Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Selective synthesis of the resveratrol analogue 4,4'-dihydroxy-*trans*-stilbene and stilbenoids modification by fungal peroxygenases

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This **Supporting Information** includes Supporting Methods, Figures S1-S6 and Scheme S1.

Supporting Methods (definitions of process parameters):

- Conversion was calculated deducting the remaining substrate from the total concentration of substrate at the beginning of the reaction.

- Selectivity is referred to percentage (%) of one product within the total amount of products.

- Turnover number (kcat) is the maximum number of chemical conversions of substrate molecules per second that a single catalytic site will execute for a given enzyme concentration. It was obtained by fitting the data to the Michaelis-Menten equation.

- Total turnover number (TTN) was calculated dividing the mol of products (multiplied by the number of transformation suffered compared to substrate) by the mol of enzyme in the reaction.

- Yield was estimated comparing the mol of product obtained (calculated by GCMS with external standard curves) with the initial mol of substrate in the reaction.

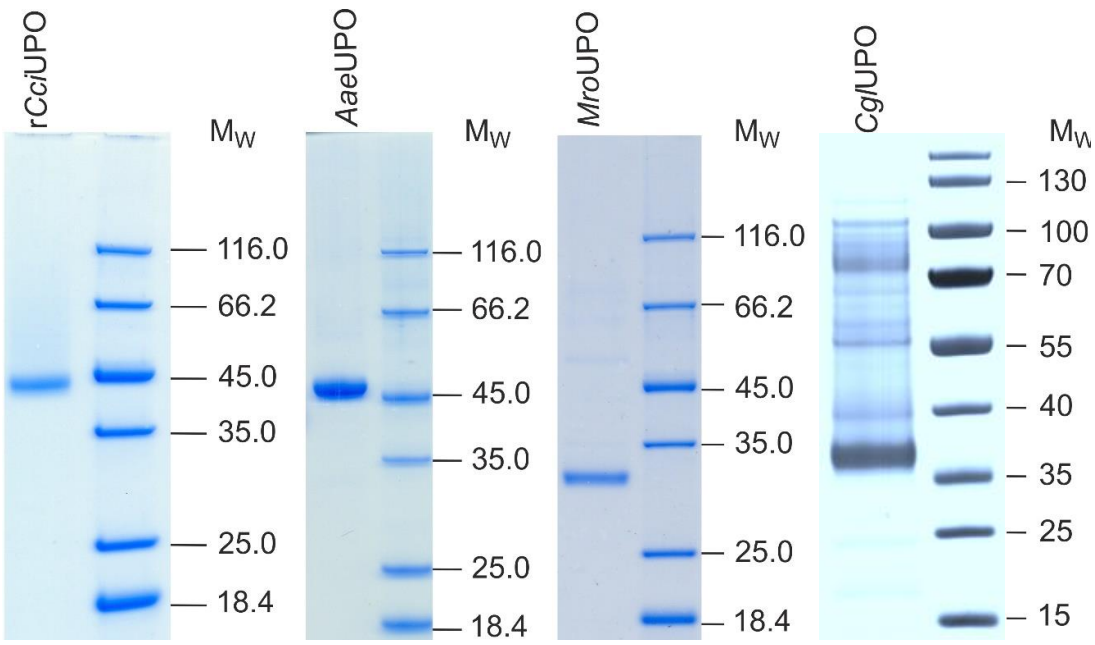

Figure S1. SDS PAGE of different UPO preparations, from left to right: r*CciUPO*, *Aae*UPO, *Mro*UPO and *Cgl*UPO. 10-12% Bis-Tris was used, and the proteins were visualized with a colloidal Blue staining (Invitrogen). Conditions (50 mM dithiothreitol) resulted in monomeric *Mro*UPO. Low molecular weight standards (Thermo Scientific, Darmstadt, Germany) were included.

