NAME:_____ Section:_____ Student Number:_____

Spring 2019 **Chemistry 2600 Midterm 1** ____/ 52 marks

INSTRUCTIONS:

1) Please read over the test carefully before beginning. You should have 7 pages of questions in addition to this cover page and a periodic table.
2) You have also been given a 6 page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE!** If you need scrap paper, use the back of any page of the test. On questions with spectra, you may also do rough work directly on the spectra.
3) You may use a molecular model kit and ruler. You may not have any papers or other written materials in your model kit.
4) You may use a calculator. It may not have wireless capability. You may not have any other electronic devices (phone, iPod, etc.) with you when you write the exam.
5) If your work is not legible, it will be given a mark of zero.
6) For full credit, explanations must be complete. In many cases, complete explanations include drawing relevant structures. If delocalization of electrons is invoked, the relevant resonance structures must be drawn.
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 2 hours to complete this test.

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00pm Mountain Time on Monday, February 11th, 2019. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/52 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____ Date: _____

Course: CHEM 2600 (Organic Chemistry II)
Semester: Spring 2019
The University of Lethbridge

Question Breakdown

Q1	/ 5
Q2	/ 12
Q3	/ 6
Q4	/ 6
Q5	/ 8
Q6	/ 15

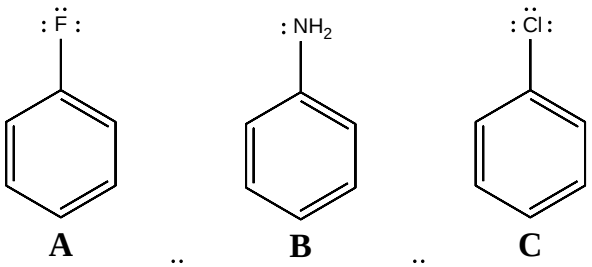
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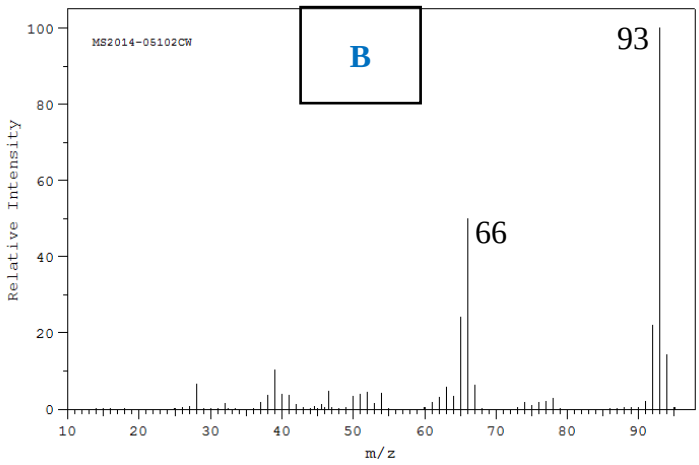
NAME:_____ Section:_____ Student Number:_____

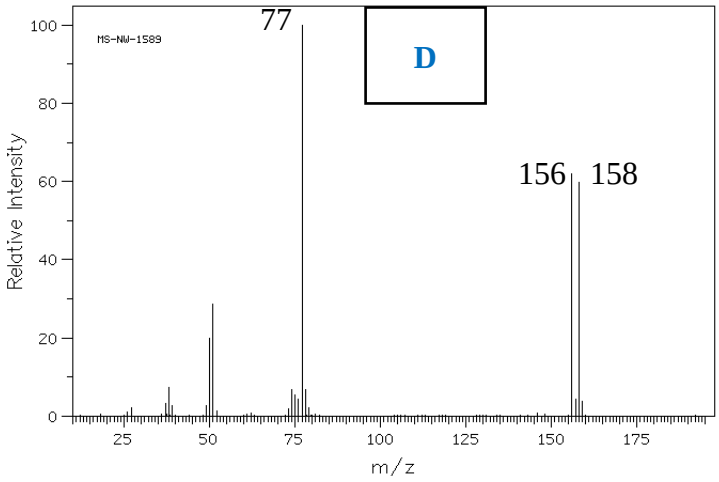
1. In the boxes provided, label each mass spectrum with the letter for the corresponding molecule (**A-E**). No explanation is required. **[5 marks]**

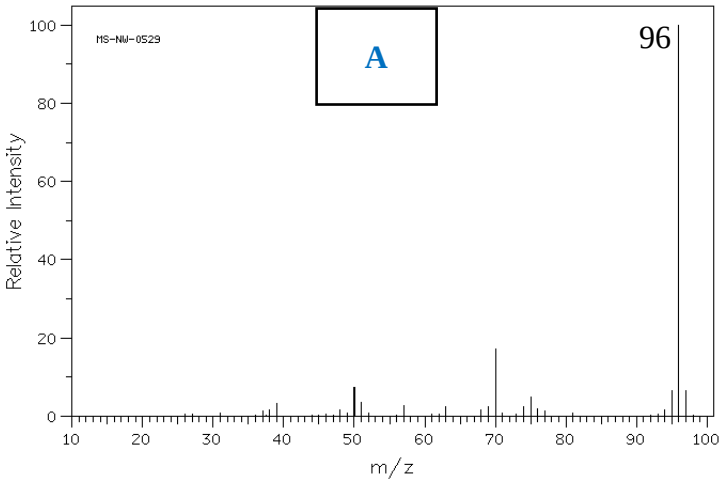
While this question can be answered by calculating the molar mass of each compound and matching that to the molecular ion of the appropriate spectrum, a few shortcuts can help:

