SHI ASYMMETRIC EPOXIDATION Reaction

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WZQ

SHI ASYMMETRIC EPOXIDATION

- B.S., Nanjing University (1983)
- M.Sc., University of Toronto (1987; Prof. I. W. J. Still)
- Ph.D., Stanford University (1992; Prof. Barry M. Trost)
- Postdoctoral Fellow, Harvard Medical School (1992-1995; Prof. Christopher T. Walsh)
- Assistant Professor, Colorado State University (1995-2000)
- Associate Professor, Colorado State University (2000-2003)
- Professor, Colorado State University (2003-Present)
- 2006-中国科学院化学研究所化学生物学研究中心主任
- 2012- 南京大学 化学化工学院教授
- 2017-常州大学自然与合成有机化学研究院院长

Yian Shi

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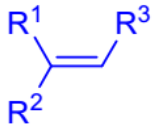
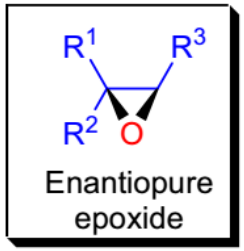


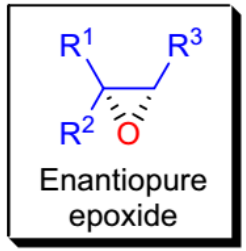
R^{1-3} = H, alkyl, aryl, substituted alkyl, substituted aryl, alkenyl, alkynyl

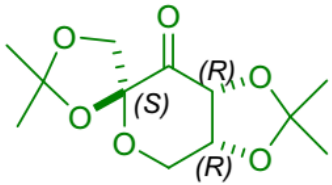
Shi's catalyst

$KHSO_5$
or 30% H_2O_2 (3.0 equiv)
H_2O / CH_3CN; pH ~7-10
50-90% yield, > 90% ee

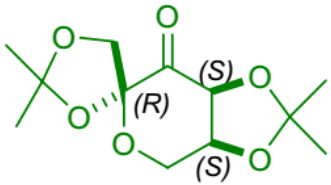


or

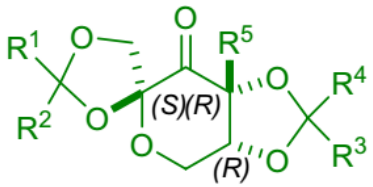




Shi's catalyst derived from D-fructose

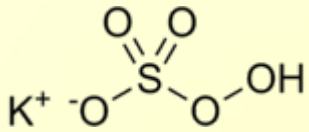


Shi's catalyst derived from L-fructose



Shi's generalized catalysts (derived from D-fructose)

R^{1-2} = Me, Et, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$
R^{3-4} = Me, Et, i-Pr, H, F, Bn, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$
R^5 = H, F



