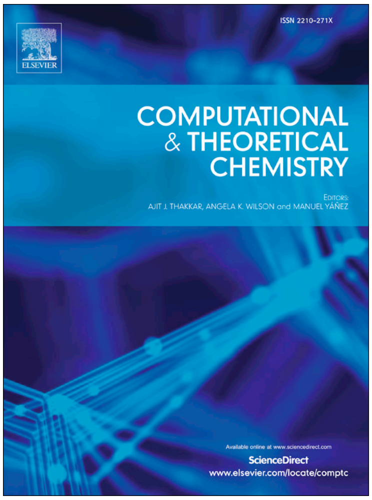

A computational mechanistic study on the chemo-, regio- and stereoselectivity of cycloaddition reactions leading to □-dihydropyran and tetrahydrocarbazol compounds

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A computational mechanistic study on the chemo-, regio- and stereoselectivity of cycloaddition reactions leading to ɤ-dihydropyran and tetrahydrocarbazol compounds

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Abstract

The reaction mechanisms of Danishefsky's diene (**1**) with 3- and 2-substituted indoles (**2** and **3**) were investigated using the DFT method. Two possible approaches of the carbonyl and carbon-carbon double bond of the dienophile to Danishefsky's diene (**1**) yield two types of compound, arising from the sequential [4+2] cycloaddition reaction. and hydrolysis of the silyl enol ether. Also, an acyclic hydroxyl product indicates that a stepwise mechanism of the Mukaiyama-type may be involved, when the reaction takes place in the presence of zinc chloride catalyst. In the cycloaddition reactions, while 3-substituted indole (**2**) tended to participate as the dienophile, 2-substituted indole (**3**) can react through a hetero Diels-Alder reaction. Then the chemoselectivity completely reverse in 2- and 3- substituted indoles, which energetical aspects and analysis of the Parr functions explained the chemoselectivity experimentally observed. The reactions were completely *ortho* regioselective with *endo* stereoselectivity in the zinc chloride catalyzed process. The Mukaiyama aldol reaction, as a stepwise mechanism, had a low activation energy relative to the concerted cycloaddition reactions. Moreover, analysis of the conceptual DFT reactivity indices allows the explanation of the reactivity, and the chemo- and regioselectivity.