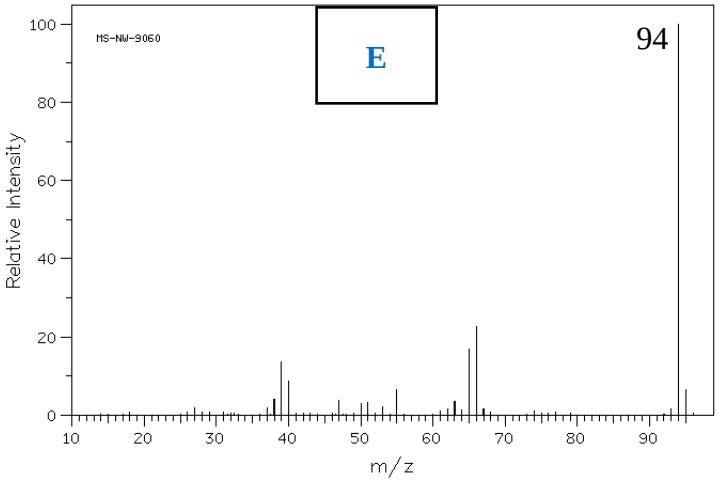
- Only one molecular ion is odd (m/z 93). That spectrum must correspond to the compound with an odd number of nitrogen atoms (B).
- Bromine exists as a 1 : 1 mixture of ^{79}Br and ^{81}Br. Bromobenzene (D) must therefore correspond to the spectrum with a 1 : 1 ratio between M^+ and $[M+2]^+$.
- Chlorine exists as a 3 : 1 mixture of ^{35}Cl and ^{37}Cl. Chlorobenzene (C) must therefore correspond to the spectrum with a 3 : 1 ratio between M^+ and $[M+2]^+$.

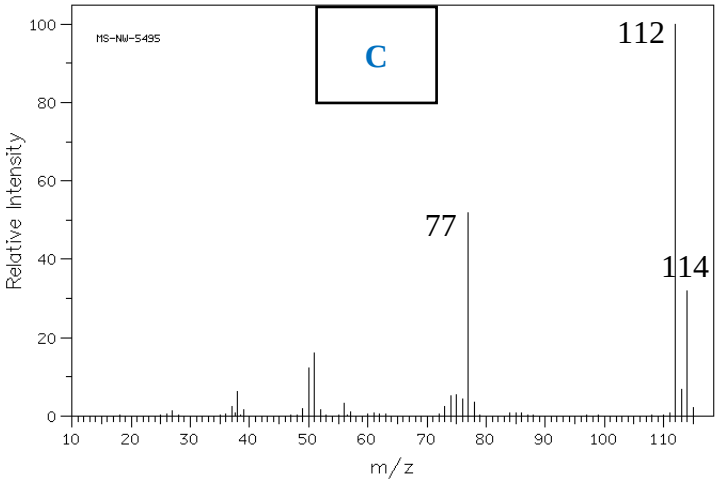










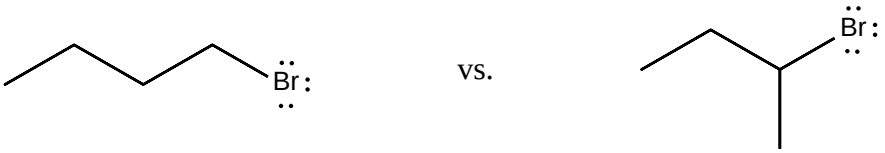


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2. *I am listing many reasonable answers. You needed two (using different types of spectroscopy).*

[12 marks]

(a)

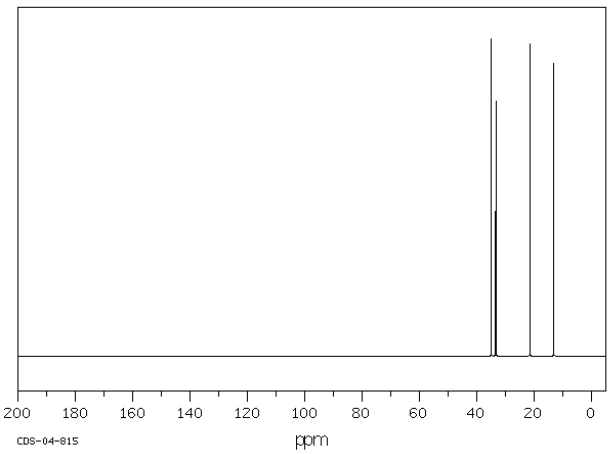


^{1}H NMR	Splitting patterns and integrations: • Triplet integrating to 3H • Sextet integrating to 2H • Pentet integrating to 2H • Triplet integrating to 2H	Splitting patterns and integrations: • Triplet integrating to 3H • Pentet integrating to 2H • Sextet integrating to 1H • Doublet integrating to 3H
	The most deshielded peak is a triplet integrating to 2H (CH_2Br) at ~3.3 ppm.	The most deshielded peak is a sextet integrating to 1H (CHBr) at ~3.9 ppm.
	Only one peak will integrate to 3H and it is a triplet.	Two peaks integrate to 3H: a triplet and a doublet.
^{13}C NMR	The most deshielded peak (for CH_2Br) is expected to appear at ~40 ppm (the upper end of the range for methylene C).	The most deshielded peak (for CHBr) is expected to appear at ~60 ppm (the upper end of the range for methane C).

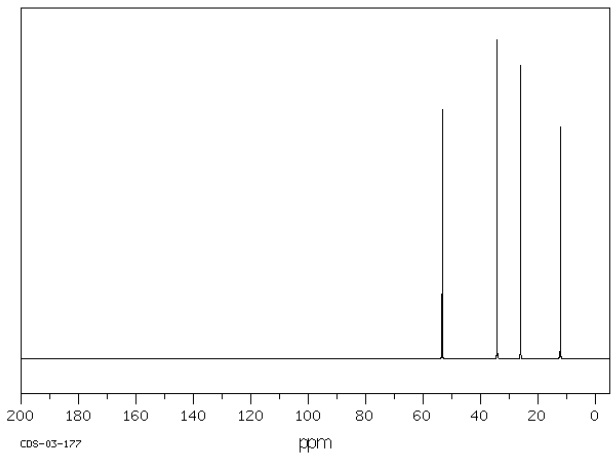
^{1}H NMR is, by far, the best way to distinguish between these two isomers.

