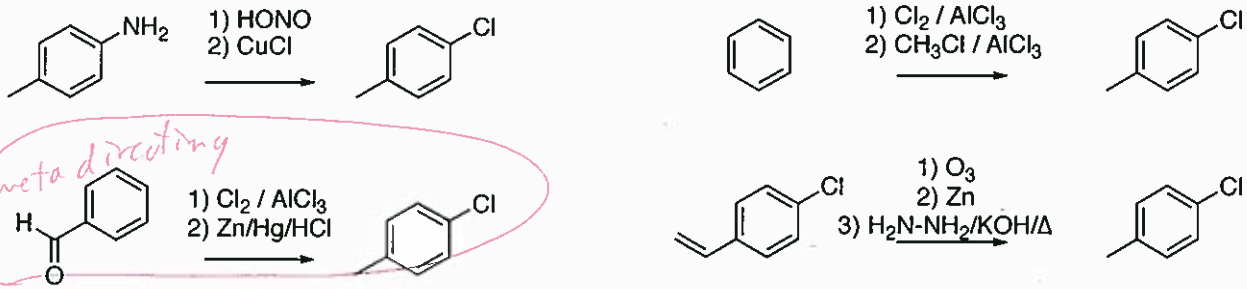
CHEM 3306 Organic Chemistry II
Exam 2, 25 points

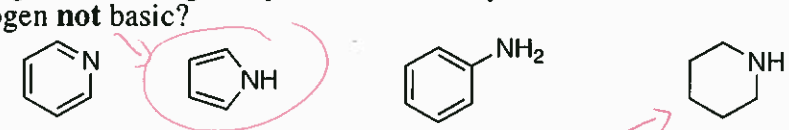
Name Answer key
In class, Monday, March 5, 2008

1. (3 points) Which substituent is **not** ortho, para-directing?

2. (3 points) Which reaction will **not** give the indicated product as the major product?

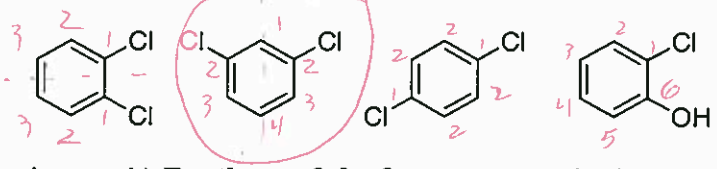


3. (3 points) Nitrogen containing compounds are usually Brönstead bases. In which compound below is the nitrogen **not** basic?



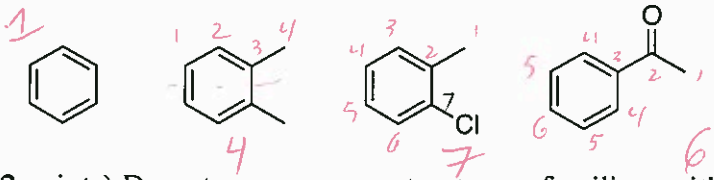
4. (3 points) Which compound above is **non-aromatic**?

5. (3 points) Which compound has peaks only at 127.0, 128.9, 130.6 and 135.1 ppm in its ^{13}C-NMR spectrum?

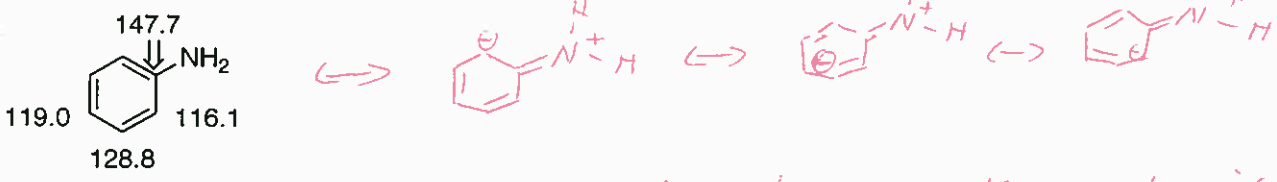


2

6. (6 points total, ~~3~~ points each) For **three of the four** compounds shown below, indicate how many peaks should be seen in the ^{13}C-NMR spectrum.

