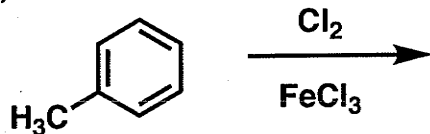


General Instructions:

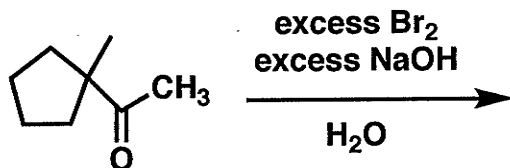
- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit.
- (ii) Print your name on each page.

1. (44 points) Show the major product or products expected from each reaction:

(a)

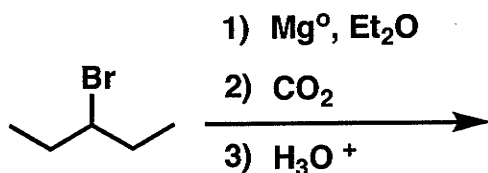


(b)

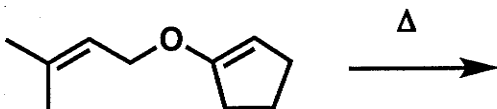


Hint: The product has a strong, broad IR signal at 3100 cm^{-1} , which is not seen in the starting material.

(c)

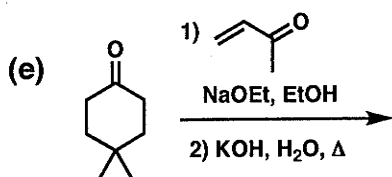


(d)

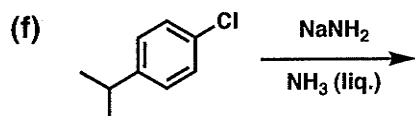


Name _____

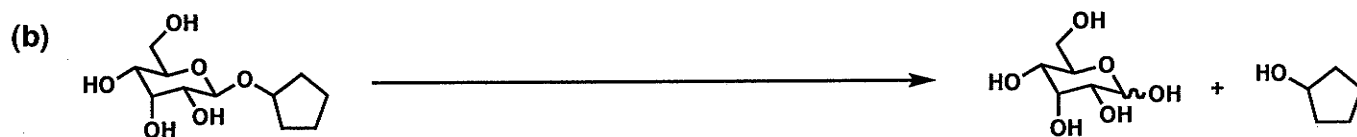
1. (cont.)



Hint: The product has a strong IR signal at 1675 cm⁻¹, and no signal ≥ 3200 cm⁻¹.



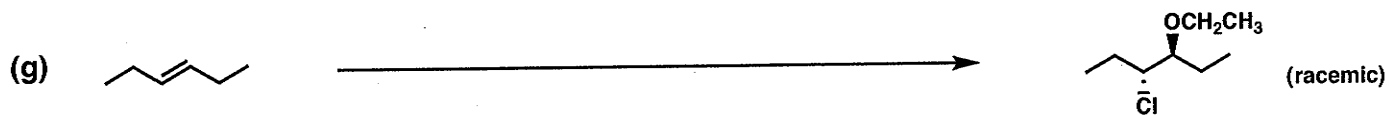
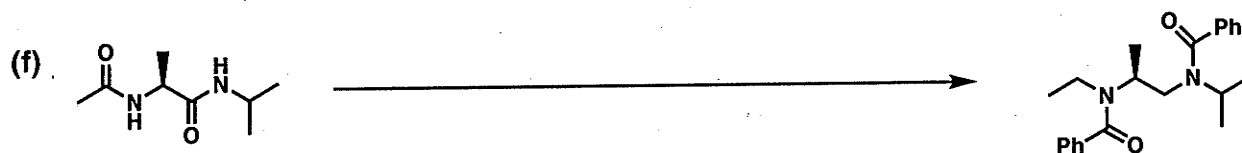
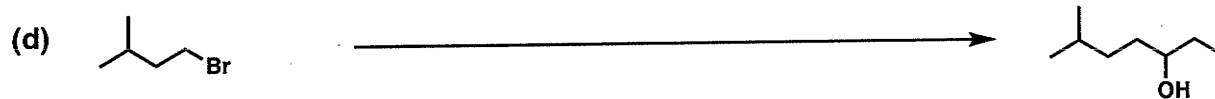
2. (47 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc.