Several students suggested looking for the number of CH_3 groups (i.e. peaks between 10 and 30 ppm) on the ^{13}C NMR. Credit was given for this suggestion as it is reasonable on paper; however, looking at the two ^{13}C NMR spectra, you can see that the CH_3 group closer to the Br in 2-bromobutane is somewhat deshielded and gives a peak with a similar chemical shift to the most shielded CH_2 group in 1-bromobutane. As such, in practice, looking for the most deshielded peak on the ^{13}C NMR would be a better strategy:

SDBS-^{13}C NMRSDBS No. 1225CDS-04-815
C_4H_9Br
1-bromobutane



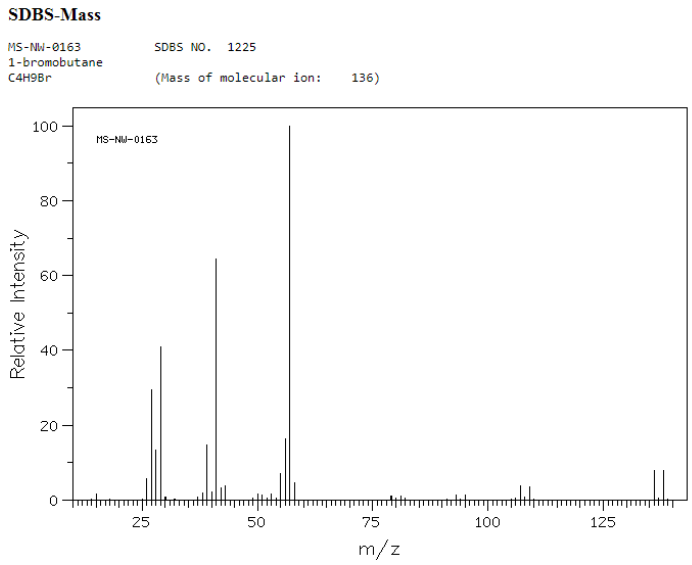
SDBS-^{13}C NMRSDBS No. 500CDS-03-177
C_4H_9Br
2-bromobutane

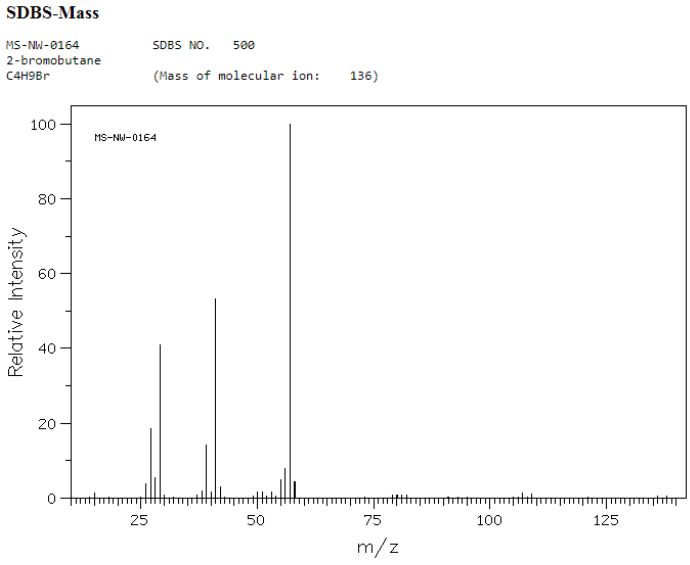


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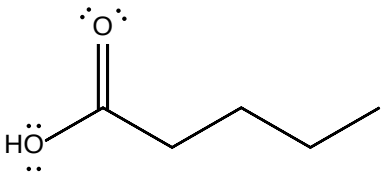
Several students suggested that you could look for gaps of m/z 14 on the mass spectrum, assuming that there would be more such gaps on the spectrum for 1-bromobutane than for 2-bromobutane. This doesn't work because the 'branches' in 2-bromobutane still contain CH_2 moieties. As we saw in class, you can't distinguish between 1-iodopropane and 2-iodopropane by mass spectrometry (without comparison to a library of reference spectra), and the same is true for these two isomers.

Mass spectra for 1-bromobutane and 2-bromobutane are shown below, and you can see that both spectra have the same major peaks.

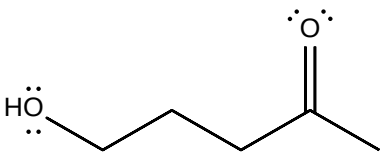




(b)



vs.



^{1}H NMR	There should be a very broad singlet above 10 ppm for the carboxylic acid OH.	There will be a (probably broad) singlet for the OH group, but it is unlikely to appear as far downfield as 10 ppm.
	Splitting patterns and integrations: • Broad singlet integrating to 1H (OH) • Triplet integrating to 2H • Pentet integrating to 2H • Sextet integrating to 2H • Triplet integrating to 3H	Splitting patterns and integrations: • Broad singlet integrating to 1H (OH) • Triplet integrating to 2H • Pentet integrating to 2H • Pentet integrating to 2H • Singlet integrating to 3H
	The peak integrating to 3H is a triplet and appears at ~1 ppm.	The peak integrating to 3H is a singlet and appears at ~2.2 ppm
	Of the peaks that are not exchangeable, the most deshielded one is a triplet integrating to 2H at ~2.2 ppm.	Of the peaks that are not exchangeable, the most deshielded one is a triplet integrating to 2H at ~3.5 ppm.

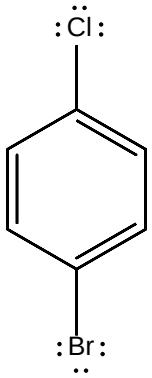
NAME:_____ Section:_____ Student Number:_____

^{13}C NMR	Carbonyl C for carboxylic acid is expected to appear between 160 and 190 ppm, so if the carbonyl C appears below 175 ppm, it is this isomer. The other four peaks on the ^{13}C NMR should all appear below 45 ppm.	Carbonyl C for ketone is expected to appear between 175 and 220 ppm, so if the carbonyl C appears above 190 ppm, it is this isomer. This isomer should also give a peak between 40 and 70 ppm for the CH_2O carbon.
IR	OH stretch is extremely broad and very likely to cross below the 3000 cm^{-1} line (possibly as far as 2800 cm^{-1})	OH stretch is broad (but not as broad as the carboxylic acid OH) and expected to appear between 3200 and 3500 cm^{-1}

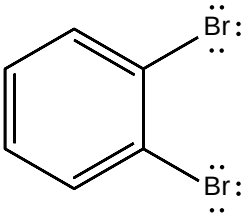
The two types of NMR are the best ways to distinguish between these two isomers.

