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RESEARCH ARTICLE

Divergent Oxidation Reactions of *E*- and *Z*-Allylic Primary Alcohols by an Unspecific Peroxygenase

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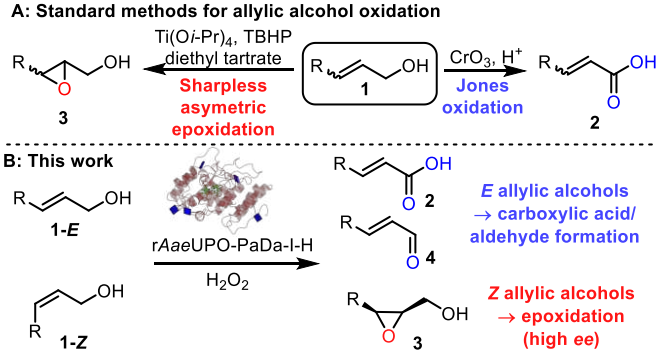
Supporting information for this article is given via a link at the end of the document.

Abstract: Unspecific Peroxygenases (UPOs) catalyze the selective oxygenation of organic substrates using only hydrogen peroxide as the external oxidant. The PaDa-I variant of the UPO from *Agrocybe aegerita* catalyses the oxidation of *Z*- and *E*-allylic alcohols with complementary selectivity, giving epoxide and carboxylic acid/aldehyde products respectively. Both reactions can be performed on preparative scale with isolated yields up to 80%, and the epoxidations proceed with excellent enantioselectivity (>99% *ee*). The divergent reactions can also be used to transform *E*/*Z* mixtures of allylic alcohols, enabling both product series to be isolated from a single reaction. The utility of the epoxidation method is exemplified in the total synthesis of both enantiomers of the insect pheromone disparlure, including a highly enantioselective gram-scale transformation. These reactions provide further evidence for the potential of UPOs as catalysts for the scalable preparation of important oxygenated intermediates.

Introduction

The selective oxygenation of organic compounds presents a challenge in organic synthesis from the perspectives of both selectivity and sustainability, each of which can in part be addressed through the use of microbes and enzymes.[1-2] In addition to the well-established whole cell oxygenations of steroid precursors[3] and amino acids such as proline,[4] the potential application of the hemoprotein cytochromes P450 (P450s) has been extensively studied.[5-6] P450s applied as *in vitro* catalysts are highly selective for a range of oxygenation reactions, but present challenges with respect to stability and also the usual requirement for expensive nicotinamide cofactor (NAD(P)H) and redox transport protein systems (P450 reductases or ferredoxin reductase/ferredoxin) for the reductive cleavage of oxygen to form the requisite catalytic iron oxoferryl species 'Compound I' in the active site of the enzyme.[7] The discovery of a further class of hemoprotein oxygenase, namely 'unspecific peroxygenases' (UPOs), by Hofrichter and colleagues nearly 20 years ago,[8,9] identified a potentially valuable new class of oxygenase that presented clear advantages for *in vitro* applications, as they depend only upon the addition of hydrogen peroxide (H_2O_2) to form Compound I.[10] The intervening years have seen the potential of UPOs advance considerably,[11-14] enabled by the identification of numerous enzymes,[15-16] the development of heterologous expression systems that permit scalable production of these enzymes,[17-19] and their application in selective oxygenation reactions.[20-24] In recent work, we have shown that UPOs can be used in a series of selective, preparative oxygenation reactions of biologically important *N*-heterocycles[25] and terpenes,[26] on up to gram scale. Despite the 'unspecific' nature that gives the enzymes their name, it is noteworthy that different UPOs, when presented with multiple susceptible oxygenation centres, often give different products selectively, thus presenting a versatile toolbox of biocatalysts for various biosynthetic applications.

This study is focused on the UPO mediated oxygenation of allylic primary alcohols **1**. Allylic alcohols are important compounds in organic synthesis capable of undergoing a range of useful transformations; for example, they can be oxidized to form carboxylic acids **2**, typically using a Cr(VI) oxidant (*e.g.* Jones oxidation), or converted into epoxides **3** using the Sharpless asymmetric epoxidation method (**Scheme 1A**).[28,29] Both of these methods have been widely used in many important synthetic applications, although both have notable drawbacks; for example, long reaction times at cryogenic temperatures are often needed to attain high *ee* using the Sharpless method,[28] while the Jones oxidation necessitates the use of stoichiometric quantities of highly toxic Cr(VI) reagents, under strongly acidic conditions.[29]



Scheme 1. a) Standard methods of allylic alcohol oxidation; b) Biotransformations of allylic alcohols by UPOs. TBHP = *tert*-Butyl hydroperoxide

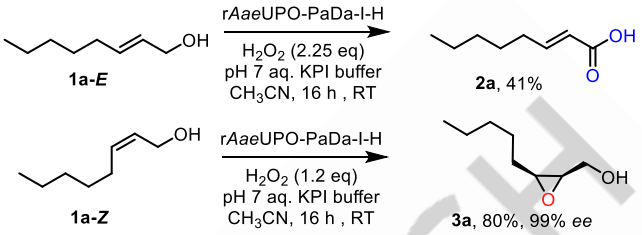
The disadvantages of conventional oxidation methods have prompted studies of the enzymatic oxidation of allylic alcohols.[30-34] In one example, the wild-type cytochrome P450 CYP154E1 from *Thermobifida fusca* was shown to transform the *E*/*Z* allylic alcohol isomers geraniol and nerol each to largely their 8-hydroxy-derivatives with 98% and 77% conversion. For nerol, the product mixture also contained 4% of the epoxide 2,3-epoxynerol.[31] Mixtures of hydroxylated and epoxidized products have also been observed in the UPO-catalyzed transformation of unsaturated fatty acids. [35-38] It has also been reported that the UPO from *Marasmius rotula* (*Mro*UPO) can be mutated to alter the balance of epoxidation and (sub)terminal hydroxylation products of oleic acid; for example, by inhibiting access of the 'bent' conformation of oleic acid to the UPO heme.[39] However, a description of the selectivity of UPOs towards carbon atoms in unsaturated fatty alcohols with allylic primary alcohol functionality has not yet been described.

Herein we describe the biotransformations of *E*- and *Z*-allylic alcohols **1** with r*Aae*UPO-PaDa-I-H, a mutant of the UPO from *Agrocybe aegerit*a (*Aae*UPO). This UPO was develop d for superior activity and ease of expression in *Pichia pastoris*,[17,18] using a modified vector and procedures previously described.[27] Remarkably, while both isomeric series are successfully transformed, *E*- and *Z*-allylic alcohols afford completely different product classes, being converted into carboxylic acids/aldehydes (**2**/**4**) and epoxides (**3**, in very high *ee*) respectively using the same enzyme and reaction conditions (**Scheme 1B**). To the best of our knowledge, we know of no other chemo- or biocatalytic method that can enable such a stark switch in chemoselectivity based solely on the allylic alcohol alkene geometry.

Results and Discussion

We started by exploring the biotransformations of the *E*- and *Z*-isomers of oct-2-ene-1-ol (**1a-*E*** and **1a-*Z***) using r*Aae*UPO-PaDa-I-H and H_2O_2 (**Scheme 2**). These biotransformations (and all biotransformations in this manuscript) were performed on preparative scale (typically ≈0.8 mmol scale), which is testament to the practicality and scalability of this system. These experiments revealed a remarkable divergence in reactivity dependent on different geometrical isomer of allylic alcohol used. Thus, the *E*-octenol **1a-*E*** was converted into carboxylic acid **2a**, using r*Aae*UPO-PaDa-I-H and 2.25 equivalents of H_2O_2, and was isolated in 41% yield on a preparative scale (47 mg). In contrast, when *Z*-isomer **1a-*Z*** was reacted with the same enzyme, using 1.2 equivalents of H_2O_2, epoxide **3a** was formed in 80% isolated yield (92 mg), as a single diastereoisomer and with excellent enantioselectivity (99% *ee*).[40] Intriguingly, the alternative product (*i.e.* carboxylic acid or epoxide) was not observed as a minor product in either series. Note, that the difference in the number of equivalents of H_2O_2 used is a consequence of the epoxidation reaction requiring one equivalent of oxidant, while the alcohol to carboxylic acid oxidation requires two.[41]

A representative class I UPO (artUPO) also led to biotransformation of the same two substrates, but was markedly less effective (see SI section 5, Scheme S1 and S2) and hence r*Aae*UPO-PaDa-I-H was used for the remainder of this study. No conversion was observed when either r*Aae*UPO-PaDa-I-H or H_2O_2 were omitted from the reaction (see SI section 5, Scheme S3). Details of optimisation of the reactions conditions, examining the reaction pH, the co-solvent, the H_2O_2 addition rate and the temperature, are all included in the Supporting Information (see SI section 5, Table S1–S4).



