Name: Irika Sinha

CHEM 337, Final Exam, Spring, 2019, Prof. Gelb

Read Before Starting Exam:

1. I pasted the topic list we wrote on the board on friday June 7, and wrote a problem for nearly every topic.

2. Be sure you have all exam pages (13 pages including this cover page).

3. Put your name on EACH exam page (upper left).

4. Only what the TA can read will be graded so be sure to write clearly. All answers need to be given in the boxes.

5. Next to each problem I give you the number of points that the problem is worth. This may help you manage your time. The exam has a total of 150 points.

6. Good luck. Take a deep breath if you get tense.

7. Don't cheat. It will only catch up with you later in life.

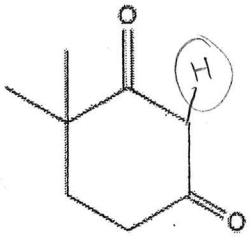
Name: Jivica Sinha

98/104

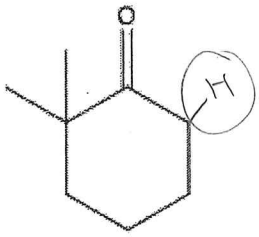
Ch 18: Enols and Enolates

pKa's

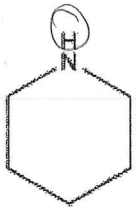
10 1. (10 pts) Next to each compound write the approximate pKa for the most acidic part of the molecule and circle the hydrogen that comes off.



9-10



18-20



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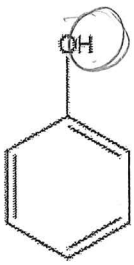

10

Enol/keto lithium enolates, alkylation, acylation:

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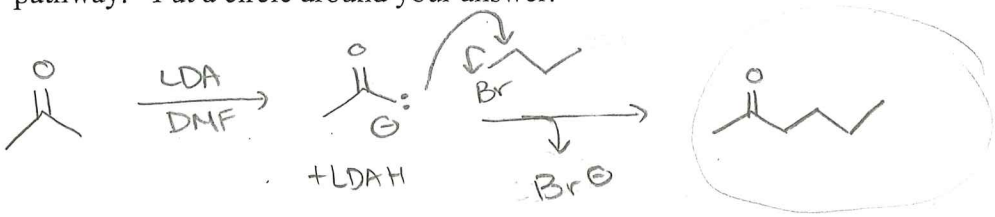
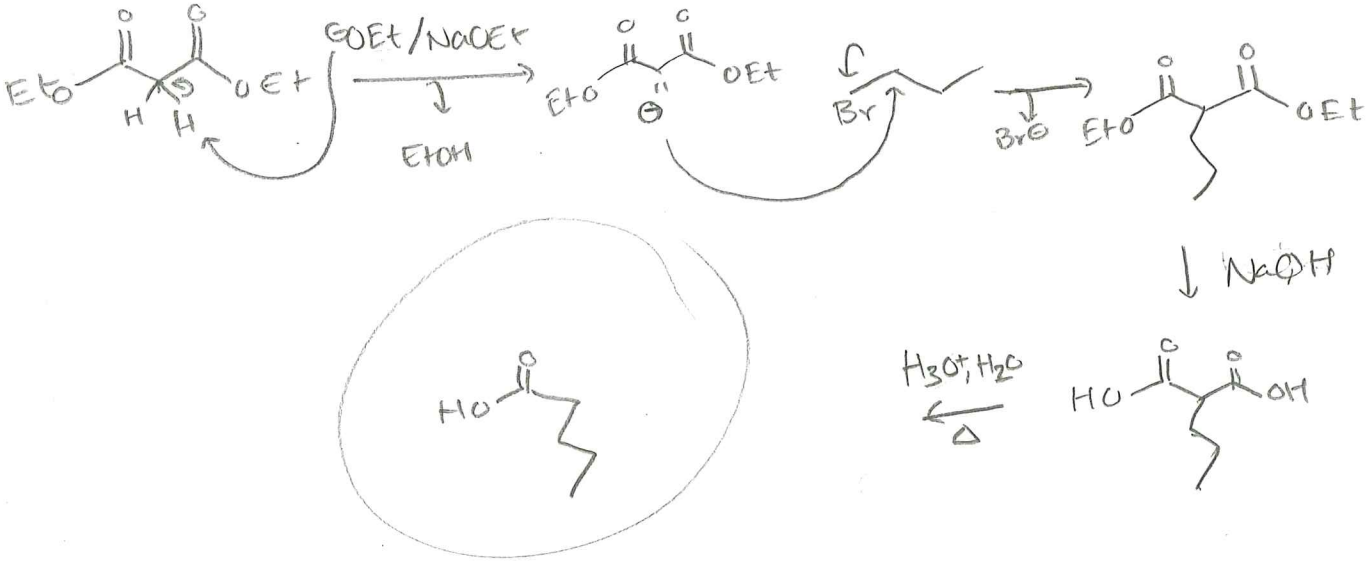
9 2. (10 pts) Draw a synthetic route using LDA, any ketone, and any alkyl halide to give the alkylated ketone. Draw a separate balanced reaction for each step of the pathway. Put a circle around your answer.



