.Massachusetts Institute of Technology
Organic Chemistry 5.13

Friday, September 30, 2005 Prof. Timothy F. Jamison

Hour Exam #1

Name _____

(please both **print** and **sign** your name)

Official Recitation Instructor _____

Directions: *Closed book exam, no books, notebooks, notes, etc. allowed. However, calculators, rulers, and molecular model sets **are** permitted.*

Please read through the entire exam before beginning, in order to make sure that you have all the pages and in order to gauge the relative difficulty of each question. Budget your time accordingly.

Show all of your work if you wish to receive partial credit.

You should have **11** pages total: **6** exam pages including this page, **3** pages of reference information, and **2** blank pages for scratchwork.

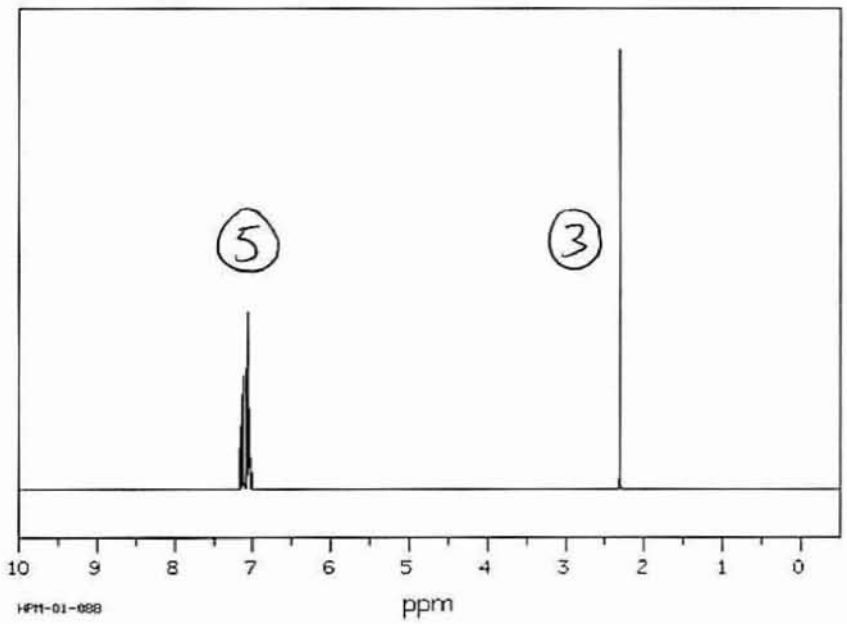
Question:		**Grader:**
1. _____/	**40 points**	_____
2. _____/	**30 points**	_____
3. _____/	**30 points**	_____
Total: _____/	**100 points**	_____

1. **(40 points total – 5 points each)** The molecular formulas and ^{1}H NMR spectra of **8 common organic solvents** are provided below and on the following 2 pages. For each, neatly **draw the entire structure** (i.e., not the acronym) in the box provided. In some cases, relative integration values (circled numbers) and/or other information have been provided.

Note: Do **not** represent functional groups with partial molecular formulas or other abbreviations. For example, do not use "Ph" or "C_6H_5" for a phenyl group. **Draw** the entire group (including hydrogen atoms).