Scheme 2. Biotransformation of *E* and *Z* isomers of **1a** by rAaeUPOPaDa-I-H.

The divergent reactivity observed depending on the *E*/*Z*-configuration of the allylic alcohol **1a**, prompted us to generate a cluster model of the r*Aae*UPO-PaDa-I-H active site to elucidate the epoxidation and oxidation pathways (**Figure 1A**). Our DFT calculations indicate that the formation of the carboxylic acid is favored over epoxidation for both **1a-*E*** and **1a-*Z***: the activation barrier is 6.3 (**1a-*E***) and 8.2 (**1a-*Z***) kcal mol^{-1} for carboxylic acid production, whereas it is 14.2 (**1a-*Z***) and 16.4 (**1a-*E***) for epoxidation (**Figure 1**, and **S17**). This static mechanistic study therefore indicates that both processes are possible under the experimental conditions. The formation of carboxylic acid in the case of **1a-*E*** is substantially more favored than epoxidation (10 kcal mol^{-1} of difference). However, the static cluster model calculations cannot provide a rationalization for the preference towards epoxidation for **1a-*Z*** as observed experimentally, thus suggesting that active site pocket flexibility helps to favor the productive binding of **1a-*Z*** toward epoxidation.

To that end, unrestrained Molecular Dynamics (MD) simulations were performed considering the iron oxoferryl species and the reactant complexes obtained from the DFT calculations with **1a-*E*/*Z*** bound (**Figure 1B-C**). The analysis of the conformational landscapes based on the distance and angle of iron oxo and C1/C2 (**Figure 1B**) indicates that **1a-*E*,** when bound in the active site, adopts a higher proportion of catalytically productive conformations for C1 oxidation (distances lower than 5 Å, angles between 120 and 150º), as compared to **1a-*Z*** (**Figure 1B** and **S18**). In contrast, **1a-*Z*** positions C2 closest to the iron center, which is consistent with it undergoing epoxidation selectively. The overlay of catalytically productive frames sampled along the MD simulations shows a large flexibility of F118, especially when **1a-*Z*** is bound, which is crucial for preferentially accommodating C2 of the substrate close to the iron center (**Figure 1C** and **S19**). This enhanced flexibility of F118 is thus crucial for favoring the epoxidation pathway. The MD simulations therefore indicate that the flexibility of the active site pocket of r*Aae*UPO-PaDa-I-H favors a different binding of **1a** depending on the *E*/Z configuration, positioning either C1 or C2 close to the iron oxoferryl center and therefore yielding selective divergent oxidation products.

