

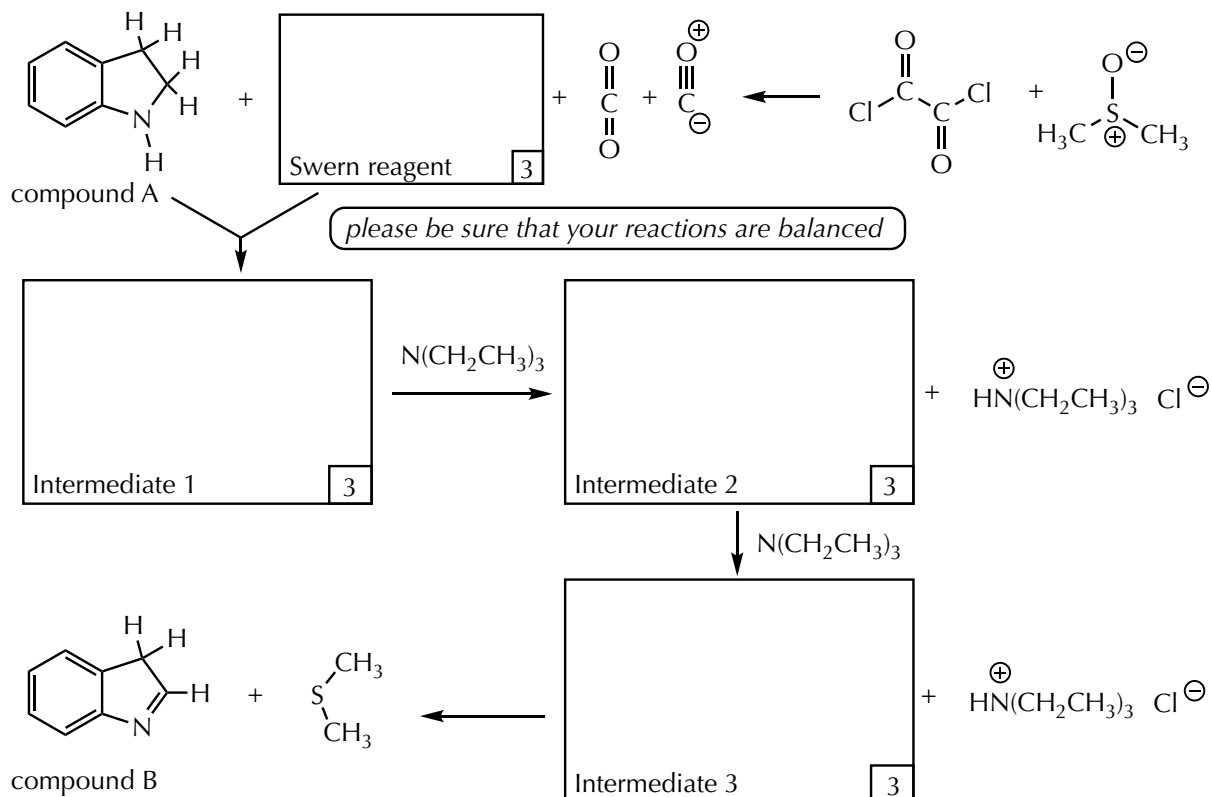
CHEM 215
WN 2022
First exam

Cover page and pKa table removed; exam = 90 minutes

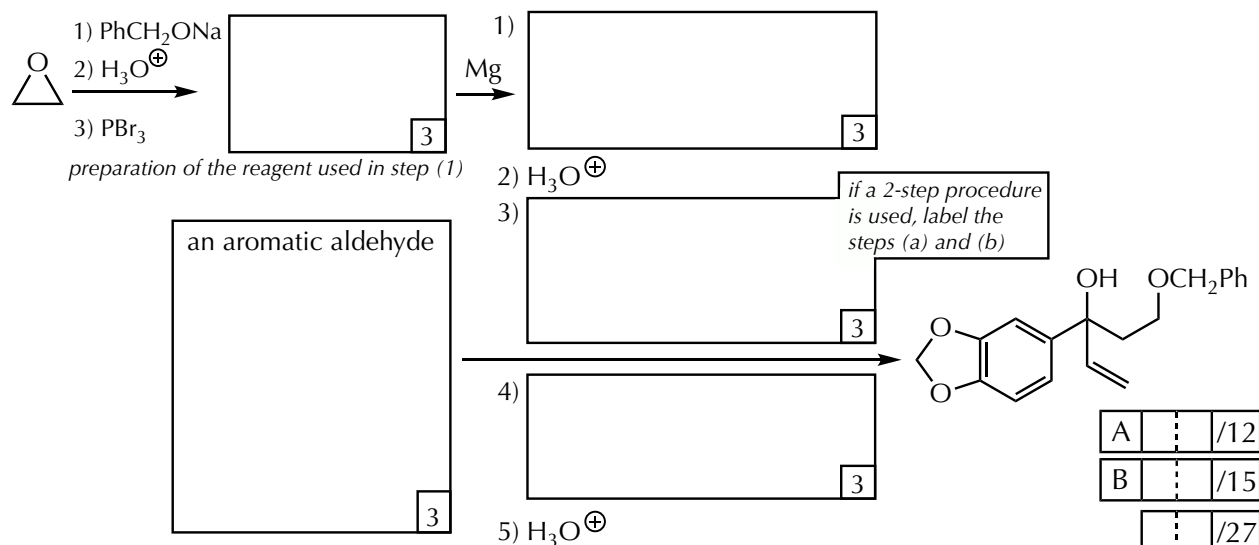
Question II (27 points)

Name: _____

- A. In 1987, it was reported that amines, such as compound A, could undergo the Swern oxidation reaction, resulting in the formation of the corresponding imine (compound B). The oxidation reaction mechanism is proposed to take place through an analogous mechanism as the one with alcohols (*J Chem Soc Chem Commun*, **1987**, 