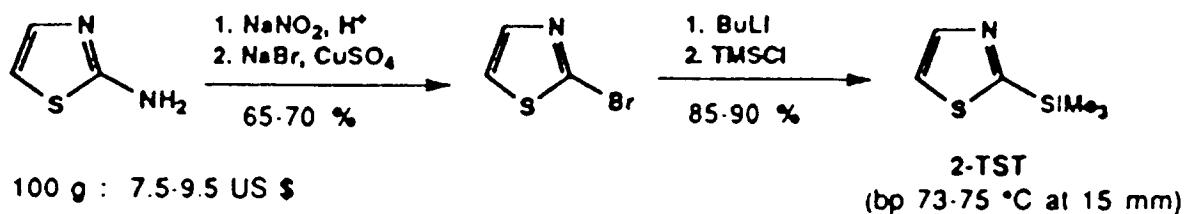
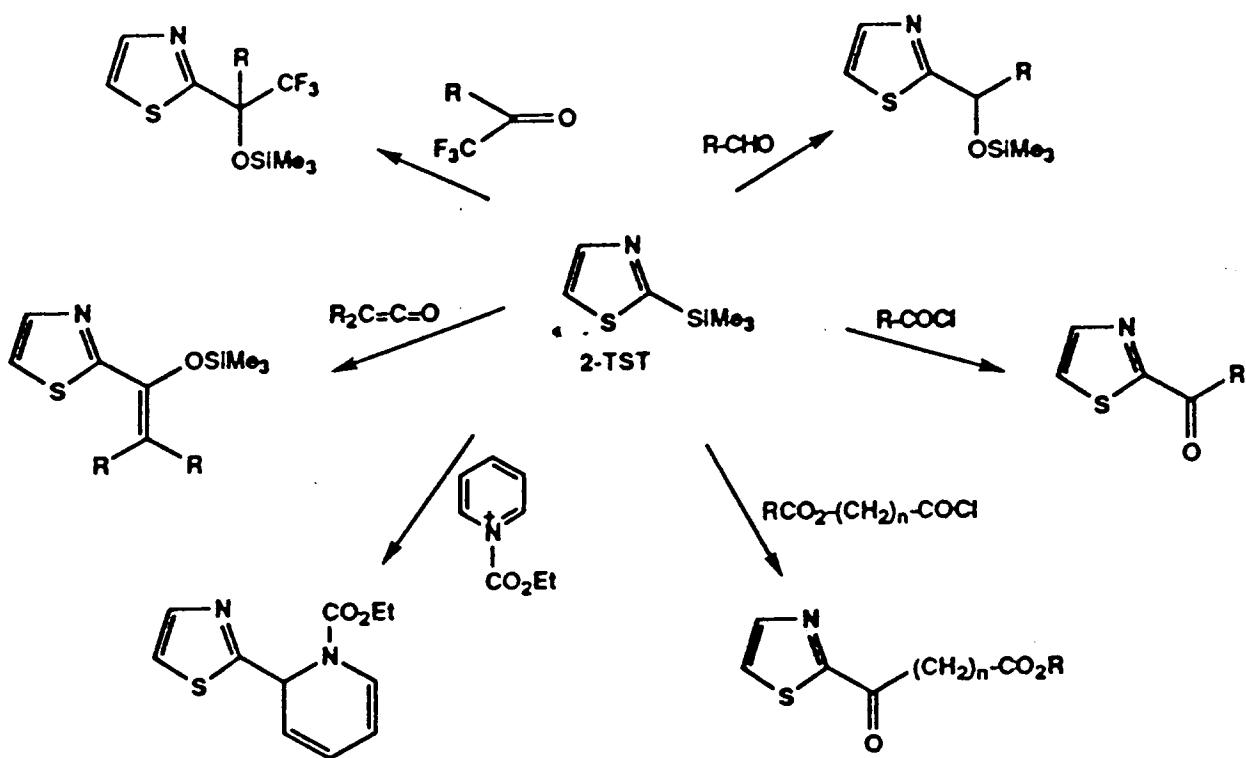


**Preparation of 2-(Trimethylsilyl)thiazole (2-TST)**



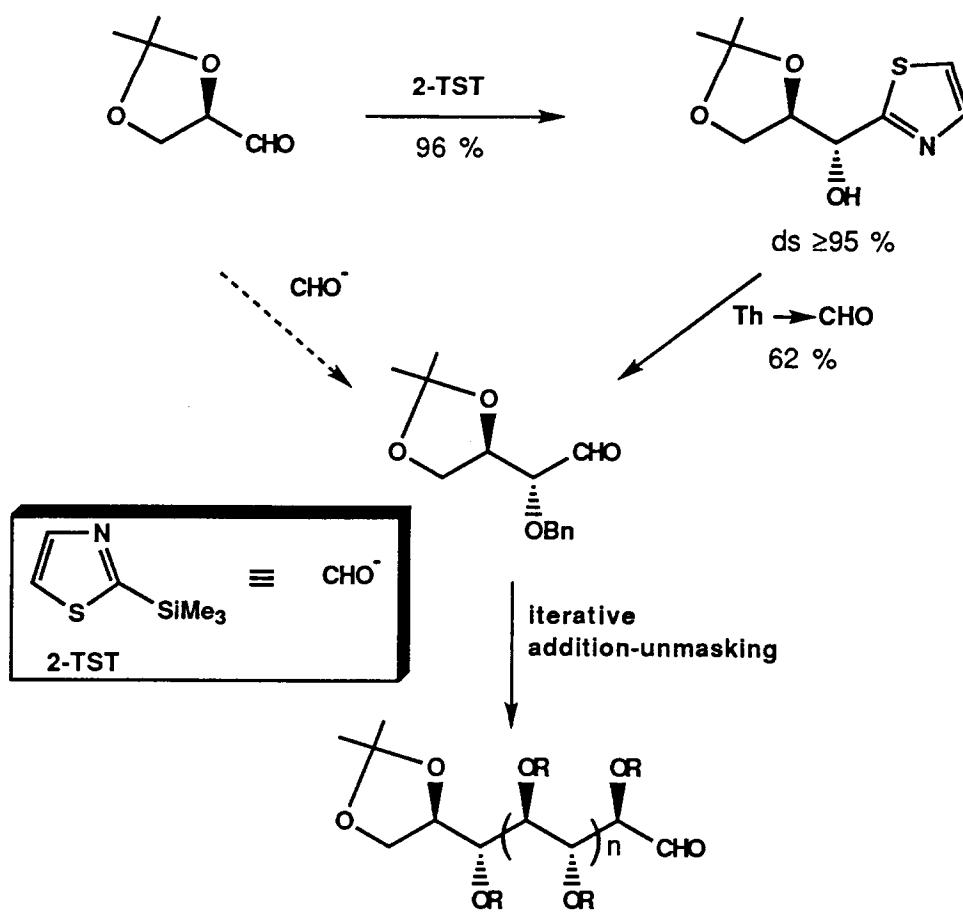
J. C. S., Chem. Commun. 1981, 655  
Org. Synth. 1993, 72, 21

**Reactivity of 2-(Trimethylsilyl)thiazole**



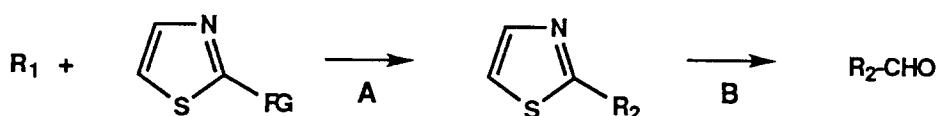
J. Chem. Soc., Chem. Commun. 1981, 655  
J. Org. Chem. 1988, 53, 1748  
Synthesis, 1994 (in press)

## 2-TST as a Formyl Anion Equivalent



Angew. Chem. Int. Ed. Engl. 1986, 25, 835  
 J. Org. Chem. 1989, 54, 693

## THE THIAZOLE-ALDEHYDE SYNTHESIS



FG = Met ( Li, SiMe<sub>3</sub>, AlEt<sub>2</sub>, MgBr)

FG = CH=PPh<sub>3</sub>

FG = COCH<sub>3</sub>

FG = COCH=PPh<sub>3</sub>

FG = CHO

FG = CNO

FG = CH<sub>2</sub>SO<sub>2</sub>Ph

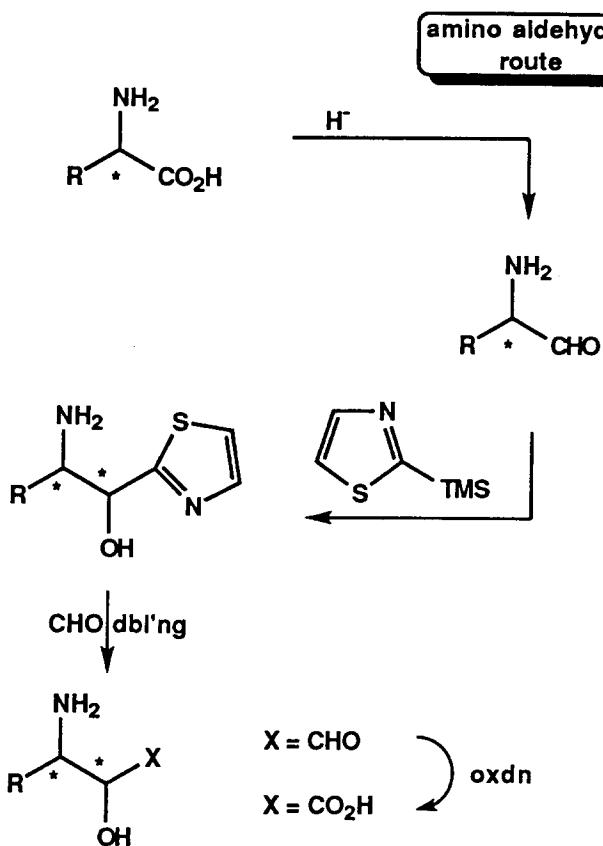
FG = CH<sub>2</sub>N=R\*

A : functionalization (C-C bond forming reaction)