9 3. (10 pts) Draw a synthetic scheme for a malonic ester synthesis starting from a malonic ester and an alkyl halide, and include the final decarboxylation step. Draw a balanced reaction for each step of the pathway. Put a circle around your answer.



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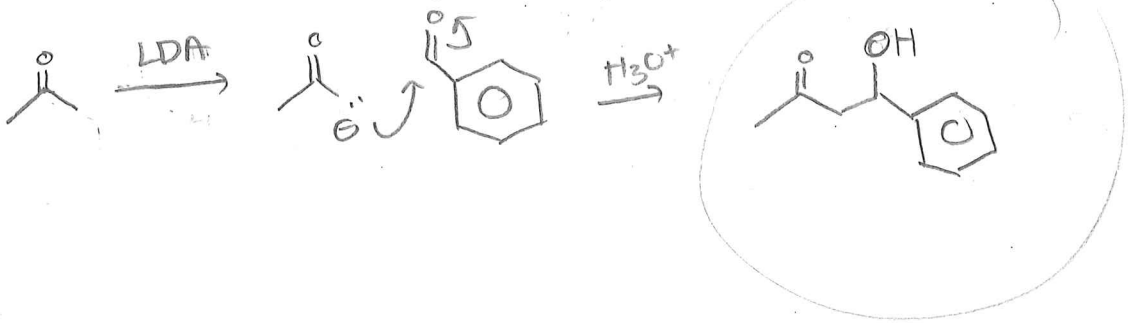
5

4. (10 pts) Draw a synthetic scheme for any cross Claisen reaction, but choose starting materials so that only a single cross Claisen product can be formed. Be sure to draw a balanced reaction for each synthetic step, and circle your answer.



6

5. (10 pts) Michael additions can be used to make a secondary amine by reaction of a primary amine with an alpha, beta-unsaturated amide.

Provide a synthesis of the compound below starting from the alpha-(4-nitrophenyl)-glycoside of D-glucose and benzene, and other compounds of 3 carbons or less. Be sure

