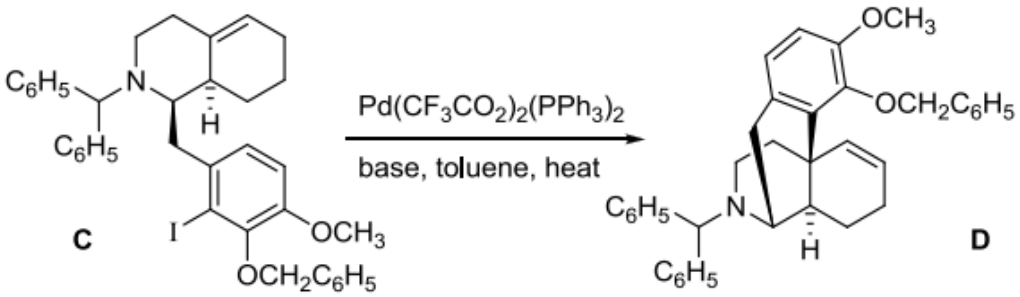
Problem Sheet

1)

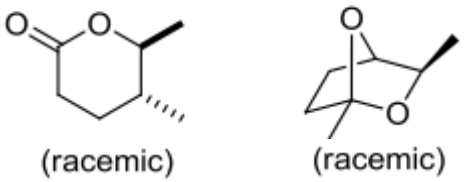
Give a mechanism for the intramolecular Heck reaction C to D shown below, explaining carefully the reasons for the position of the alkene double bond in the product D.



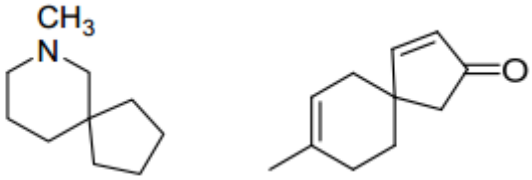
2)

Devise a synthesis of the compounds shown below. Each starting materials should have 5 carbons or fewer. Show clearly your retrosynthetic analysis and synthetic equivalents where appropriate. Optimally, no more than 3 steps are required. Propose reagents for your forward synthesis.

a)



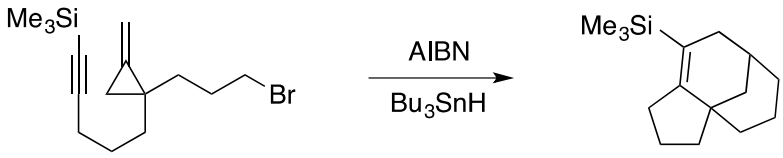
b)



3)

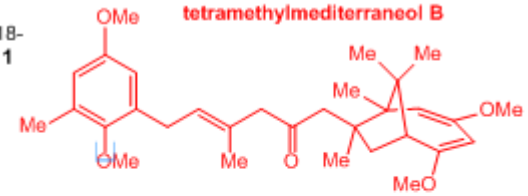
a) Suggest a radical-based method for carrying out the following transformations (how is it called?), giving reagents and a mechanism.

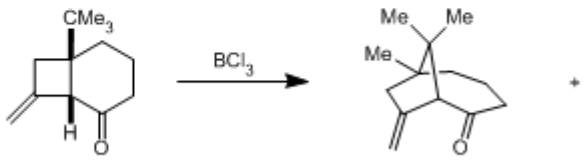
b) Provide a detailed, annotated mechanism for the transformation shown below commenting on all aspects of selectivity.



4)

The synthesis of racemic tetramethylmediterraneol B was reported by workers in Japan (*J. Org. Chem.* **1995**, 60, 3318-33). The pivotal step was the rearrangement of compound **1** into the [4.2.1] bicycle **2**, as found in the natural product. Provide a mechanism for the formation of **2** and **3**.





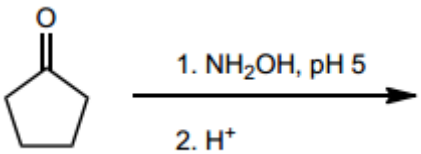
1

2, 66% yield

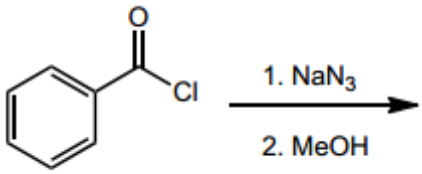
3, 11% yield

5) Name the following transformations and provide complete curved-arrow mechanisms, and fill in the structures of the products in each case.

a)



b)

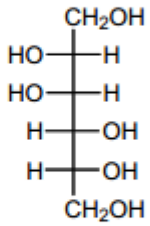


6)

Give structures for the products formed in the following reactions and identify all unknown compounds. Explain any issues of selectivity.

a) D-glucose $\xrightarrow[ZnCl_2]{2 \times Me_2CO}$ **F** $\xrightarrow[MeI]{NaH,\ CS_2;}$ **G** $\xrightarrow[AIBN,\ PhH,\ reflux]{Bu_3SnH,}$ **H**

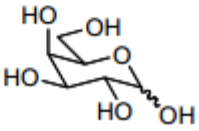
b)



D-mannitol

$\xrightarrow[ZnCl_2]{2 \times Me_2CO}$ **I** $\xrightarrow{Pb(OAc)_4}$ **J**

c)



D-galactose

$\xrightarrow[ZnCl_2]{2 \times Me_2CO}$ **K** $\xrightarrow[NaH,\ THF]{PhCH_2Br,}$ **L**