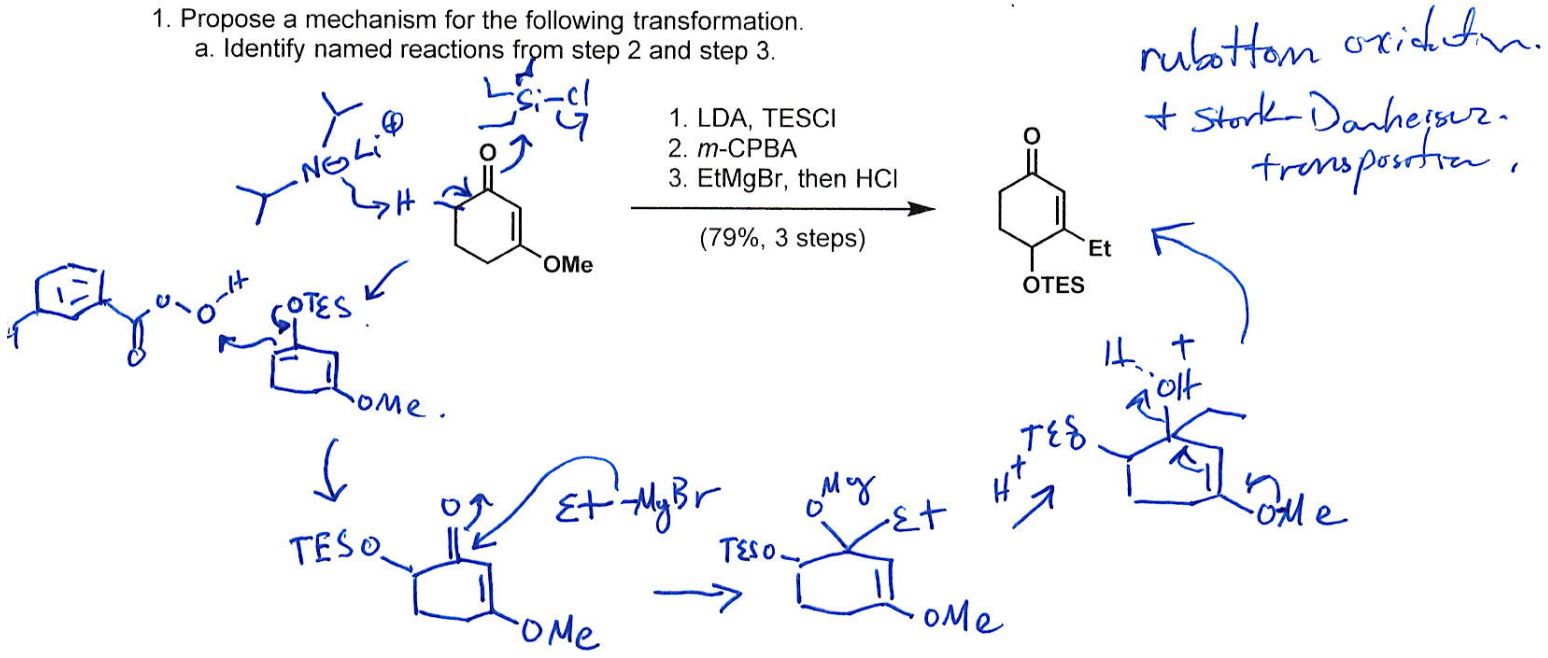
1. Propose a mechanism for the following transformation.
   a. Identify named reactions from step 2 and step 3.



rubottom oxidation.
+ Stork-Danheiser transposition.

Thomson, R. J. *Chem. Sci.* **2014**, *5*, 1794.