B : CHO-unmasking [one pot : a) MeI or CF<sub>3</sub>SO<sub>3</sub>Me; b) NaBH<sub>4</sub>; c) Hg<sup>++</sup> or Cu<sup>++</sup>/H<sub>2</sub>O]

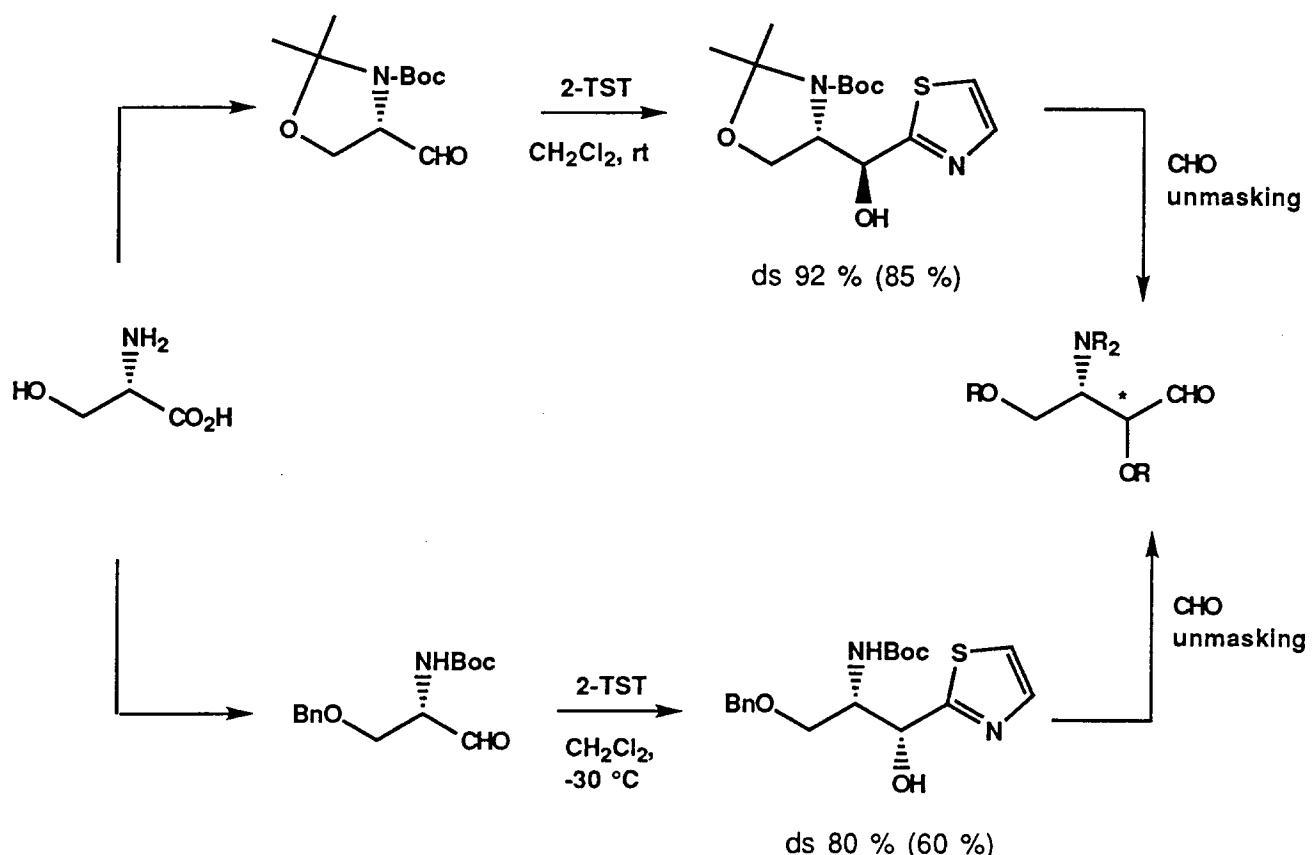
Review : A. Dondoni, In 'Modern Synthetic Methods,' R. Scheffold, Ed., Verlag Helvetica Chimica Acta, Basel, 1992, p. 379.

**Thiazole-based Route to  $\beta$ -Amino- $\alpha$ -Hydroxy Acids from  $\alpha$ -Amino Acids**



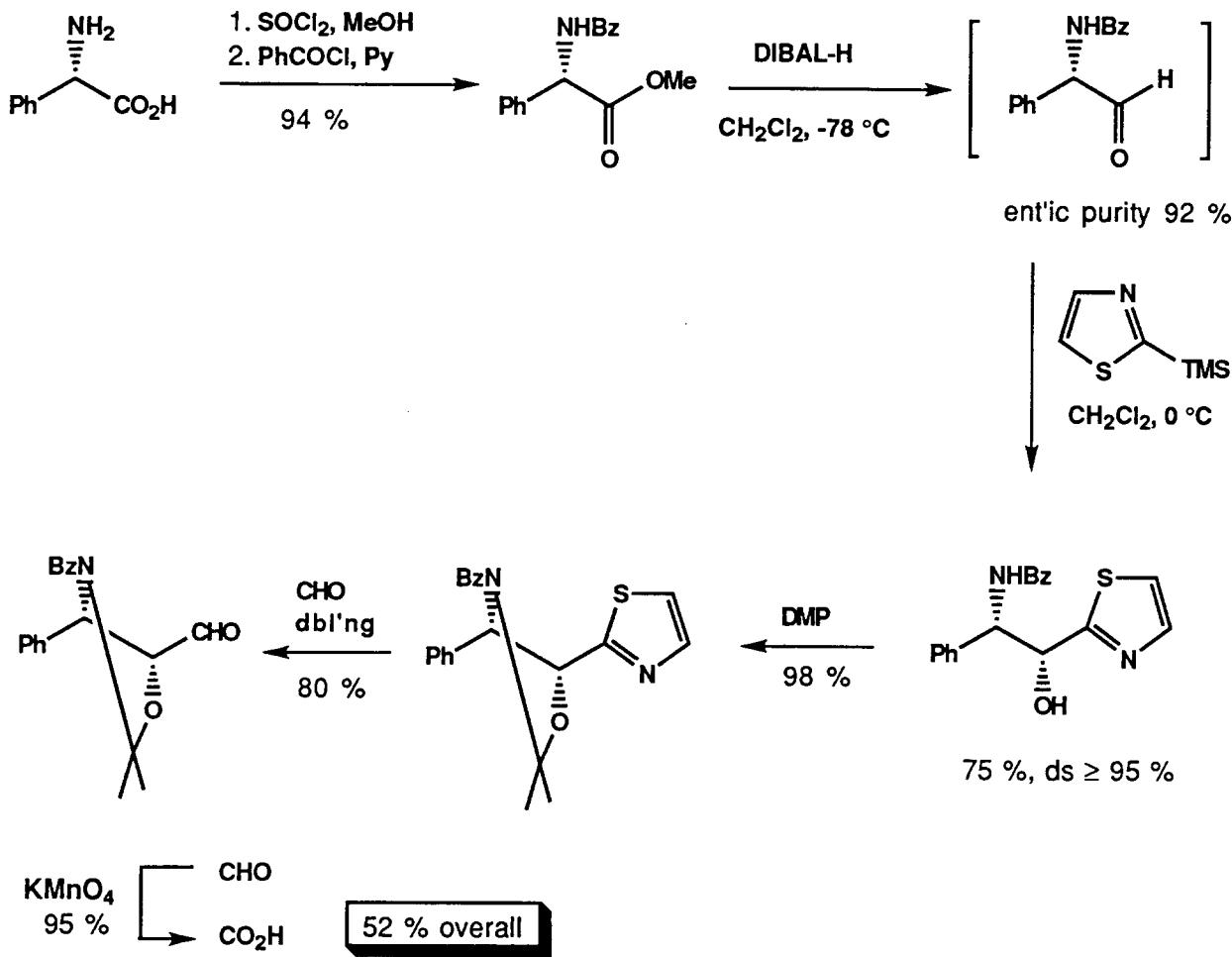
## Addition of 2-TST to $\alpha$ -Amino Aldehydes

Tunable Diastereoselectivity by *N*-Protecting Groups



J. C. S. Chem. Commun. 1988, 10  
J. Org. Chem. 1990, 55, 1439

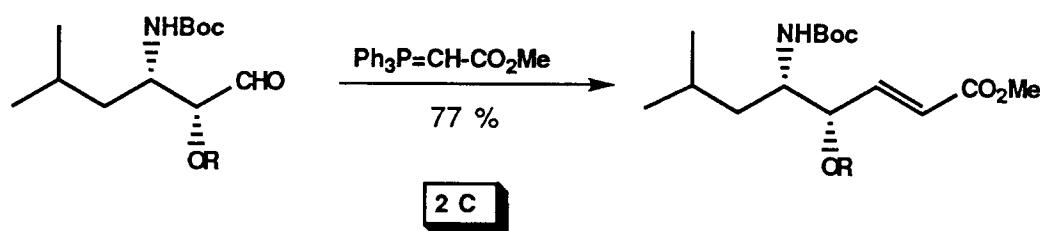
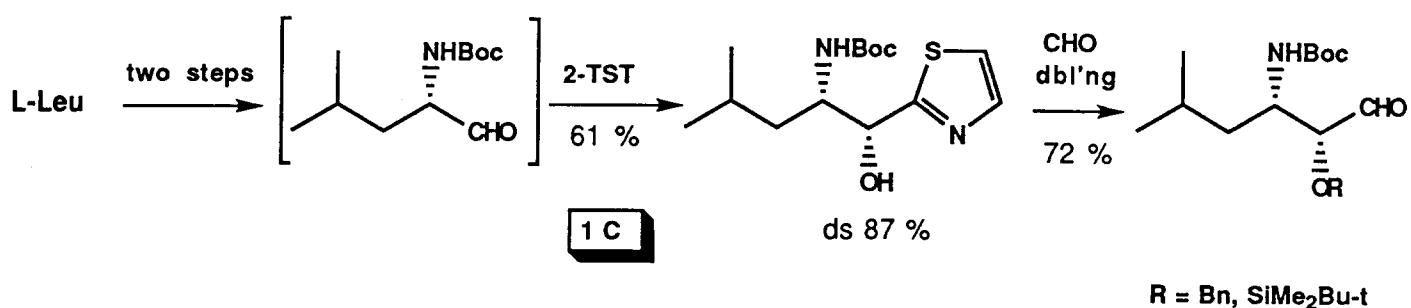
THE THIAZOLE ROUTE TO TAXOL SIDE CHAIN FROM L-PHENYLGLYCINE



same strategy for the *N*-Boc derivative (35 % overall yield)