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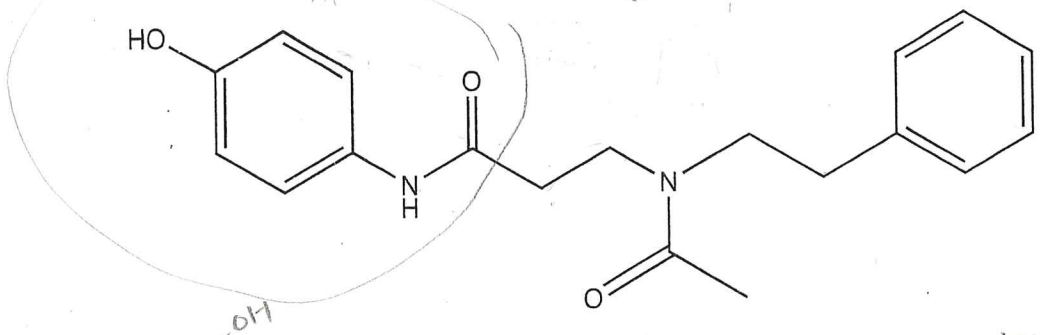
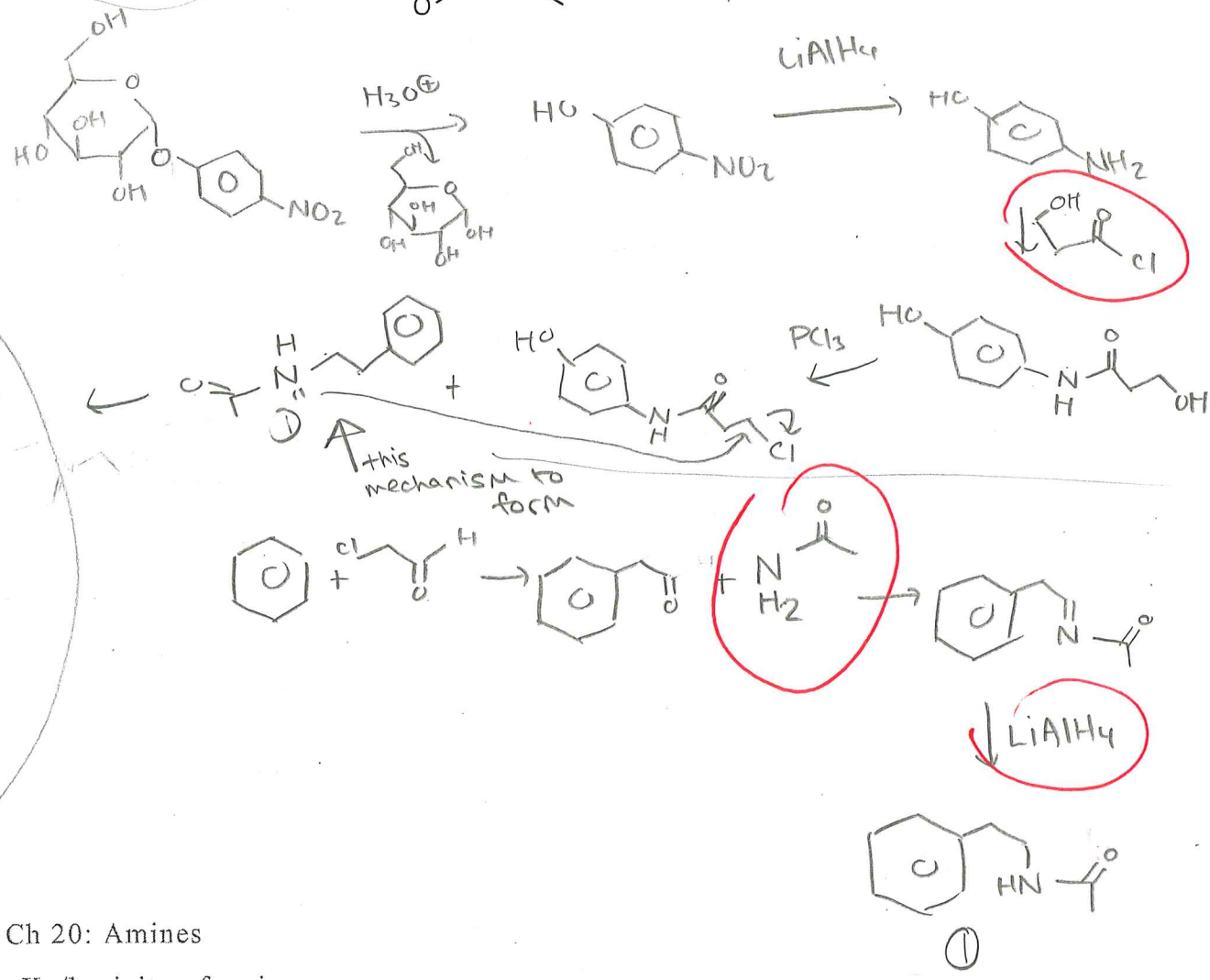
to show a balanced reaction for all synthetic steps. Also draw the chemical structure of all compounds including all reagents, and circle your final answer.

alpha-glycoside of D-glucose with  +3C





Ch 20: Amines

pKa/basicity of amines

6. (6 pts) Give the approximate equilibrium constant for the following reaction and circle your answer.

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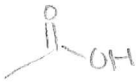


