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TOPIC(s) : Alternative solvents / Homogenous, heterogenous and biocatalysis

Combination of metal- and bio-catalyzed organic reactions in Deep Eutectic Solvents and water

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PURPOSE OF THE ABSTRACT

Due to the increasing rate of production of the Chemical Industry, it is necessary to design new cleaner and more efficient one-pot multi-step cascades in green solvents (i.e., water or Deep Eutectic Solvents). These one-pot transformations are emerging as exciting alternatives to highly-costly and tedious step-by-step processes, which also: i) minimise chemical waste; ii) save time; and iii) simplify practical aspects.[1] In this sense, we have previously reported the successful combination of the Ru(IV)-catalyzed redox isomerization of allylic alcohols (for the transient formation of the desired pro-chiral ketones) with a concomitant bioreduction (promoted by ketoreductases, KREDs) or bioamination (promoted by α -transaminases, α -TA).[2] In this communication, we present:

- the unprecedented combination of the following reactions in aqueous media: i) Pd(II)- or Au(I)-catalyzed cycloisomerizations of alkynols, alkynoic acids or alkynyl amides;[3] ii) spontaneous and concomitant hydrolysis of the obtained 5-membered heterocycles; and iii) enantioselective bioreduction of the corresponding prochiral ketones.[4]
- the first application of Deep Eutectic Solvents (DESs) in the asymmetric bioreduction of ketones employing isolated ketoreductases (KREDs). The performance of the biocatalysts was enhanced by increasing the percentage of neoteric solvent in DES-buffer mixtures. At buffer content of 50% and even 20%, either the combination of choline chloride (ChCl)/glycerol (Gly) (1:2) or (ChCl/sorbitol) (1:1) proved to be most effective for achieving up to >99% conversion and up to >99% enantiomeric excess of the corresponding secondary alcohols. Moreover, this reaction medium was used to perform the first example of chemoenzymatic cascade process in DES-buffer mixtures,[5] namely the ruthenium-catalyzed isomerization of racemic allylic alcohols coupled with a further enantioselective bioreduction, in both sequential and concurrent mode.

FIGURES

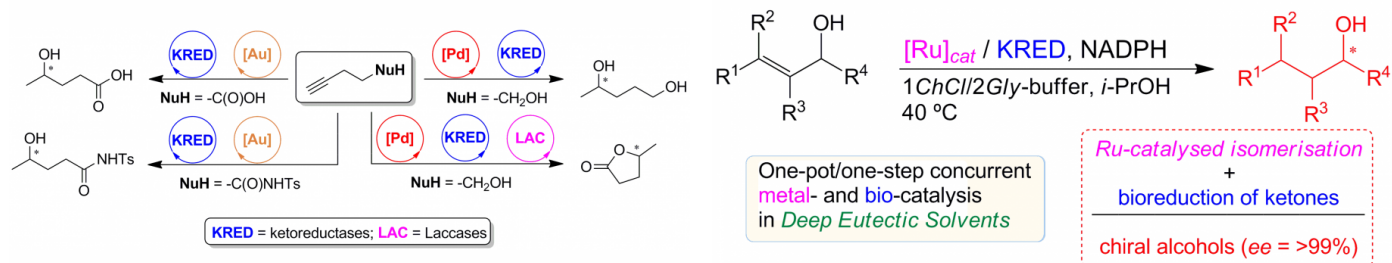


FIGURE 1

Scheme 1

Combination of metal- and bio-catalyzed organic reactions in aqueous media

FIGURE 2

Scheme 2

Combination of metal- and bio-catalyzed organic reactions in DESs

KEYWORDS

Metal-catalyzed | Bio-catalyzed | Deep Eutectic Solvents | Water

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