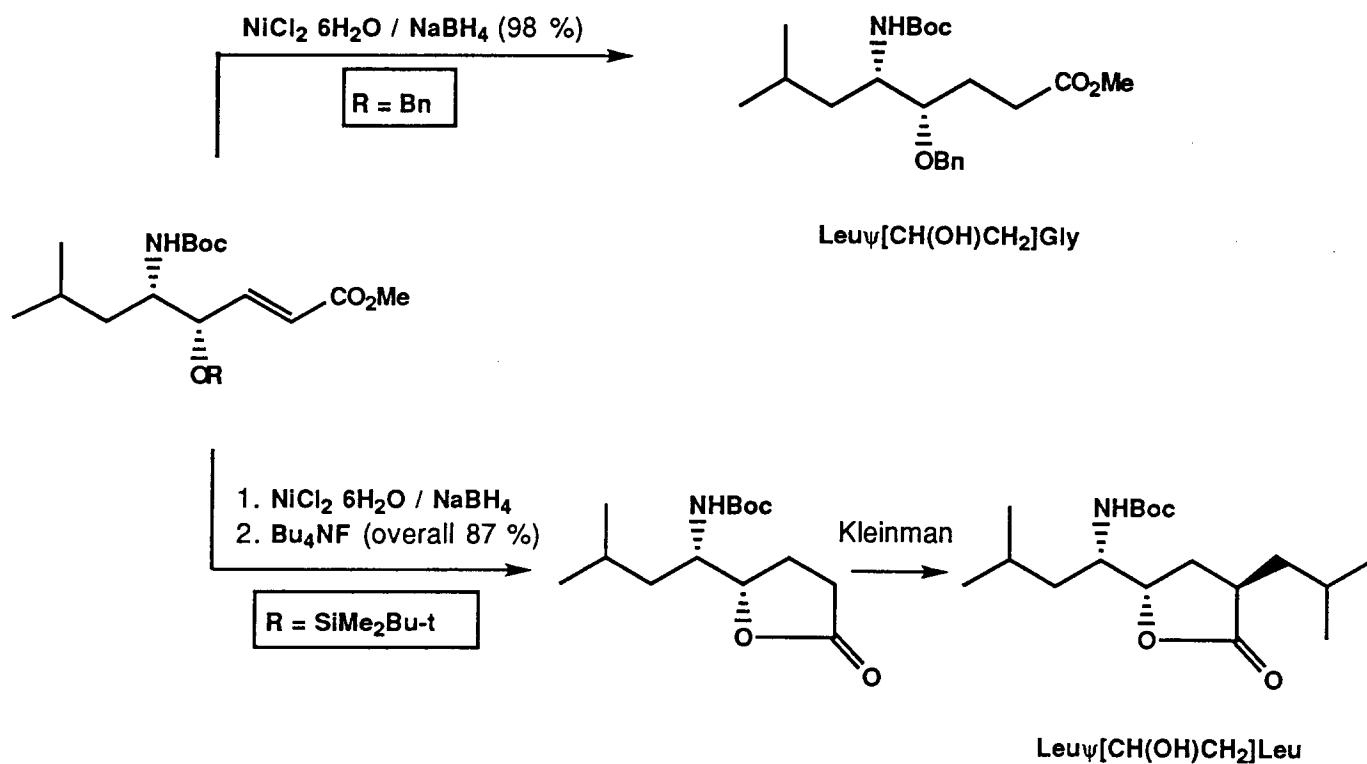
## Synthesis of Hydroxyethylene Leu-Gly and Leu-Leu Isosteres from L-Leucine

### A. One- and Two-carbon Chain Elongation



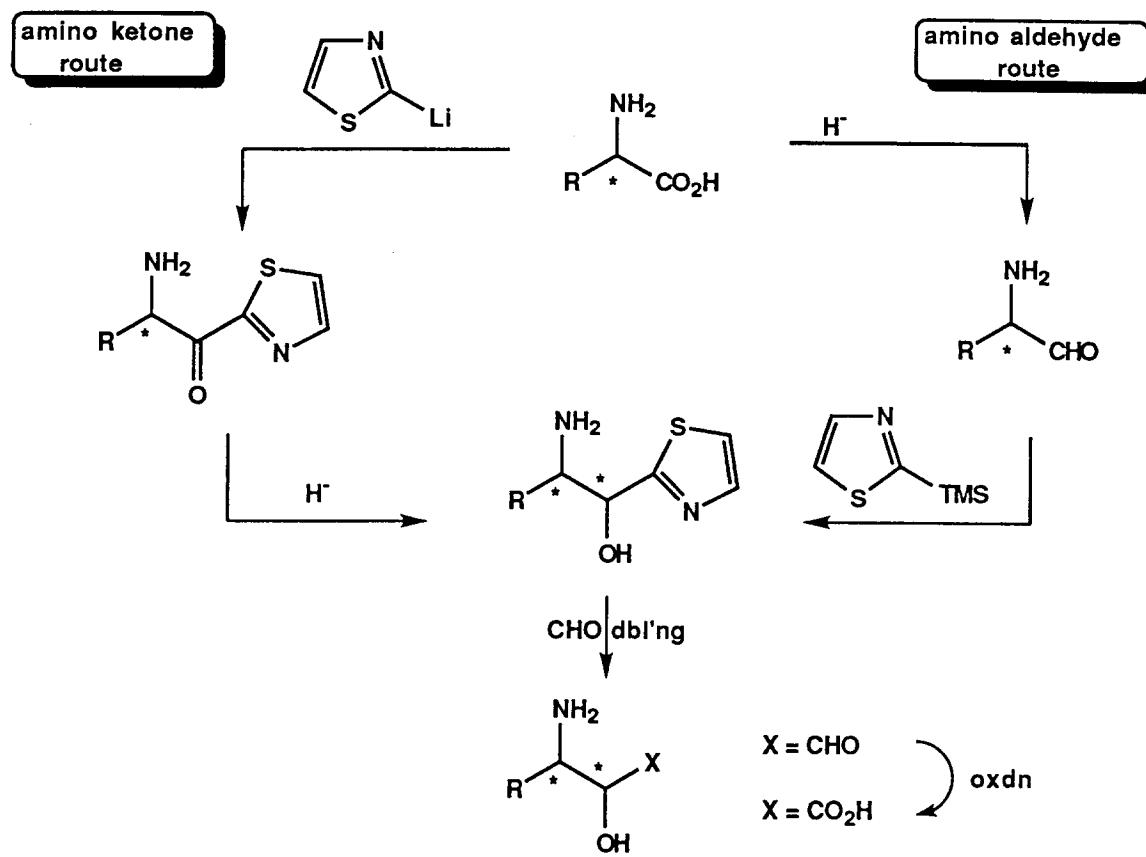
**Synthesis of Hydroxyethylene Leu-Gly and Leu-Leu Isosteres from L-Leucine**

