

DOCTORAL THESIS

CaSH (camphor sulfonyl hydrazine) and CSI (chiral sulfonimide) organocatalysis

Chen, Lingyan

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**CaSH (Camphor Sulfonyl Hydrazine) and CSI (Chiral
Sulfonimide) Organocatalysis**

CHEN Lingyan

**A thesis submitted in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy**

Principal Supervisor: Professor Albert W. M. LEE

Hong Kong Baptist University

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Abstract

Organocatalysts can be broadly classified as Lewis bases, Lewis acids, Brønsted bases, and Brønsted acids. In this thesis, two new types of Lewis base and Brønsted acid organocatalysts were designed.

For Lewis base organocatalysis, CaSH (camphor sulfonyl hydrazine) was developed as a new functionality in organocatalysis. *N*^α-alkylated CaSH catalyzed enantioselective aza-Michael addition between nitrogen nucleophiles and α,β -unsaturated aldehydes was explored. With trichloroacetic acid (TCA) as the co-catalyst, good enantioselectivity up to 90% has been achieved. In addition, *N*^α-phenyl CaSH was also synthesized from a totally different route. However, it did not show any catalytic effect on the aza-Michael addition reactions.

For Brønsted acid organocatalysis, CSI (chiral sulfonimide) was synthesized as a new type of organocatalyst. Starting from racemic BINOL, a convergent approach to the synthesis of a series of chiral 3,3'-diaryl CSIs was developed. It involved Newman-Kwart rearrangement, oxidative chlorination, resolution, hydrogenation and Suzuki-Miyaura coupling. The use of these chiral sulfonimides (CSIs) as Brønsted acid organocatalysts in asymmetric aza-Friedel-Crafts reactions of indoles to aldimines was explored.

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