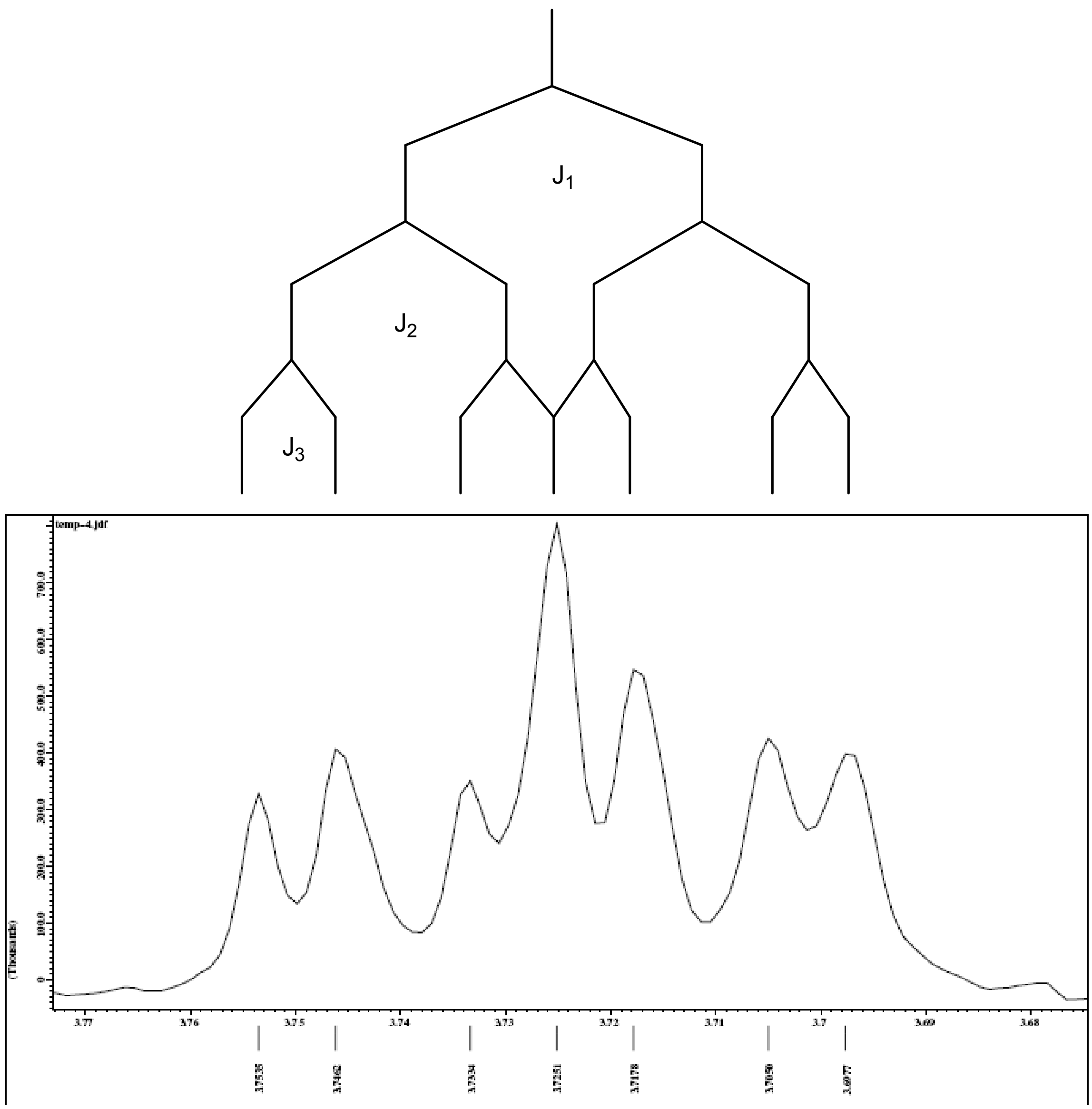
381 Homework Set - Key **Name: ______________________________**
Due Monday, April 27, 2009

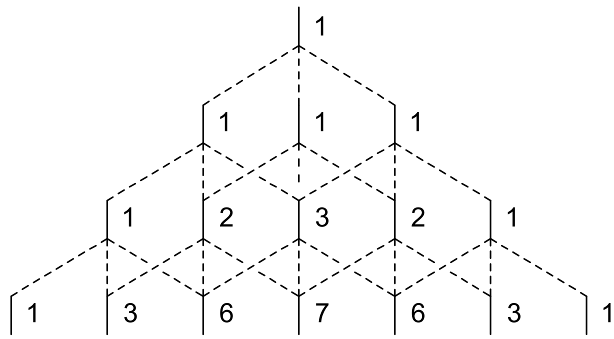
Write all your answers on a separate answer sheet. Clearly and fully label your answers.

1.



Remember to multiply the peak difference in ppm by 400 Hz/ppm to get the value in Hz.

2. relative intensities are shown



3. Below are a number of transition metal complexes. Give a valence electron count for each of the complexes. For the octahedral complexes (those with six ligands), predict whether the complex is high or low field. Also, for the octahedral complexes draw out the *d*-orbitals and show the electronic configuration.

