**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 stereo-selective 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.

**Model reaction:**

\[
\text{CO}_2\text{Bn} + \text{RS-Pr}_3\text{SiOH} \xrightarrow{\text{hv}, \text{PhMe}, \text{r.t.}, 2\text{h}} \text{CO}_2\text{Bn} \xrightarrow{\text{B}} \text{CO}_2\text{Bn} + \text{BuO}\text{t}-\text{BuPh}_2
\]

**Selected examples:**

- 94% yield, dr = 94:6, er = 94.5:5.5
- 93% yield, dr > 95:5, er = 95:5
- 92% yield, dr (C3/C4) > 97:3, er (C1/C3-4) = 94:6, er (major) = 95:5, er (minor) = 94.5:5.5
- 98% yield, dr (C3/C4) = 95:5, er (C1/C3-4) = 56:44, er (major) = 95:5, er (minor) = 94.5:5.5