Highly Enantioselective [5+2] Annulations through Cooperative N-Heterocyclic Carbene (NHC) Organocatalysis and Palladium Catalysis


**Enantioselective [5+2] Annulations with a Cooperative Catalytic System**

![Representative examples](image)

**Significance:** Synthetic chemists have long sought to combine N-heterocyclic carbene (NHC) organocatalysis and metal catalysis. However, because NHCs are excellent ligands for late-transition metals, the design of cooperative catalytic systems remains a formidable challenge (M. H. Wang, K. A. Scheidt Angew. Chem. Int. Ed. 2016, 55, 14912). Reported is the first highly enantioselective [5+2] annulation between an NHC enolate and a π-allyl palladium intermediate through a dual catalytic process.

**Comment:** The authors expand their previous studies on NHC/Pd-based catalytic systems (*J. Am. Chem. Soc.* 2016, 138, 7840; *ibid.* 2017, 139, 4443) by using a bidentate phosphine ligand to prevent NHC coordination to the active palladium catalyst. A matched combination of a chiral NHC and a chiral phosphine ligand promotes high levels of enantioselectivity, which has previously been a challenge for seven-membered rings due to both unfavorable entropy effects and transannular interactions (see, for example: Y.-N. Wang et al. *Angew. Chem. Int. Ed.* 2018, 57, 1596).