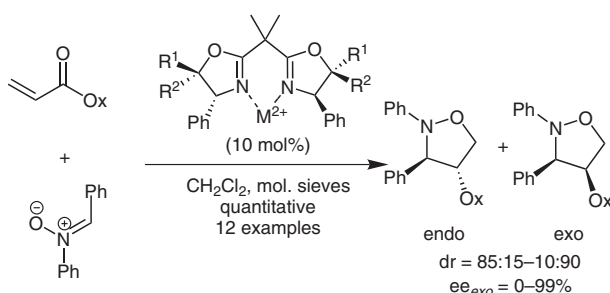


exo-Selective Catalysts for 1,3-Dipolar Nitrono Cycloaddition



Significance: There are numerous methods for *endo*-selective cycloaddition reactions; however, few examples addressing *exo*-selectivity can be found. 1,3-Dipolar nitrono cycloadditions serve as templates for developing selective catalysts, as regio-, diastereo- and enantioselectivity must all be addressed. Using Ph-BOX ligands and Lewis acids such as Mg(II), Co(II), Ni(II) and Zn(II), selectivity can be tuned for the 1,3-dipolar cycloaddition between acryloyloxazolidinone and diphenylnitrone. Under the optimal *exo*-selective conditions, >98:2 regioselectivity, 10:90 *endo/exo* selectivity and 99% ee_{exo} was obtained with *trans*-diphenyl-BOX ligand and Ni(ClO₄)₂ as Lewis acid.

Comment: All of the Lewis acid catalysts used produce quantitative conversion of the cycloaddition products. Addition of 4Å molecular sieves tends to favor formation of the *exo*-adduct, as well as the use of *trans*-disubstituted BOX ligands. One exception is the use of Zn(II), which showed reversed selectivity with the *trans*-ligands. In the absence of substituents on the 5-position of the BOX ligand, all cases show *endo*-selectivity. Overall, Ni(II) and Mg(II) performed the best, allowing access to the elusive *exo*-adduct.