Deprotonation of peptides in the presence of zinc chloride gives rise to highly reactive nucleophiles which can be subjected to palladium-catalyzed allylic alkylations. Excellent diastereoselectivities are obtained nearly independent on the allylic substrate used. By this protocol also highly functionalized side chains can be incorporated with excellent yields and selectivities. The stereochemical outcome of the reaction is exclusively controlled by the peptide chain as long as terminal π-allyl-palladium complexes are involved. Probably, the deprotonated peptide chain coordinates at least threefold to the chelating zinc ion. In such metal peptide complexes one face of the generated enolate is shielded by the side chain of the adjacent amino acid, directing the electrophilic attack to the opposite face. This explains while an (S)-amino acid always generates an (R)-amino acid (and \textit{vive versa})