N G R D

*Exam 2*
**Chem 22**
March 10, 2010

*Name* Gary Snyder

page **1** (25) _____
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**5** (40) _____
**6** (25) _____
**7** (15) _____

_____ total (200)

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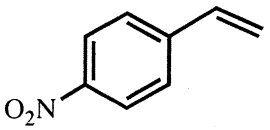
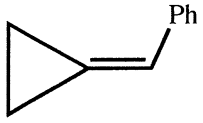
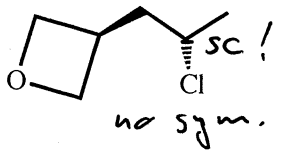
No scribbling in this space, please.

**1.** (18 points) For each compound below, how many separate signals would you expect to see in a room-temperature proton-decoupled $^{13}$C NMR spectrum, and how many in a $^{1}$H NMR spectrum?

3 pts each

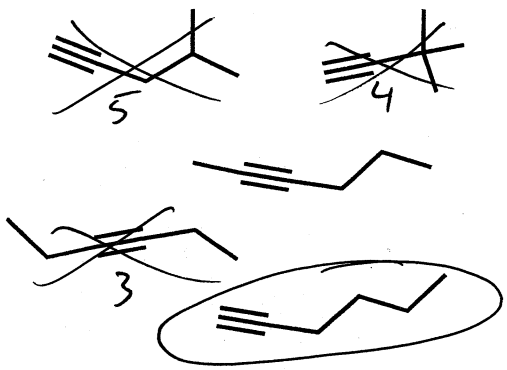


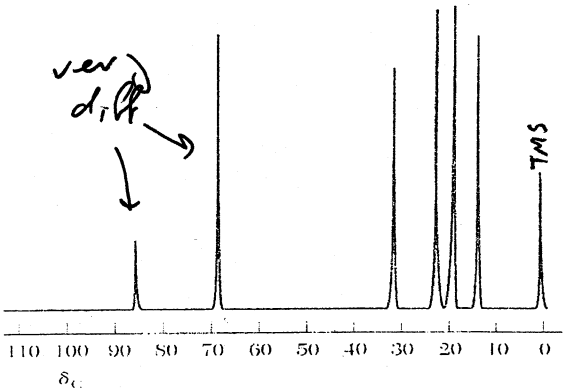




| | | | |
|---|---|---|---|
| # $^{13}$C NMR signals: | 6 | 8 | 6 |
| # $^{1}$H NMR signals: | 5 | 6 | 9 |

**2.** (7 points) The proton-decoupled $^{13}$C NMR spectrum below belongs to *one* of the alkynes shown. (a) Draw an **X** through each alkyne that is ruled out based on the *number* of NMR signals.




(b) Circle the alkyne that you believe is most likely responsible for the spectrum. (You do not need a table of chemical shifts.)

