

# Functional Group Modification of Metal-Organic Frameworks for Synthesis of Enol Carbamates

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## Abstract

In this work, we succeeded to synthesis enol carbamates using modified MOFs in short times and excellent yields. In this procedure we utilized 1, 3- dicarbonyl compounds, DMF, TBHP as oxidant and MOFs as catalyst. Products were obtained with excellent yield and in short times.

## Introduction

The development of heterogeneous catalysts is a crucial requirement for sustainable chemistry due to ease of their separation. Metal-organic frameworks (MOFs) are a new class structured nonporous materials built up from organic linkers and inorganic connectors. Various organic linkers with functional groups can be used in synthesis of MOFs and these linkers are able to give them different applications [1-3]. Interestingly, MOFs have been used as heterogeneous catalyst in the synthesis of organic compounds. The catalytic performance of MOFs takes place at the metal centers. However, only a few proofs of concept of MOFs with catalytically-active functional organic sites have been reported [4-5]. The modification of amino groups on linkers of MOFs with second metal make them active catalysts for organic synthesis [6]. MOFs are widely used as a catalyst for recyclability and stability reasons during reaction. In this study, we synthesis of enol carbamates catalyzed by salen-Co(II) complex incorporated into  $\text{Cu}_2(\text{NH}_2\text{-BDC})_2\text{DABCO}$ . Products obtained in excellent yields.

## Experimental

### *Materials and instrumentation*

All chemical compounds and solvents were purchased from commercially available sources such as Sigma–Aldrich and Merck. All the chemicals were used as received without further purification. FT-IR spectra were recorded with a Shimadzu 8400s FT-IR spectrometer using potassium bromide pellets.  $^1\text{H}$  (500 MHz) NMR measurements were recorded on a Bruker 500 MHz spectrometer in  $\text{CDCl}_3$  using TMS as the internal reference.

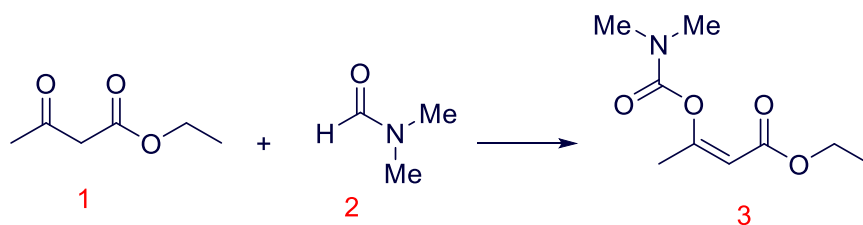
### General procedure for synthesis of enol carbamates

The mixture of 1, 3- dicarbonyl compounds (1 mmol), dimethylformamide (4 mL), TBHP (1.5 eq) and 0.03g solid catalyst were added into 10 mL round bottom flask. The reaction mixture was stirred and heated for 5-15 min. Afterward, catalyst was separated by filtration. The products were purified by plate chromatography. The yield of products was good to excellent.

## Results and discussion

Inhere,  $\text{Cu}_2(\text{NH}_2\text{-BDC})_2\text{DABCO}$  was prepared by solvothermal method. Then it modified using salicylaldehyde and cobalt (II) acetate tetrahydrate to form  $[\text{Cu}_2(\text{NH}_2\text{-BDC})_2\text{DABCO -Sal-Co (II)}]$ . The FT-IR spectra of samples were recorded to identify the structures of prepared samples. We used prepared catalyst in synthesis of enol carbamates. To optimize reaction condition, reaction of 1, 3- dicarbonyl compound **1** and DMF **2** was chosen as the model reaction. A systematic study considering different factors such as amounts of catalyst, various oxidants and the effect of temperature were investigated. The results are summarized in table 1. We found that reaction present desired yield when 30 mg from catalyst was used at 80 °C in the presence of t-butyl hydroperoxide (TBHP) as oxidant (entry 5). Preliminary optimization experiments indicated that the no product was obtained in the absence of any catalyst or oxidant in even under high thermal condition or at ambient temperature (entries 1-3).

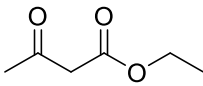
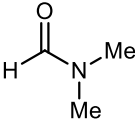
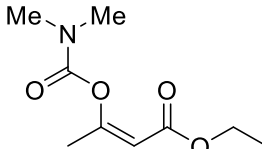
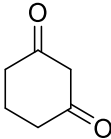
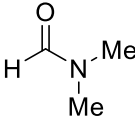
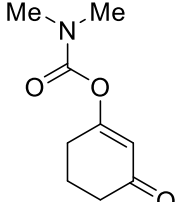
**Table 1.** Optimization of the reaction conditions.

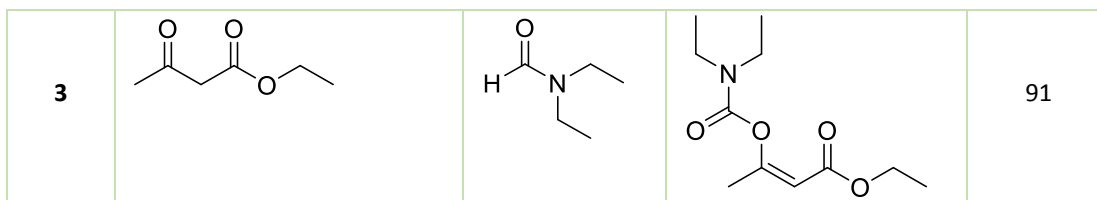


Entry	Catalyst (mg)	Oxidant	Oxidant (eq.)	Time (min)	T (°C)	Yield (%)
1	20-30	Air	-	90	80-100	NR
2	-	TBHP	3	90	80-100	NR
3	20-30	TBHP	1.5	90	25	NR
4	30	H <sub>2</sub> O <sub>2</sub>	1.5	60	80	NR
5	30	TBHP	1.5	5	80	94

According to the obtained results, 30 mg of catalyst and 1.5 eq from TBHP at 80 °C, as optimized conditions, was developed to other derivatives of enol carbamates. The results are summarized in Table 2.

**Table 2.** Synthesis of enol carbamates under optimized conditions.

Entry	1, 3- dicarbonyl compound	Amide	product	Yield (%)*
1				94
2				85



\* The yield of reaction determined by GC.

## Conclusion

We have been successfully synthesized metal-salen complex incorporated into  $\text{Cu}_2(\text{NH}_2\text{-BDC})_2\text{DABCO}$ . It was found that  $\text{Cu}_2(\text{NH}_2\text{-BDC})_2\text{DABCO}$  -Sal-Co behaves as desirable catalyst for synthesis of enol carbamates. This catalyst exhibits good recyclability as heterogeneous catalyst in synthesis of enol carbamates.

## Acknowledgements

The authors gratefully acknowledge from Iran University of Science and Technology (IUST) for financial support of this work.

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