Detailed Mechanism  Provide a detailed mechanism [i.e., explicitly show (using curly arrows) EVERY intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step] to account for the following transformations:

a) The conversion of the highly substituted tetrahydropyran 1 to the ethyl ester analogue 2. Predict the configuration of the new stereocenter (*) and provide a 3D drawing of the transition state to support your reasoning for that prediction.

b) The Lewis acid-catalyzed, tandem polycyclization of the linear precursor 3 to the (racemic) tricyclic lactam 4. Show the geometry of the transition state for the initial intramolecular Diels-Alder (IMDA) reaction that accounts for all of the relative configurations in 4. [Hint: Read about the Schmidt rearrangement on pp 396–397 in Kurti and Czako.]

c) The conversion of a substituted phenol 5 into the racemic tricyclic enone 6 upon exposure to hexa-2,4-dien-1-ol and PhI(OCOCF₃)₂ (PIFA) followed by refluxing in mesitylene. [Hint: The first step involves initial reaction between 5 and PIFA.]
d) Formation of ring-expanded products 8 and 9 from pyran 7 upon treatment with NaHMDS.

![Diagram of reaction](image)

**Other Problems**

1. A lithiation-borylation strategy is a powerful method for stereospecific homologation of chiral boronic esters. In the following scheme: i) deduce and provide the structures of the missing species (10 and 14), and ii) provide a detailed mechanism for transformation of 11 into 12.

![Diagram of reaction scheme](image)

**Reaxys Database Search**

a) According to the Reaxys database, how many single step reactions convert the C–C double bond in a substrate containing both a 1,2-disubstituted alkene (cis or trans) and a sulfide (containing at least 1 sp³-hybridized carbon) to an epoxide without converting the sulfide to a sulfoxide or sulfone? [Hint: Explore how to limit the results to only sulfides and not sulfoxides or sulfones and to limit the results to only alkenes and not aromatic rings.]

b) According to the Reaxys database, how many single step reactions convert a substrate containing both a 1,2-disubstituted alkene (cis or trans) and a sulfide (containing at least 1 sp³-hybridized carbon) to a sulfoxide without forming the epoxide? [Hint: Explore how to limit the results to only sulfoxides and not sulfones.]