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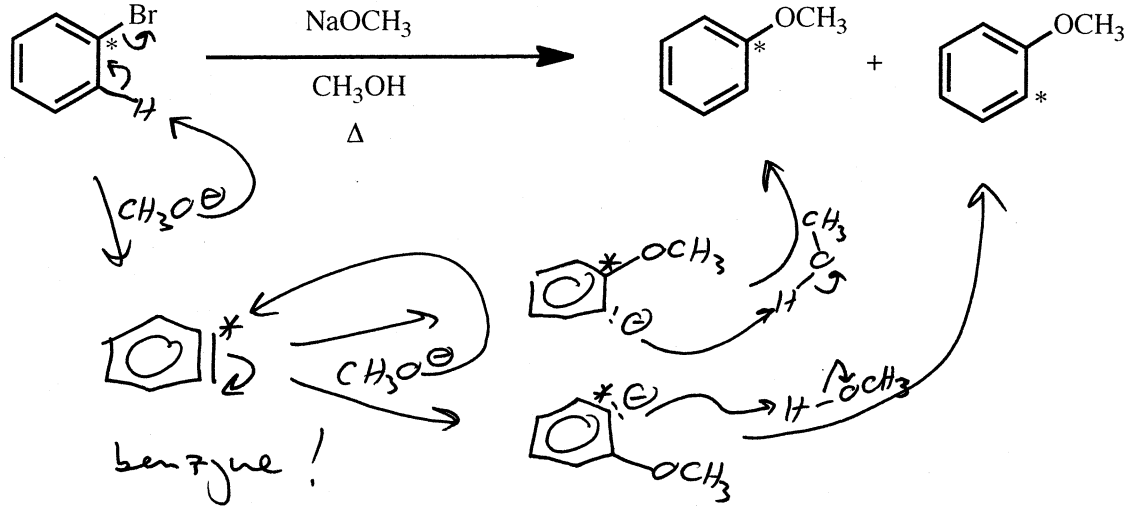
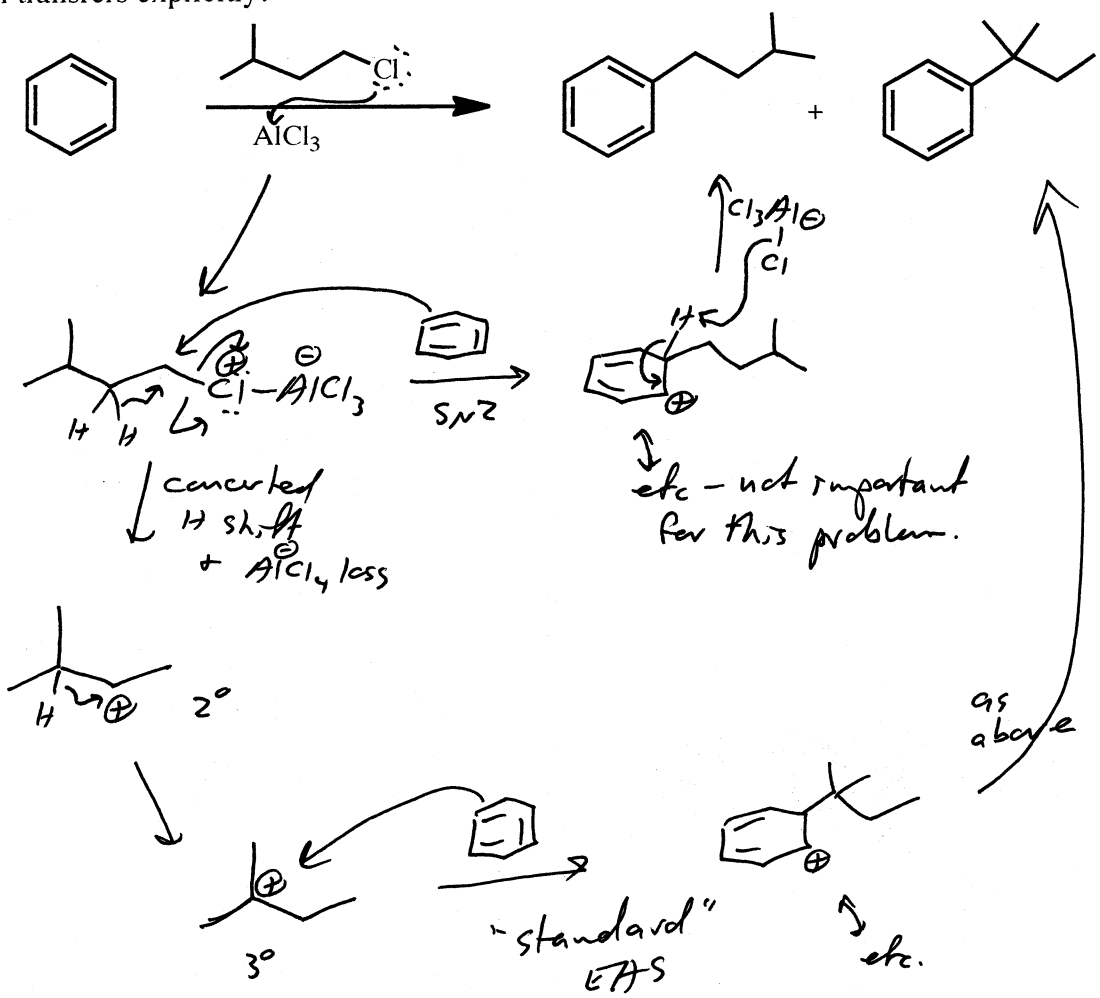
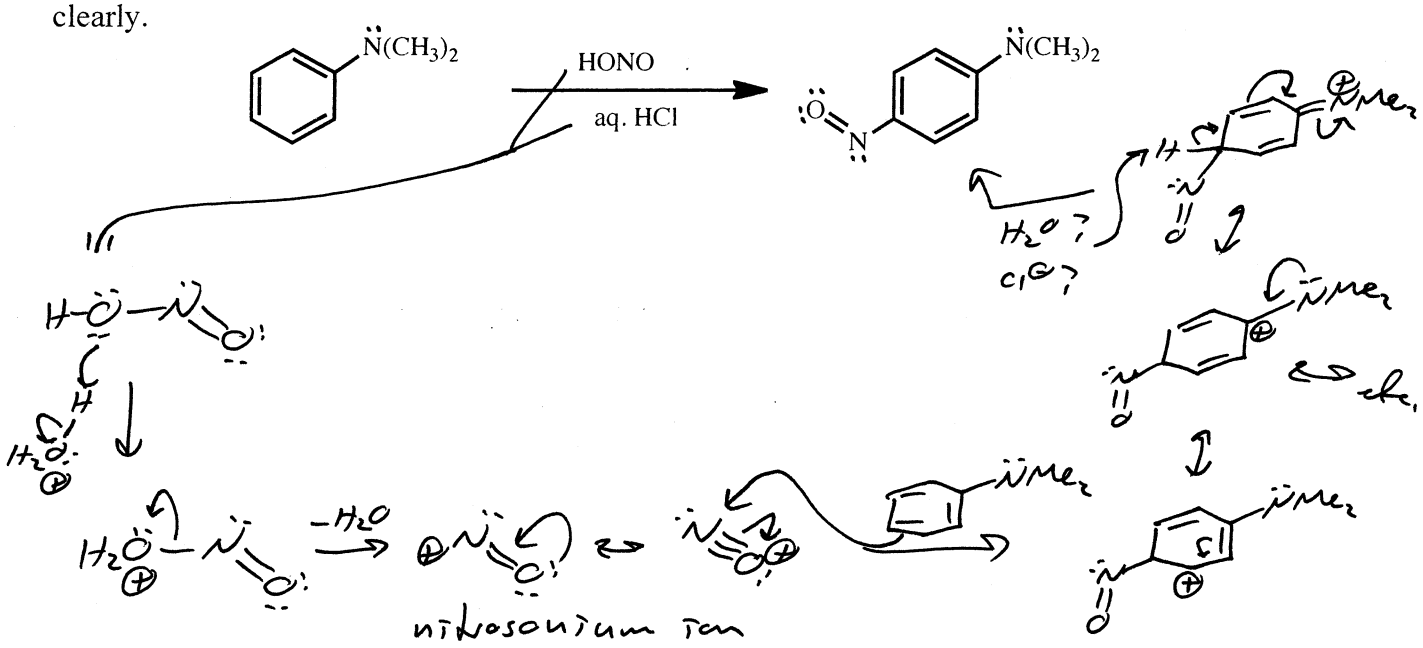
**3.** (13 points) Suggest a mechanism that accounts for the following transformation. As always, show each step clearly with curved arrows, and show all proton transfers explicitly. The * indicates a radioactive $^{14}C$.