It is likely that you would be able to identify each molecule by comparing the shapes of the O-H stretches on the IR spectra (but, given that hydrogen bonding can change the shape of O-H stretches, it is not guaranteed). You cannot distinguish between a ketone and a carboxylic acid by looking at the C=O stretch on the IR; they both appear between 1700 and 1725 cm^{-1}.

(c)



vs.



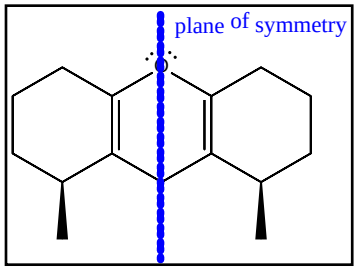
MS	Molecular ion is m/z 190 $M^+ : [M+2]^+ : [M+4]^+ = 3:4:1$ because the molecule contains one Cl and one Br	Molecular ion is m/z 234 $M^+ : [M+2]^+ : [M+4]^+ = 1:2:1$ because the molecule contains two Br
^{13}C NMR	4 signals	3 signals
^{1}H NMR	2 signals, both of which are doublets (long range coupling is not possible)	2 signals, both of which are doublets of doublets (due to long range coupling)

Given that these two molecules contain different numbers of Cl and Br atoms, mass spectrometry is the easiest way to distinguish them. They are also quite easily distinguished by counting the number of peaks on the ^{13}C NMR spectrum.
As long as the peaks don't coincidentally overlap, the shape of the peaks on the ^{1}H NMR can also be used to distinguish between the two molecules since long range coupling (4-bond coupling) is possible in 1,2-dibromobenzene but not in 1-bromo-4-chlorobenzene. Remember that equivalent hydrogen atoms do NOT couple to each other, so there are no triplets on the spectrum for 1,2-dibromobenzene.

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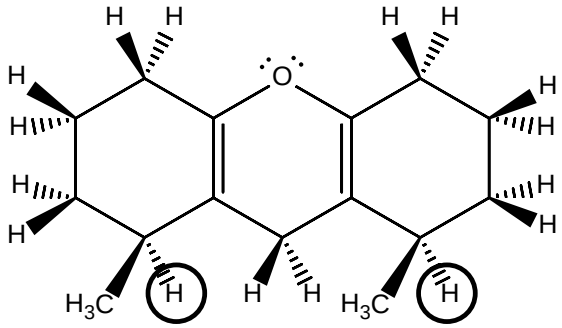
3. The following pictures are all of the same molecule (also shown in the box at the right). Below each picture, write one of the following abbreviations (H, E, D or CD) to indicate the relationship between the circled hydrogen atoms: **[6 marks]**

- Homotopic (H)
- Enantiotopic (E)
- Diastereotopic (D)
- Constitutionally different (CD)



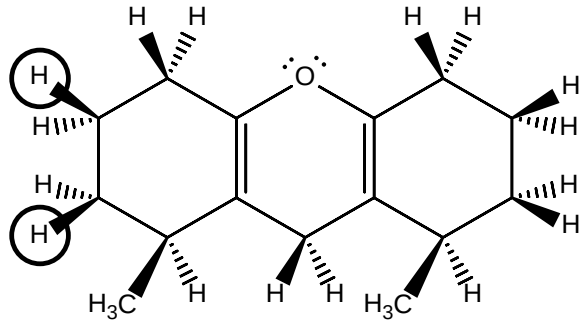
This molecule has a plane of symmetry (shown at right). Because both methyl groups are "up", it does not have rotational symmetry. As such, it may be easiest to think of the hydrogen atoms in terms of their relationship to the two methyl groups (how close? cis/trans?).

(a)



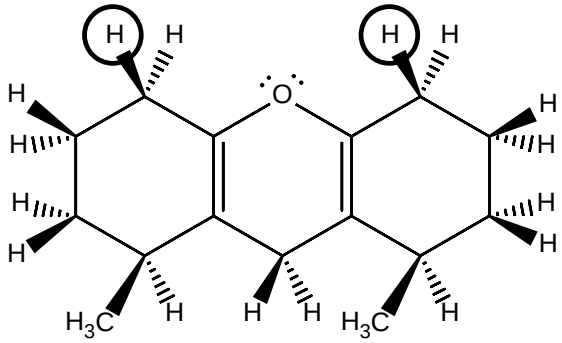
E

(b)



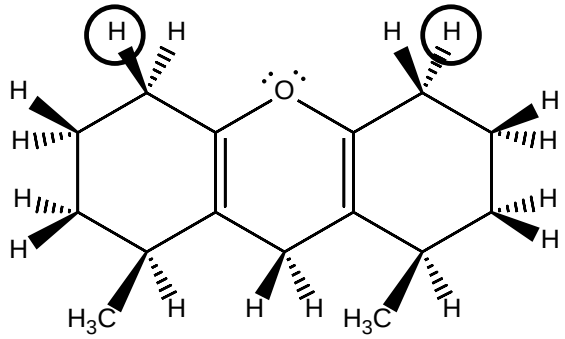
CD

(c)



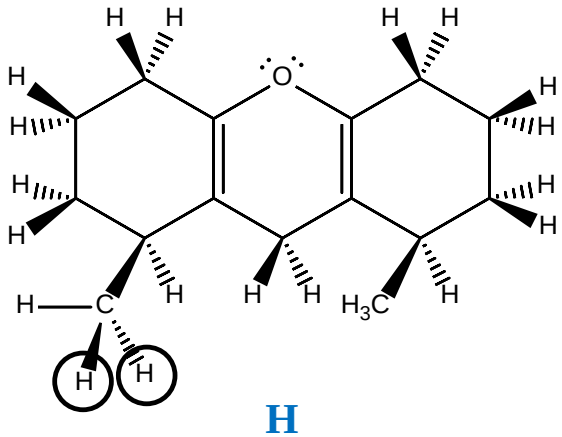
E

(d)