0 ammonia + acetic acid < > ammonium + acetate

$NH_3 + CH_3OH \longrightarrow NH_4 + C_2H_3O^{\ominus}$

Gabriel synthesis

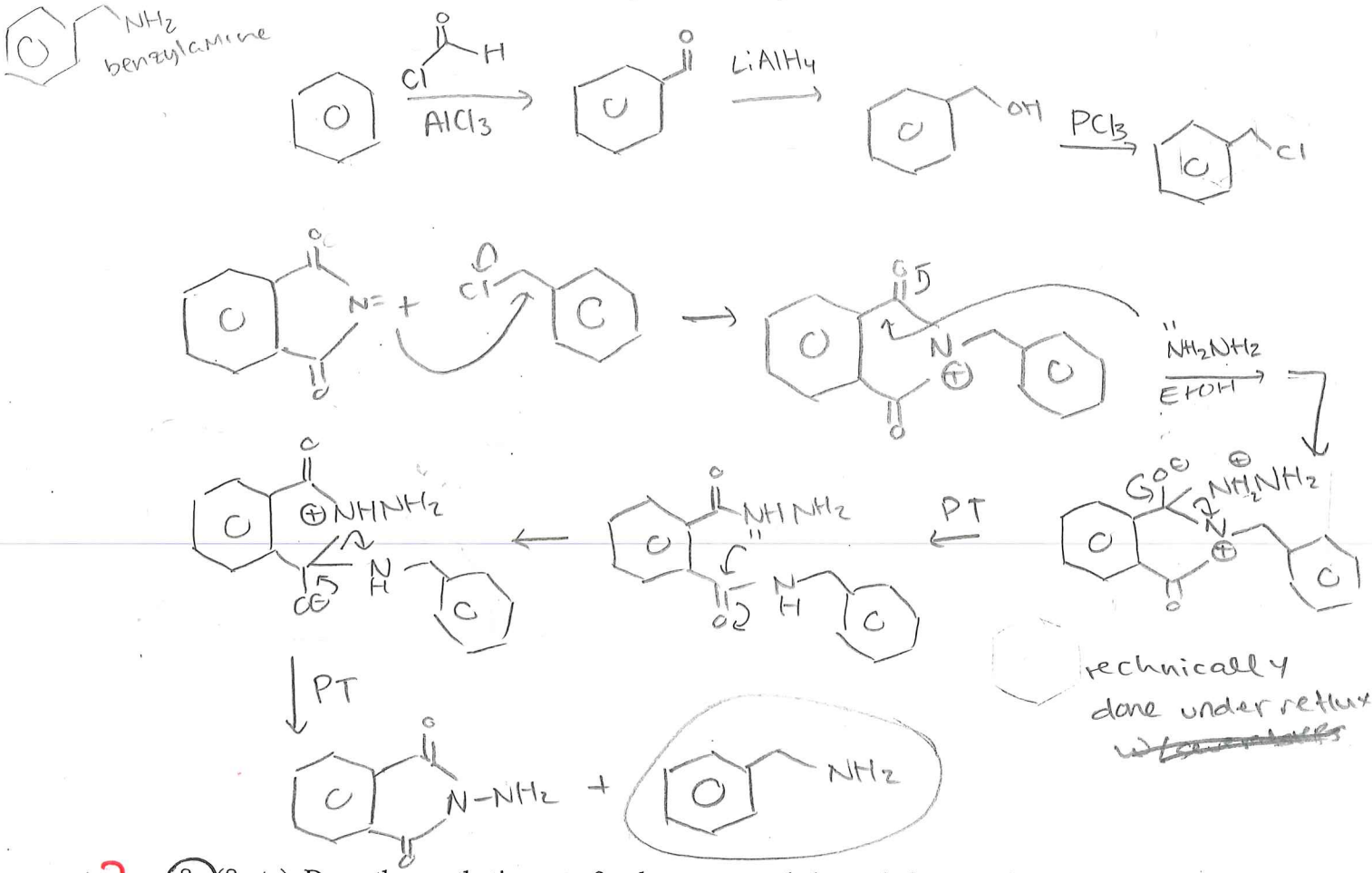
$pK = -\log\left(\frac{[NH_4][C_2H_3O]}{[NH_3][CH_3OH]}\right) = pK_a(NH_3) + pK_a(CH_3OH)$

$= 15 + 4 = 19$

($pK_a = 15$, $pK_a = 4$)