Oxone/Caroat/Potassium peroxymonosulfate

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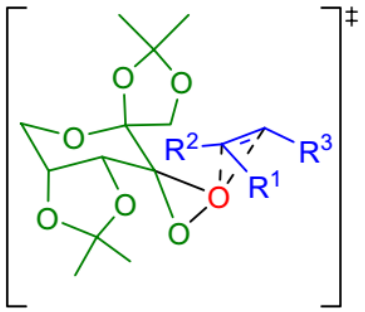
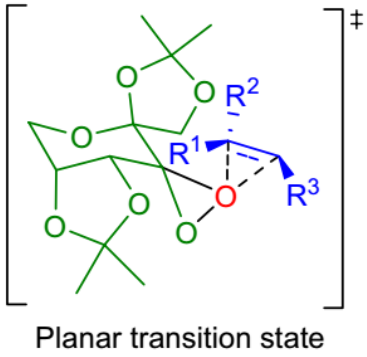
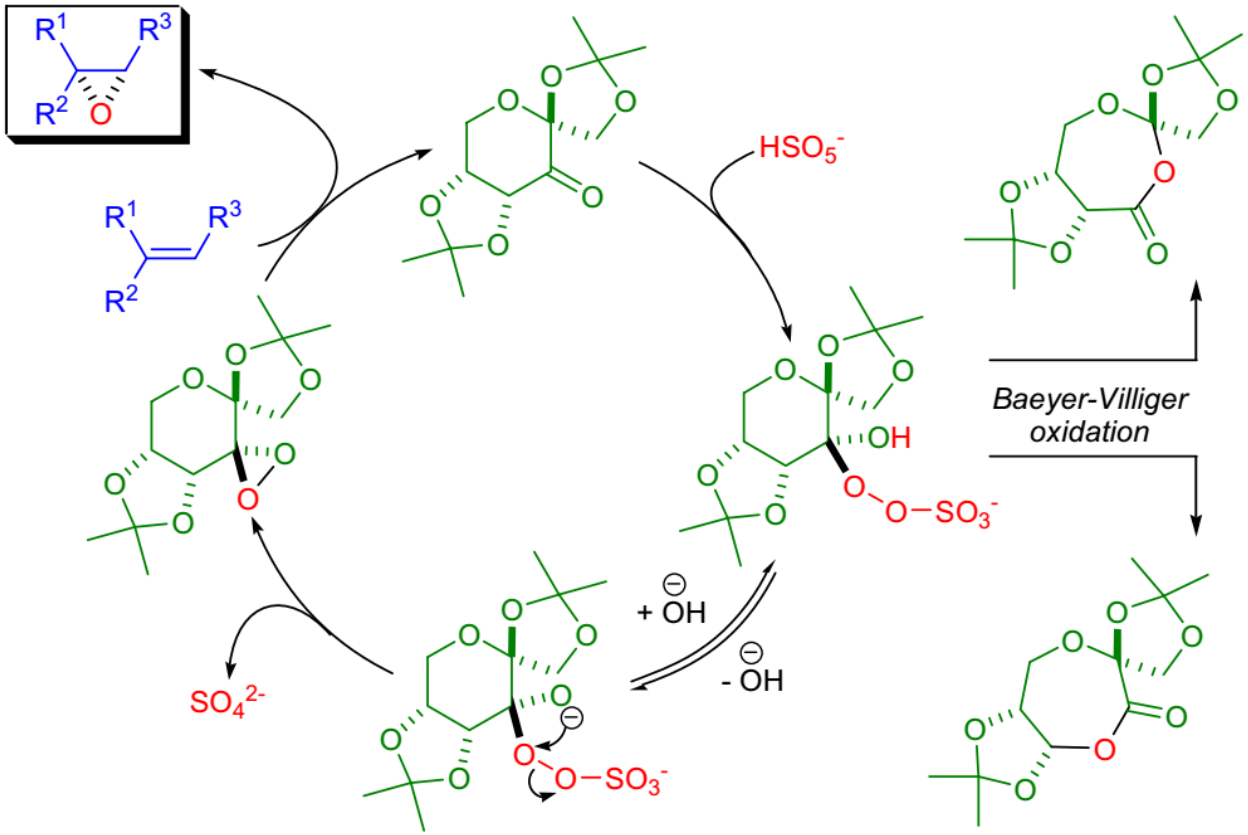
Mechanism







