Organocatalysis —
Hydrazine and Sulfonimide as New Functionalities in
Asymmetric Organocatalysis

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Abstract

Two new types of organocatalysts, camphor sulfonyl hydrazine and chiral sulfonimide are designed respectively for Lewis base and Brønsted acid organocatalysis.

Camphor sulfonyl hydrazine (CaSH) was synthesized for the first time as a new Lewis base organocatalyst. After modification by $N^\alpha$- and $N^\beta$-alkylation or $N^\alpha$-acylation, a series of six-member cyclic CaSHs were explored as organocatalysts in asymmetric Diels-Alder reactions. Trichloroacetic acid was found to be the best co-catalyst when the loading amount was controlled at 0.1 equivalent to the dienophiles and 0.5 equivalent to the catalysts. The reactions were carried out in brine without any additional organic solvent. Excellent yields and enantioselectivity up to 96% were achieved. It is the first report that hydrazine is used as the functionality in asymmetric organocatalysis.

Chiral sulfonimide (CSI) is synthesized as a new type of Brønsted acid organocatalyst. Starting from racemic BINOL, the corresponding 2,2’-bissulfonylchloride was synthesized in good yield. Resolution was achieved by forming the diastereomeric cyclic sulfonimide with optically pure (S)-(-)-α-methylbenzylamine. Lithiation followed by bromination at the 3,3’- positions was mediated by the sulfonyl groups. A series of 3,3’-diaryl CSIs were then synthesized via Suzuki coupling. The use of these chiral sulfonimides (CSI) as Brønsted acid organocatalysts in asymmetric aza-Friedel-Crafts reaction was explored.
CaSH
Camphor Sulfonyl Hydrazine

CSI
Chiral Sulfonimide
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