Chemicals From Renewable Sources: Metal-Catalyzed Oxidation of the 2-phenoxyethanol Lignin Model

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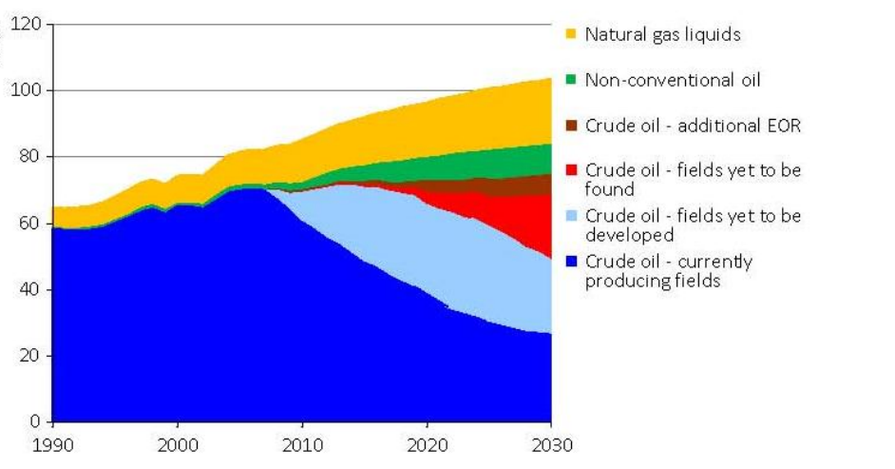
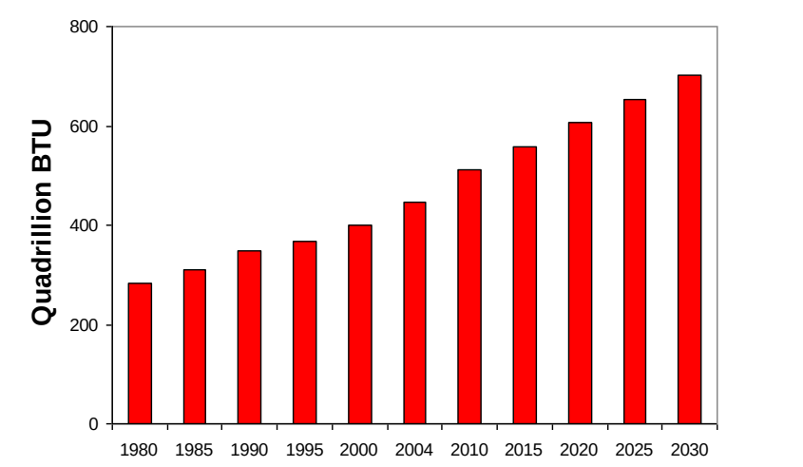
INTRODUCTION

Projected World Oil Production



Source: International Energy Agency (http://www.worldenergyoutlook.org/2008.asp)

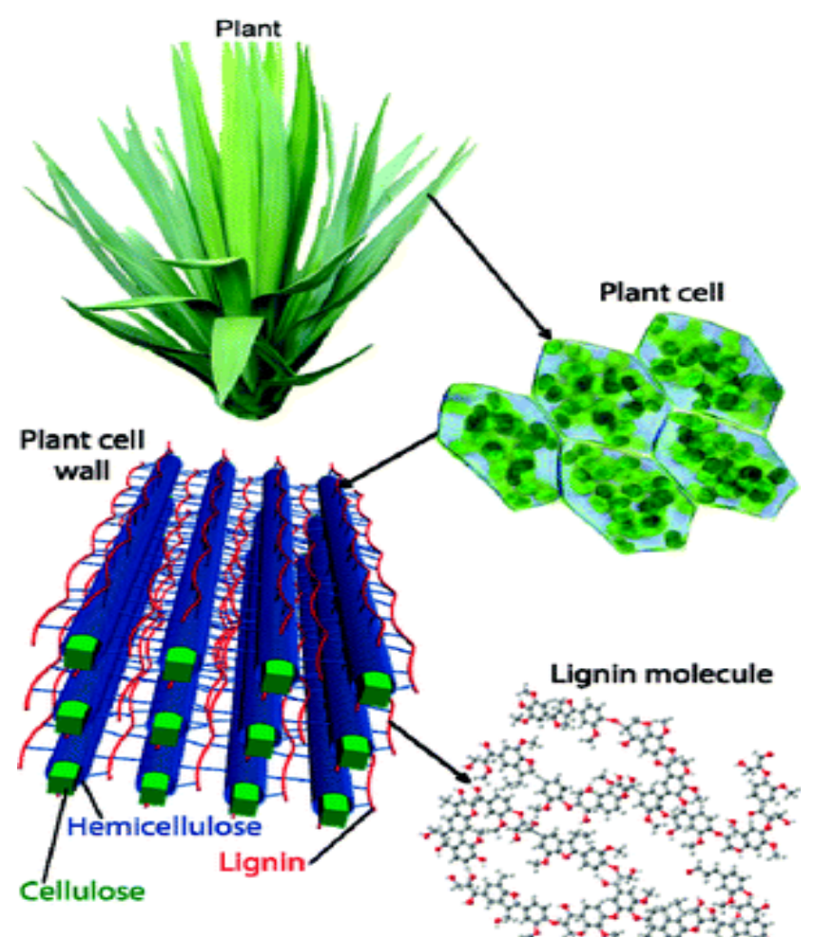
Projected World Energy Consumption

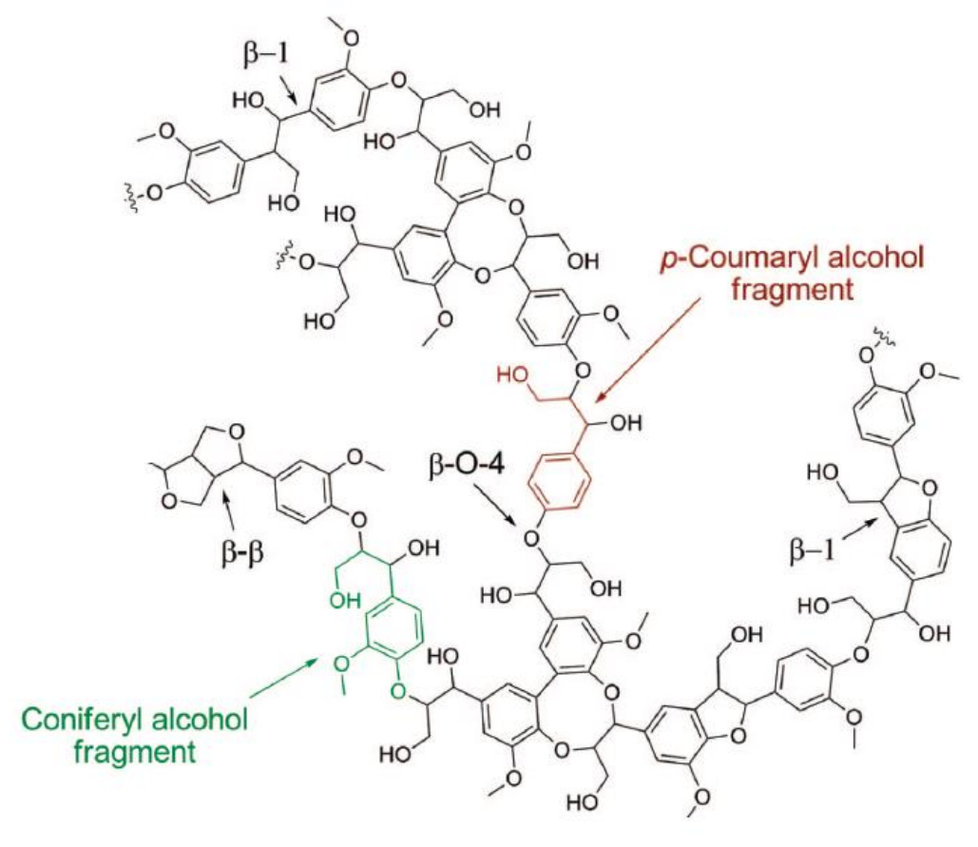


Source: Energy Information Administration (www.eia.doe.gov)

Petroleum and other fossils fuels are useful sources for energy, fuels, and chemicals. However, we are observing the rapid depletion of fossil fuel resources and higher costs. With an exponential increase in world energy demand, this impending energy crisis is driving a shift of interest towards cheaper and renewable sources of fuel and chemicals.

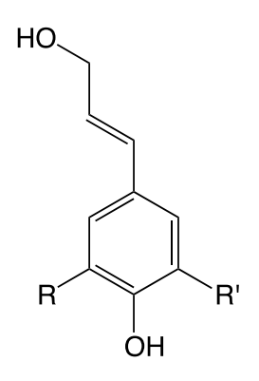
Non-food based biomass (lignocellulose) is one of the renewable carbon feedstocks available. It consists of lignin (up to 30% by weight), hemicellulose, and cellulose. Several methods have transformed cellulose into valuable materials such as glucose and ethylene glycol, but less progress has been made with the valorization of lignin.





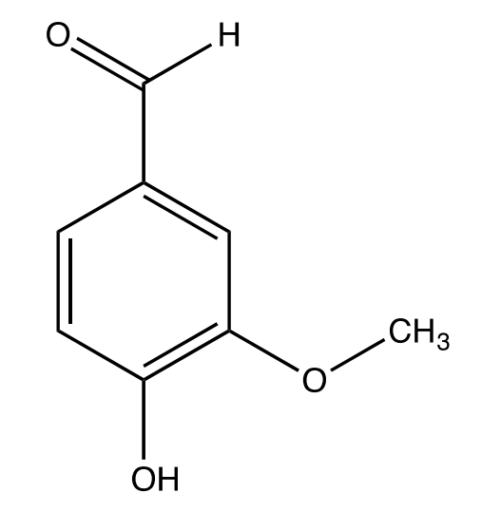
Partial structure of lignin macromolecule

