

# Highly enantioselective arylation of aromatic aldehydes, promoted by chiral phosphinite ligands

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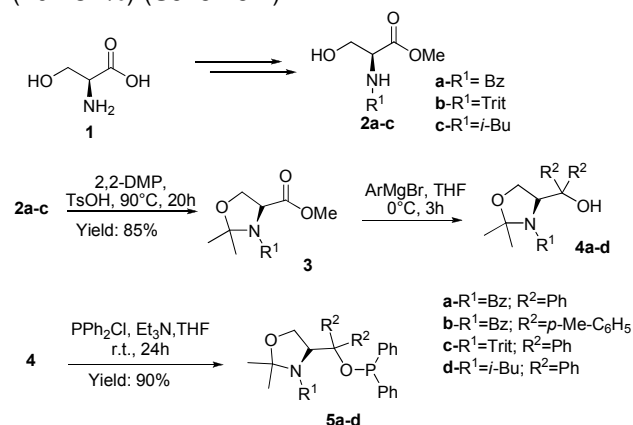
## INTRODUCTION

Enantiopure compounds production is becoming increasingly important, and for this purpose the asymmetric synthesis, particularly asymmetric catalysis, have been highlighted as an efficient method. In this context the nucleophilic addition to carbonyl compounds have received much attention, specially the asymmetric arylation of aldehydes and ketones.

In this work we present the synthesis of new phosphinite ligands with an oxazolidinic ring in its structure. In order to modulate the structure of the ligands aiming the optimization of the asymmetric induction, based on a six member ring N,P transition state, some variations of substituents in strategic positions of the basic structure of the ligand were made.

## RESULTS AND DISCUSSION

The asymmetric amino-phosphinite ligands can be prepared from *L*-Serine, in satisfactory global yields (10 - 32%) (Scheme 1).



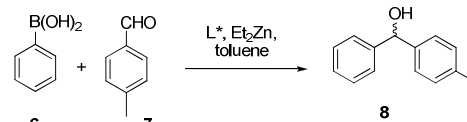
**Scheme 1:** Synthesis of phosphinites from *L*-serine.

This strategy permits a flexibility in the synthetic route. The versatility in introducing different groups at positions R<sup>1</sup> and R<sup>2</sup> as well as on carbon 2 of the oxazolidine ring allows the modulation of steric and electronic features of the ligand.

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Some results of the catalytic activity of the phosphinites are shown in table 1. The reaction furnished the product in good yields and when ligand **5d** was used excellent enantiomeric excesses were obtained.

**Table 1:** Enantioselective arylation of *p*-tolualdehyde



| Entry | Ligand | Temperature | mol% <b>5a</b> | Yield* | e.e. |
|-------|--------|-------------|----------------|--------|------|
| 1     | 5a     | r.t.        | 10             | 98%    | 39%  |
| 2     | 5a     | 0 °C        | 10             | 75%    | 67%  |
| 3     | 5a     | 0 °C        | 20             | 83%    | 66%  |
| 4     | 5a     | -15 °C      | 20             | 65%    | 53%  |
| 5     | 5c     | 0 °C        | 10%            | 46%    | 52%  |
| 6     | 5d     | 0 °C        | 0%             | 50%    | 92%  |

\*Isolated yields.

## CONCLUSION

These preliminary results showed that phosphinite ligands have a good activity as catalysts as well as inducers of asymmetry in the proposed reaction. Further studies are in progress in order to analyze the efficiency of these ligands against different substrates.

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## REFERENCES

- 1 Paixão, M. W. ; Braga, A. L., Lüdtkke, D. S. J. *Braz. Chem. Soc.*, **2008**, 5, 813.
- 2 Bolm, C.; Gladysz, J., Eds. *Chem. Rev.* **2003**, 103, 2761
- 3 Rudolph, J.; Bolm, C.; Norrby, P. O. *J. Am. Chem. Soc.* **2005**, 127, 1548.
- 4 Fontes, M. Verdaguer, x. Solá, L. Pericás, M. A. Riera, A. J. *Org.Chem.* **2004**, 69, 253