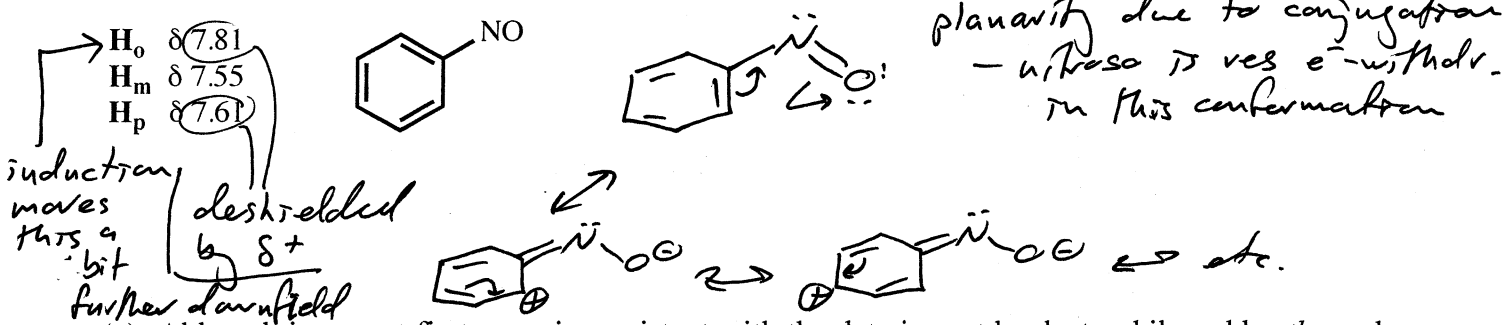

**4.** (22 points) The Friedel-Crafts alkylation below produces a mixture of products. Write a mechanism that explains this reaction. Show each step clearly with curved arrows, and show all proton transfers explicitly.