Nature builds lignin by radical coupling of arylpropenyl alcohols



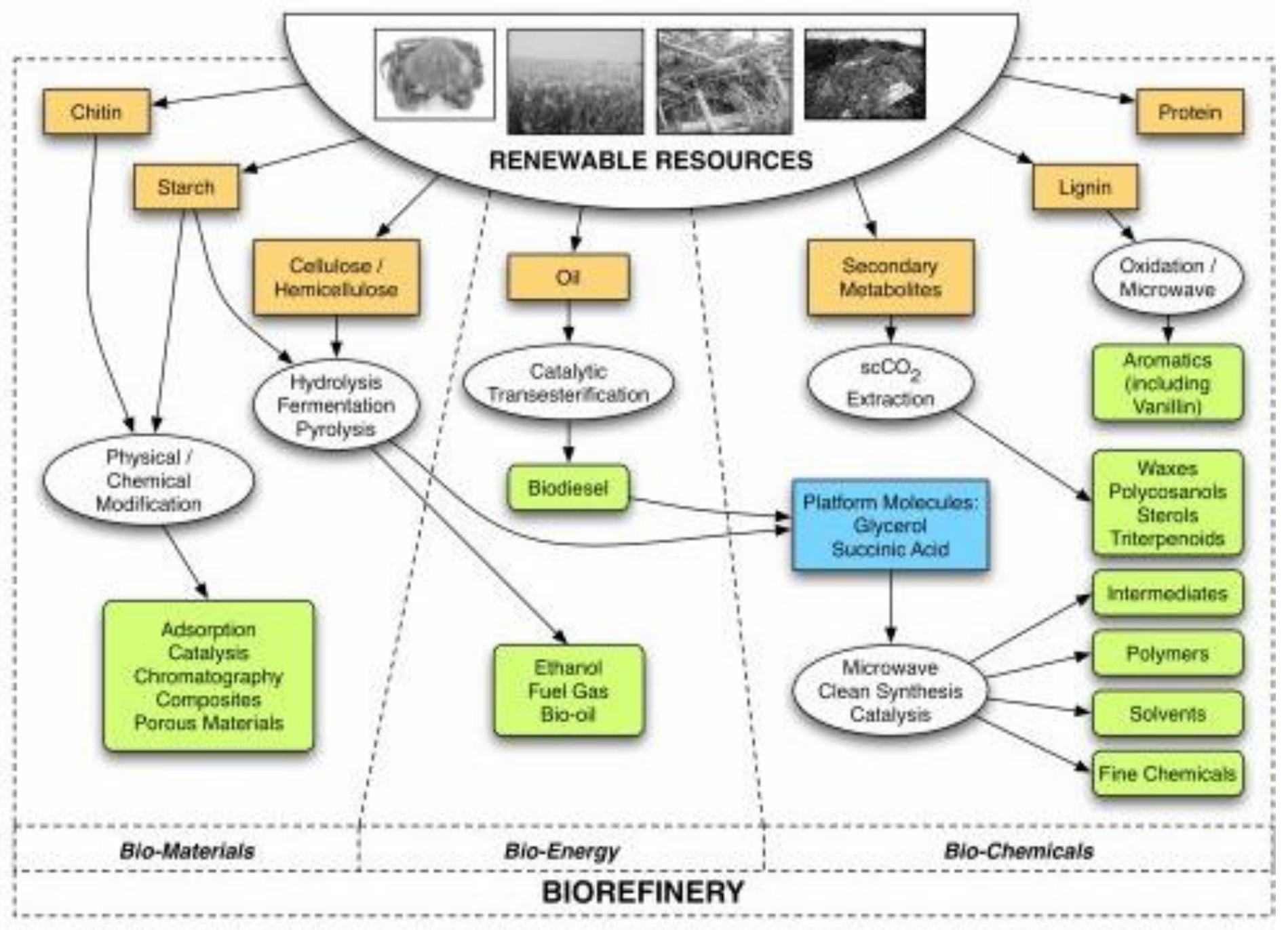
p-coumaryl: R, R’ = H
coniferyl: R = OMe
syringyl: R,R’ = OMe

Lignin is a large, amorphous polymer in nature that provides plants with their structural integrity. One of the most prevalent linkages in lignin is the β-O-4 linkage (up to 50%). **Aerobic oxidative C-C bond cleavage of lignin may afford valuable aromatic aldehydes and other products for further chemical transformations.**



Vanillin

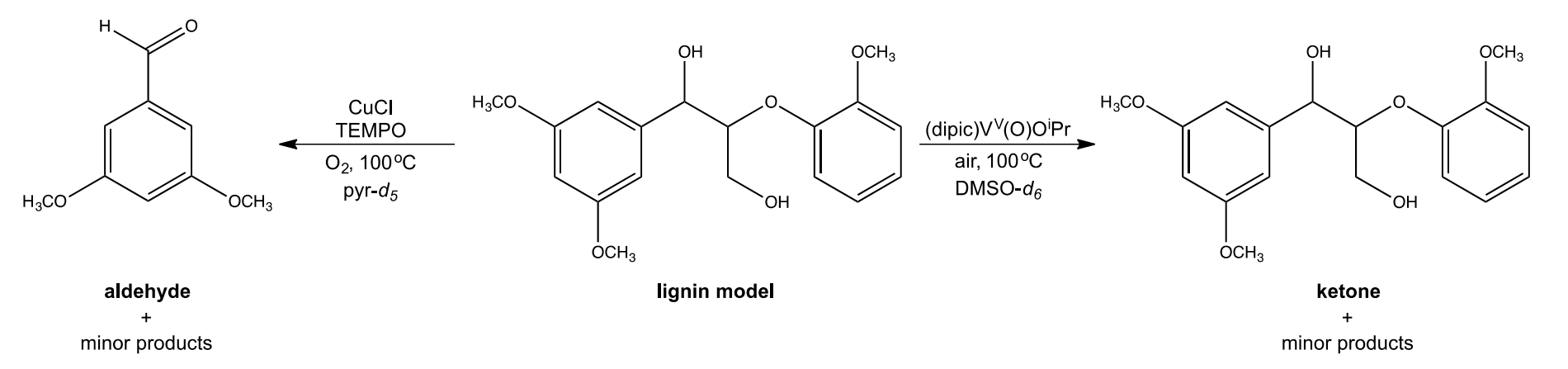
- ✓ Flavouring (vanilla extract)
- ✓ Fragrances (perfumes)
- ✓ Masking unpleasant odours and tastes in medicines
- ✓ General purpose stain in thin layer chromatography