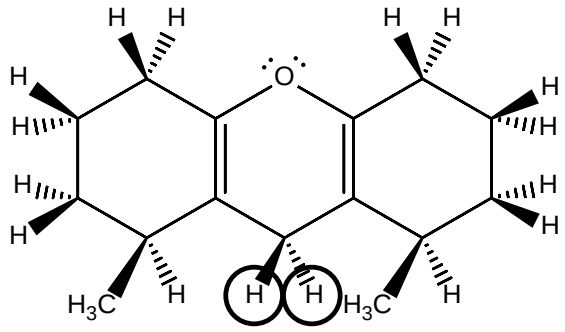
D

(d)



H

(e)

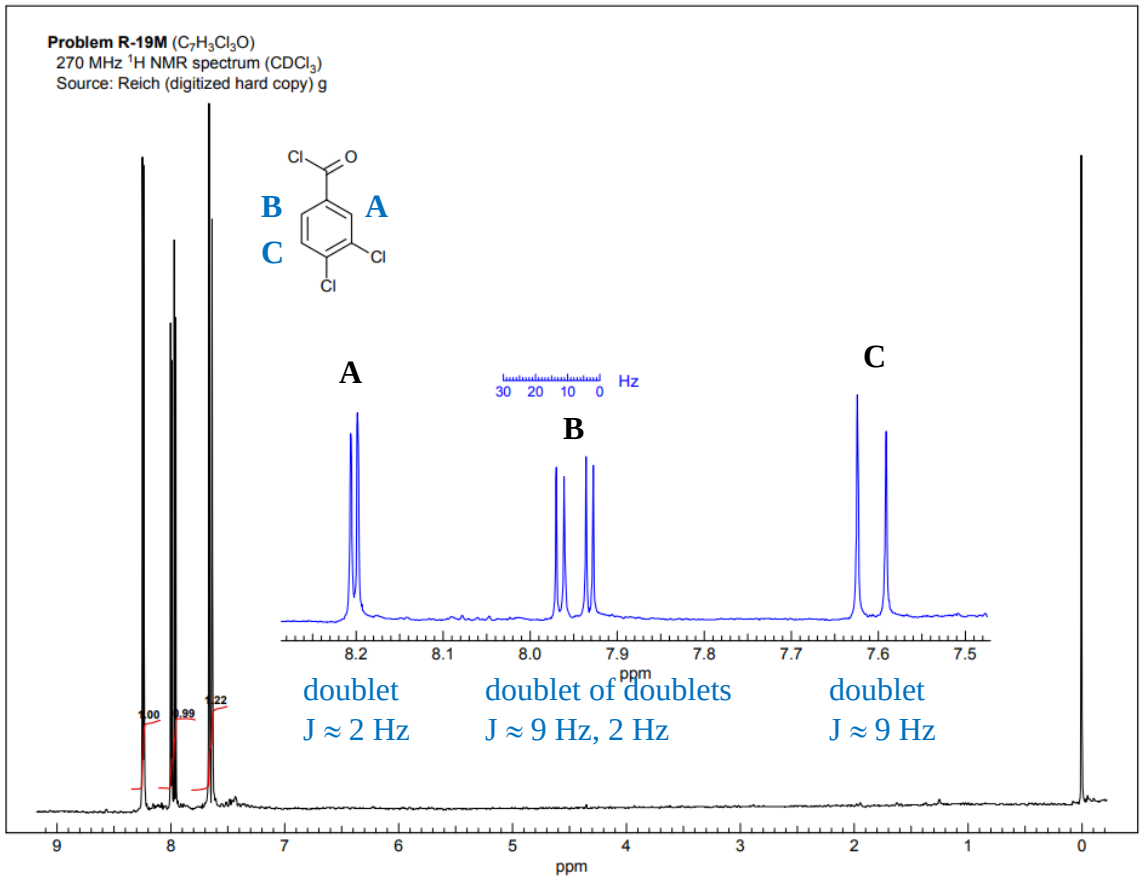


D

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4. Consider the ^{1}H NMR spectrum below. The peaks have been labeled A, B and C for your convenience. **[6 marks]**

*If a question provides you with a labeling system, please do **NOT** use those same letters for a completely different labeling system. Using the same letters to mean two completely different things can easily lead to you losing marks (either through confusing yourself or the person marking your paper).*



Clearly identify which hydrogen atom corresponds to each peak and justify your answer. For full marks, your explanation must address the multiplicity (splitting pattern) of each peak.

The spectrum shows two doublets and a doublet of doublets. Coupling constants were approximated using the scale provided (which suggests that 1 mm = 2 Hz).

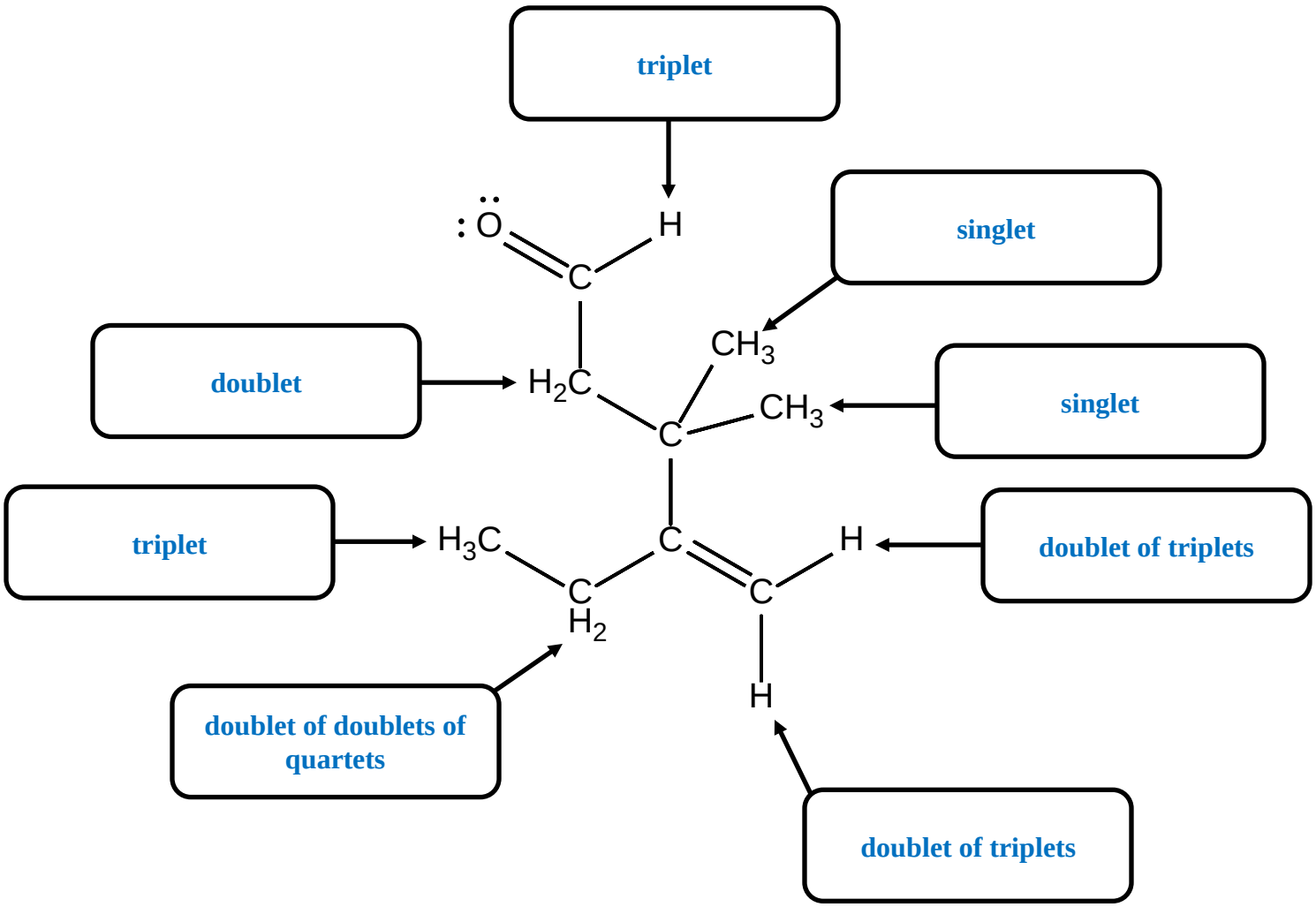
- Peak B is a doublet of doublets. The hydrogen atom labeled B experiences 3-bond coupling to hydrogen C (J ≈ 9 Hz) and 4-bond coupling to hydrogen A (J ≈ 2 Hz) and should therefore give a doublet of doublets.
- Peak A is a doublet with J ≈ 2 Hz. This corresponds to hydrogen A which experiences 4-bond coupling to hydrogen B and does not couple to hydrogen C (5 bonds away).
- Peak C is a doublet with J ≈ 9 Hz. This corresponds to hydrogen C which experiences 3-bond coupling to hydrogen B and does not couple to hydrogen A (5 bonds away).

The chemical shifts of the three peaks are consistent with the assignments made based on multiplicity. The strongest electron withdrawing group is the carbonyl, and it deshields hydrogen atoms ortho and para to it. So, A and B are downfield of C. The question asked you to use multiplicity to assign the peaks, so answers based only on chemical shift did not get full marks.

Also, the term "doublet of singlets" is awkward and not generally used. It's just a "doublet".

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5. Consider the molecule below. In the boxes provided, label each proton (or set of protons) with the multiplicity (splitting pattern) it would be predicted to exhibit in a ^{1}H NMR spectrum. *Assume that any long range coupling has J > 0 Hz.* **[8 marks]**



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6. The following page contains spectra for Unknown X ($C_6H_6O_4$). **[15 marks]**

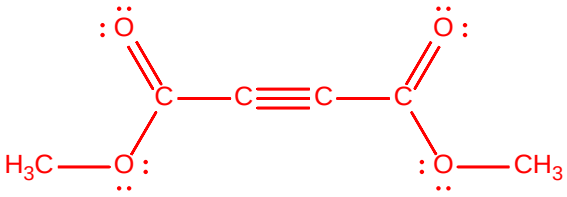
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your reasoning.

(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, drawing Unknown X in the box provided, and labeling each carbon or hydrogen atom with the appropriate peak number. *For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.*

(d) Label any important peaks on the IR.

Unknown X:



General breakdown of marks:
1 mark for correct answer
1 marks for IR peak assignment
1 marks for ^{1}H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)
3 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
1 mark for calculating DU
8 marks for logic (this page plus legible rough work on spectra, etc.)

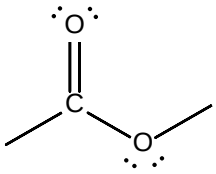
One Way to Arrive at the Answer

Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(6)+2-6}{2} = \frac{8}{2} = 4$
- Each degree of unsaturation corresponds to either a pi bond (double bond = 1 DU; triple bond = 2 DU) or a ring.

Step 2: Look at IR for relevant peaks

- The large peak at ~1700-1720 cm^{-1} strongly suggests a C=O bond.
  - There is a peak on the ^{13}C NMR at about 152 ppm. This is quite far upfield for a carbonyl carbon (they usually appear downfield of 160 ppm) and definitely too far upfield for a ketone or aldehyde. Given that the only elements in the molecular formula are C, H and O, that means the carbonyl must come from a carboxylic acid or ester. (Anhydrides give two C=O stretches on the IR.)
  - To decide whether the carbonyl is ester or carboxylic acid, check the ^{1}H NMR for a broad stretch above 10 ppm (indicative of a carboxylic acid). There is none (and there is also no O-H stretch on the IR). So, a carboxylic acid is not likely. An ester is therefore, the most probable type of carbonyl.
  - The stretch on the IR is low for an ester, so the ester is probably part of a conjugated pi system.