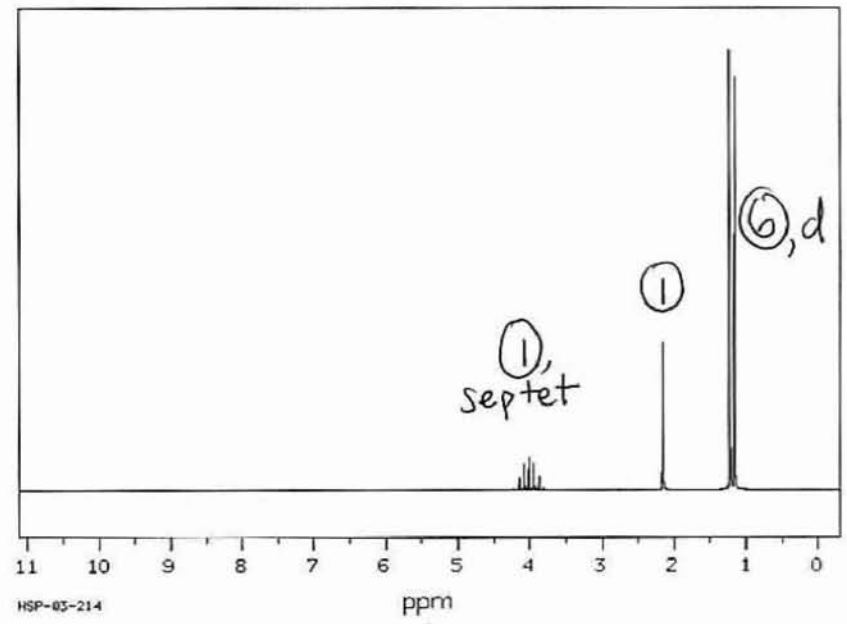
a. C_7H_8

Draw structure here



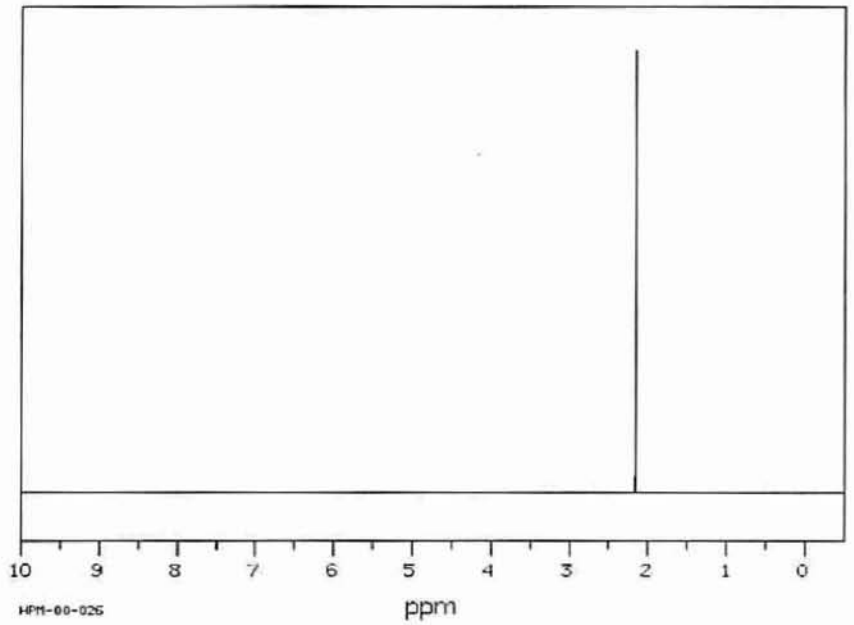
b. C_3H_8O

Draw structure here



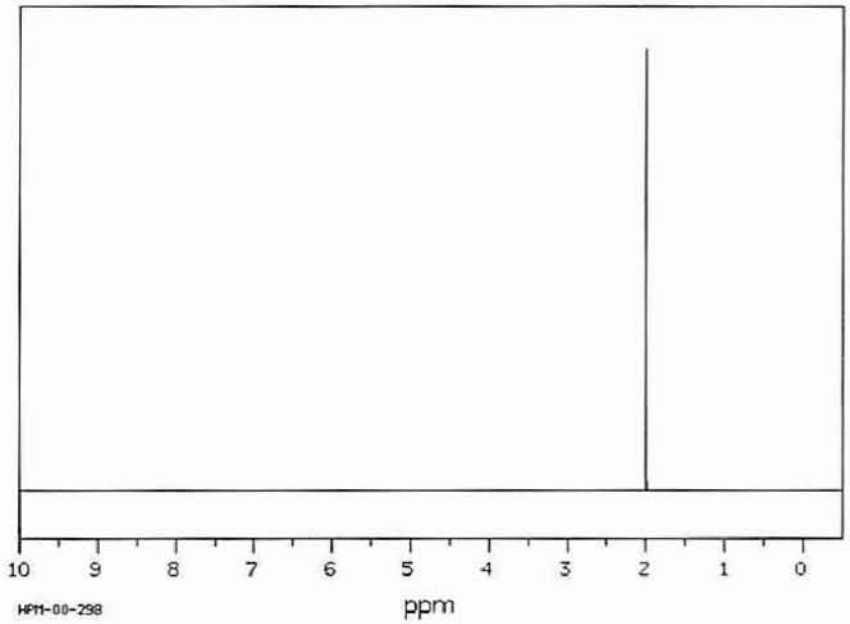
c. C_3H_6O

Draw structure here