$K = 10^{-19}$

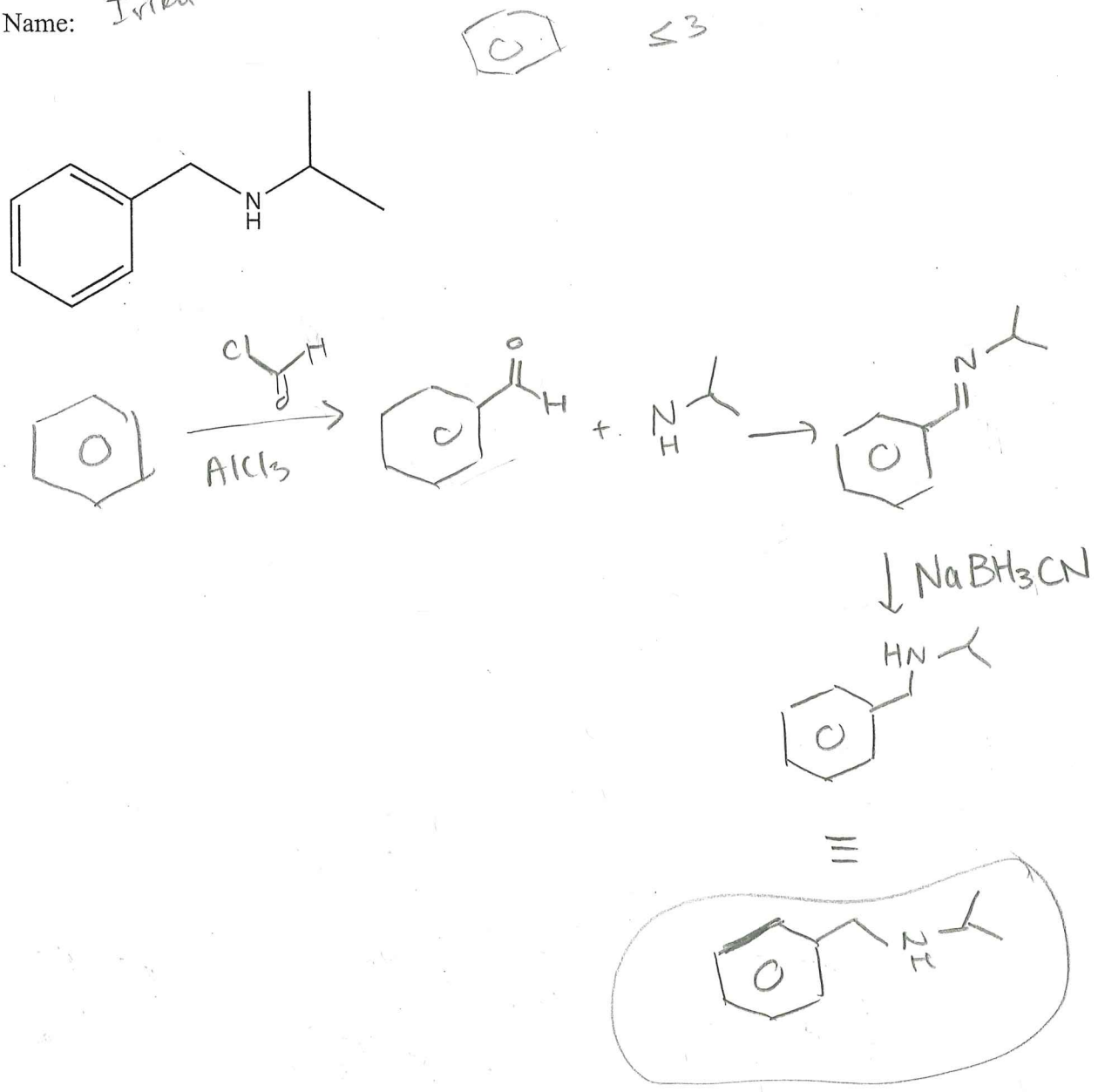
6 (7.) (6 pts) Draw the route of a Gabriele synthesis for the synthesis of benzylamine starting from phthalimide, benzene and all other needed reagents. Draw a balanced chemical reaction for each synthetic step, and circle your answer.



technically done under reflux

7 (8.) (8 pts) Draw the synthetic route for the compound shown below starting from benzene and any other carbons of 3 carbons or less. Be sure to provide a balanced chemical reaction for each synthetic step, and circle your answer.

Name: Iriku Suzuki



Names of common heterocyclic amine from textbook

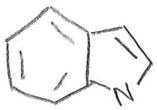
12 9. (12 pts) Draw the chemical structure of the indicated compounds, and circle your answers.

