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GTHNL CATALYZES OXIDATIVE C=C BOND CLEAVAGE

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PURPOSE OF THE ABSTRACT

GtHNL is a hydroxynitrile lyase that was successfully utilized for the synthesis of cyanohydrins (Scheme 1B) and nitro aldol products, in batch and in flow [1,2,3]. GtHNL has moderate similarity (35%) with Tm1459 and the same catalytic metal ion, Mn(II) (Scheme 1A). Enzymes display high selectivity for one type of reaction. Therefore, lyases are not expected to catalyze oxidative C=C bond cleavage reactions as Tm1459 does (Scheme 1C) [4]. However, examining the structure of GtHNL there is no obvious reason why it should not catalyze the oxidative C=C bond cleavage, as described for Tm1459. Equally a hydroxynitrile lyase activity for Tm1459 cannot be ruled out.

GtHNL was employed under condition earlier successful for Tm1459 [4]. tert-butyl hydroperoxide (TBHP) was used as oxidizing reagent and GtHNL satisfactorily catalyzed the oxidative cleavage of a number of styrene derivatives. Enzyme and reaction engineering led to improved selectivities and yields. On the other hand Tm1459 displayed only modest hydroxynitrile lyase activity without selectivity. These results question our concepts of enzyme selectivity and at the same time open new routes to novel enzyme activities.

FIGURES

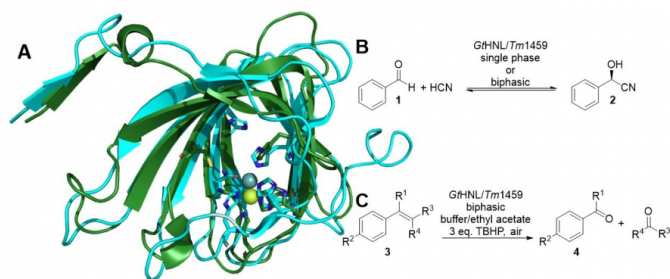


FIGURE 1

Scheme 1

A) Superimposition of GtHNL (PDB code: 4BIF) in blue with Mn(II) in grey coordinated by four histidines and glutamine and Tm1459 (PDB code: 1VJ2) in green with Mn(II) in lime coordinated by four histidines. B) Cyanohydrin synthesis C) Oxidative cleavage.

FIGURE 2

KEYWORDS

Hydroxynitrile lyase | oxidative cleavage | promiscuity

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