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

Representative examples:

- **Ph**
  - 75% yield, >99% ee

- **Ph**
  - 30% yield, 99% ee

- **Ph**
  - 86% yield, >99% ee

- **Ph**
  - 62% yield, 99% ee

- **Ph**
  - 52% yield, >99% ee

- **Ph**
  - 67% yield, 99% ee

**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).