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

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Category

Synthesis of Heterocycles

Key words

organocatalysis

N-heterocyclic carbenes

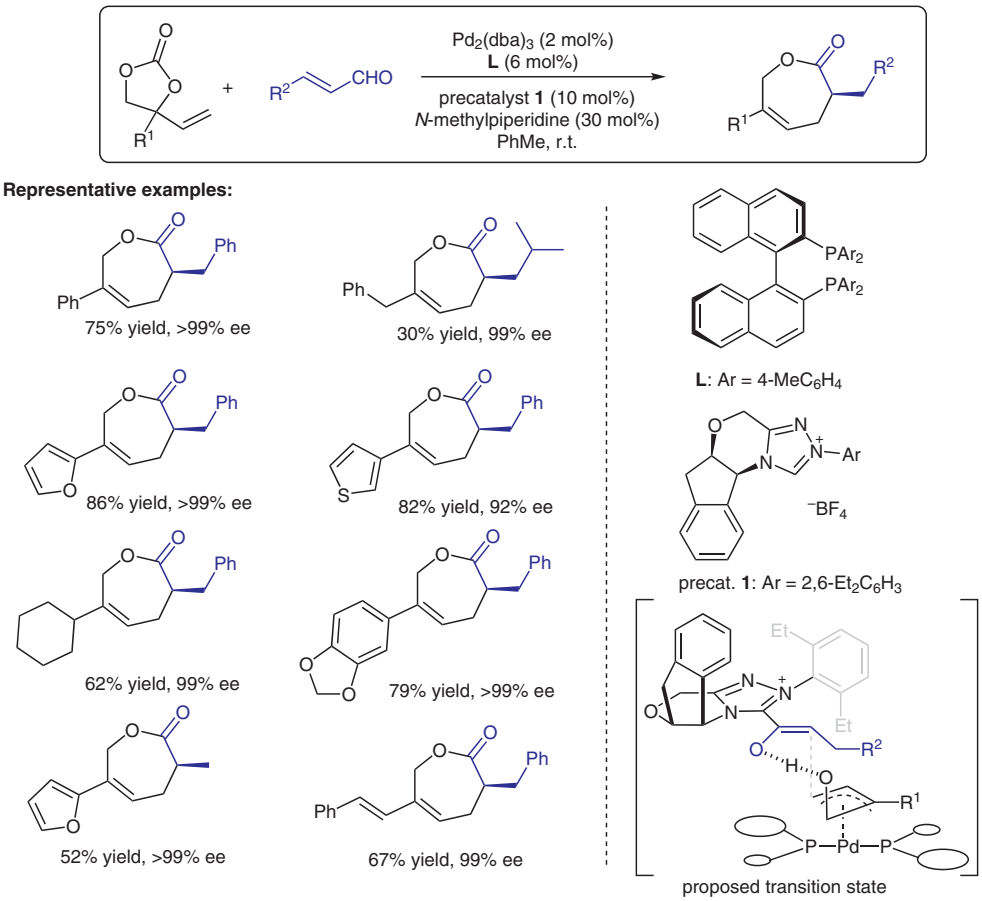
palladium catalysis

enantioselectivity

[5+2] annulation

lactones

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



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).

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