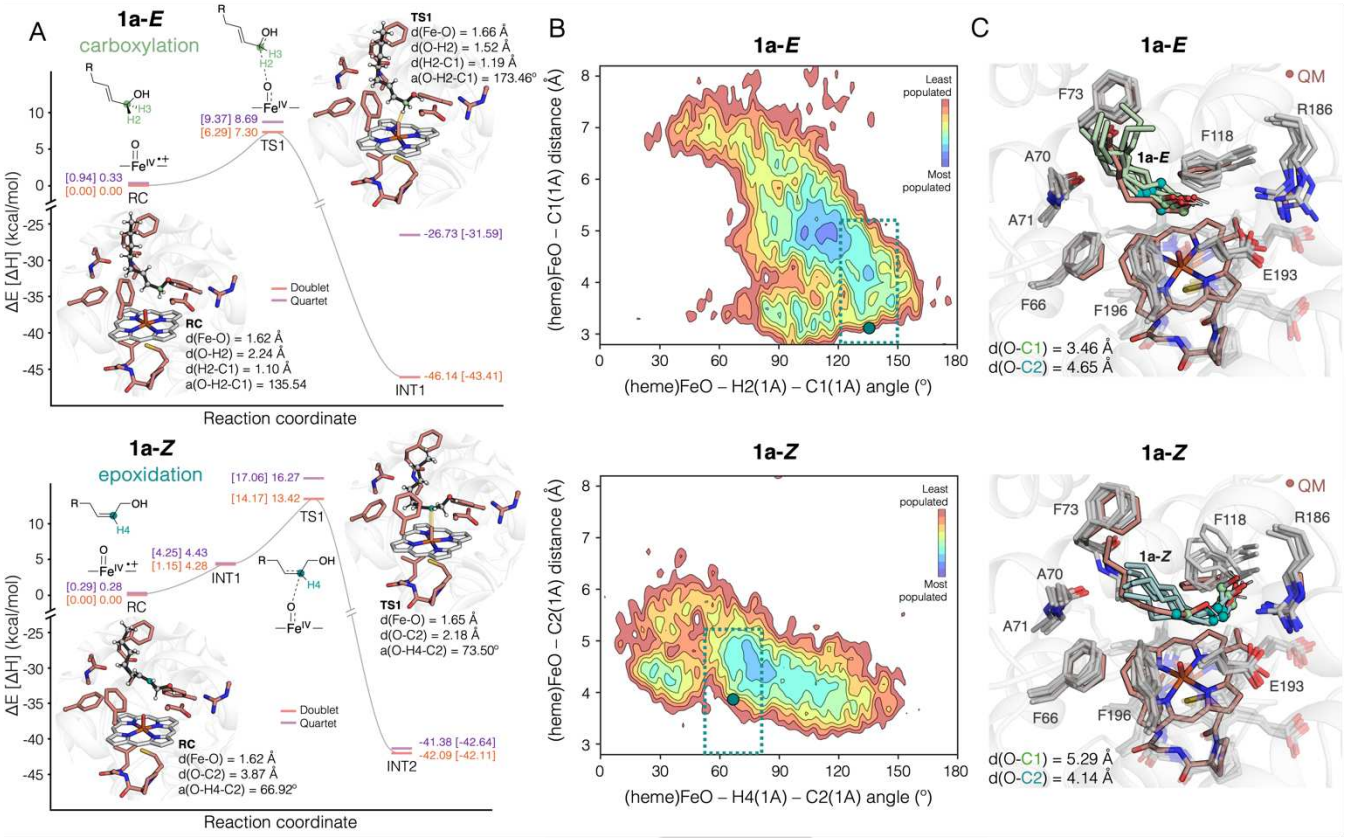
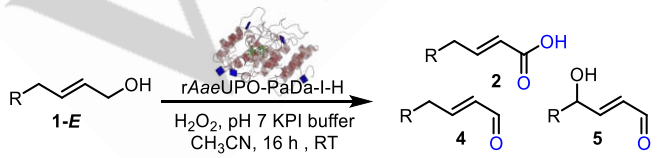
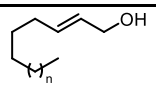
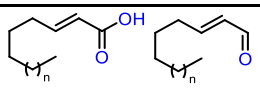
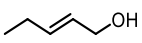
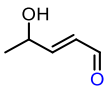
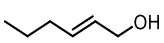
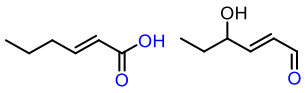
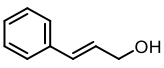
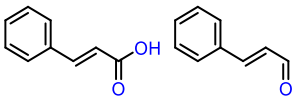
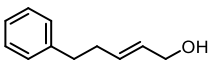
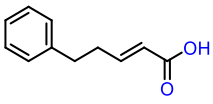