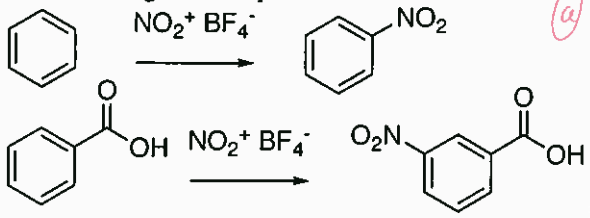


7. (6 points total) a. (2 points) Draw two resonance structures of aniline, with four bonds to the nitrogen, and a positive charge on the nitrogen.
b. (4 points) Use these resonance structures to explain the trends in the ^{13}C-NMR chemical shifts of aniline as compared to benzene (128.5 ppm).

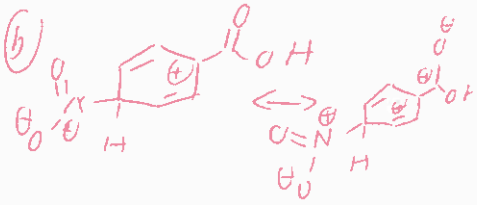


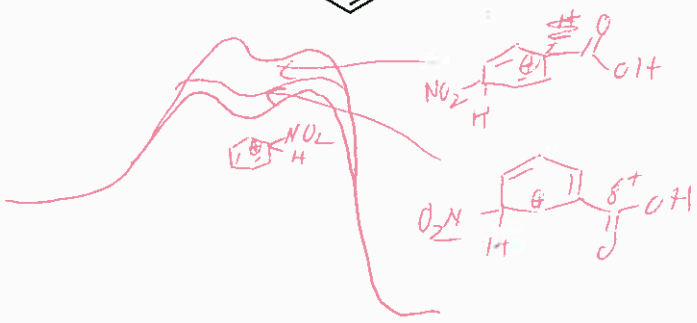
b 147.7 ppm is downfield because the carbon is bonded to nitrogen, an electronegative element. also, it is quartenary. 116.1 and 119.0 are upfield as compared to benzene, because of the negative charge from the resonance structures. 128.8 is unchanged from benzene.

8. (12 points total) a. (2 point) Draw the intermediate in the nitration of benzene.
b. (4 points) Nitration of benzoic acid gives the meta product, as shown below. Draw the intermediate you would get for the **para** product showing the resonance structure that **disfavors** the **para** product.
c. (6 points) Draw an energy vs. reaction coordinate diagram comparing the nitration of benzene with that of benzoic acid. Use it to explain why the carboxylic acid group (-CO_2H) in benzoic is deactivating as compared to benzene.



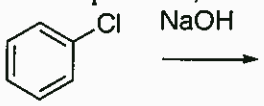
(a) 

(b) 

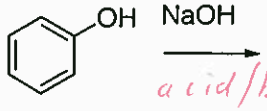


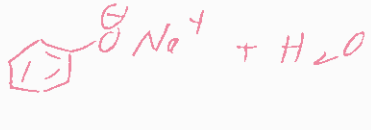
since the intermediates in nitration of benzoic acid are destabilized relative to the intermediate in benzene, the barrier to making them is higher and the reaction is slower

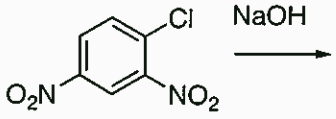
9. (8 points total, 2 points each) Predict the product of **each** reaction below. For **one and only one** of the equations, there will be no reaction.

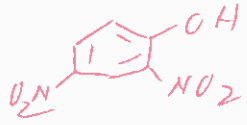


N.R.