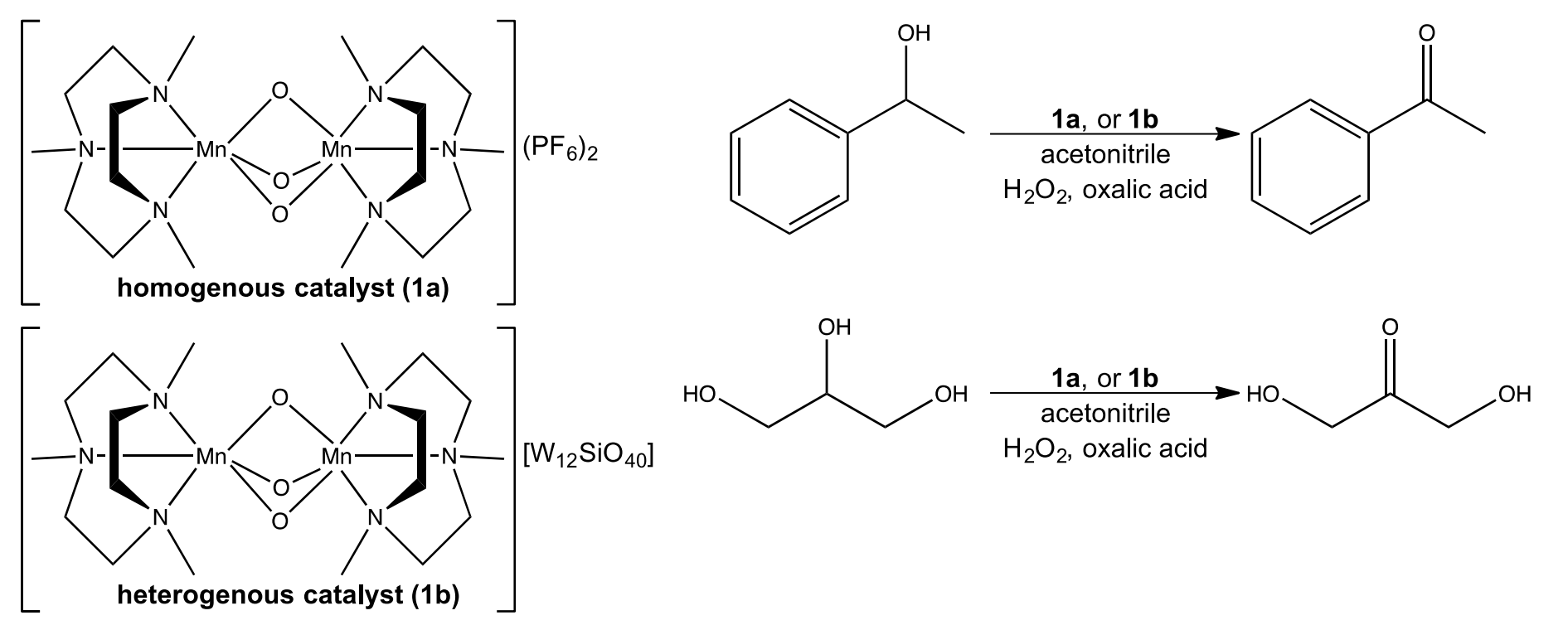
Catalysis is a key enabling technology for biomass conversion and for fulfilling the promise of lignin valorization. Using an inexpensive, earth-abundant transition metal complex as a catalyst and air as an oxidant can provide advantages in terms of process cost and simplicity.

PREVIOUS WORK

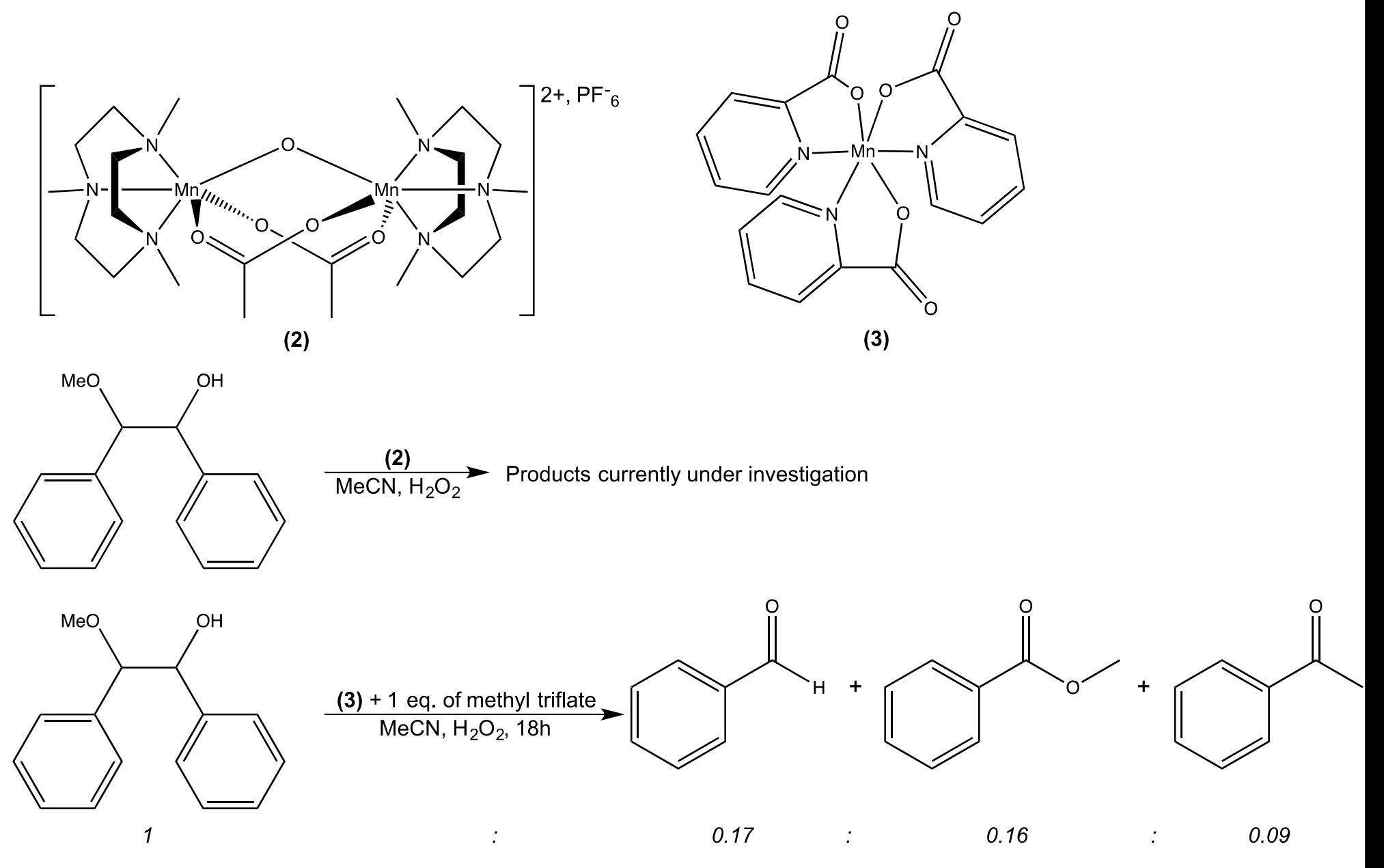
Baker Group – Homogenous Copper and Vanadium Catalysts