**B. Elaboration of the *E*-Enoate**

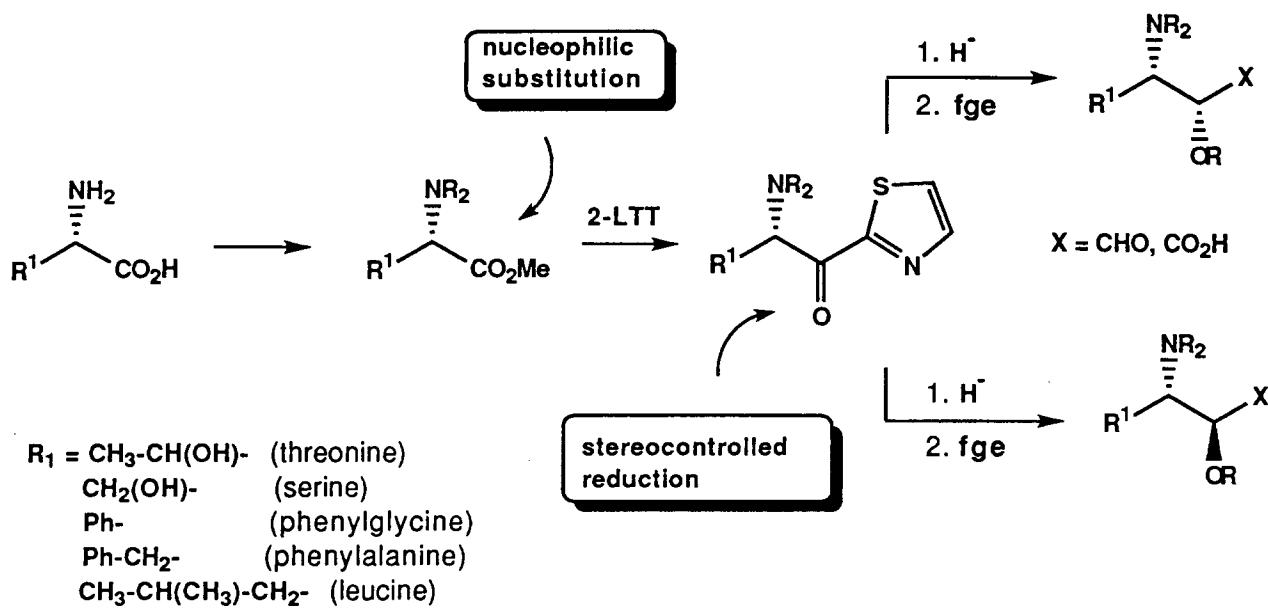


16

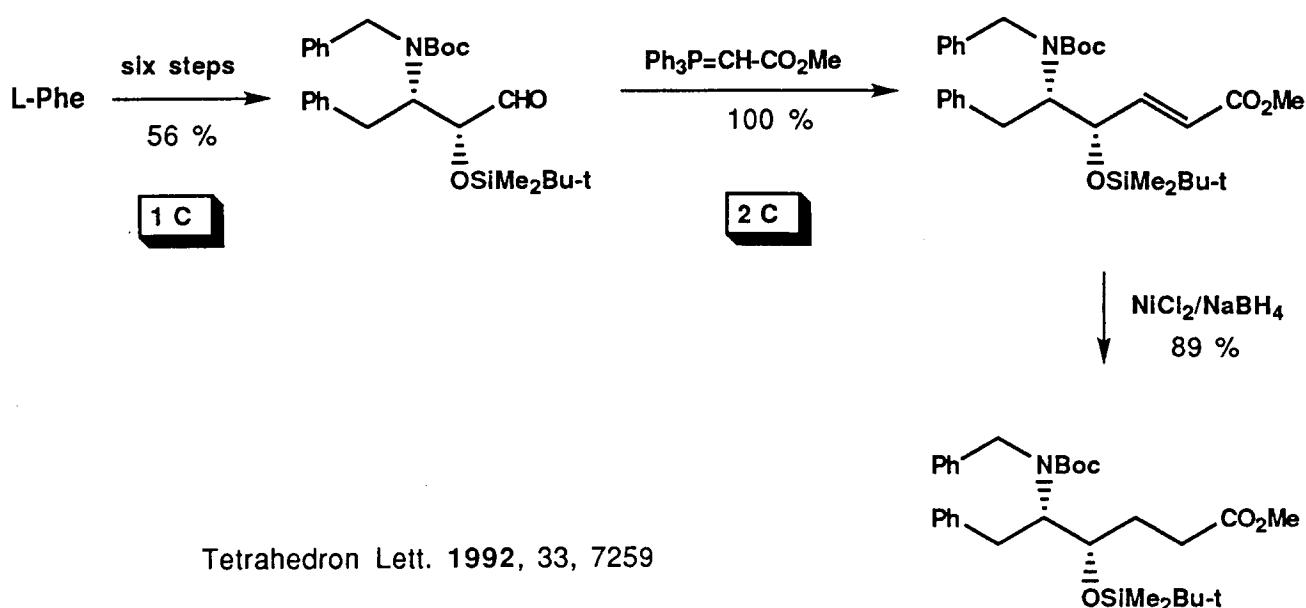
### Thiazole-based Strategies to $\beta$ -Amino- $\alpha$ -Hydroxy Acids from $\alpha$ -Amino Acids



