Category

Synthesis of Heterocycles

Key words

enynes

cobalt catalysis

hydroboration

γ-lactams

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Versatile Cobalt-Catalyzed Enantioselective Entry to Boryl-Functionalized All-Carbon Quaternary Stereogenic Centers

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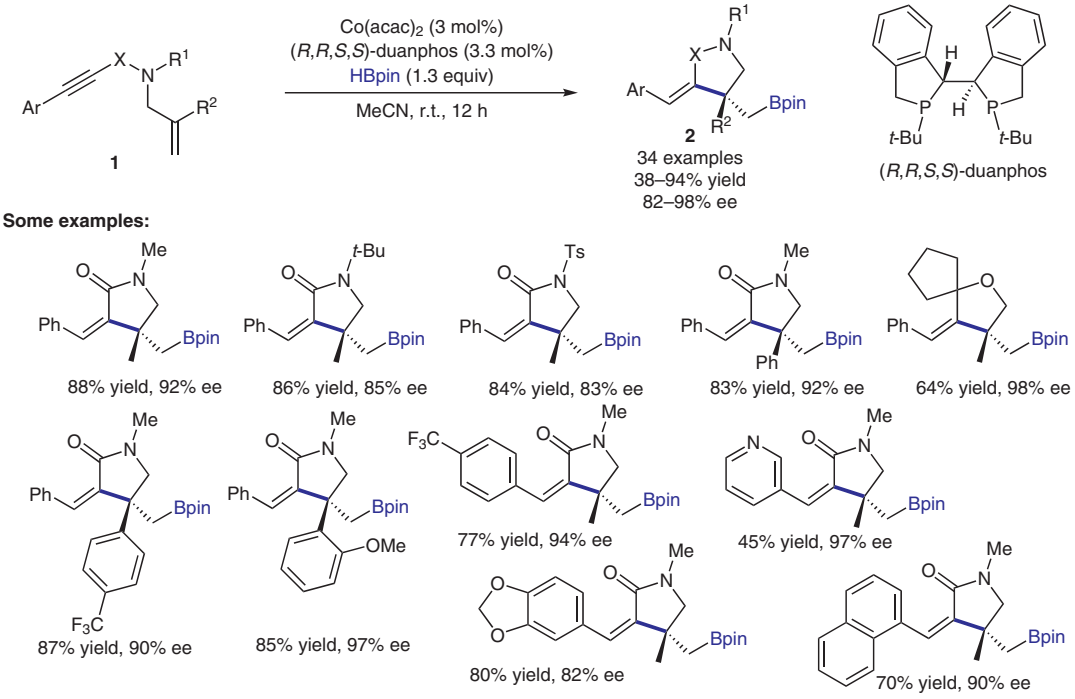
Cobalt-Catalyzed Hydroboration/Cyclization Synthesis of γ-Lactams



Significance: Compounds containing the γ-lactam ring are widely distributed in nature and are present in many biologically active compounds. Besides other methods described for preparing this scaffold, transition-metal-catalyzed cyclization has gained much attention (S. Soleimani-Amiri et al. *RSC Adv.* **2017**, *7*, 28407). Wang and Ge report a Co-catalyzed preparation of chiral γ-lactams bearing a boron functionality that has not previously been described and that adds to the limited number of reported reactions for the preparation of all-carbon quaternary stereogenic centers.

Comment: Reported is the asymmetric Co-catalyzed hydroboration/cyclization of amide-tethered 1,6-enynes **1** to produce γ-lactams **2**. Substrates with aliphatic or aromatic substituents on the nitrogen atom and the allyl group (R^1, R^2 = alkyl, aryl) were suitable for the reaction conditions. O- and N-tethered 1,6-enynes **1** also gave the corresponding cyclization products **2** efficiently. Steric hindrance around the nitrogen atom led to slightly decreased enantioselectivities. Enynes **1** (Ar = EWG- or EDG-bearing aryl or hetaryl) also gave products **2** in good yields and with high enantioselectivities. A gram-scale synthesis of **2** and a series of transformations including oxidations, homologations, cross-couplings, and alkenylations demonstrated the synthetic utility of this method. A reaction mechanism was proposed on the basis of deuterium-labeling and control experiments.

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