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GIORNATA DI STUDIO DEDICATA ALLA CHIMICA ORGANICA  
DELLE MOLECOLE BIOLOGICAMENTE ATTIVE

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## HANNO CONTRIBUITO ALLA REALIZZAZIONE DEL CONVEGNO:

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**EXPANDING THE SCOPE OF ATROPISOMERIC MONODENTATE P-DONOR  
LIGANS IN ASYMMETRIC CATALYSIS. HYDROGEN TRANSFER  
REDUCTION AND HYDROGENATION OF  $\alpha,\beta$ -UNSATURATED ACIDS  
DERIVATIVES BY RHODIUM/PH-BINEPINE CATALYSTS.**

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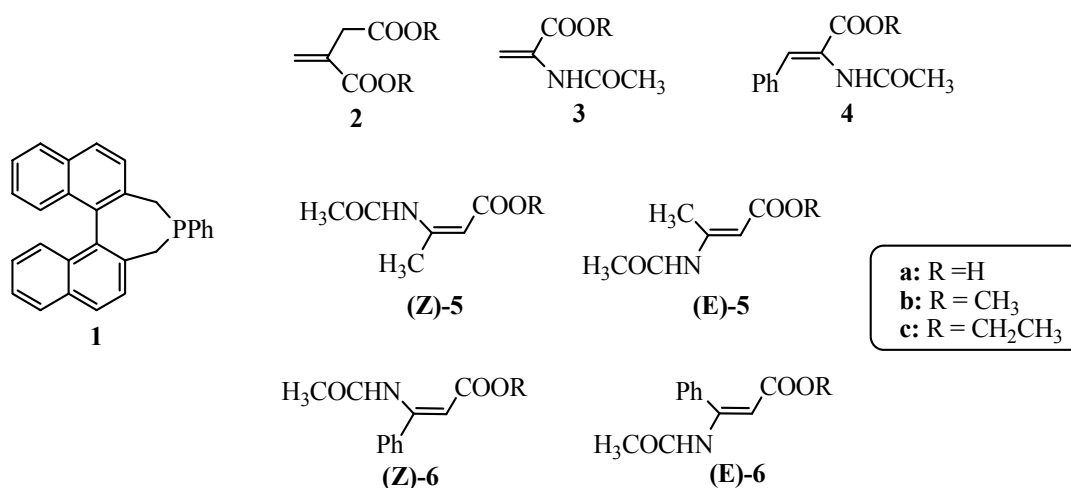
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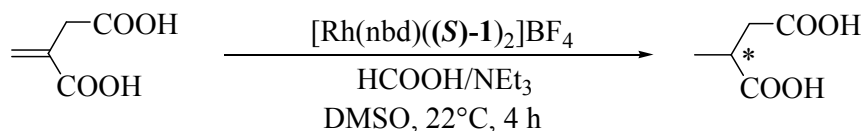
Cationic complexes of rhodium with binaphthophosphepine **1** (Ph-BINEPINE) [1], an axially chiral binaphthalene-core monodentate P-donor ligand (Figure 1),  $[\text{Rh}(\text{nb})((S)\text{-Ph-BINEPINE})_2]^+\text{X}^-$ , where  $\text{X}^- = \text{BF}_4^-, \text{CF}_3\text{SO}_3^-, \text{BarF}^-$ , have been prepared. These complexes have been tested as catalyst precursors in the asymmetric reduction of  $\alpha,\beta$ -unsaturated acid derivatives (Scheme 1) by both molecular hydrogen [2] and formic acid as a hydrogen donor source [3].



**Figure 1**

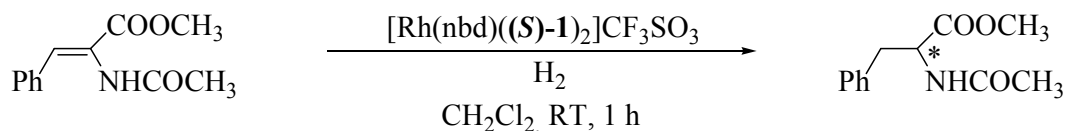
**Scheme 1**

Through optimization of reaction conditions, complete conversion and enantioselectivity up to 97% were achieved with itaconic acid **2a** in the hydrogen transfer reduction (Scheme 2).



**Scheme 2**

In the reduction with molecular hydrogen (*Z*)-methyl 2-acetamido-3-phenylacrylate **4b** gave the product with the highest optical purity (92% ee) providing a complete conversion (Scheme 3).



**Scheme 3**

Transfer hydrogenation has been applied for the first time to reduction of precursors of  $\beta$ -aminoacids. The stereoselectivity obtained with (*Z*)-**5c** in this process (12% ee) is lower than the one obtained with molecular hydrogen (92% ee).

A detailed description of the different outcome of reduction as to substrates and hydrogen source will be reported in the poster.

### References

- [1] a) S. Gladiali, A. Dore, D. Fabbri, O. De Lucchi, M. Manassero, *Tetrahedron :Asymmetry* **1994**, *5*, 511. b) Y. Chi, X. Zhang, *Tetrahedron Lett.* **2002**, *43*, 4849. c) K. Junge, G. Oehme, A. Monsees, T. Riermeier, U. Dingerdiessen, M. Beller, *Tetrahedron Lett.* **2002**, *43*, 4977.
- [2] S. Gladiali, E. Alberico “Transferhydrogenations” in M. Beller, C. Bolm (Eds), *Transition Metals for Organic Synthesis*, 2<sup>nd</sup> Ed., Wiley-VCH, **2004**, 145-156.
- [3] a) I. D. Gridnev, T. Imamoto, *Acc. Chem. Res.*, **2004**, *37*, 633-644. b) D. Heller et al., *Angew. Chem. Int. Ed.* **2005**, *44*, 1184-1.