

(R)-TRIP and (S)-TRIP – Very Recent Applications

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José Tiago Menezes Correia was born in Brazil in 1986. He received his B.Sc. in chemistry from the Federal University of Bahia – UFBA (Bahia, Brazil) in 2010 and his M.Sc. in sciences from the State University of Campinas – UNICAMP (São Paulo, Brazil). He is currently a PhD candidate under the supervision of Prof. Dr. Fernando Coelho also at UNICAMP. His research focuses on the development of organocatalysed strategies to access indolizidinic and quinolizidinic cores, starting from Morita–Baylis–Hillman adducts.



Introduction

(R)- and (S)-3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diylhydrogenphosphates, also known as (R)-TRIP and (S)-TRIP are chiral phosphoric acids (CPA's) derived from BINOL. They are available from commercial sources, and they can be prepared through a three-step sequence that starts with a Kumada coupling between compound **1** and two equivalents of 2,4,6-(triisopropoxy)phenylmagnesiumchloride. This reaction is followed by a deprotection and a high-yielding phosphorylation step (Scheme 1a).¹

Since their first application in enantioselective organocatalytic hydrogenations by the List Group, in 2005,² these catalysts have been applied in numerous enantioselective transformations, including strategies involving cooperative catalysis.³

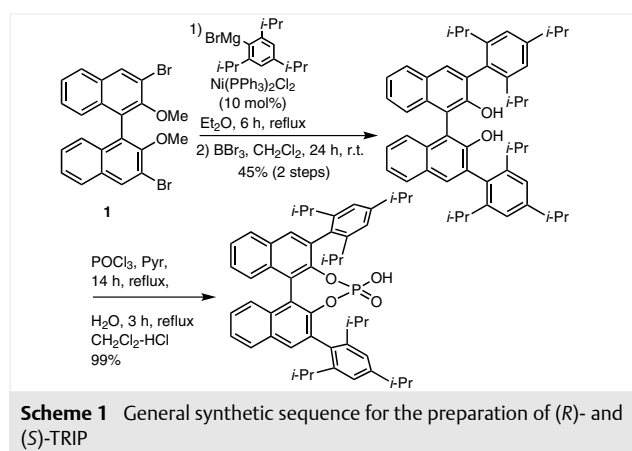
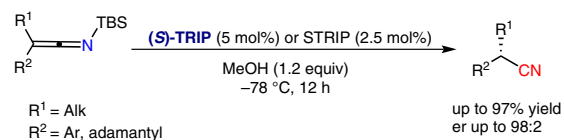
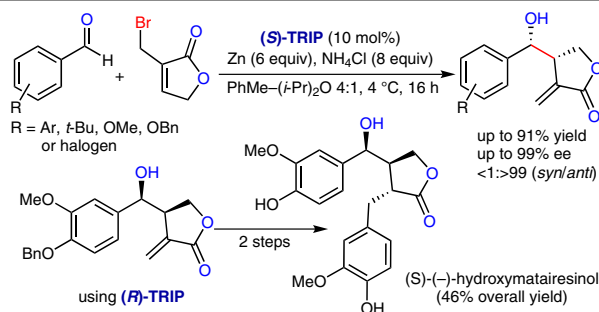


Table 1 Use of (R)-TRIP and (S)-TRIP – Very Recent Applications

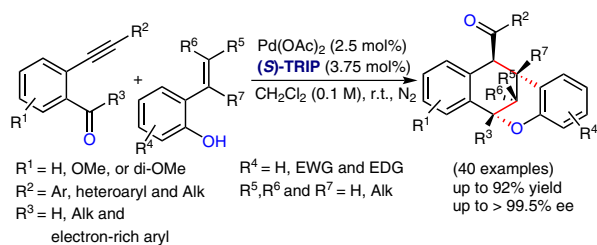
(A) Early in 2013, List and co-workers reported an asymmetric protonation of silyl ketene imines (SKI's) catalyzed by (S)-TRIP or STRIP (a spiroderivative of TRIP).⁴ During the catalyst screening both of these showed high efficiency. This transformation has no precedents in literature and showed to be a mild and straightforward strategy to access α -branched nitriles with high enantiopurity.



