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One-pot catalytic cascade for the depolymerization of the lignin ?-O-4 motif to non-phenolic dealkylated aromatics

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PURPOSE OF THE ABSTRACT

Lignin is the most abundant sustainable aromatic source from which various bio-aromatics can be obtained.1 Towards bio-aromatics, a series of lignin catalytic depolymerization strategies have been developed in the past 20 years.2 These depolymerization approaches, which can be grouped to reductive, oxidative, acid/base catalyzed and thermal methods, achieve the production of aromatics mainly by the cleavage of the most abundant ?-O-4 linkage in lignin (Scheme a). However, lignin-derived platform chemicals usually consist of a wide range of phenolic aromatic monomers with different alkyl side chains and various functional groups, for which further energy-intensive upgrading steps are necessary to transform them to industrial drop-in chemicals. In this work, we demonstrate the development of a one-pot cascade catalytic lignin depolymerization strategy, targeting the lignin ?-O-4 motif to selectively yield uniform defunctionalized aromatic monomers. This is achieved by selective acceptorless dehydrogenation of the ?-hydroxy group of the ?-O-4 motif, subsequent retro-aldol reaction to cleave the C?-C? bond followed by in situ acceptorless decarbonylation of the relevant aldehydes (Scheme b) This three-step cascade reaction catalyzed by an iridium(I)-BINAP complex, allows the efficient breaking of the internal ?-O-4 linkage selectively resulting in non-phenolic monomer 1,2-dimethxybenzene from G-type lignin structures alongside synthesis gas (CO:H2 = 2:1). By applying this method to a G-type lignin model, a selectivity of approximately 75% can be achieved. The obtained 1,2-dimethxoybenzene can be further transformed to cyclohexane, cyclohexanol or benzene using hydroprocessing with a catalyst of Ni/SiO2-Al2O3 under different conditions. This reveals a potentially more facile route from lignin to these important drop-in chemicals.

FIGURES

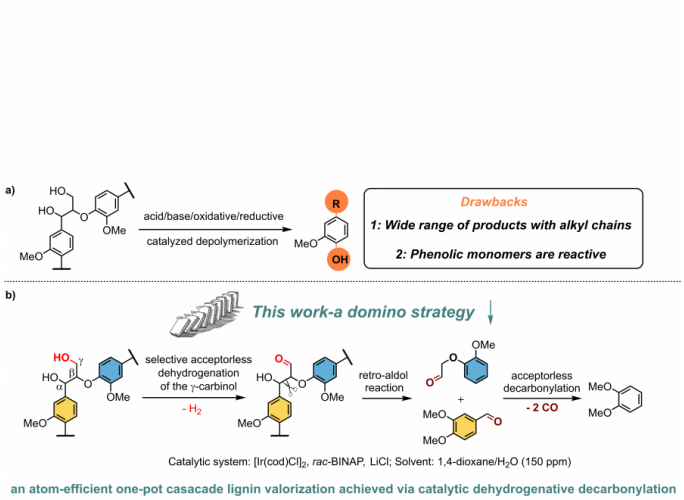

FIGURE 1

Scheme: a) current lignin valorization strategies and their typical products, b) 100% atom-efficient one-pot tandem lignin valorization achieved via dehydrogenative decarbonylation

FIGURE 2

KEYWORDS

lignin conversion | cascade reaction | atomic-efficient | domino strategy

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