

## DOCTORAL THESIS

### Second generation camphor sulfonyl hydrazine (CaSH II) organocatalysis

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**Second Generation Camphor Sulfonyl Hydrazine  
(CaSH II) Organocatalysis**

**LI Qing Hua**

**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**

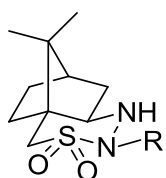
**August 2013**

## Abstract

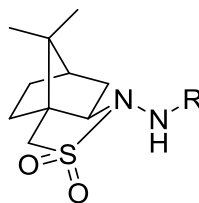
Based on the studies of the first generation camphor sulfonyl hydrazine (CaSH I), primary sulfonyl hydrazine functionality is introduced to the development of new organocatalysts.

As a new Lewis base type organocatalyst, the second generation camphor sulfonyl hydrazine (CaSH II) and its derivatives have been successfully designed and synthesized. The activity and enantioselectivity of CaSH II were investigated in three different kind of asymmetric reactions, Diels-Alder, Friedel-Crafts alkylation of indoles and intra-molecular oxo-Michael addition. In all cases, CaSH II showed excellent activity towards  $\alpha$ ,  $\beta$ -unsaturated ketones and cyclohexadienones, which would be attributed to the primary hydrazine functionality and the  $\alpha$ -heteroatom effect. This remedied the limitation of CaSH I that could only activate aldehyde substrates.

In the study of Diels-Alder reactions, the key iminium intermediate was isolated and characterized. We further propose that asymmetric organocatalysis can be viewed as *in situ* chiral auxiliary. The thermo rearrangement of CaSH II to CaSH I and other sulfinyl compounds were also probed.



**CaSH I**



**CaSH II**

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