Applications of Lewis Acidic $[ZnCl_2]_2[ChCl]$ Deep Eutectic Solvents (DESs) in the Synthesis of Unsymmetrical Ethers via Dehydrative Cross Etherification of Alcohols

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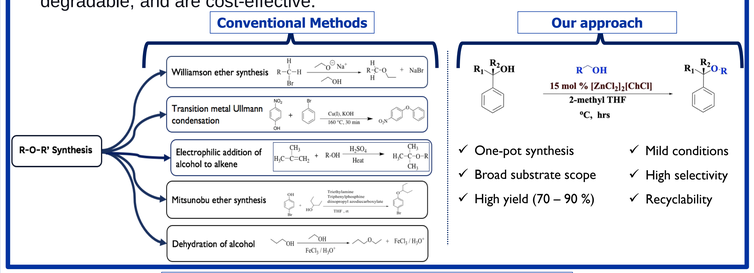
Introduction

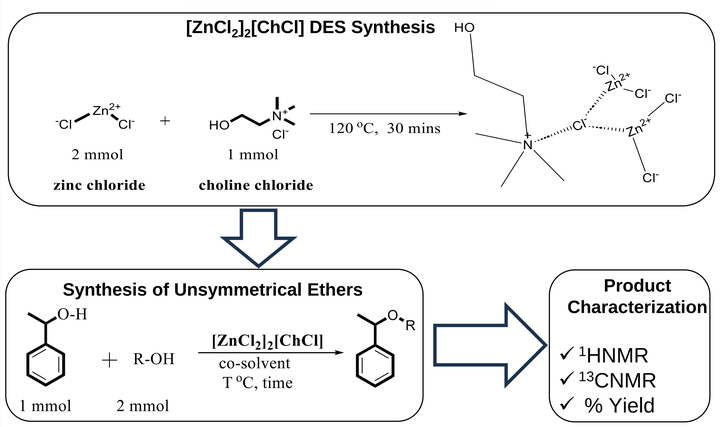
- The etherification reaction has ubiquitous applications as solvents, herbicides, building blocks of polymers, and drug precursors.
- Although the synthesis of symmetrical ethers is facile, the synthesis of unsymmetrical ethers via dehydrative cross-coupling of alcohols is still a challenge.
- Thus, **the project's goal is to develop environmentally benign homogenous catalysts** based on Lewis acidic (LA) $[ZnCl_2]_2[ChCl]$ deep eutectic solvents (DESs) for dehydrative cross etherification of alcohols under mild conditions.
- DES is a mixture of two or more pure compounds. It is a combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) with a melting point lower than their components.
- They have high thermal stability, low volatility, tunable polarity, high viscosity, are easily degradable, and are cost-effective.



Key Notes

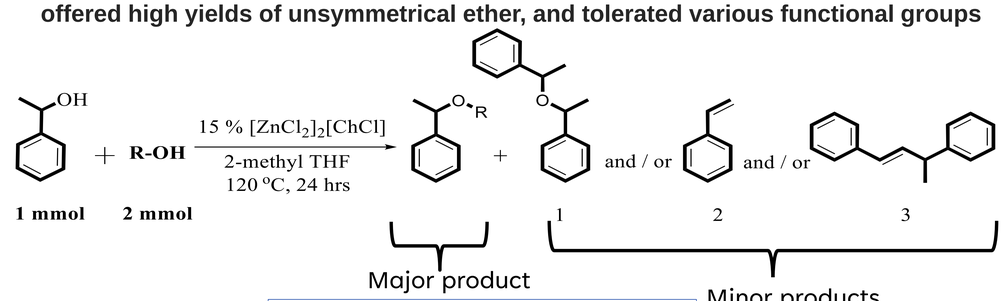
- The use of Lewis acidic $[ZnCl_2]_2[ChCl]$ DES as catalyst serves as green alternative to precious metals previously employed for the catalytic synthesis of unsymmetrical ether.
- Zinc-based DES ($[ZnCl_2]_2[ChCl]$) poses little or no toxicity risk to human health and the environment, its constituents are cheap and obtained from renewable sources (the choline chloride in the deep eutectic solvent is a feedstock for animals), and its synthesis requires minimal energy consumption.
- Lewis acidic Zn^{2+} centers in $[ZnCl_2]_2[ChCl]$ DES are active catalysts for the activation of 1-phenyl ethanol (1-PHE) via benzylic carbocation formation.

