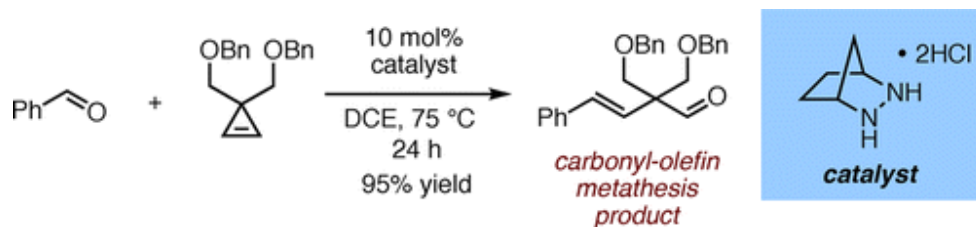


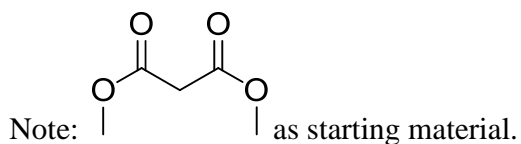
## Organocatalytic Carbonyl-Olefin Metathesis

*Problem:*



1) Propose a mechanism for this catalytic carbonyl-olefin metathesis using hydrazine; Explain the complete (**E**)-olefin selectivity observed in this reaction.

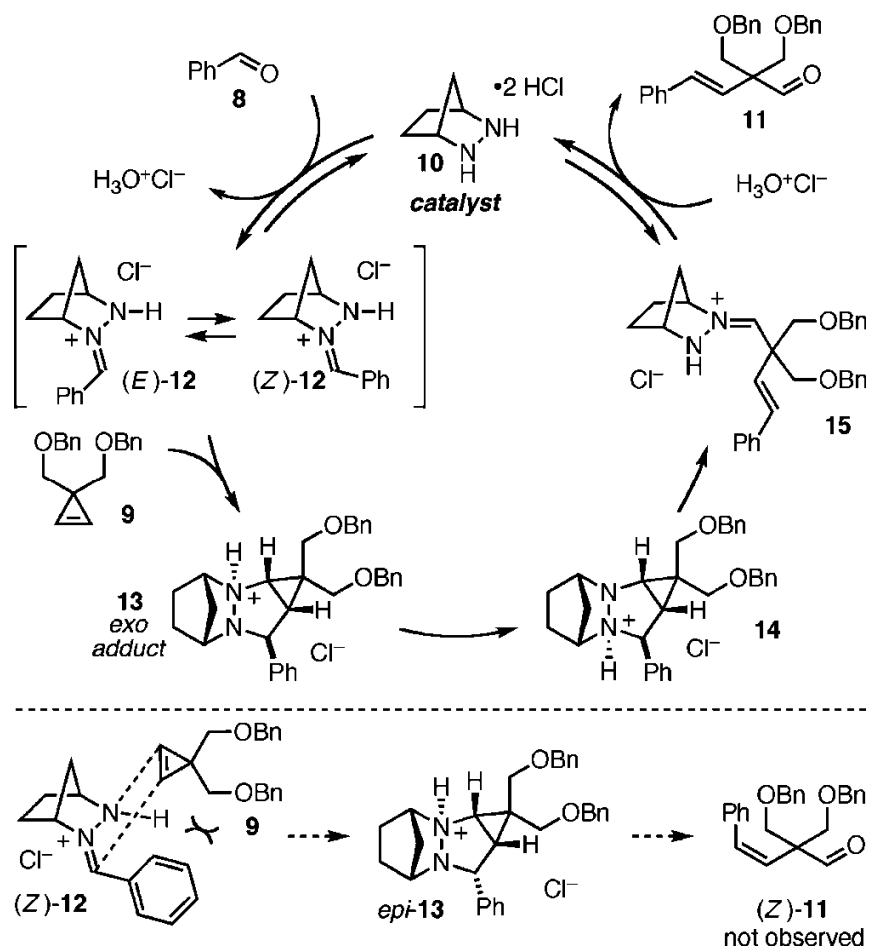
2) How to synthesize the cyclopropene?



### 1. Mechanistic rationale for catalytic carbonyl-olefin metathesis using hydrazine

Catalyst **10** is used as its dihydrochloride salt, they assume that the reaction proceeds via hydrazone ion **12**, the protonated form of the putative azomethine imine. Cycloaddition of **12** with cyclopropene **9** produces pyrazolidinium salt **13**. It is plausible that cycloaddition and not cycloreversion is the ratedetermining step in this transformation due to the high strain of the three-membered ring. Conversion of **13** to **14** by proton transfer would then facilitate strain-relieving cycloreversion to produce hydrazone ion **15**. Upon hydrolysis of **15**, the metathesis aldehyde **11** would be produced with concomitant regeneration of hydrazine catalyst **10**.

The complete (**E**)-olefin selectivity observed in these reactions can be rationalized by invoking cycloaddition of hydrazone (**E**)-**12** via an *exo* transition state due to the minimization of steric congestion. The alternative cycloaddition of (**Z**)-**12** (via the *exo* transition state) to produce *epi*-**13** is expected to be disfavored due to a significant destabilizing interaction between the phenyl substituent and a benzyloxymethyl group on the cyclopropene **9**.



## 2. Synthesis of Cyclopropenes:

