[Tetrahedron: Asymmetry, **7**, 1199-1204 (1996)] [Lab. of Pharm. Synthetic Chemistry]

Highly Stereoselective Hetero Diels-Alder Reactions of Chiral 3-(*p*-Tolylsulfinyl)-2-furaldehyde with Danishefsky's Diene Promoted by a Lanthanoid Lewis Acid.

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Hetero Diels-Alder reaction of optically active 3-(*p*-tolylsulfinyl)-2-furaldehyde with 1-methoxy-3-(trimethylsilyloxy)-buta-1,3-diene (Danishefsky's diene) in the presence of a Lewis acid has been examined. The reaction in the presence of 1.0 equiv. of $Ln(OTf)_3$ (Ln = Yb, Nd and Sm) followed by acidic work-up produced in good yields (68-88%) the hetero Diels-Alder adduct with high diastereoisomeric excesses (93-98% d.e.'s), whereas in the presence of an NMR shift reagent, tris(2,2,6,6-tetramethyl-3,5-heptanedionate)europium [$Eu(thd)_3$] the corresponding diastereoisomer was obtained as the major adduct in excellent yield with 77% d.e.

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Synthesis of D-*erythro*-Sphingosine from D-Glucosamine.

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D-*erythro*-Sphingosine was synthesized from D-glucosamine as a chiral pool through stereoinversion of the C(3)-hydroxyl group via an oxidation-reduction sequence, transformation to the *erythro*-amino-alcohol chiron protected as the oxazolidinone, and elongation of the side chain at the C(6)-position of the derived chloride .

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Synthesis of (3*S*,4*S*)-Statine and a Related Compound, (3*S*,4*S*)-AHPPA, from D-Glucosamine as a Chiral Pool.

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Biologically important *threo*-β-hydroxy-γ-amino acids, (3*S*,4*S*)-statine ((3*S*,4*S*)-4-amino-3-hydroxy-6-methylheptanoic acid) and (3*S*,4*S*)-AHPPA ((3*S*,4*S*)-4-amino-3-hydroxy-5-phenylpentanoic acid), were synthesized starting from D-glucosamine as a chiral pool. Two routes for the transformation of D-glucosamine to key intermediates, which are applicable to the synthesis of *threo*-β-hydroxy-γ-amino acids, were investigated. The successful route involved C(6)-carbon degradation and elimination of the C(4)-hydroxy group of D-glucosamine in 8 steps and 30% overall yield to furnish (4*R*,5*S*)-2-oxo-5-vinyloxazolidine-4-carbaldehyde dimethyl acetal, which has been utilized as a versatile intermediate for synthesizing the target compounds.