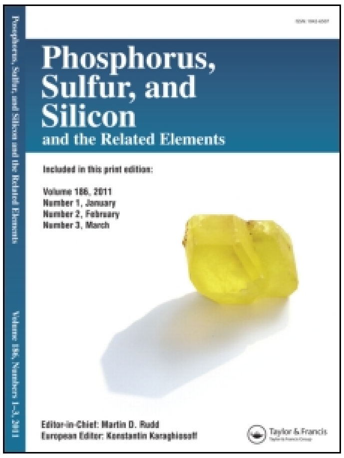

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Synthesis of Chiral Bis-Thiazolines and Asymmetric Diels-Alder Reactions

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Synthesis of Chiral Bis-Thiazolines and Asymmetric Diels–Alder Reactions

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*New chiral ligands, bis-thiazoline derivatives (sulfur analogues of known oxazolines) were prepared from chiral bis-(*N*-acylamino alcohols) with Lawesson's reagent. Bis-thiazolines thus obtained proved to be useful chiral ligands for metal in asymmetric Diels–Alder reaction.*

Keywords Asymmetric catalyst; bis-(*N*-acylamino) alcohol; chiral bis-thiazoline; Diels–Alder reaction; Lawesson's reagent

INTRODUCTION

Chiral bis-oxazolines have been successfully used in asymmetric synthesis.[1] However, the sulfur analogues, bis-thiazolines, have received little attention.[2] Several of them are known, but the variety of structures is restricted because the most useful sulfur-containing precursors are not easily available. Recently, we have reported the novel synthesis of sulfur-containing heterocycles by treating bifunctional compounds with Lawesson's reagent (LR).[3] We report herein the facile synthesis of chiral bis-thiazolines starting from bis-(*N*–acylamino alcohols) and the ability of new chiral ligands for metals in asymmetric Diels–Alder reactions.

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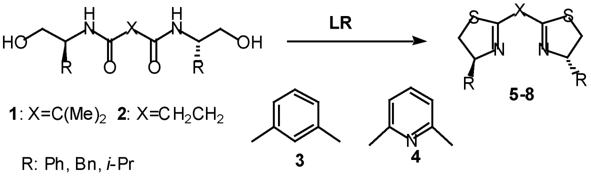
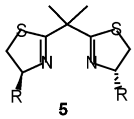
RESULTS AND DISCUSSION

Treatment of chiral bis-(*N*-acylamino alcohols) **1–4** with LR in toluene at reflux temperature yielded chiral bis-thiazolines **5–8** in good yields. Chiral thiazoline **9** was also obtained by treatment of *N*-picolinoylamino-2-phenylethanol. Chiral bis-thiazolines **5–8** and **9** thus obtained, sulfur analogues of known oxazolines, can be expected to be new chiral ligands for metals in asymmetric Diels–Alder reactions.





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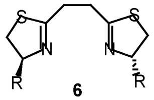

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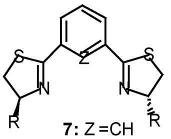
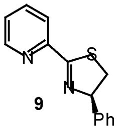
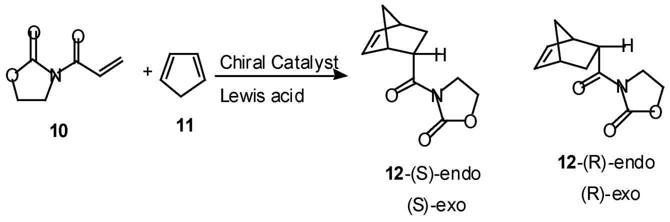


7: Z =CH
8: Z =N



9

For example, when 3-acryloyloxazolidine-2-one **10** was treated with cyclopentadiene **11** in the presence of zinc triflate and bis-thiazoline **6** (R=Ph), the cycloadducts **12** were obtained as a 94:6 diastereomers where the major diastereomer formed with good enantioselectivity (92% ee).



In summary, the results achieved here establish the new and facile method for the synthesis of bis-thiazolines as promising chiral ligands.

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