Shul’pin *et al.* – Homogenous and Heterogenous Manganese Catalysts



Baker Group – Homogenous Manganese Catalysts

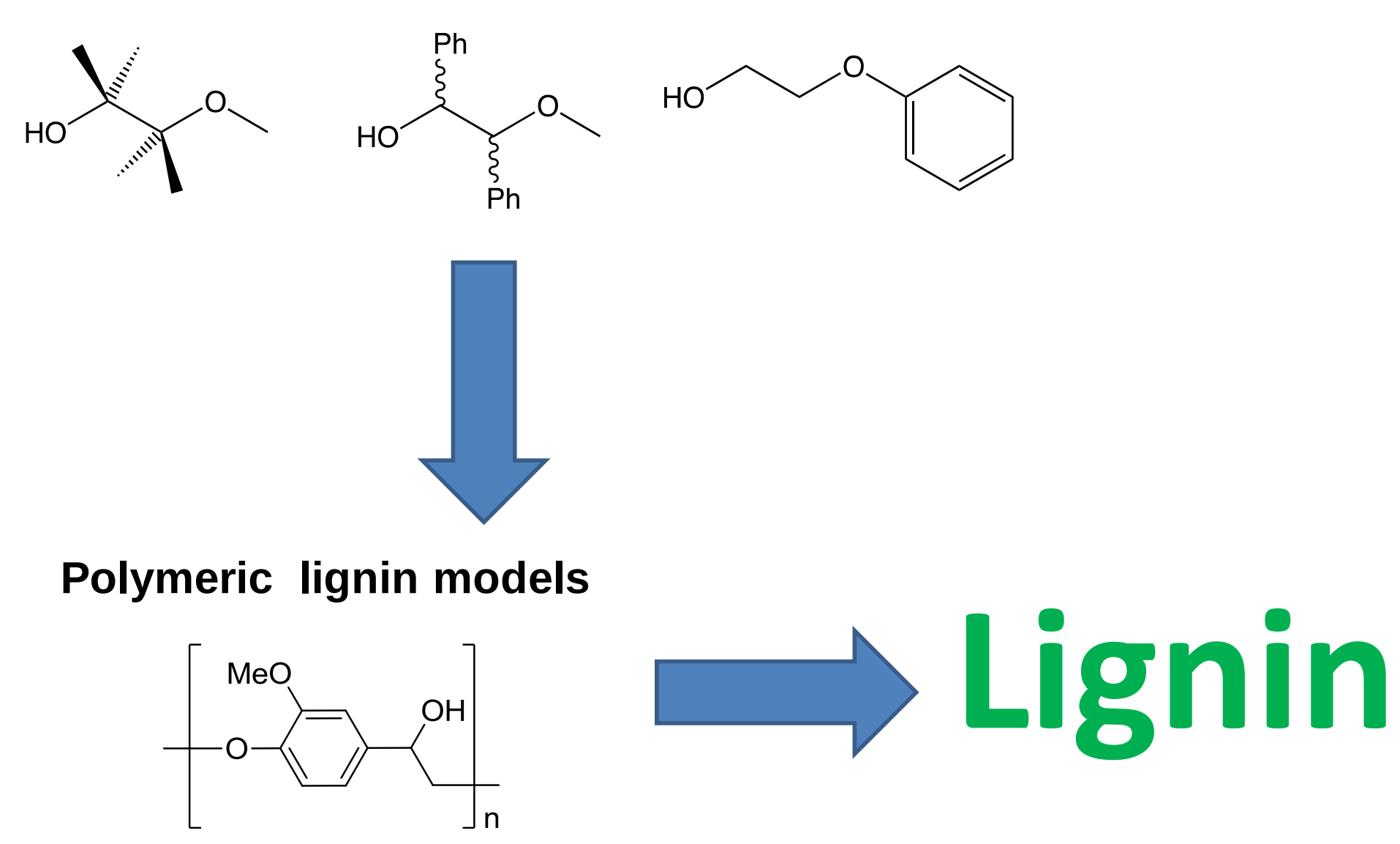


(2): $[(TMTACN)Mn(\mu\text{-}O)(\mu\text{-}OOCCH_3)_2Mn(TMTACN)](PF_6)_2$, TMTACN = 1,4,7-triazacyclononane
(3): $Mn(pic)_3$, pic = picolinate

RESEARCH APPROACH

Progressively scaling up the complexity of the lignin models used, starting from simple lignin models containing the β-O-4 linkage. These simple models allow for the investigation of catalyst selectivity

Simple β-O-4 lignin models

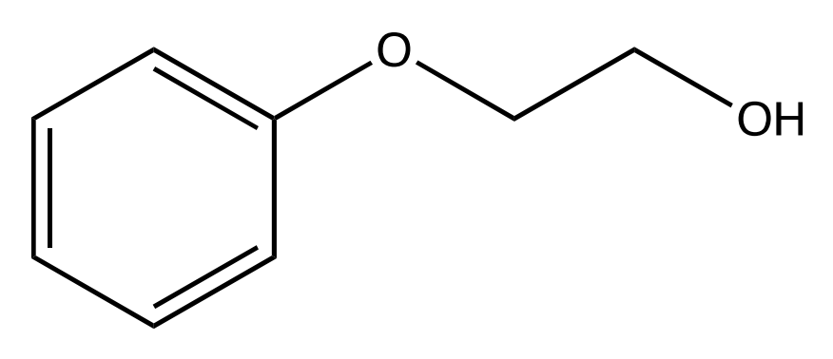


Polymeric lignin models

Lignin

OBJECTIVE

The primary objective of this project is to determine the catalytic oxidative potential of the manganese catalyst (2) on the lignin model compound 2-phenoxyethanol under optimized conditions. Secondary objectives include studying the coordination of (2) with 2-phenoxyethanol to understand how the two substances interact prior to oxidation, and examining the effect of H_2O_2 alone on (2).

