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C₂-Symmetric Bis-Thioglycosides as Useful Ligands in Palladium-Catalyzed Asymmetric Allylic Alkylation: Synthesis of Both Enantiomers Using Natural Sugars as Ligand Precursors

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C₂-Symmetric Bis-Thioglycosides as Useful Ligands in Palladium-Catalyzed Asymmetric Allylic Alkylation: Synthesis of Both Enantiomers Using Natural Sugars as Ligand Precursors

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Keywords Carbohydrates; C₂-symmetric s/s ligands; pd-catalyzed asymmetric alkylation

INTRODUCTION

In our continuous interest in the synthesis and utilization of chiral sulfur compounds in asymmetric synthesis,¹ we have recently reported the synthesis of a new family of S/S ligands such as **L-1**, Figure 1, using carbohydrates as cheap starting material.² In this communication we report on the origin of the enantioselectivity observed with these ligands and on the synthesis of both enantiomers of the allylic alkylation using natural sugars as ligands precursors.

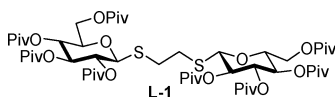


FIGURE 1 Structure of C₂-symmetric bis-thioglycoside **L-1**.

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RESULTS

The NMR studies of $[\text{Pd}(\eta^3\text{-1,3-PhC}_3\text{H}_3\text{Ph})(\text{L-1})]\text{SbF}_6$ have shown that the high enantioselectivity observed is a result of both the sulfur control stereochemistry and the ability of the hydroxyl protective groups to reach the remote reactive allylic center. On the other hand, one of the major drawbacks when using carbohydrates as chiral auxiliaries or chiral ligands is inherent in generating both enantiomers of a given process. To solve this problem we have noticed that α -D-arabinose, a cheap commercially available D-pentapyranose that exists mainly in the ${}^1\text{C}_4$ conformation, is quasi mirror image of β -D galactose. The synthesis of *per*-pivaloylated bis-arabinoside **L-2**, Figure 2, has been carried out in three high-yielding steps from arabinose tetraacetate.

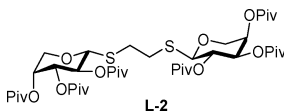
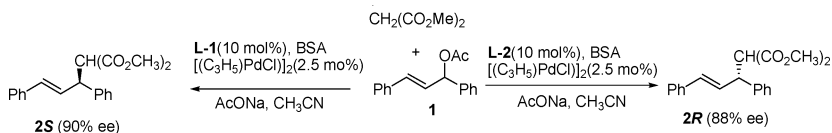


FIGURE 2 Structure of C_2 -symmetric bis-thioglycoside **L-2**.

The use of **L-2** as ligand in $\text{Pd}(0)$ -catalyzed allylic alkylation of 1,3-diphenylpropenylacetate **1** with dimethyl malonate afforded the **2R** isomer with 88% ee, while **L-1** afforded the **2S** isomer in 90% ee, Scheme 1.



SCHEME 1

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