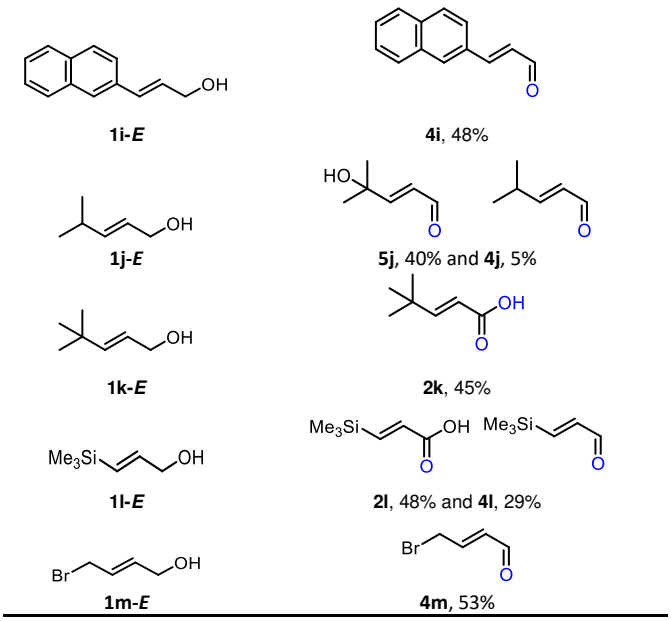
Figure 1. Computational evaluation of the divergent reactivity depending on the *E*/*Z*-configuration of the allylic alcohol **1a**. **A.** DFT reaction mechanism towards carboxylic acid formation of **1a-*E*** (top panel), and epoxidation pathway of **1a-*Z*** (bottom panel). Electronic energies and enthalpies (between brackets) are provided in kcal mol^{-1} for the doublet (pink values) and quartet (purple) states. The cluster model of the optimized reactant complexes and transition states are represented, and key distances and angles are provided in Å and degrees, respectively. The substrate **1a-*E*/*Z*** is shown as spheres and black sticks. **B.** Conformational landscapes of the substrate-bound MD simulations based on the FeO-H2/4-C1/2 angle (x-axis) and key catalytic FeO-C1/2 (y-axis). The values from the DFT-optimized reactant complex are marked using a teal dot. The area taken as catalytically productive is highlighted with a discontinuous box. **C.** Overlay of representative structures extracted from the catalytically productive area in the conformational landscape. The DFT-optimized cluster model of the reactant complex is shown with brown sticks. **1a-*E*/*Z*** substrates and key C1/C2 atoms are colored with light green and teal, C1 and C2 positions are shown as spheres. The mean distance for FeO-C1/C2 is also included in both **1a-*E*/*Z*** cases.

Having explored the basis for the selective divergent oxidation reactions of **1a-*E*** and **1a-*Z***, our attention turned to exploring the scope of this phenomenon, starting with a range of *E*-allylic alcohol substrates **1-*E*** (**Table 1**).

Table 1. Biotransformation of *E*-allylic alcohols **1-*E*** by r*Aae*UPO-PaDa-I-H.[a]



Alkene	Product(s), yield/%
	
1a-*E*, n = 1	**2a**, 41% and **4a**, 0%
1b-*E*, n = 2	**2b**, 49% and **4b**, 0%
1c-*E*, n = 3	**2c**, 47% and **4c**, 8%
1d-*E*, n = 5	**2d**, 10%[b] and **4d**, 34%
	
1e-*E*	**5e**, 68%[c]
	
1f-*E*	**2f**, 15% and **5f**, 61%
	
1g-*E*	**2g**, 38% and **4g**, 20%
	
1h-*E*	**2h**, 57%



[a] r*Aae*UPOPaDa-I-H, H_2O_2 (2.25 equiv. slow addition), pH 7 KPI buffer, CH_3CN 16 h, RT. Yield refers to isolated product after column chromatography. [b] NMR yield – based on the ratio of product by ^1H NMR in a partially purified fraction. [c] *ee* not determined as the product **5e** is unstable.

Longer chain allylic alcohols were first tested. r*Aae*UPO-PaDa-I-H was able to transform each of allylic alcohols **1a–d-*E*** to the expected carboxylic acids **2a**–**d** in all cases, albeit with partially oxidised aldehyde products **4c** and **4d** also obtained in reactions of the longer homologues. Shorter chain aliphatic homologues **1e-*E*** and **1f-*E*** were also tested; in these cases, competing allylic oxidation reactions were observed, as well as alcohol oxidation to form hydroxy aldehydes **5e** and **5f** as the major products (in 60% isolated yield in both cases). The reduction in length in the alkyl chain presumably facilitated the ease with which the oxygenated allylic position can access the UPO active site.

