



## Metal–Organic Framework $\text{Cu}_2(\text{OBA})_2(\text{BPY})$ as efficient catalyst for C–O bond formation via oxidative cross-coupling reaction of benzaldehyde and 1,4-dioxane

Huynh Quoc Thai<sup>1</sup>, Nguyen Thi Ngoc Tran<sup>1</sup>, Ha Thanh My Phuong<sup>1</sup>, Dang Huynh Giao<sup>1,2</sup>, Doan Hoai Son<sup>1</sup>, Phan Thanh Son Nam<sup>1\*</sup>

<sup>1</sup> Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, VNU-HCM, Vietnam

<sup>2</sup> College of Engineering Technology, Can Tho University, Vietnam

\*Email: [ptsnam@hcmut.edu.vn](mailto:ptsnam@hcmut.edu.vn)

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### ABSTRACT

A metal-organic framework  $\text{Cu}_2(\text{OBA})_2(\text{BPY})$  was synthesized, and was used as an efficient heterogeneous catalyst for the oxidative cross-coupling reaction of benzaldehyde and 1,4-dioxane to form 1,4-dioxan-2-yl benzoate as major product. The coupling reaction could proceed readily, with more than 80 % reaction yield being achieved after 24 h at 80 °C in the presence of 2 mol%  $\text{Cu}_2(\text{OBA})_2(\text{BPY})$  catalyst and *tert*-butyl hydroperoxide in water as an oxidant. The  $\text{Cu}_2(\text{OBA})_2(\text{BPY})$  was reutilized numerous times for the reaction without a noteworthy decline in catalytic efficiency. This Cu-MOF exhibited higher activity than other MOFs and traditional homogeneous catalysts in the oxidative coupling reaction. To the best of our knowledge, this transformation using heterogeneous catalyst was not previously mentioned in the literature.

### Introduction

The direct activation and cleavage of C–H bonds for the construction of carbon-carbon and carbon-heteroatom bonds catalyzed by transition metals has become an attractive strategy in modern organic [1]. The transformation showed remarkable potential for step economy, atom economy, and environmental sustainability as compared with traditional cross couplings which usually required the prefunctionalization of the reactants [2-4]. Considerable attention has been paid to the oxidative couplings involving C(sp<sup>3</sup>) H bonds [5-10]. However, studies involving the activation of C–H bond adjacent to an ethereal oxygen atom are still rare [11-14].  $\alpha$ -acyloxy ethers are ubiquitous structural motifs found in natural products and pharmaceutically active molecules [15-19]. The traditional methods of the

esterification of a hemiacetal, the nucleophilic substitution of a carboxylic acid and an  $\alpha$ -halo substituted ether or the addition of a carboxylic acid to an alkenyl ether, represented many disadvantages because it required substrate prefunctionalization and it was not atom economic. Recently, some processes have been developed to address these problems [20-23]. The Patel group synthesized benzylic esters via cross dehydrogenative coupling of aldehydes with alkylbenzenes in the presence of  $\text{Cu}(\text{OAc})_2$  catalyst and *tert*-butyl hydroperoxide as a oxidant [24]. The Patel group also reported an efficient Cu-catalyzed directed O-arylation process (esterification) between alkylbenzenes and *o*-carbonylphenols and  $\beta$ -dicarbonyl compounds using TBHP as the oxidant [25]. The Sharma group developed an efficient method of synthesizing 2-carbonyl substituted benzoates via copper-catalyzed esterification of 2-carbonyl