Name: Erika Sinke

a. Furan 

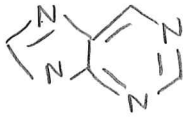
b. pyrimidine 

pyrol pyrazole ipmidazole indole
pyridine pyridazine pyrimidine quinoline

c. indole 

d. imidazole

e. purine



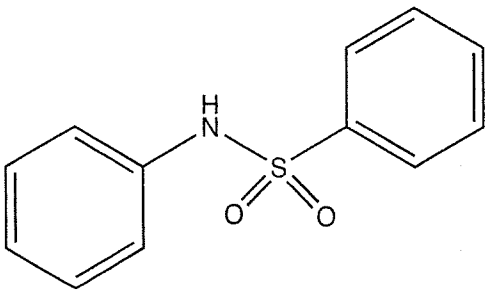
f. pyridine

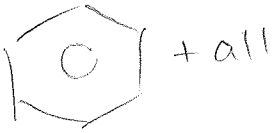
$Ar\text{-}NO_2$ → $Ar\text{-}NH_2$ → acylation with acyl chlorides of sulphonyl chlorides

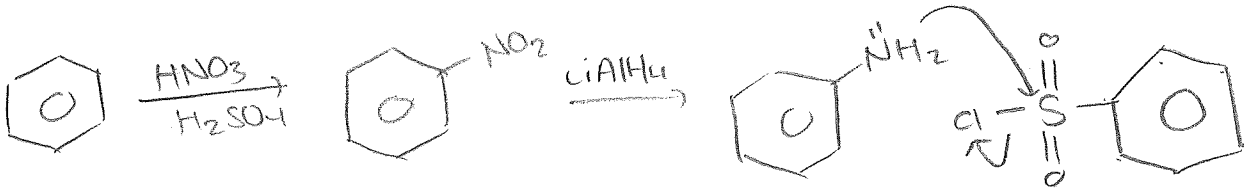
6

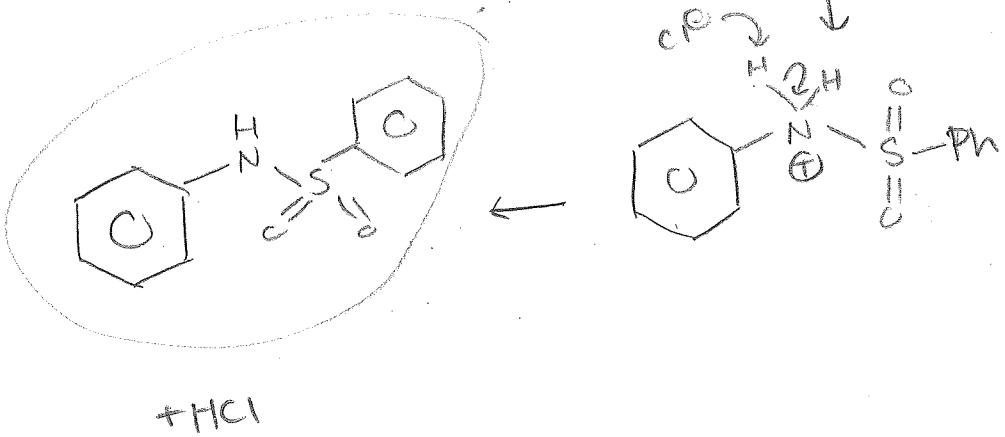
10. (10 pts) Provide a synthesis for the following compound starting from benzene and all other needed reagents. Draw a balanced reaction for each chemical step, and circle your answer.

Name: Ivika Sinha







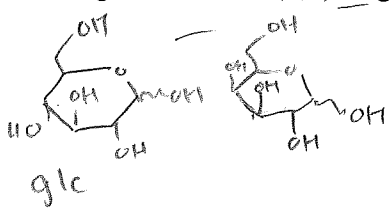


+HCl

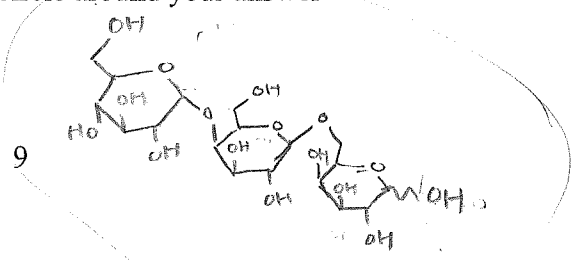
Carbohydrates

Structures of galactose and glucose α, β, D, L, numbering of carbons

6 (11.) (6 pts) Draw the structure of the tri-saccharide D-glucose-alpha(1,4)-~~D-~~galactose-beta(1,6)-D-galactose. Put a circle around your answer