## HOMOLOGATION OF $\alpha$ -AMINO ACIDS via THIAZOLYL $\alpha$ -AMINO KETONES

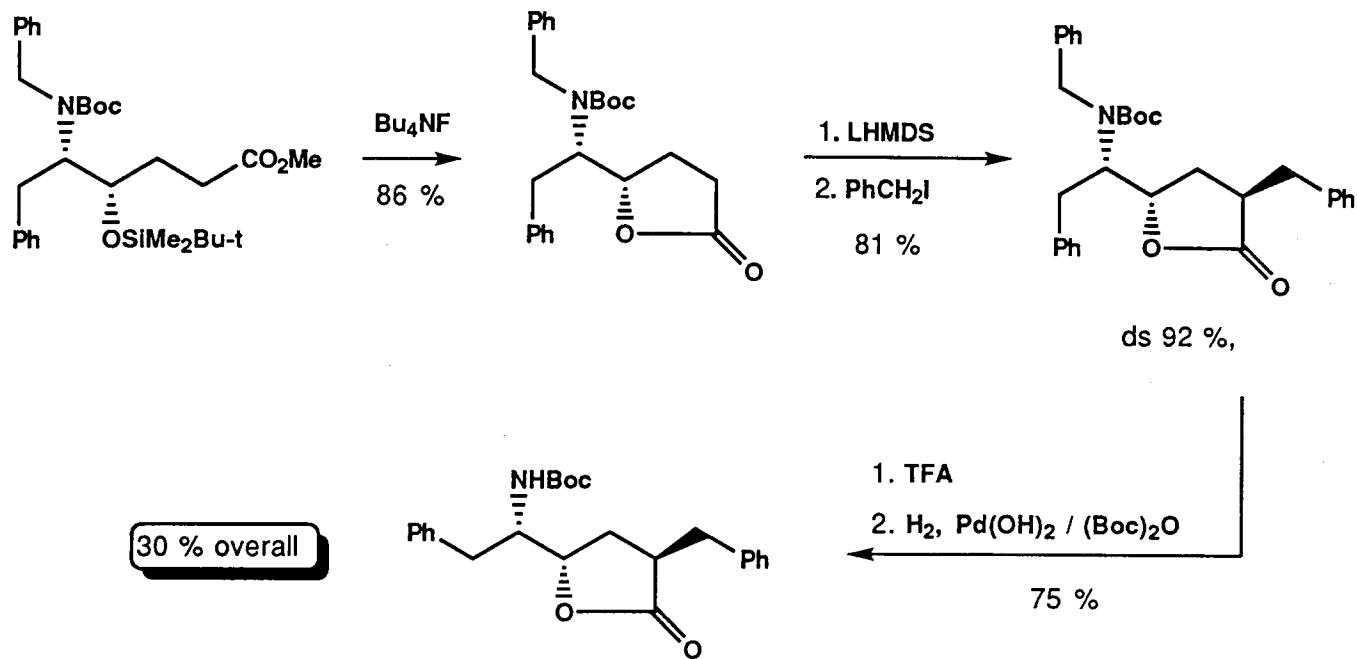


Synthesis of Hydroxyethylene Phe-Phe Isostere from L-Phenylalanine



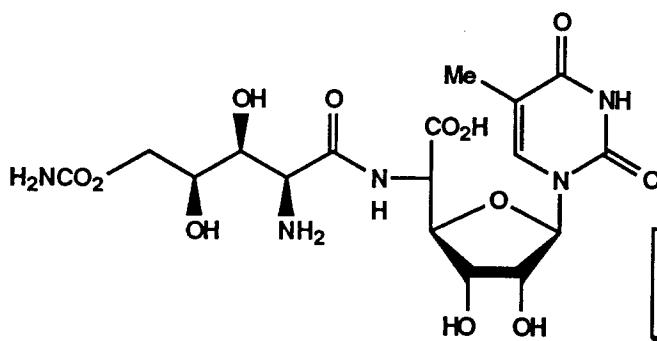
Tetrahedron Lett. 1992, 33, 7259

Synthesis of Hydroxyethylene Phe-Phe Isostere from L-Phenylalanine

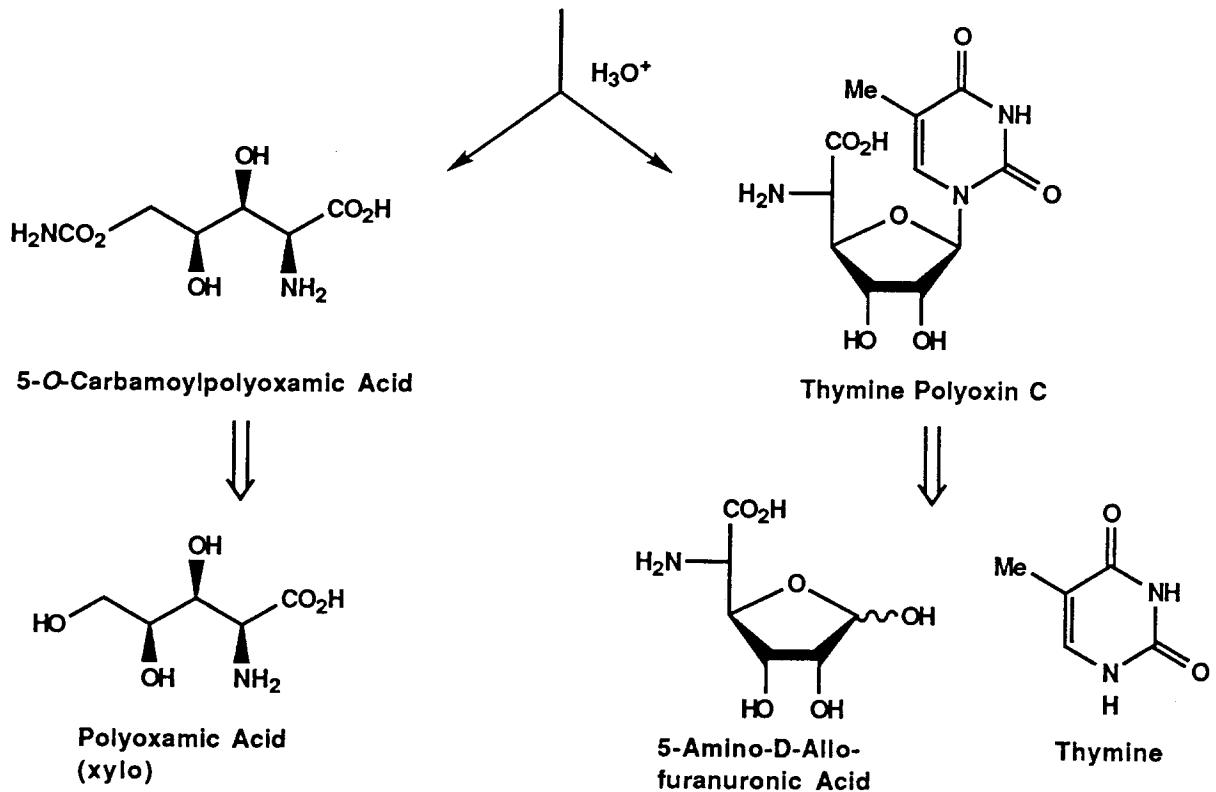


Tetrahedron Lett. 1992, 33, 7259

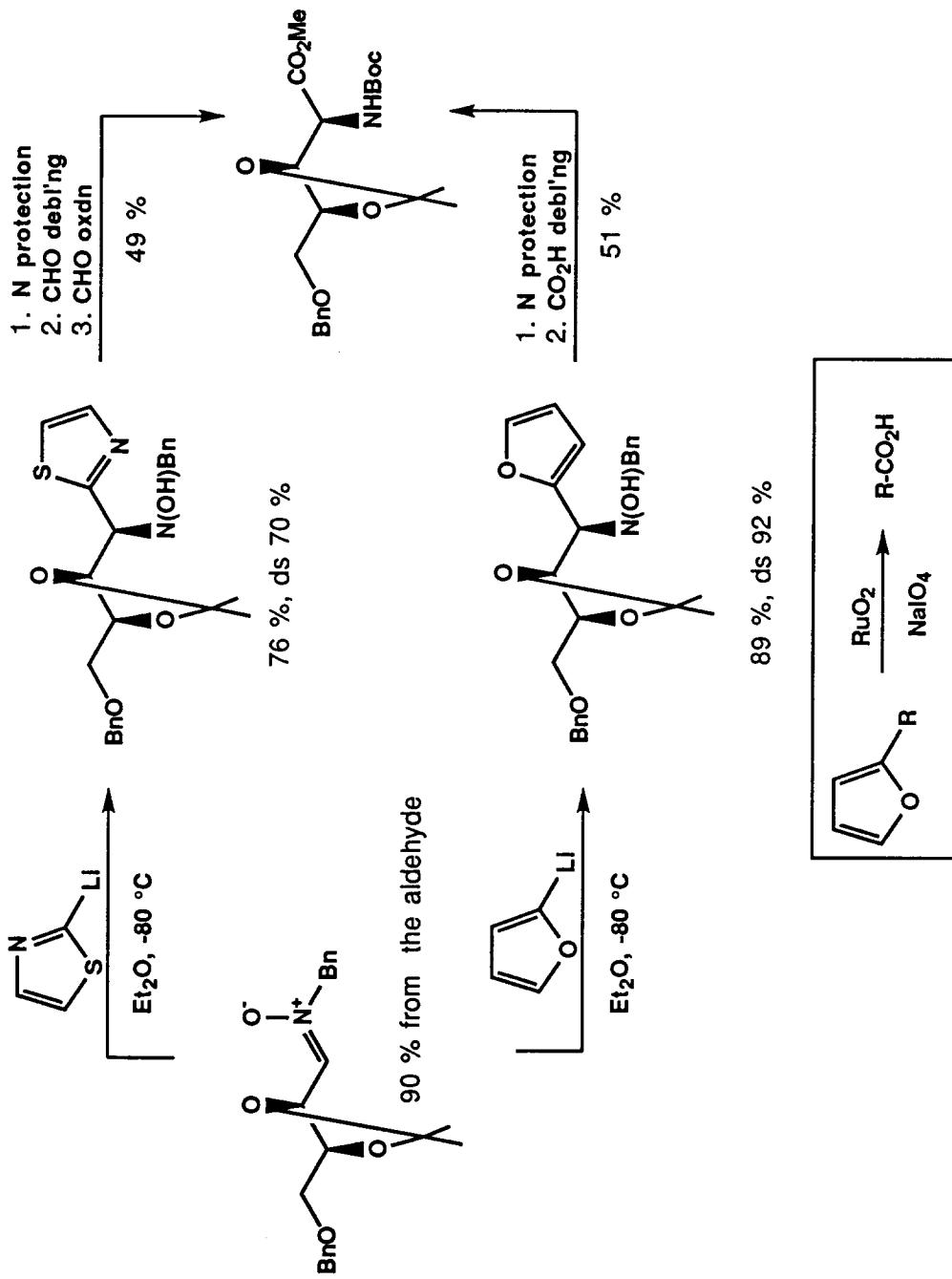
## POLYOXIN J : Skeletal Disconnection



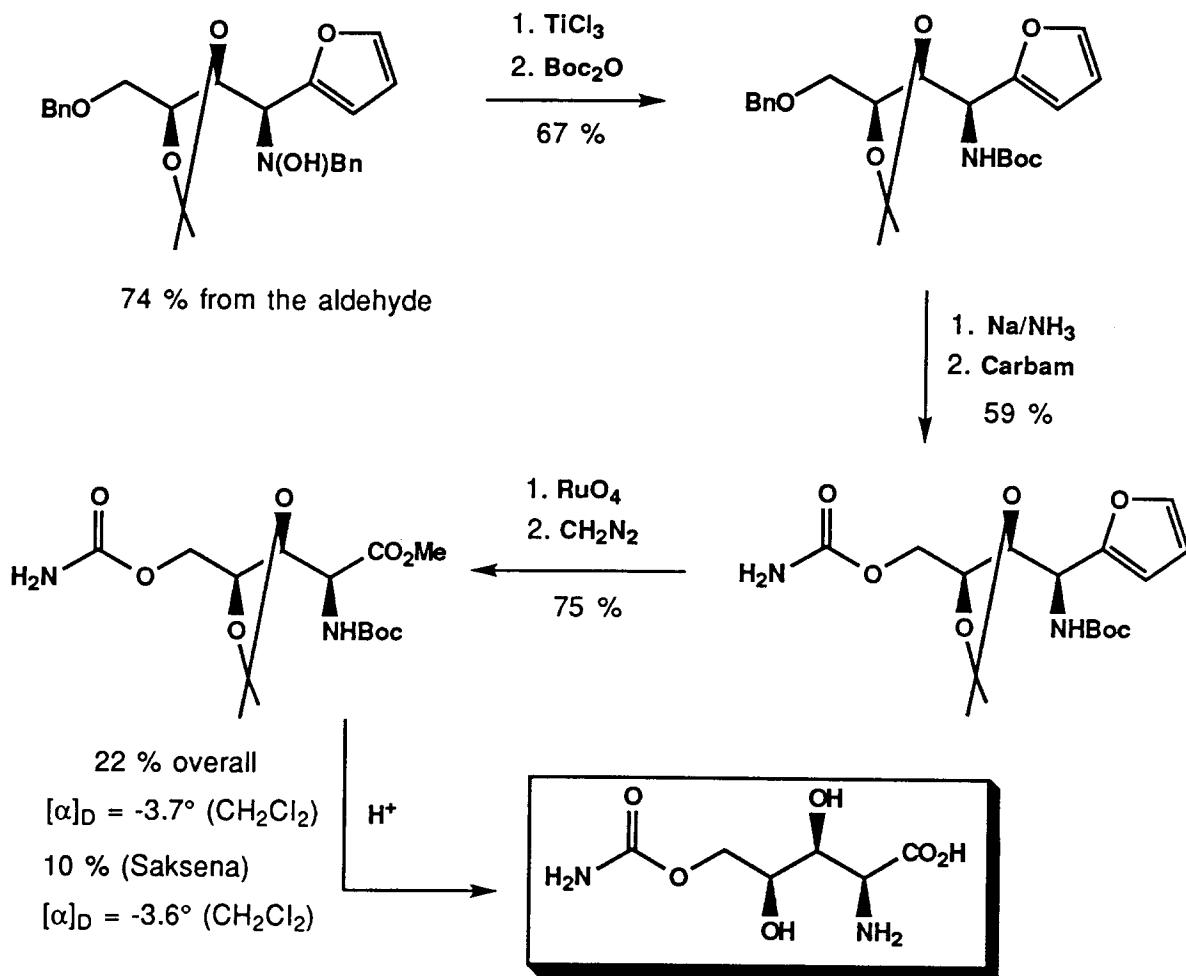
Peptidyl pyrimidine  
nucleoside antibiotic  
(fungicide)