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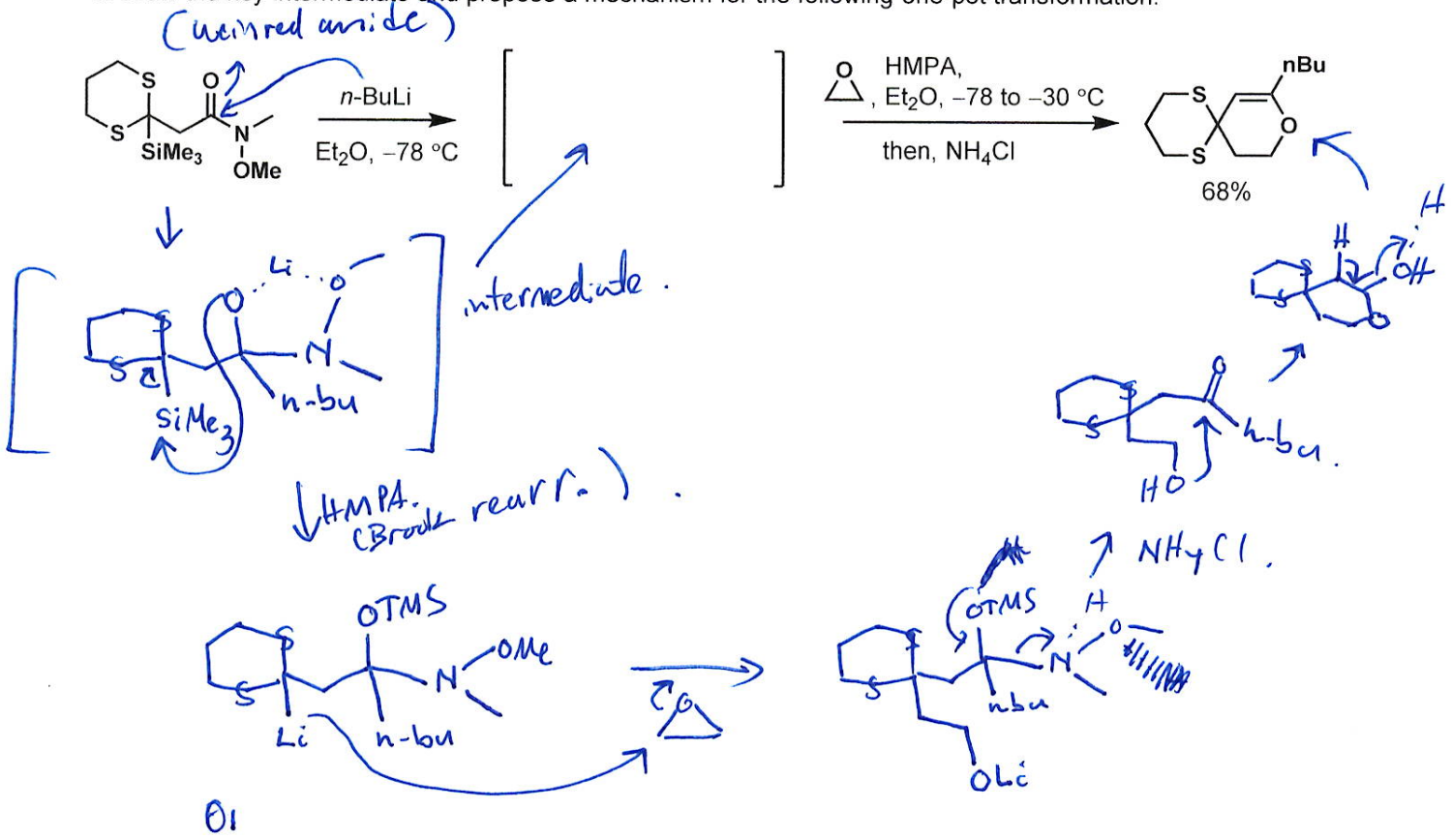
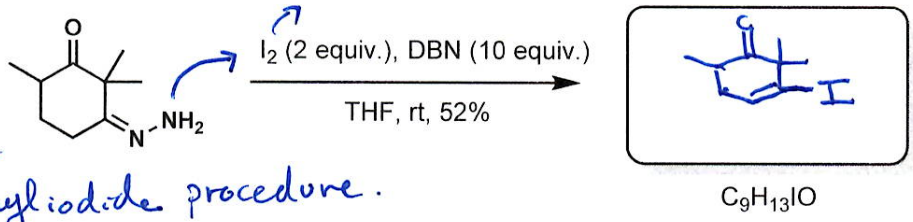
2. Draw the key intermediate and propose a mechanism for the following one-pot transformation.