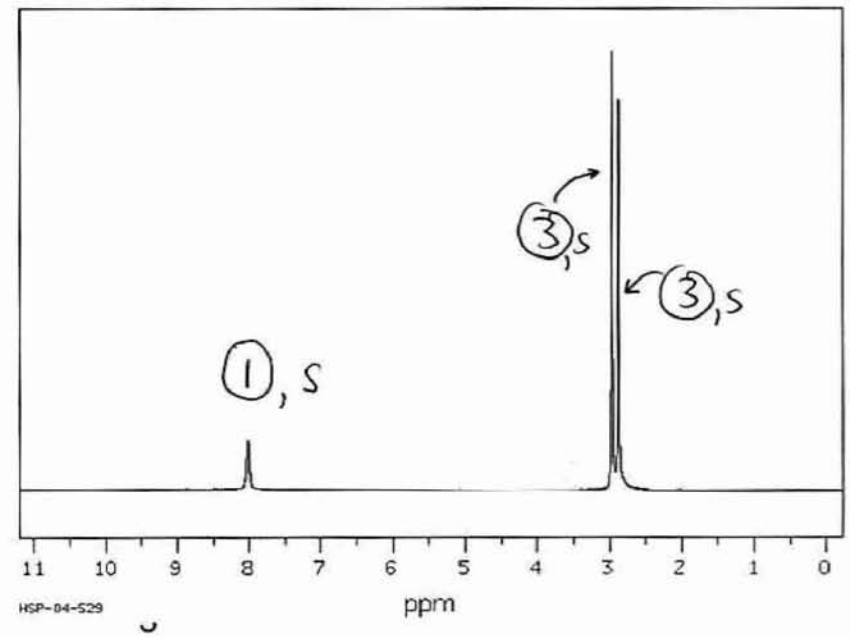
d. C_2H_3N

Draw structure here



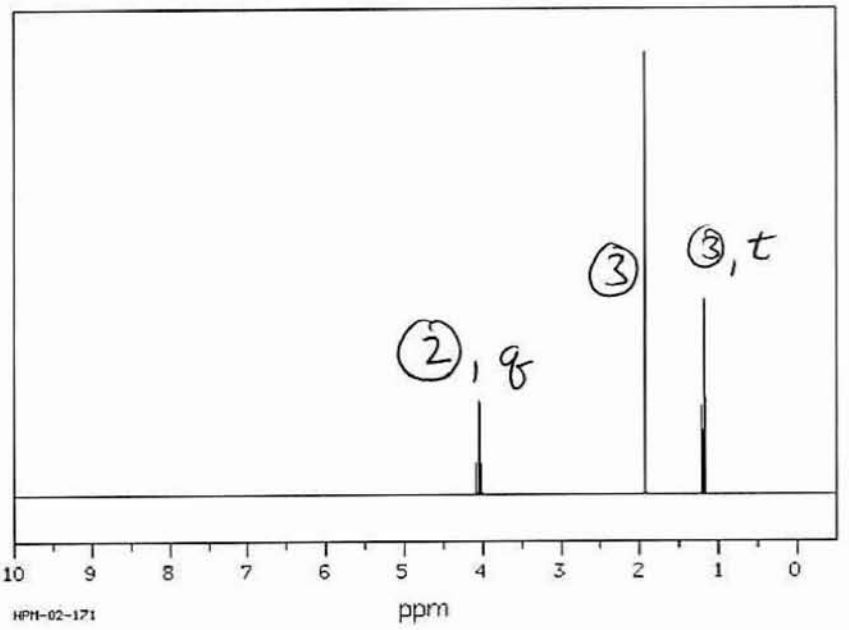
e. C_3H_7NO

Draw structure here



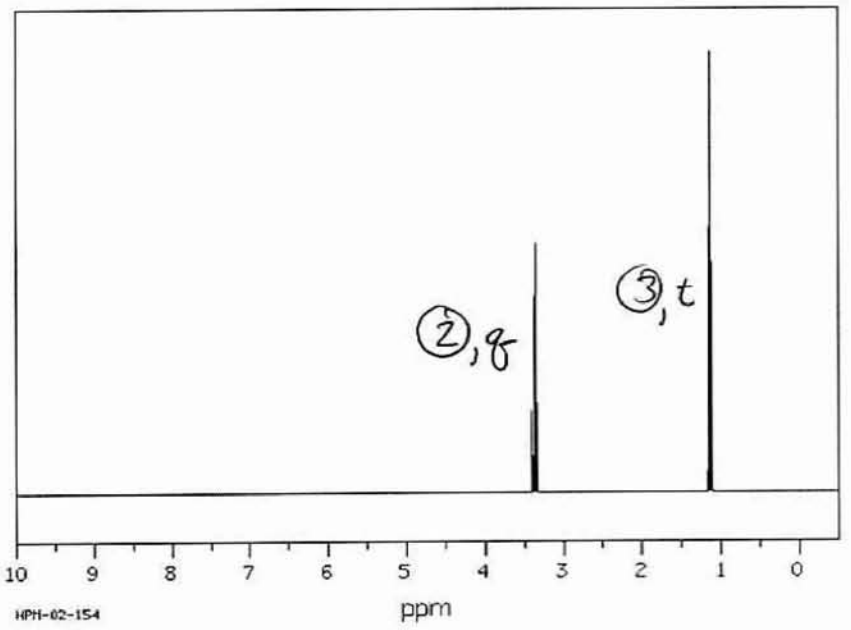
f. $C_4H_8O_2$

Draw structure here