Methods

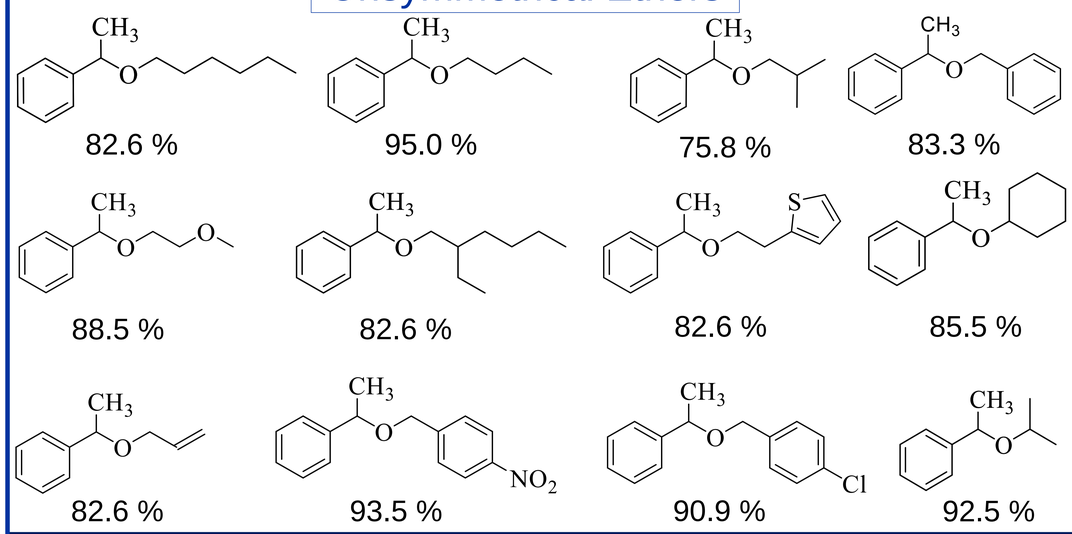


Results

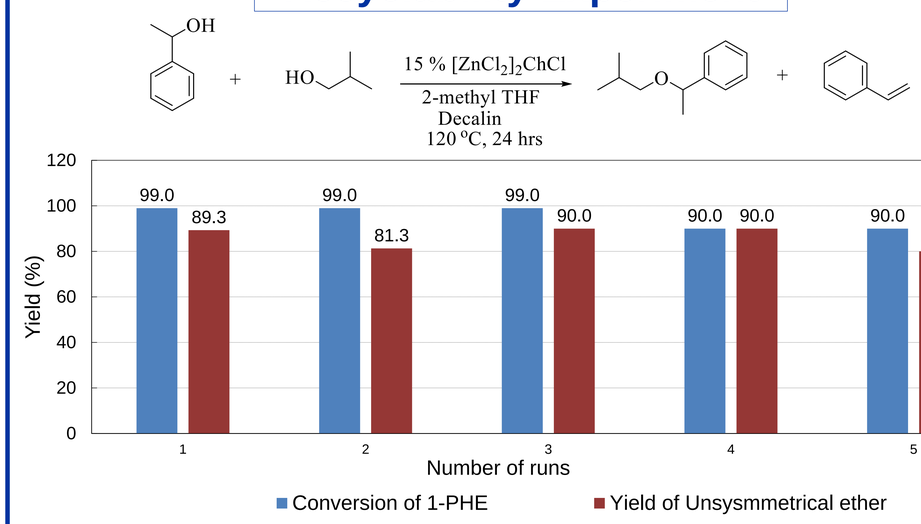
- **Dehydrative cross etherification of 1-phenyl ethanol (1-PHE) employing $[ZnCl_2]_2[ChCl]$ offered high yields of unsymmetrical ether, and tolerated various functional groups**



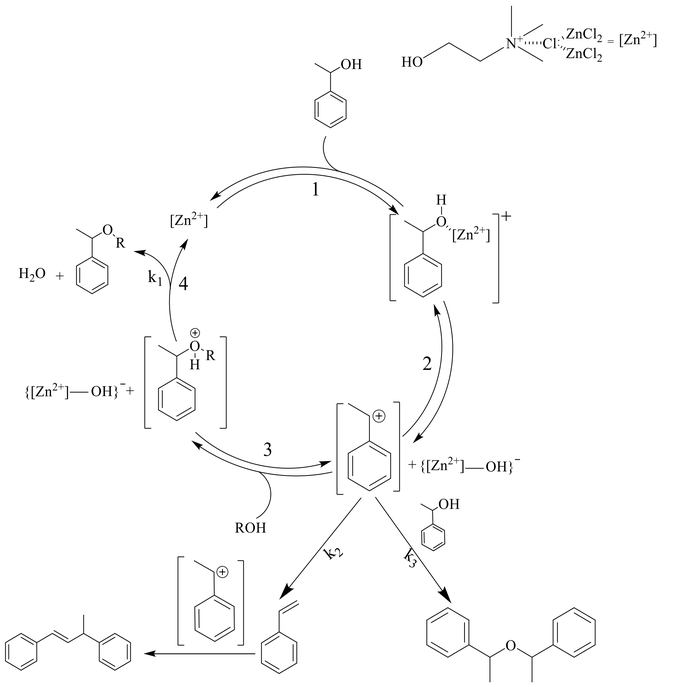
Unsymmetrical Ethers



Recyclability Experiment



Proposed Mechanism



Conclusions

- The synthesis of a C-O bond via cross etherification reaction using environmentally benign LADESs has been accomplished selectively under air.
- The novel catalyst $[ZnCl_2]_2[ChCl]$ derived DES mixture served as an effective Lewis acid in the synthesis of unsymmetrical ether in high yields.
- The synthetic route for unsymmetrical ether is tolerable of methoxy, nitro, halide, thienyl, allylic and sterically hindered alcohol functional groups.

References

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