Smith, A. B. *Angew. Chem., Int. Ed.* **2016**, *55*, 232

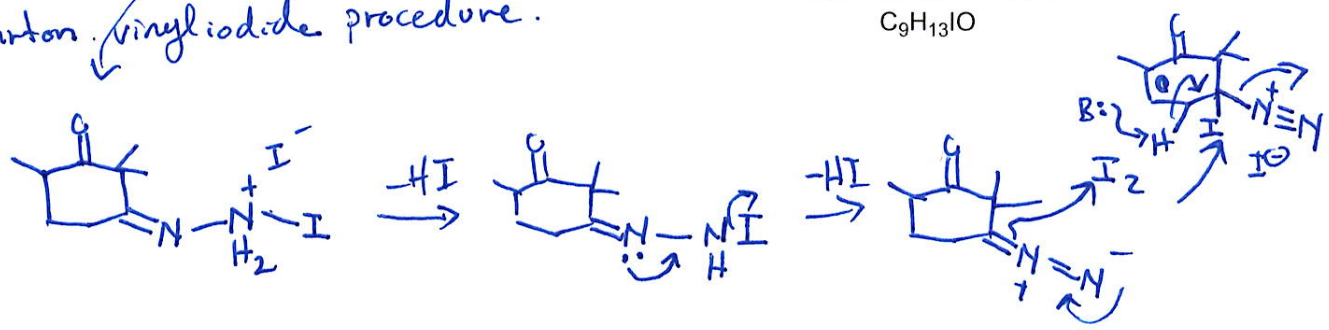
3. Draw the product, and propose a mechanism for the following transformation.

DBN



$C_9H_{13}IO$

Barton vinyliodide procedure.



Danishefsky S.J. *J. Am. Chem. Soc.* **1996**, *118*, 2843

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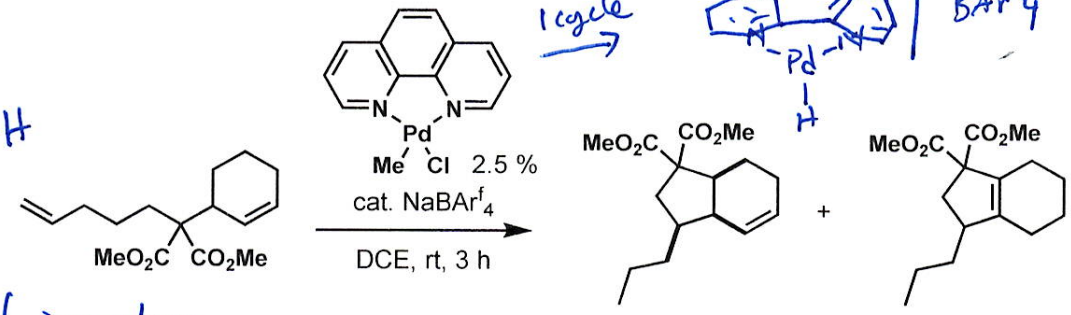
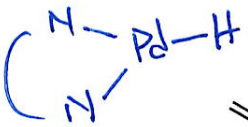
4. Propose a mechanism for the following transformation.
   a. Identify the active catalyst. (Hint: What catalyst is turned over in a closed catalytic cycle?)
   b. Explain the product ratio with respect to reaction time.



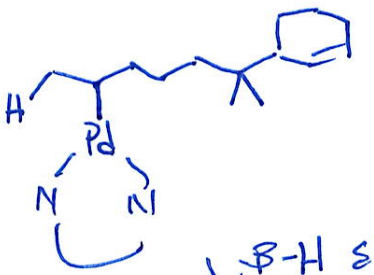
reaction time	A	Yield (%)	B
2 h	83		6
24 h	63		33

1 cycle

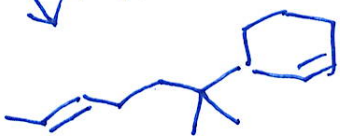
= active catalyst.



