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

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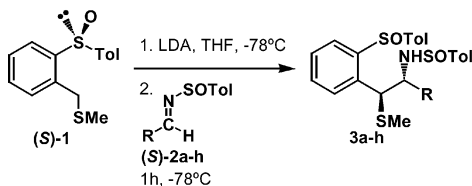
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The significance of enantiomerically pure β -aminosulfides as chiral building blocks¹ and their use as effective chiral ligands in enantioselective reactions,² underlies the importance of developing new methods for their synthesis as single enantiomers.

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	<i>o</i> -BrC ₆ H ₄	78	>98
3c	<i>p</i> -MeOC ₆ H ₄	72	>98
3d	<i>p</i> -CNC ₆ H ₄	60	>98
3e	2-Naphthyl	70	>98
3f	<i>i</i> -Pr	55	>98
3g	<i>n</i> -Pr	50	>98
3h	<i>n</i> -Bu	70	>98

and in a completely stereoselective way (only the *anti* β -aminosulfides are formed in <98% de, measured by ¹H-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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