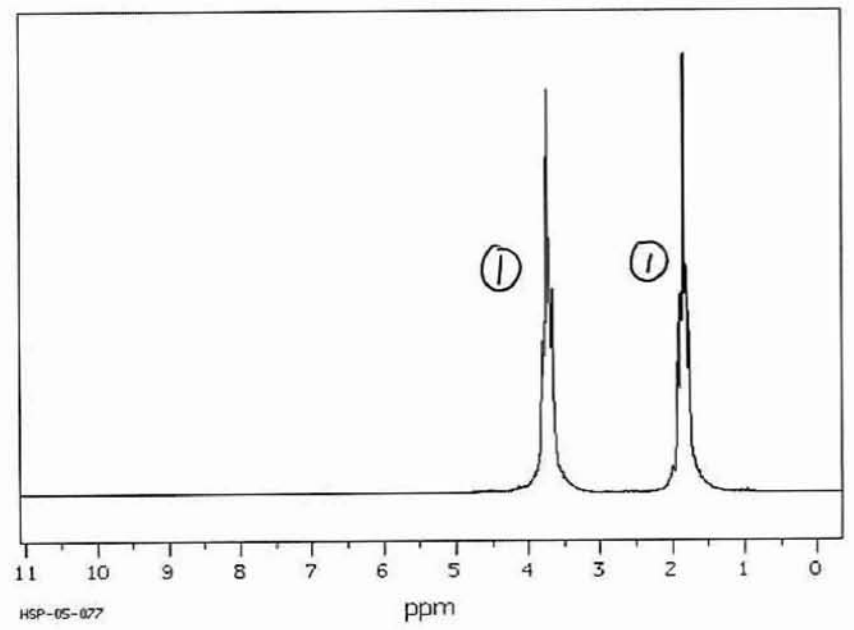
g. $C_4H_{10}O$

Draw structure here



h. C_4H_8O

Draw structure here



2. (30 points total) Answer the questions below about the structure that has the following data:

EA	C, 81.61; H, 11.06; N, 7.32
MS	191, 176.
^{13}C NMR	162.7, 136.5, 118.9, 35.1, 31.9
^{1}H NMR	7.59 (t, J = 7.8, 1H), 7.14 (d, J = 7.8, 2H), 1.34 (s, 18H)

a. (10 points) Determine the **molecular** formula. **Circle** your final answer.

b. (5 points) Calculate the **Index of Hydrogen Deficiency** (IHD). **Circle** your final answer.

c. (2 points) How many "types of carbon" (chemically non-equivalent) does this compound have? **Circle** your final answer.

d. (3 points) How many "types of hydrogen" (chemically non-equivalent) does this compound have? **Circle** your final answer.

e. (10 points) **In the space below, draw the structure of the molecule that is consistent with all of the data provided**. **Circle** your final answer.

3. (30 points total) Answer the questions below about the structure that has the following data:

EA	C, 75.69; H, 8.80
M^+	206
IR	3430 (broad), 1705 (strong)
^{13}C NMR	181.4, 140.9, 137.0, 129.5, 127.4, 45.9, 44.1, 30.3, 22.5, 18.2
^{1}H NMR	11.9 (broad s, 1H), 7.21 (d, J = 7.7, 2H), 7.09 (d, J = 7.7, 2H), 3.70 (q, J = 7.0, 1H), 2.44 (d, J = 6.8, 2H), 1.84 (nonet (9 lines), J = 6.8, 1H), 1.49 (d, J = 7.0, 3H), 0.89 (d, J = 6.8, 6H)

a. (7 points) Determine the **molecular** formula. **Circle** your final answer.

b. (5 points) Calculate the **Index of Hydrogen Deficiency** (IHD). **Circle** your final answer.

c. (8 points) Which protons are coupled to which? Complete the tables below using the NMR data above. Write H1, H2, etc. or "none", as appropriate, in the box provided, and list **all protons** to which a given proton is coupled.

Proton(s)	∂ (ppm)	Coupled to
H1	11.9	
H2	7.21	
H3	7.09	
H4	3.70	

Proton(s)	∂ (ppm)	Coupled to
H5	2.44	
H6	1.84	
H7	1.49	
H8	0.89	

d. (10 points) Draw **all** of the possible **enantiomers and diastereomers of the unknown compound** that are consistent with all the data given. **Circle** your final answers.

e. (**Extra credit** – 5 points total) What is the common name of this over-the-counter pharmaceutical (3 points), and for which symptoms is it indicated (2 points)?

Infrared Spectra: Tables of Reference

X-H Region

Phenols and Alcohols	**ROH**	3700-3500 sharp or 3200-3600 broad (H-bonded)
Acids	**RCO_2H**	2800-3600 very broad
Amides and Amines	**RCONHR** **R_2NH**	3300-3500
C-H bonds	**C≡C-H** **C=C-H** **C-C-H** **RCHO**	3100-3300 3000-3200 2850-3000 2700-2800

sp Region

Acetylenes	**C≡C**	2100
Nitriles	**C≡N**	2200
Ketenes	**C=C=O**	2150
Allenes	**C=C=C**	1950

Double Bond Region

Alkenes	**C=C**	1600-1670 weak unless conjugated
Imines	**C=N**	1600-1700
Nitro	**$-NO_2$**	1350-1550 (two bands)

Carbonyl Groups

Note: subtract ca. 30 cm^{-1} for conjugation (e.g. with a double bond or aromatic ring)

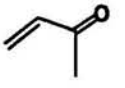
Anhydrides	**$RC(O)OCOR$**	1740-1780, 1800-1840 (two bands)
Acid Chlorides	**RCOCl**	1790-1815
Esters	**RCO_2R**	1725-1755
Acids	**RCO_2H**	1700-1725
Amides	**$RCONR_2$**	1630-1700
Urethanes	**R_2NCO_2R**	1700
Aldehydes	**RCHO**	1720-1740

Ketones

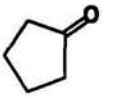
$R_2C=O$ 1710 (subtract ca. 30 cm^{-1} for conjugation)