1660). Provide the anticipated three intermediates in the mechanism of this oxidation reaction (no curved arrows needed, only the Swern reagent and the three intermediates). Paying attention to the byproducts shown in these **BALANCED EQUATIONS** can help guide you.



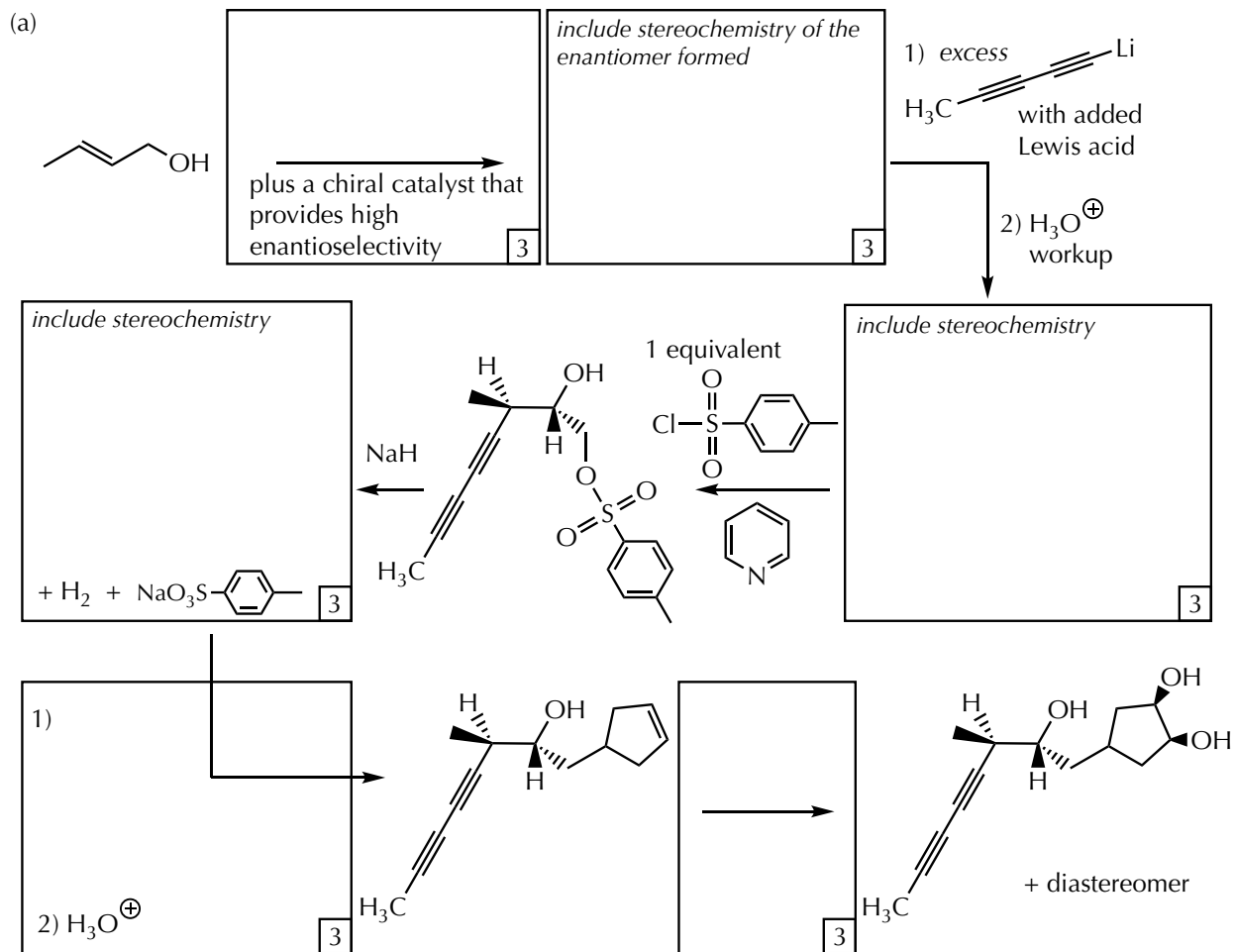
- B. The following tertiary alcohol was prepared in 5 steps during the synthesis of a naturally occurring alkaloid named crinine. Provide the missing compounds used in the production of this alcohol.



