Part 1. Provide the product, starting material or reagents (as indicated) for 6 of the following 8 reactions. Specify the stereochemical outcome of the reaction wherever appropriate. If you attempt more than 6, be sure to cross out the ones you don’t want me to mark. Otherwise, I will go in order.

A.  

B.  

C.  

D.  

E.  

F.  

G.  

H.  

I.  

J.  

K.  

L.  

M.  

N.  

O.  

P.  

Q.  

R.  

S.  

T.  

U.  

V.  

W.  

X.  

Y.  

Z.  

[Diagram of reactions and products]
Part 2. Provide a reasonable mechanism for 2 out of the following 3 transformations (here, and on the following two pages). If you attempt all 3, be sure to cross out the one you don’t want me to mark. Otherwise, I will go in order.

/ 10

A. $\text{CH}_3\text{COOH} + \text{N=C=N} \xrightarrow{\text{LDA}} \text{O}$

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{N=C=N} & \xrightarrow{\text{LDA}} \text{O} \\
\end{align*}
\]
B.  \[
\text{H}_2\text{N}\begin{array}{c}
\text{HO} \\
\text{H} \\
\text{O}
\end{array}\text{O}\text{NH}_2 \xrightarrow{\text{PhI(OAc)}_2} \text{Rh}_2\text{(OAc)}_4 / \text{MgO} \Rightarrow \text{O}\begin{array}{c}
\text{H} \\
\text{N} \\
\text{O}
\end{array}\text{N} \begin{array}{c}
\text{O} \\
\text{H}
\end{array}\]
This very useful two-step synthesis of differentially protected carbohydrates was recently developed by Dave MacMillan. *Angew. Chem. Int. Ed.* **2004**, *43*, 2152.

For this question, provide a precise mechanism for the first step (i.e. up to the big black question mark), and discuss what is happening in the second step. How is it that three different sugars are accessible from the same two precursors?
Part 3. The following synthesis of ircinal A and manzamine A was completed Steve Martin’s group in 1999. Fill in the blanks corresponding to reagents or intermediates where indicated. For the two requested mechanisms (A and B), please write your responses on the subsequent pages. In a few cases, I have used blue circles to highlight where the molecule has been transformed. In other steps, I have left the products unannotated, so you will need to figure out for yourself what reaction has taken place.

next page
Space for mechanisms is provided on the next two pages.
Mechanism for Step A:
Mechanism for Step B:
Part 4. Propose an **enantioselective** synthesis for 2 out of the following 4 natural products. Your approach should begin with commercially available reagents. You can assume that you have access to:

(a) **simple** alkyl, alkenyl or alkynyl reagents with up to 4 carbon atoms, for example:

\[
\begin{align*}
\text{Br} & \quad \text{or} \quad \text{H} \\
\text{Li} & \quad \text{or} \quad \text{Cl} \\
\text{O} & \quad \text{or} \quad \text{O}
\end{align*}
\]

(b) aryl or heteroaryl molecules with a **maximum of 2 substituents**, for example:

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{Me} & \quad \text{or} \quad \text{N}
\end{align*}
\]

(c) **simple** penta- or hexacycles, for example:

\[
\begin{align*}
\text{Cl} & \quad \text{or} \quad \text{Cl}
\end{align*}
\]

(d) other reagents or catalysts that we’ve seen in class.

You will **not** have access to organotin or organoborane compounds, so you’ll have to make those yourself. Please write your final answers on the next two pages – I’ve also provided some scrap paper you can use for working through your ideas, but this will not be submitted with your exam so make sure you have something good in the allotted space.

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**hydroxysovalerylshikonin**
- suppresses tumor necrosis factor proteins
- induces apoptosis

**bacilysin**
- antibiotic

**cocaine**
- used extensively in the entertainment industry

**genipin**
- enhances acid-independent secretory capacity of hepatocytes.
Synthesis #1:
Synthesis #2:

END