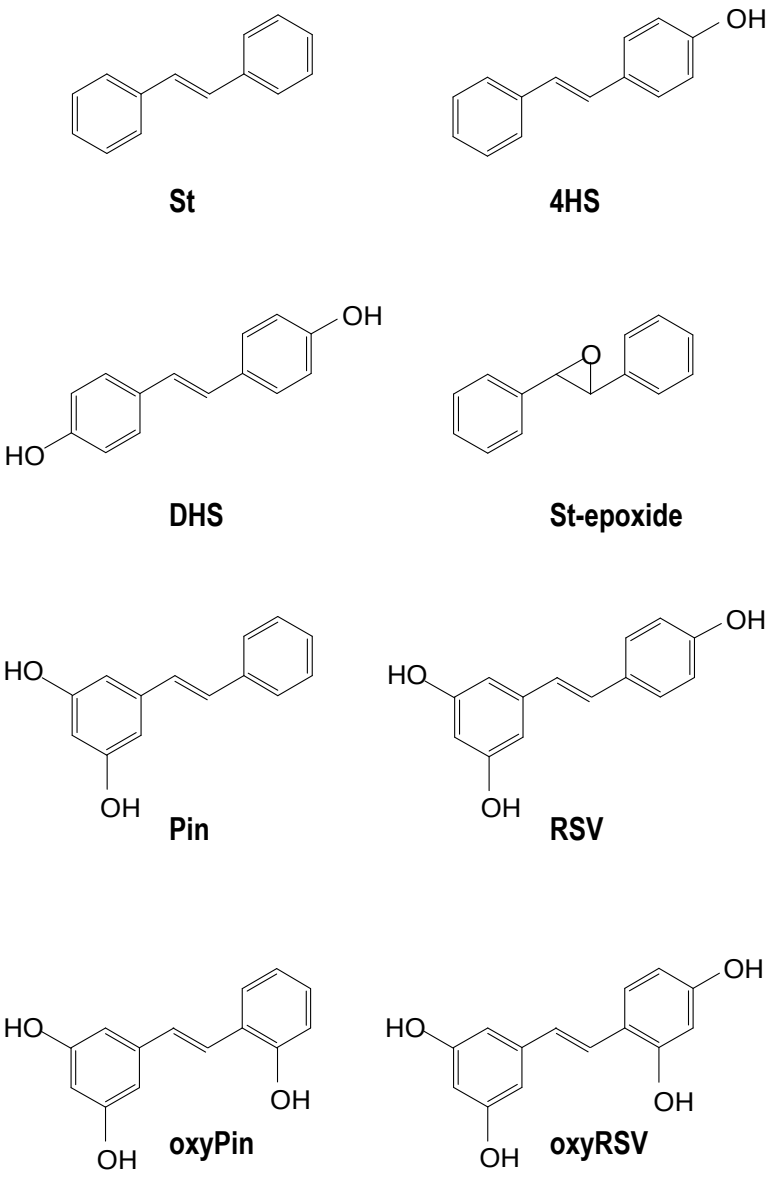

Figure S2. Chemical structures of *trans*-stilbene (St); 4-hydroxy-*trans*-stilbene (4HS); 4,4'-dihydroxy-*trans*-stilbene (DHS); *trans*-stilbene epoxide (St-epoxide); pinosylvin (Pin), resveratrol (RSV), oxypinosylvin (oxyPin) and oxyresveratrol (oxyRSV).