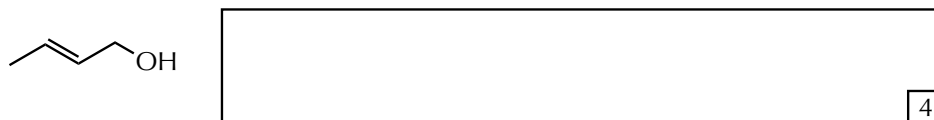
Question III (27 points)

Name: _____

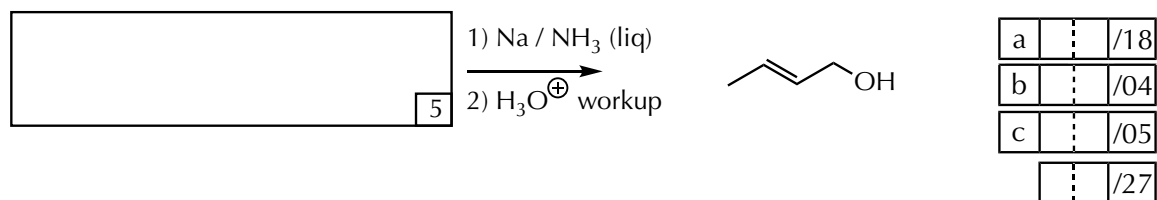
Complete the following organic transformations, used in a synthesis of rhizoxin D, an anticancer agent (*Angew Chem Int Ed*, 2019, 131, 254). **Using the available information backwards and forward is important for answering this question.** Draw out structures for reagents (no names, abbreviations, or acronyms).



(b) What is the complete name for the starting material in this sequence?



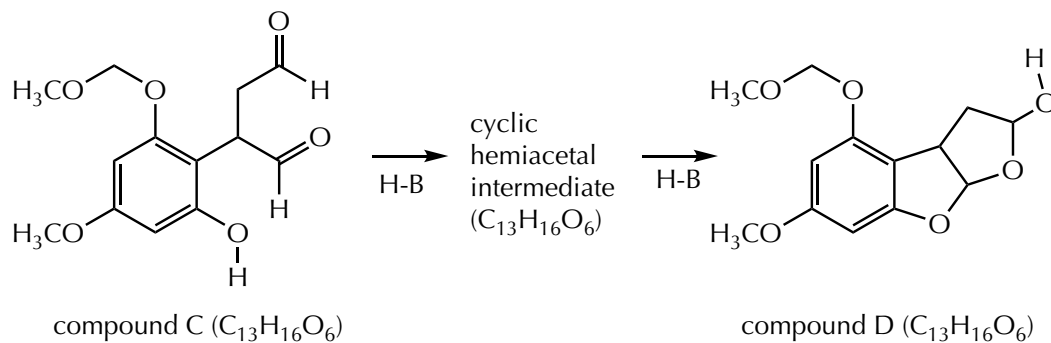
(c) What compound is used to prepare the starting material under these reaction conditions?



