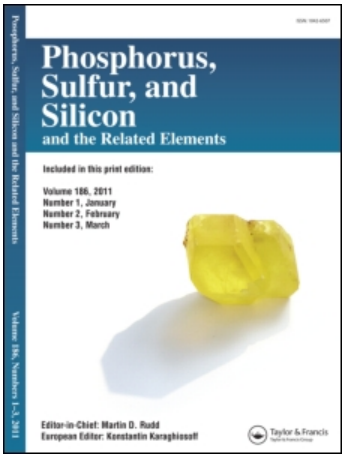


## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Chiral Vinyl Sulfoxides as Useful Reagents for the Synthesis of β-Amino Acid Derivatives

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(*S*)- and (*R*)-β-amino acid derivatives were synthesized by the asymmetric conjugate addition of ammonia and piperidazine to *t*-butyl (*E*)-2-[(*R*)- and (*S*)-*p*-tolylsulfinyl]cinnamates, respectively.

KEY WORDS: CHIRAL VINYL SULFOXIDES; CONJUGATE ADDITION; β-AMINO ACID DERIVATIVES; (*S*)-CELACINNINE



## INTRODUCTION

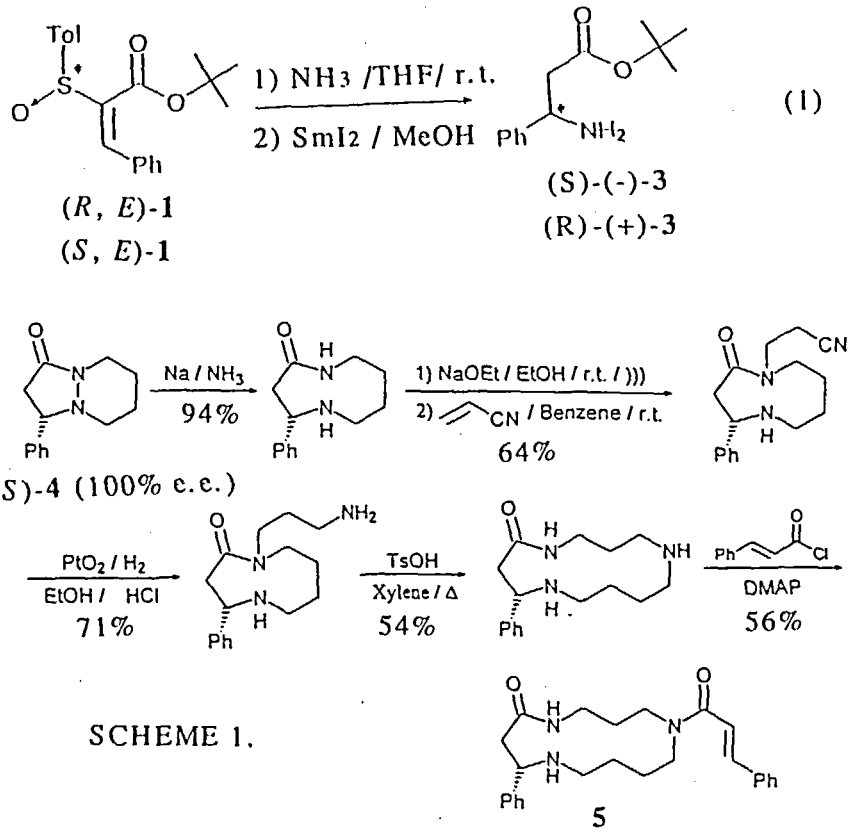
Many classes of natural products contain β-amino acid derivatives as fragments. For example, β-phenylalanine derivatives are constituents of many of the polyamine alkaloids, which are antibiotics and antihypertensive.[1]

## SYNTHESIS OF β-AMINO ACID DERIVATIVES

Recently, enantiomerically pure vinyl sulfoxides have proved to be useful reagents in stereoselective synthesis.[2] Our synthetic approach to β-amino acid derivatives is outlined in Equation 1. The conjugate addition of ammonia to chiral vinyl sulfoxides[3] (*R*)-**1** and (*S*)-**1**, followed by successive reduction of *p*-tolylsulfinyl group of the adducts **2** with $SmI_2$ proceeded smoothly at room temperature in THF to give (*S*)-(-)- and (*R*)-(+)-*t*-butyl β-amino-β-phenylpropionates (**3**) in 68% yield with good optical purity (74 and 81% e.e.), respectively. In the reactions of (*R*)-**1** and (*S*)-**1** with benzylamine in THF at room temperature, the stereoselectivity was moderate (52% e.e.).

## SYNTHESIS OF (*S*)-(-)-CELACINNINE

In the reactions of (*R*)-**1** and (*S*)-**1** with six-membered hydrazine, piperidazine, in the presence of potassium *t*-butoxide in THF at room temperature, the conjugate addition-cyclization proceeded stereoselectively and (*S*)-**4** and (*R*)-**4** were obtained in 73 and 75% yields with high enantiomeric purity (95% e.e.), respectively. The bicyclic compound **4** is a key intermediate in the total synthesis of natural thirteen-membered polyamine alkaloids,[1] celacinnine and *N*(1)-acetyl-*N*(1)-deoxymayfoline, and the first synthesis of (*S*)-(-)-celacinnin (**5**) {$[\alpha]_D$ -16.5° (*c* 0.10, $CHCl_3$); natural celacinnine[3] $[\alpha]_D$ -19° (*c* 0.16, $CHCl_3$)} was accomplished by the ring-expansion method starting from (*S*)-(-)-**4** (100% e.e.) (Scheme 1).




SCHEME 1.

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