# Dynamic catalytic diastereoconvergent (3+2) cycloaddition with α-keto ester enolates

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Induced-fit in response to substrate binding is a key mechanistic basis in enzymes. Such structural changes allow for active site preorganization, rate acceleration relative to other undesired pathways, and efficient turnover. Advancements in asymmetric catalysis have been made toward mimicking and surpassing enzyme. However, most approaches in asymmetric catalysis have mainly used a set of structurally constrained catalyst(s)/ substrates to reduce the number of possible diastereomeric transition states (TSs).

Here, we will present our studies on the stereochemical dynamics in the Ni(II)-catalyzed diastereoconvergent (3 + 2) cycloadditions of isomerizable nitrile-conjugated nitrones with α-keto ester enolates.[1] Even in the presence of multiple equilibrating species, our protocol enables the selective access to the CN-containing molecules having adjacent stereocenters. Our experimental and computational investigations suggest that weak H-bonding, CH/N, and CH/π interactions between the nitrone and ligand in **TS-*Z/Z*** play key roles in selectively recognizing the *Z*-nitrone to promote the cycloaddition.
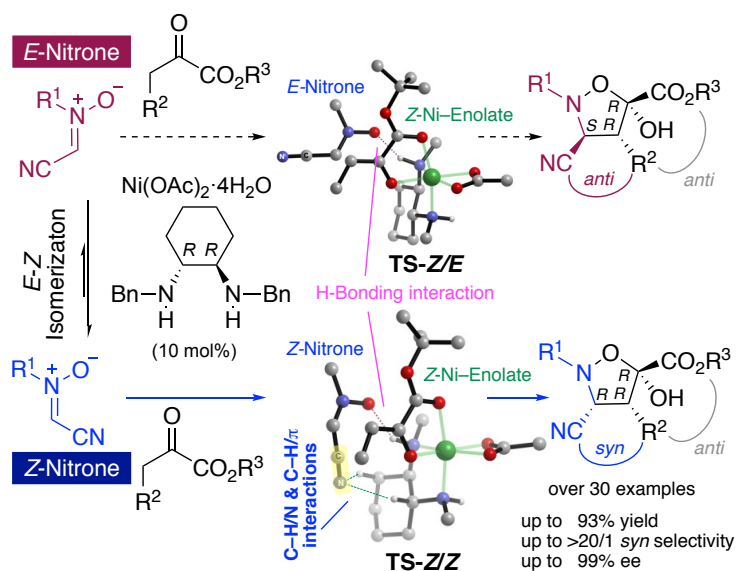
1) Ezawa, T.; Sohtome, Y.; Hashizume, D.; Adachi, M.; Akakabe, M.; Koshino, H.; Sodeoka, M. *J. Am. Chem. Soc.* **2021** *143*, 9094–9104.