

Name: _____

CHEM 322. Midterm 2
Spring 2011
Prof Donald Watson, Prof Mary Watson

Please write your answers clearly in the boxes provided. If your answer is illegible or outside the box, it will not be graded. You may use the back of test pages for scratch work.

You may use molecular models.

Use of calculators, cell phones, headphones, or any other electronic device during this exam is prohibited.

No notes or books may be used during this exam. Tables of spectral data and a periodic table are provided on page 14 of this exam.

You may raise your hand to ask a question if you are not sure what is being asked of you.

There are 16 pages in this exam. Please check that your test has 16 pages before you begin. The last 2 pages are blank and may be used as scratch paper.

Please circle your lab section:

Mon 12:20–3:20 (Amber, 031)

Mon 3:35–6:35 (Tatsiana, 032)

Mon 7–10 (Craig, 033)

Tues 9:30–12:30 (Srimoyee, 020)

Tues 12:30–3:30 (Neo, 021)

Tues 3:30–6:30 (Peter, 022)

Tues 7–10 (Peter, 023)

Wed 12:20–3:20 (Tatsiana, 034)

Wed 7–10 (Tatsiana, 035)

Thurs 9:30–12:30 (Srimoyee, 024)

Thurs 12:30–3:30 (Neo, 026)

Thurs 3:35–6:35 (Srimoyee, 027)

Thurs 7–10 (Neo, 030)

Fri 9:05–12:05 (Amber, 036)

Fri 12:20–3:20 (Amber, 028)

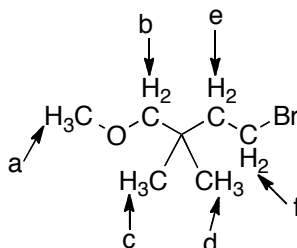
Fri 3:35–6:35 (Jesse, 025)

Fri 7–10 (Jesse, 039)

| Question | Points |
|--------------|-----------|
| 1 | ____ /8 |
| 2 | ____ /10 |
| 3 | ____ /6 |
| 4 | ____ /8 |
| 5 | ____ /10 |
| 6 | ____ /20 |
| 7 | ____ /8 |
| 8 | ____ /8 |
| 9 | ____ /8 |
| 10 | ____ /14 |
| Total | ____ /100 |

Name: _____

1. (8 points) Consider the structure of 1-methoxy-2,2-dimethyl-4-bromobutane to answer the following questions.



(a) How many signals do you expect to see in the ^1H NMR spectrum?

(b) Which of the indicated protons should appear the furthest upfield?

(c) What should be the splitting pattern of the protons labeled **e** (singlet, doublet, etc)?

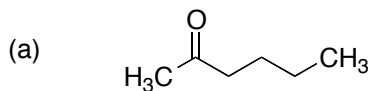
(d) What should be the splitting pattern of the protons labeled **a** (singlet, doublet, etc)?

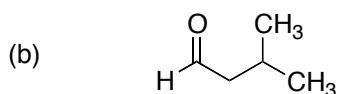
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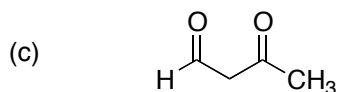
2. (10 points) Are H_a and H_b in the following molecules homotopic, enantiotopic or diastereotopic? Do you expect to see 1 or 2 signals corresponding to those protons in the 1H NMR spectrum?

| | Compound | Homotopic, enantiotopic or diastereotopic? | 1 or 2 signals? |
|-----|----------|--|-----------------|
| (a) | | | |
| (b) | | | |
| (c) | | | |
| (d) | | | |
| (e) | | | |

3. (6 points) Please provide the IUPAC names for each of the following molecules.