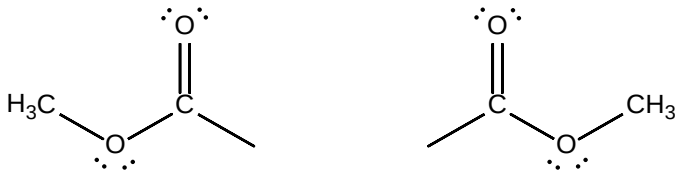
Step 3: Recognize symmetry

- There is only one peak on the ^{1}H NMR, so all six H are shift equivalent.
- The ^{13}C NMR has three peaks, but the molecular formula has 6C. So, there are only three different environments for six carbon atoms.
- Both of these points strongly suggest a symmetrical molecule.

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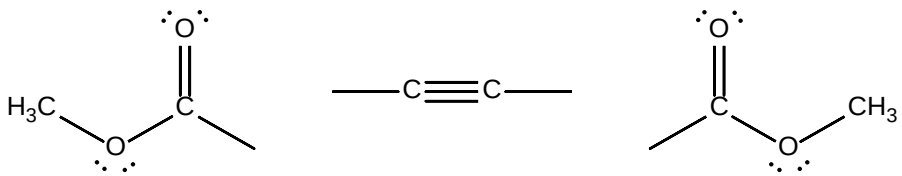
Step 4: Consider the peak on ^{1}H NMR

- There is a single peak on the ^{1}H NMR spectrum – a singlet at ~3.8 ppm. The most likely way for all six H to be equivalent is for there to be two CH_3 groups, and the chemical shift suggests that each CH_3 group is attached to O.
- That means the unknown must contain two methyl esters, and the only two atoms not used yet are two C, and two degrees of unsaturation remain unaccounted for



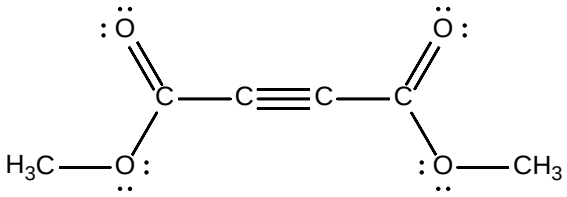
Step 5: Look at ^{13}C NMR for C=O, C=C or C≡C peaks to account for the remaining atoms and DU

- The peak at ~152 ppm is most likely the C=O for the ester discussed in the IR section.
- There is also a peak at ~75 ppm. This is too far upfield for an alkene but could be an alkyne. It could also be C attached to O, but the peak at ~54 ppm would be a good match for $–OCH_3$. So, given that there are two C and two DU left, an alkyne is likely the best answer:



Step 6: Assemble the pieces.

- There is only one way to assemble the pieces that maintains the required symmetry:

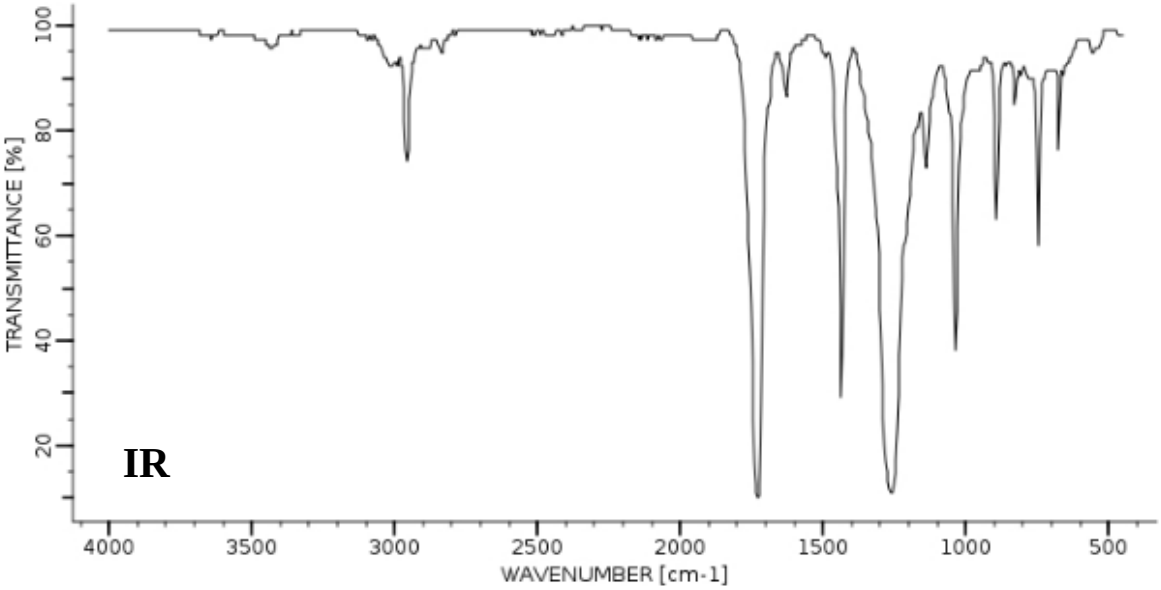


Step 7: Check your answer against the spectra and assign the peaks.