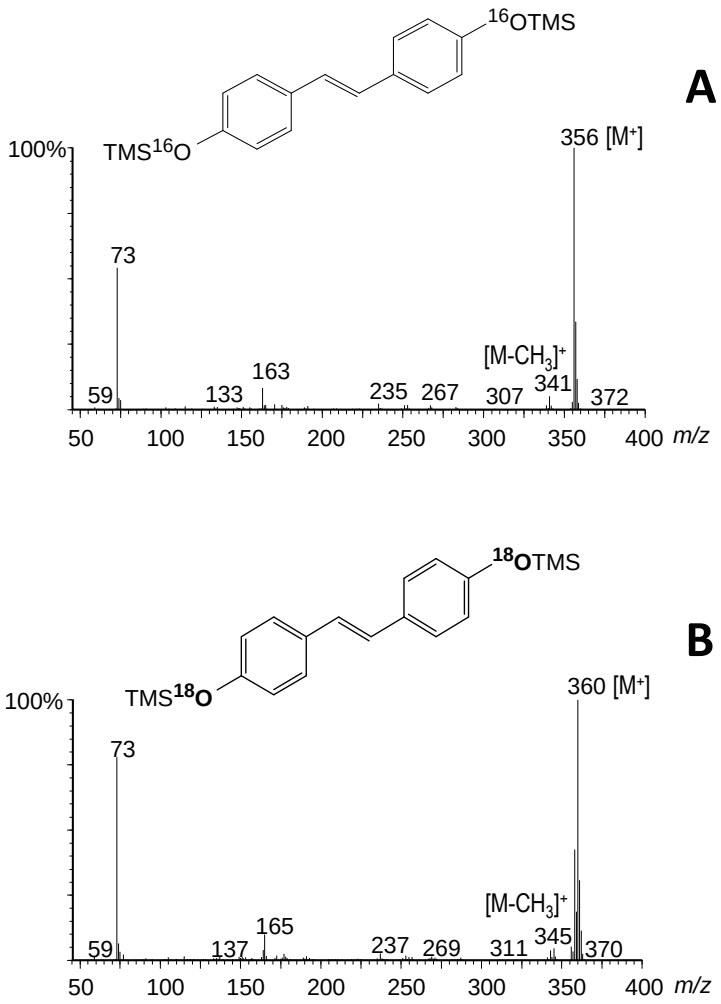

Figure S3. Mass spectra of 4,4'-dihydroxy-*trans*-stilbene from enzymatic reactions of *Aae*UPO, r*Cci*UPO and *Mro*UPO with *trans*-stilbene in O-labeling experiments (**B**) and controls (**A**). The formulae for the unlabeled compounds (A) and the labeled compounds (B) are shown as trimethylsilyl (TMS) derivatives.

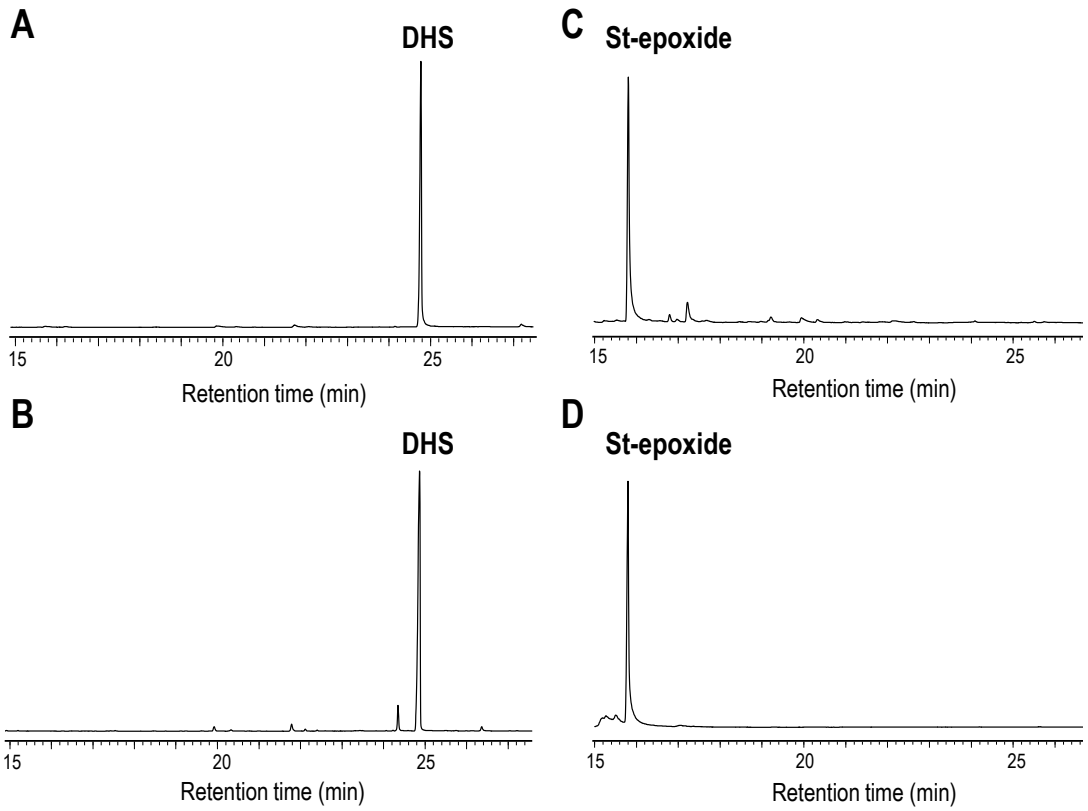

Figure S4. GC-MS chromatograms of 4,4'-dihydroxy-*trans*-stilbene (DHS) from *trans*-stilbene reaction with *Aae*UPO (**A**) and DHS standard (**B**); and of *trans*-stilbene epoxide (St-epoxide) from *trans*-stilbene reaction with *Cgl*UPO (**C**) and St-epoxide standard (**D**).