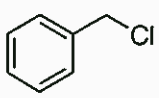
acid/base 





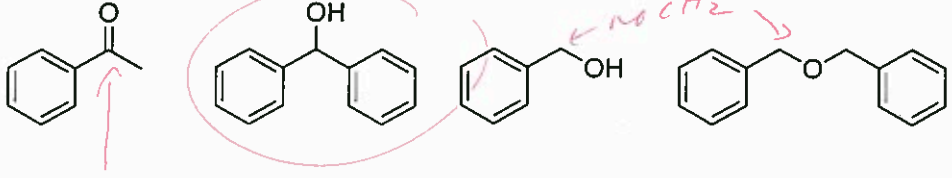
+ HCl

~~electrophilic~~ nucleophilic aromatic substitution



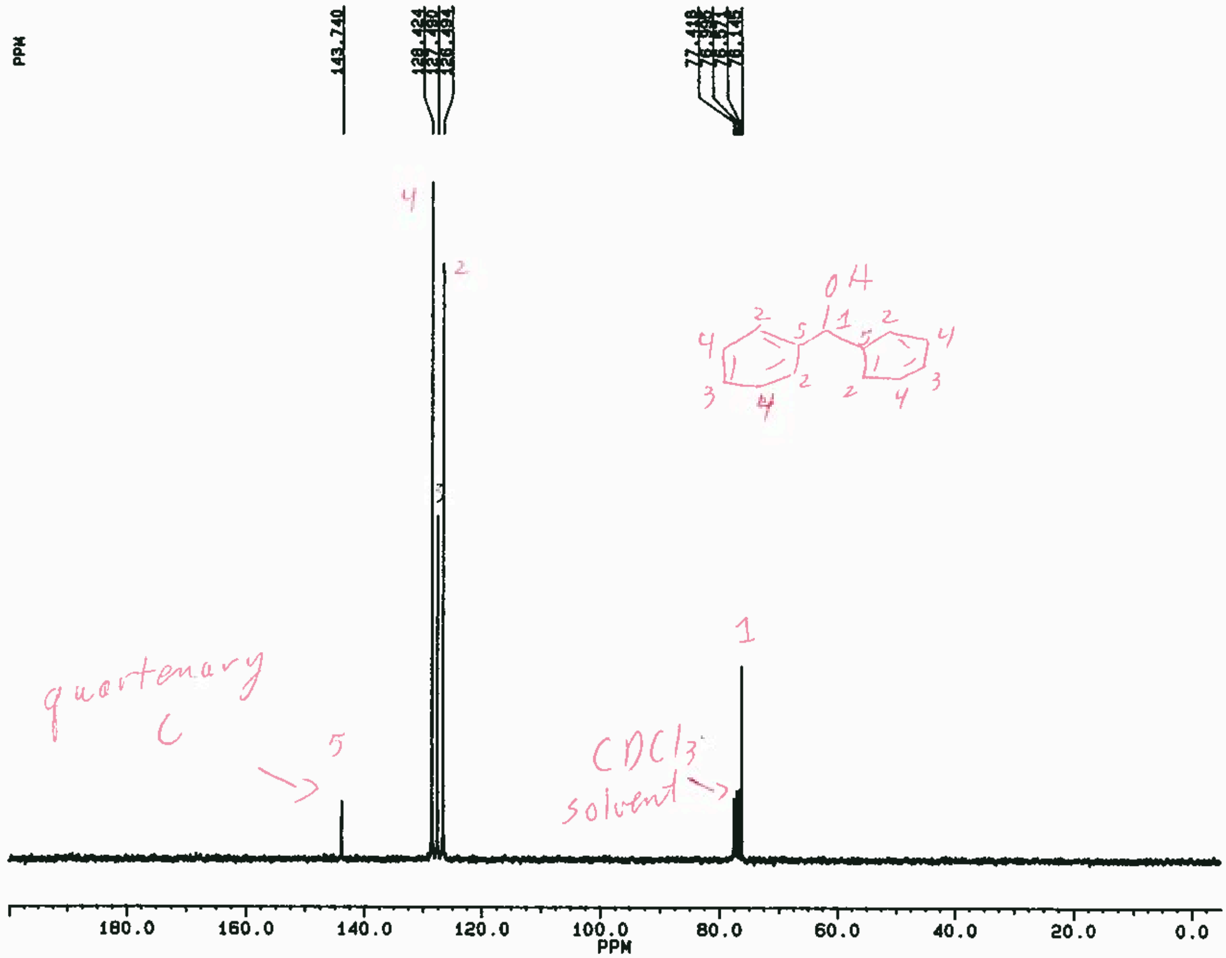
SN2 

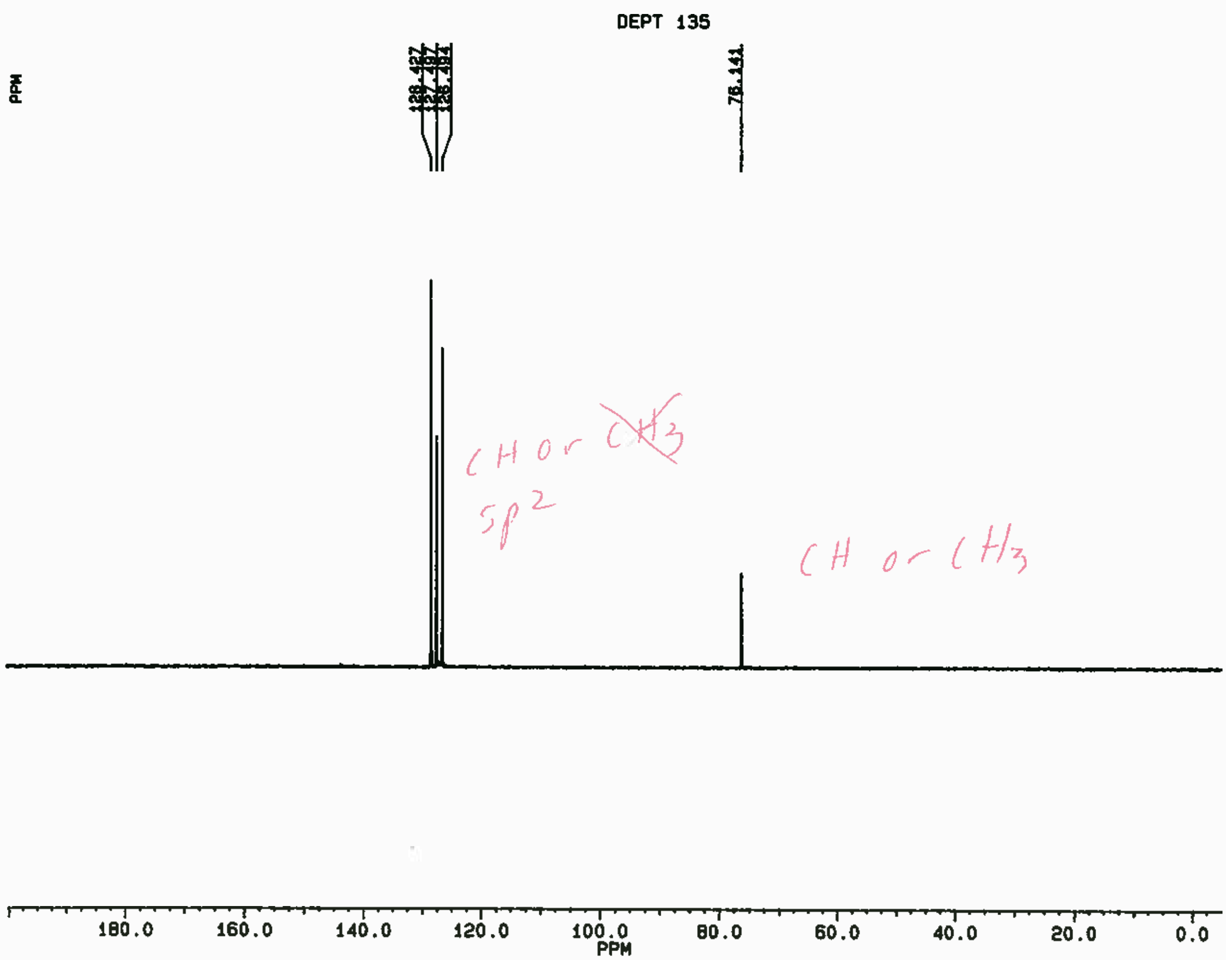
10. (6 points) On the next page is a ^{13}C-NMR and a DEPT-135 spectrum. Which compound is compatible with these spectra? Briefly explain your reasoning.



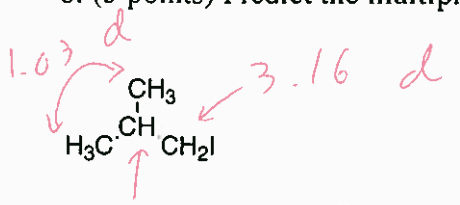
no CH_2

no carbonyl

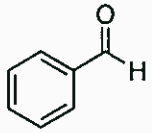

PPM
143.740
128.424
77.418
quartenary C
5
4
2
OH
CDCl3 solvent
1
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
PPM


DEPT 135
PPM
128.427
76.141
CH or CH3
sp2
CH or CH3
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
PPM

11. (7 points total) a. (4 points) Assign these chemical shifts (3.16, 1.72, 1.03 ppm) to the hydrogens in 1-iodo-2-methylpropane.
b. (3 points) Predict the multiplicity (singlet, doublet, triplet, etc.) of the peaks.



