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Improved oxovanadium catalysts for aerobic oxidation of lignin models and extracts

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Introduction

The challenge of converting biomass to valuable chemicals is a worthwhile endeavor for green chemistry. Lignin, the most abundant aromatic biopolymer on Earth, is a complex molecule that still needs more efficient synthetic methods in order to obtain value-added products.

Previously in the Baker group, selective C-C bond cleavage of lignin model compounds using oxovanadium catalysts with tethered bases was examined (Figure 1). To create improved catalysts, electron-withdrawing groups are being installed on the amino-diphenolate ligands of the complexes with the hope of suppressing undesired side-reactions observed previously.

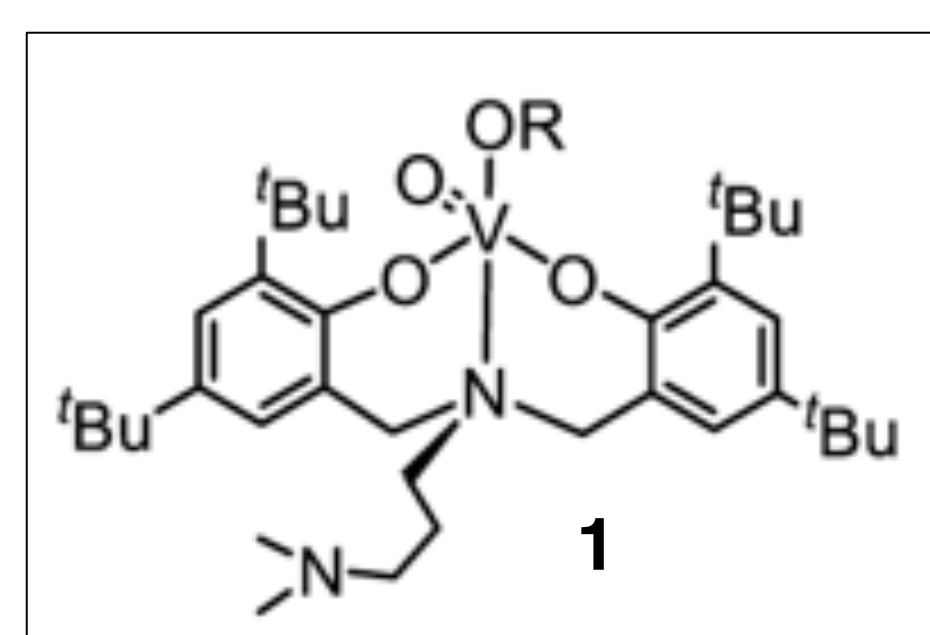


Figure 1. Previous oxovanadium catalyst, AP1

Once the ligands and oxovanadium catalysts are successfully synthesized and their purity confirmed by multinuclear nuclear magnetic resonance (NMR) spectroscopy, the latter will be tested on lignin model compounds starting with 1,2-diphenyl-2-methoxyethanol (LM2). Those catalysts that show improved selectivity with a number of lignin models will then be tested on Organosolv Lignin with the aim of obtaining value-added products. The success of these catalysts may provide a step forward in the valorization of lignin, helping to accelerate the shift towards a sustainable bio-based economy.

Goal

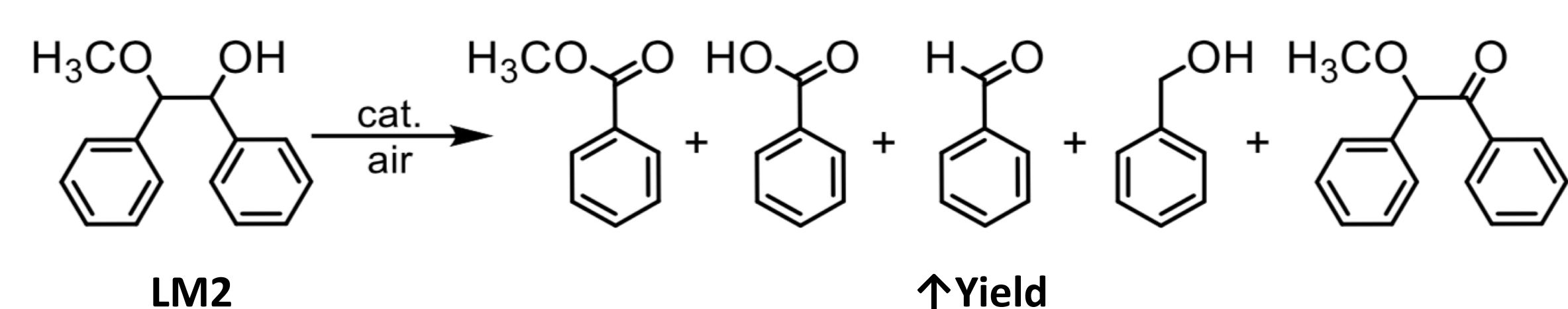


Figure 2. Possible products from C-C bond cleavage of LM2 using the oxovanadium catalyst (Díaz-Urrutia, 2016).

