Modifications of Peptides via Chelate Claisen Rearrangements of Manganese Enolates

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Deprotonation of allylic esters of peptides at -70 °C in the presence of metal salts results in the formation of metal peptide enolate complexes which undergo Claisen rearrangement during warm-up to room temperature to produce stereoselectively modified peptides. By far the best results are obtained with manganese enolates. With these enolates the amino acids incorporated in the peptide chain have no significant influence on the rearrangement, neither on the yield nor on the stereochemical outcome of the reaction. Therefore this protocol is extremely suitable for the stereoselective modification of peptides by using esters of chiral allylic alcohols. α-Alkylated amino acids can be incorporated into peptides as well.