Tandem Addition/Cycloisomerisation Reactions Catalyzed by [Ag(I)(Pc-L*)]$^+$ Complexes

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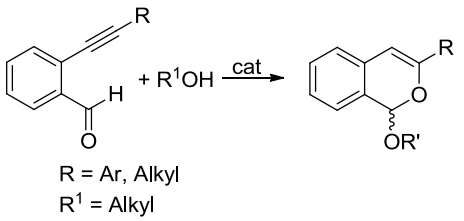
The tandem emiacetalization/cycloisomerization of *ortho*-alkynylbenzaldehydes (**Scheme 1**), originally reported by Yamamoto using $Pd(OAc)_2$ or CuI as a catalysts,[1] gives 1*H*-isochromene derivatives that can have useful medicinal properties.[2] Although several related tandem processes[3] are known, no enantioselective version of this reaction has appeared until the very recent report by Slaughter and coworkers.[4] Their study, is based on the use of chiral gold(I) acyclic diaminocarbene complexes as catalysts in the presence of $LiNTf_2$ (Tf = trifluoromethanesulfonyl) as a necessary additive to achieve useful activity.



Scheme 1

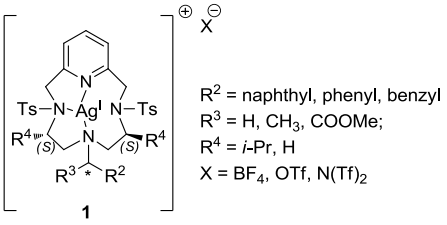


Figure 1

Recent studies in our research group demonstrated the efficacy of Cu(I) complexes, derived from novel macrocyclic ligands containing a pyridine ring (**Pc-L***), in cyclopropanation reactions.[5] The excellent results obtained up to now with copper prompted us to verify the application of silver(I) complexes of these ligands in catalysis. We herein report the synthesis and characterization of the new Ag(I) macrocyclic complexes, **1** (**Figure 1**) and their catalytic activity in the synthesis of oxygenated heterocycles by addition/cycloisomerization reactions of alcohols and *ortho*-alkynylbenzaldehydes. Reactions are characterized by mild conditions, complete regioselectivity and 1*H*-isochromene derivatives are obtained in good to excellent yields starting from both electron rich and electron poor *ortho*-alkynylbenzaldehydes. When optically pure ligands are used, chiral induction in the reaction products is observed, although, up to now, with modest enantiomeric excesses.

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