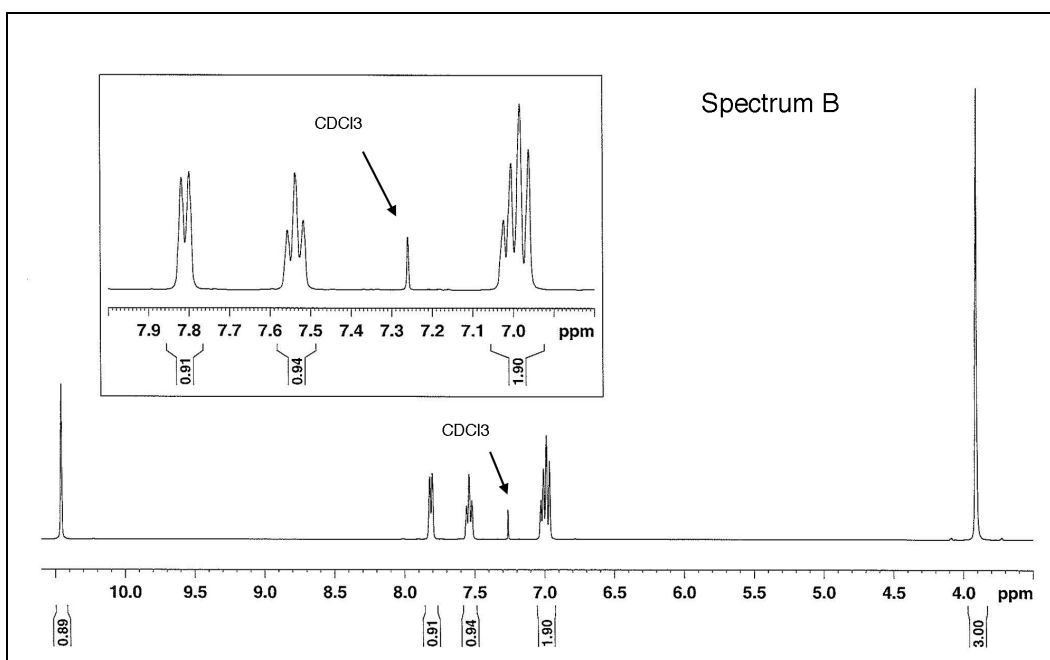
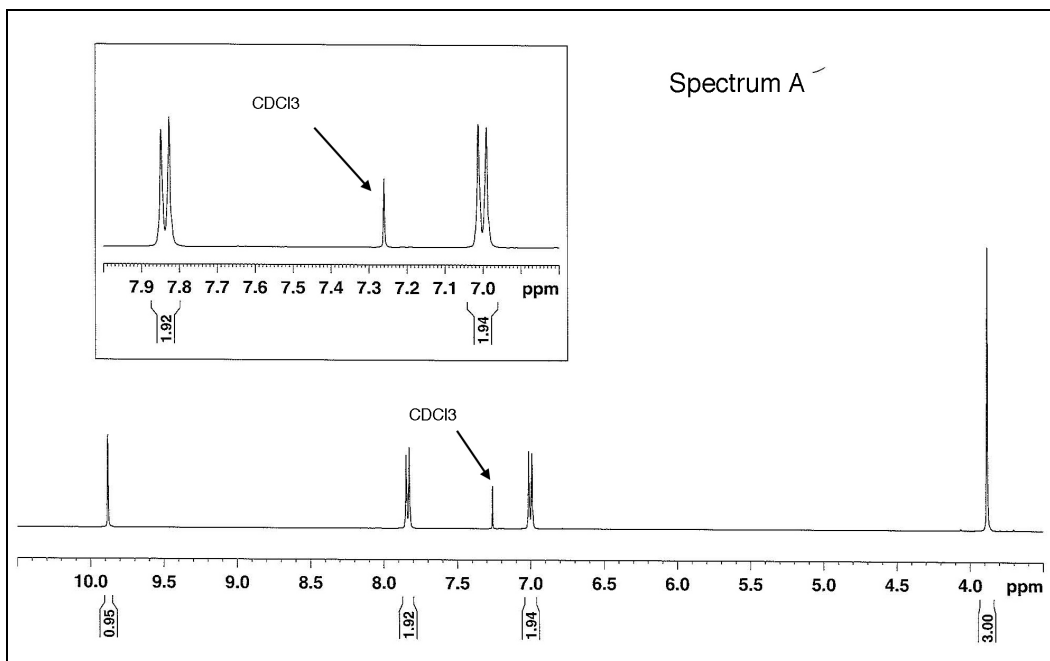
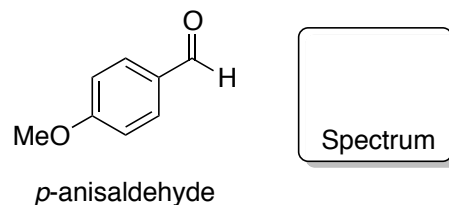
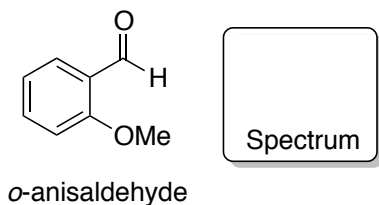






