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

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### C<sub>2</sub>-Symmetric Bis-Sulfoxides: Synthesis of Both Enantiomers and Utilization in Organometallic Chemistry and in Asymmetric Catalysis

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**To cite this Article** Fernández, Inmaculada , Araújo, Cristina S. , Alcudia, Felipe and Khier, Nouredine(2005) 'C<sub>2</sub>-Symmetric Bis-Sulfoxides: Synthesis of Both Enantiomers and Utilization in Organometallic Chemistry and in Asymmetric Catalysis', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1509 — 1510

**To link to this Article:** DOI: 10.1080/10426500590913447

**URL:** <http://dx.doi.org/10.1080/10426500590913447>

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## **C<sub>2</sub>-Symmetric Bis-Sulfoxides: Synthesis of Both Enantiomers and Utilization in Organometallic Chemistry and in Asymmetric Catalysis**

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**Keywords** C<sub>2</sub> symmetric bis-sulfoxides; C<sub>2</sub> symmetric bis-thioesters; Pd-catalyzed asymmetric alkylation

## **INTRODUCTION**

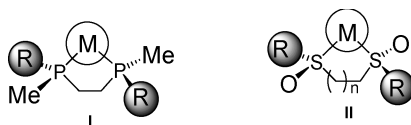
Although the utilization of chiral sulfoxides as chiral controllers in asymmetric synthesis is well documented, their utilization as ligands in asymmetric catalysis has met with little success.<sup>1</sup> In a clear analogy to the well-known bis-phosphine with a chiral phosphorus atom **I**, we contemplate the possibility of using C<sub>2</sub>-symmetric bis-sulfoxides such as **II** (Figure 1) as chiral ligands in asymmetric catalysis.

## **RESULTS**

Various aryl and alkyl ethane-bridged C<sub>2</sub>-symmetric bis-sulfoxides were synthesized, applying our recently developed methodologies based

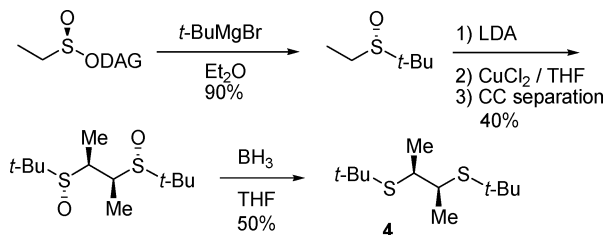
Received July 9, 2004; accepted October 5, 2004.

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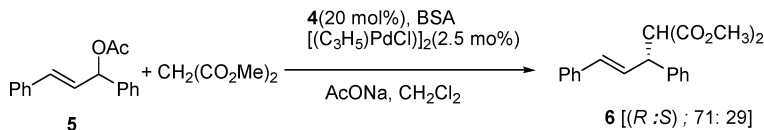
**FIGURE 1** Bis-phosphines and bis-sulfoxides metal complexes.

on the dynamic kinetic resolution of sulfinyl chlorides.<sup>2,3</sup> The study of the chelation properties of these compounds with transition metals by NMR and IR has shown that they chelate Pd and Ru efficiently through the sulfur atoms. Surprisingly, when used as chiral ligands in Pd(0)-catalyzed asymmetric alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate, they were completely inactive.



**SCHEME 1**

Keeping in mind the idea of maintaining the stereogenic centers close to the metal center, bis-thioethers with a chiral backbone were considered as an alternative. C<sub>2</sub>-Symmetric bis-thioether **4** was synthesized from DAG (*S*)-ethanesulfinate in three steps, Scheme 1. The use of **4** as ligand in Pd(0)-catalyzed allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate afforded the *R* isomer with a promising 42% ee, Scheme 2.



**SCHEME 2**

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