Electronic Supplementary Information (ESI) to

A bifunctional old yellow enzyme from *Penicillium roqueforti* is involved in the ergot alkaloid biosynthesis

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Table S1 ¹H-NMR data for festuclavine

The spectra were taken at 500 MHz in CD₃OD whose signal was used as reference (3.31 ppm). The data correspond well to the NMR data for festuclavine published previously (Wallwey et al., Org. Biomol. Chem., 2010, 8, 3500-3508).
Table S2 ¹H-NMR data for chanoclavine-I aldehyde

The spectra were taken at 500 MHz in CDCl₃ whose signal was used as reference (7.26 ppm). The data correspond well to the NMR data for chanoclavine-I and chanoclavine-I aldehyde published previously (Wallwey et al., Microbiology, 2012, 158, 1634-1644).
Figure S1 LC-MS analysis of the in vitro assays with ChaDH, FgaOx3Pr3 and EasG. The reaction mixtures contained 1 mM chanoclavine-I, 10 µg enzymes, 5 mM of the respective cofactors and different concentrations of GSH and were incubated at 30°C for 16h.
Figure S2 Determination of the kinetic parameters for FgaDH\textsubscript{Pr}.

Figure S3 Determination of the kinetic parameters for FgaDH\textsubscript{Pr} in the presence of FgaOx3\textsubscript{Pr}.3.
Figure S4 Determination of the kinetic parameters for FgaDHPCa.

Figure S5 Determination of the kinetic parameters for FgaDHPCa in the presence of FgaOx3PC3.
Figure S6: Structure-based sequence alignments of different OYE s involved in the ergot alkaloid biosynthesis. The protein sequences were taken from the NCBI database with the accession numbers EAL94095 (FgaOx3 from A. fumigatus), CDM30151 (IfgG from P. roqueforti), CDM33403 (FgaOx3Pr3 from P. roqueforti), CAG28312 (EasA from C. purpurea) and AFM84626 (FgaOx3PC from P. commune).