(cont. on next page)

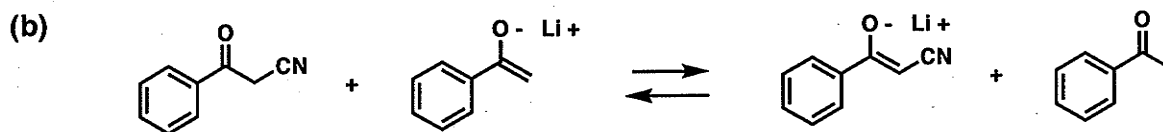
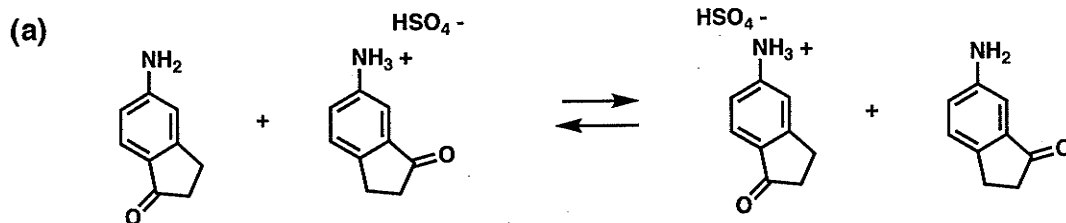
Name _____

2. (cont.)



Name _____

3. (14 points) For each equilibrium shown below, circle the form (left side or right side) that you expect to be favored in each case. BRIEFLY explain your choice, using structures as necessary to bolster your explanation.



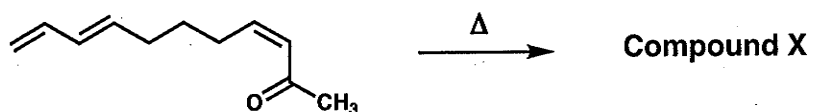
Name _____

4. (8 points) When the molecule shown below is heated, compound X is formed. Propose a structure for compound X based on the observations below.

-- Compound X is an isomer of the starting material.

-- The ^1H NMR spectrum of the starting material has seven resonances (all multiplets) above 4.5 ppm, while NMR spectrum of compound X has only two resonances in this region of the NMR spectrum.

-- Compound X takes up only one equivalent of H_2 upon treatment with H_2 and Pd/C.

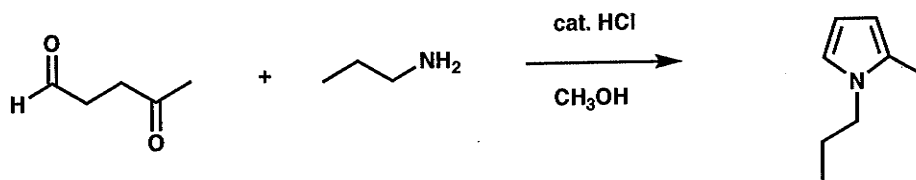


Compound X =

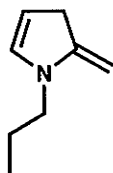
Name _____

5. (25 points)

(a) Draw a mechanism (curved arrows) for the reaction shown below.

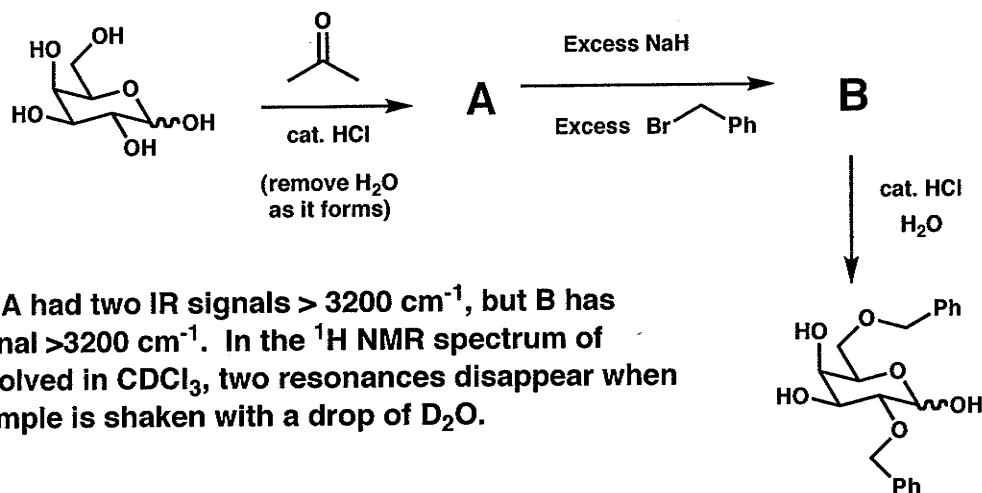


(b) Give a brief rationale (one sentence) for the fact that the product indicated above is obtained in preference to the isomer shown below.