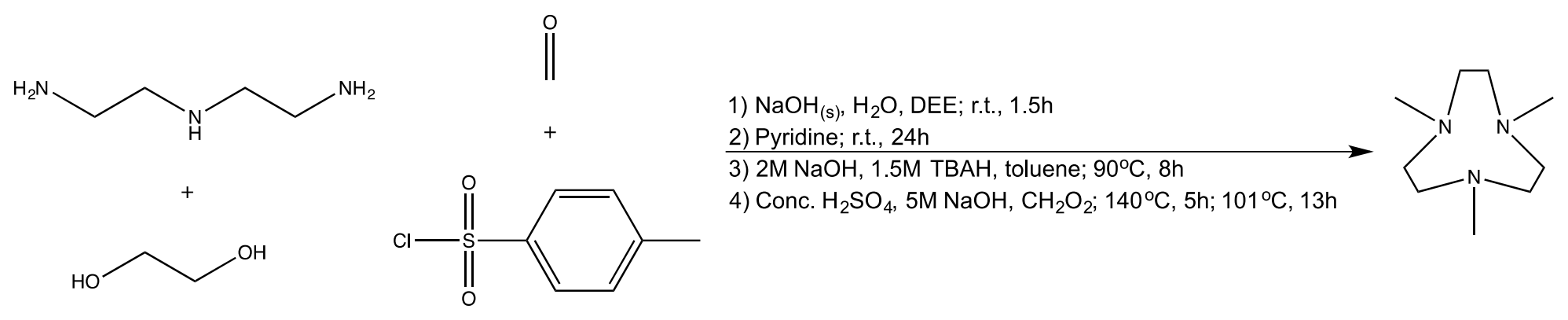


2-phenoxyethanol

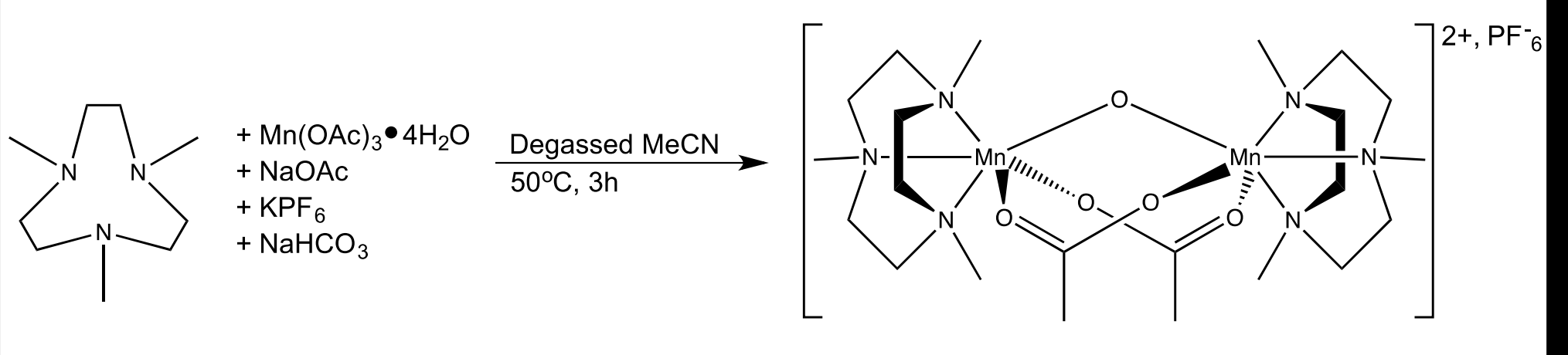
METHODOLOGY

Following literature procedures, the TMTACN ligand was prepared by a 4-step synthesis, and then subjected to a one-pot reaction that generated (2). Both compounds were characterized by IR and ^1H NMR. Hydrogen peroxide (H_2O_2) was reacted with a small quantity of (2) to assess its effect on the catalyst’s structure.

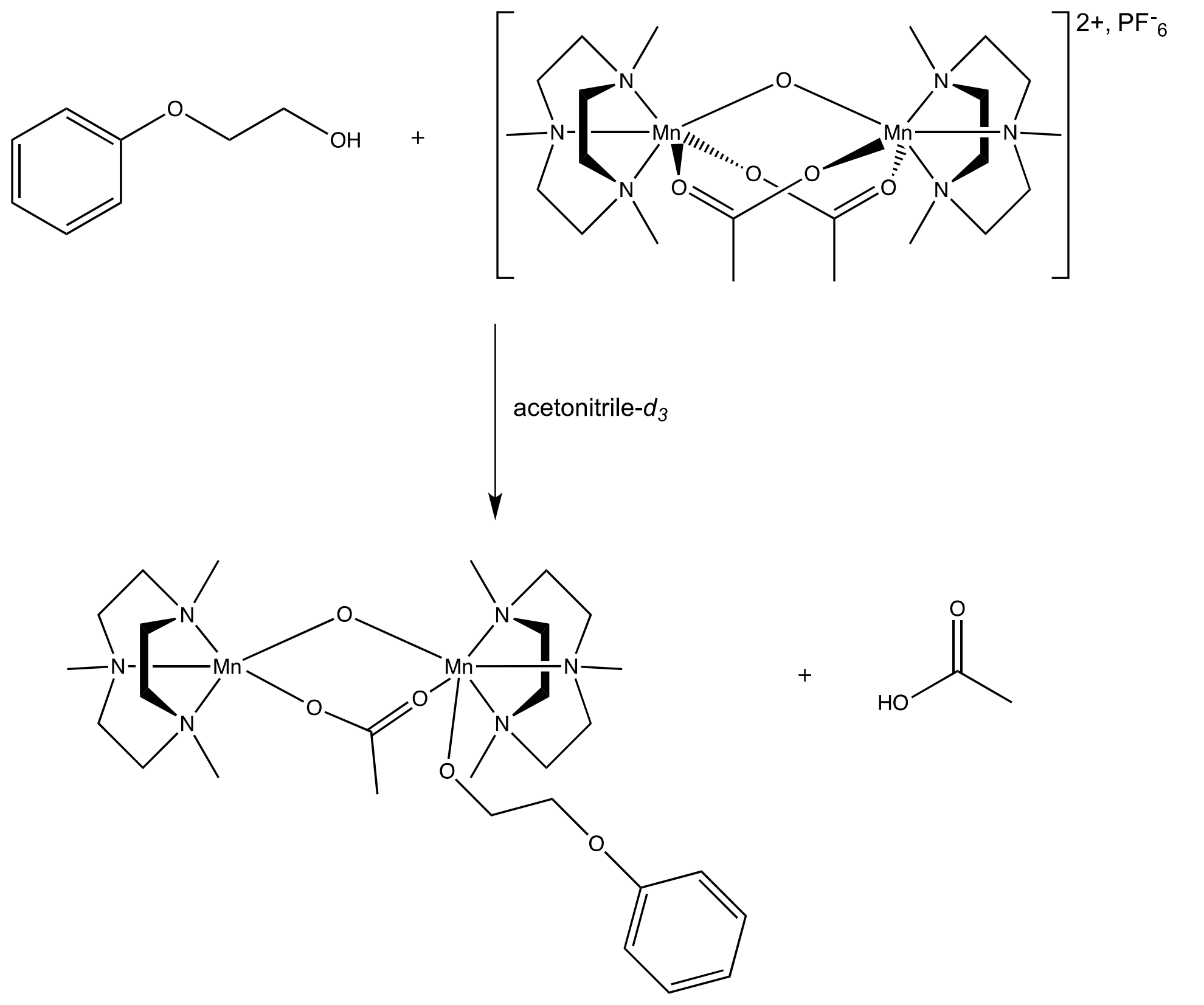
Under a nitrogen atmosphere, 10 mg of (2), 30 µL of dimethylsulfone (DMS) as an internal standard, and 800 µL of acetonitrile-d_3 were added to a screw-cap NMR tube, then an initial ^1H NMR was taken. In addition to adding equivalent aliquots of 2-phenoxyethanol, other reaction conditions such as adding an equivalent of H_2O_2 as an oxidant and heating the solution were employed. ^1H NMR spectra were obtained after each successive reaction condition was implemented into the solution to observe any chemical reactions.