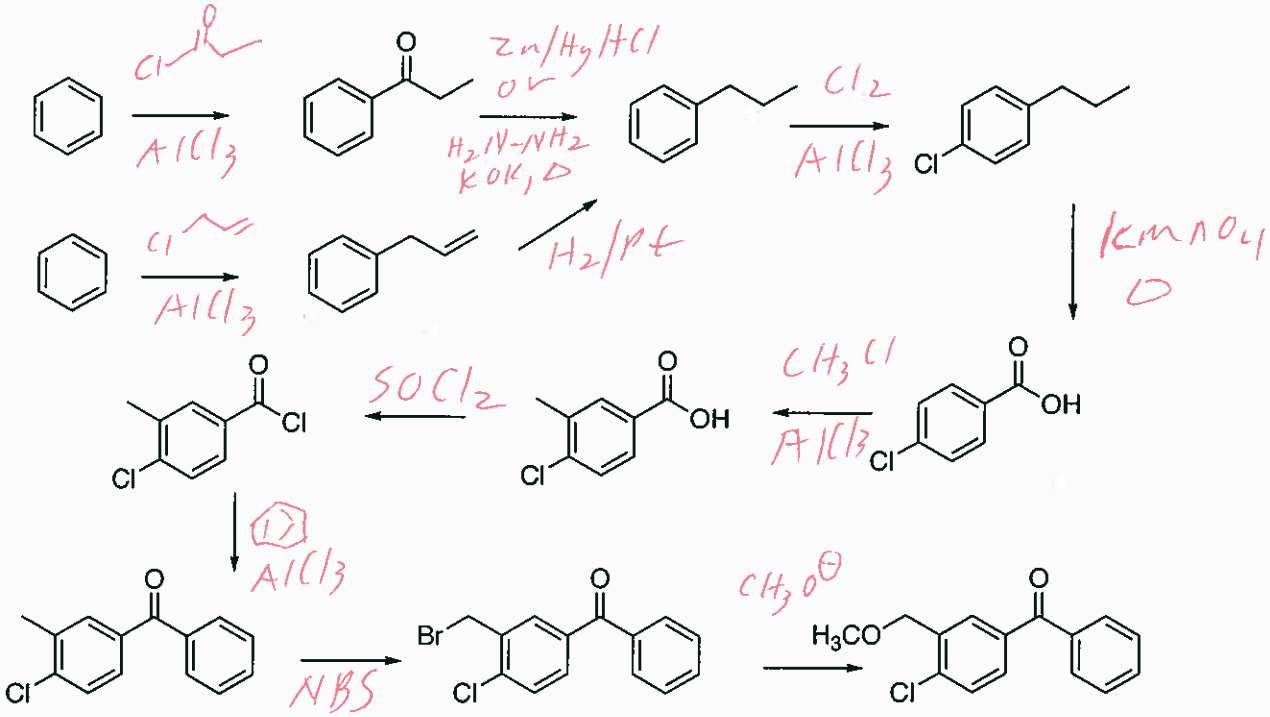
12. (10 points total) On the next page are the ^{1}H-NMR and ^{13}C-NMR spectra of benzaldehyde. Impurities are marked with an X.



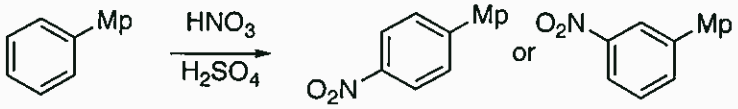
a. (2 points) What compound gives rise to the three peaks at 77.42, 76.99 and 76.57 ppm in the ^{13}C-NMR spectrum?

b. (8 points) Assign all of the peaks in the ^{1}H-NMR and ^{13}C-NMR spectra.

13. (12 points total) Suggest reagents for **six of the eleven** of the reaction arrows below.



