**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 sterically unhindered quadrants - low stereoinduction, 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 diasterecontrol between a possible stereocenter at C1 and the anti-configured stereodiad at C3 and C4.