Question IV (22 points)

Name: _____

With a catalytic drop of HCl, compound C undergoes an isomerization reaction in which an intermediate with a cyclic hemiacetal forms, and then that intermediate gives compound D. Provide the complete, curved arrow mechanism for the acid catalyzed transformation of compound C to compound D. Use H-B as your generic Brønsted acid and B:[⊖] as its conjugate base (*Org Lett*, **2021**, 23, 2222).



compound C (C₁₃H₁₆O₆)

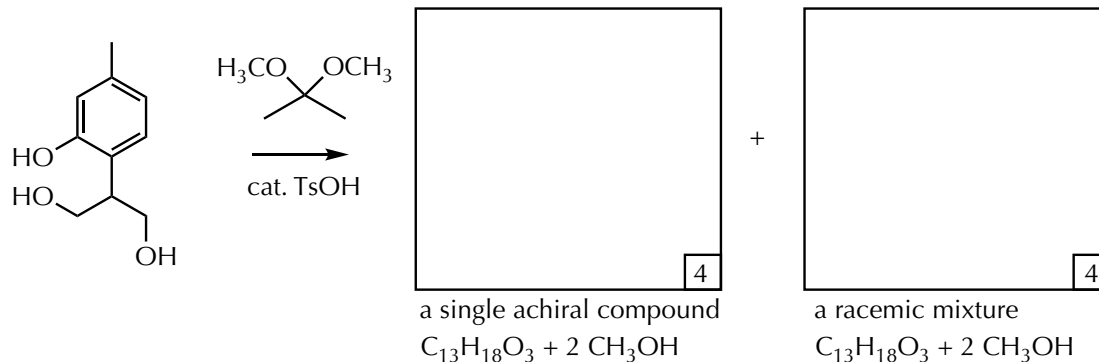
cyclic hemiacetal intermediate
and the next step in the mechanism

22

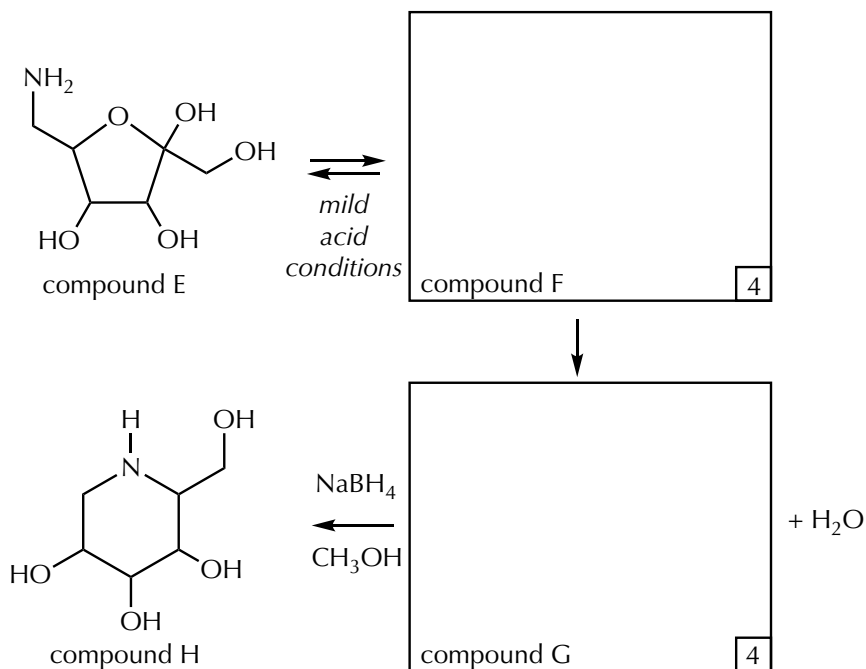
Question V (16 points)

Name: _____

- A. In principle, two different isomeric products could form in the following reaction (*Org Lett*, **2006**, *8*, 2479). Both products are $C_{13}H_{18}O_3$ and both reactions release two equivalents of methanol. Based on this information and the stereochemical descriptions provided below, what are the structures of the possible products?



- B. The following reaction sequence was used in the synthesis of DGJ, a potential drug candidate for lysosomal storage disorders (*Org Lett*, **2011**, *13*, 4064). Under mild acid conditions, compound E exists in equilibrium with an open chain form containing a ketone (compound F) which, in turn, can cyclize to give a different compound (compound G) along with an equivalent of water. Compound G can be reduced ($NaBH_4$ in methanol) to give compound H, as shown. What are the structures for compounds F and G?



A	:	/08
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B	:	/08
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