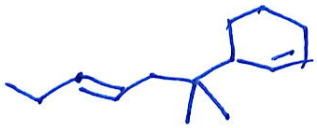
↓ insertion.



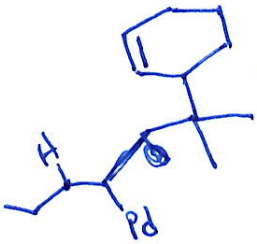
↓ β-H elim.



→ insertion, βH elim.

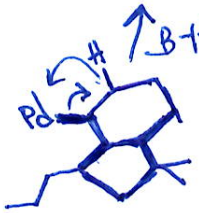


→ insertion.



intramolecular insertion.

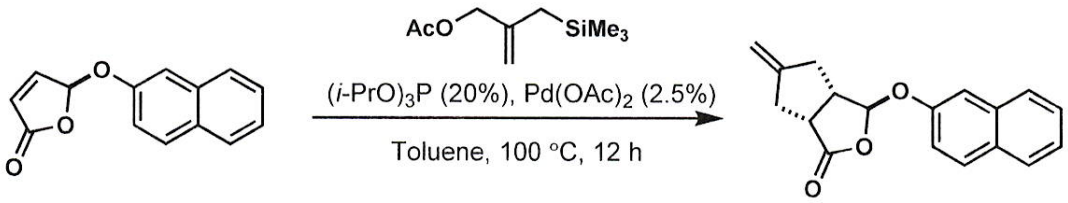
(A)



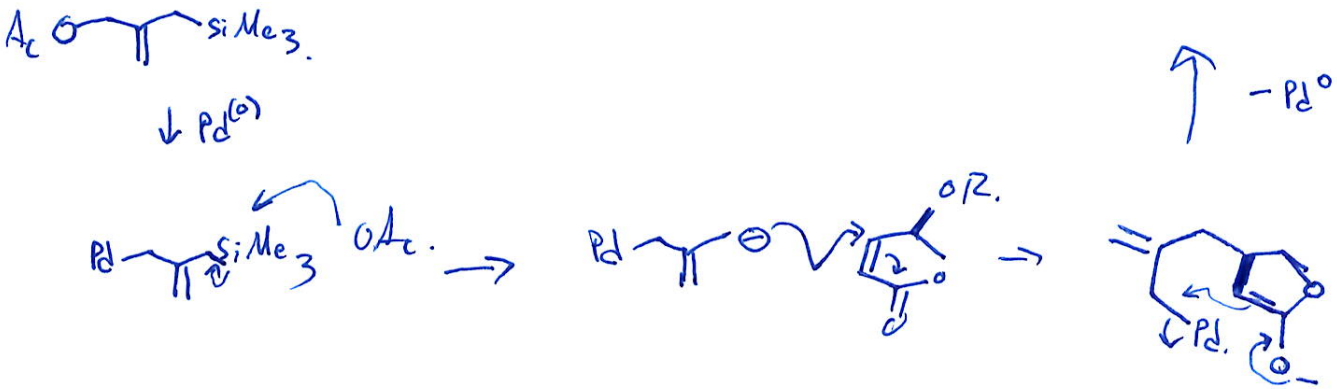
(B) arises from re-insertion to pdt (A).

Kochi, T. *J. Am. Chem. Soc.* **2012**, *134*, 16544.

5. Propose a mechanism for the following transformation.



93%, 98:2 dr



Trost, B.M. *J. Am. Chem. Soc.* **2002**, *124*, 9328.

