Highly Enantioselective Organocatalysis with a Mechanically Interlocked Molecule

**Significance:** Niemeyer and co-workers report that the [2]-catenane (S,S)-3, containing two chiral 1,1'-binaphthylphosphoric acids (initial report: *Chem. Commun.* 2016, 52, 5977), imposes dramatically superior enantioinduction on the transfer hydrogenation of 2-aryl-substituted quinolines, compared with both the corresponding non-interlocked macrocycle (S)-4 and acyclic catalyst (S)-5.

**Comment:** Computational studies, in which the mechanically interlocked nature of (S,S)-3 was mimicked by assuming a simplified non-dissociative dimeric structure, suggest that the interlocked catalyst proceeds through a sandwich-like transition state in the enantiodetermining step. The authors propose that this motif, involving two phosphoric acid moieties bound together in proximity to the reaction site, is responsible for the increase in enantioselectivity.