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Enantioselective Baeyer–Villiger Oxidation: Desymmetrization of Meso Cyclic Ketones and Kinetic Resolution of Racemic 2-Arylcyclohexanones

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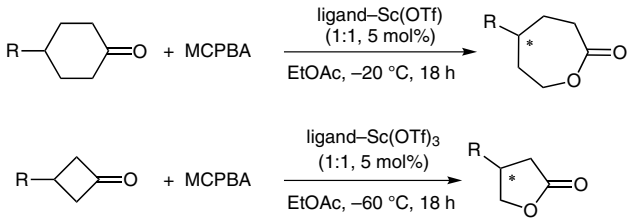
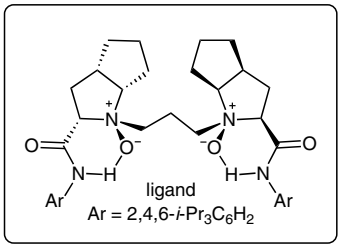
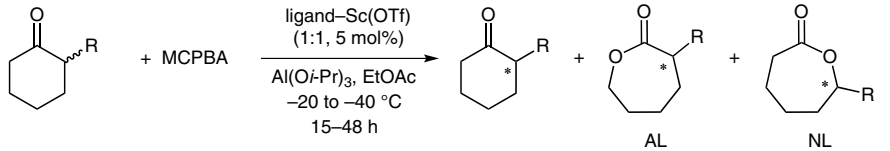
Enantioselective Baeyer-Villiger Oxidation

Desymmetrization of *meso*-cyclic ketones:

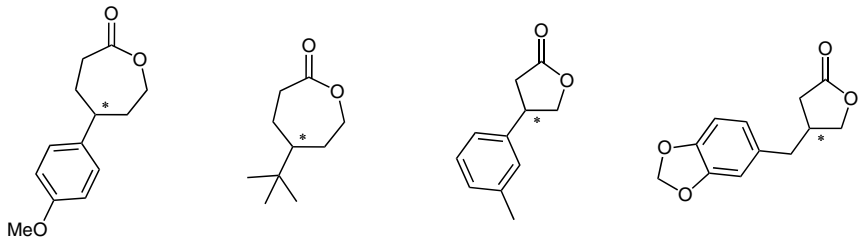




Kinetic resolution of racemic cyclohexanones:

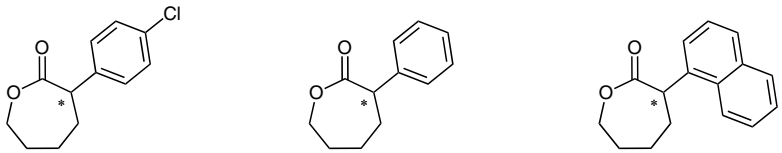


Selected examples of desymmetrization:



81% yield, 95% ee | 81% yield, 94% ee | 80% yield, 91% ee | 99% yield, 80% ee

Selected examples of kinetic resolution:



AL/NL > 19:1
93% ee (AL)

AL/NL = 16.5:1
90% ee (AL)

AL/NL > 19/1
99% ee (AL)

Significance: The asymmetric Baeyer–Villiger oxidation of prochiral and racemic cyclic ketones effectively synthesized optically active ε- and γ-lactones. The desymmetrization of racemic cyclohexanones interestingly showed a reversal of migratory aptitude with high levels of enantioselectivity.

Comment: The authors continued their use of chiral *N*,*N*′-dioxide-metal catalysts for the Baeyer–Villiger oxidation reaction. During the desymmetrization of *meso*-cyclohexanones and *meso*-cyclobutanones, the electronic and steric nature of the substituents appeared to have no effect on enantioselectivity; the opposite was true for the kinetic resolution of racemic cyclohexanones.

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

Baeyer–Villiger oxidation

scandium

desymmetrization