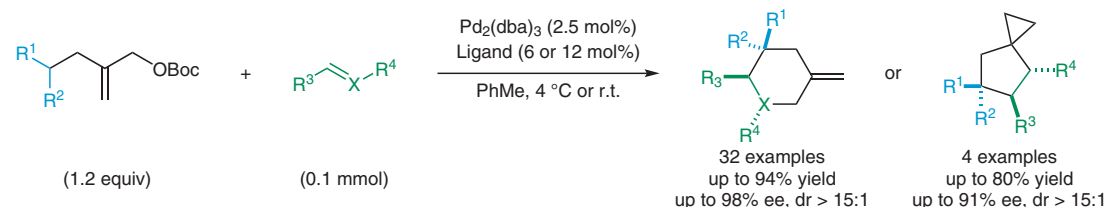
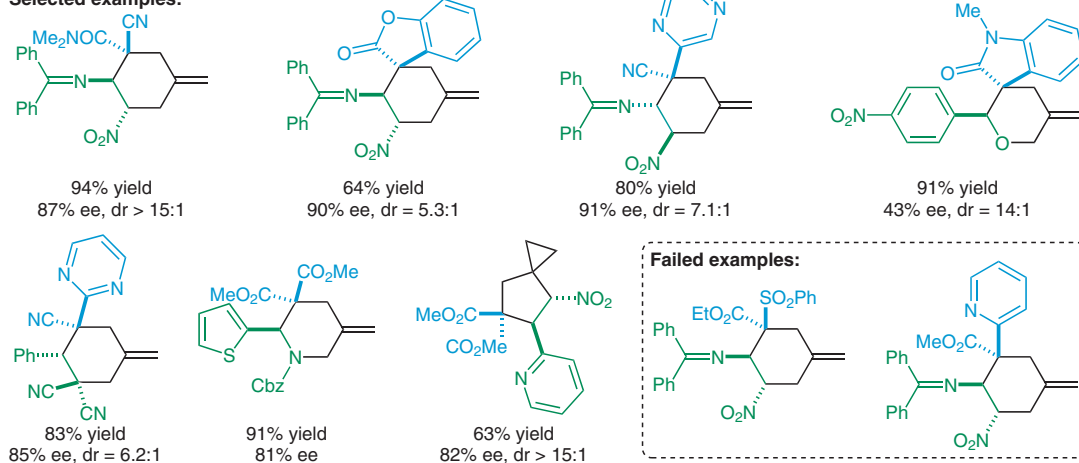


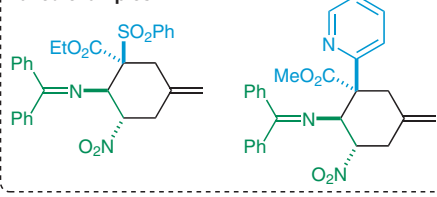
# Enantioselective Pd-Catalyzed Trimethylenemethane Cycloadditions of All-Carbon 1,4-Dipoles



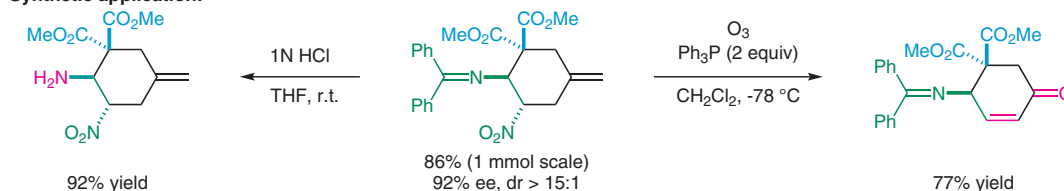
## Selected examples:



## Failed examples:



## Synthetic application:



**Significance:** Trost and co-workers report the asymmetric syntheses of all-carbon chiral cyclohexanes and spiro[2.4]heptanes using palladium-catalyzed cycloadditions of aliphatic 1,4-dipoles. Using various phosphoramidite and diamidophosphite ligands, several biologically relevant scaffolds were generated in good regio-, diastereo- and enantioselectivity. The synthetic utility was demonstrated through gram-scale syntheses of each scaffold, and derivatizations included the ozonolysis and hydrolysis reactions shown.

**Comment:** Upon scale up, the palladium and ligand loading could be decreased to 2 and 4 mol%, respectively, and the cyclohexane products were formed with higher regioselectivity than the spirocycles. Interestingly, a resonance effect between the pyridine nitrogen and palladium cation center was found to be necessary for the examples with heterocyclic arenes as the second electron-withdrawing group.