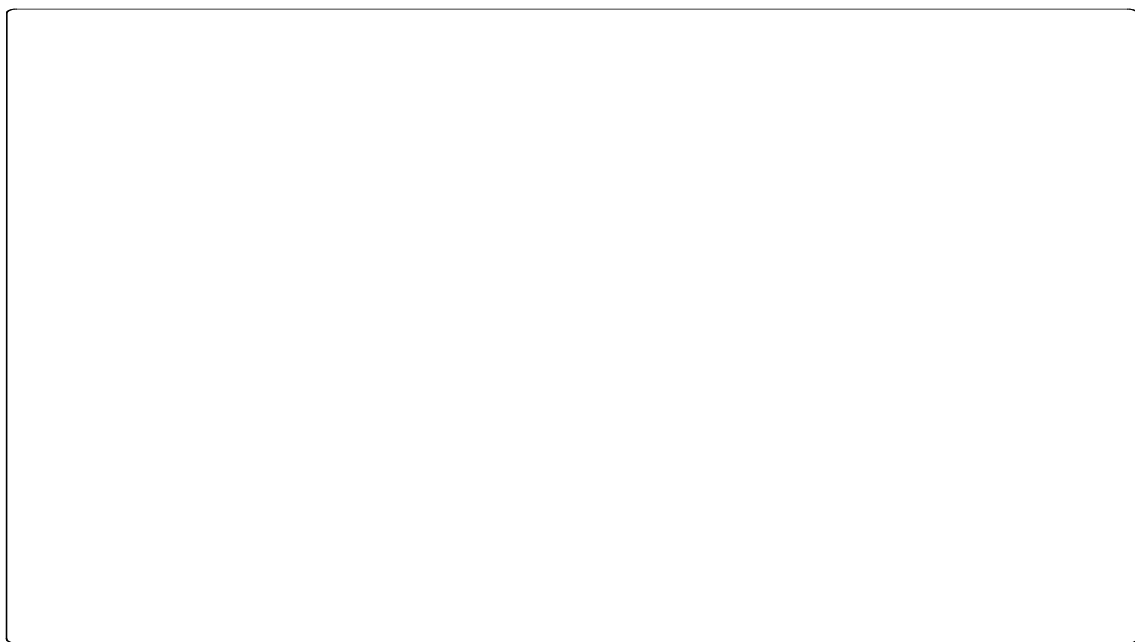
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4. (8 points) (a) Match *o*-anisaldehyde and *p*-anisaldehyde to the ^1H NMR spectra below (A or B). Write the letter of the spectrum in the box next to the structure,



Name: _____

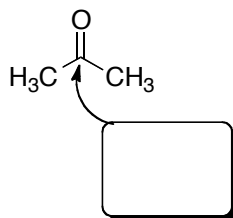
(b) Briefly (20 words or less), in the space below, explain how you determined which compound matched which spectrum.



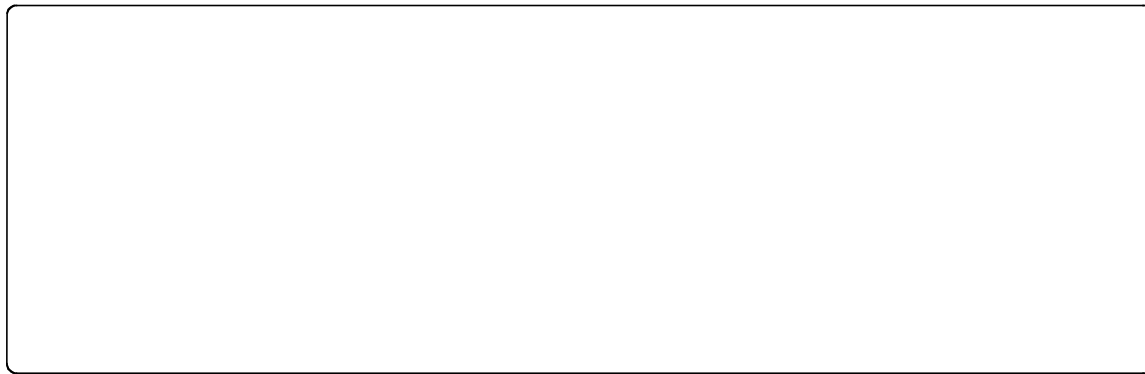
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5. (10 points)

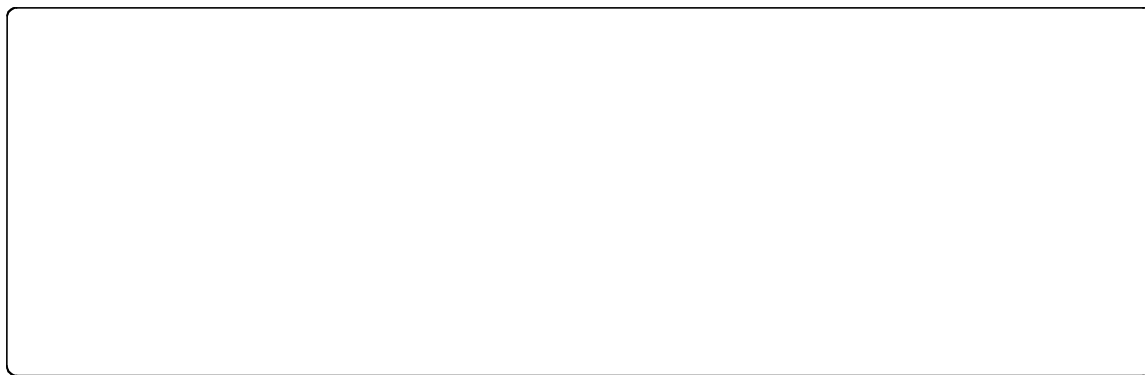
(a) In acetone, what is the hybridization of the carbonyl C?



