

## DOCTORAL THESIS

### New benzyne precursors: the chemistry of benzobisoxadisilole and benzotrisoxadisilole

Chen, Yali

*Date of Award:*  
2006

[Link to publication](#)

#### General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

**New Benzyne Precursors —  
The Chemistry of Benzobisoxadisilole and  
Benzotrisoxadisilole**

**CHEN Yali**

**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**

**July 2006**

## Abstract

The syntheses of linear and angular benzobisoxadisiloles **2.9** and **2.13** as well as benzotrisoxadisilole **2.28** were accomplished. They can serve as new benzyne precursors. Generation of benzynes (**2.15**, **2.22** and **2.30**) from benzobisoxadisiloles and benzotrisoxadisilole *via* the phenyliodination / fluoride induced elimination protocol were investigated.

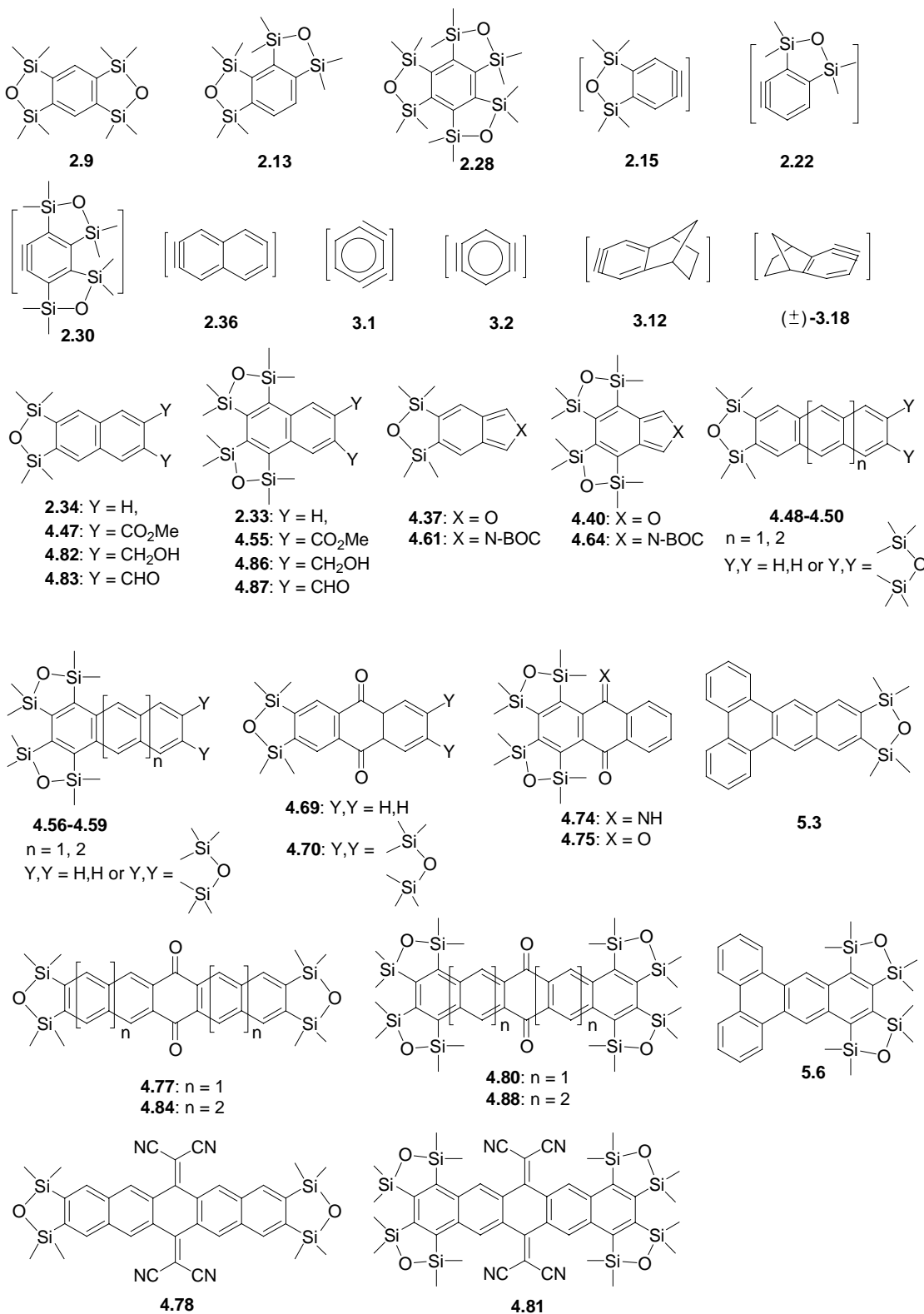
The linear and angular benzobisoxadisiloles can serve as synthetic equivalents of 1,4- and 1,3-benzdiyne (**3.2** and **3.1**) respectively *via* the phenyliodination / fluoride induced elimination protocol.

Mono- and bis-oxadisilole fused isobenzofurans (**4.37** and **4.40**) and isoindoles (**4.61** and **4.64**) were synthesized and isolated for the first time, they were used as the synthons for a series of mono- and bis-oxadisilole fused linear acenes (**4.47-4.50** and **4.55-4.58**) and acenequinones (**4.69**, **4.70** and **4.75**). The electrochemical and photo-physical properties of these oxadisilole fused acenes were characterized.