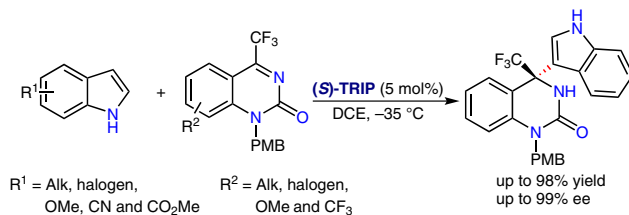
(B) Faber, Orthaber and co-workers reported an asymmetric allylation reaction between a zinc(II)-allylbutyrolactone species and (hetero)aromatic aldehydes using TRIP as catalyst.⁵ DFT studies showed that a complex ion-pair involving TRIP, Zn²⁺ and substrates is formed prior to enantioenriched β -substituted α -methylenebutyrolactone formation. Although high enantioselectivities had been reached, a two-step total synthesis of natural product (S)-(-)-hydroxymatairesinol was also performed in order to demonstrate the applicability of the methodology.



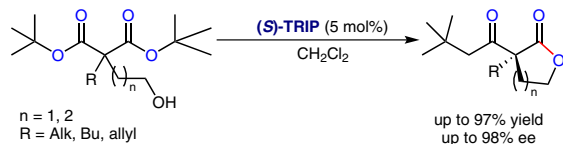
(C) In order to expand the applicability of isochromenyliums in enantioselective transformations, an asymmetric [4+2] annulation between 2-hydroxystyrenes and isochromenyliums prepared in situ from 2-alkynylbenzaldehydes or 1-(2-alkynylphenyl)ketones was developed by Yao and co-workers.⁶ Among the catalytic conditions investigated, the combination of Pd(OAc)₂ with (*S*)-TRIP gave the best results. This cooperative catalytic system showed to be applicable for a broad spectrum of substrates. Good to excellent enantioselectivities were achieved.



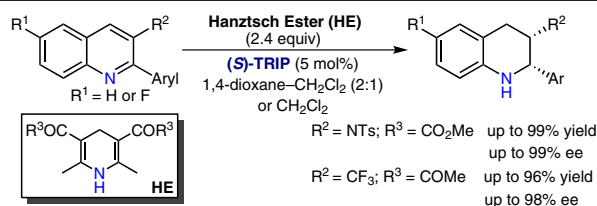
(D) Still in 2013, an asymmetric synthesis of cyclic trifluoromethyl-dihydroquinazolines via a TRIP-catalyzed aza-Friedel-Crafts reaction between indoles and cyclic *N*-acylketimines was developed by Ma and co-workers.⁷ This work was based on a previous report in which aryl-imines generated in situ from hemi-acetals were used as electrophiles.^{8a} In 2011, Bolm and co-workers had also reported another example using trifluoropyruvate derived *N*-Boc-imines as electrophiles.^{8b}



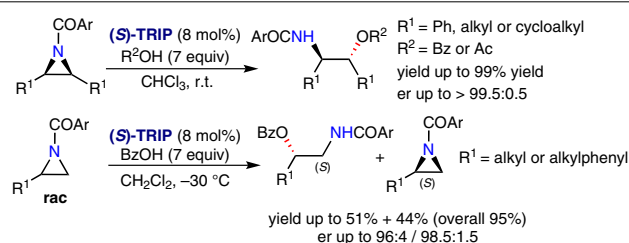
(E) Recently, the desymmetrization of pro-chiral diesters by an intramolecular transesterification catalyzed by TRIP was disclosed and had its scope explored by Petersen and co-workers.⁹ The process showed to be scalable and robust, leading to the preparation of several enantioenriched lactones with all-carbon chiral quaternary centers, which showed to be useful small building blocks.



(F) Organocatalysed transfer hydrogenation of heteroaromatic compounds has been widely investigated over the last years. Recently, Zhou and co-workers reported the use of TRIP on the asymmetric hydrogenation of 2-aryl-quinolone-3-amines and 3-(trifluoromethyl)quinolones with up to 99% and 98% ee, respectively.^{10a,b}



(G) Taking advantage of a highly favoured heterodimerization of carboxylic acids with TRIP, List and co-workers investigated the desymmetrization of *meso*-aziridines and the kinetic resolution of terminal aziridines using this catalyst.¹¹ The catalytic system proved useful for the conversion of cyclic and acyclic aziridines into *O*-protected amino alcohols with high yields and enantioselectivities. This was the first report of a CPA's catalyzed reaction using carboxylic acids as nucleophiles instead of only as additives, which has opened new perspectives in the field.



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