bifunctional

ammonium betaines

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Chiral Ammonium Betaines: A Bifunctional Organic Base Catalyst for Asymmetric Mannich-Type Reaction of α -Nitrocarboxylates

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Chiral Ammonium Betaines as Bifunctional Organocatalysts

Catalysts with comparable activity:

Only the betaine catalyst is selective:

Betaine Structured ion-pair

Significance: The authors established a new ammonium betaine catalyst in asymmetric Mannichtype reactions. The reaction of α -nitrocarboxylates with N-Boc imines proceeded in the presence of catalyst $\mathbf{1}$ in excellent yields and enantioselectivities, albeit diastereoselectivities of the products were only moderate, in favor of the syn isomer. Although the activity was comparable to betaine $\mathbf{1}$, almost no stereoselectivity was observed when catalyst $\mathbf{2}$ was used. This points out the crucial role of the betaine structure, since it is able to form a structured ion pair in the reaction course.

Comment: In the present work a new class of organocatalysts is introduced. Although the reported reaction is well established in organocatalysis (e.g., A. Singh, J. N. Johnston *J. Am. Chem. Soc.* **2008**, *130*, 5866), this work demonstrates the power of new bifunctional ammonium betaines like **1** as enantioselective organic base catalysts. Especially the high enantioselectivities at low catalyst loadings (1 mol%) are remarkable. The importance of the zwitterionic nature of the catalysts was shown nicely. Reports on new organic betaine catalysts and further applications can be anticipated.

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