted benzene.
- Eight distinct ^{13}C NMR signals, four definitely aliphatic, four probably aromatic, one of which is extremely weak and further downfield from others.
- IR shows aromatic C-H stretches, C=C stretch cluster of weak signals ~1700-1950 cm^{-1}, no other obvious functionality.

Step 2: look closer at ^{1}H signals.

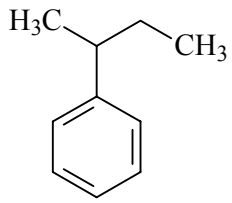
- 3H triplet at ~0.8 ppm almost certainly C**H**$_3$CH$_2$–
- 3H doublet at ~1.2 ppm almost certainly C**H**$_3$CH–
- 1H multiplet at ~2.55 consistent with CH$_3$C**H**(Ph)CH$_2$–
- 2H multiplet at ~1.6 ppm consistent with CH$_3$C**H**$_2$CH– (doublet of quartets, overlapped).

Step 3: look closer at ^{13}C signals.

- A monosubstituted benzene ring would have four different types of C atoms, in a ratio of 1:2:2:1. Three of these atoms have hydrogens and would be expected to yield stronger signals due to NOE. They would also be expected to have similar chemical shifts. The fourth carries an alkyl substituent and would be shifted downfield. This is what is observed.
- Four aliphatic C atoms is consistent with a butyl chain. Signal at 42 ppm consistent with connection to phenyl ring.

Step 4: propose a structure.

- ^{1}H strongly suggests a 2-butyl chain and a linked phenyl group. ^{13}C confirms. Structure is:



4. $C_{10}H_{14}O$: 4-t-butylphenol

Step 1: the obvious stuff.

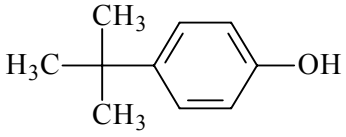
- ^{1}H NMR shows four signals, integration 2:2:1:9, doublet, doublet, broad singlet, singlet.
- Pair of ^{1}H doublets at ~6.85 and ~7.35 ppm strongly suggest *para*-disubstituted phenyl ring.
- Broad ^{1}H signal at ~4.9 consistent with exchangeable O**H**.
- Six distinct ^{13}C NMR signals, four probably aromatic (two of which are weak and two strong) and two aliphatic (one weak and one very strong).
- IR definitely says OH, broad signal at 3250 cm^{-1}.

Step 2: look closer at ^{1}H and ^{13}C signals.

- 9H ^{1}H singlet at ~1.35 ppm combined with ^{13}C signals at 34 and 31.5 ppm can only be a tertiary butyl group, CH_3C–
- Aromatic ^{13}C signals and ^{1}H doublet pattern say para-disubstituted for sure.

Step 3: propose a structure.

- The only possibility given the formula is:



5. $C_6H_{12}O_2$: isobutyl acetate

Step 1: the obvious stuff.

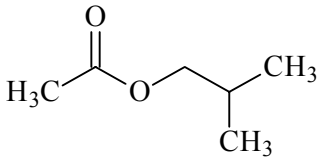
- ^{1}H NMR shows four signals, integration 2:3:1:6, doublet, singlet, multiplet, doublet.
- ^{13}C NMR shows five signals, a carbonyl, no alkenyl or aryl, one aliphatic probably attached to a heteroatom and three other aliphatics.
- IR carbonyl at 1745 probably ester, no OH.

Step 2: look closer at the ^{1}H signals.

- 3H singlet at ~2.05 ppm almost certainly C**H**$_3$C(O)–
- 2H doublet at ~3.85 ppm consistent with –CHC**H**$_2$O–
- 6H doublet at ~0.95 ppm consistent with (C**H**$_3$)$_2$CH–
- 1H multiplet at ~1.9 ppm consistent with (CH$_3$)$_2$C**H**CH$_2$–

Step 3: propose a structure.

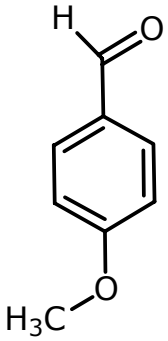
- Given that IR and ^{13}C NMR say it is an ester, and the proton signals suggesting an isobutyl group, the structure can only be:



6. $C_8H_8O_2$: p-methoxybenzaldehyde

Note that the molecular formula indicates 5 degrees of unsaturation - that is, rings and/or double bonds.

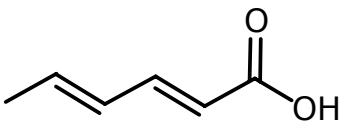
- Infrared Spectrum
  - no OH stretches.
  - strong C=O at 1684 - conjugated ketone or aldehyde.
- ^{1}H NMR Spectrum
  - 1-proton singlet at ~9.9 ppm - aldehyde.
  - 2-proton doublets at 7.85 and 7.0 - *para*-disubstituted phenyl ring.
  - 3-proton singlet at ~3.9 ppm - OCH_3
- ^{13}C NMR Spectrum
  - 190.7 - conjugated aldehyde C
  - 164.6 - quaternary aromatic C attached to O.
  - 131.9, 114.3 - aromatic CH (2 each).
  - 130.0 - quaternary aromatic C attached to C=O.
  - 55.5 - OCH_3



7. $C_6H_8O_2$: E,E-2,4-hexadienoic acid

4 degrees of unsaturation.

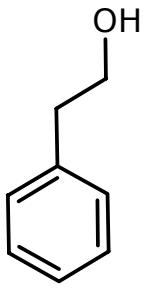
- Infrared Spectrum
  - broad OH stretch.
  - strong C=O at 1693 - conjugated carbonyl.
  - strong bands at 1637, 1612 - conjugated alkene, probably asymmetric diene.
- ^{1}H NMR Spectrum
  - 1-proton broad signal at ~11.8 ppm - COOH.
  - 1-proton wide multiplet at ~7.8 ppm, 2-proton multiplet at ~6.2 ppm, 1-proton doublet at ~5.75 ppm large *J* suggests R-CH=CH-CH=CH-COOH.
  - 3-proton broad doublet at 1.87 ppm - CH-CH_3
- ^{13}C NMR Spectrum
  - 172.8 - COOH
  - 147.3, 140.8, 129.6, 118.2 - CH=CH-CH=CH.
  - 18.4 - CH_3.



The double bonds are probably both *E*, as suggested by the large *J* seen in the doublet at 1.87 and the width of the multiplet at 7.8 (i.e. one large coupling constant).

8. $C_8H_{10}O$: 2-phenylethanol

4 degrees of unsaturation.



- Infrared Spectrum
  - strong OH stretch.
  - no C=O.
  - C-H stretches at >3028, weak overtone bands 1800-1950, medium to weak bands 1604, 1498, 1454 indicate phenyl ring, probably monosubstituted.
  - medium to strong bands 748, 700 also suggest monosubstituted phenyl.
- ^{1}H NMR Spectrum
  - 5-proton multiplet 7.15-7.35 ppm - phenyl.
  - two 2-proton triplets, same *J* - X-CH_2-CH_2-Y.
  - broad singlet at ~2 ppm - OH. The integral is a bit high but this may simply indicate that the OH is exchanging with water in the solvent.
- ^{13}C NMR Spectrum
  - 138.7 - quaternary aromatic.
  - 129.1, 128.5 - aromatic CH, two each.
  - 126.4 - aromatic CH, *para* to substituent.
  - 63.5 - CH_2-OH.
  - 39.2 - CH_2-phenyl.