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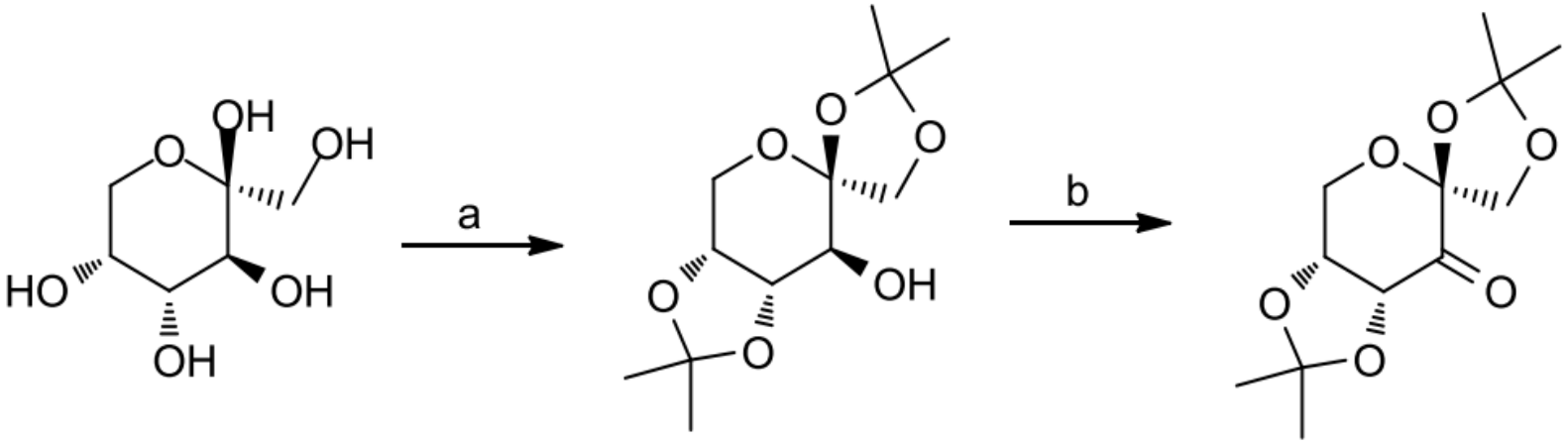
Either enantiomer of the catalyst can be prepared easily from D- or L-fructose in two steps:



59 **60** **61**

Reagents and conditions: (a) acetone, $HClO_4$, 0 °C, 53%. (b) PCC, CH_2Cl_2, rt, 93%.

Scheme 19: Synthesis of Shi's D-fructose-derived ketone

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General features:

- the pH of the reaction medium has a crucial effect on the outcome of the reaction
- catalyst loadings:20-30 mol%
- trans-disubstituted and trisubstituted olefins give high enantioselectivities, whereas for cisdisubstituted and terminal olefins the ee's are lower

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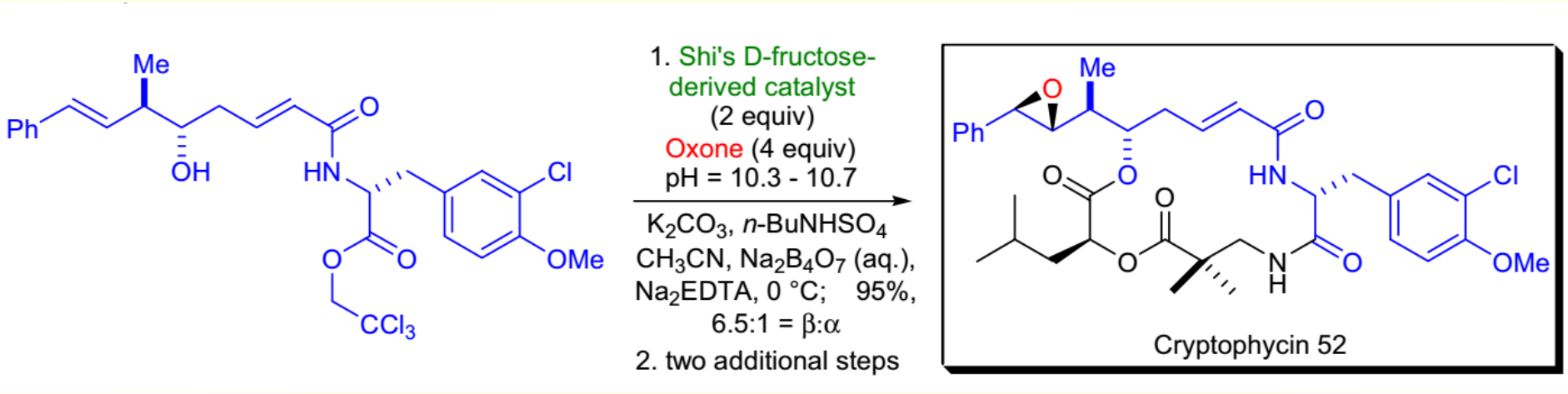
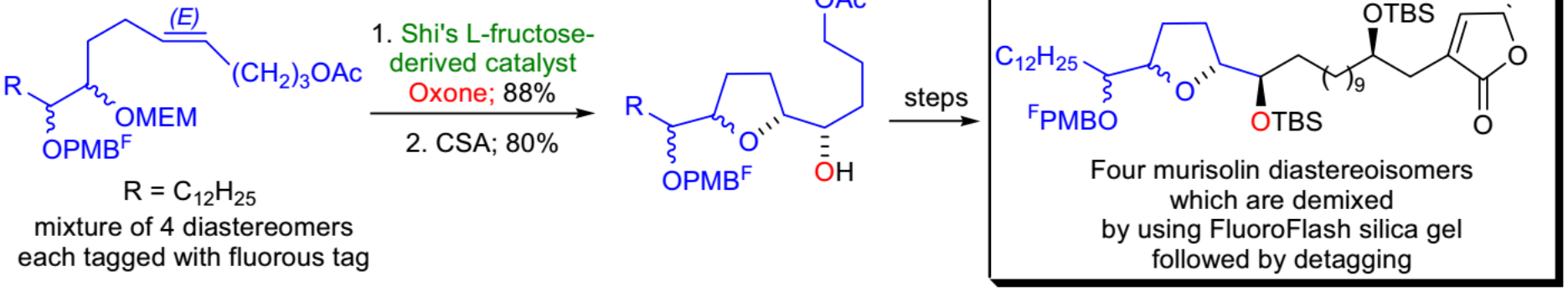
Synthetic Applications