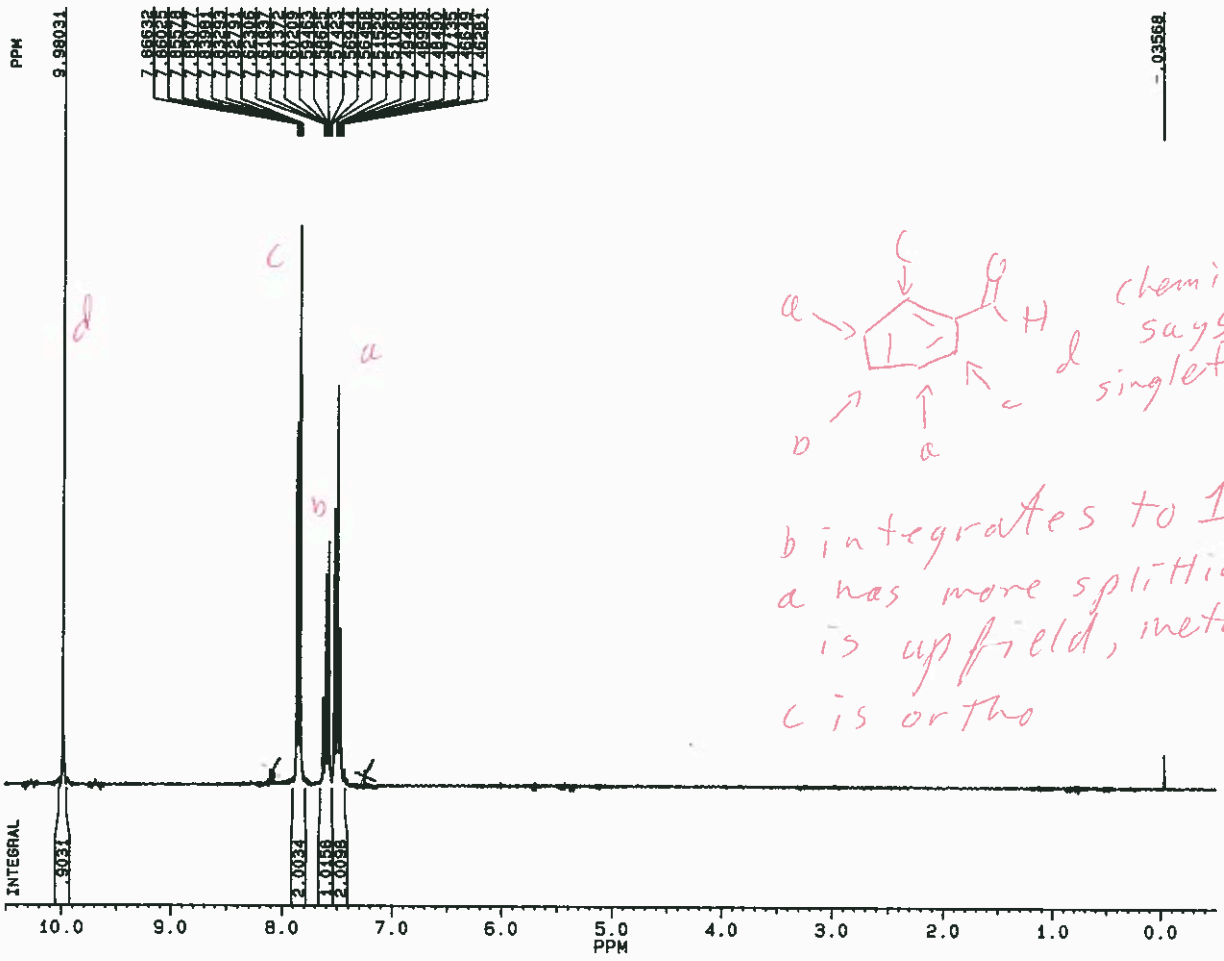
Extra Credit (4 points) You have just discovered a new functional group, abbreviated Mp. You want to learn whether it is ortho-para or meta directing, so you run a nitration and isolate a single product. Suggest an experiment to decide which product you obtained.