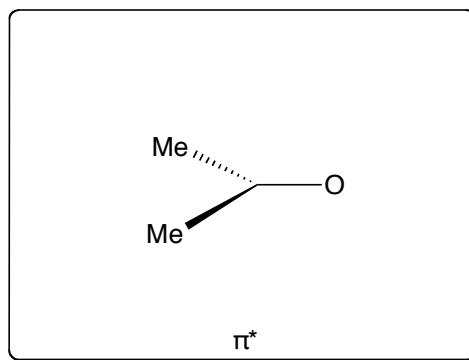
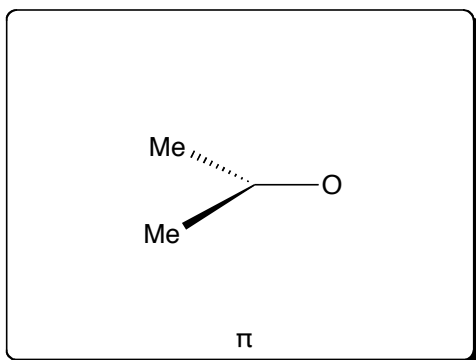
(b) Draw the major resonance structures of acetone.



(c) In a carbonyl fragment ($\text{C}=\text{O}$), which atom is electrophilic and which is nucleophilic?

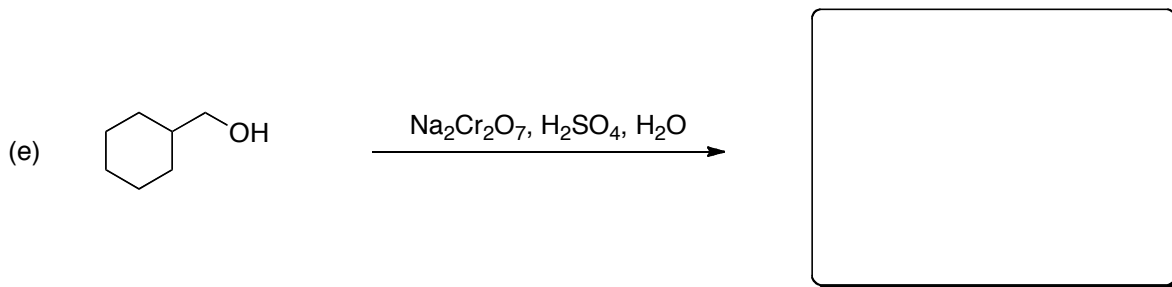
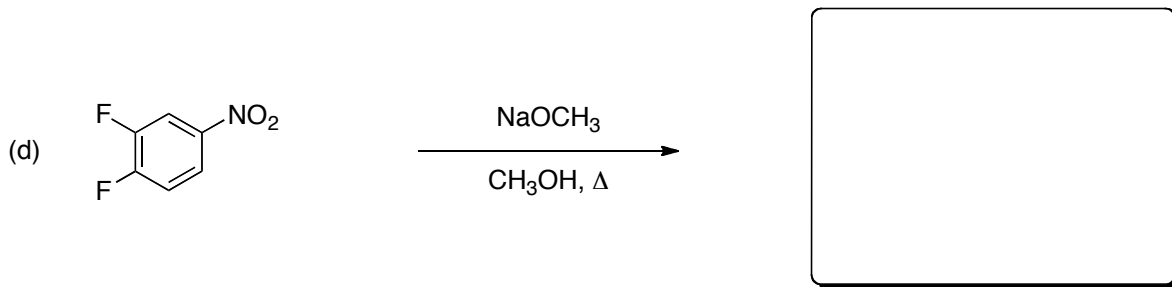
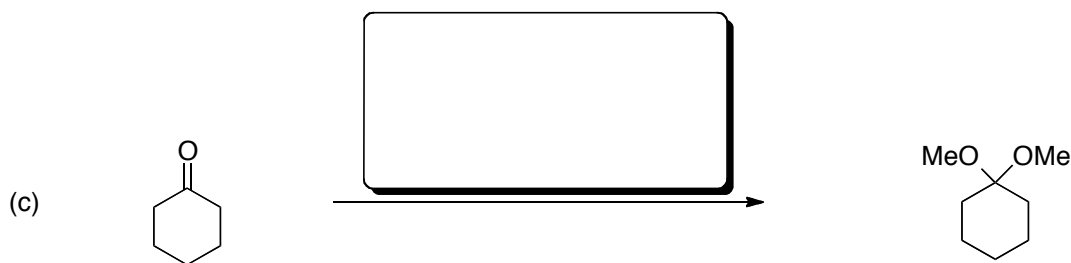
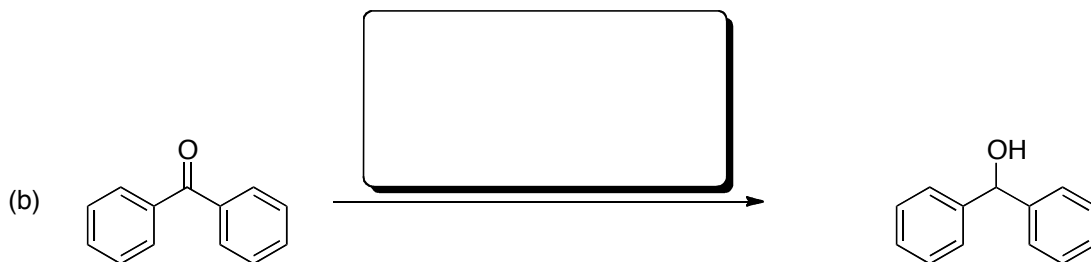
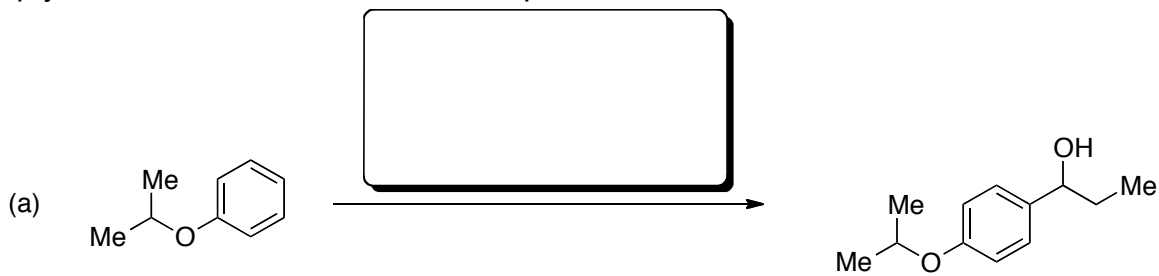