ROUTES TO THE POLYOXAMIC ACID SKELETON

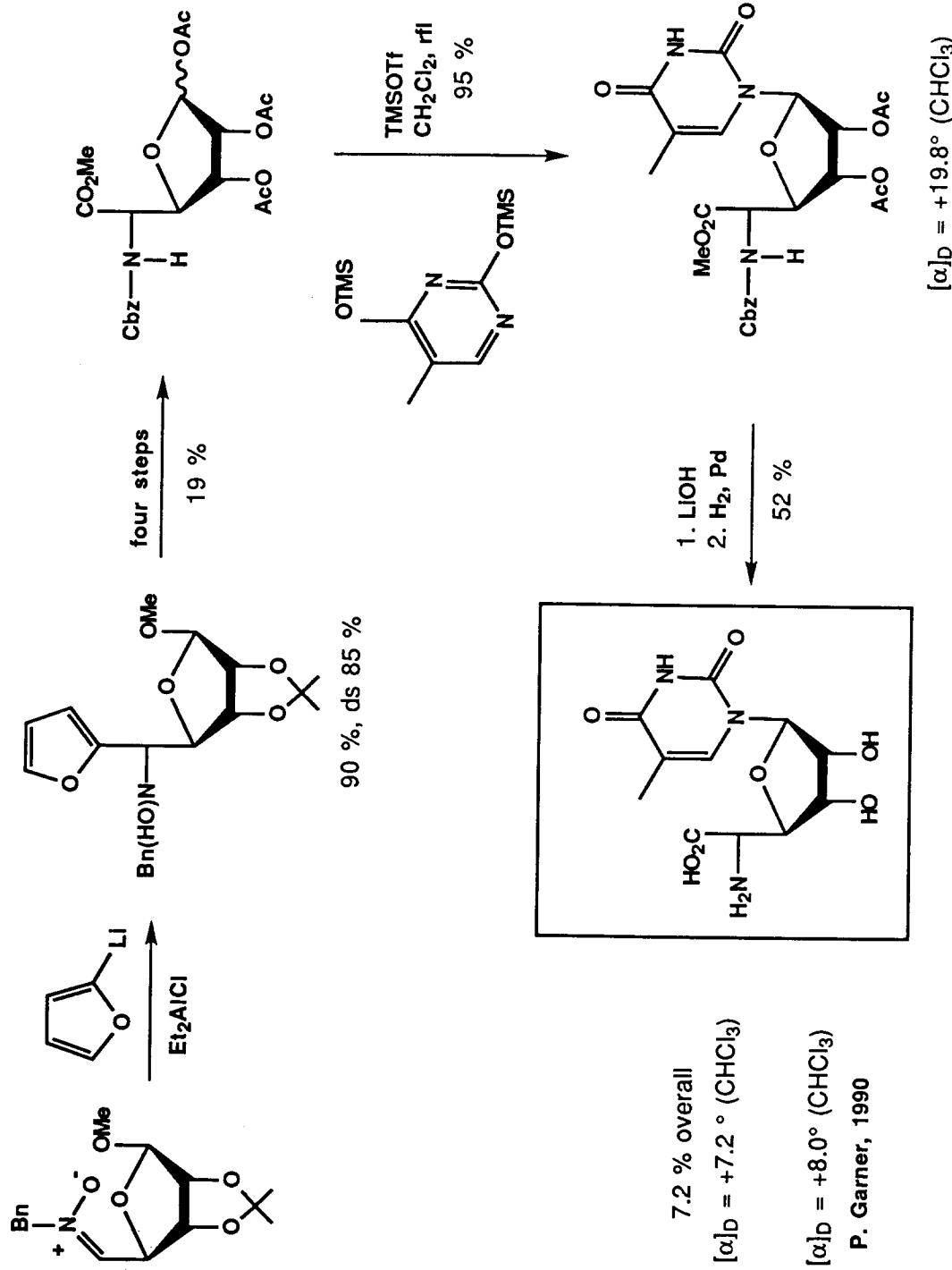


**SYNTHESIS OF 5-O-CARBAMOYLPOLYOXAMIC ACID**



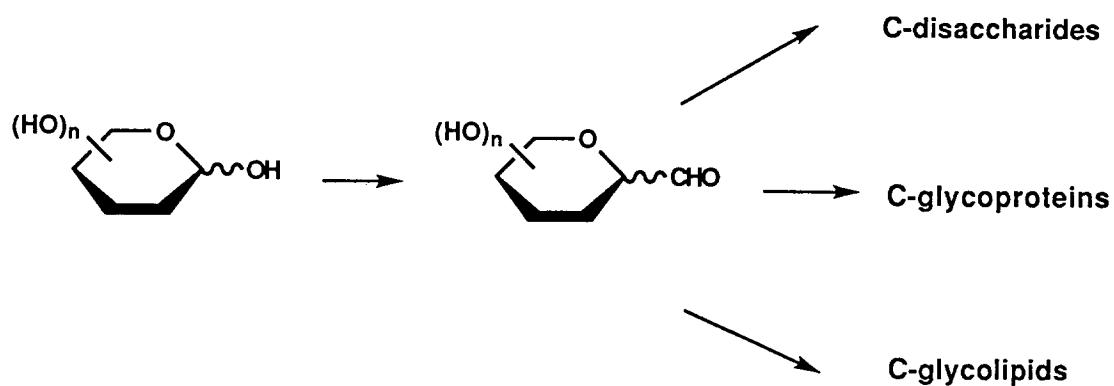
Tetrahedron Lett. 1993, 34, 5479

TOTAL SYNTHESIS OF THYMINE POLYOXIN C FROM D-RIBOSE NITRONE

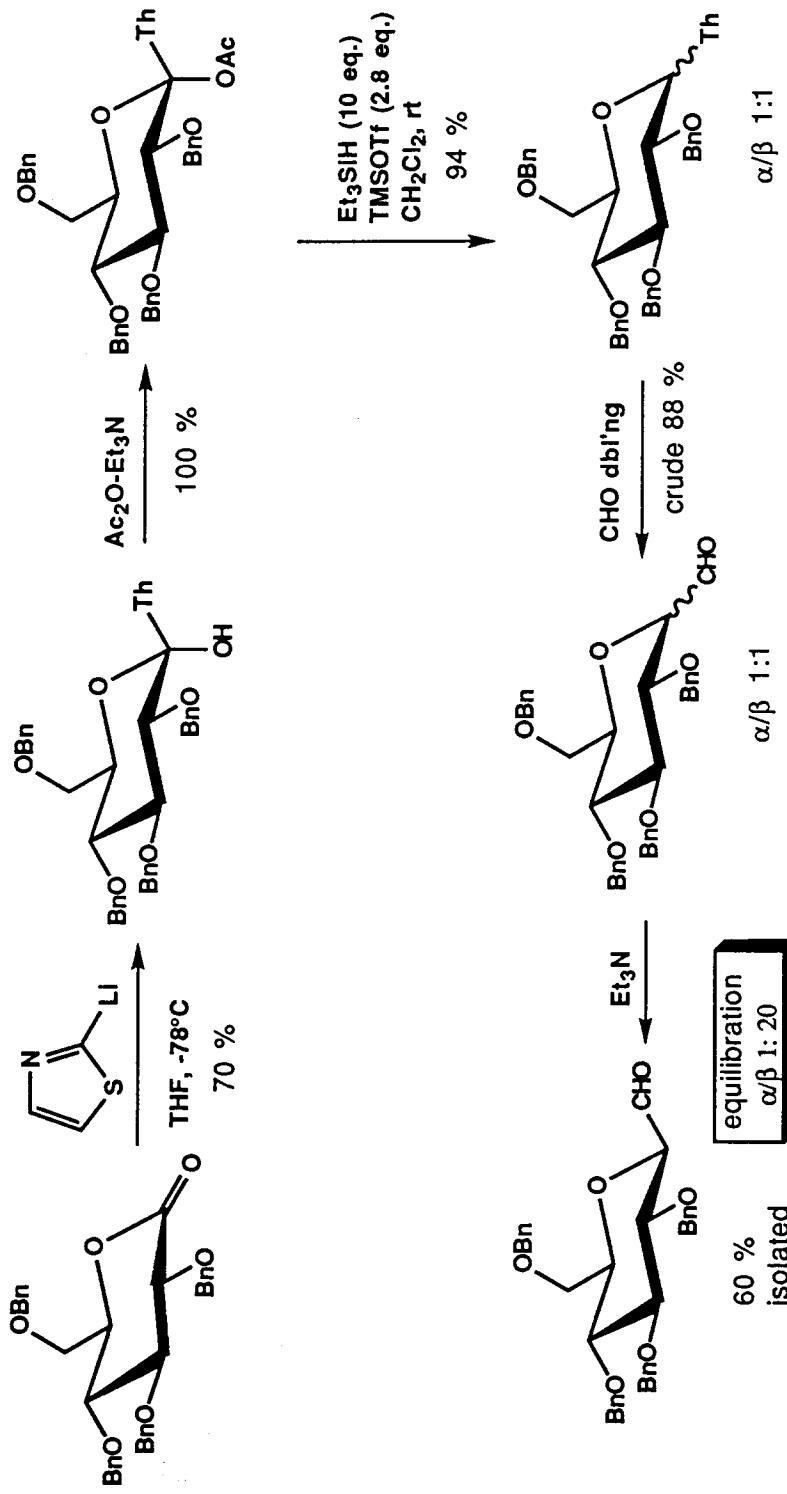


FORMYLATION AT THE ANOMERIC POSITION OF SUGARS.