Allylic alcohols with aromatic substituents were tested next. Substrates **1g-*E***, **1h-*E*** and **1i-*E*** were all converted well, with carboxylic acids **2g–i** the major product in each case. Hydroxylated aldehyde **5j** was obtained from allylic alcohol **1j-*E***, with the formation of this side product likely favored by a combination of the short alkyl chain, and the comparatively easy oxidation of the *iso*-propyl allylic position. Allylic alcohols **1k-*E*** and **1l-*E***, substituted with bulky *tert*-butyl and trimethyl silyl substituents, were well tolerated, affording carboxylic acids **2k** and **2l** as the major products respectively. Finally, bromide containing substrate **1m-*E*** was also transformed by the UPO, to form aldehyde **4m** in good yield. While it is not obvious why oxidation stalls at the aldehyde in this example, it is notable that the relatively sensitive allyl bromide group is tolerated and retained in the isolated product.

We then moved onto exploring the scope of the biotransformation of *Z*-allylic alcohols **1-*Z*** (**Table 2**). In this series, the divergent selectivity for alkene epoxidation was observed across all substrates tested; the expected epoxide products (**3a**–**b**, **3d**–**f**, **3j** and **3n**) were obtained as the major product and isolated in good yield in all cases. An additional aldehyde product arising from alcohol oxidation was also observed in longer carbon chain substrates (**1b-*Z***, **1d-*Z*** and **1n-*Z***) only.

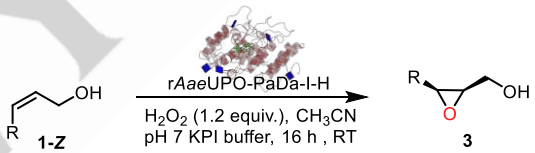
Z-Cinnamyl alcohol **1g-*Z*** can also undergo selective epoxidation, to form epoxide **3g** in 42% isolated yield and 99% *ee*.

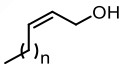
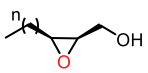
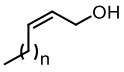
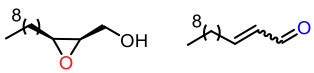
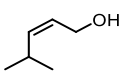
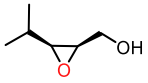
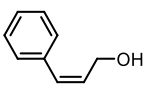
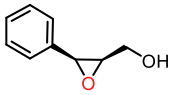
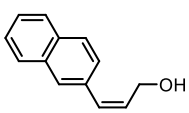
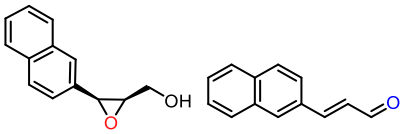
The analogous β-naphthalene substrate **1i-*Z*** also delivered the expected epoxide in high *ee* but in comparatively low isolated yield; in this case, aldehyde **4i** was also obtained *via* oxidation of the alcohol group. Notably, aldehyde **4i** was isolated exclusively as the *E*-isomer shown; it is not clear whether the alkene isomerization took place before or after oxidation in this example.

Crucially, the formation of the epoxide product **3** as a single diastereoisomer and in excellent *ee* was observed across all examples in this series. This method therefore offers a very effective way to prepare highly enantioenriched epoxides from allylic alcohols, complementing the Sharpless Asymmetric Epoxidation method.[28]

Making allylic alcohols as single geometrical isomers is not always trivial – especially in the case of *Z*-isomers. Partial hydrogenation of a propargylic alcohol using Lindlar's catalyst is the most common synthetic method used to prepare *Z*-allylic alcohols, including most of the *Z*-allylic alcohols used in this study. However, despite the expectation that *Z*-alkenes should be formed by this method, in reality, inseparable mixtures of *E*/*Z* mixtures are often obtained.[42,43] We recognised that an advantage to the divergent reactivity enabled in this study could be its ability to effectively transform allylic alcohols that are only available as *E*/*Z* mixtures. Because the expected products in each series (epoxy alcohols vs. carboxylic acids/aldehydes) typically have very different physical properties, this would permit the

Table 2. Biotransformation of *E*-allylic alcohols **1-*Z*** by r*Aae*UPOPaDa-I-H.[a]

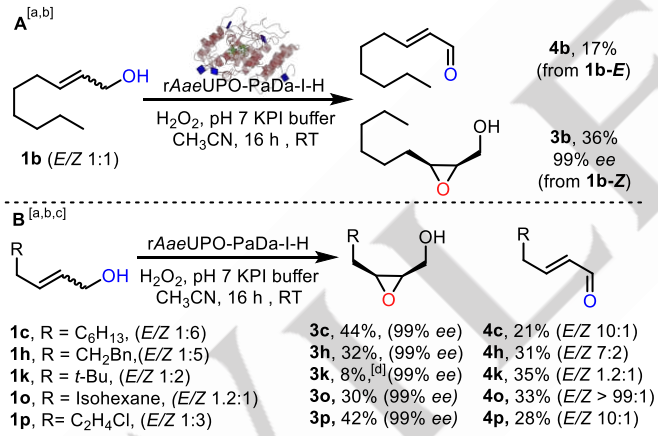


Alkene	Product, yield/% (% *ee*)[b]
	
1a-*Z*, n = 4	**3a**, 80% (99% *ee*)
1e-*Z*, n = 1	**3e**, 45% (92% *ee*)
1f-*Z*, n = 2	**3f**, 45% (99% *ee*)
	
1b-*Z*, n = 5	**3b**, 56% (99% *ee*) and **4b**, 14%
1d-*Z*, n = 8	**3d**, 42% (99% *ee*) and **4d**, 14% (*E*/*Z* 5:1)
1n-*Z*, n = 9	**3n**, 30% (99% *ee*) and **4n**, 12% (*E*/*Z* 6:1)
	
1j-*Z*	**3j**, 56% (99% *ee*)
	
1g-*Z*	**3g**, 42% (99% *ee*)
	

1i-*Z*	**3i**, 28% (99% *ee*)[c] and **4i**, 35% (E isomer)

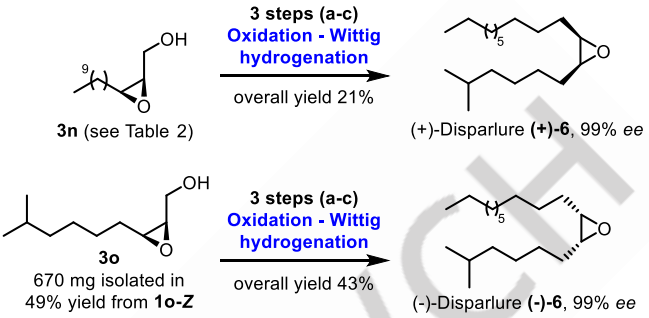
[a] r*Aae*UPOPaDa-I-H, H_2O_2 (1.2 equiv. slow addition), pH 7 KPI buffer, CH_3CN 16 h, RT. Yield refers to isolated product after column chromatography. [b] *ee* determined by GC unless stated (see SI); [c] *ee* determined by HPLC (see SI)

isolation of separable products from both isomers in a single reaction. This idea is exemplified in **Scheme 3A**; in this biotransformation, a 1:1 mixture[44] of *E*- and *Z*-allylic alcohol **1b** was reacted with r*Aae*UPO-PaDa-I-H and H_2O_2 (1.2 equiv.) under the standard epoxidation conditions. Both isomers of **1b** were fully converted by the UPO, with the major products observed in the reaction mixture being the *E*-aldehyde **4b** (likely derived from the *E*-allylic alcohol **1b-*E***) and epoxide **3b** (likely derived from *Z*-allylic alcohol **1b-*Z***). Both products were duly separated by column chromatography to deliver pure samples of both products **4b** and **3b** in reasonable yields on preparative scale. As previously, the *ee* of the isolated epoxide **3b** was high (99% *ee*). The formation of aldehyde **4b** rather than carboxylic acid **2b** in this reaction is likely to be a consequence of 1.2 equivalents of H_2O_2 being used, rather than the 2.25 equivalents favoured for the standard carboxylic-forming method used in Table 1. Pleasingly, similar results were obtained in four other cases in which *E*/*Z*-mixtures of allylic alcohols were used, with the respective epoxides (**3c**, **3h**, **3o**, **3p**) and aldehydes (**4c**, **4h**, **4o**, **4p**) all being formed and isolated cleanly using the same approach (**Scheme 3B**). In the case of the *t*-butyl substituted starting material **1k**, only the aldehyde product **4k** was obtained cleanly; *E*/*Z* isomerisation of the starting material likely contributed to low yield and purity of epoxide **3k** in this case.



Scheme 3. Biotransformations of allylic alcohols that exist as E/Z mixtures. [a] r*Aae*UPOPaDa-I-H, H_2O_2 (1.2 equiv. slow addition), pH 7 KPI buffer, CH_3CN 16 h, RT. Yield refers to isolated product after column chromatography. [b] *ee* determined by GC (see SI). [c] *E*/*Z* ratio based on analysis by ^1H NMR. [d] Compound **3k** could not be isolated cleanly. The yield quoted is adjusted considering the impurities, details of which are included in the Supporting Information (see Figure S45).

Finally, the utility and scalability of the epoxide-forming biotransformation was illustrated using the total synthesis of both enantiomers of the insect pheromone disparlure **6**, each of which were obtained in 99% *ee* (**Scheme 4**).[45] The (+)-enantiomer was synthesised from epoxide **3n** (itself prepared from **1n-*Z***, see **Table 1**), following an established sequence of alcohol oxidation, Wittig olefination and hydrogenation,[46] to afford disparlure **(+)-6** in 21% unoptimised yield over the 3-step sequence. To prepare the (–)-enantiomer **(–)-6**, an alternative epoxide **3o** was prepared using the standard r*Aae*UPO-PaDa-I-H method; notably, this reaction was done on gram-scale, and resulted in the isolation of 670 mg of analytically pure epoxide **3o** from a single biotransformation (49% yield, 99% *ee*). The analogous oxidation/Wittig/hydrogenation sequence was then performed starting from **3o**, which furnished (–)-disparlure **(–)-6** in 43% yield over the 3-step sequence.



Scheme 4. Total synthesis of both enantiomers of natural product disparlure. (a) TEMPO, $PhI(OAc)_2$, CH_2Cl_2, 0 °C → RT, 6 h; (b) n-BuLi, $RPPh_3Br$ (Wittig reagent), THF, –78 °C then add aldehyde, RT, 16 h; (c) Wilkinson's catalyst, H2, benzene, RT, 3 h, then $NaBH_4$, ethanol, RT, 30 min. For full synthetic details, see SI

Conclusion

In summary, r*Aae*UPO-PaDa-I-H and H_2O_2 can be used to promote the divergent oxidation of *E*- and *Z*-allylic alcohols with complementary selectivity, giving carboxylic acid/aldehyde and epoxide products respectively. Notably, we know of no chemical oxidation method that is able to discriminate between *E*- and *Z*-allylic alcohols in this way. The oxidations of *E*- and *Z*- substrates can be performed on preparative scale in good yields, with the epoxidations proceeding with excellent enantioselectivity (>99% ee). The divergent reactions can also be used to transform *E*/*Z* mixtures of allylic alcohols; this is especially useful in cases where the allylic alcohol is not available as a single geometrical isomer, as both product series can be isolated from a single reaction using the mixed starting material. Together, these results constitute a further illustration of the useful reaction scope of UPOs, but also of their scalability with respect to selective oxidation reactions, many more examples of which remain to be discovered.

Supporting Information

The authors have cited additional references within the Supporting Information.[47-125]

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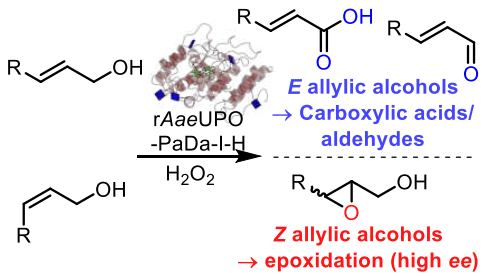

The Unspecific Peroxygenase r*Aae*UPO-PaDa-I-H catalyses the oxidation of *Z*- and *E*-allylic alcohols with complementary selectivity, giving epoxide and aldehyde/acid products respectively. Both reactions were performed on preparative scale with yields of up to 80%, and the epoxidations proceed with excellent enantioselectivity (>99%).

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