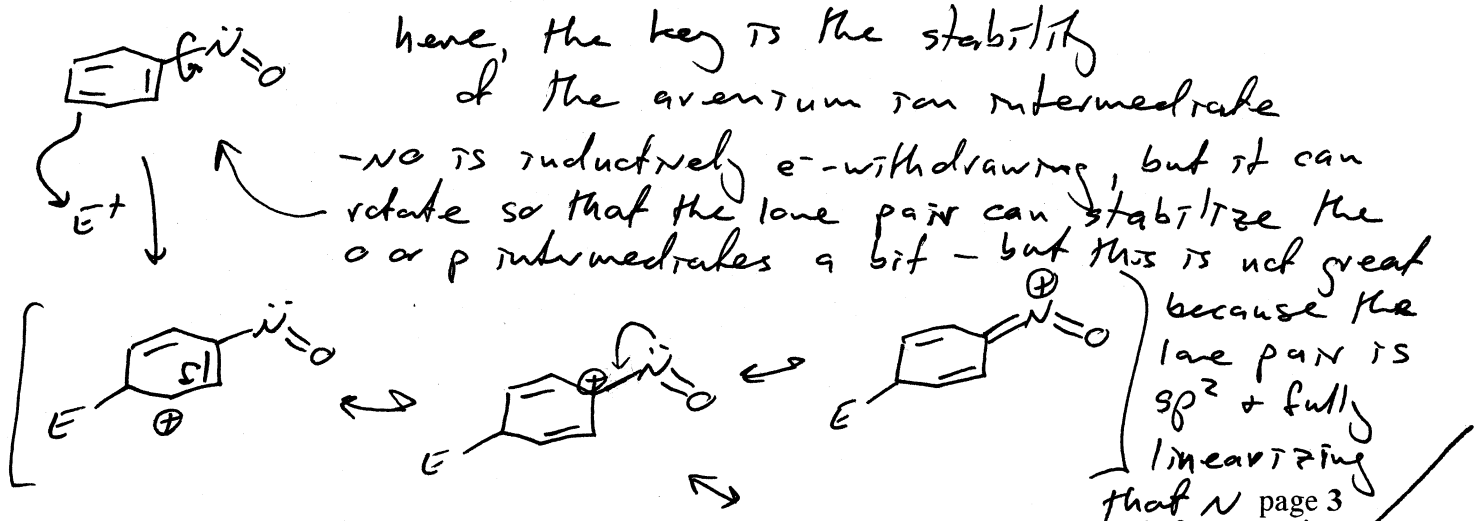
**5.** (30 points) (a) We learned that nitrous acid, HONO, reacts with primary aromatic amines to form diazonium ions. But a tertiary aromatic amine cannot form a diazonium ion. Instead, the reaction below occurs. Write a mechanism that accounts for this reaction. Show every step clearly.




(b) At first glance, it may not be obvious whether a nitroso group should be electron-donating or electron-withdrawing. Based on the $^1$H NMR data below, which is it? Explain. Draw structures.

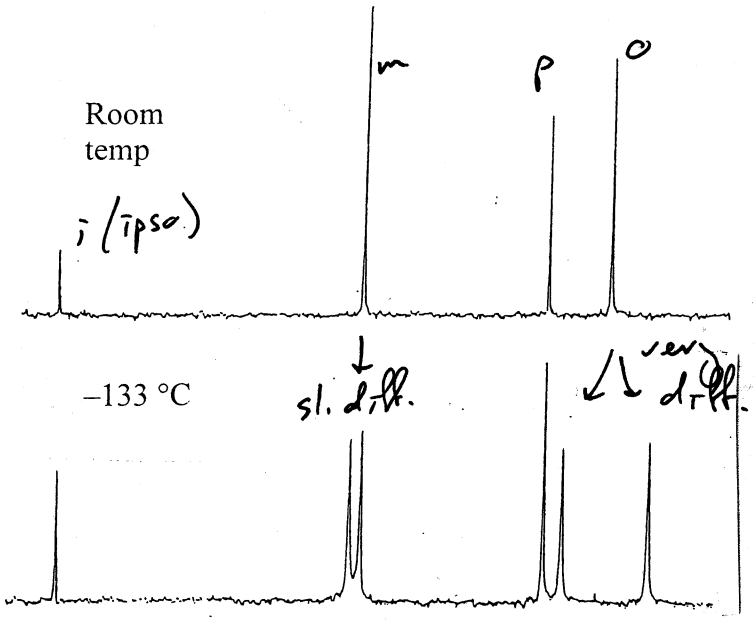



(c) Although it may at first seem inconsistent with the data in part b, electrophiles add *ortho* and *para* to the nitroso group. This reaction is a bit slower than the reaction with benzene. The nitroso group is therefore in the same directing-effect category as the halogens. Explain how this group can function as a mild deactivator and as an *o,p*-director. Draw structures.



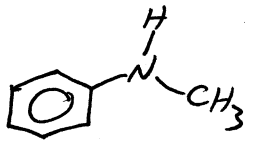
**6.** (23 points) N-methylaniline, Ph–$NHCH_3$, displays the following $^1$H-decoupled $^{13}$C NMR spectra. Only the aromatic region is shown. The upper spectrum was recorded at room temperature; the lower at –133 °C.

