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?

Note: as starting material.
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 hydrazonium 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 rate-determining 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 hydrazonium 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 hydrazonium (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 benzyloxyethylmethyl group on the cyclopropene 9.
2. Synthesis of Cyclopropenes: