Effects of Unsymmetric Amine(bis)phenol Ligands and Molybdenum Complexes in the Deoxydehydration Reaction

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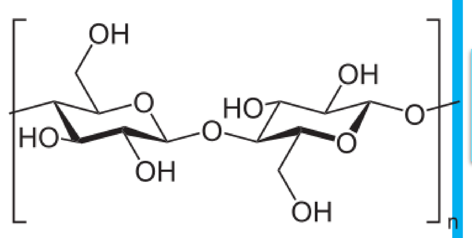
Introduction

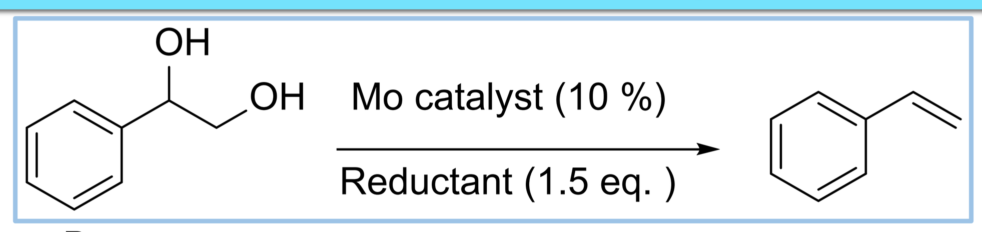
- Finding alternatives to produce chemical feedstock is essential to:
  - Preserving limited fossil resources that are available
  - Ensuring chemical supply beyond their depletion
- Production of value-added chemical resources such as biomass (cellulose, starch, glycerol, etc.)
- Biomass is rich in oxygen-containing functional groups

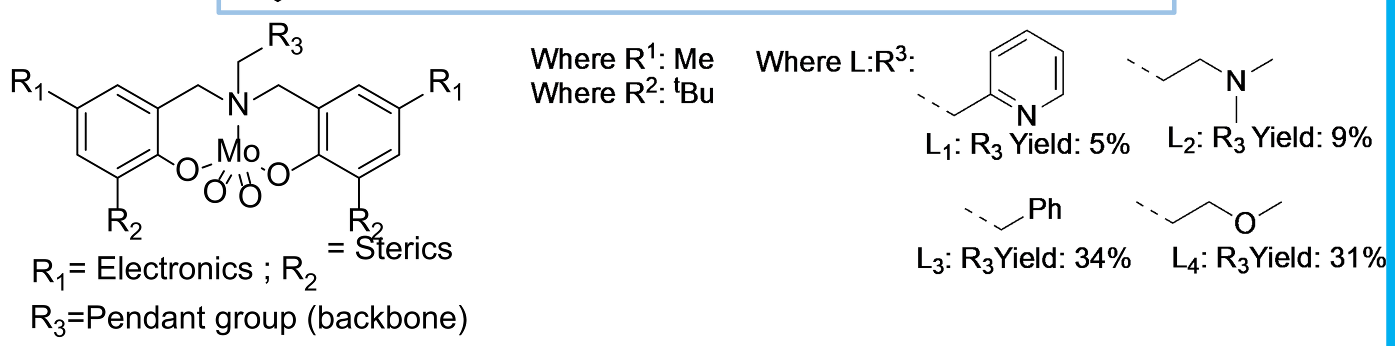


Deoxydehydration (DODH)

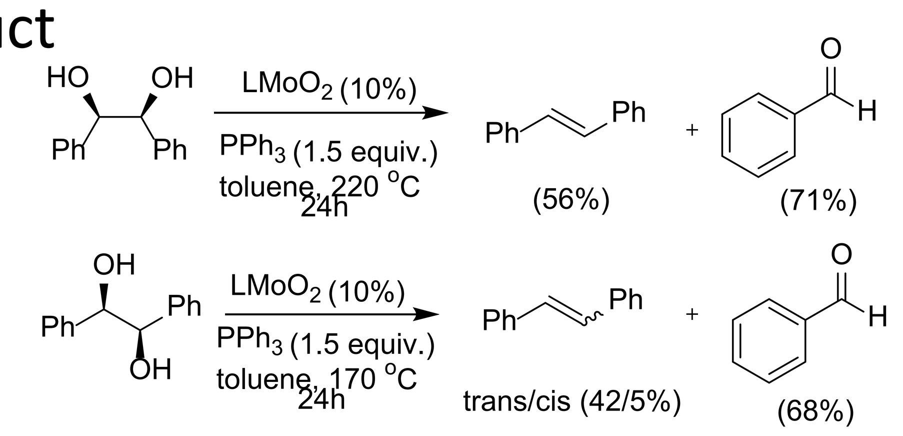
- Oxygen and water removal for conversion of product into olefins (alkenes)
- Use of metal catalyst and reductant.
- Variations of metal catalysts :
  - Rhenium: effective in DODH producing high yields, however, it is limited and expensive.
  - Molybdenum and Vanadium: inexpensive and readily available in large amounts, but yield to less product, and require longer reaction times at higher temperatures.

Current Findings





- Multiple amine(bis)phenol ligands were evaluated, as well as the catalytic promise of dioxomolybdenum complexes in the DODH reaction
- The catalytic reaction of the complex with a Ph backbone resulted in higher yields of alkene product

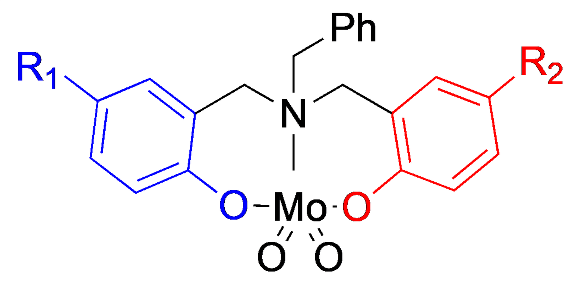


- Explored the effects of temperature and catalyst loading on the DODH of styrene glycol and other alcohols

Siu, T. C.; Silva, I.; Lunn, M. J.; John, A **2020**, *44* (23), 9933–9941

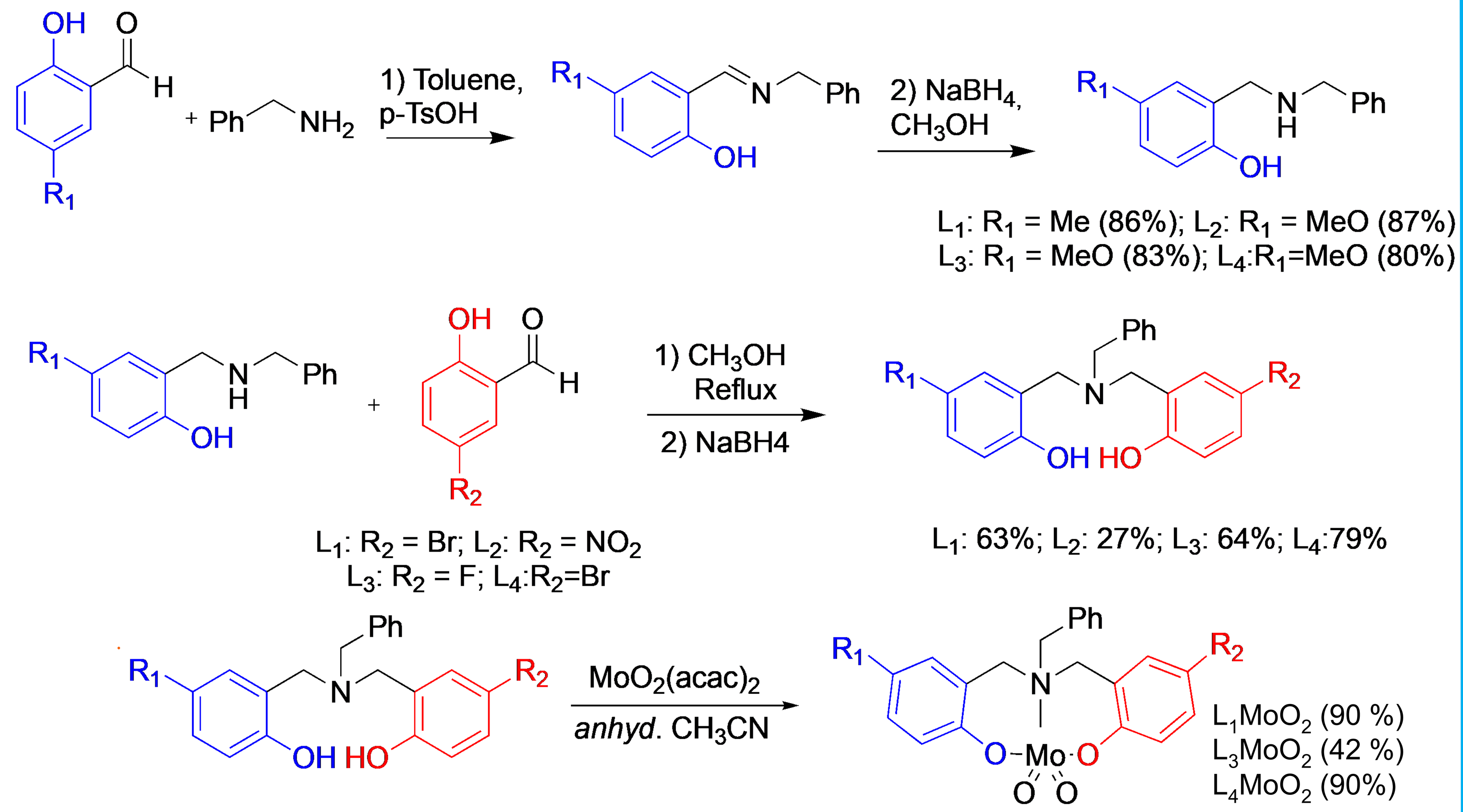
Project Goal

- Synthesis of asymmetric ligands and complexes characterized by NMR spectroscopy, IR spectroscopy and X-ray crystallography

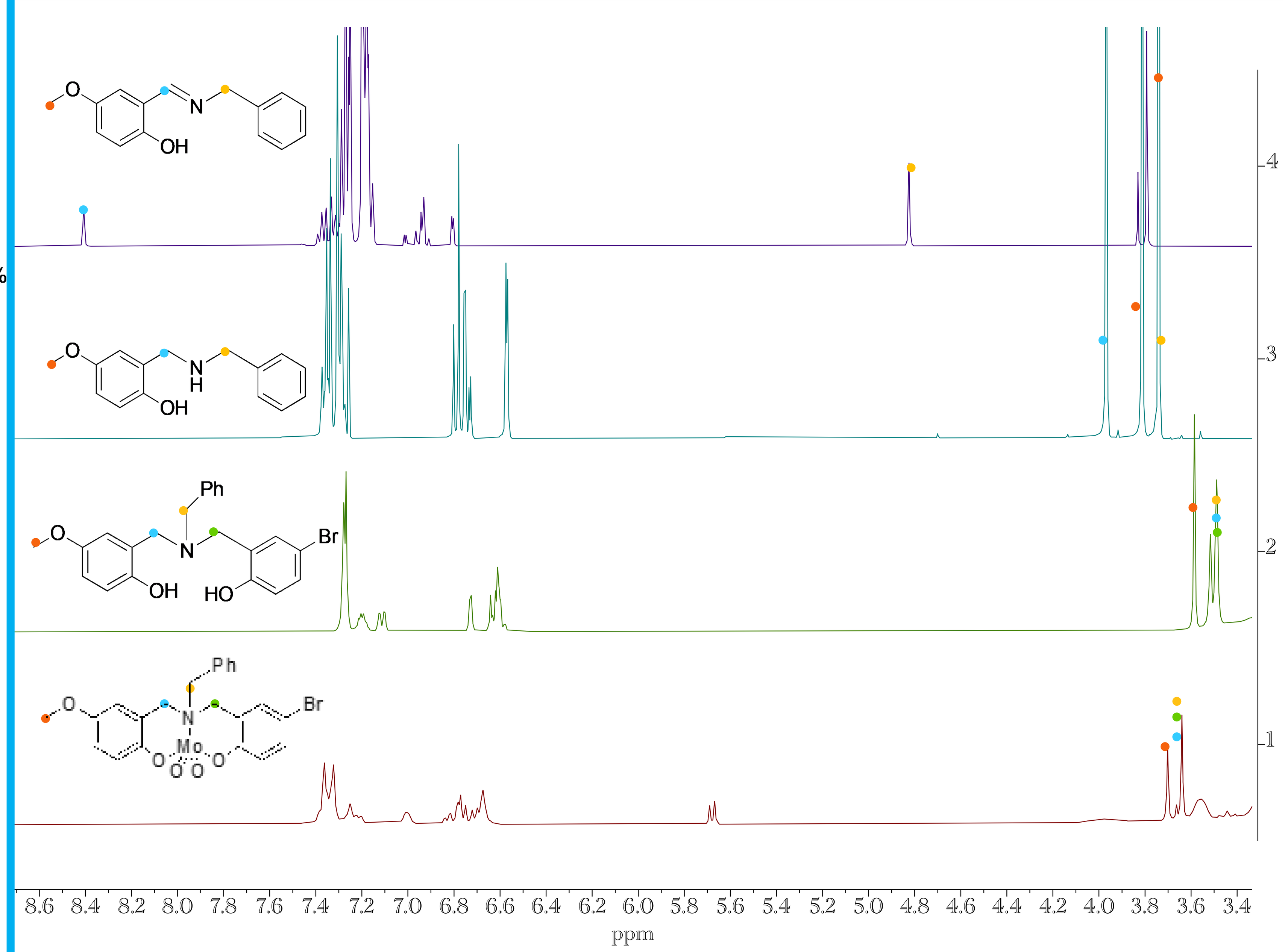


- Investigate the effects of asymmetric ligands may have on electronic properties of Molybdenum catalysts and its efficiency

