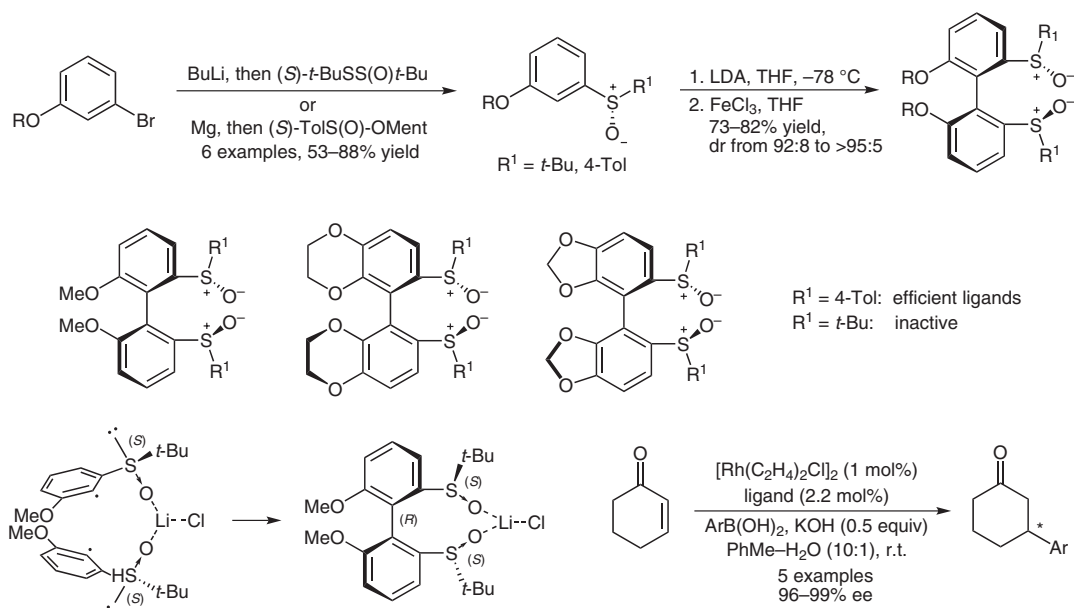


Q.-A. CHEN, X. DONG, M.-W. CHEN, D.-S. WANG, Y.-G. ZHOU,* Y.-X. LI* (DALIAN INSTITUTE OF CHEMICAL PHYSICS, UNIVERSITY OF SCIENCE AND TECHNOLOGY OF CHINA, HEFEI AND SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA) Highly Effective and Diastereoselective Synthesis of Axially Chiral Bis-sulfoxide Ligands via Oxidative Aryl Coupling
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Diastereoselective Synthesis of Axially Chiral Bis-sulfoxide Ligands



Significance: Chiral auxiliaries containing sulfinyl groups have recently received considerable attention due to their optical stability, efficient transfer of chiral information, and accessibility in both enantiomeric forms. However, limited studies have been carried out on sulfoxide ligands of axial chirality. In this study the authors have successfully developed a highly diastereoselective synthetic approach towards axially chiral sulfoxide ligands via oxidative coupling. A range of products were obtained with excellent diastereoselectivities (up to >95:5) and 73–82% yields; some of those were converted into partially and fully desoxygenated derivatives. The prepared 4-tolyl-substituted ligands were successfully employed in the rhodium-catalyzed asymmetric addition of arylboronic acids to 2-cyclohexenone to furnish the corresponding products with 96–99% ee.

Comment: The series of enantiopure substrates were prepared via the reaction of aryl Grignard reagents with (S_S) -menthyl-4-toluenesulfinate; *tert*-butyl analogues were accessed via quenching of the aryllithio intermediates with the corresponding thiosulfinate. Deprotonation with LDA followed by introduction of FeCl_3 furnished the desired biaryl bis-sulfoxides. The use of *S-tert*-butyl and *S-4-tolyl* substrates was shown to be equally successful in terms of chirality transfer. The authors proposed that the asymmetric induction of the coupling stems from the repulsion between the alkyl groups on sulfur (e.g., *tert*-butyl) and the coordination of lithium with the sulfinyl groups. In this consideration the major isomer is favorable both kinetically and thermodynamically.

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