SYNLETT
Spotlight 118

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Copper(II) Trifluoromethanesulfonate[1]

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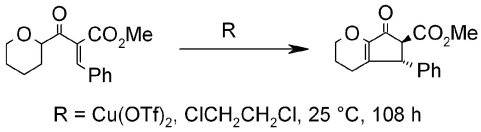
Introduction

Copper(II) trifluoromethanesulfonate is a mild and efficient catalyst and is commonly known as copper triflate. It is commercially available as a white powder and, when freshly prepared, it is in the form of a blue powder. It is prepared most conveniently from copper(II) carbonate and triflic acid (trifluoromethanesulfonic acid) in acetonitrile.[2] The freshly prepared salt is precipitated from Et_2O and is pale blue in colour. It is soluble in MeOH, EtOH, DMF, MeCN, formamide, *i*-PrCN and acetone. It is moisture stable and can be handled in air for quick transfer. Pure samples are only mildly corrosive. It appears to be indefinitely stable in the absence of air, moisture and light. Copper triflate has been used extensively, effecting various organic transformations such as oxidative coupling,[3] reactions of diazo-compounds,[4] formation of oxazoles from ketones,[5] and oxidation of alkyl radicals,[2] among others.[6]

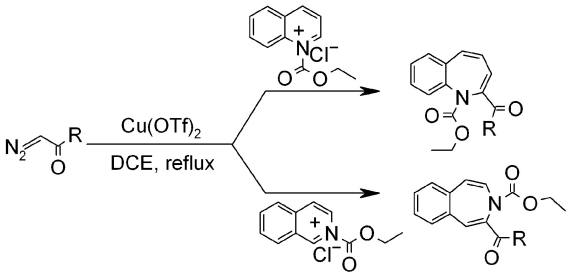
Abstracts

A) He et al. reported a mild and efficient copper(II) triflate-catalyzed procedure for the Nazarov cyclization of polarized divinyl ketones.[7]

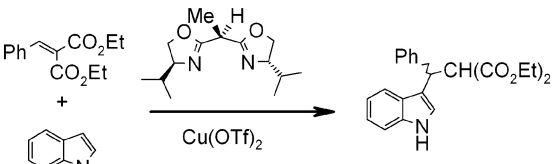


R = $Cu(OTf)_2$, $ClCH_2CH_2Cl$, 25 °C, 108 h

B) Our group reported unexpected ring expansion from activated quinoline and isoquinoline by using diazocarbonyl compounds via C–C insertion in the presence of 5 mol% of copper triflate to produce ethyl 1*H*-benzo[*b*]azepine-1-carboxylate and ethyl 3*H*-benzo[*d*]azepine-3-carboxylate, respectively, in excellent yields and with a high degree of selectivity.[8] The products represent an important moiety in many pharmaceutically active naturally occurring molecules.[9,10]



C) The combination of a bis(isopropyloxazole) and $Cu(OTf)_2$ proved to be an efficient catalyst in the asymmetric Friedel–Crafts reaction of indoles with arylidene malonates. In isobutanol, the *S*-enantiomer was obtained in up to 97% ee, while the opposite enantiomer was obtained in up to 78% ee in CH_2Cl_2 or 1,1,2,2-tetrachloroethane.[11]



For *S*-enantiomer, solvent = *i*-BuOH
For *R*-enantiomer, solvent = CH_2Cl_2 or $CHCl_2CHCl_2$

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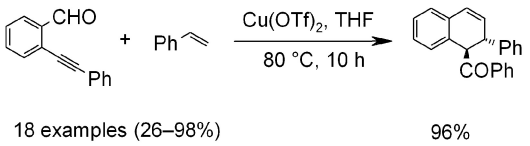
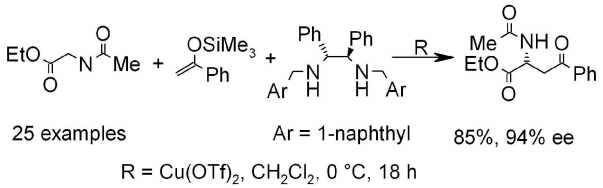
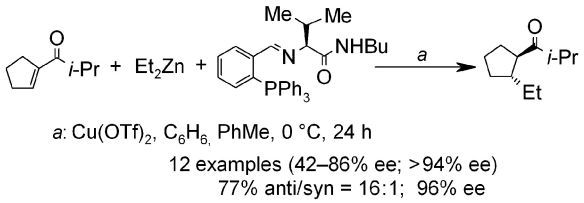
D) Asao and co-workers reported the [4+2] cycloaddition reaction between *o*-alkynyl(oxo)benzene and olefins in the presence of catalytic amount of $Cu(OTf)_2$. The reaction affords 1,2-dihydronaphthalene derivatives bearing an oxo function at the 1-position. The reaction proceeds most probably through the formation of benzo[*c*]pyrylium cupric ate complex.[12]



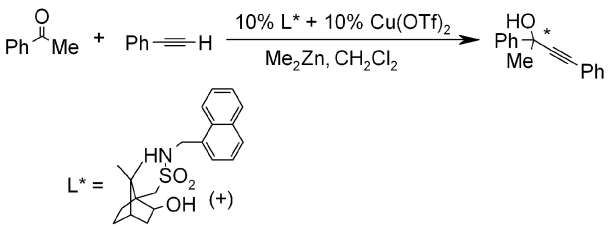
E) Kobayashi et al. developed catalytic asymmetric Mannich-type reactions of *N*-acyl esters with silyl enol ethers or alkyl vinyl ethers using $Cu(OTf)_2$–chiral diamine complexes as the catalyst.[13] The reaction proceeded smoothly at 0 °C in most cases, and high yields and high diastereoselectivies were attained. This method is useful for the preparation of N-acetylated amino acid derivatives, which are often observed in biologically important compounds such as peptides and ceramide.[14]



F) Degrado et al. reported an efficient and highly selective Cu-catalyzed asymmetric conjugate addition of alkylzincs to trisubstituted cyclic enones. This transformation is catalyzed by Schiff base derivatives of a single amino acid that is commercially available and inexpensive (L- or D-valine). The ligand can be prepared and used directly, without isolation or purification, to afford products with high enantioselectivities.[15]



G) Lu et al. reported the smooth addition of phenylacetylene to aromatic ketones in the presence of catalytic amounts of $Cu(OTf)_2$ and camphorsulphonamide. The corresponding tertiary propargylic alcohols were obtained in high yields and with up to 97% ee. This reaction represents a highly enantioselective catalytic addition of dialkynyl zinc reagents to simple ketones.[16]



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