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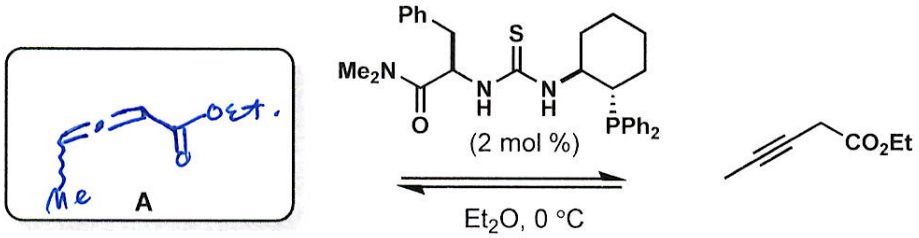
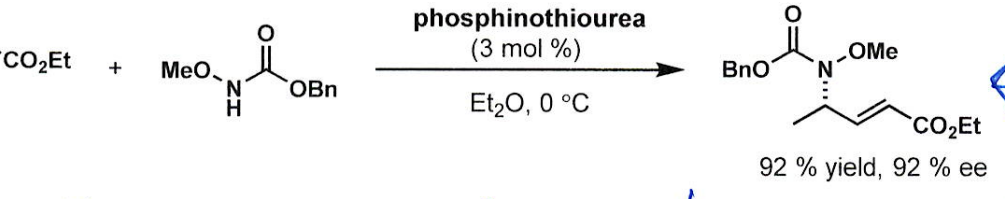
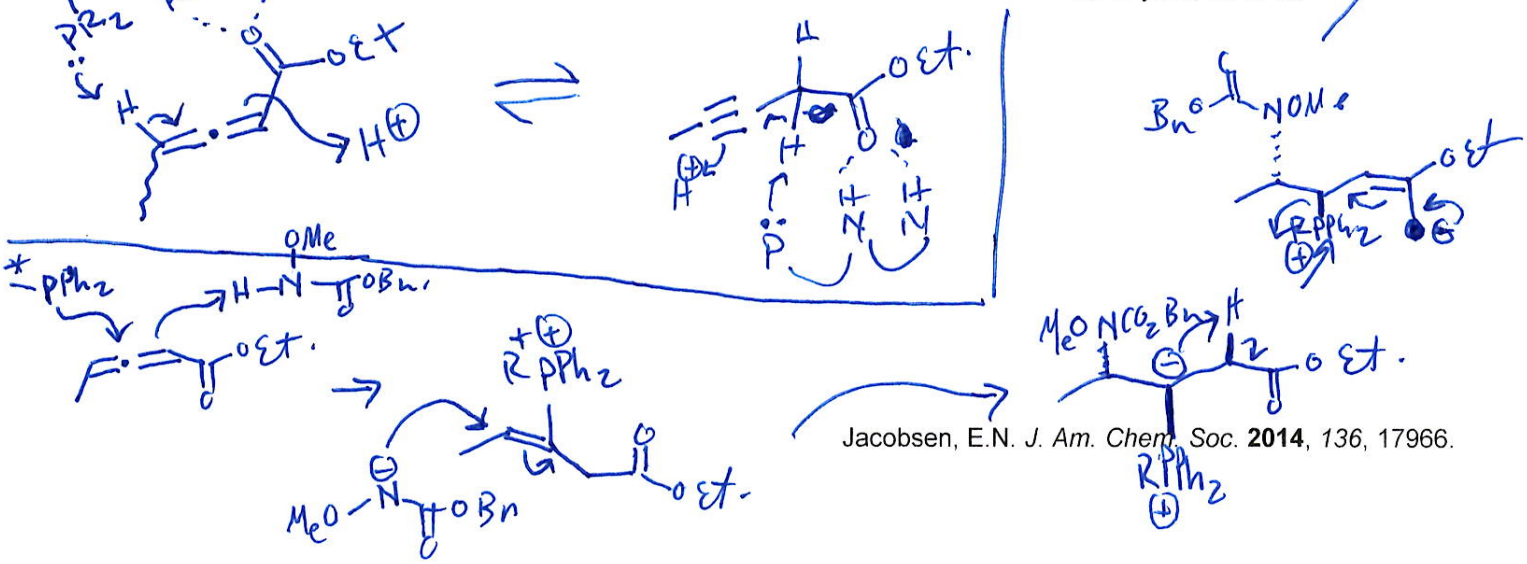
6. Upon treatment with a phosphinothiourea catalyst, compound **A** was found to isomerize to a propargyl ester. Compound **A** is the active isomer in the amination reaction that follows. Draw a mechnism for both the isomerization of **A**, and its transformation to the unsaturated ester.





92 % yield, 92 % ee



Jacobsen, E.N. *J. Am. Chem. Soc.* **2014**, *136*, 17966.