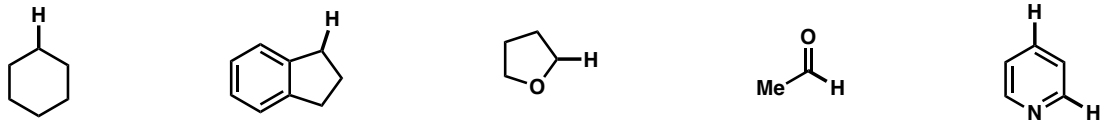
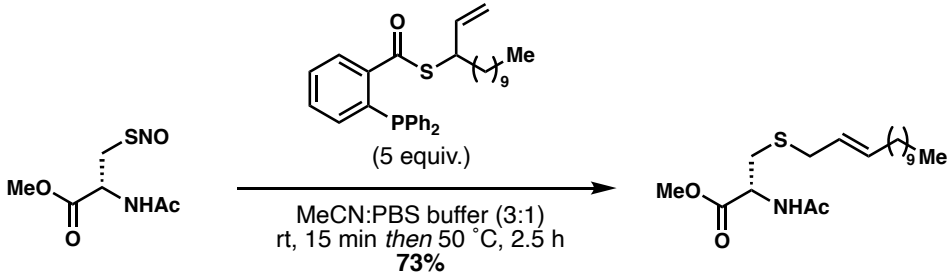
Problem Set
07/11/23
Nick Falcone & Sam He

1. **Warm-up:** Estimate the bond dissociation energies of the indicated C–H bonds in the following organic molecules (In *Comprehensive Handbook of Chemical Bond Energies*, Yu-Ran Luo, CRC Press, 2007).



2. **Mechanism:** Nitric oxide (NO)-mediated protein *S*-nitrosation is an important post-translational modification which has dynamic interactions with redox-signaling. Detecting *S*-nitrosation is challenging due to the instability of *S*-nitrosothiols (RSNO). Xian and coworkers developed the following one-pot protocol to convert these unstable functional groups to detectable thioether conjugates. Propose a mechanism for this transformation.



Org. Lett. **2010**, *12*, 5674–5676.

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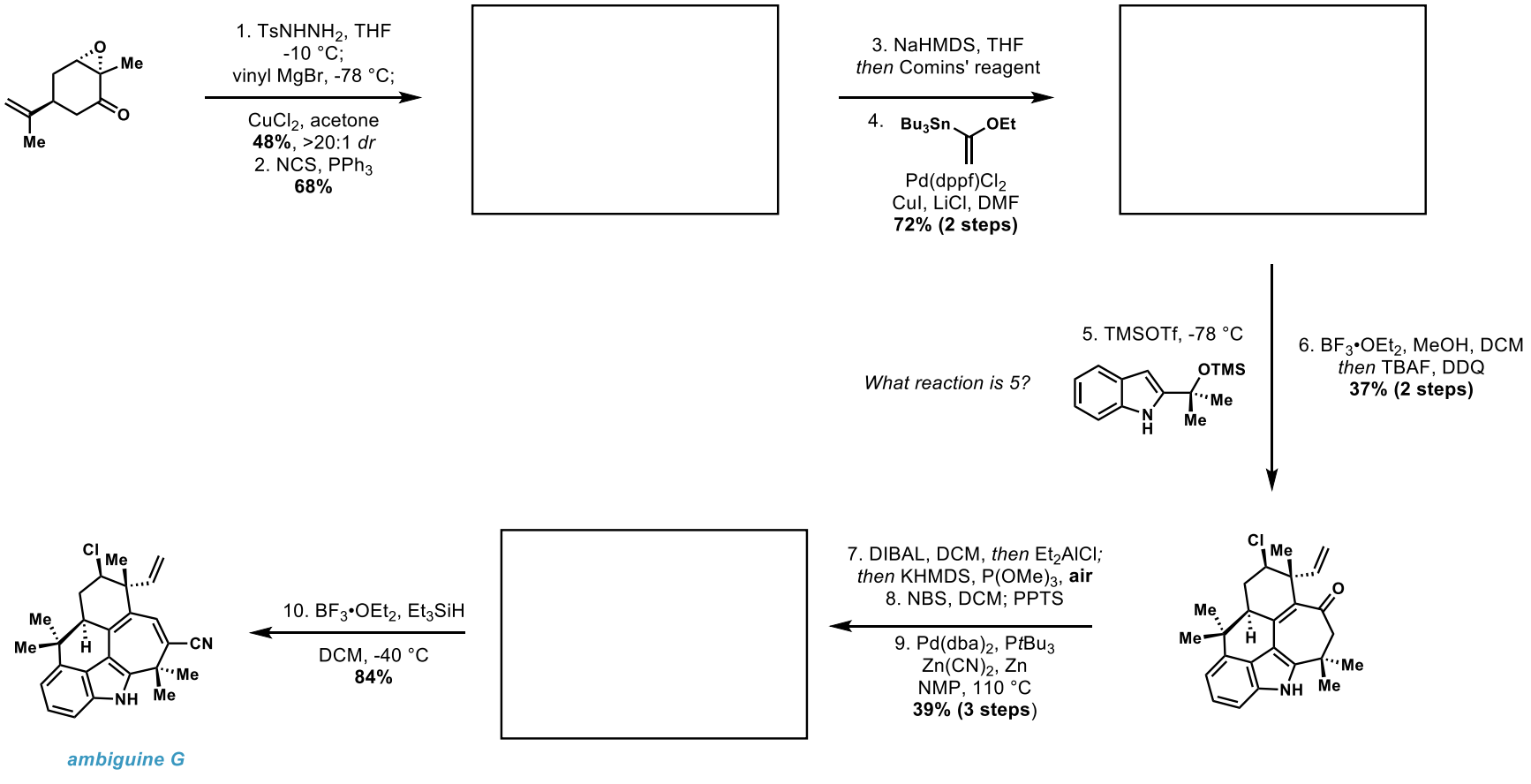
3. Denskport: Please provide the following structures in the blanks below in the total synthesis of ambiguine G. *(J. Am. Chem. Soc.* **2021**, *143*, 10872-10875).



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4. **Undergraduate problem:** Farnesyl pyrophosphate has been postulated to be the precursor of a variety of sesquiterpene skeletons. Please provide a mechanism of the depicted rearrangement of farnesyl pyrophosphate to the cedrane skeleton. *Hint*: The first step is loss of OPP. (*In Bioactive Natural Products (Part L)*; Studies in Natural Products Chemistry; Atta-ur-Rahman, Ed; 2005, Vol.32, p 395.)