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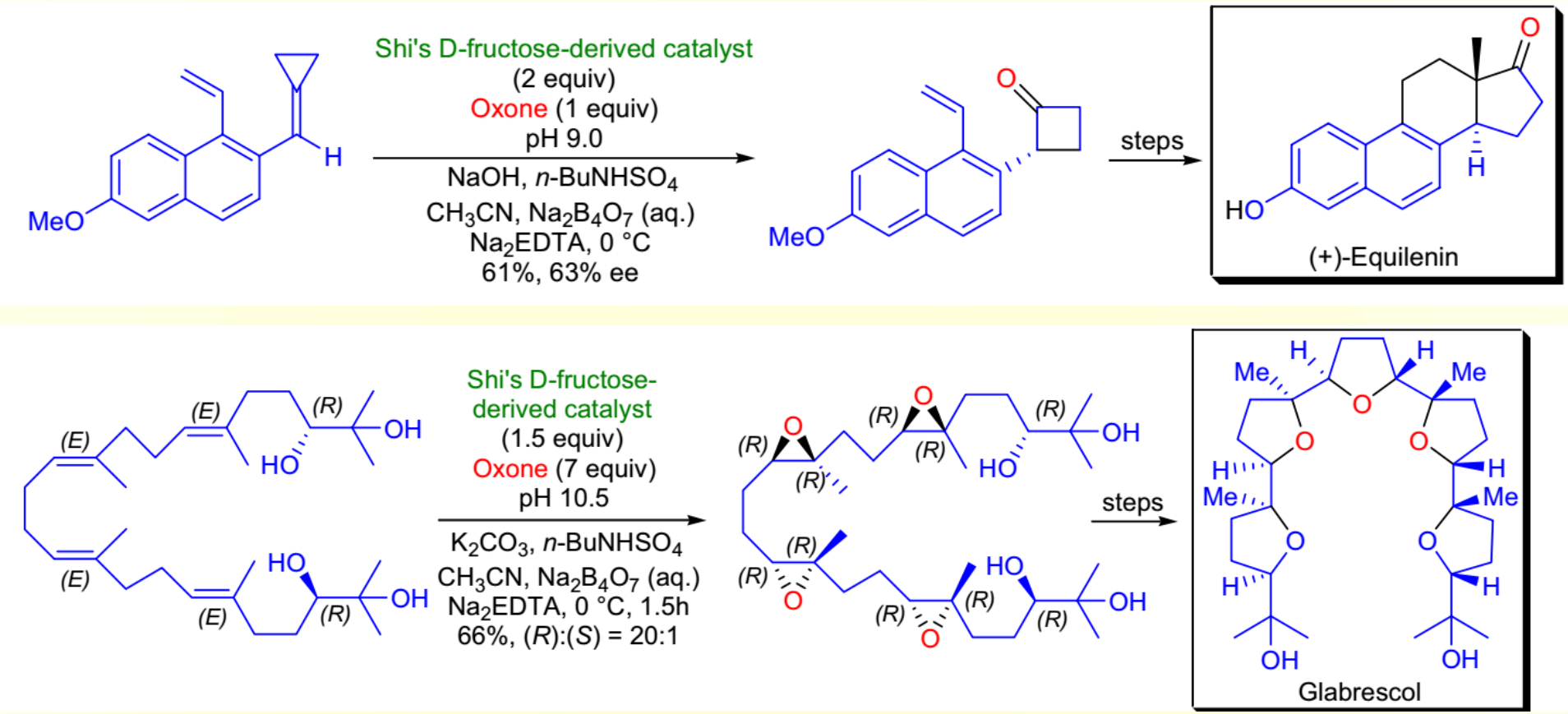

