



Dehydrogenative Methanol Activation and its application as Transfer Hydrogenating reagent under homogeneous catalysis



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Hydrogen Economy

- ✓ Sustainable alternative
- ✓ Fuel of the future



Limitations

- ✓ Safe-storage
- ✓ Cost-effective transportation

LOHC

Liquids/materials with high-hydrogen content, and hydrogen can be liberated from them when and where it is required

Why Methanol as LOHC?

- ✓ High hydrogen content (12.5%), low cost
- ✓ Availability from renewable feedstock (coal/natural gas/CO₂ reduction)
- ✓ Liquid at ambient temperature, easy to handle and safe to transport
- ✓ Compatible with already established diesel oil and gasoline-based infrastructure

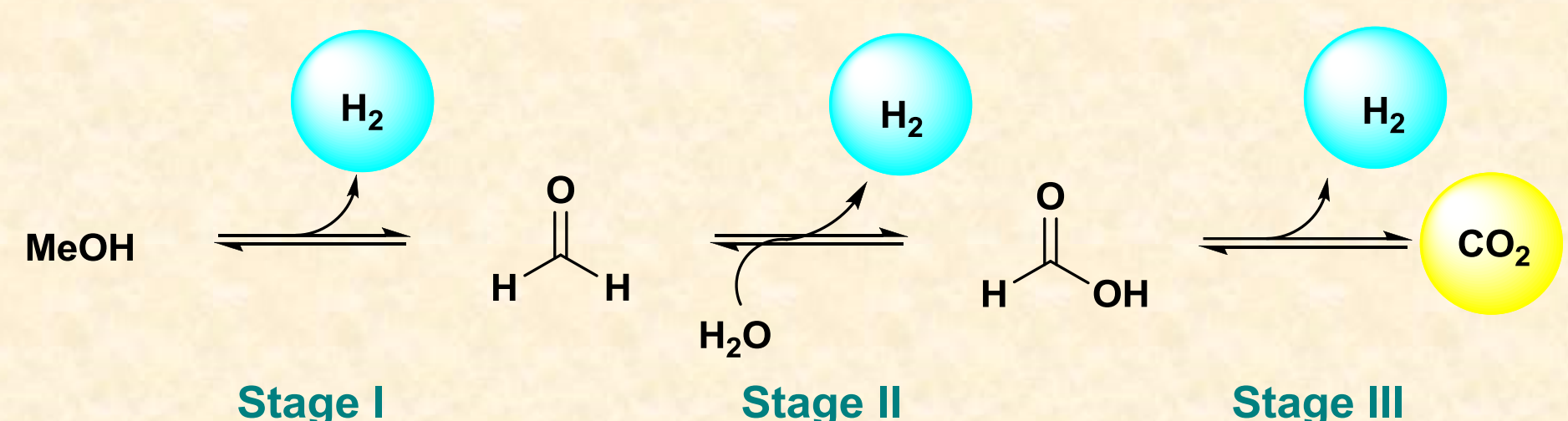
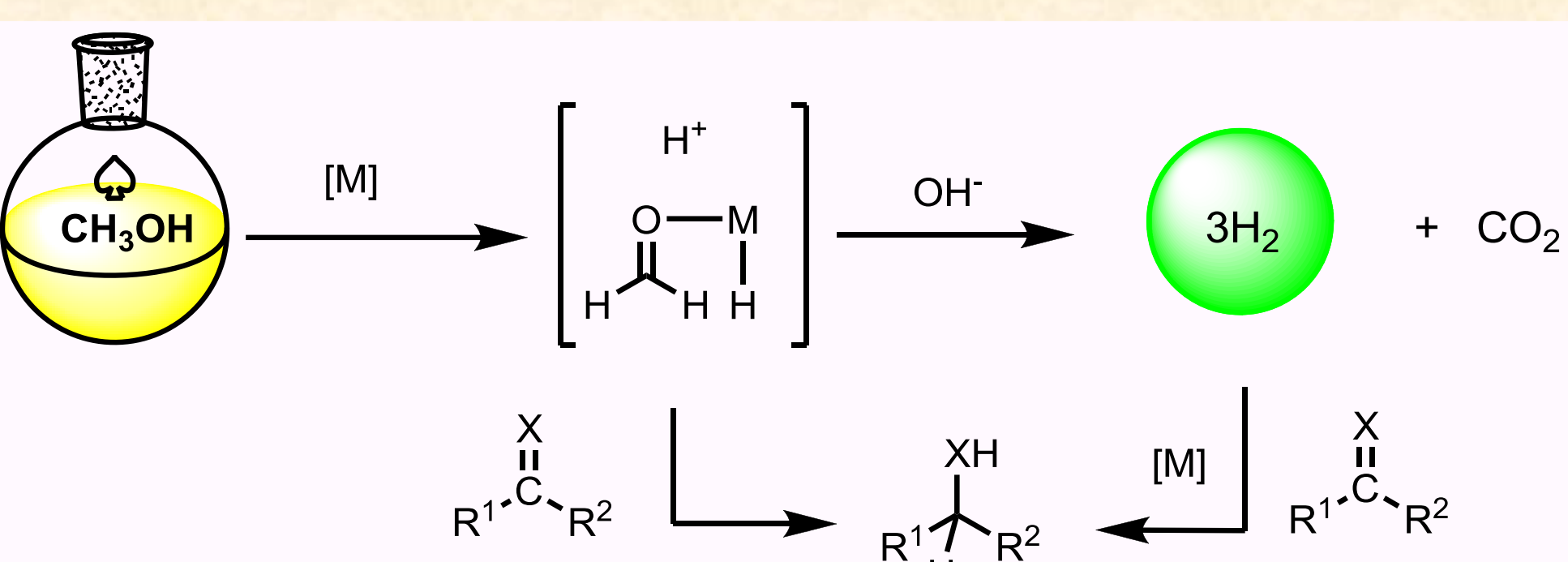
Limitations

Dehydrogenation of methanol is an uphill process (63.7 kJ/mol) and requires high temperature and high pressure conditions [1,2]