(a) Explain the difference between the two spectra in terms of the structure of the compound. (b) Assign the four peaks in the room temperature spectrum to the aromatic Cs of the compound.

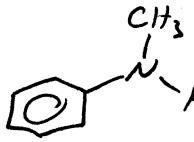



note e⁻-donation from N shields o & p Cs

from the dynamic NMR lab (the management apologizes for the lack of originality)



at low T all the ring Cs are diff.



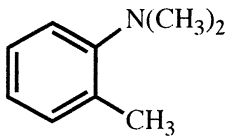
at high T these two confs. interconvert rapidly – this averages the diff environments of o & m Cs

(c) If the upfield region of these spectra had also been recorded, how many signals would have been observed for the methyl C at each temperature?

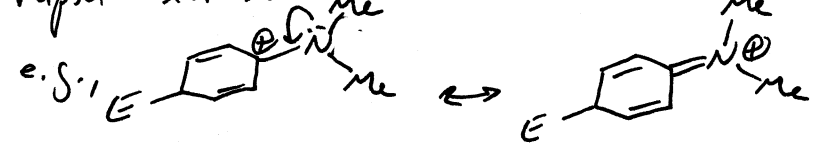
Room temp __1__ –133°C __1__

me e is in the same environment regardless of which way it points.

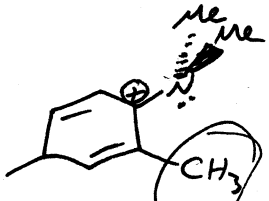
**7.** (12 points) As we would expect, N,N-dimethylaniline, Ph–$N(CH_3)_2$, reacts rapidly with electrophiles. But under the same conditions, the *ortho*-methyl derivative (below) reacts much more slowly. Why? Explain clearly. Draw structures.