6-membered and larger cyclic ketones

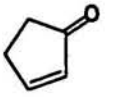
1710



1680

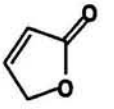


1740

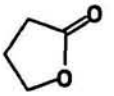


1715

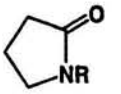
1780



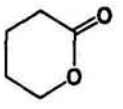
1740



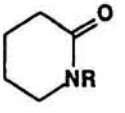
1770



1690-1740



1730



1650

^{1}H NMR Spectra: Tables of Reference

Average Chemical Shifts (δ) of α-Hydrogens in Substituted Alkanes*

X	CH_3X	RCH_2X	R_2CHX
H	0.233	0.9	1.25
CH_3 or CH_2	0.9	1.25	1.5
F	4.26	4.4	—
Cl	3.05	3.4	4.0
Br	2.68	3.3	4.1
I	2.16	3.2	4.2
OH	3.47	3.6	3.6
OR	3.3	3.4	—
OAr	3.7	3.9	—
OCOR	3.6	4.1	5.0
OCOAr	3.8	4.2	5.1
SH	2.44	2.7	—
SR	2.1	2.5	—
SOR	2.5	—	2.8
SO_2R	2.8	2.9	3.1
NR_2	2.2	2.6	2.9
NR-Ar	2.9	—	—
NCOR	2.8	—	3.2
NO_2	4.28	4.4	4.7
CHO	2.20	2.3	2.4
COR	2.1	2.4	2.5
COAr	2.6	3.0	3.4
COOH	2.07	2.3	2.6
COOR	2.1	2.3	2.6
$CONH_2$	2.02	2.2	—
$CR{=}CRCR^1$	2.0-1.6	2.3	2.6
Phenyl	2.3	2.7	2.9
Aryl §	3.0-2.5	—	—
C≡CR	2.0	—	—
C≡CN	2.0	2.3	2.7

* The tabulated values are average values for compounds that do not contain another functional group within two carbon atoms from the indicated hydrogens.

§ Includes polycyclic and many heterocyclic aromatics.

Chemical Shifts of Hydrogens Bonded to Unsaturated Centers

Type	Unconjugated	Conjugated*
$R_2C{=}CH_2$	4.6-5.0	5.4-7.0
$R_2C{=}CHR$	5.0-5.7	5.7-7.3
Aromatic	6.5-8.3	-----
Nonbenzenoid aromatic	6.2-9.0	-----
Acetylenic	2.3-2.7	2.7-3.2
Aldehydic	9.5-9.8	9.5-10.1
R_2NCHO	7.9-8.1	-----
ROCHO	8.0-8.2	-----

* The position depends on the type of functional group in conjugation with the unsaturated group.

Chemical Shifts of Hydrogen Bonded to Oxygen, Nitrogen, and Sulfur

Functional Group		Chemical Shift, δ	
OH	Alcohols	0.5 0.5-5	(Monomeric) (Associated)
	Phenols	4.5 4.5-8	(Monomeric) (Associated)
	Enols	15.5	
	RCO_2H	9-12	(Dimeric)
	H-bonded to C=O	13-16	
NH_2	Alkylamine	0.6-1.6	
	Arylamine	2.7-4.0	
	Amide	7.8	
NH	Alkylamine	0.3-0.5	
	Arylamine	2.7-2.8	
R_3NH^+	Ammonium salts	7.1-7.7	(in CF_3COOH)
SH	Aliphatic	1.3-1.7	
	Aromatic	2.5-4	

Characteristic Functional Group Chemical Shifts in ^{13}C NMR (ppm)

Alkanes	
Methyl (RCH_3)	0-30
Methylene (RCH_2R')	15-55
Methine (RCH(R')(R"))	25-55
Quaternary (RC(R')(R")(R'"))	30-40
Alkenes	100-150
Aromatic	120-160
Alkynes	70-90
Nitriles	110-125
Alcohols, Ethers	50-90
Amines	40-60

Organohalogen	
C–F	70-80
C–Cl	25-50
C–Br	10-40
C–I	–20-10
Ketones, Aldehydes	185-220
Carboxyl Derivatives	
Acids	150-185
Esters	155-180
Amides	150-180
Carbamates	150-160