A KEY REACTION TOWARD CARBON-LINKED GLYCOCONJUGATES

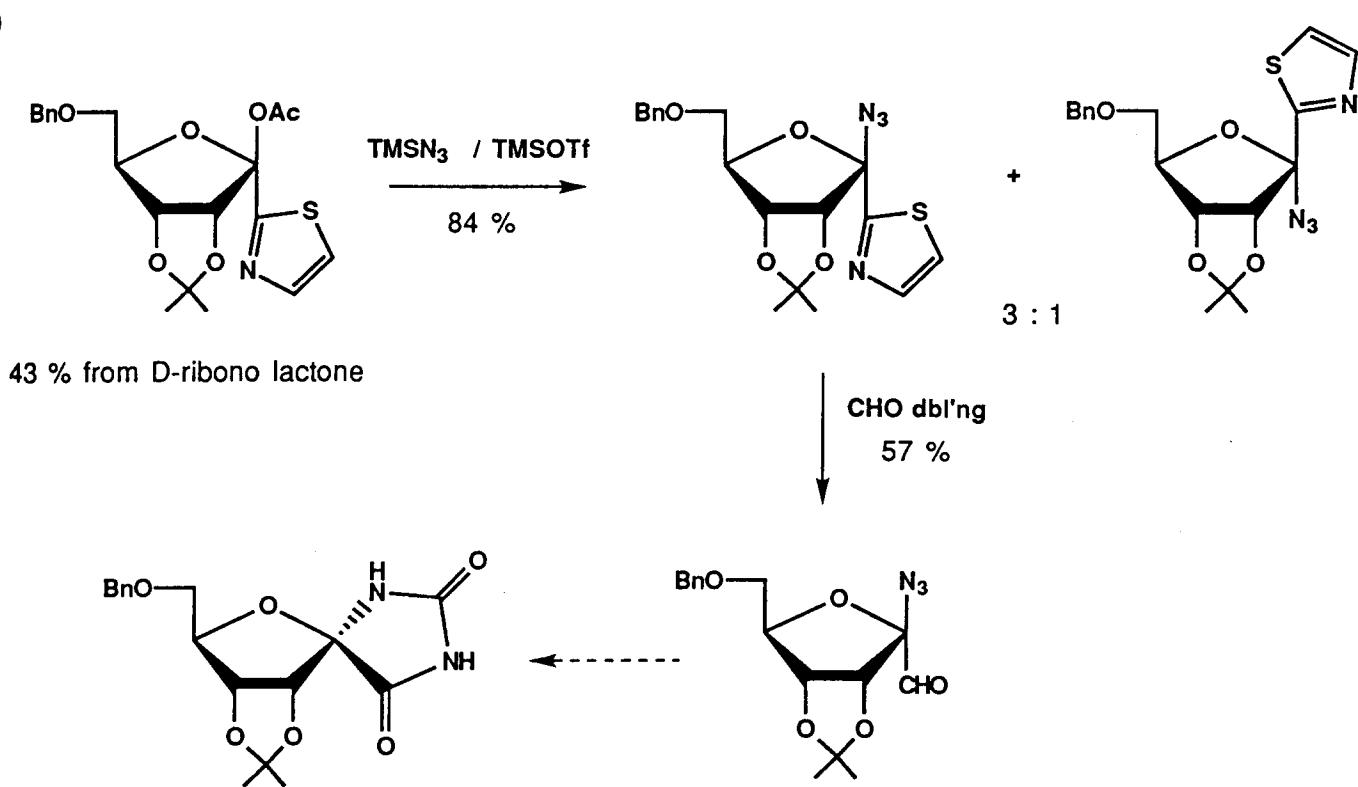


FORMYLATION OF TBG BY THIAZOLE-MASKED FORMYL ANION

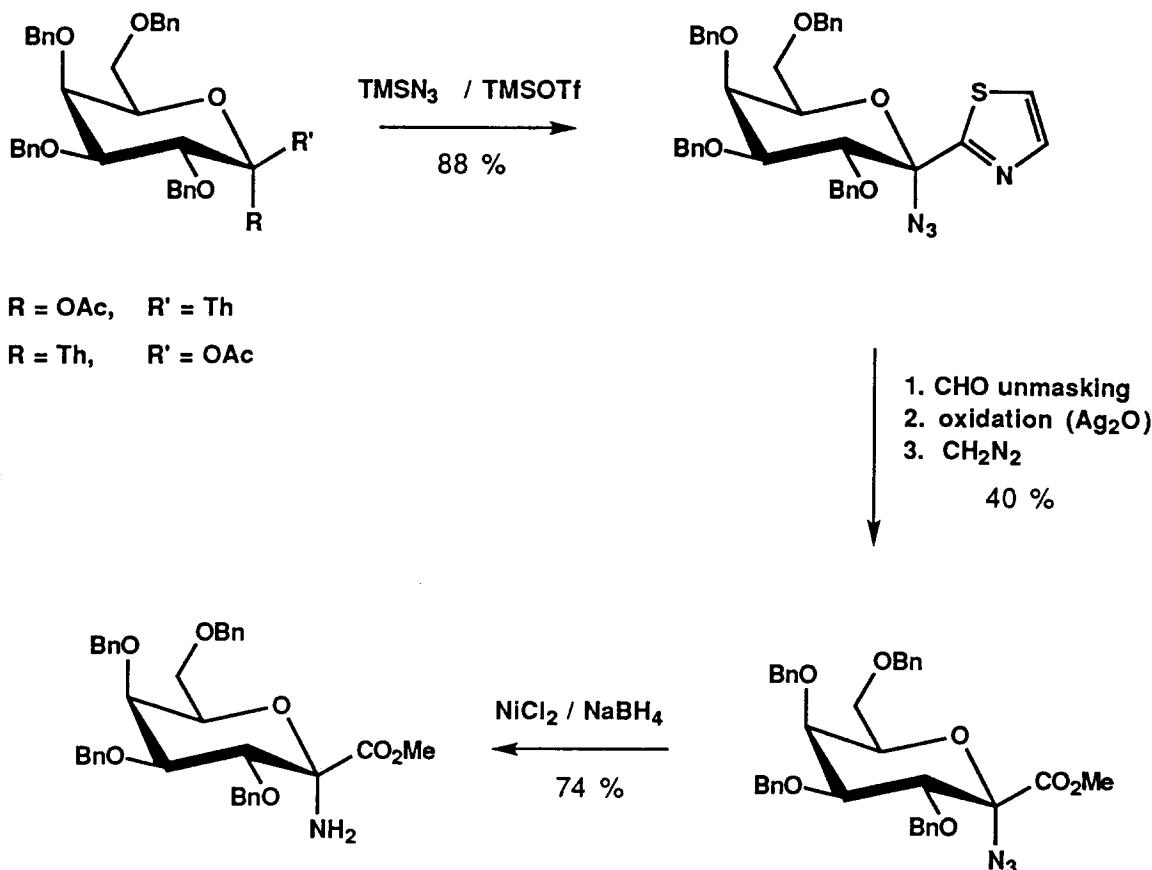


Tetrahedron Lett. 1993, 34, 7319

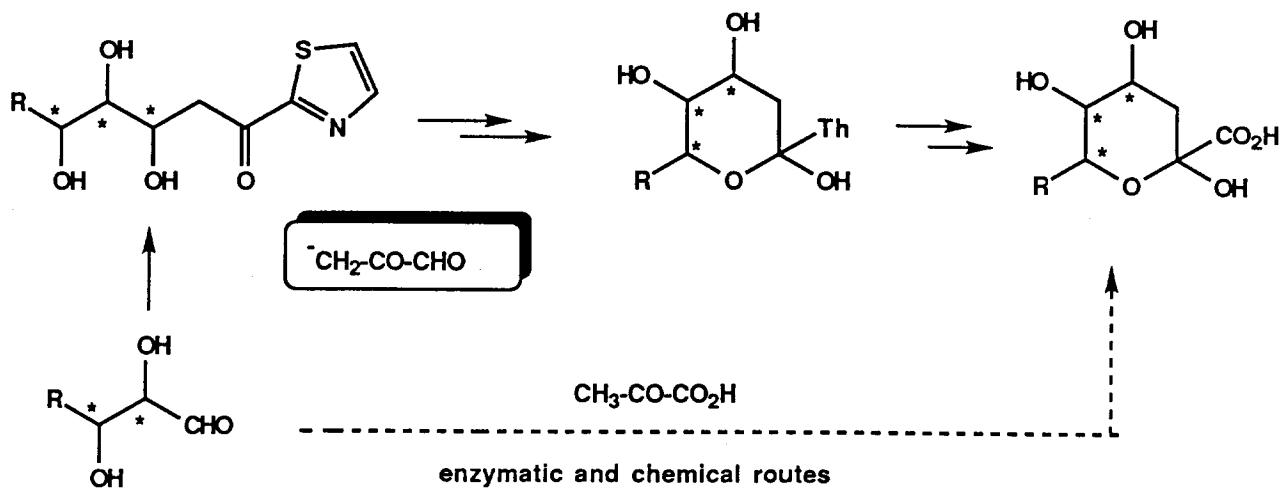
# FORMAL SYNTHESIS OF HYDANTOCIDIN



Synthesis of Novel Sugar  $\alpha$ -Azido and  $\alpha$ -Amino Acids



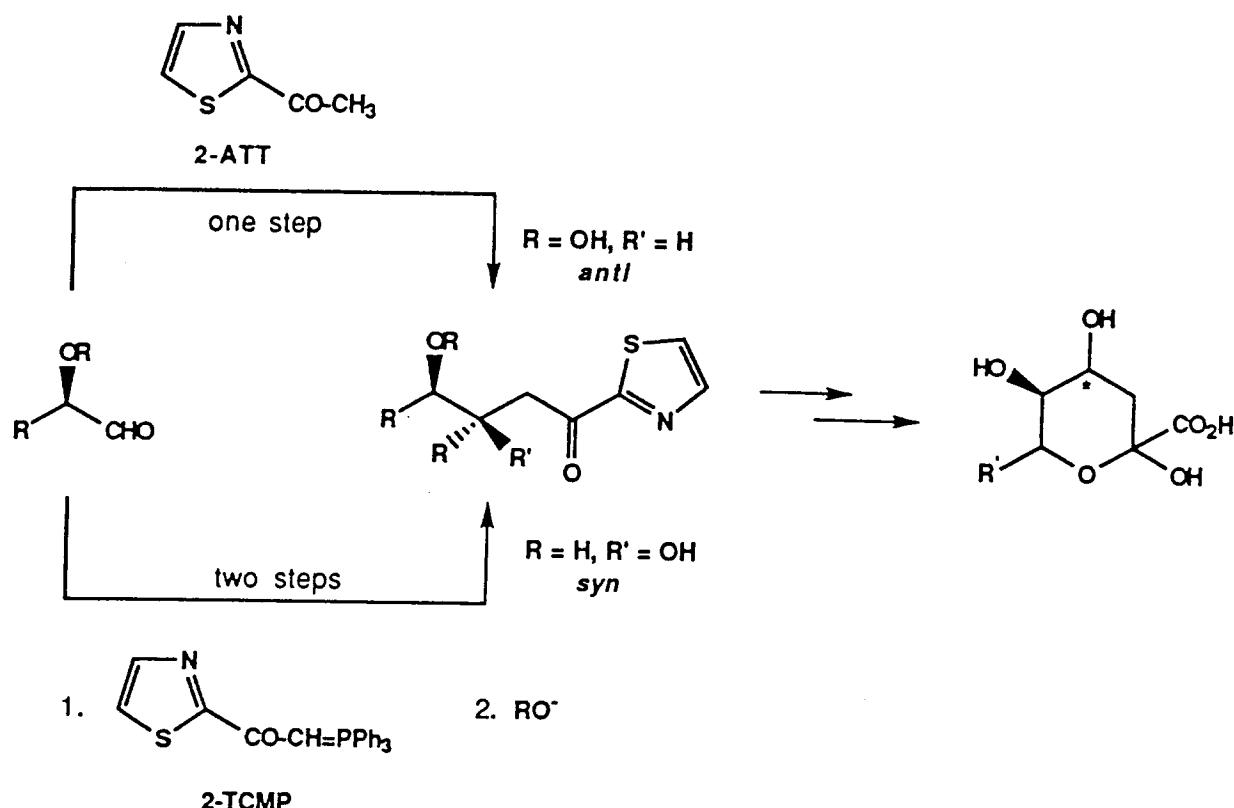
### Three-Carbon Chain Extension of Aldoses to 3-Deoxy 2-Ulosonic Acids