Bis- and tetra-oxadisilole fused pentacenequinones (**4.77** and **4.80**) and heptacenequinones (**4.84** and **4.88**) were synthesized *via* double Diels-Alder or 4-fold Aldol-condensation reactions.

Mono- and bis-oxadisilole fused dibenz[*a,c*]anthracenes **5.3** and **5.6** were also synthesized *via* palladium-catalyzed [2+2+2] cyclotrimerization reaction and aromatization. The electrochemical and photo-physical properties of these dibenz[*a,c*]anthracene derivatives was characterized.

The structures of 14 new compounds were also confirmed by X-ray analyses.



# Table of Contents

<b>Declaration</b>		i
<b>Abstract</b>		ii
<b>Acknowledgements</b>		iv
<b>Table of Contents</b>		v
<b>List of Tables</b>		ix
<b>List of Figures</b>		x
<b>List of Schemes</b>		xii
<b>List of Abbreviations and Symbols</b>		xviii
<b>Chapter 1</b>	<b>Introduction</b> .....	1
1.1	Benzyne and Aryne .....	1
1.2	Benzyne Precursors .....	3
1.3	Benzynes in Organic Synthesis .....	7
1.4	Benzynes in Natural Product Synthesis .....	15
1.5	References .....	16
<b>Chapter 2</b>	<b>Benzobisoxadisilole and Benzotrisoxadisilole as New Benzyne Precursors</b> .....	22
2.1	Introduction .....	22
2.2	Linear and Angular Benzobisoxadisiloles .....	26
2.2.1	Synthesis of Linear and Angular Benzobisoxadisiloles ..	26

2.2.2	Benzynes from Linear and Angular Benzobisoxadisiloles	29
2.3	Benzotrisoxadisilole .....	34
2.3.1	Synthesis of Benzotrisoxadisilole .....	34
2.3.2	Benzyne from Benzotrisoxadisilole .....	36
2.4	2,3-Naphthalene from 2,3-Naphthoxadisilole .....	38
2.5	Silica Gel Absorbed Benzyne Precursor .....	39
2.6	Summary .....	41
2.7	References .....	42
<b>Chapter 3</b>	<b>Linear and Angular Benzobisoxadisiloles as Synthetic Equivalents for the Stepwise Generation of 1,3- and 1,4-Benzdiynes</b> .....	<b>44</b>
3.1	Introduction .....	44
3.2	Stepwise Generation of 1,4-Benzdiyne from Linear Benzobisoxadisilole .....	47
3.3	Stepwise Generation of 1,3-Benzdiyne from Angular Benzobisoxadisilole .....	50
3.4	Summary .....	51
3.5	References .....	52
<b>Chapter 4</b>	<b>Oxadisilole Fused Isobenzofurans and Isoindoles. Synthesis and Characterization of Oxadisilole Fused Acenes and Quinones</b> .....	<b>55</b>
4.1	Introduction .....	55

4.1.1	Generation and Reaction of Isobenzofuran .....	55
4.1.2	Generation and Reaction of Isoindole .....	59
4.1.3	Acenes .....	62
4.2	Mono- and Bis-Oxadisilole Fused Isobenzofurans .....	69
4.2.1	Synthesis of Mono- and Bis-Oxadisilole Fused Isobenzofurans .....	69
4.2.2	Acenes from Mono- and Bis-Oxadisilole Fused Isobenzofurans .....	71
4.2.3	Optical and Electrochemical Properties of Oxadisilole Fused Acenes .....	73
4.3	Mono- and Bis-Oxadisilole Fused Isoindoles .....	80
4.3.1	Synthesis of Mono- and Bis-Oxadisilole Fused Isoindoles	80
4.3.2	Reactions of Mono- and Bis-Oxadisilole Fused Isoindoles	82
4.4	Bis- and Tetra-Oxadisilole Fused Pentacenequinones ...	84
4.5	Bis- and Tetra-Oxadisilole Fused Heptcenequinones ...	86
4.6	Summary .....	88
4.7	References .....	90
<b>Chapter 5</b>	<b>Synthesis and Characterization of Oxadisilole Fused Dibenz[<i>a,c</i>]anthracenes .....</b>	<b>97</b>
5.1	Introduction .....	97
5.2	Synthesis of Mono- and Bis-Oxadisilole Fused Dibenz[ <i>a,c</i> ]anthracenes .....	100

5.3	Optical and Electrochemical Properties of Oxadisilole	
	Fused Dibenzo[ <i>a,c</i> ]anthracenes .....	105
5.4	Summary .....	109
5.5	References .....	110
<b>Chapter 6</b>	<b>Conclusion</b> .....	<b>113</b>
<b>Chapter 7</b>	<b>Experimental Section</b> .....	<b>117</b>
7.1	General Procedures and Requirements .....	117
7.2	Experimental Details for Chapter 2 .....	118
7.3	Experimental Details for Chapter 3 .....	137
7.4	Experimental Details for Chapter 4 .....	140
7.5	Experimental Details for Chapter 5 .....	163
<b>Appendix 1</b>	<b>NMR Spectra</b> .....	<b>166</b>
<b>Appendix 2</b>	<b>Tables of Crystallographic Data</b> .....	<b>261</b>
	<b>Curriculum Vitae</b> .....	<b>299</b>
	<b>List of Publications and Conference Presentations</b> .....	<b>300</b>