$V(CO)_6$ – 5 + 6×2 = 17 (5 d electrons, high field)

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$Pt(PtBu_3)_2$ – 10 + 2×2 = 14

$W(CO)_3[P(C_6H_{11})_3]_2$ (C_6H_{11} = cyclohexyl) – 6 + 5×2 = 16

$CrCl_3(THF)_3$ (THF = tetrahydrofuran, acts like water as a ligand) – 6 + 3×1 + 3×2 = 15
(6 d electrons, low field)

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$[Cu(H_2O)_6]^{2+}$ - 11 + 6×2 − 2 = 21 (9 d electrons, low field – but it doesn't matter)

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$[PtCl_4]^{2-}$ - 10 + 4×1 − (−2) = 16

$[Fe(CN)_6]^{4-}$ - 8 + 6×1 − (−4) = 18 (6 d electrons, high field)

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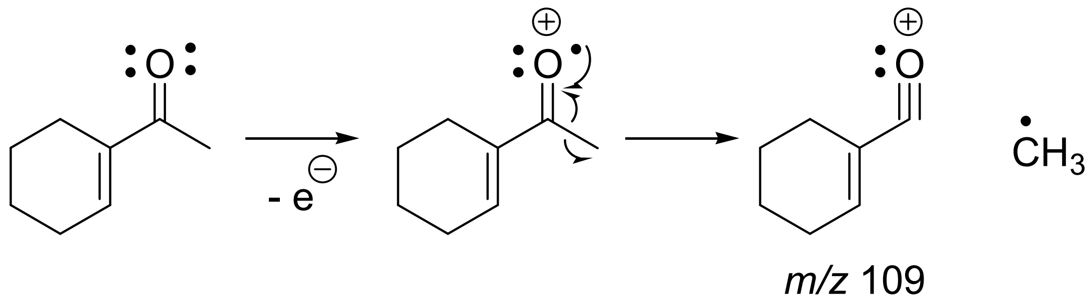
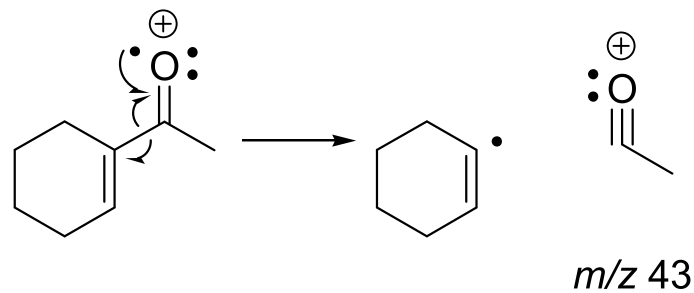
$[PtCl_3(\eta^2\text{-}C_2H_4)]^{1-}$ - 10 + 3×1 + 1×2 − (−1) = 16

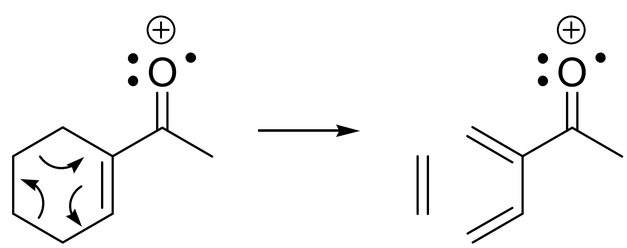
4. Remember that the fragmentation mechanisms must *exactly* explain the products. Every electron and changed bond must be described by your mechanism arrows.

Two oversized examples





The Diels-Alder is nothing special. Several answers are possible. All correct answers are a single step and lead to the exact product.



5. All the lines intersect at 50% conversion. Half the material (0.50 mol) is product and half the material (0.50 mol) is starting material. For E = 5, the starting material and product lines intersect at roughly 50% e.e. An e.e. of 50% corresponds to a 3:1 ratio of enantiomer. For the product, the *R*-enantiomer predominates. So, the product at 50% conversion and 50% e.e. is a mixture of 0.375 mol *R*-alcohol and 0.125 mol *S*-alcohol. Similarly, for the starting material, the *S*-ester predominates, with 0.375 mol *S*-ester and 0.125 mol *R*-ester.

In total, we have accounted for a full 1.0 mol of material (0.375 mol *R*-alcohol, 0.125 mol *S*-alcohol, 0.375 mol *S*-ester, and 0.125 *R*-ester).

Parts B and C and be taken from either the graphs (harder) or from the Excel spreadsheets (easier).

In part B, the E = 5 and E = 10 enzymes never have a product with an e.e. of 0.90, so the question is non valid for these cases. For E = 25, the product has an e.e. of at least 0.90 until about 30% conversion – so potentially 30% yield of *R*-alcohol with an e.e. of at least 0.90.

In part C, all enzymes do have a starting material line that reaches at least 90% e.e. at some point in the reaction. For E = 5, the starting material hits 0.90 e.e. at around 75% conversion, or 25% unreacted starting material. So, this would be a 25% yield. For E = 10, the starting material hits 0.90 e.e. at about 61% conversion – a 39% yield. For E = 25, it happens at around 53% conversion – a 47% yield.