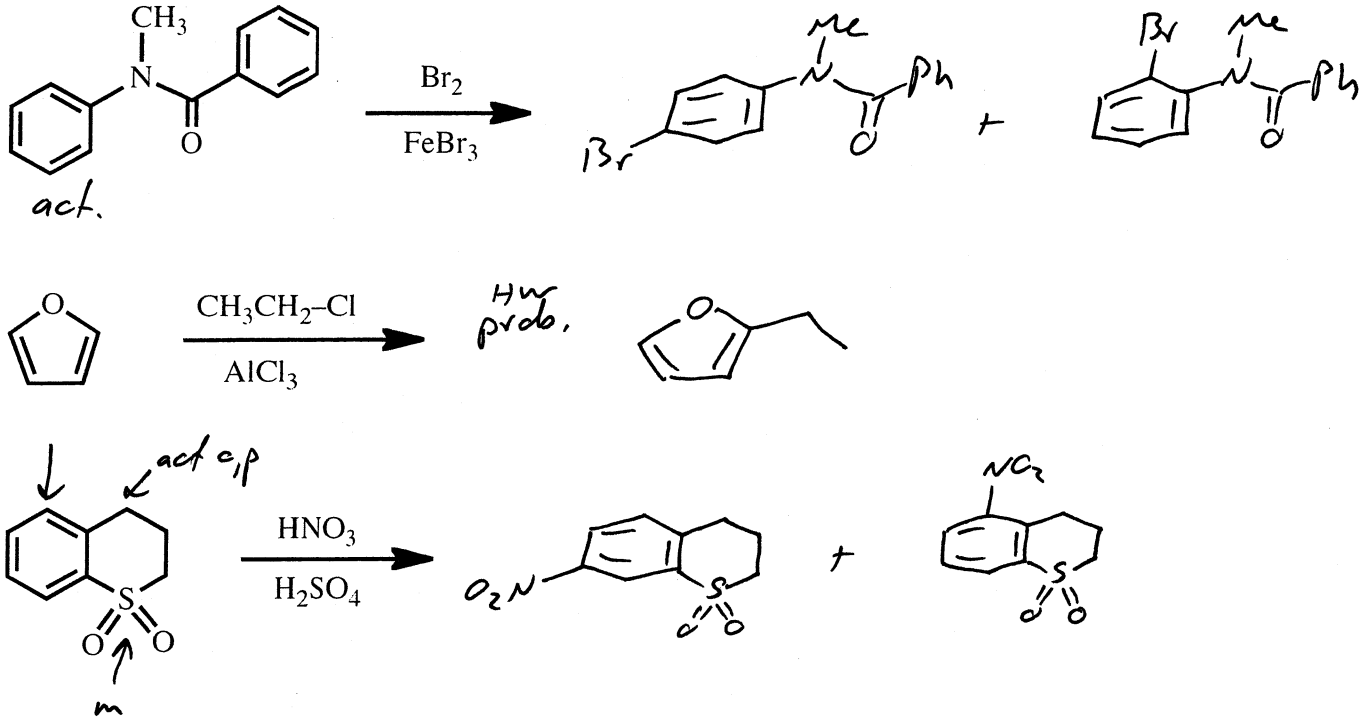

rapid rxn is due to res.-e⁻-donation by N



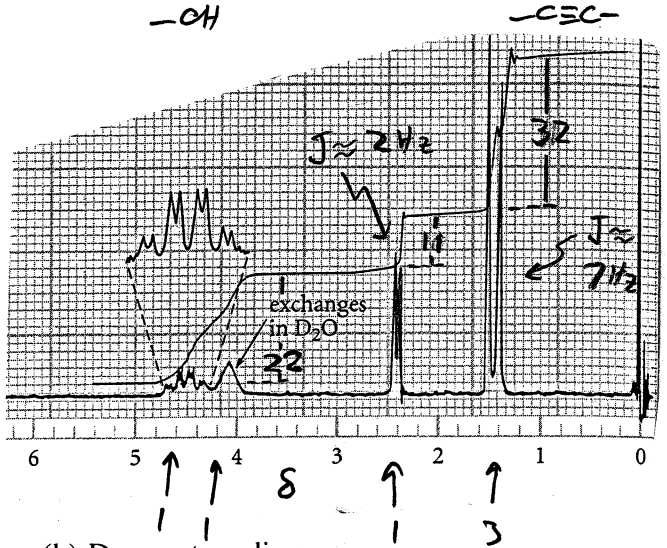

here, steric clash forces the N to rotate so that the lone pair is not aligned with the empty p-orb (or poorly aligned, at best)



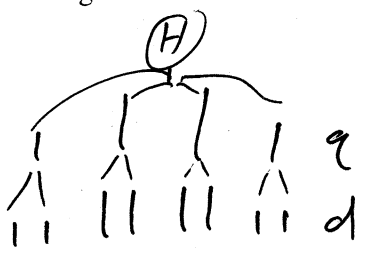
**8.** (20 points) Draw the organic products of the following EAS reactions. Assume one equivalent of electrophile adds in each case.

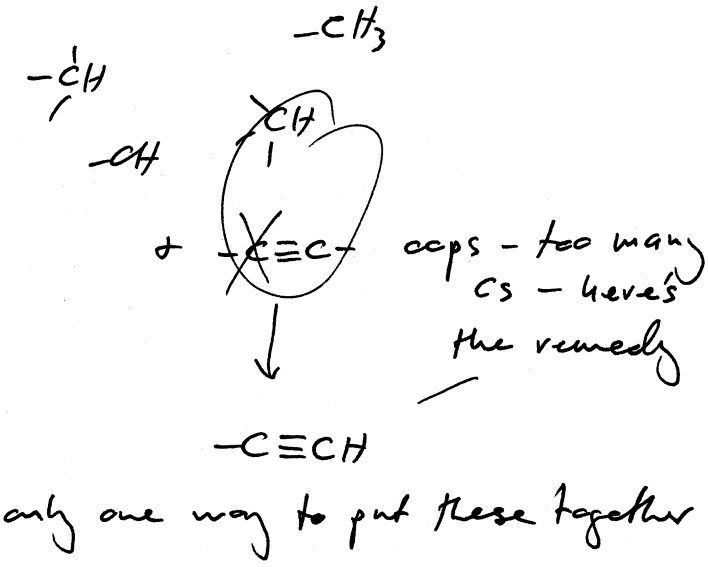


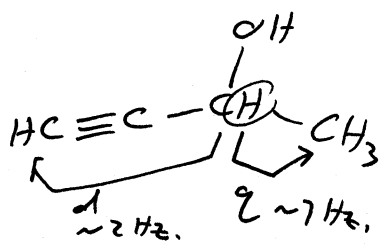

**9.** (20 points) A compound with the formula $\mathbf{C_4H_6O}$ has the 60-MHz $^1$H NMR spectrum shown below. The integral step heights are in mm. The compound's IR spectrum has a broad absorption around 3400 $cm^{-1}$ and a sharp peak at 2150 $cm^{-1}$. (a) Draw the structure.




(b) Draw a tree diagram to account for the appearance of the δ 4.6 signal.