Name _____

6. (14 points) Provide structures for molecules A and B, which are intermediates in the conversion of D-galactose (the starting material) to 2,6-dibenzyl-D-galactose (the final product).



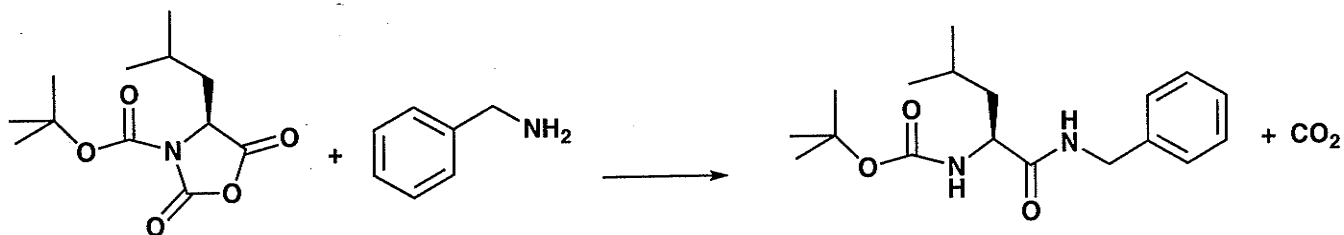
Note: A had two IR signals $> 3200\text{ cm}^{-1}$, but B has no signal $> 3200\text{ cm}^{-1}$. In the $^1\text{H NMR}$ spectrum of A dissolved in CDCl_3 , two resonances disappear when the sample is shaken with a drop of D_2O .

A =

B =

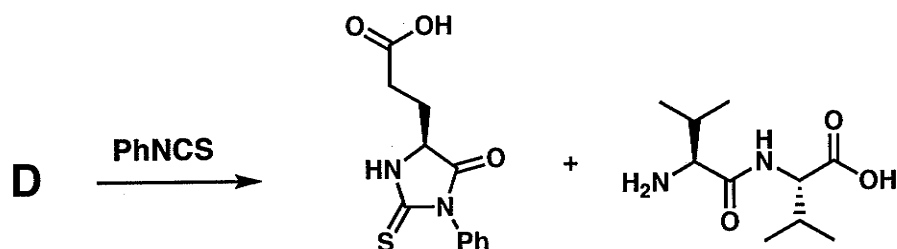
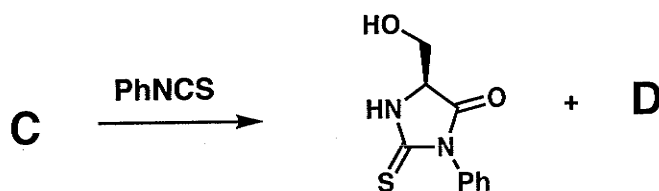
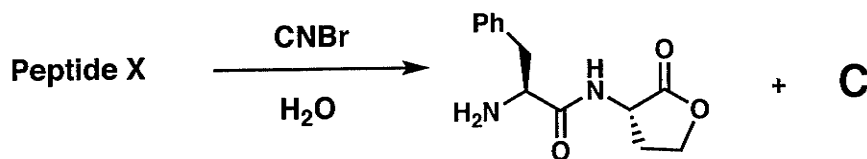
Name _____

7. (15 points) Draw a mechanism (curved arrows) for the reaction shown below. Show resonance forms where appropriate.



Name _____

8. (15 points) Peptide X is analyzed as indicated below. What are the structures of peptide X and the two unknown intermediates?



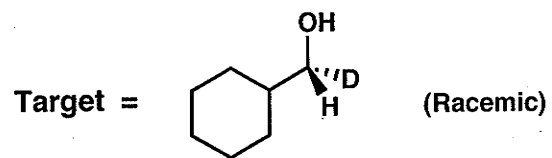
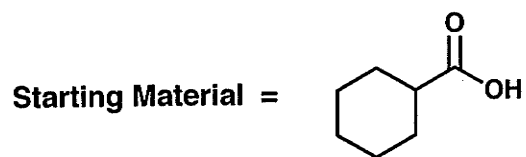
D =

C =

Peptide X =

Name _____

9. (18 points) Propose a synthesis of each target molecule shown below from the indicated starting material shown. You may use any other reagents.



Name _____

<u>Problem</u>	<u>Score</u>
1	/ 44
2	/ 47
3	/ 14
4	/ 8
5	/ 25
6	/ 14
7	/ 15
8	/ 15
9	/ 18

Total:**/ 200**

TABLE 14.4 Approximate Chemical Shifts of Various Hydrogens^{a,b}

Hydrogen	δ (ppm)
CH ₃	0.8–1.0
CH ₂	1.2–1.5
CH	1.4–1.7
C=C–CH (allylic hydrogens)	1.8–2.3
O=C–CH	2.0–2.5
Ph–CH (benzylic hydrogens)	2.3–2.8
=C–H	2.5
R ₂ N–CH	2.0–3.0
I–CH	2.8–3.3
Br–CH	2.8–3.5
Cl–CH	3.1–3.8
F–CH	4.1–4.7
O–CH	3.1–3.8
–CH ₂ (terminal alkene)	5.0
C=CH (internal alkene)	4.5–5.5
Ph–H (aromatic hydrogens)	7.0–7.5
O–CH (aldehyde hydrogens)	9.0–10.0
RCOOH	10–13

^aThese values are approximate. There will surely be examples that lie outside the ranges indicated them as guidelines, not "etched in stone" inviolable numbers.

^bWatch out for loose talk. For example, "aromatic hydrogen" means a hydrogen attached to a ring.

TABLE 14.3 Typical Infrared Absorptions of Functional Groups^a

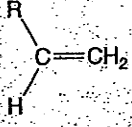
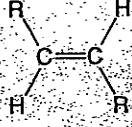
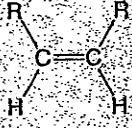
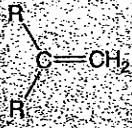
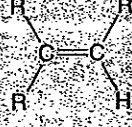

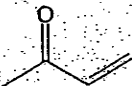
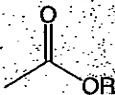
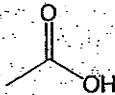
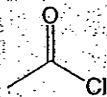
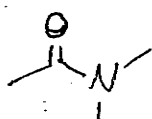
Functional Group	Position (cm ⁻¹)	Intensity ^b
Alkanes		
C-H	2980-2850	m-s (stretch)
C-C	1480-1420	m (bend)
Alkenes		
=C-H	3150-3000	m (stretch)
C=C	1680-1620	m-w (stretch)
(conj) C=C	1630-1600	m-w (stretch)
	995-985 915-905	s (out-of-plane bend)
	980-960	s (out-of-plane bend)
	730-665	s (out-of-plane bend) (br, variable)
	895-885	s (out-of-plane bend)
	840-790	m (out-of-plane bend)
Alkynes		
≡C-H	3350-3300	s (stretch)
C≡C	2260-2100	m-w (stretch)
Alcohols		
D-H		
free	3650-3580	m (stretch)
hydrogen bonded	3550-3300	br, s (stretch)
C-O	1350-1250 1150-1050	s (stretch)
Amines		
N-H	3500-3100 (two bands for primary amines one band for secondary amines)	br, m (stretch)

TABLE 14.3 (CONTINUED)

Functional Group	Position (cm ⁻¹)	Intensity ^b
C-N	~1200	m (stretch)
Aromatic compounds		
=C-H	3080-3020	m-w (stretch)
C=C	1650-1580	m-w (stretch)
C-H		
mono	770-730	s (out of plane bend)
ortho	710-690	s (out-of-plane bend)
meta	770-735	s (out-of-plane bend)
meta	900-860	m (out of plane bend)
meta	810-750	s (out-of-plane bend)
meta	725-680	m (out-of-plane bend)
para	860-800	s (out-of-plane bend)
Carbonyl compounds		
aldehydes, ketones		
		
C=O	1730-1700 (higher in strained cyclic molecules)	s (stretch)
		
C=O	1680-1660	s (stretch)
C-H (aldehydes)	2900-2700 (two bands)	w (stretch)
Esters		
		
	1750-1735 1300-1000	s (C=O) (stretch) s (C-O) (stretch)
Acids		
		
	1730-1700 3200-2800	s (C=O) (stretch) s, br (O-H) (stretch)
Acid chlorides		
		
	1820-1770	s (C=O) (stretch)

Amides



1620-1680 s (C=O) (stretch)

