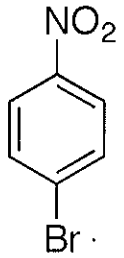
Chem 333, Exam 1
Professor Fox
FALL 2009

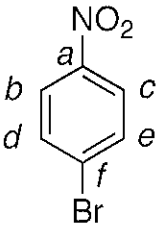
Your Name Key

1)	9 points
2)	9 points
3)	12 points
4)	22 points
5)	48 points

1. Calculate the chemical shifts for each of carbons in the following molecule. Place your answers on the line after the appropriate carbon atom. (9 points total)
Your answers must match the correct answer within +/– 1 ppm



Carbon a 147.1 ppm
Carbon b 125.4 ppm
Carbon c 125.4 ppm
Carbon d 132.8 ppm
Carbon e 132.8 ppm
Carbon f 129.1 ppm



You may use the area below for scratch work, but it will not be graded

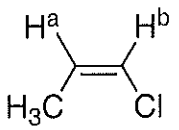
$C^a = 128.5 \; (+19.6) \; (-1.0) = 147.1$
$^1C - NO_2 \quad ^4C - Br$

$C^b = C^c = 128.5 \; (-5.3) \; (+2.2) = 125.4$
$C^2 - NO_2 \quad C^3 - Br$

$C^d = C^e = 128.5 \; (+0.9)(+3.4) = 132.8$
$C^3 - NO_2 \quad C^2 - Br$

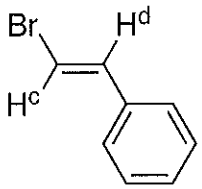
$C^f = 128.5 \; (+6.0) \; (-5.4) = 129.1$
$C^4 - NO_2 \quad C^1 - Br$

2. Calculate the chemical shifts for each of protons in the following molecules. Place your answers on the line after the appropriate carbon atom. (9 points total)
Your answers must match the correct answer within +/– 1 ppm



H^a 5.72 ppm

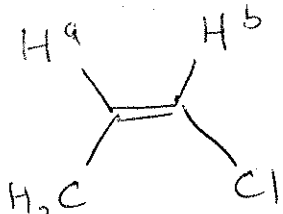
H^b 5.96 ppm



H^c 6.66 ppm

H^d 7.00 ppm

You may use the area below for scratch work, but it will not be graded



ALKYL
Gem to a
trans to b

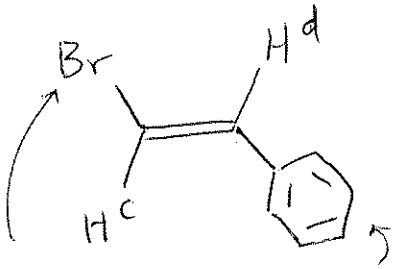
Cl
Gem to b
trans to a.

$H^a = 5.25 (+0.44)(+0.03) = 5.72$

Gem ALKYL trans Cl

$H^b = 5.25 (-0.29)(+1.00) = 5.96$

trans ALKYL gem Cl



Br:
cis to Hd
Gem to Hc

Aromatic
cis to Hc
Gem to Hd.

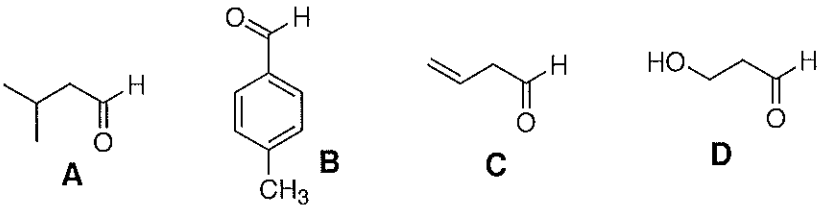
$H^c = 5.25 (+0.37)(+1.04) = 6.66$

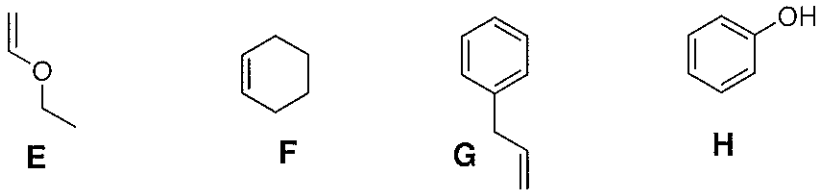
cis Aromatic Gem Br

$H^D = 5.25 (1.35)(0.40) = 7.00$

Gem Aromatic Cis Br

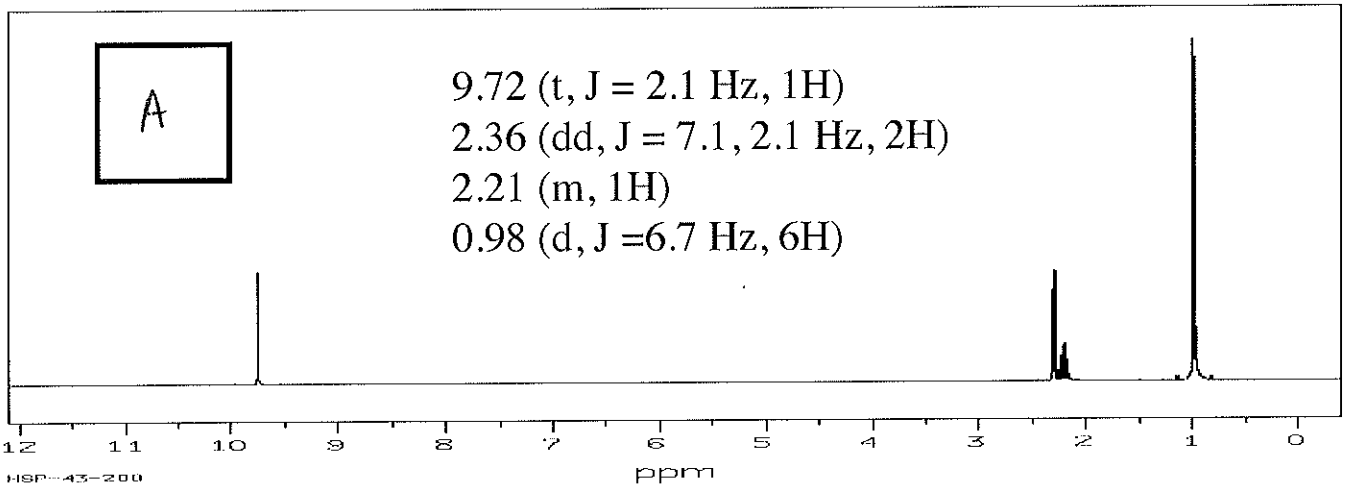
3. Match the following ^1H NMR spectra with one of the following substances. Write your answer in the box along side the spectrum. (6 points each)