Schematic of the 4-step synthesis for preparing the TMTACN ligand

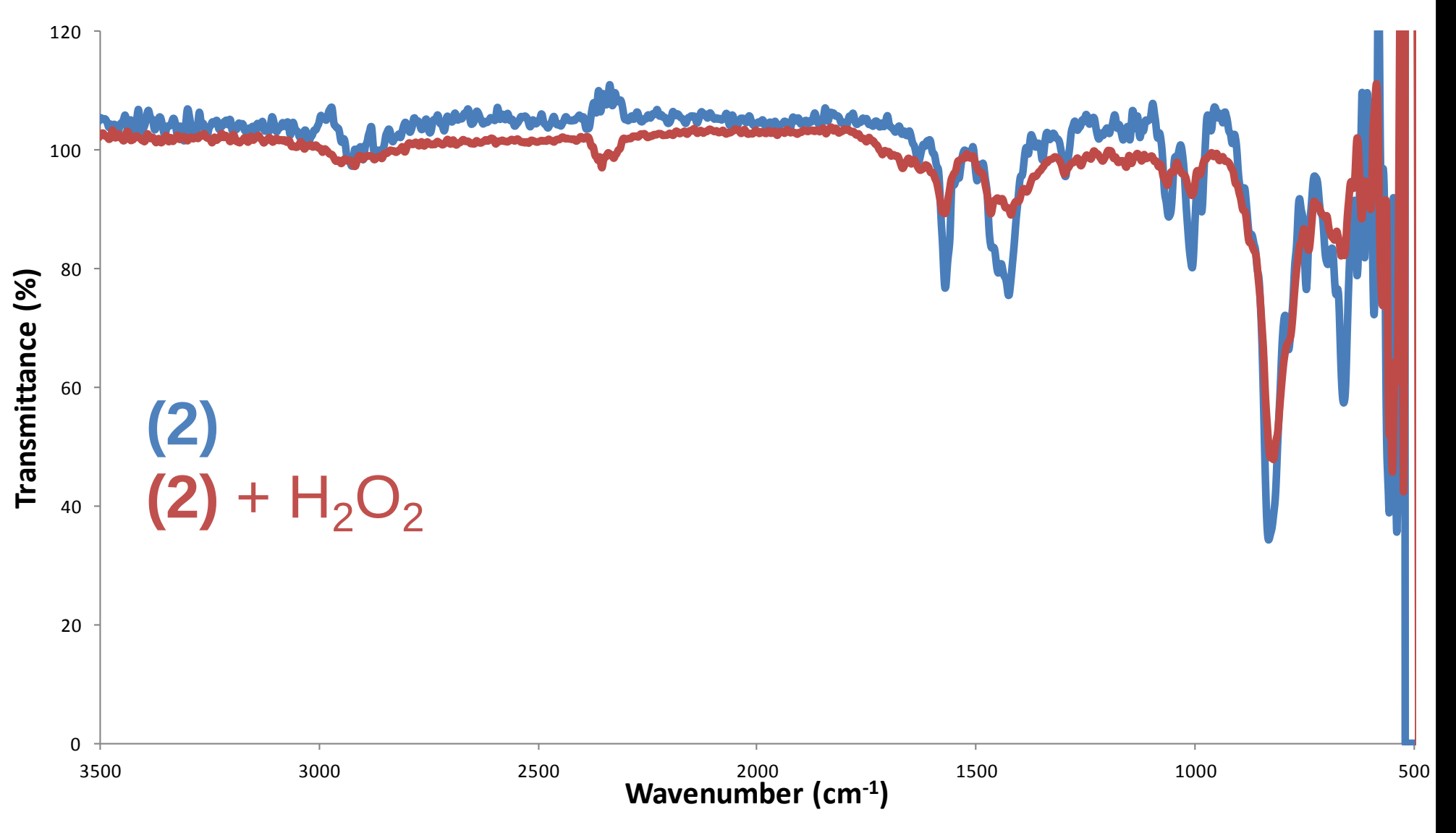


Schematic of the one-pot reaction that generates (2)

