

Substituent Effect on Cycloaddition [2+2+2] Reactions using the Wilkinson's Catalyst.

DFT calculations

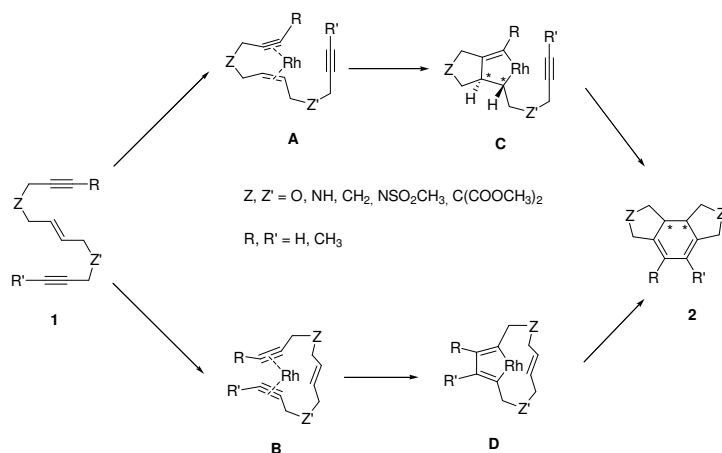
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The intramolecular [2+2+2] cycloaddition reaction of various enediynes using transition metal has been studied in several works.¹ Recently, Shibata and co-workers reported an enantioselective intramolecular [2+2+2] cycloaddition of various enediynes using Rh-H₈-BINAP catalyst.¹ They assumed that the asymmetric induction depends on the structure of tethers.

In this work, Density Functional Theory calculations were performed in order to study the oxidative coupling step of several enediynes analyzing the role of the carbon and heteroatom-tethered and also comparing the reactivity with the ligand phosphines present in the Rh-catalyst.²



¹ a) Bennacer, B.; Fujiwara, M.; Lee, S-Y.; Ojima, I. *J. Am. Chem. Soc.* **2005**, *127*, 17756-17767. b) Tanaka, K.; Nishida, G.; Sagae, H.; Hirano, M. *Synlett*, **2007**, 1426-1430. c) Shibata, T.; Kurokawa, H.; Kanda, K. *J. Org. Chem.* **2007**, *72*, 6521-6525.

² Dachs, A.; Roglans, A.; Solà, M. *in preparation*.