(d) On the partial structures below, draw a 3-D picture of the $\text{C}=\text{O}$ π and π^* molecular orbitals of acetone. Clearly indicate the geometry, phasing and relative sizes of the lobes.



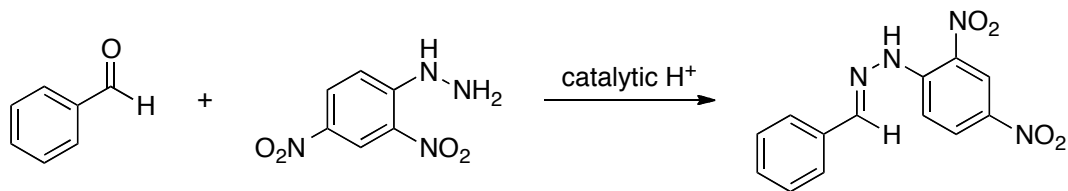
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6. (20 points) Please provide the missing reagent(s) or expected major product in the empty boxes below. If no reaction is expected, write "No Reaction."



Name: _____

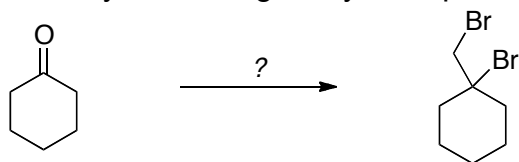
7. (8 points) Please draw a reasonable arrow-pushing mechanism for the following reaction.



Blank area for drawing the arrow-pushing mechanism.

Name: _____

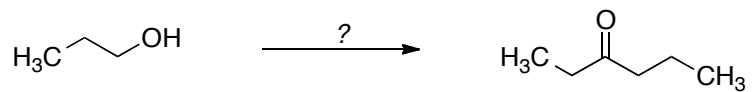
8. (8 points) Provide a synthesis of 1-bromo-1-bromomethylcyclohexane from cyclohexanone. You may use any other reagents you require.



A large empty rectangular box with rounded corners, intended for the student to write the synthesis procedure.

Name: _____

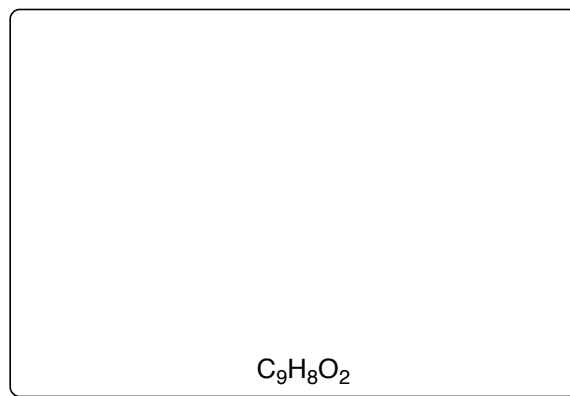
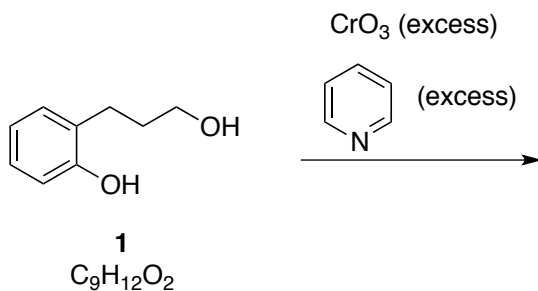
9. (8 points) Using 1-propanol as your only source of carbons, provide a synthesis of the 3-hexanone. You may use any inorganic reagents.



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10. (14 points) When diol **1** is treated with CrO_3 and pyridine, the product is *not* the product normally expected for this reaction. The product has a molecular formula of $\text{C}_9\text{H}_8\text{O}_2$. The ^1H NMR, ^{13}C NMR and IR spectra of the product are shown on the next page.

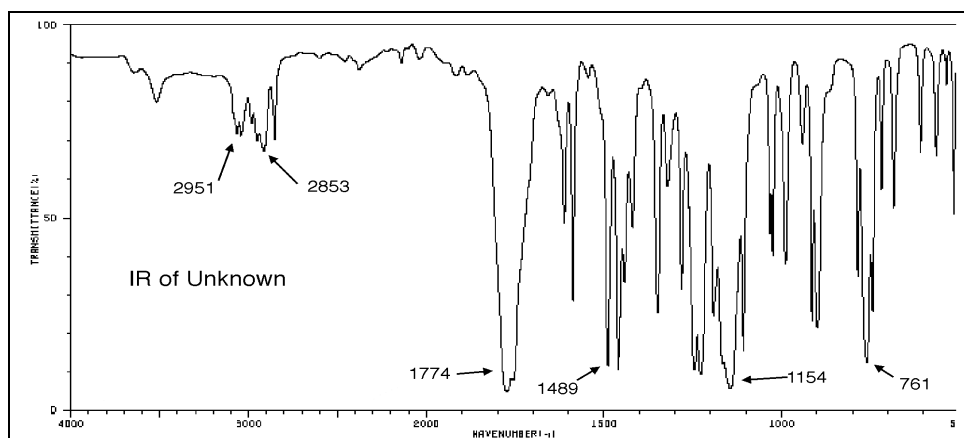
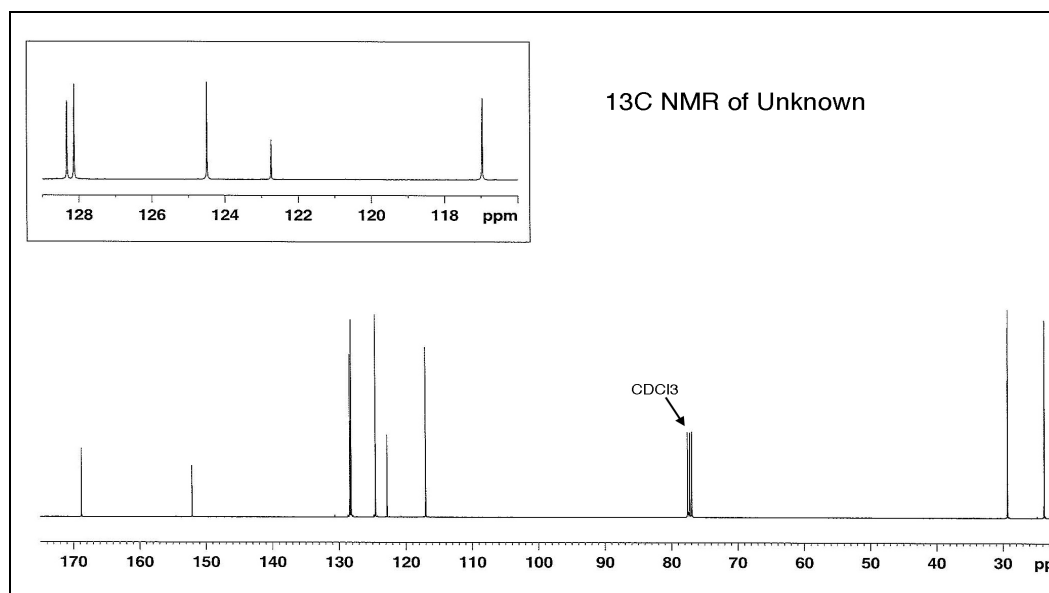
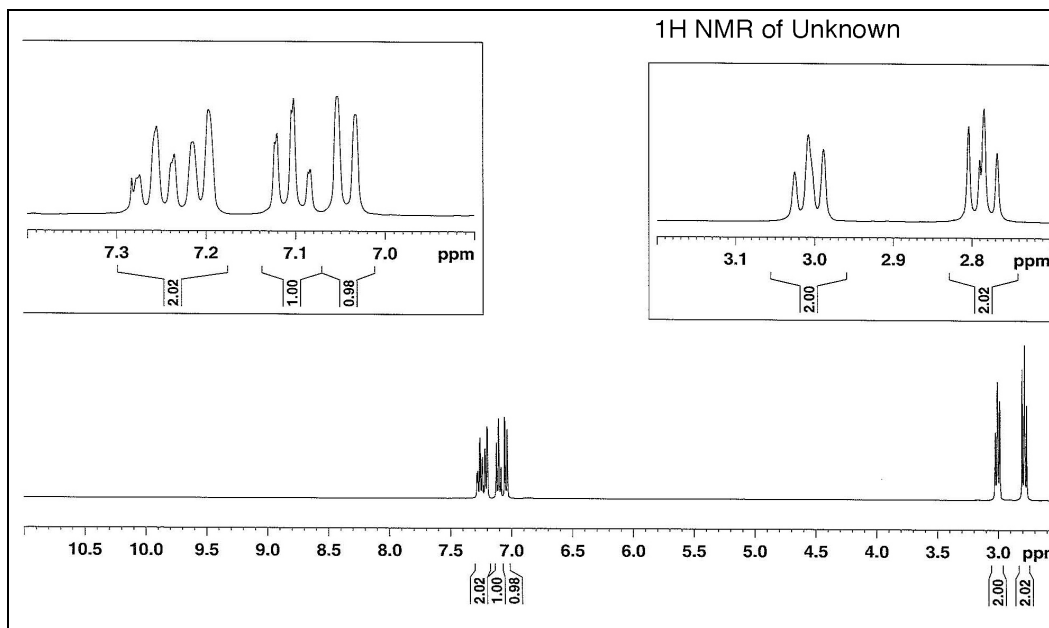
(a) Based on this information, please draw the product of this reaction.