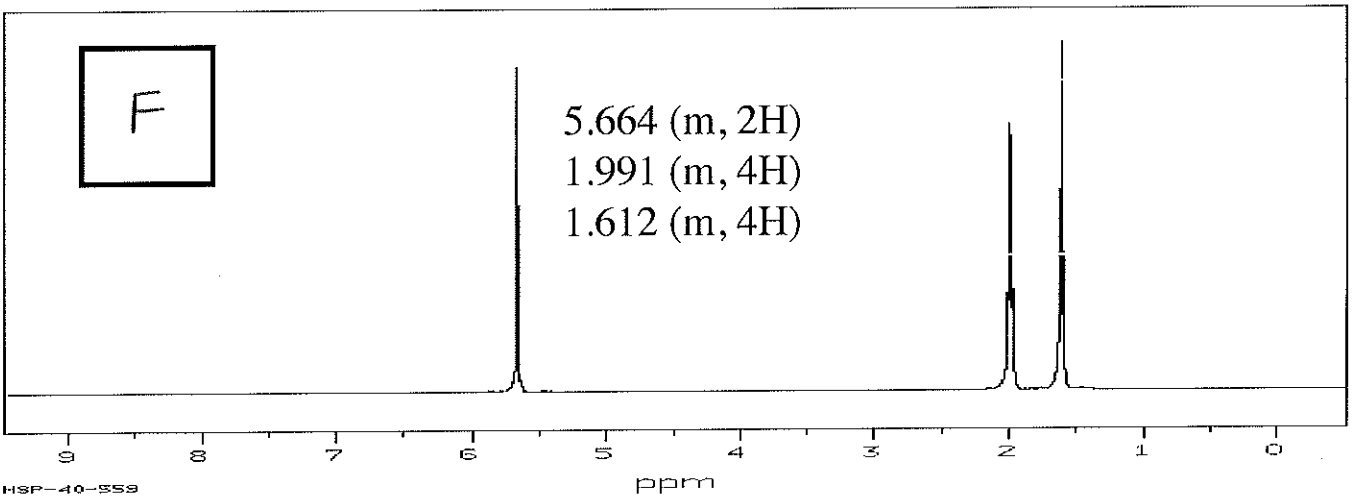
A

9.72 (t, J = 2.1 Hz, 1H)
2.36 (dd, J = 7.1, 2.1 Hz, 2H)
2.21 (m, 1H)
0.98 (d, J =6.7 Hz, 6H)



F

5.664 (m, 2H)
1.991 (m, 4H)
1.612 (m, 4H)



4. Elucidate the following structure based on the ^{13}C NMR data

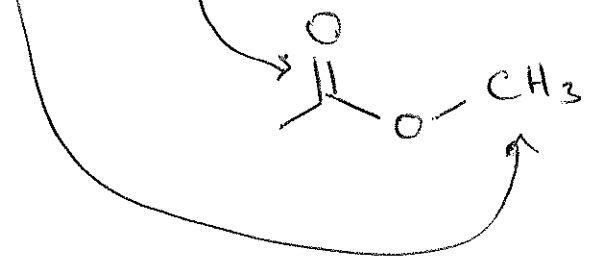
$C_6H_{11}BrO_2$

C^{13} NMR
173.4, s
51.5, q
33.1, t
32.9, t
32.0, t
23.5, t

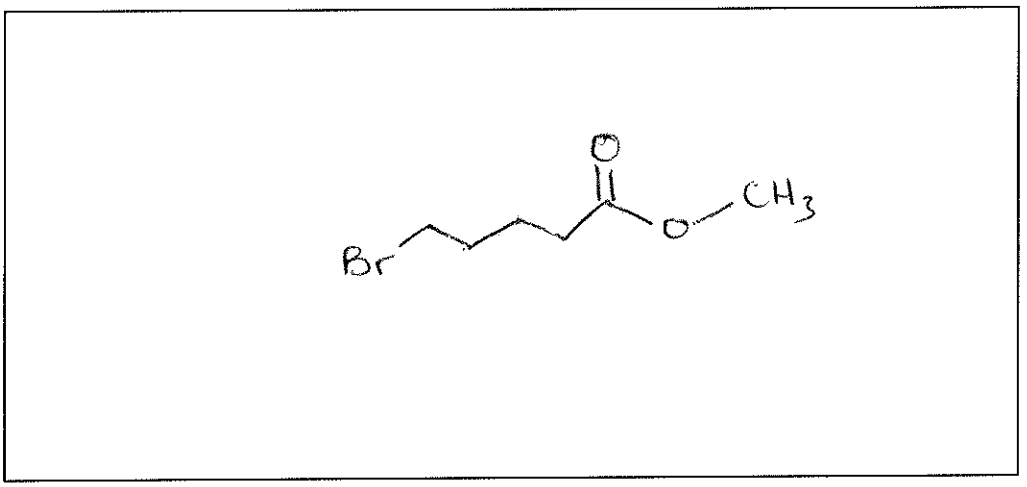
a) Calculate the IHD: 1 (1 point)

b) Show the substructure that is associated with the following ^{13}C NMR resonances (7 points)

173.4, s
51.5, q



c) Draw the structure (14 points)



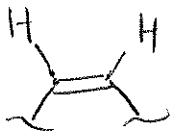
5. Elucidate the following structure based on the following ^{1}H NMR and ^{13}C NMR data $C_{10}H_{18}O_2$.

