Studies on the Regio- and Enantioselective Heck Arylations of Acyclic Allylic Alcohols.

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INTRODUCTION

Allylic alcohols is one of the most used substrates in the Heck reaction, not only because they are privileged building block in organic synthesis but also due the challenging control of the regioselectivity of the carbopalladation step. Although the stilbene adducts 3a and 4a are usually obtained as the major products, the aryl-carbonyl compounds such as 3b and 4b also represent interesting structural motifs for chemical synthesis if obtained in an enantioselective fashion (Scheme 1).

Very recently, we reported the intramolecular desymmetrization of both cyclic and acyclic olefins by enantioselective Heck-Matsuda arylations (Scheme 2). As a further demonstration of the power of this method, we describe herein the more challenging arylation of non-symmetrical acyclic allylic alcohols and its applications in the synthesis of enantioenriched α- and β-aryl-aldehydes.

RESULTS AND DISCUSSION

After optimization, we found that E-allylic alcohols provided the β-aryl-aldehydes as the major products in excellent ee values. On the other hand, the Z-allylic alcohols exhibited the opposite preference during the carbopalladation, furnishing the α-aryl-aldehydes (Scheme 3).

CONCLUSION

In this preliminary work, we have shown that simple acyclic allylic alcohols can be arylated by the enantioselective Heck-Matsuda reaction with good yields and ee values. Although the regioselectivity for those reactions were modest, either α- or β-aryl-aldehydes could be synthesized according to the double bond configuration present in the substrate.

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REFERENCES

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Scheme 1. Heck reactions with allylic alcohols.

Scheme 2. Heck reactions of allylic alcohols.