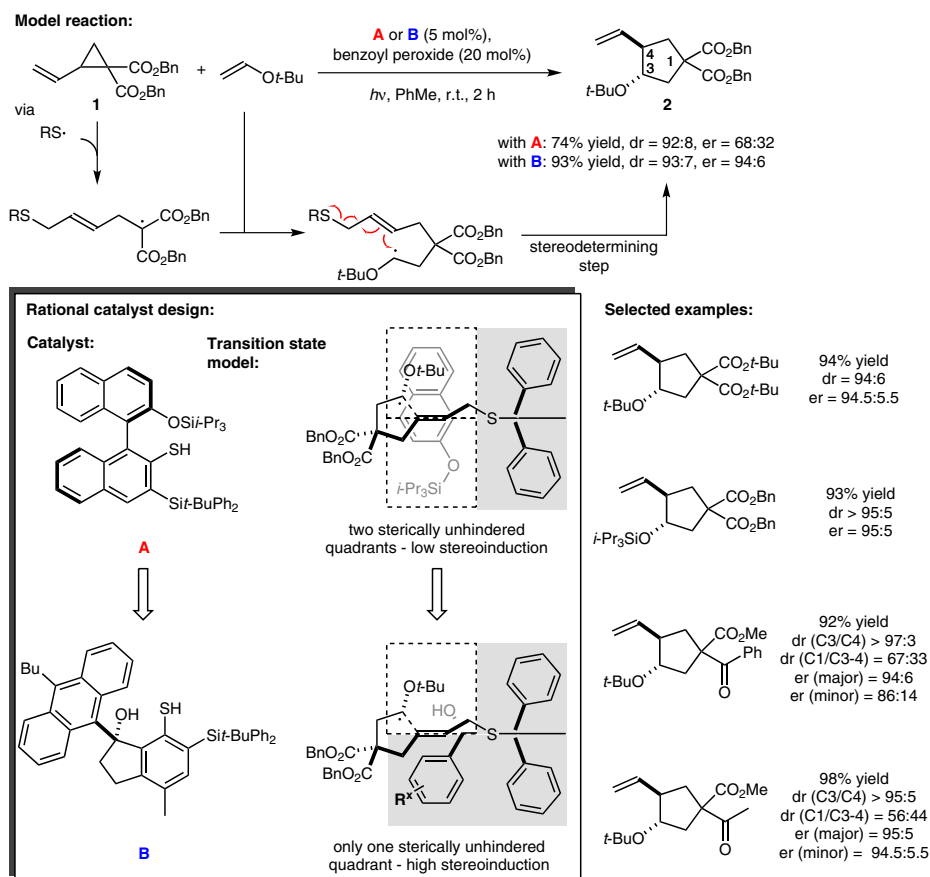


Thiyl Radical Catalyzed Enantioselective Cyclizations



Significance: Maruoka and co-workers report an enantioselective radical cyclization catalyzed by the newly designed thiyl radical catalyst **B**. The reaction starts from acceptor-substituted vinyl cyclopropanes **1**, which are opened by the catalyst and reclose to cyclopentane **2** after addition to a vinyl ether. Based on the low selectivity obtained with catalyst **A** and the transition state model with two quadrants available for the formation of opposite enantiomers, catalyst **B** was designed blocking of the quadrants and enabling high enantioselectivities.

Comment: Through rational catalyst design, the Maruoka group has achieved the first highly stereoselective C–C bond formation using a thiyl radical catalyst. This proof of principle is expected to spur further research towards the application of catalysts similar to **B** and the development of novel thiyl radical catalysts with innovative chiral backbones. Further research is also expected to address the currently poor diastereocontrol between a possible stereocenter at C1 and the *anti*-configured stereodiad at C3 and C4.