Part 1. Provide the product, starting material or reagents (as indicated) for 5 of the following 6 reactions. Specify the stereochemical outcome of the reaction wherever appropriate. If you attempt all 6, be sure to cross out the one you don’t want me to mark. Otherwise, I will go in order.
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.

**Leftovers... not just for lunch anymore!**

In a recent Nature paper, Brian Stoltz published a beautiful synthesis of (-)-cyanthiwigin F that relied on a 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.

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A.

1. NaH, toluene, reflux
2. K_2CO_3 / Mel, acetone, reflux

1:1 mixture of racemic : meso diastereomers

not chiral

chiral!

1. *chiral ligand* Pd^0, diethyl ether, room temp.

99% enantiomeric excess

(CR,R)-3

Cyanthiwigin F

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**Stereoablative:**

Initially formed stereocentres (from alkylation step) are lost (ablated) then new centres are formed under the control of a chiral ligand.
In the presence of a photosensitizer and light (hv), oxygen (O₂) can participate in Diels-Alder reactions, which opens up all kinds of interesting synthetic possibilities. In 1993, Dale Boger (Scripps) synthesized isochrysohermidin from a bis-pyrrole precursor. Propose a mechanism, and comment on the expected stereochemical outcome for the reaction.

Note: the purpose of the photosensitizer and light is to generate singlet oxygen (oxygen in the ground state is a triplet). Don't worry about this too much, though. You can just push arrows from O=O if that makes you happier.
In a synthesis of the briarellin diterpenes, Larry Overman formed the central bicycle by reacting precursors 1 and 2 in an efficient 2-step procedure. Propose a mechanism for the formation of 3.

Don't worry about the relative stereochemistry for this reaction.
Part 3. The following synthesis of (±)-isocyclechellene was completed by Steven Welch’s group in 1985. 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 couple of 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.

**Note:** pay attention to regiochemical control in these reactions, but don’t worry too much about stereochemistry.
Space for mechanisms is provided on the next two pages.
Mechanism for Step A:

\[ \text{reaction steps} \]

\[ \text{products} \]

"T&I."

*Pins mechanism would be ok here, too."
Mechanism for Step B: