Nazarov Reaction

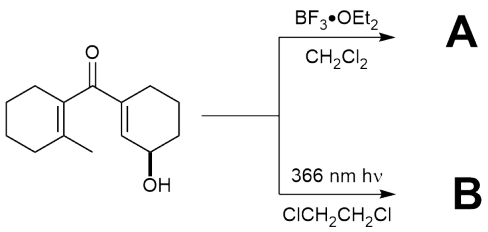
5% of total							
Question	8.1	8.2	8.3	8.4	8.5	8.6	**Total**
Points	5	2	6	2	8	8	**31**
Score							

The Nazarov reaction is a frequently used reaction of divinyl ketones to give cyclopentenones. It proceeds either photochemically or via acid catalysis and is an electrocyclization, followed by a proton transfer.

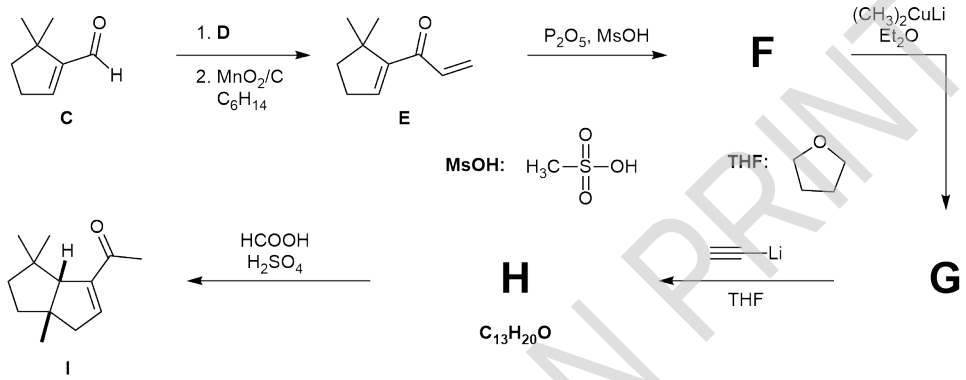
8.1 **Draw** the pi molecular orbitals to describe the Nazarov reaction. **Fill in** the electrons into the respective energy levels. **Mark** with an X the **i)** HOMO (highest occupied molecular orbital) and **ii)** LUMO (lowest unoccupied molecular orbital). For this exercise, you can consider the divinyl ketone as a pentadienyl cation with five p-orbitals. 5pt

8.2 From the pi molecular orbitals you derived in **Task 8.1**, **predict** under which conditions the Nazarov reaction of the divinyl ketone will proceed in a disrotatory or conrotatory fashion. In the **table on the answer sheet**, **mark** with an X the conditions under which the reaction is allowed. 2pt

8.3 The Nazarov reaction was used as key reaction in a synthesis of Farnesin. For both conditions below, **draw** one possible structure for each of **A** and **B**, including stereochemistry. Note that the products of both reactions show a signal at 6.70 - 6.73 ppm in the ^{1}H NMR. 6pt



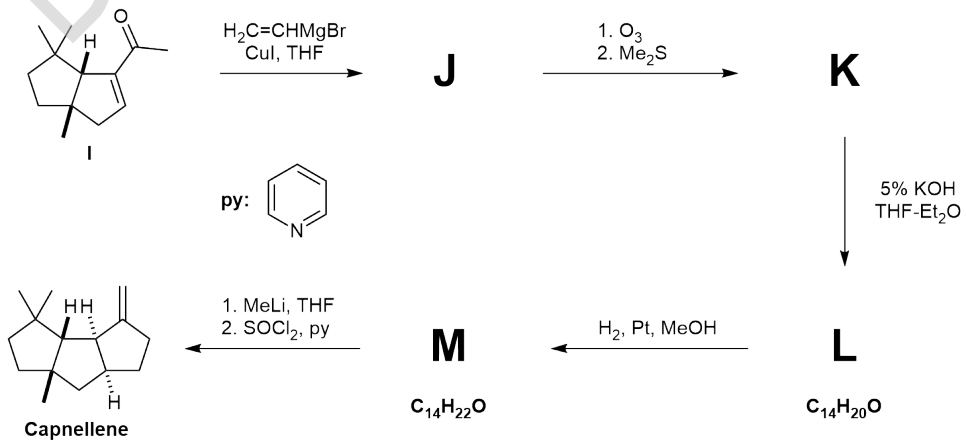
The synthesis of Capnellene commences with unsaturated aldehyde **C** shown below. Treatment with conditions **D**, followed by reaction with MnO_2 supported on carbon gave divinyl ketone **E** shown below. Exposure to a mixture of P_2O_5 and MsOH yielded **F**, which was elaborated via a sequence of reactions to the unsaturated ketone **I**.



8.4	**Choose** the reagent(s) from the list **on the answer sheet** that would be suitable as **D**.	2pt

8.5	**Give** the structures of intermediates **F**, **G**, and **H**, including their stereochemistry.	8pt

Enone **I** was then subjected to $H_2C{=}CHMgBr$ and CuI in THF to give intermediate **J**, followed by ozonolysis to yield intermediate **K**, which shows a signal at 9.61 ppm in the ^1H NMR. Treatment with 5% KOH in a mixture of THF and ether yielded intermediate **L**. Hydrogenation with a Pt-catalyst and under an atmosphere of H_2 yielded **M**, which finally gave rise to Capnellene.



8.6	**Give** the structures of **J**, **K**, **L**, and **M**, including their stereochemistry.	8pt