

DOCTORAL THESIS

Organocatalysis: hydrazine and sulfonimide as new functionalities in asymmetric organocatalysis

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**Organocatalysis —
Hydrazine and Sulfonimide as New Functionalities in
Asymmetric Organocatalysis**

HE Hao

**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

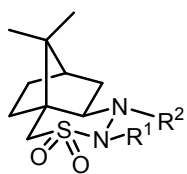
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Abstract

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

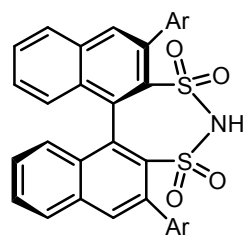
Camphor sulfonyl hydrazine (CaSH) was synthesized for the first time as a new Lewis base organocatalyst. After modification by N^α - and N^β -alkylation or N^α -acylation, a series of six-member cyclic CaSHs were explored as organocatalysts in asymmetric Diels-Alder reactions. Trichloroacetic acid was 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 Sulfonyl Imide

Table of Contents

Declaration.....	i
Abstract.....	ii
Acknowledgements.....	iv
Table of Contents.....	v
List of Tables.....	viii
List of Figures.....	ix
List of Schemes.....	x
List of Abbreviations.....	xii
Chapter 1 Introduction	1
1.1 Asymmetric Synthesis.....	1
1.2 Organocatalysis.....	7
1.2.1 Lewis Base Type Organocatalyst.....	9
1.2.2 Lewis Acid Type Organocatalyst.....	12
1.2.3 Brønsted Acid Type Organocatalyst.....	14
1.2.4 Hydrazine and Sulfonimide as New Functionalities in Organocatalysis.....	16
Chapter 2 Camphor Sulfonyl Hydrazines (CaSH) as Lewis Base	
Organocatalysts in Enantioselective Diels-Alder Reactions	17
2.1 Design and Synthesis of Camphor Sulfonyl Hydrazines (CaSH).....	17
2.2 Camphor Sulfonyl Hydrazines (CaSH) Catalyzed Enantioselective Diels-Alder Reactions.....	22
2.2.1 Background.....	22

2.2.2	CaSH Catalyzed Enantioselective Diels-Alder Reactions.....	23
2.3	Mechanism and Stereochemistry.....	31
2.4	CaSH in Other Asymmetric Transformations.....	32
2.5	Summary.....	33
Chapter 3 Chiral Sulfonimides (CSI) as Brønsted Acid Organocatalysts in		
	Aza-Friedel-Crafts Alkylations.....	34
3.1	Design and Synthesis of Chiral Sulfonimides (CSI).....	34
3.2	Chiral Sulfonimides (CSI) catalyzed Asymmetric Aza-Friedel-Crafts Alkylations.....	39
3.2.1	Background.....	39
3.2.2	CSI Catalyzed Asymmetric Aza-Friedel-Crafts Alkylations.....	41
3.2	Summary.....	44
Chapter 4 Conclusion.....		
Chapter 5 Experimental.....		
5.1	General Experimental Details.....	46
5.2	Experimental Details for Chapter 2.....	47
5.2.1	Synthetic Procedures and Characterization of CaSHs.....	47
5.2.2	CaSH Catalyzed Asymmetric Diels-Alder Reactions.....	55
5.3	Experimental Details for Chapter 3.....	63
5.3.1	Synthetic Procedures and Characterization of CSIs.....	63
5.3.2	CSI Catalyzed Asymmetric Aza-Friedel-Crafts Alkylations.....	69
Chapter 6 References.....		
HPLC Chromatograph and NMR Spectra.....		
		82

HPLC Chromatograph for Asymmetric Diels-Alder Reactions	82
HPLC Chromatograph for Asymmetric Aza-Friedel-Crafts Alkylations.....	89
NMR Spectra for CaSH	91
NMR Spectra for Asymmetric Diels-Alder Reactions	110
NMR Spectra for CSI	120
NMR Spectra for Asymmetric Aza-Friedel-Crafts Alkylations.....	133
Curriculum Vitae	136