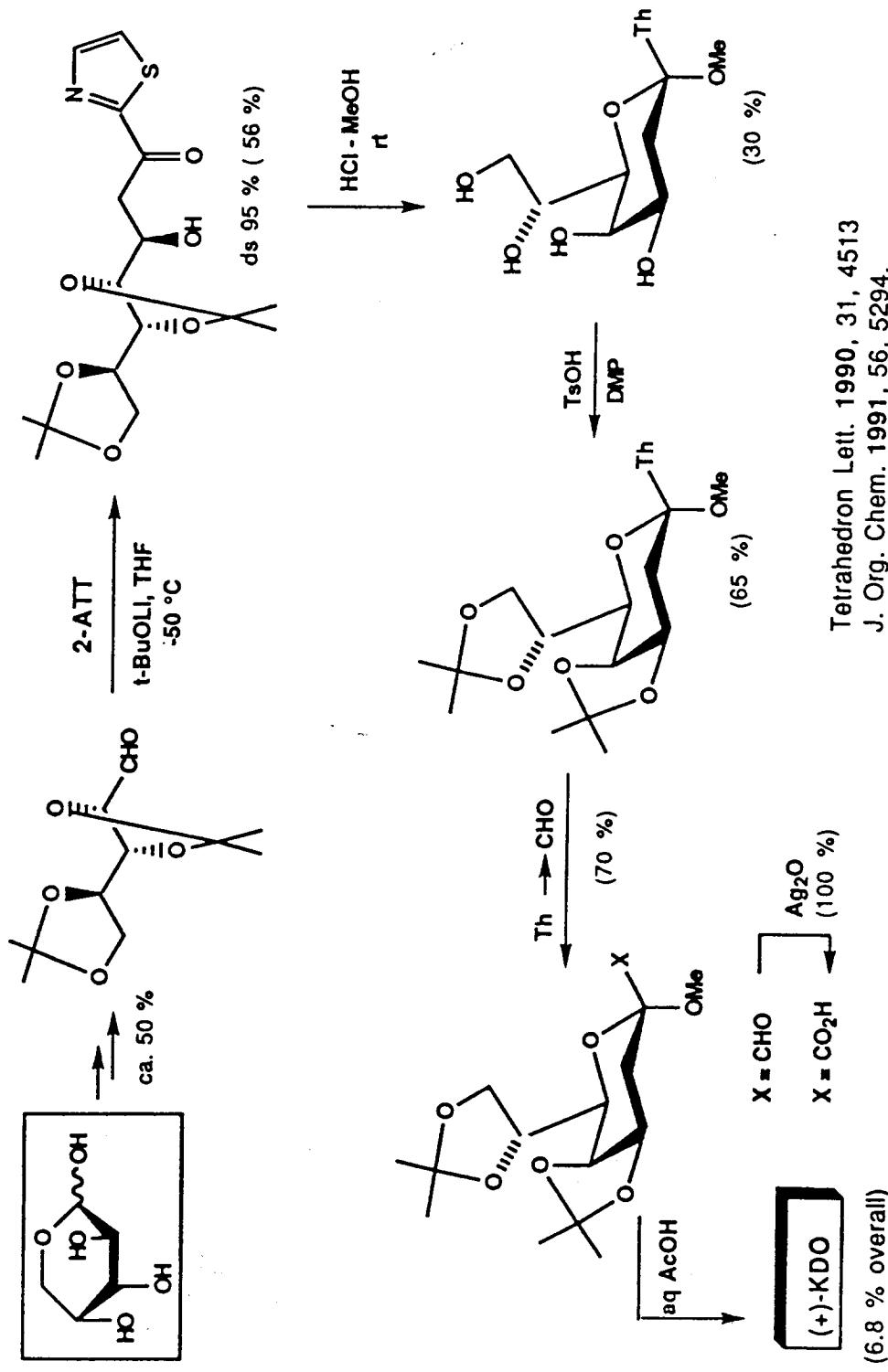
S. David                            R. R. Schmidt  
C.-H. Wong                        A. Vasella  
G. M. Whitesides                 T.-H. Chan  
                                      B. Giese

3-Deoxy 2-Ulosonic Acids via 2-Thiazolyl  $\beta$ -Hydroxy Ketones

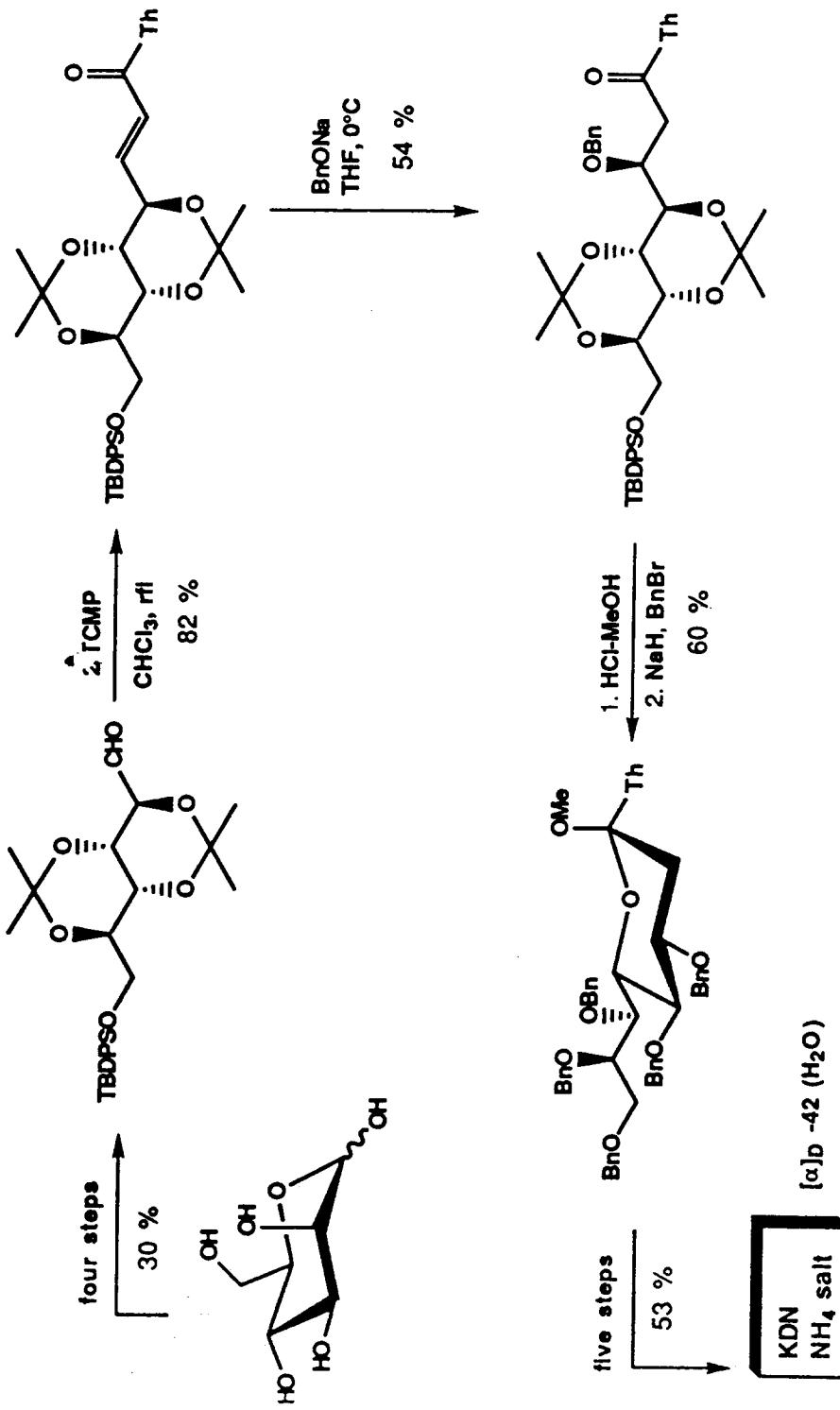
Stereocontrol at C-4



Total Synthesis of 3-Deoxy-D-manno-2-octulosonic Acid (KDO) from D-Arabinose



Total Synthesis of 3-Deoxy-D-glycero-D-galacto-2-nonulosonic Acid (KDN)



J. Am. Chem. Soc. 1994, 116, 3324

**Synthesis of iso-Neu4Ac from D-Mannose**

(Trimethylsilyl Azide Route)

