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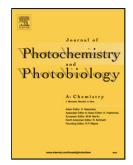
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DFT study on α-regioselectivity of photo-organocatalytic

functionalization of aldehydes

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ABSTRACT

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Density functional theory (DFT) study has been conducted to elucidate the key mechanistic transformations and the unique α -regioselectivity of alkylidene malonates towards the photoinitiated α -alkylation of aldehydes. The reaction between n-butyl aldehyde and diethyl methylenemalonate was chosen as model reaction and the possible reaction pathways were computed. Our calculations reveal that α -alkylation of aldehydes with alkylidene malonates proceeds through a radical-radical coupling pathway, instead of the radical chain or radical propagation pathway. This work demonstrates the details of the mechanistic framework and rationalizes the α -regioselectivity of alkylidene malonates.

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1. Introduction

Carbonyl compounds are widely used as inexpensive raw materials in pharmaceuticals. Consequently, direct functionalization of carbonyls has been an important goal in the research area of organic synthesis [1]. Many strategies such as

asymmetric organocatalysis have been developed by chemists to install functional groups at the carbonyl α - and β -positions [2, 3]. In recent years, photo-organocatalytic functionalization of aldehydes has emerged as a new activation mode [4-14]. By merging photoredox catalysis with organocatalysis, the

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