

GS4-1 Enantioselective amination reactions catalyzed by dirhodium(II) carboxylates: Catalytic asymmetric synthesis of biologically active nitrogen-containing compounds

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Transition metal-catalyzed nitrene transfer reactions with (arenesulfonylimino)phenyliodinane offer useful means for the synthesis of aziridines, and amides or amines. Consequently, many studies on enantioselective nitrene-transfer reaction have carried out with chiral metal complexes as catalysts. Recently we reported that $\text{Rh}_2(\text{S-TCPTTL})_4$, a chiral Rh(II) carboxylate characterized by substitution of chlorine atoms for four hydrogen atoms on the phthalimido group in the parent Rh(II) complex, is an effective catalyst for enantioselective amination of benzylic C–H bonds (up to 88% ee) with $p\text{NsN=IPh}$ ($p\text{Ns} = 4\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2$). As a logical extension of our studies in this area, we now address the enantioselective aziridination of silyl enol ethers catalyzed by chiral Rh(II) carboxylates.

The Rh(II)-catalyzed aziridination of acyclic silyl enol ethers with NsN=IPh followed by treatment with aq. TFA has led to the formation of optically active α -amino ketone derivatives. The fluorinated catalyst, $\text{Rh}_2(\text{S-TFPTTL})_4$, has proven to be the catalyst of choice for this process, exhibiting the highest enantioselectivity of 95% ee. The effectiveness of the present catalytic method has been demonstrated by the enantioselective synthesis of (–)-ritodrine and (–)-metazocine. The amination of silylketene acetals derived from methyl phenylacetates with NsN=IPh under the catalysis of $\text{Rh}_2(\text{S-TCPTTL})_4$ afforded phenylglycine derivatives in high yields and with up to 99% ee.

