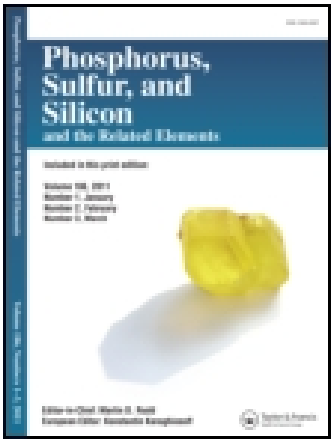

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A New Access to the Synthesis of Optically Pure β-Aminosulfides

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The significance of enantiomerically pure β-aminosulfides as chiral building blocks[1] and their use as effective chiral ligands in enantioselective reactions,[2] underlies the importance of developing new methods for their synthesis as single enantiomers.

We present herein a new route to synthetically useful chiral β-aminosulfides **3**, based on the reaction of the lithium α-sulfenylcarbanion Li-1 (derived from enantiomerically pure (*S*)-*ortho*-2-p-tolylsulfinyl-α-thiomethyltoluene **1**) with several (*S*)-N-*p*-toluensulfinylimines **2**. As in the case of other previously studied *ortho*-sulfinyl benzyl carbanions,[3] reactions take place in high yields

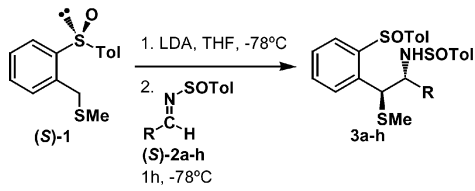

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TABLE I Lithiation and Subsequent Electrophilic Substitution of (S)-1 with (S)-N-sulfinylimines 2a–h

Products	R	Isolated yield (%)	de (%)
3a	Ph	85	>98
3b	*o*-BrC_6H_4	78	>98
3c	*p*-$MeOC_6H_4$	72	>98
3d	*p*-CNC_6H_4	60	>98
3e	2-Naphthyl	70	>98
3f	*i*-Pr	55	>98
3g	*n*-Pr	50	>98
3h	*n*-Bu	70	>98

and in a completely stereoselective way (only the *anti* β-aminosulfides are formed in <98% de, measured by ^{1}H-NMR). It is remarkable that only using clear solutions of n-BuLi to prepare LDA, one diastereoisomer was formed in reactions from **3g** and **3h** (Table I).

The α-sulfenyl carbanion Li-**1** is configurationally unstable according to the Hoffmann rule.[4] Thus, the high level of stereoselectivity achieved in these processes should arise through a dynamic kinetic resolution.

Chemical manipulation of compounds **3** have allowed us to obtain a wide variety of enantiomerically pure *anti*-1,2-diaryl (or 1-alkyl-2-aryl) 2-(methylthio)ethylamines and derivatives.

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