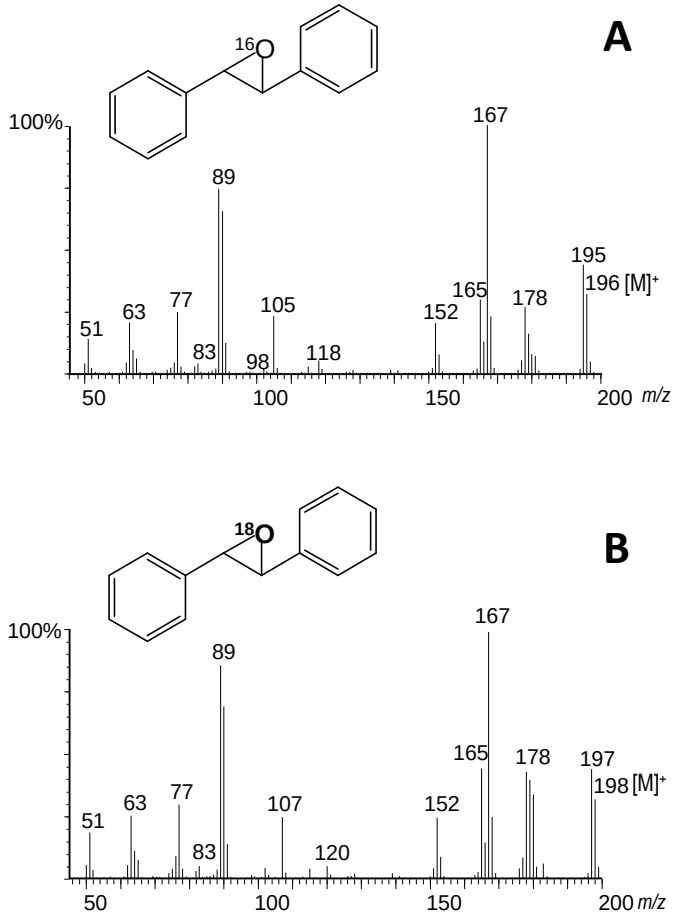

Figure S5. Mass spectra of *trans*-stilbene epoxide from enzymatic reactions of *Cgl*UPO with *trans*-stilbene in O-labeling experiments (**B**) and controls (**A**). The formulae for the unlabeled compounds (A) and the labeled compounds (B) are shown.

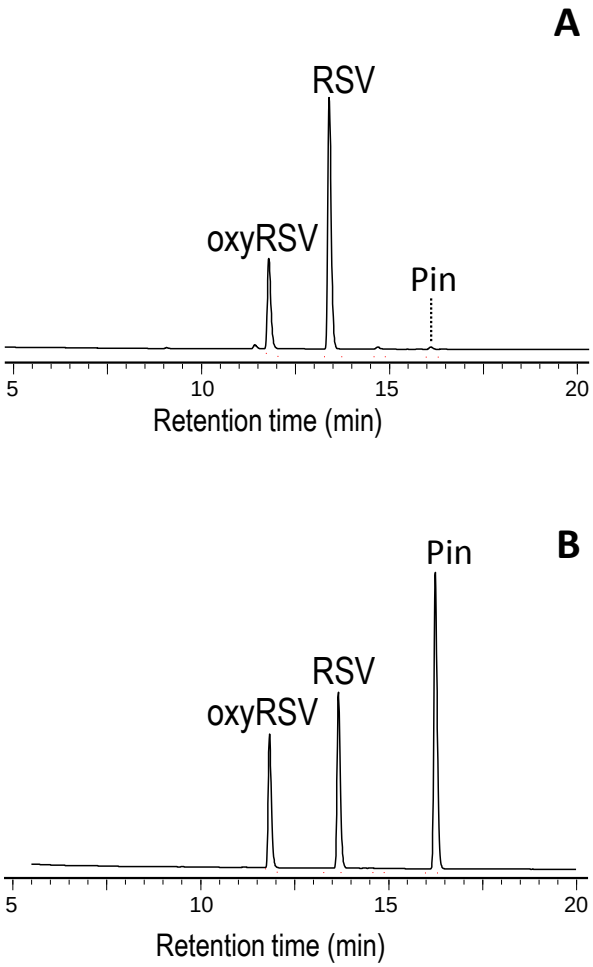

Figure S6. HPLC chromatograms of pinosilvin (Pin), resveratrol (RSV) and oxyRSV from Pin reaction with *Aae*UPO (**A**) and a mixture of autenthic standards (0.1 mM each) of Pin, RSV and oxyRSV (**B**).

Scheme S1. Comparison of step number and yield in (a) chemical,[7] and (b) enzymatic using UPO (this study) synthesis of 4,4'-dihydroxy-*trans*-stilbene (DHS).