Ideally, yield and specificity for benzaldehyde would be increased as this product is chemically useful for further modifications.

Proposed Mechanism

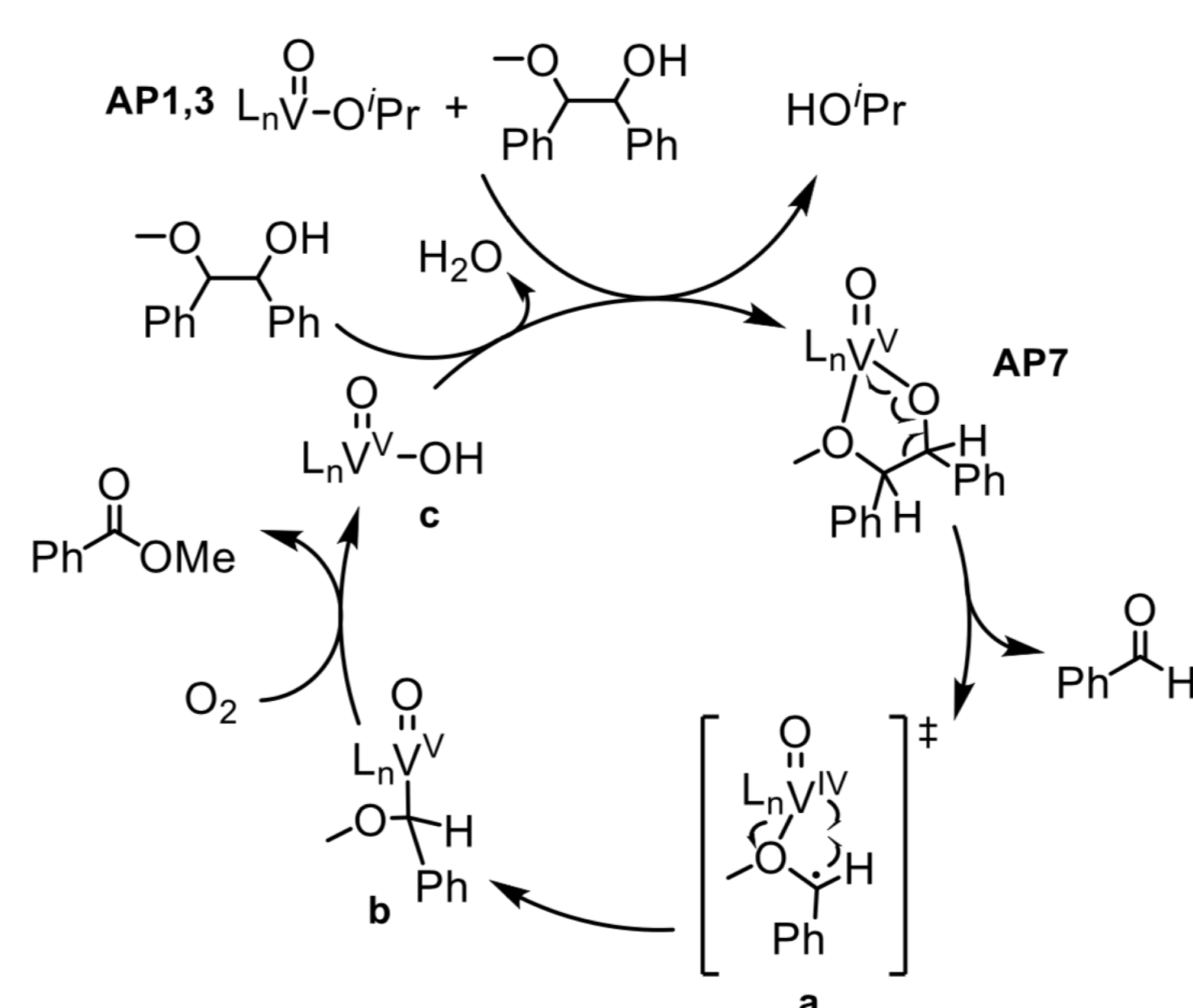


Figure 3. Proposed mechanism for the C-C bond cleavage of LM2 using amine bisphenolate catalysts (Díaz-Urrutia, 2016).

