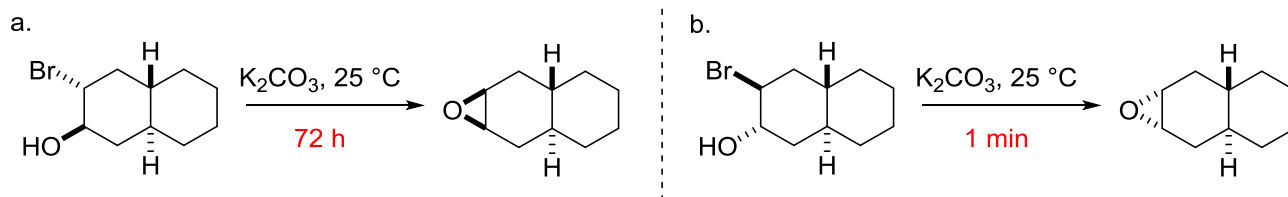
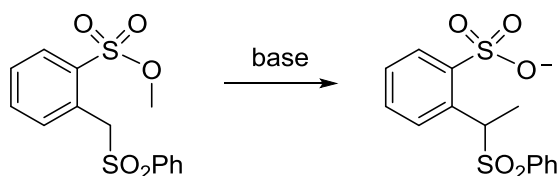


Answer the following questions:

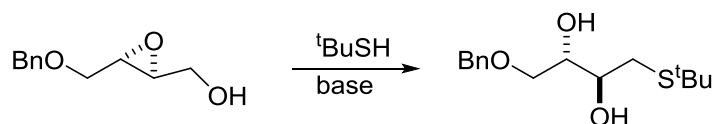
1. Explain the following:



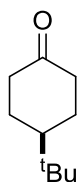
2. Draw a possible mechanism for this reaction (hint: uses Baldwin's rules):



3. Write a mechanism for the following transformation.

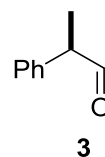
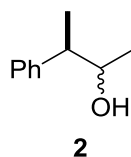
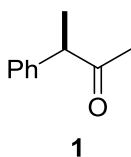


4. Rank the following reagents in terms of their ability to add to the ketone shown via equatorial attack (thex = thexyl =  $-\text{CMe}_2\text{CHMe}_2$ ).

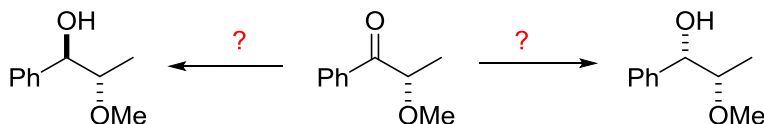


- a.  $\text{NaBH}^t\text{Bu}_3$
- b.  $\text{NaBH}(\text{thex})_3$
- c.  $\text{LiAlH}_4$
4.  $\text{Na} / \text{ROH}$

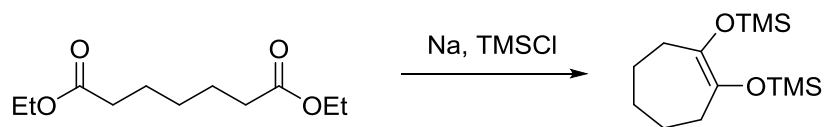
5. Suggest a reaction that would selectively convert ketone **1** into one diastereomer of the alcohol **2**, and another that would transform the aldehyde **3** preferentially into the other diastereomer of **2**.



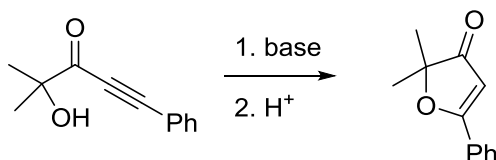
6. Provide reagents and draw appropriate diagrams of key intermediates to explain the following.



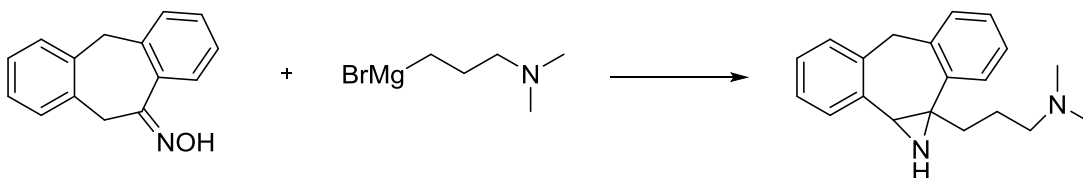
7. Indicate the mechanism of the following acyloin reaction (it takes several steps).



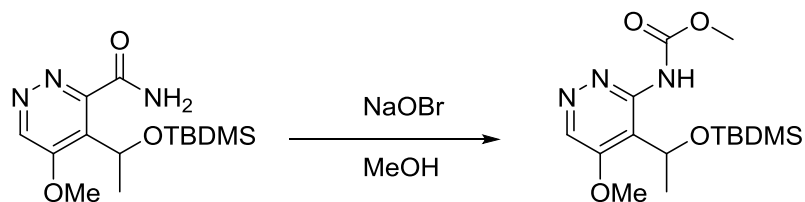
8. Draw orbitals of the alkyne in the following substrate and suggest why the following 5-endo-dig reaction (and all other 5-endo-dig reactions, according to Baldwin's rules) should be favoured?



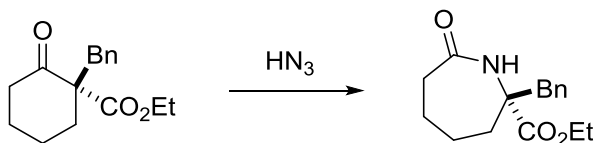
9. Draw clear curly arrows to express a reasonable mechanism for the following reaction. (Why does this reaction not undergo a Beckman rearrangement?)



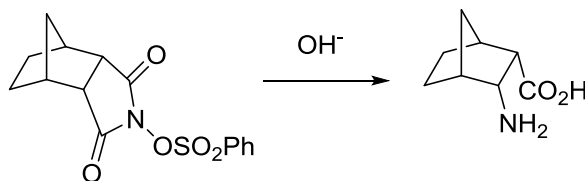
10. Write a mechanism for the following rearrangement.



11. Outline a mechanism for the following reaction of a ketone to an amide.



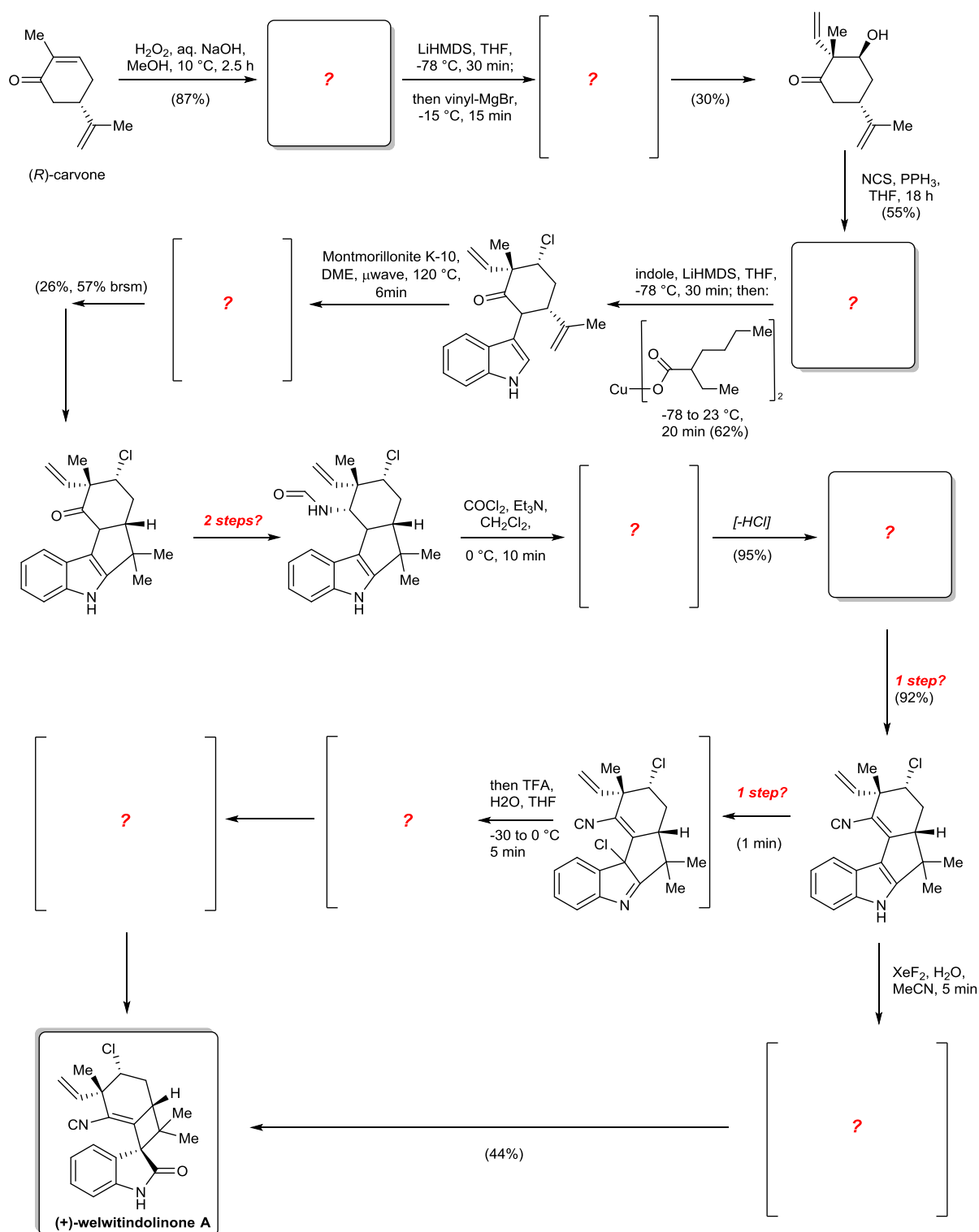
12. Outline a mechanism for the following rearrangement process.



Welwitindolinone A was discovered by Moore and colleagues in 1994 from *Hapalosiphon welwitschii*, collected from Queensland, Australia. Some of the welwitindolinones are cytotoxic agents active against multidrug resistant ovarian cancer cell lines.

Phil S. Baran and coworkers at The Scripps Research Institute reported the first total synthesis of welwitindolinone A in 2005. In 2006, John L. Wood and colleagues, then at Yale University, described a second total synthesis of this compound. Both synthetic routes have been outlined below – fill in the missing steps and provide a mechanistic explanation for each step. Which total synthesis is the more elegant?

### Baran's Total Synthesis



# Wood's Total Synthesis

