Question 1. Provide the product, reactant, or reagent for four of the following five reactions. Specify stereochemistry wherever appropriate. If you attempt all five, be sure to cross out the one you don’t want me to mark. Otherwise, I will go in order.

A. \[
\text{PPh}_3 / \text{CBr}_4 \\
n-\text{BuLi (2 equiv)} \\
\rightarrow \\
\text{OMe} \\
\text{CH}_3
\]

B. \[
\begin{align*}
\text{Pd}(\text{PPh}_3)_4 \\
\text{NMe}_2 \quad \text{to give} \quad \text{Ia} \\
\text{N-CBr}_3
\end{align*}
\]

C. \[
\text{Nal} \\
\text{DMSO} / \text{H}_2\text{O} \Delta \\
\rightarrow \\
\text{CH}_3 \\
\text{O}
\]

D. \[
\begin{align*}
\text{Pd}_2(\text{dba})_3 \quad (+/-)-\text{BINAP} \\
\text{NaHCO}_3 \\
\rightarrow \\
\text{O}
\end{align*}
\]
Question 2. Provide a reasonable mechanism for one out of the following two transformations. If you attempt both, be sure to cross out the one you don’t want me to mark. Otherwise, I will go in order.

A. Silyl groups have the ability to stabilize positive charges at the position β to the silicon group (the so-called “silicon β-effect”). This effect was exploited by Scott Denmark’s group to convert a series of bis-alkylidene ketones (1) to functionalized cyclopentenes (2) in high yield. Surprisingly, when trienyl ketones (1a) were used, the anticipated product (2a) was not formed – instead, the unexpected product 3 was isolated. Provide mechanisms for both the expected formation of 2a, and the observed formation of 3.
B. In a recent Nature paper, Brian Stoltz published a beautiful synthesis of (-)-cyanthiwgin F that relied on a fantastically cool desymmetrization reaction as the key step. Provide mechanisms to account for the formation of 2 and 3. In words, briefly summarize how it is that Stoltz is able to "correct" the stereochemistry at the chiral quaternary centres, in proceeding from 2 to 3. Bonus marks for using (appropriately) the word "stereablative"!

1. [Reaction 1]
2. [Reaction 2]
3. [Reaction 3]

1:1 mixture of racemic : meso diastereomers

99% enantiomeric excess

Cyanthiwgin F

The initially formed stereocentres are removed ("obliterated") to give flat enolates on route to the final product.

The new stereocentres are formed under the control of the chiral ligand on Pd. This is therefore a stereoablative desymmetrisation.

Repeat.
Question 3. Propose a synthesis for one out of the following two compounds. If you attempt both, be sure to cross out the one you don't want me to mark. Otherwise, I will go in order. 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:

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

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

(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. Your syntheses can be racemic, but please explain how you will control relative stereochemistry.