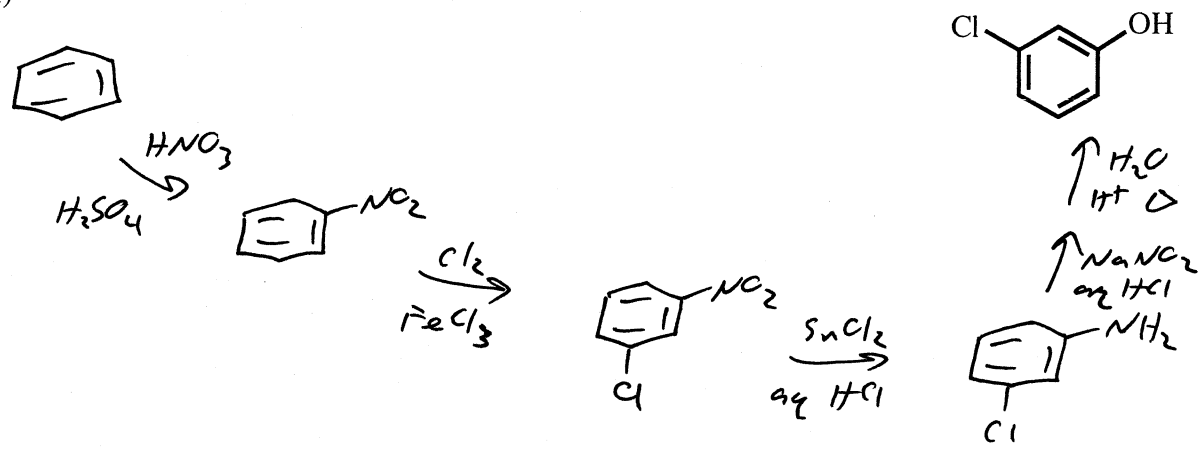


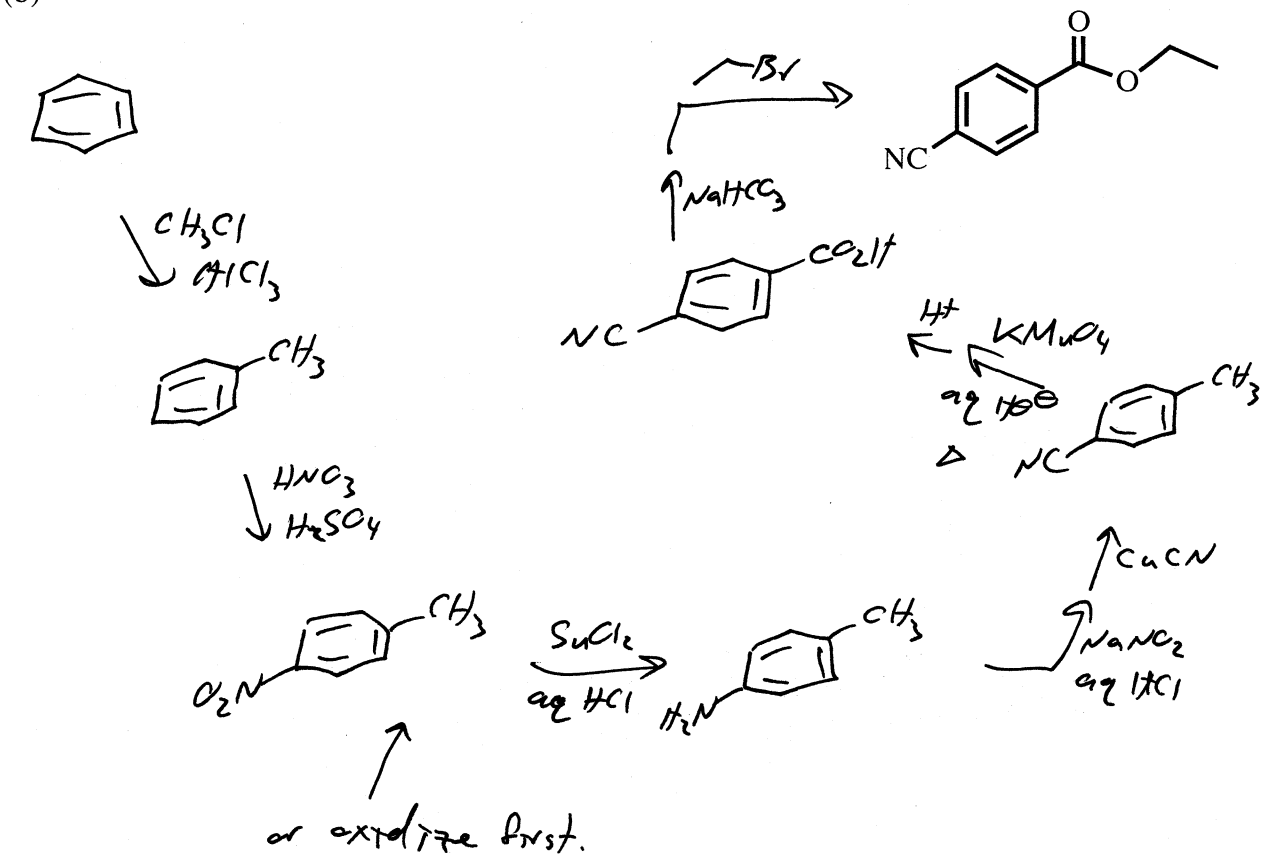



**10.** (25 points) Suggest a synthesis of each compound below starting with benzene.

(a)