^{13}C or ^{1}H NMR

^{13}C 4 peaks 6 peaks

^{1}H two d d Singlet, 2 d, a triplet

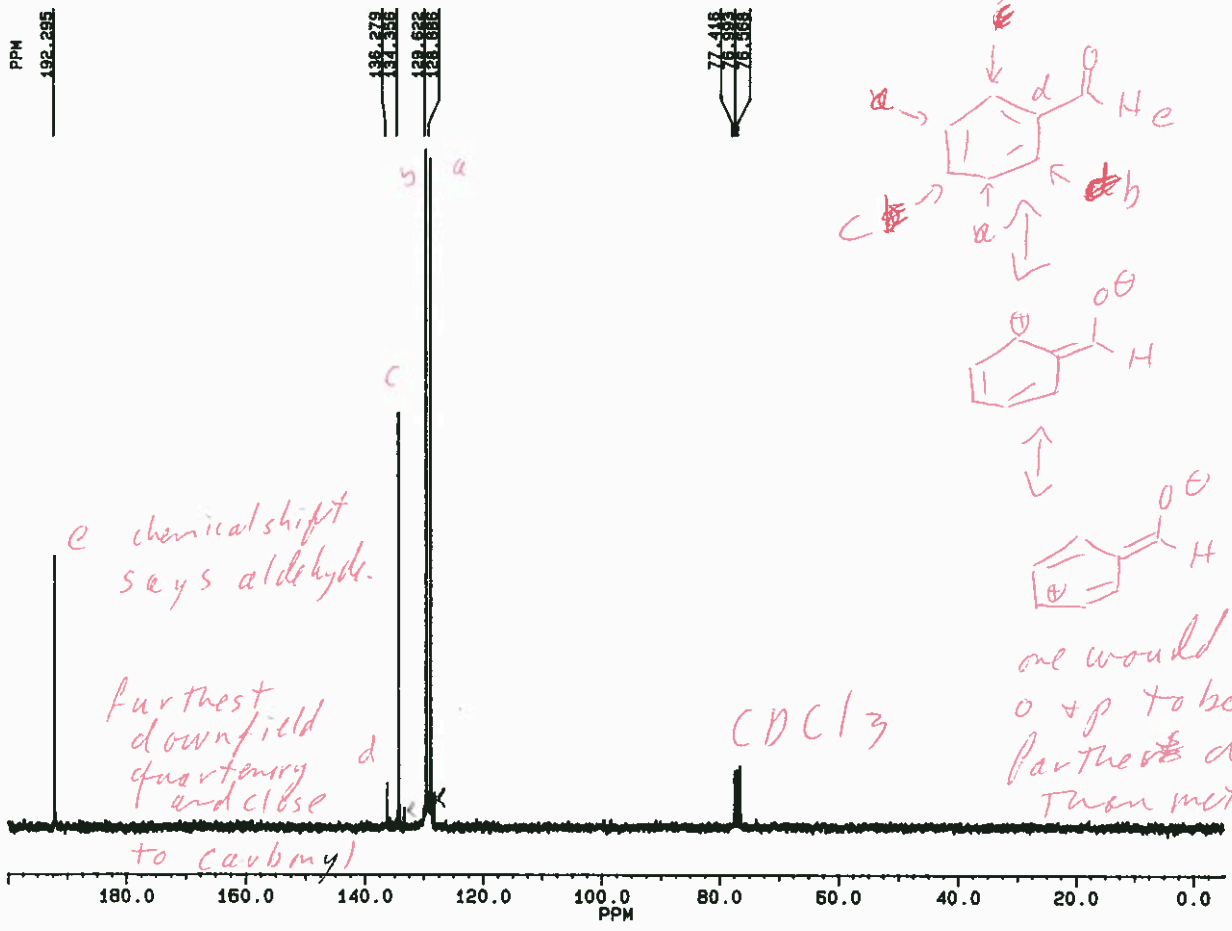


d chemical shift says aldehyde. singlet

b integrates to 1 ⇒ para

a has more splitting and is upfield, meta

c is ortho

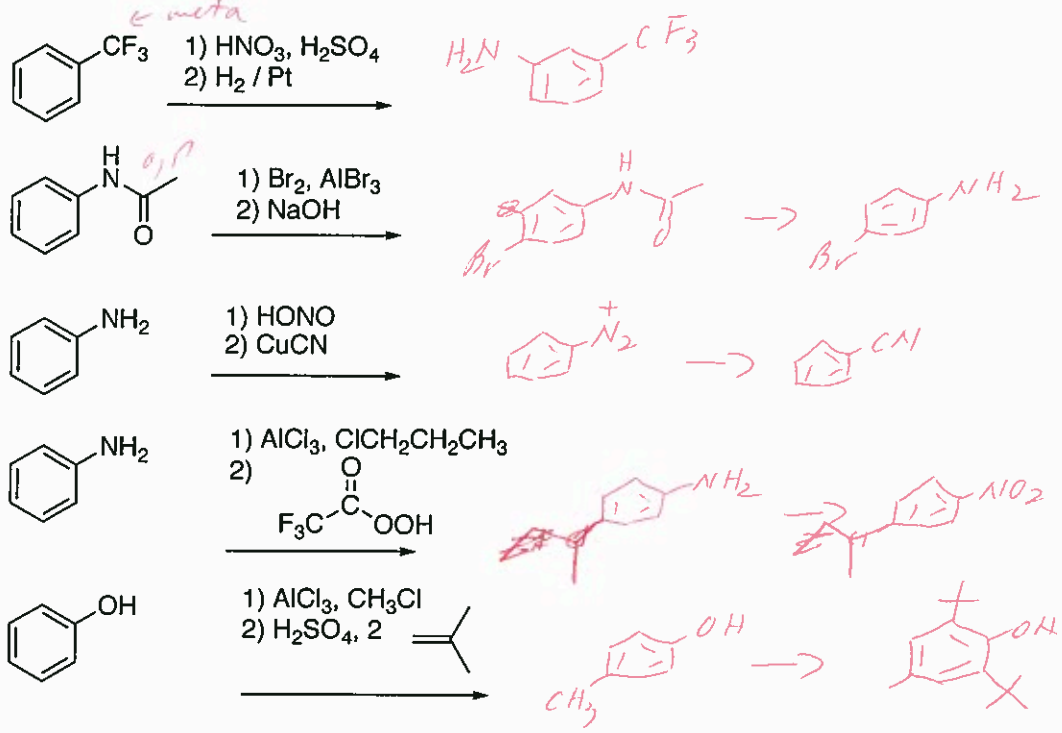


e chemical shift says aldehyde.

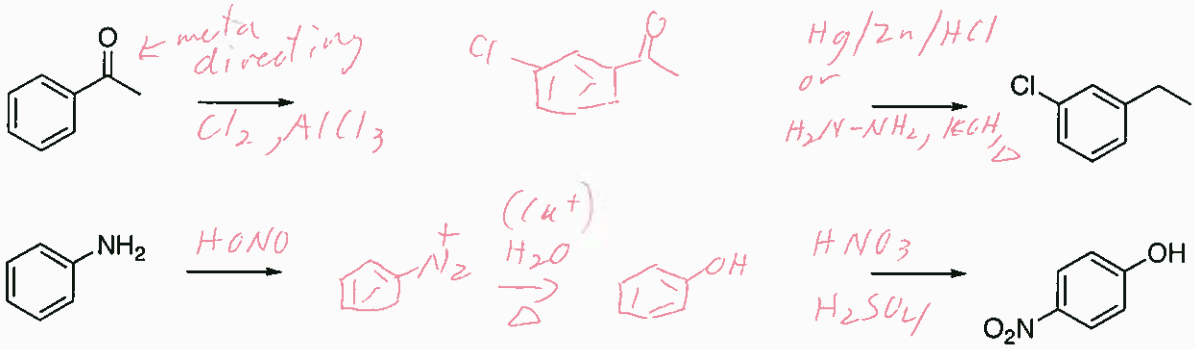
Furthest downfield quartenary and close to carbonyl

one would expect o + p to be farthest downfield from meta.

14. (12 points total, 4 points each) Predict the product of **three of the five** reactions below. (The last product is BHT (butylated hydroxytoluene, used as a free radical inhibitor and a preservative in food packaging.)



15. (6 points) For **one of the two** sequences, suggest a method for making the indicated product. We have not learned a way to do this in one step, but you know chemistry to do each in two or three steps. Show the intermediate product(s) as well.



Extra Credit (4 points) One of the steps in the formation of lignin (in woody plants) involves this reaction. Suggest a simple catalyst for this reaction. Why does the new bond form where it does on the aromatic ring?