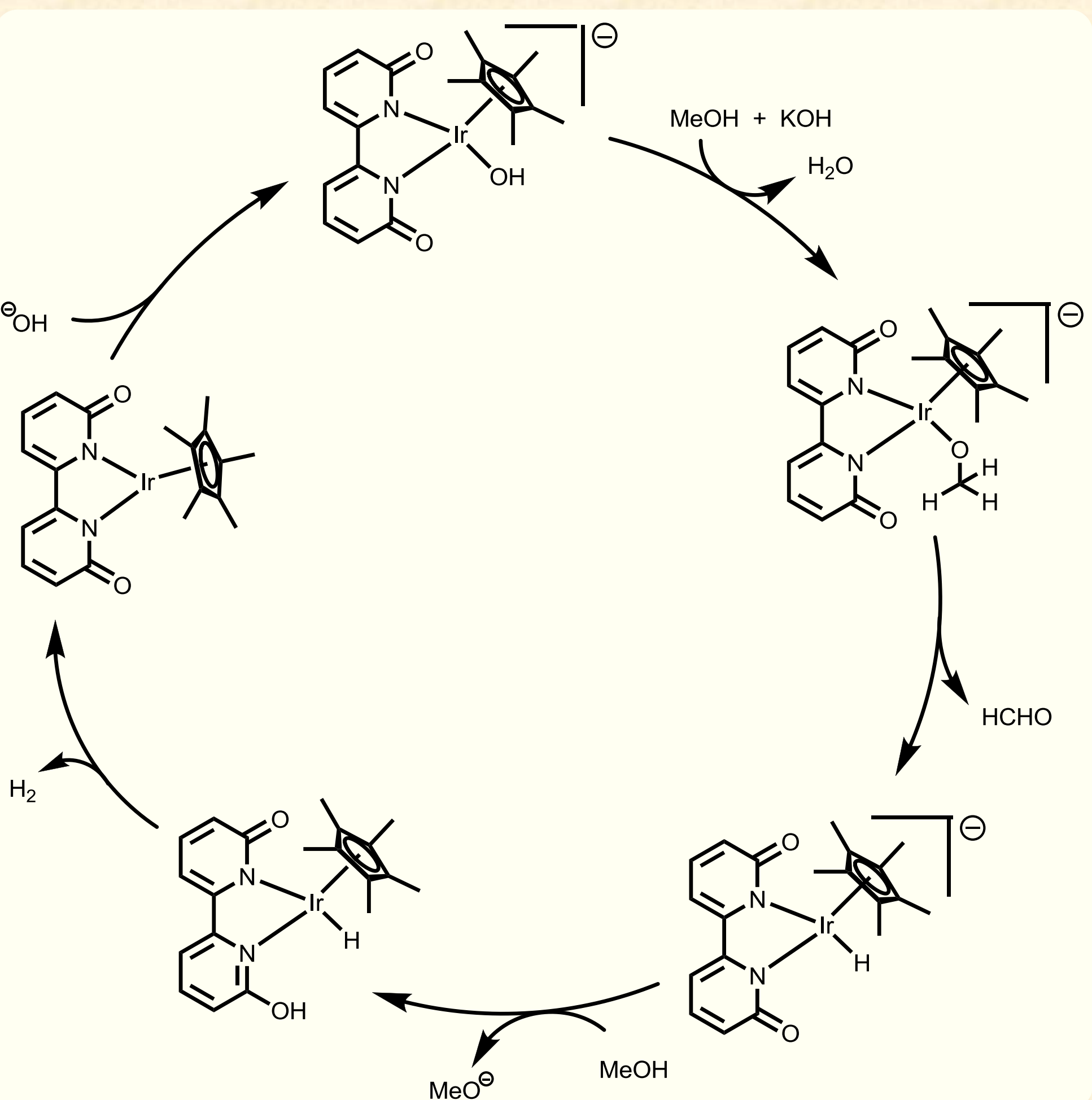
Transfer Hydrogenation (TH)

- ✓ Avoids special equipment for pressure handling and hazardous hydrogen gas
- ✓ Safe and practical approach
- ✓ Avoids stoichiometric amount of toxic reducing agents
- ✓ Availability of a wide range of inexpensive sacrificial donors in adequate amounts

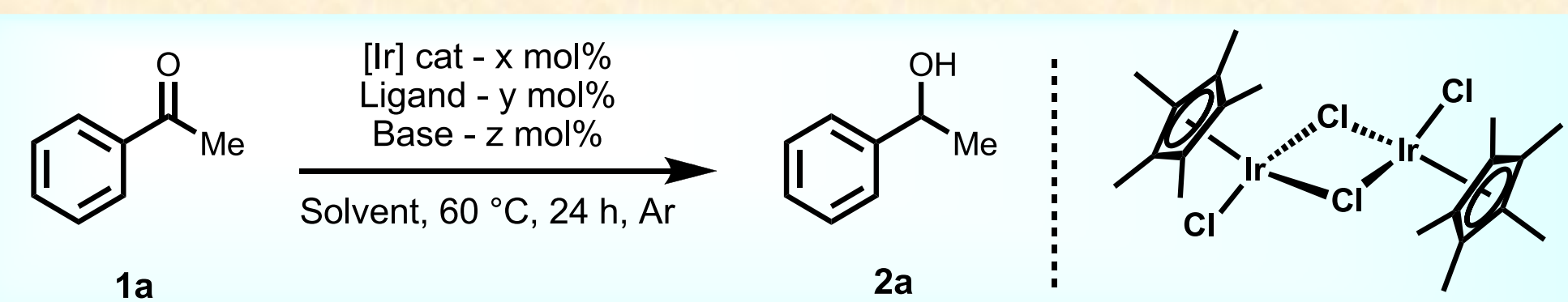
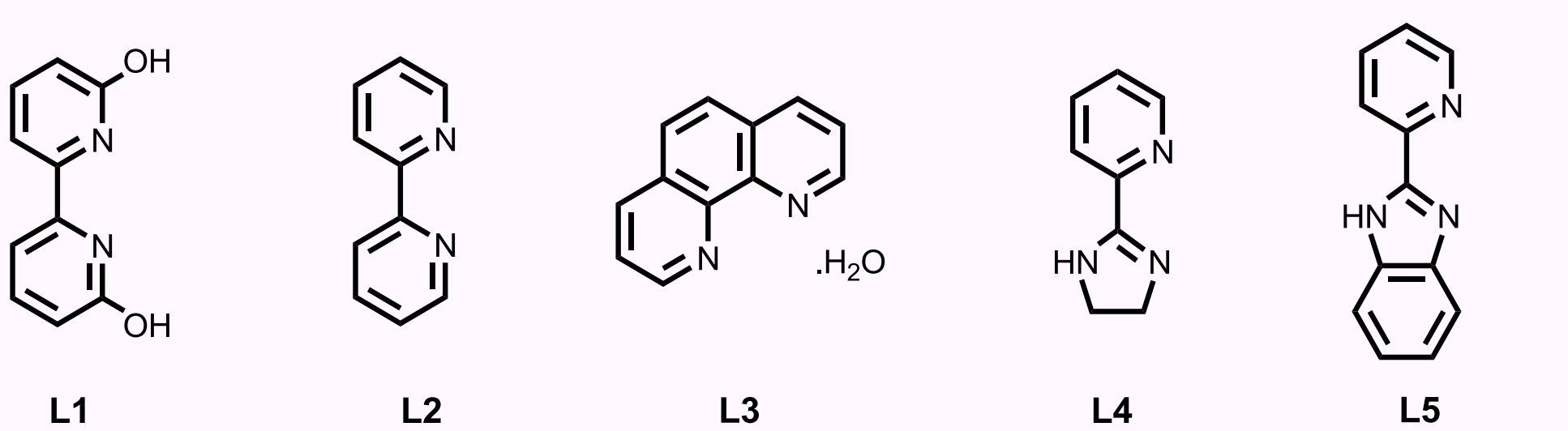
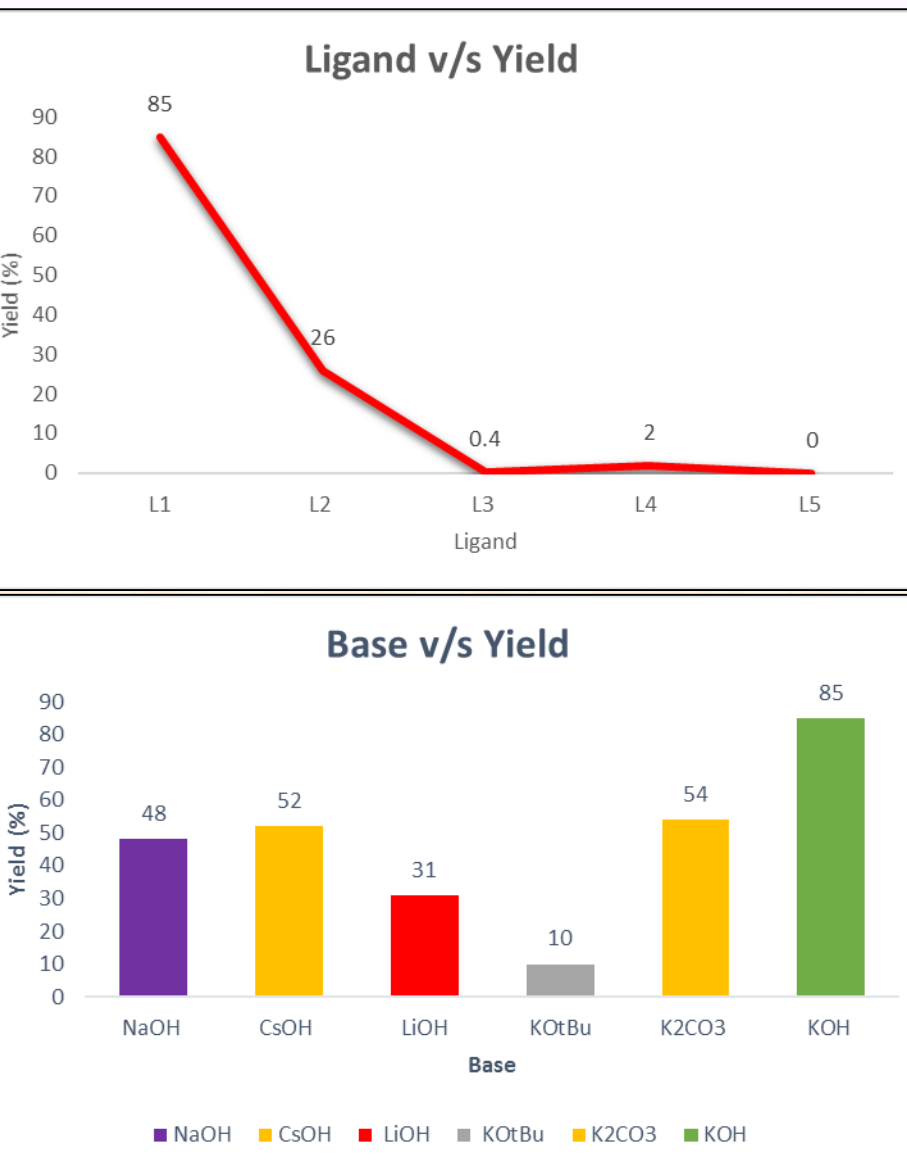
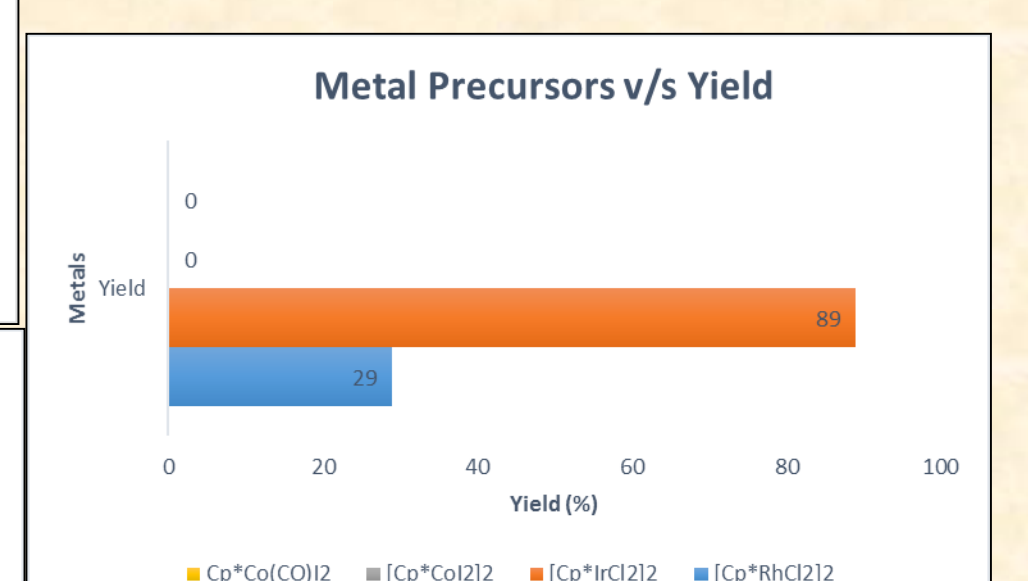
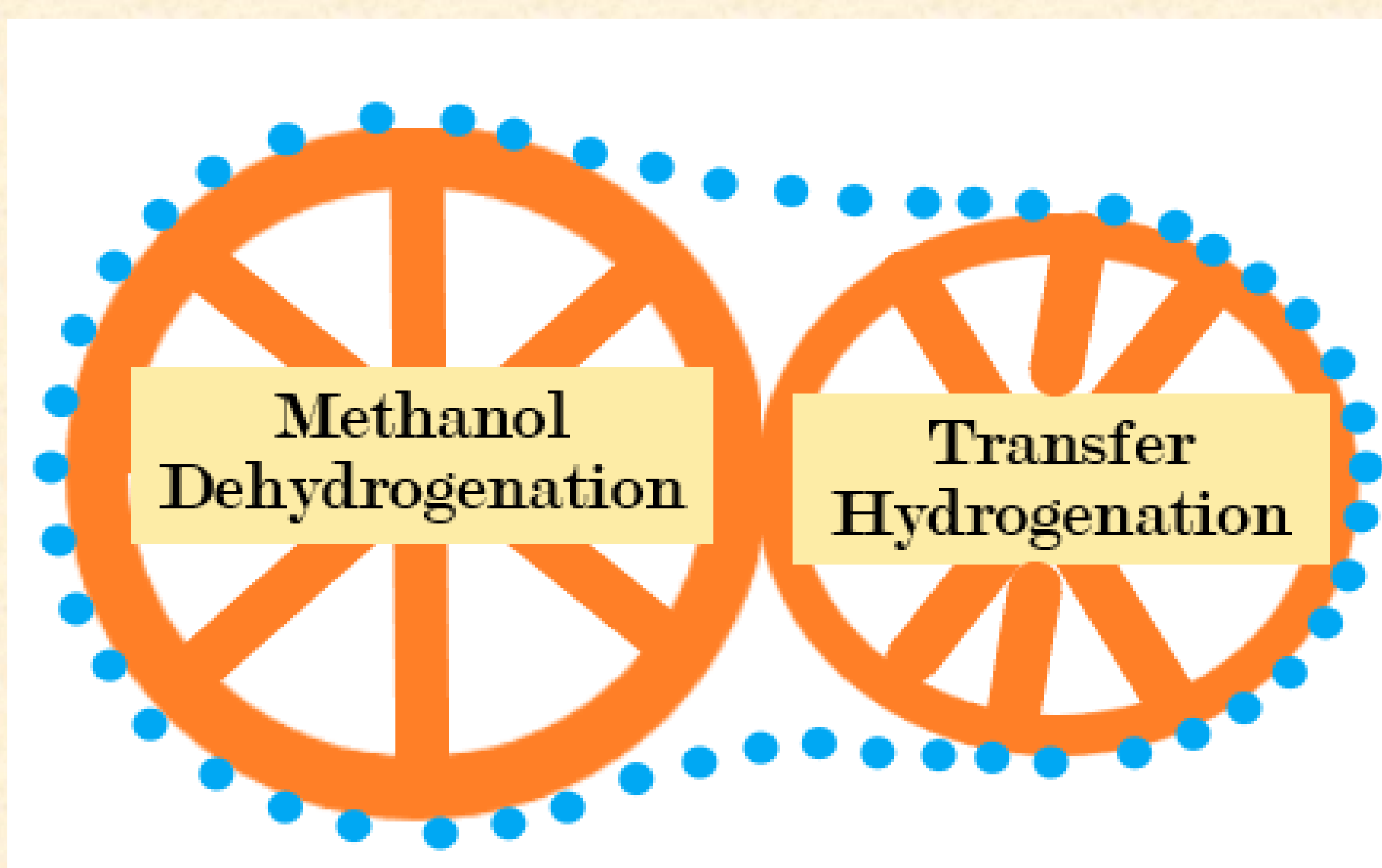
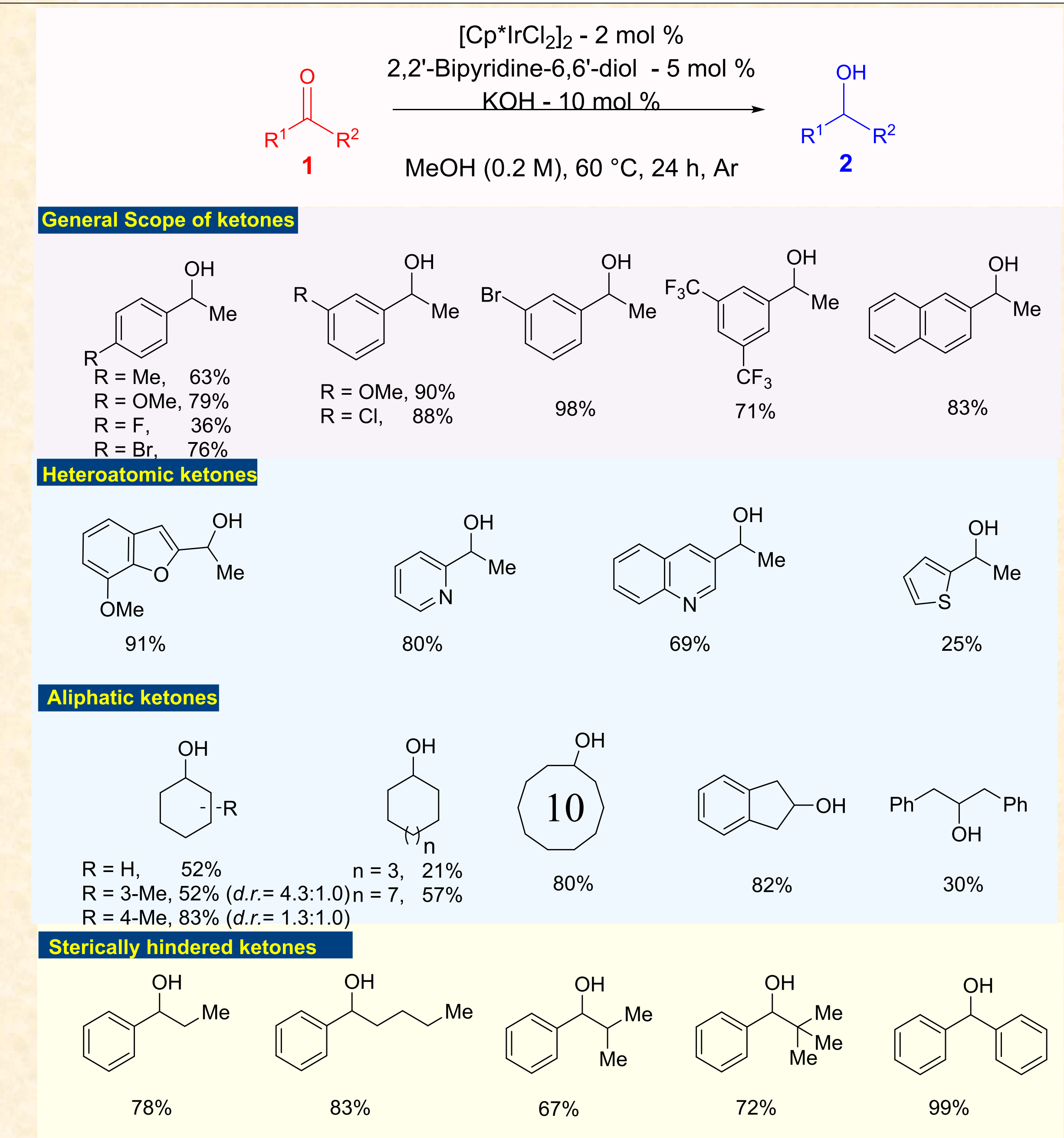
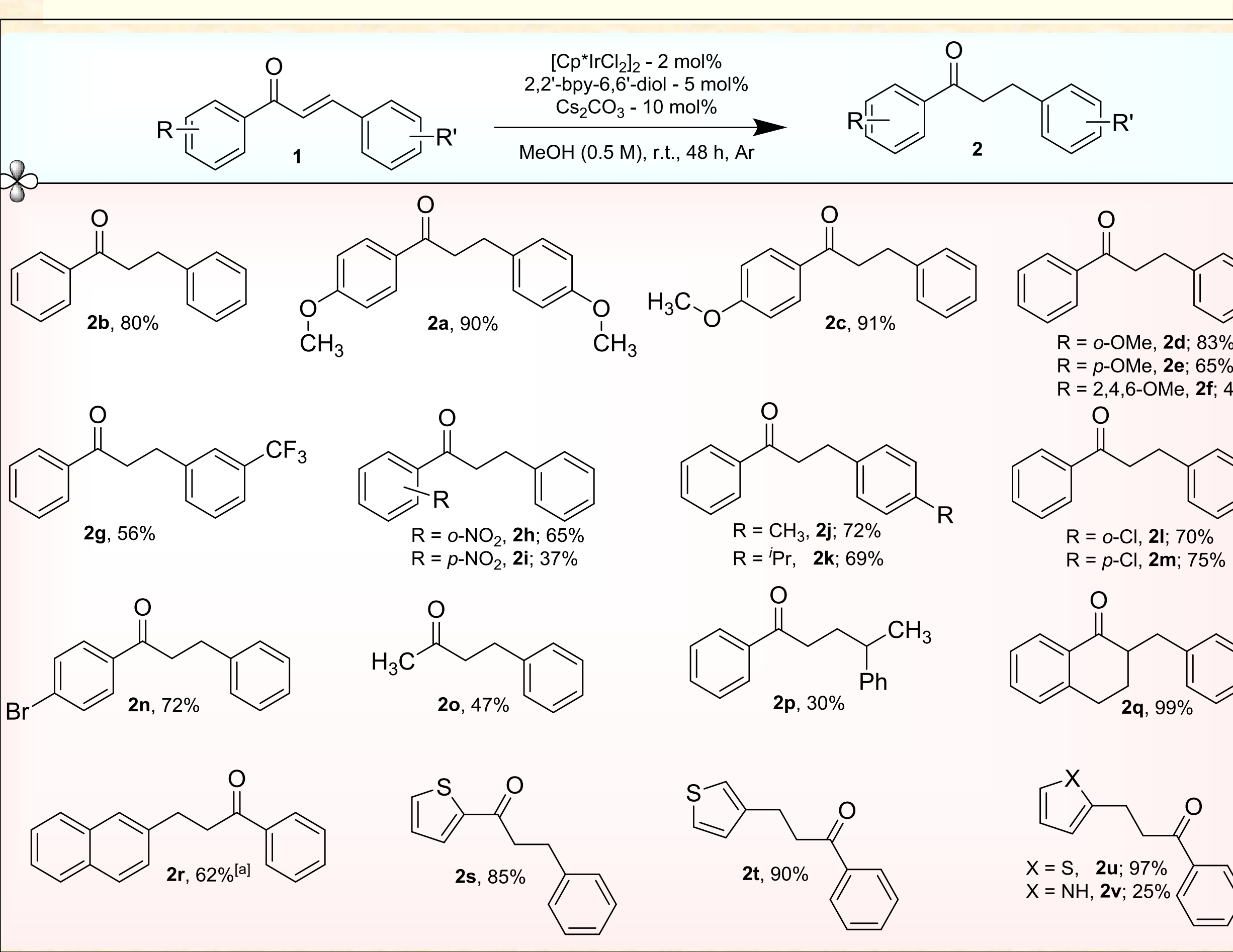
TM-catalyzed Methanol Dehydrogenation



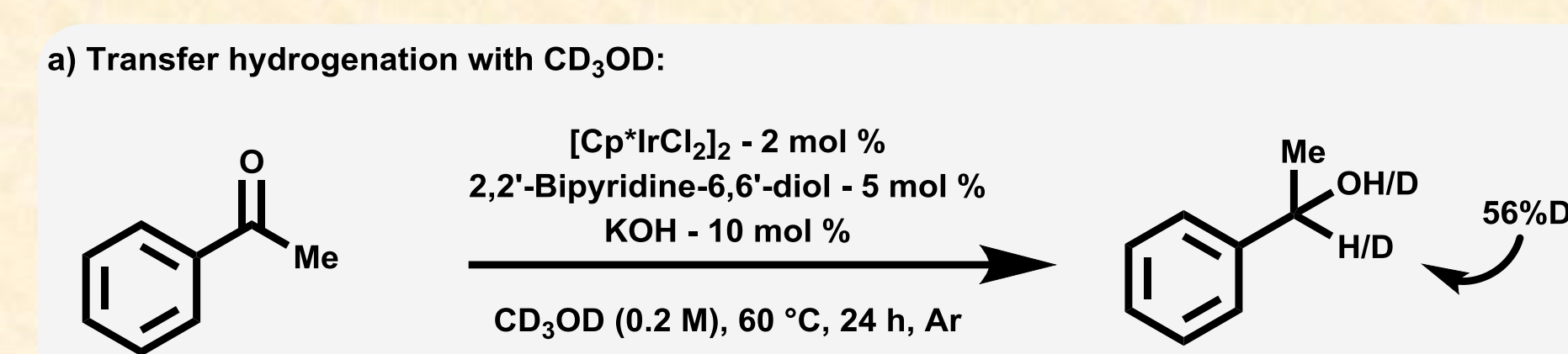
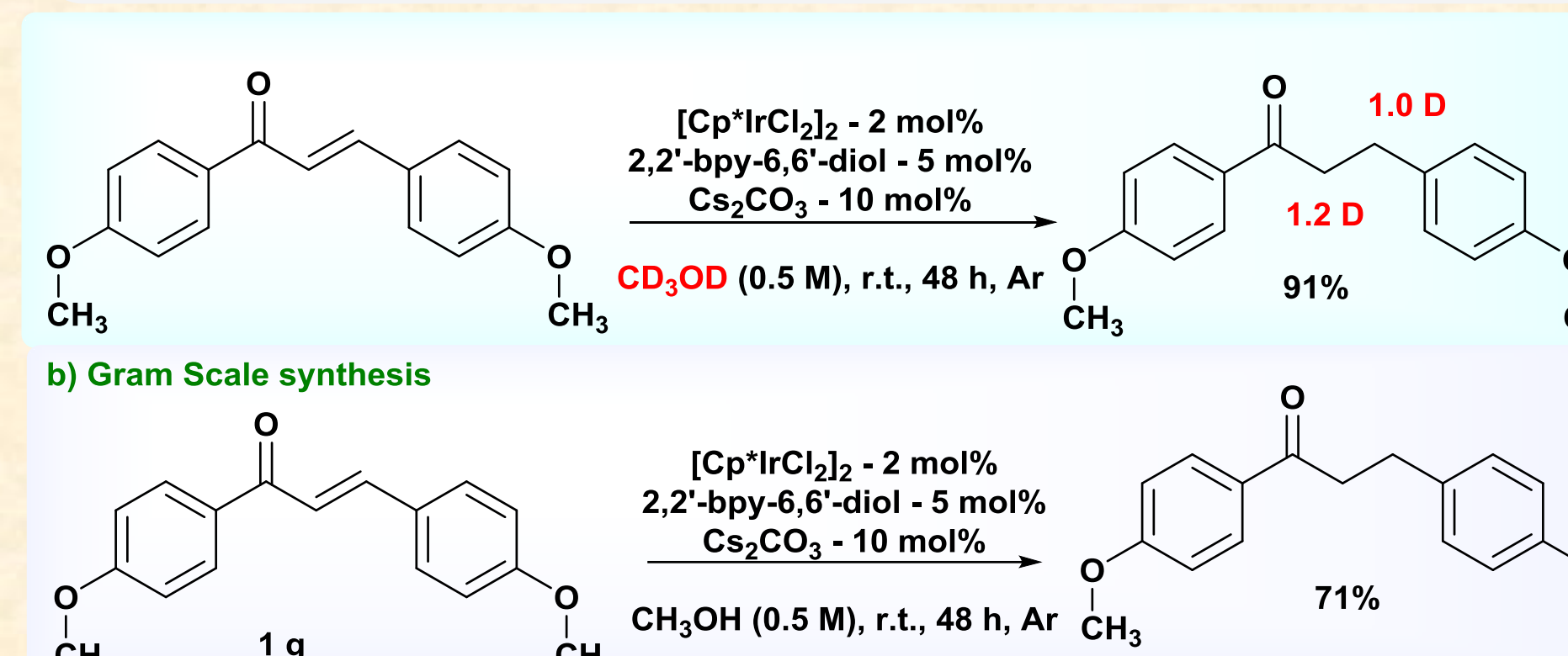
Plausible Mechanism