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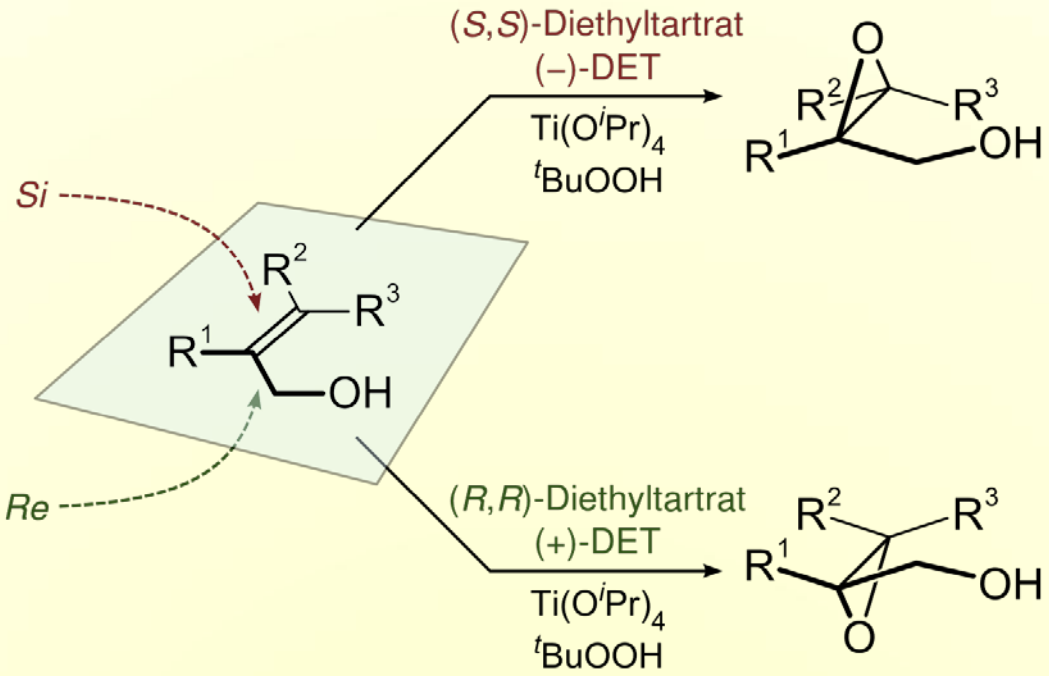
Sharpless epoxidation:



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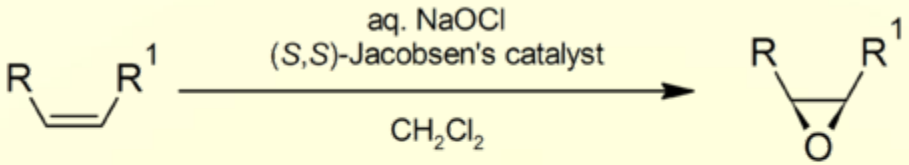
Jacobsen epoxidation or Jacobsen-Katsuki epoxidation :



R = aryl, alkenyl, alkynyl, alkyl group

R^1 = bulky alkyl group

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More：

The application of organocatalytic Asymmetric Epoxidation

By

Mohammed I. Alahmdi

Doctoral Thesis A thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy