Title: DFT study on α-regioselectivity of
photo-organocatalytic functionalization of aldehydes

Authors: Yuhua Liu, Haizhu Yu, Qing-Xiang Guo

PII: S1010-6030(17)31388-6
DOI: https://doi.org/10.1016/j.jphotochem.2017.10.060
Reference: JPC 11060

To appear in: *Journal of Photochemistry and Photobiology A: Chemistry*

Received date: 21-9-2017
Revised date: 26-10-2017
Accepted date: 31-10-2017

Please cite this article as: Yuhua Liu, Haizhu Yu, Qing-Xiang Guo, DFT study on α-regioselectivity of photo-organocatalytic functionalization of aldehydes, Journal of Photochemistry and Photobiology A: Chemistry https://doi.org/10.1016/j.jphotochem.2017.10.060

ELSEVIER
Journal of Photochemistry and Photobiology A: Chemistry
journal homepage: www.elsevier.com

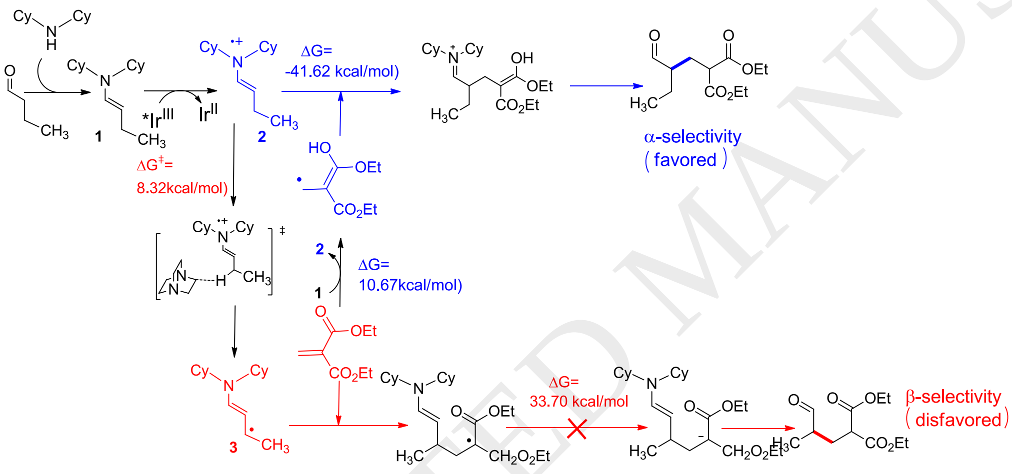
DFT study on α-regioselectivity of photo-organocatalytic functionalization of aldehydes

Yuhua Liu,[a] Haizhu Yu[b]* and Qing-Xiang Guo[b]

[a] *School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou, Guangdong 510006, China*

[b] *School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui 230601, China*
Email: yuhaizhu@ahu.edu.cn

Graphical abstract



ARTICLE INFO

Article history:
Received
Revised
Accepted
Available online

Keywords:
Alkylation
Mechanism
Regioselectivity
Density functional theory

ABSTRACT

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.

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

Dedicate to Professor Chen-Ho Tong on the occasion of his 80th birthday