- The IR shows a C=O stretch at ~1700-1720 cm^{-1}. This is low for an ester, but is reasonable because the two esters are conjugated to the alkyne. We do not expect to see a C≡C stretch on the IR because the alkyne is symmetric; only terminal alkynes give C≡C stretches on IR.
- The single peak at ~3.8 ppm on the ^{1}H NMR spectrum is consistent with two equivalent methyl groups each attached to the O of an ester.
- The three peaks on the ^{13}C NMR are consistent with the three carbon environments of this symmetrical molecule.
    - The signal at ~152 ppm must correspond to the carbonyl; it is unusually far upfield for a carbonyl but that must be due to the extended pi system (conjugated esters and alkyne).
    - The signal at ~75 ppm is in the right region for an alkyne C
    - The signal at ~54 ppm is in the right region for a methyl group attached to O

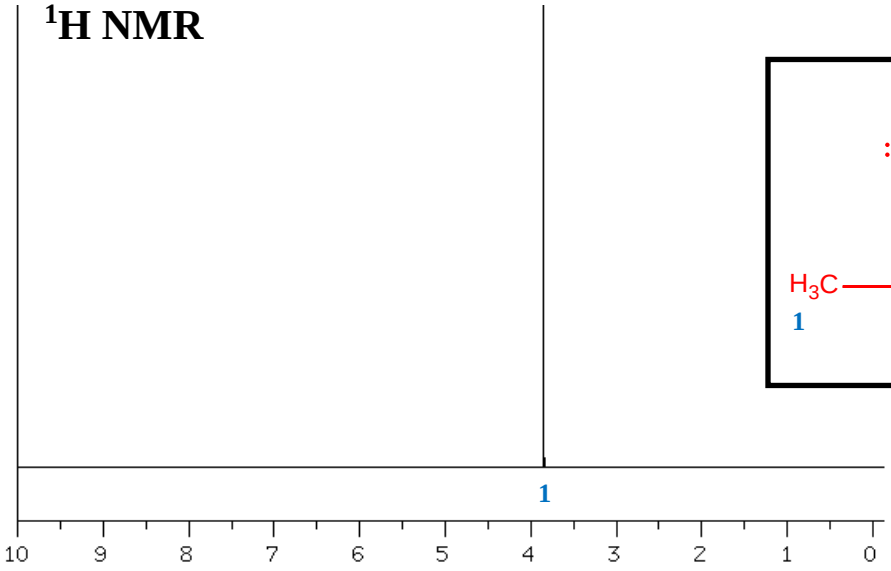
NAME:_____ Section:_____ Student Number:_____

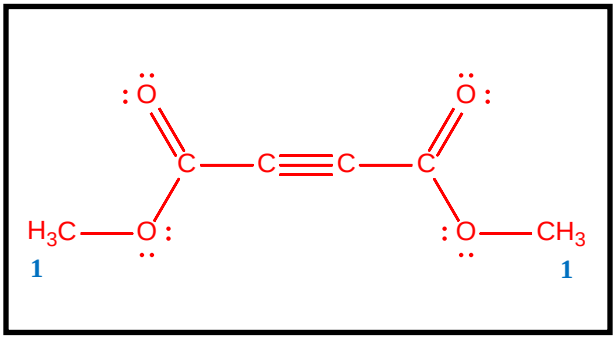
$C_6H_6O_4$



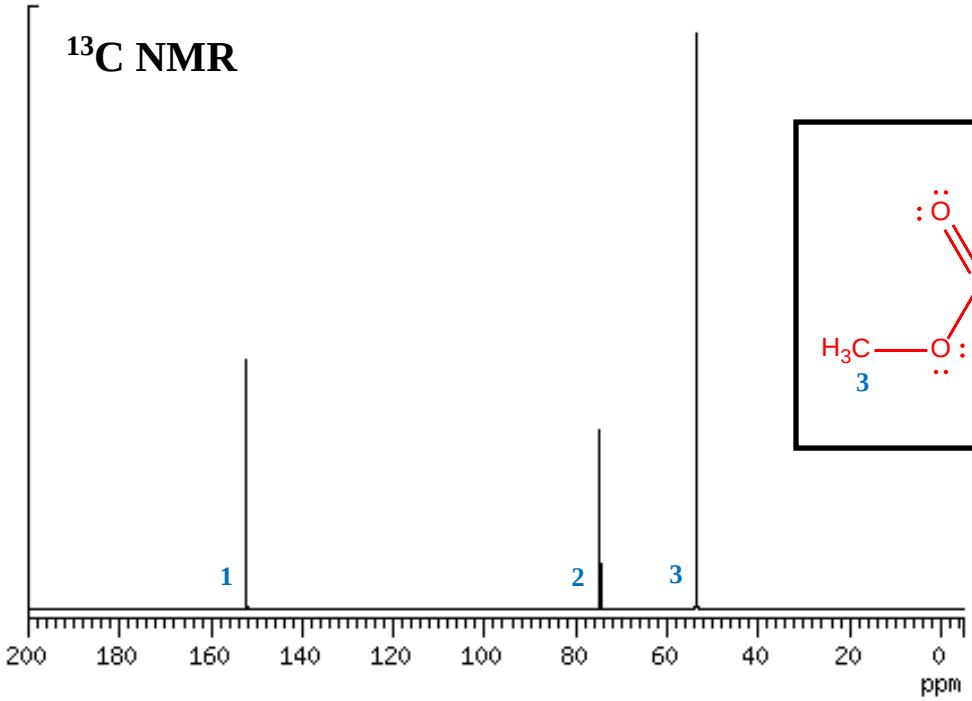
IR

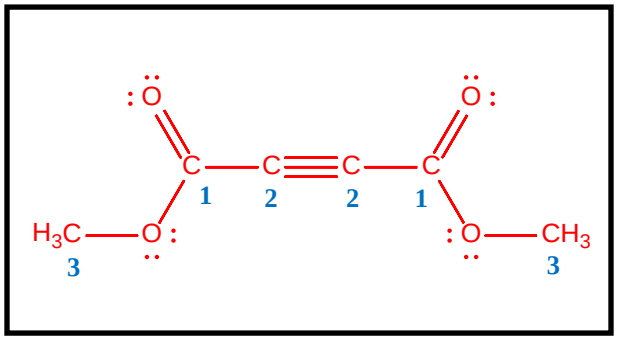
^{1}H NMR





^{13}C NMR





NAME:_____ Section:_____ Student Number:_____

CHEM 1000 Standard Periodic Table

1												13	14	15	16	17	18
1.0079 **H** 1	**2**																4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Nh** 113	(289) **Fl** 114	(288) **Mc** 115	(293) **Lv** 116	(294) **Ts** 117	(294) **Og** 118

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2016)