(b) In the space below, briefly (20 words or less) explain how your proposed structure is consistent with the data.

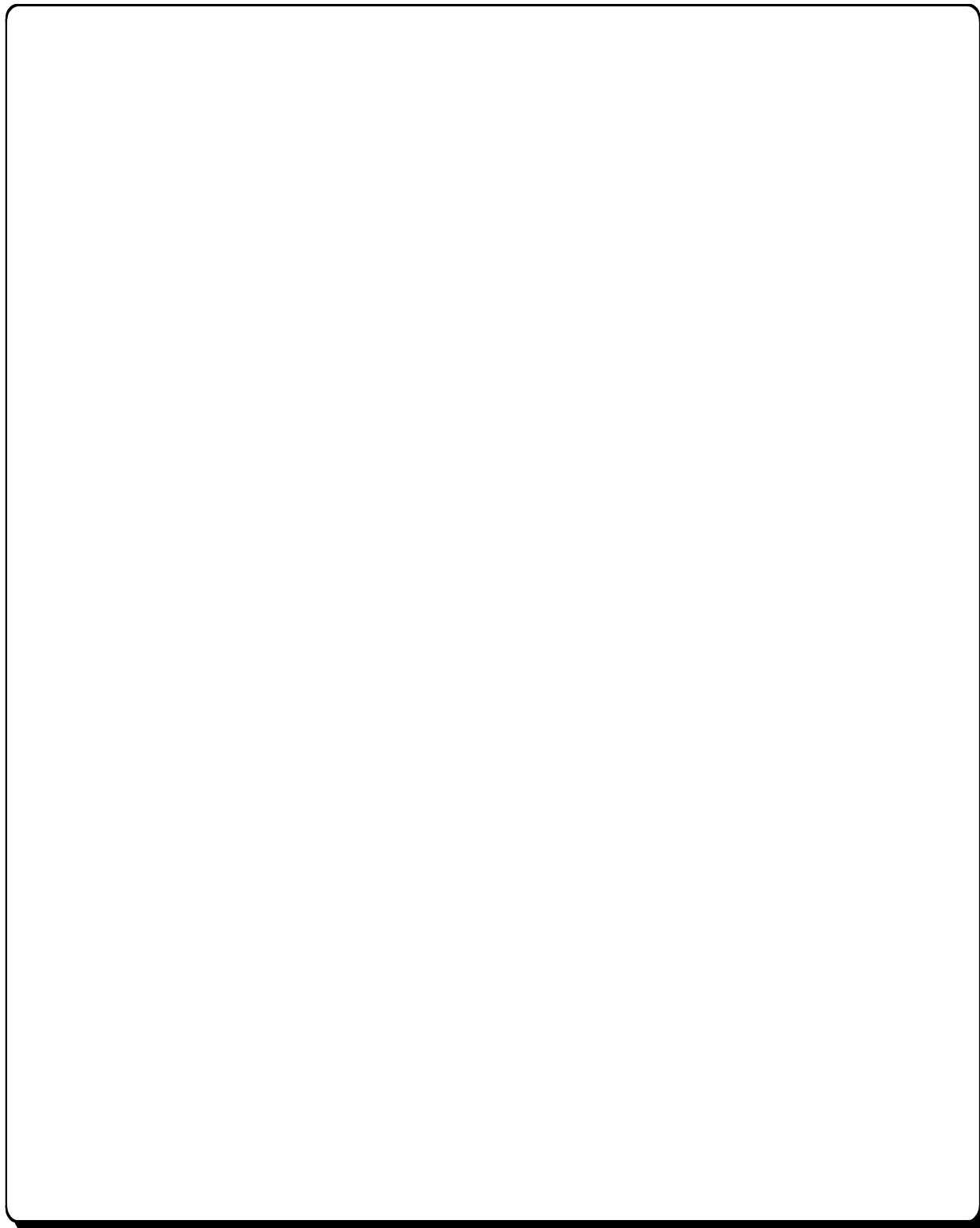
Empty space for explanation.

