The asymmetric construction of quaternary carbon stereogenic centers, particularly in acyclic systems, remains one of the most significant challenges facing synthetic organic chemistry. In this regard, the transition metal-catalyzed allylic substitution reaction has emerged as a powerful method, owing to the enhanced electrophilicity of metal-allyl intermediates, which permits the generation of sterically congested bonds. This seminar will focus on the development of highly stereoselective rhodium-catalyzed allylic substitution reactions with nitrile-stabilized carbanions for the construction of quaternary stereocenters. Moreover, two distinct reaction manifolds shall be discussed, which serve to highlight the versatility of this class of carbanions. Firstly, tert-butyldimethylsilyl-protected cyanohydrins serve as acyl anion equivalents for the construction of \( \alpha \)-quaternary ketones, in which the nitrile group serves to stabilize the anion before being cleaved \textit{in situ}. On the other hand, lithiated \( \alpha \)-alkyl benzyl nitriles permit the synthesis of homoallylic tertiary nitriles, which constitutes the first example of the asymmetric alkylation of a nitrile anion. Finally, the synthetic utility of these novel transformations will be delineated via the preparation of useful motifs for target-directed synthesis applications.