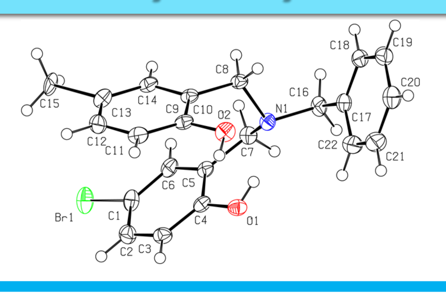
Synthesis

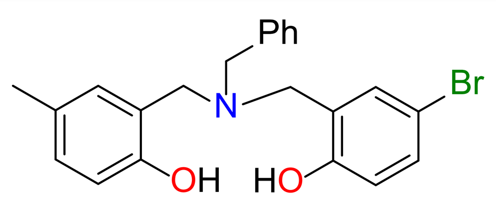


Analysis of Asymmetric Ligand & L_4MoO_2: Proton NMR

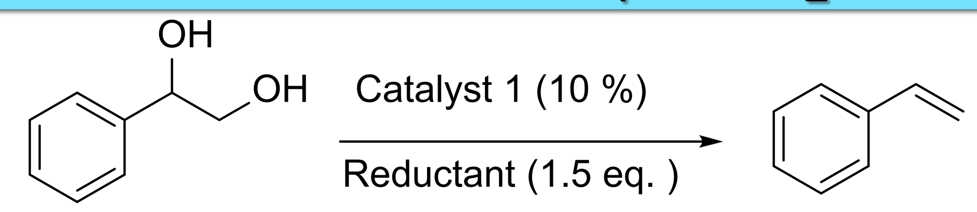


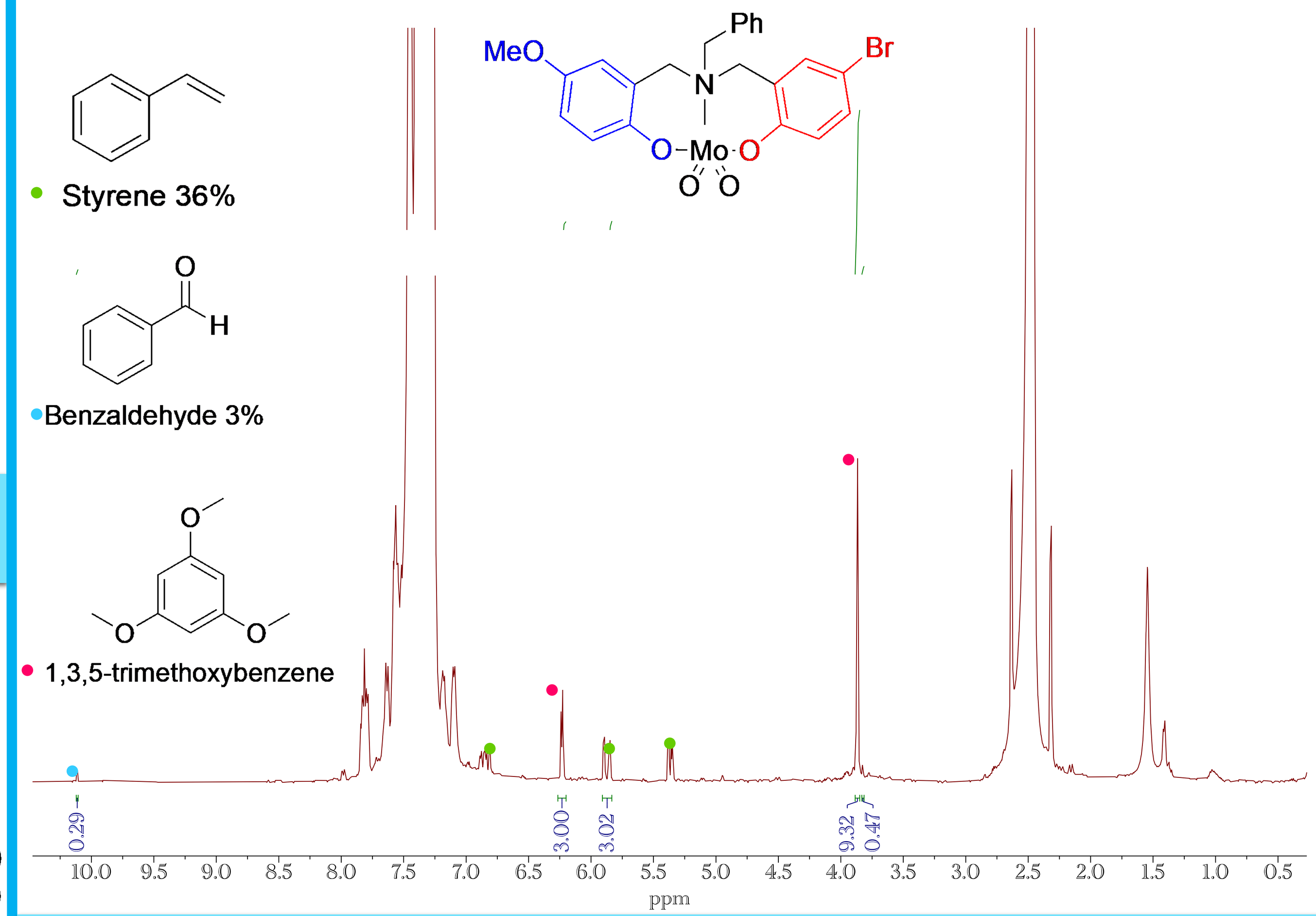
X-Ray Crystallography of L_1R_1





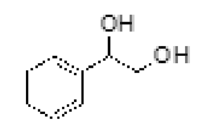
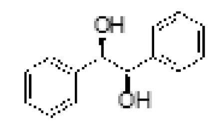
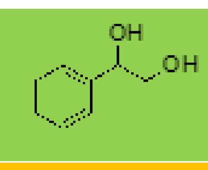
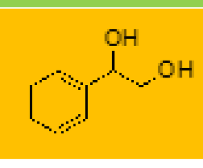
DODH with L_4MoO_2





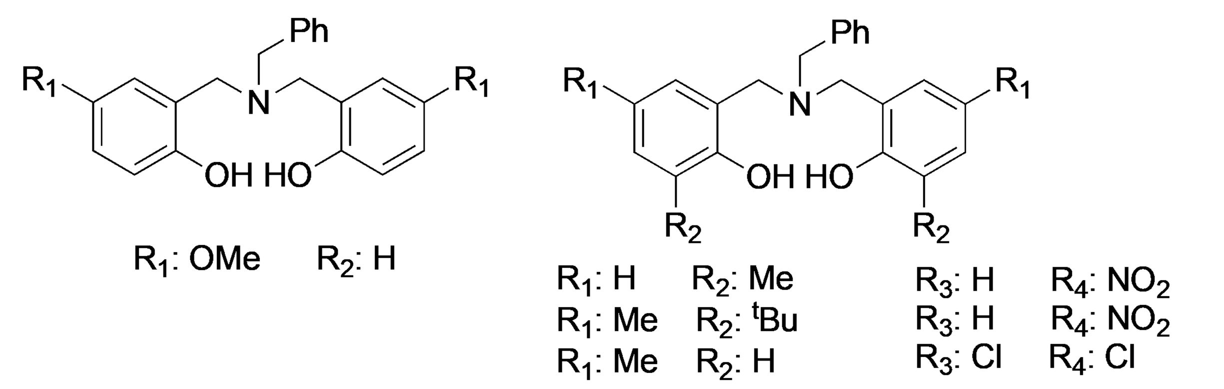
Data table entry for L_1MoO_2 and L_4MoO_2

Table 1. Substrate scope for DODH using L1MoO2 and L4MoO2 in toluene

Entry	Substrate	Catalyst	T (°C)	Yields C=C	Yields C=O
1.		1b	170	36%	3%
		4b		25%	<1%
2.		1b	170	80%	4%
		4b		80%	4%
3.		1b	170- 210	0	0
		4b		0	0
4.		1b	170	8%	1%
5.		1b	170	4%	8%

Future Work

- Use other reductants for styrene glycol.
- Variations of the asymmetric ligand will be made to study the effects of steric modulation on catalytic activity in DODH reactions



Acknowledgments

- Chemistry and Biochemistry Department, California State Polytechnic University, Pomona
- National Science Foundation - Chemical Catalysis
- Dr. Alex John, Principal Investigator
- Dr. Francis Flores
- The John Lab Research Group