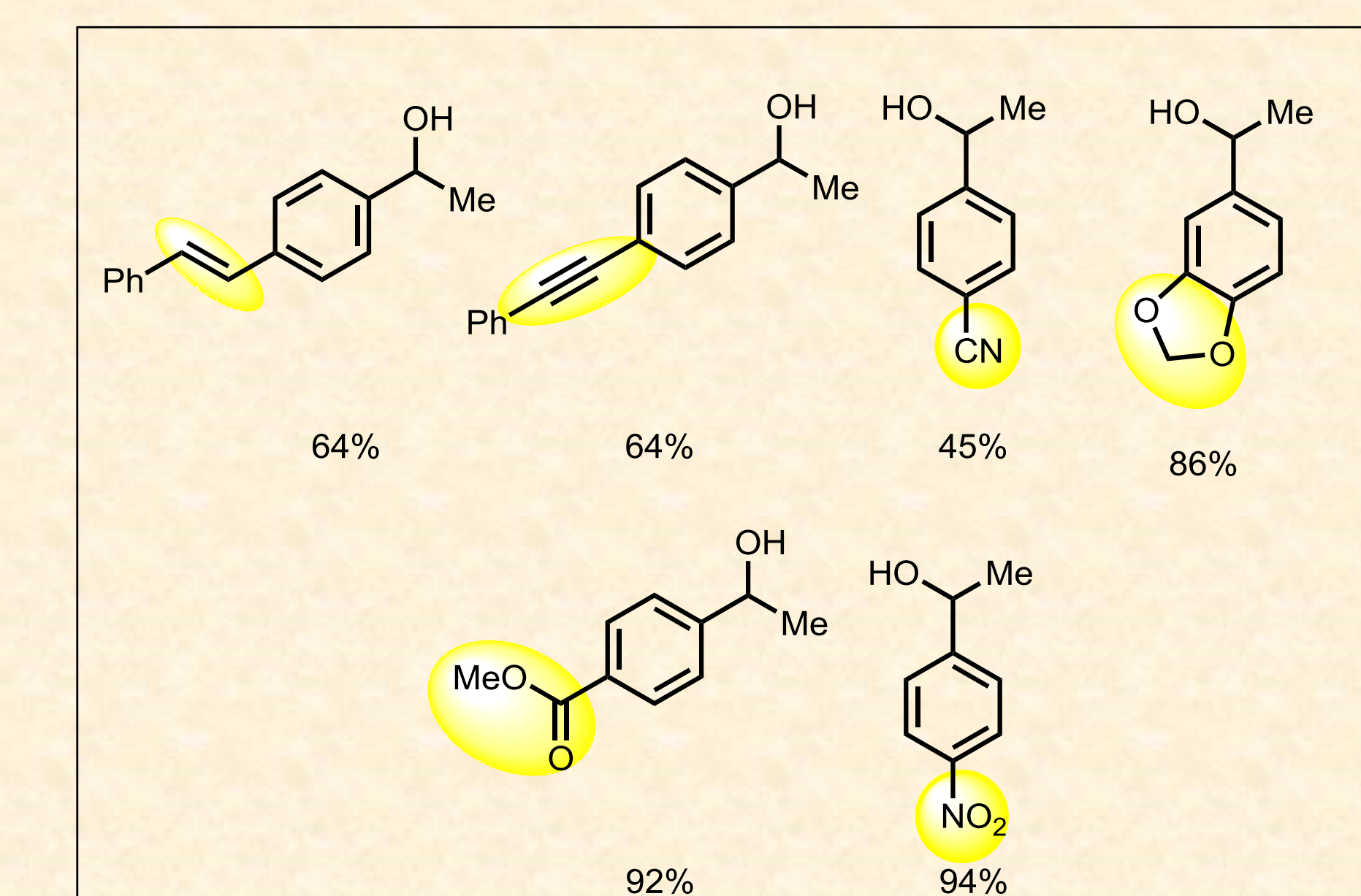
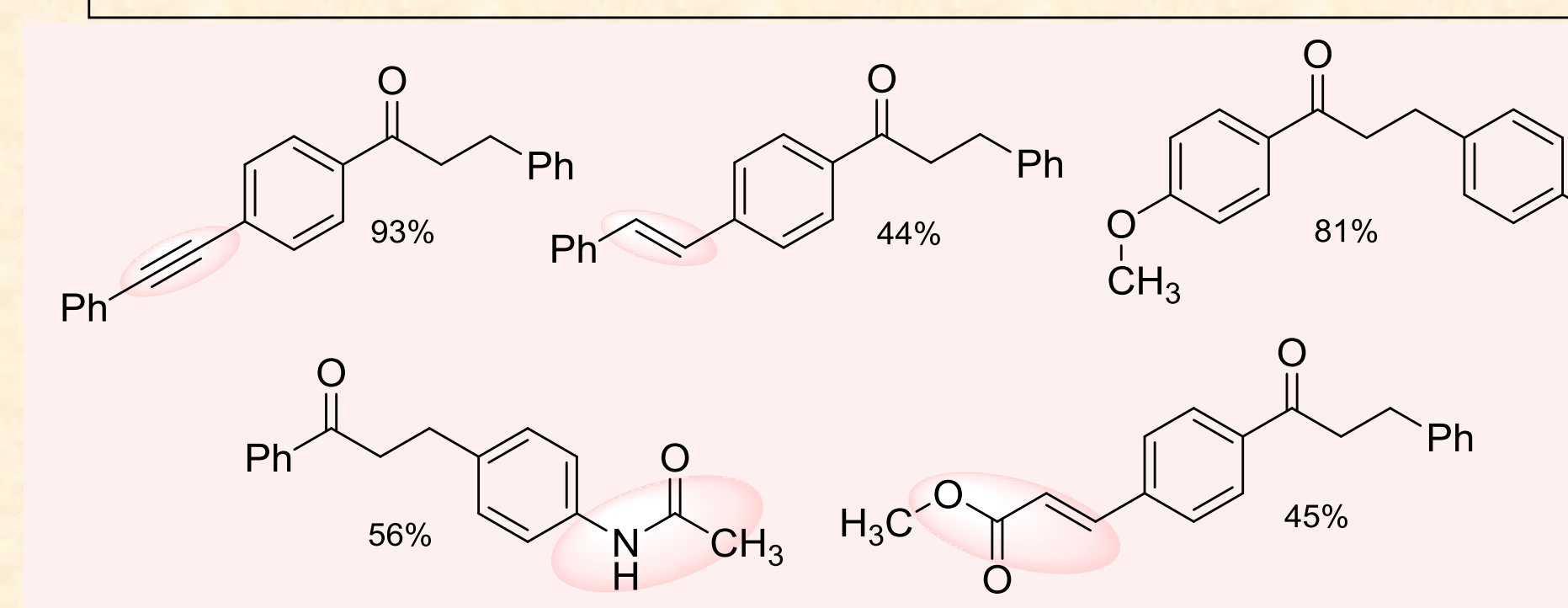
Reaction Optimization



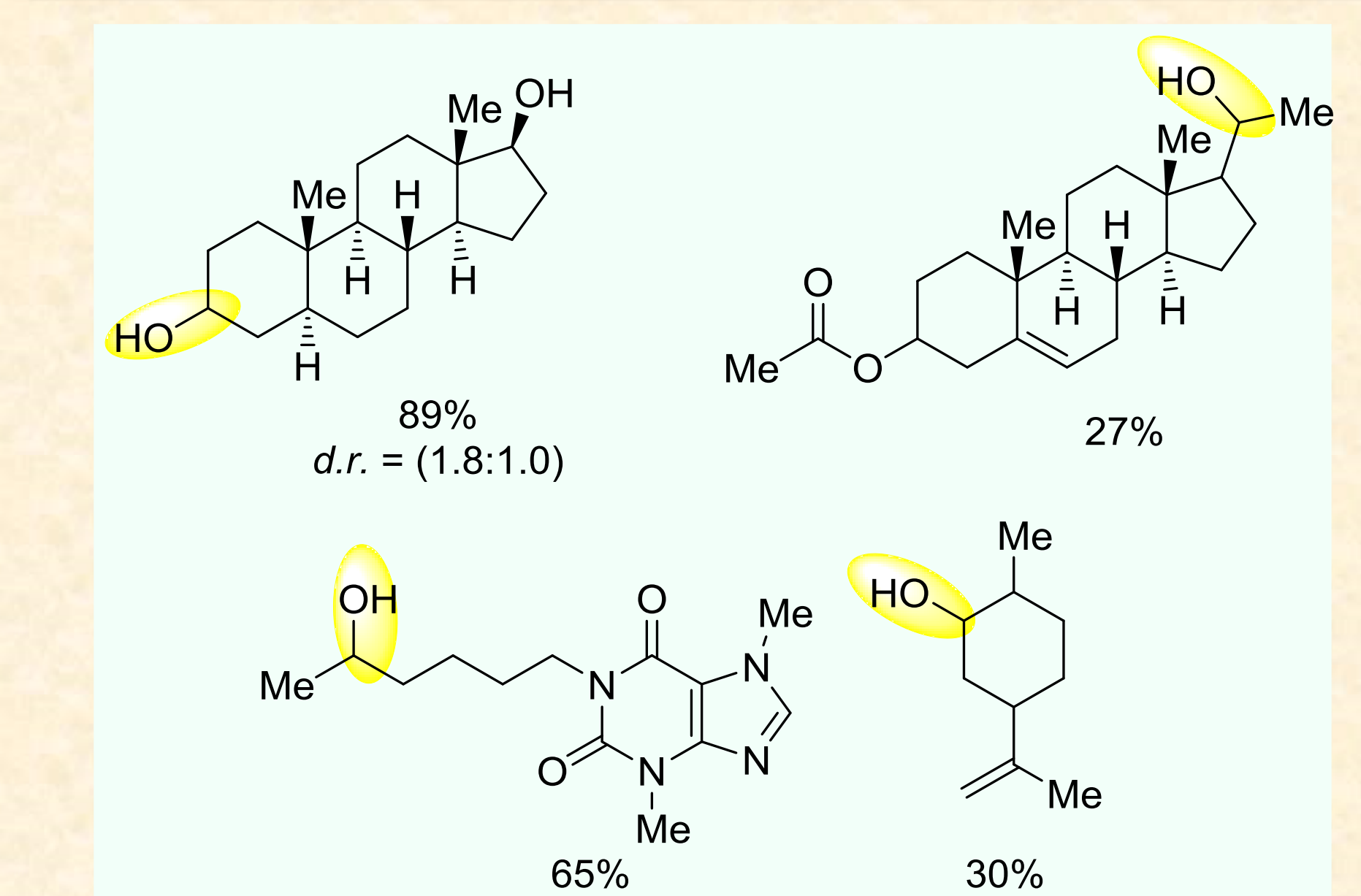
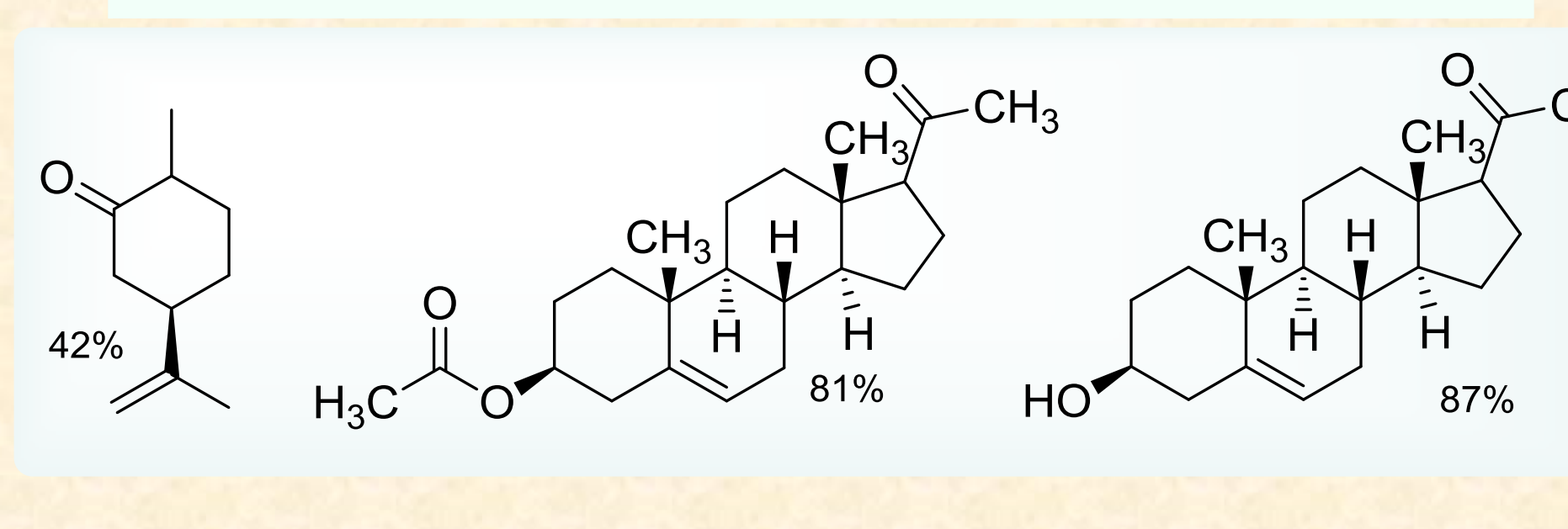
Preliminary mechanistic investigations



Chemoselective Reduction



Late-stage Functionalization



In conclusion, we demonstrated an efficient homogeneous iridium-catalyzed transfer hydrogenation of ketones using methanol as hydrogen source. The methodology was compatible with a wide range of ketones and shows excellent chemoselectivity. The key to the success of the described catalytic system is the well-defined metal ligand system that works well under moderately basic conditions. Further improvements in the catalytic conditions as well as catalytic reduction of other functional groups are currently underway in our laboratory. [3,4]

References : 1. D. R. Palo, R. A. Dagle, J. D. Holladay, *Chem. Rev.* **2007**, *107*, 3992.

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