Name: _____



Name: _____

(c) Draw a reasonable arrow-pushing mechanism for the transformation of **1** to your proposed product.



Name: _____

Approximate IR Absorption Frequencies


| Bond | Frequency (cm ⁻¹) | Intensity |
|-----------------------|-------------------------------|--------------------|
| O-H (alcohol) | 3650–3200 | Strong, broad |
| O-H (carboxylic acid) | 3300–2500 | Strong, very broad |
| N-H | 3500–3300 | Medium, broad |
| C-H | 3300–2700 | Medium |
| C≡N | 2260–2220 | Medium |
| C≡C | 2260–2100 | Medium to weak |
| C=O | 1780–1650 | Strong |
| C-O | 1250–1050 | Strong |

Approximate ¹H NMR Chemical Shifts

| Hydrogen | δ (ppm) |
|----------------------------------|----------|
| CH ₃ | 0.8–1.0 |
| CH ₂ | 1.2–1.5 |
| CH | 1.4–1.7 |
| C=C-CH _x | 1.7–2.3 |
| O=C-CH _x | 2.0–2.7 |
| Ph-CH _x | 2.3–3.0 |
| ≡C-H | 2.5 |
| R ₂ N-CH _x | 2.0–2.7 |
| I-CH _x | 3.2 |
| Br-CH _x | 3.4 |
| Cl-CH _x | 3.5 |
| F-CH _x | 4.4 |
| O-CH _x | 3.2–3.8 |
| C=CH | 4.5–7.5 |
| Ar-H | 6.8–8.5 |
| O=CH | 9.0–10.0 |
| ROH | 1.0–5.5 |
| ArOH | 4.0–12.0 |
| RNH _x | 0.5–5.0 |
| CONH _x | 5.0–10.0 |
| RCOOH | 10–13 |

Approximate ¹³C NMR Chemical Shifts

| Carbon | δ (ppm) |
|-------------------------|---------|
| <i>Alkanes</i> | |
| Methyl | 0–30 |
| Methylene | 15–55 |
| Methine | 25–55 |
| Quaternary | 30–40 |
| <i>Alkenes</i> | |
| C=C | 80–145 |
| <i>Alkynes</i> | |
| C≡C | 70–90 |
| <i>Aromatics</i> | |
| Benzene | 128.7 |
| <i>Alcohols, Ethers</i> | |
| C-O | 50–90 |
| <i>Amines</i> | |
| C-N | 40–60 |
| <i>Halogens</i> | |
| C-F | 70–80 |
| C-Cl | 25–50 |
| C-Br | 10–40 |
| C-I | -20–10 |
| <i>Carbonyls, C=O</i> | |
| R ₂ C=O | 190–220 |
| RXC=O (X = O or N) | 150–180 |



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|------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1 | 1 | | | | | | | | | | | | | | | 18 | | |
| 1 | H | | | | | | | | | | | | | | | He | | |
| 2 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | | |
| 2 | Li | Be | | | | | | | | | | B | C | N | O | F | Ne | |
| 3 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | | |
| 3 | Na | Mg | | | | | | | | | | Al | Si | P | S | Cl | Ar | |
| 4 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| 5 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| 6 | Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
| 7 | Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | |
| 8 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 |
| 8 | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | | | |
| 9 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 |
| 9 | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | | | |

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