^{13}C NMR		^{1}H NMR
166.4, s	0	5.92, dd, J=7.9, 11.5 Hz, 1H
149.0, d	1	5.68, d, J=11.5 Hz, 1H
118.2, d	1	✓ 4.15, q, J=7.2 Hz, 2H
59.7, t	2	2.40, m, 1H
39.2, t	2	✓ 1.27, t, J=7.2 Hz, 3H
32.4, d	1	1.2-1.3, m, 4H
20.7, t	2	0.99, d, J=6.6 Hz, 3H
20.2, q	3	0.88, t, J=7.1 Hz, 3H
14.2, q	3	
14.1, q	3	→ ALL H'S ON C
	18	

a) Calculate the IHD: 2 (1 point)

b) Show the substructure that is associated with the following ^{13}C NMR resonances (5 points)

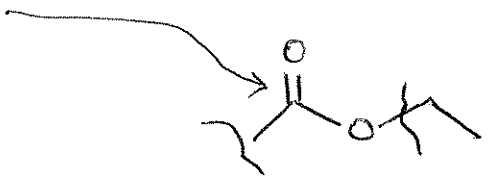
149.0, d
118.2, d



1,2 disubstituted ALKENE.

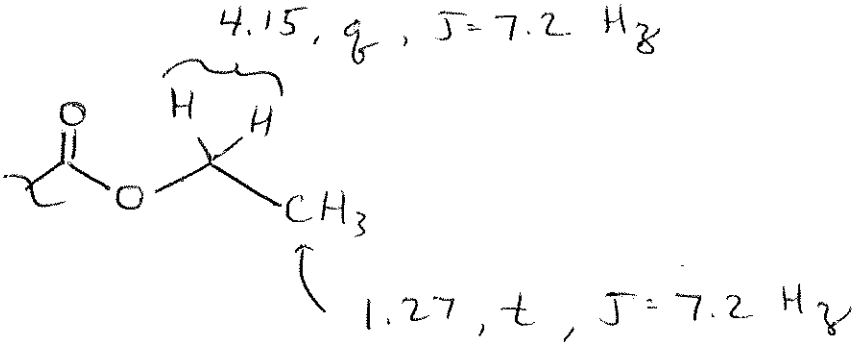
c) Show the substructure that is associated with the following ^{13}C NMR resonances (5 points)

166.4, s



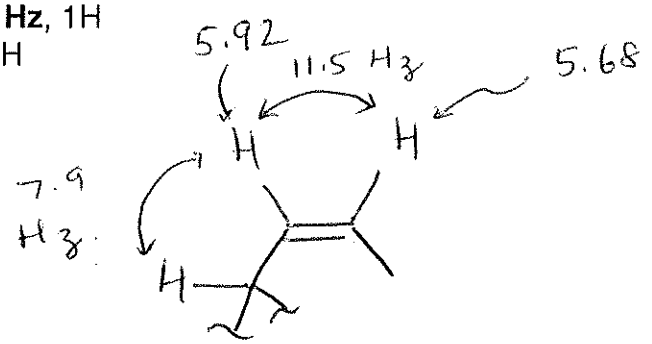
d) Show the substructure that is associated with the following ^{1}H NMR resonances (5 points)

4.15, q, J=7.2 Hz, 2H
1.27, t, J=7.2 Hz, 3H



e) Show the substructure that is associated with the following ^{1}H NMR resonances. Be sure to comment on the significance of the 11.5 Hz coupling constant. (12 points)

5.92, dd, J=7.9, **11.5 Hz**, 1H
5.68, d, **J=11.5 Hz**, 1H



f) Show your final structure (20 points)