Chem 333, Exam 1
Professor Fox
FALL 2013

Your Name Key

Q1) 12 points
Q2) 12 points
Q3) 16 points
Q4) 25 points
Q5) 33 points

tables at back of exam
Calculate the chemical shifts for each of carbons in the following molecule. Place your answers on the line after the appropriate carbon atom. A correct answer should be precise to one decimal place (e.g., 128.5; NOT 129 ppm). Your answers must match the correct answer within ± 0.5 ppm.

(12 points total)

\[
\begin{align*}
\text{Carbon } a & \quad 136.2 \text{ ppm} \\
\text{Carbon } b & \quad 116.3 \text{ ppm} \\
\text{Carbon } c & \quad 148.7 \text{ ppm} \\
\text{Carbon } d & \quad 114.1 \text{ ppm} \\
\text{Carbon } e & \quad 130.8 \text{ ppm} \\
\text{Carbon } f & \quad 119.2 \text{ ppm}
\end{align*}
\]

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

\[
\begin{align*}
\text{C}^a & = 128.5 \left( +6.4 \right) \left( +1.3 \right) = 136.2 \\
\text{C}^1 & = \text{Cl} \quad \text{C}^3 & = \text{NH}_2 \\
\text{C}^b & = 128.5 \left( +0.2 \right) \left( -12.4 \right) = 116.3 \\
\text{C}^2 & = \text{Cl} \quad \text{C}^2 & = \text{NH}_2 \\
\text{C}^c & = 128.5 \left( +1.0 \right) \left( +19.2 \right) = 148.7 \\
\text{C}^3 & = \text{Cl} \quad \text{C}^1 & = \text{NH}_2 \\
\text{C}^d & = 128.5 \left( -2.0 \right) \left( -12.4 \right) = 114.1 \\
\text{C}^4 & = \text{Cl} \quad \text{C}^2 & = \text{NH}_2 \\
\text{C}^e & = 128.5 \left( +1.0 \right) \left( +1.3 \right) = 130.8 \\
\text{C}^3 & = \text{Cl} \quad \text{C}^3 & = \text{NH}_2 \\
\text{C}^f & = 128.5 \left( +0.2 \right) \left( -9.5 \right) = 119.2 \\
\text{C}^2 & = \text{Cl} \quad \text{C}^4 & = \text{NH}_2
\end{align*}
\]

(for graders only) page total: ________
2. Calculate the chemical shifts for each of labeled protons in the following molecules. Place your answers on the line after the appropriate atom. A correct answer should be precise to two decimal places (e.g. 5.25 ppm; NOT 5.3 ppm)
Your answers must match the correct answer within \( +/- 0.05 \) ppm
(12 points total)

\[
\begin{align*}
H^a & \quad 7.81 \\
H^b & \quad 6.18 \\
\end{align*}
\]

\[
\begin{align*}
H^a & \quad 5.74 \\
H^b & \quad 5.57 \\
\end{align*}
\]

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

\[
\begin{align*}
H^a &= 5.25 \left( +1.35 \right) \left( +1.21 \right) = 7.81 \\
&\quad \text{gem} \quad \text{trans} \quad \text{aldehyde} \\
&\quad \text{aromatic} \\
H^b &= 5.25 \left( +1.03 \right) \left( -0.10 \right) = 6.18 \\
&\quad \text{gem} \quad \text{trans} \quad \text{aldehyde} \quad \text{aromatic} \\
N &= 5.25 \left( +0.78 \right) \left( -0.29 \right) = 5.74 \\
&\quad \text{cis} \quad \text{trans} \quad \text{-C=CH}_2 \\
H^b &= 5.25 \left( +0.58 \right) \left( -0.26 \right) = 5.57 \\
&\quad \text{trans} \quad \text{cis} \quad \text{-C=CH}_2
\end{align*}
\]
3. Match the following $^1$H NMR spectra with one of the following substances. Write your answer in the box along side the spectrum. (8 points each)

A

O-H

B

O-H

C

 vinyl

D

 OH

E

H$_2$N

F

OH

G

O

H

O

I

O-CH$_3$

J

OH

9.96 (s, 1H)
7.78 (d, J = 8.1 Hz, 2H)
7.34 (d, J = 8.1 Hz, 2H)
2.71 (d, J = 7.6 Hz, 2H)
1.26 (t, J=7.6 Hz, 2H)

5.81 (ddt, J=18.1, 12.4, 7.4 Hz, 1H)
4.99 (d, J=18.1 Hz, 1H)
4.93 (d, J=12.4 Hz, 1H)
3.63 (t, J = 7.1 Hz, 2H)
2.04 (m, 2H)
1.78 (bs, 1H)
1.56 (m, 2H)
1.46 (m, 6H)

(for graders only) page total_______
4. Elucidate the following structure based on the $^{13}$C NMR data

$$C_8H_{14}O$$

146.3, d  
112.6, t  
72.5, s  
39.9, t (2 carbons)  
22.0, t  
21.5, t (2 carbons)

a) Calculate the IHD: 2 (1 pt)

b) How many hydrogens are on carbons? 13 (1 pt)

c) Circle the substructure that is associated with the following $^{13}$C NMR resonances. If none of the below functional groups exist, then circle "none of the above" (6 points)

145.3 d  
112.6, t

monosubstituted alkene

cis-disubstituted alkene

trans-disubstituted alkene

trisubstituted alkene
	tetrasubstituted alkene

ketone  
aldehyde  
acid  
ester  
amide  
nitro  
nitrile

$\text{C} = \text{C} - \text{C} - \text{H}$  
$\text{C} = \text{C} - \text{C} - \text{H}$  
$\text{OH}$  
$\text{OH}$  
$\text{OH}$  
$\text{OH}$  
$\text{NH}_2$  
$\text{NH}_2$  
$\text{NH}_2$

monosubstituted benzene  
1,4-disubstituted benzene  
1,3-disubstituted benzene  
1,2-disubstituted benzene  
trisubstituted benzene

none of the above
4. Elucidate the following structure based on the $^{13}$C NMR data

\[ C_9H_{14}O \]

145.3, d
112.6, t
72.5, s
39.9, t (2 carbons)
22.0, t
21.5, t (2 carbons)

d) Identify the functional group associated with 72.5, s.
If the correct functional group is not listed, then circle "none of the above" (6 points)

![Functional groups diagram](image)

none of the above

e) Draw the structure (11 points)

![Structure diagram](image)
5. Elucidate the following structure based on the $^1$H and $^{13}$C NMR data (continued)

C$_{13}$H$_{19}$O$_2$

$^1$H NMR
7.70 ppm (d, J=8.0 Hz, 2H)
6.91 ppm (d, J=8.0 Hz, 2H)
3.86 ppm (m, 1H)
2.45 (s, 3H)
1.67 (m, 2H)
1.43 (d, J=7.2 Hz, 3H)
1.33 (m, 2H)
0.96 (t, J=6.9 Hz, 3H)

$^{13}$C NMR
197 (s)
163 (s)
129 (s)
128 (2 carbons, d)
114 (2 carbons, d)
73 (d)
39 (t)
23 (q)
20 (q)
17 (t)
14 (q)

a) Calculate the I:ID: ________ (1 pt)

b) How many hydrogens are on carbons? ________ (1 pt)

c) Identify the substructure that is associated with the following. (6 pts)

197 (s)

mono-substituted alkene
cis-disubstituted alkene
trans-disubstituted alkene
trisubstituted alkene
tetrasubstituted alkene
ketone
aldehyde
acid
ester
amide
nitro
nitrite

$\equiv$-C≡C-\(\equiv\) terminal alkyne
$\equiv$-C≡C-\(\equiv\) internal alkyne
primary alcohol
secondary alcohol
tertiary alcohol
primary amine
secondary amine
tertiary amine

monosubstituted benzene
1,4-disubstituted benzene
1,3-disubstituted benzene
1,2-disubstituted benzene
trisubstituted benzene

none of the above
5. Elucidate the following structure based on the $^1$H and $^{13}$C NMR data

$$C_{13}H_{18}O_2$$

$^1$H NMR
- 7.70 ppm (d, J=8.0 Hz, 2H)
- 6.91 ppm (d, J=8.0 Hz, 2H)
- 3.86 ppm (m, 1H)
- 2.45 (s, 3H)
- 1.67 (m, 2H)
- 1.43 (d, J=7.2 Hz, 3H)
- 1.33 (m, 2H)
- 0.96 (t, J=6.9 Hz, 3H)

$^{13}$C NMR
- 197 (s)
- 163 (s)
- 129 (s)
- 128 (2 carbons, d)
- 114 (2 carbons, d)
- 73 (d)
- 39 (t)
- 23 (q)
- 20 (q)
- 17 (t)
- 14 (q)

d) Identify the substructure that is associated with the following. (7 points)
- 7.70 ppm (d, J=8.0 Hz, 2H)
- 6.91 ppm (d, J=8.0 Hz, 2H)

e) Draw the structure (18 points)