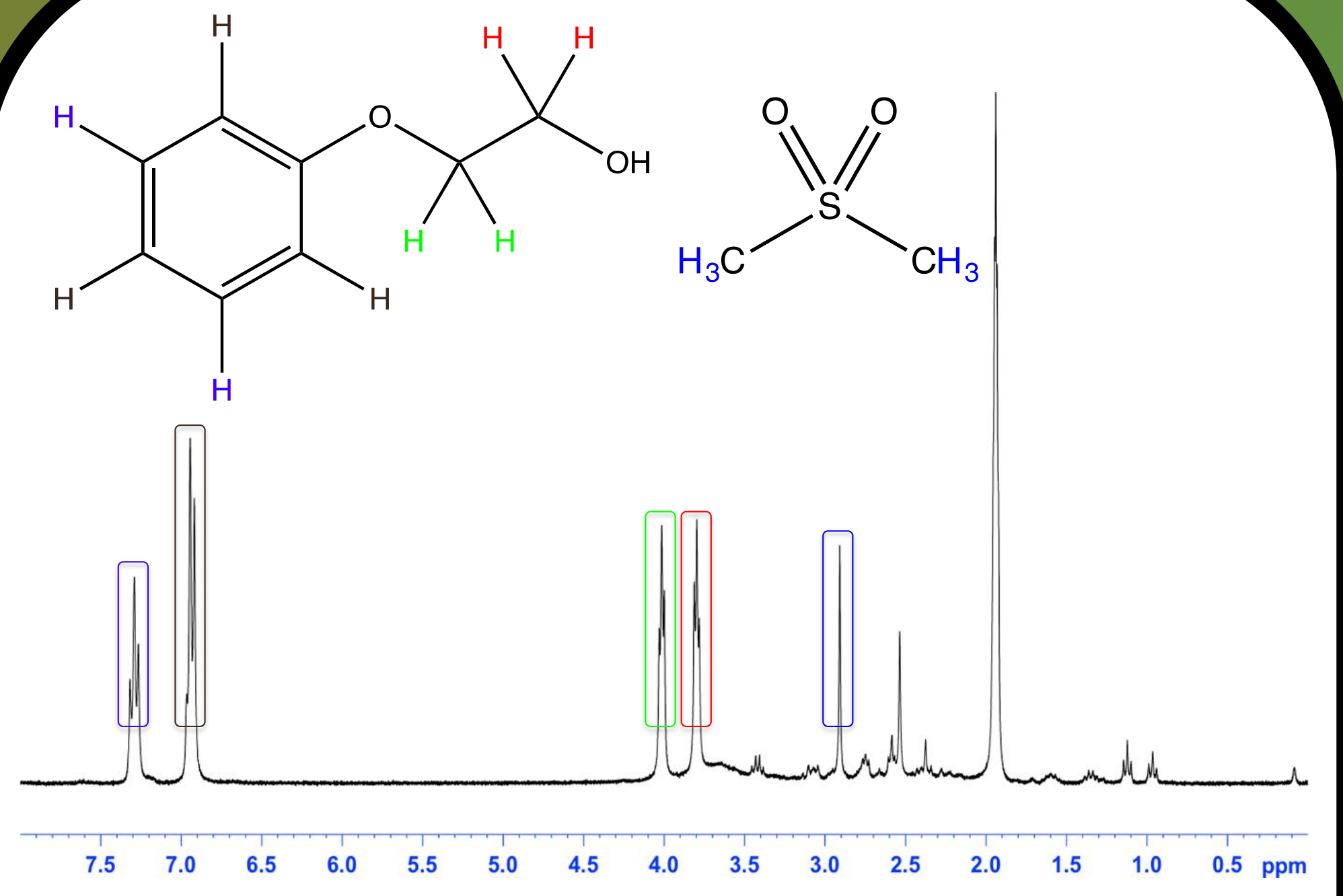


Predicted coordination of (2) with 2-phenoxyethanol prior to oxidation

RESULTS



Examining effect of H_2O_2 on (2) by comparison of the IR spectrum of (2) before and after addition of H_2O_2.



^1H NMR [300 MHz] of (2), DMS, and 3 eq. of 2-phenoxyethanol in acetonitrile-d_3. All labeled peaks represent the correspondently coloured proton(s) in either 2-phenoxy ethanol (left) or DMS (right). All unlabeled peaks correspond exclusively to (2).

Conditions	Ar-H 7.25 ppm	Ar-H 6.90 ppm	Aliphatic H 4.00 ppm	Aliphatic H 3.80 ppm
• Initial Set-Up	0	0	0	0
• 1 eq. 2-phenoxyethanol	0.2491	0.3725	0.233	0.2589
• 2 eq. 2-phenoxyethanol	2.2380	3.4108	2.4745	2.7307
• 2 eq. 2-phenoxyethanol • Heating @ 50°C for 1 hour	2.7073	4.0770	2.7856	2.9424
• 3 eq. 2-phenoxyethanol	3.3823	5.1502	3.4932	3.5233
• 3 eq. 2-phenoxyethanol • 1 eq. H2O2	4.2832	6.5052	4.3598	4.3905
• 3 eq. 2-phenoxyethanol • 1 eq. H2O2 (few days)	5.1717	7.7893	5.3112	5.3054
• 3 eq. 2-phenoxyethanol • 1 eq. H2O2 • Heating @ 50°C for 1 hour	25.3527	38.5238	25.2687	25.2870

Integration of the labeled peaks in the ^1H NMR spectrum above after each condition was implemented. All peaks were calibrated to the internal standard (DMS) to monitor for any changes in the spectrum over time.

CONCLUSIONS

Hydrogen peroxide has no noticeable effect on the structure of the manganese catalyst (2). Additionally, catalytic oxidation of the 2-phenoxyethanol lignin model by (2) was unsuccessful under the tested reaction conditions. Finally, the coordination of (2) and 2-phenoxyethanol was not observed

FUTURE WORK

Testing additional conditions for the successful catalytic oxidation of 2-phenoxyethanol by (2).

Reacting (2) with other simple B-O-4 lignin models.

Designing manganese catalysts with different tri-nitrogen ligands.

Synthesizing a monomeric version of (2) and determining its catalytic activity, if any.

ACKNOWLEDGEMENTS

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