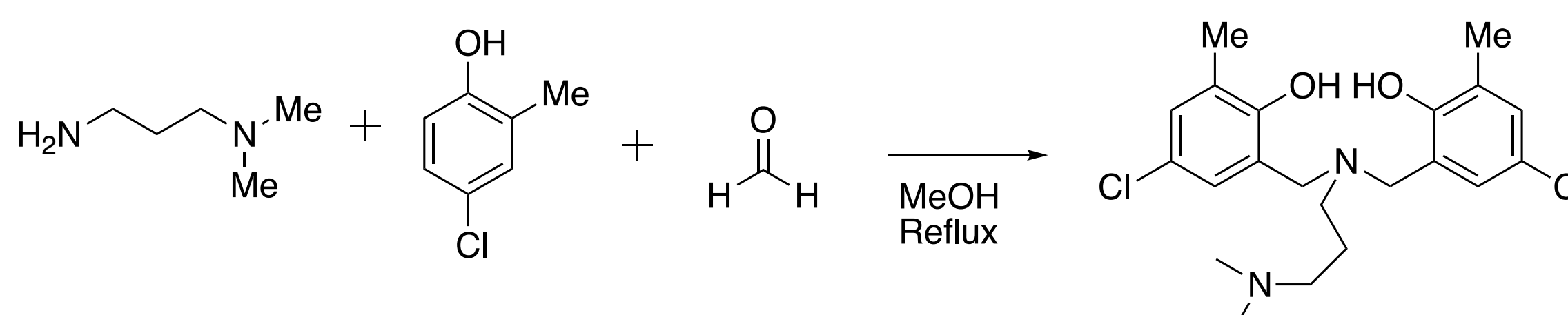
Methods

3 Components:

1. Synthesis of ligand
2. Synthesis of catalyst
3. Testing of catalyst on LM2

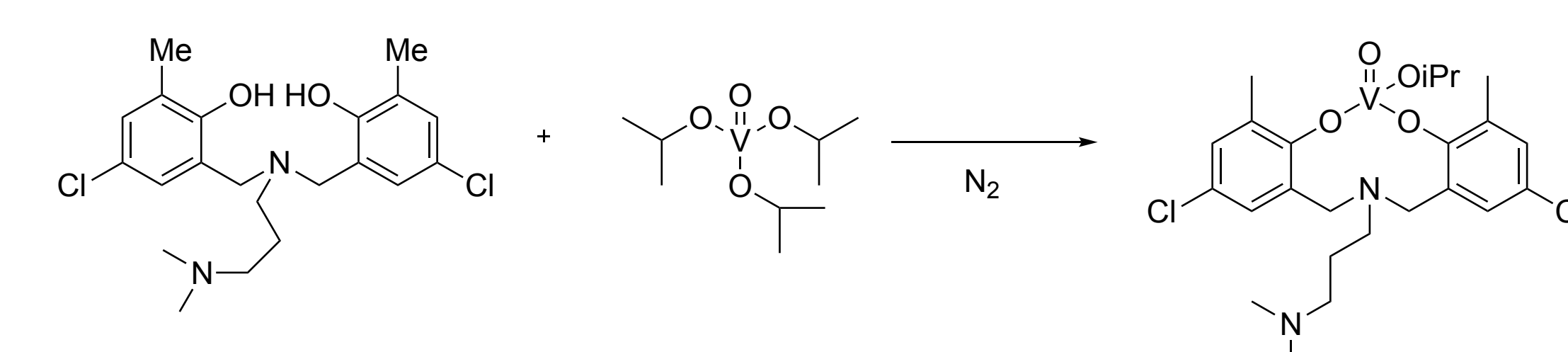
Results

Synthesis of ligand



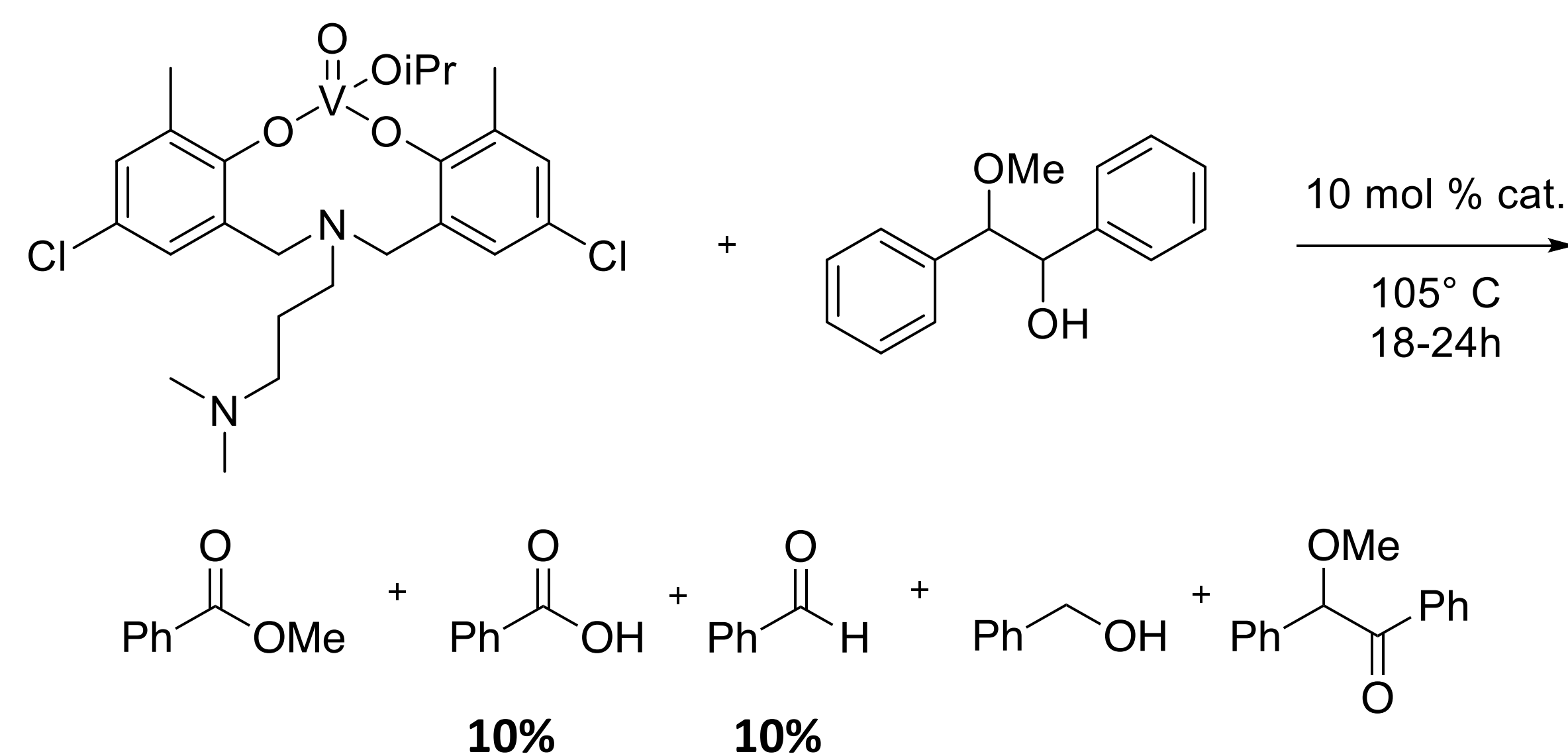
Confirmation of product made via ^1H NMR Yield: 30.2%

Synthesis of catalyst



Confirmation of product made via ^1H NMR. Yield: 51.3%

Reaction of catalyst on LM2



The reaction of the catalyst and LM2 was performed in a non-polar solvent (toluene), a medium-polarity solvent (pyridine), and a highly polarity solvent (DMSO). Toluene did not show sufficient product formation. ^1H NMR was used to determine the products made.

Mesitylene or 1,3,5-trimethoxybenzene was used as the internal standard in order to determine the amount of product made via ^1H NMR.

A 1:1 ratio of benzoic acid to benzaldehyde was observed based on NMR integration in both pyridine and DMSO. However some products which are still unidentified differed among the reaction in pyridine vs DMSO.

