M. L. COOKE, K. XU, B. BREIT* (ALBERT-LUDWIGS-UNIVERSITÄT FREIBURG, GERMANY) Enantioselective Rhodium-Catalyzed Synthesis of Branched Allylic Amines by Intermolecular Hydroamination of Terminal Allenes

Angew. Chem, Int. Ed. 2012, 51, 10876-10879.

Rhodium-Catalyzed Enantioselective Hydroamination of Allenes

Proposed mechanism:

NHAr
$$H(D)$$

$$H(D)$$

$$ArNH_{2}(ArND_{2})$$

$$ArHN-[Rh]$$

$$ArHN-[Rh]$$

$$H(D)$$

$$H(D)$$

$$H(D)$$

$$H(D)$$

$$H(D)$$

$$H(D)$$

$$H(D)$$

$$H(D)$$

Significance: Despite the versatility of α -chiral allylic amines, synthetic methods to access them have been underdeveloped. The authors reported the first example of the enantioselective intermolecular hydroamination of mono-substituted allenes.

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Comment: A variety of substituted anilines, even bearing unprotected alcohol and indole moieties, were employed to give good yields and high enantioselectivities. Further mechanistic study is desirable to explain the regioselectivity of the hydrometalation step.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

rhodium

hydroamination

allenes

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