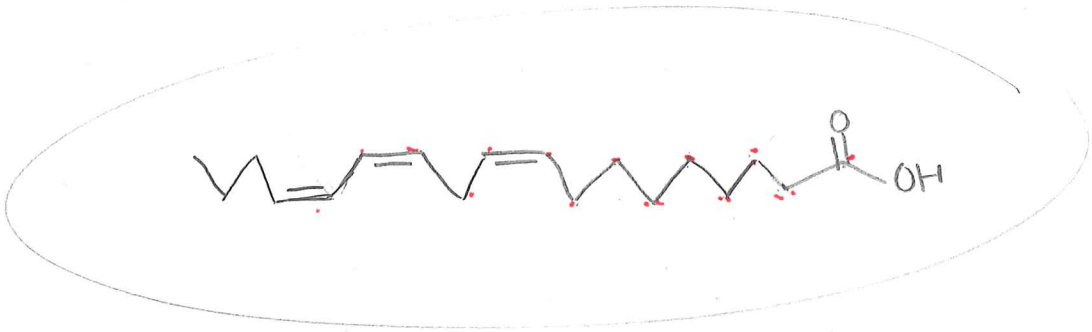
glc



Name: Mike Sinko

Lipids

6 12. (6 pts) Draw the structure of all-cis delta-9, 12, 14-18:3 fatty acid and put a circle around your answer



7 13. (10 pts) Draw an electron pushing mechanism for the formation of geranyl-fuc diphosphate from isopentyl-diphosphate and dimethylallyl-diphosphate, be sure to draw a balanced chemical step for each reaction, and circle your answer.

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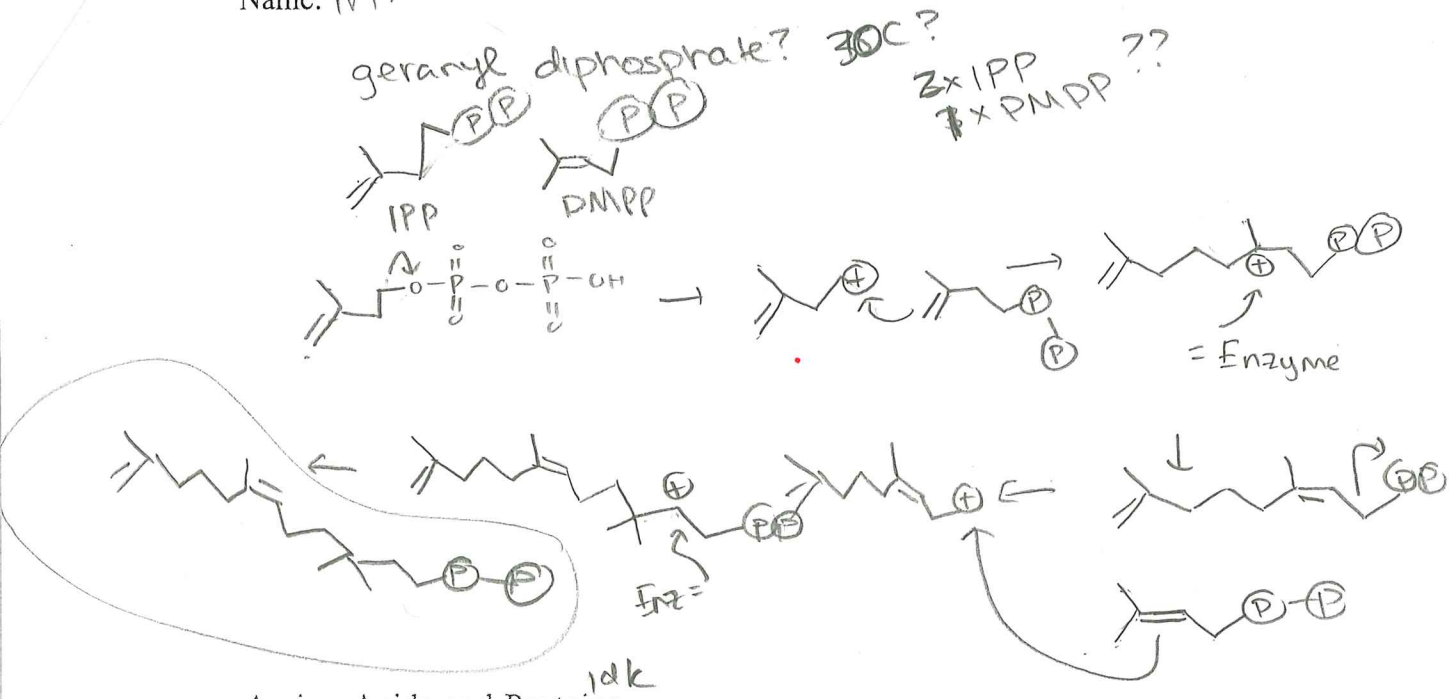
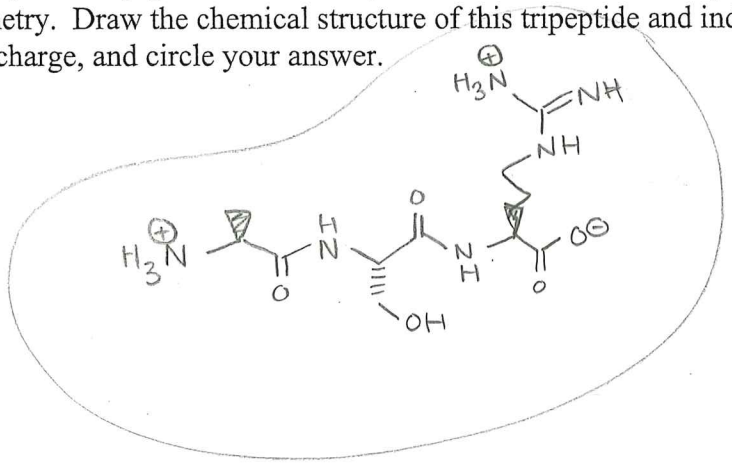


