Rhodium-Catalyzed Enantioselective Cyclopropanation of Electron Deficient Alkenes and Acceptor/Acceptor Diazo Reagents.

Rh-catalyzed cyclopropanation reactions have been extensively documented with electron-rich alkenes, as their intrinsic reactivity makes them highly compatible with catalytically active electrophilic rhodium carbenes. In contrast, the cyclopropanation of electron-deficient alkenes using diazo compounds poses a considerable challenge due to their lower nucleophilicity and reduced ability to interact efficiently with rhodium carbenes. Overcoming this limitation requires the development of tailored catalytic systems and optimized reaction conditions to achieve high efficiency and selectivity. Moreover, only one reaction has utilized diazo diacceptor compounds with electron-deficient olefins.

Herein, we report the enantioselective cyclopropanation of electron-deficient alkenes using diazo diacceptor derivatives, with $Rh_2((S)-BTPCP)_4$ or $Rh_2((R)-BTPCP)_4$ as chiral catalysts. This reaction enabled the synthesis of highly functionalized cyclopropanes, which were obtained in moderate to excellent yields, with high diastereoselectivities and excellent enantiomeric ratios. Finally, the versatility of these enantioenriched cyclopropanes was demonstrated through various functional group transformations.