Side Reactions

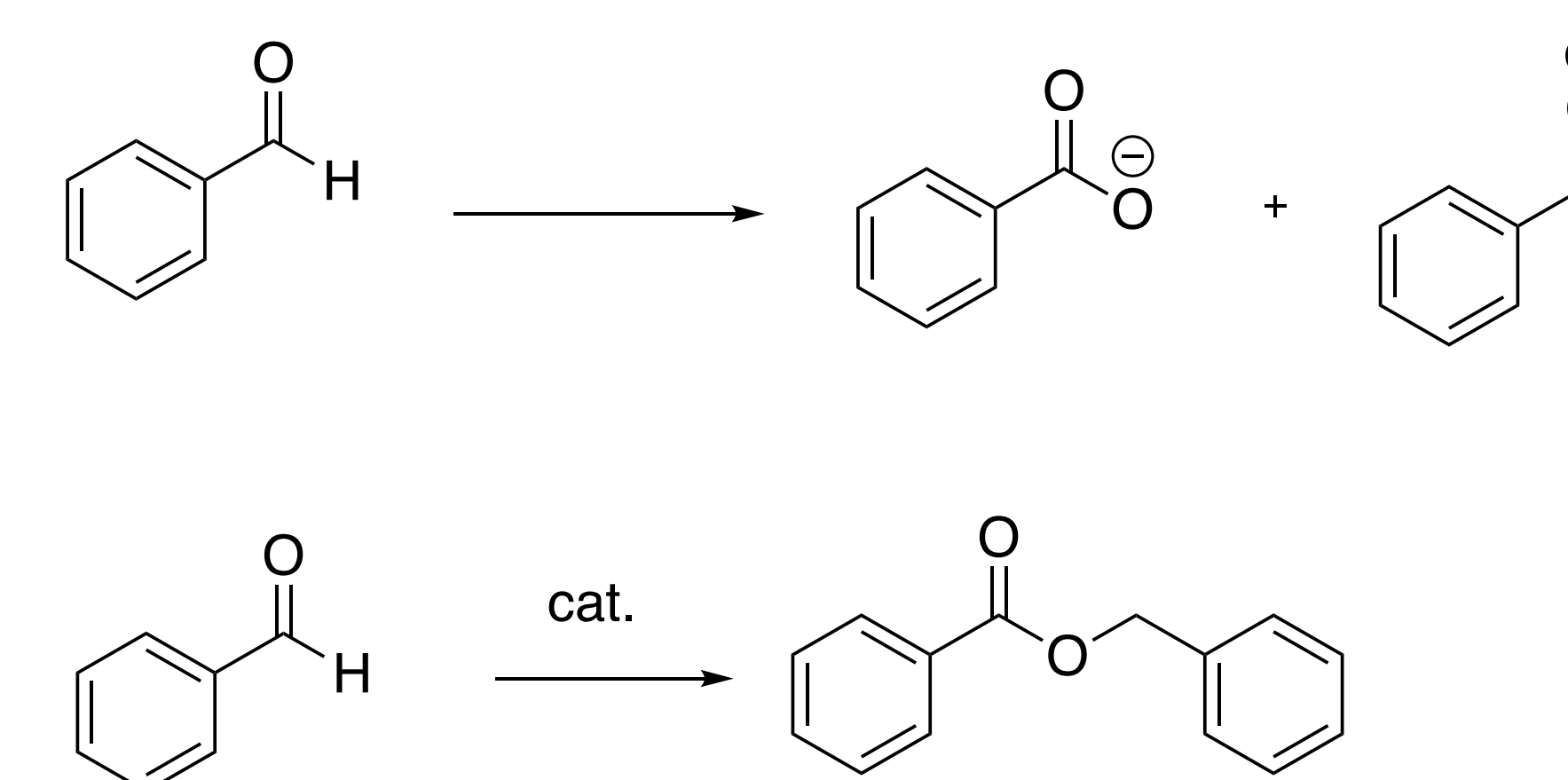


Figure 4. Suggested reactions for the overoxidation of benzaldehyde. The first reaction is a Cannizzaro Reaction while the second is a Tishchenko Reaction.

A timed reaction in which NMRs were taken at frequent time intervals to assess the rate and selectivity of product formation was done. Over oxidation of benzaldehyde into other products such as benzoic acid was observed after 16h. This may occur through a Tishchenko or Cannizzaro reaction (Refer to Figure 4).

Conclusions

Replacing the t-Butyl groups with more electron withdrawing groups seems to have no significant impact on the selectivity of the catalyst. While C-C bond cleavage of lignin model compounds was successful with high conversion, the selectivity for higher value products still needs to be improved. Despite varying polarity of the solvent for the catalyst, a significant increase in selectivity was not observed. However, the solvent does seem to have an effect on the products made.

Future Work

- Obtaining more quantitative data on conversion and selectivity of the catalyst made.
- Testing of the catalyst on Organosolv lignin once the above data are obtained.

Bibliography

1. Díaz-Urrutia, C. (2016). *Vanadium-Catalyzed Aerobic Oxidation of Diols and Lignin Models/Extracts*. University of Ottawa. Retrieved from <http://dx.doi.org/10.20381/ruor-833%0A>

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