Amino Acids and Proteins

6 (14) (6 pts) The tripeptide ASR readily forms a +2 ion in electrospray mass spectrometry. Draw the chemical structure of this tripeptide and indicate the sites of positive charge, and circle your answer.



10 15. (10 pts) The active site hisitidine has two catalytic roles in the complete reaction cycle for hydrolysis of an amide by serine proteases. In words, state these two roles.

- specific base (accepts hydrogen from serine & water)
- specific acid (donates hydrogen to =NH R & serine)

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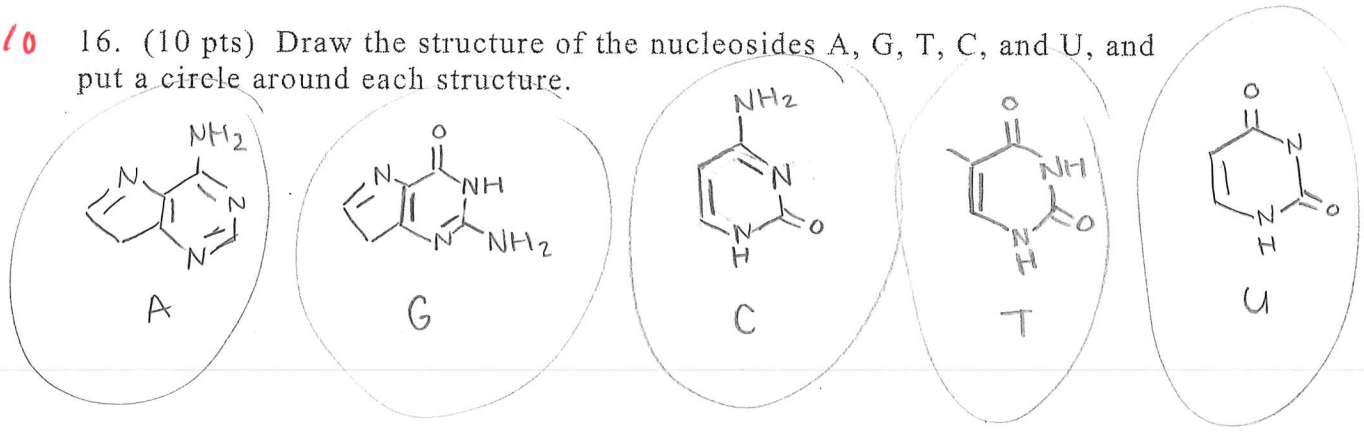
DNA/RNA

10 16. (10 pts) Draw the structure of the nucleosides A, G, T, C, and U, and put a circle around each structure.



10 17. (10 pts)

a. Draw all of the steps of one cycle of solid-phase oligonucleotide synthesis starting from trityl-nucleoside on the resin bead and ending up with a dinucleotide on the resin with the trityl group removed. Be sure to indicate each step of the reaction.