(b)



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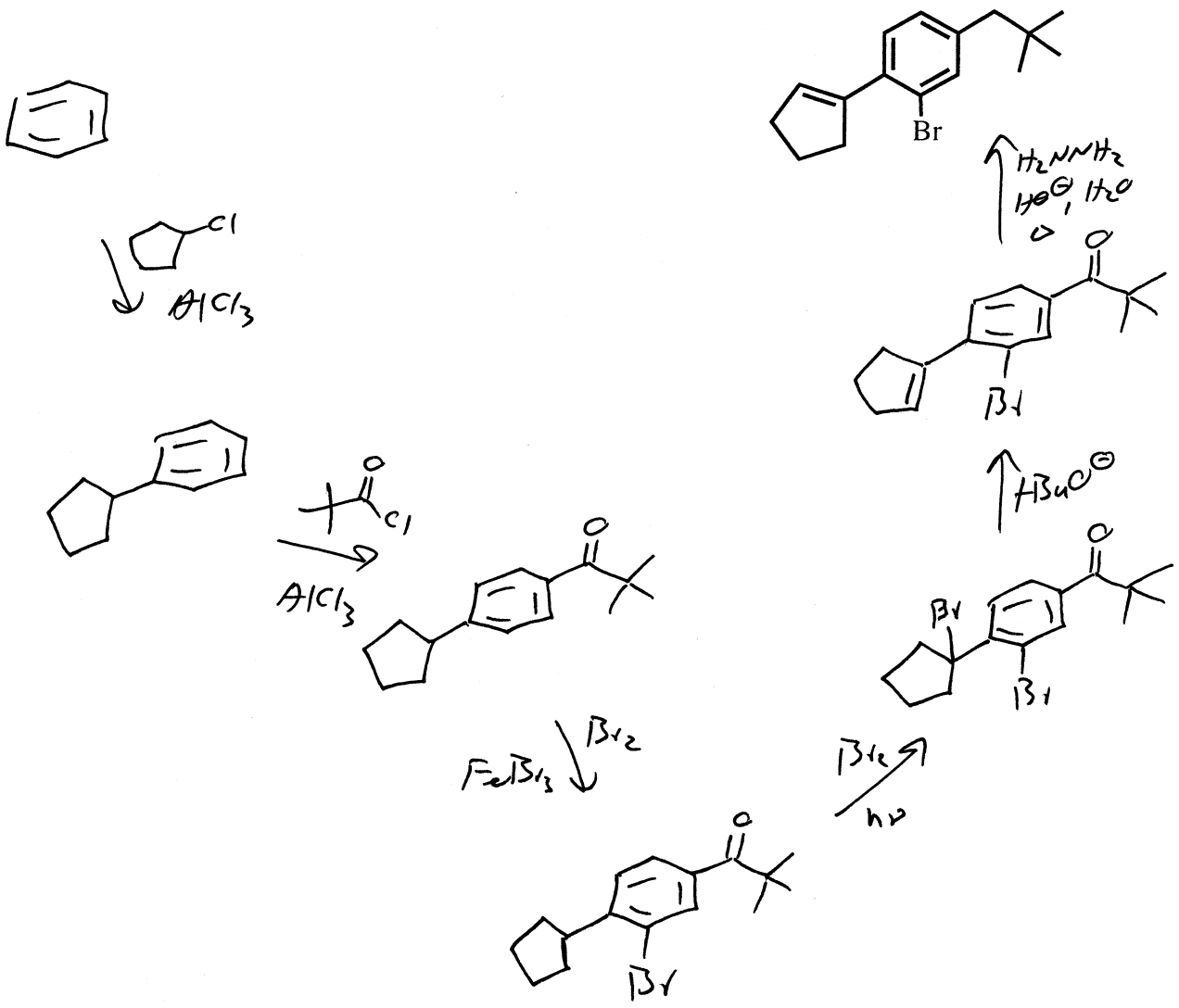
**11.** (15 points) Suggest a synthesis of the compound below starting with benzene.



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