Supplementary Table 1. Selected P450 enzymes used in this study. Sequence identity with respect to the heme domain of P450$_{BM3}$ was determined using ClustalW2.1.

Host organism	CYP	PDB ID	Sequence identity [%]
Bacillus megaterium P450$_{BM3}$	CYP102A1	2IJ2	100
Pseudomonas putida P450$_{cam}$	CYP101	3L62	17
Streptomyces turgidiscabies TxtE	-	4L36	17
Sulfolobus solfataricus	CYP119	1IO7	21
Mycobacterium sp. HXN-1500	CYP153A6	-	16

Supplementary Figure 1. Sequence alignment of P450 enzymes used in this study (ClustalW2.1). The highly conserved cysteine at the axial position is depicted in bold. The cysteine pocket is highlighted in gray.

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                                              Cys pocket
CYP119      YVRVWIASANRDEEVF-HDGEKFIPDRN-------PNPHLSFGSGIHLCLGAPLARLEAR 327
CYP153A6    KVVMWYVSGNRDPEAI-DNPDTFIIDRAK------PRQHLSFGFGIHRCVGNRLAELQLN 374
TxtE        TLALFLGSANRDANMF-ERPNDFDLDRPN------SARHLSFGQGVHACLAAQLISLQLK 367
P450cam     QILLPQMLSGLDEREN-ACPMHVDFSRQ-------KVSHTTFGHGSHLCLGQHLARREII 368
P450BM3     ELMVLIPQLHRDKTIWGDDVEEFRPERFENPSAIPQHAFKPFGNGQRACIGQQFALHEAT 411
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Supplementary Figure 2. Electronic absorption spectra of ferric (blue), dithionite reduced ferrous (red) and carbon monoxide bound ferrous (green) of **A)** CYP153A6-C363S **B)** P450$_{cam}$-C357S **C)** CYP119-C316S purified enzymes were normalized according to the hemochrome assay [4 µM].

A) CYP153A6-C363S: Fe^{III}, 405; Fe^{II}, 416, 427; Fe^{II}-CO, 413. Fe^{II}-CO displays α and β bands at 536 and 568 nm. The shoulder at 416 nm for the ferrous spectrum is due to incomplete reduction to Fe^{II} under aerobic conditions.
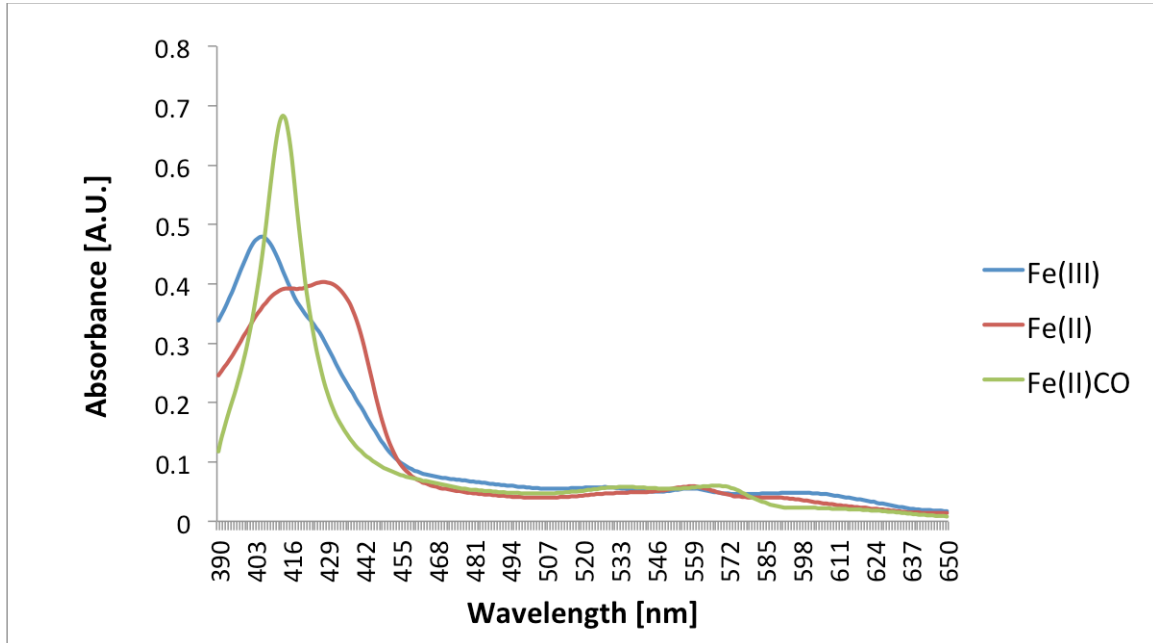
B) P450$_{cam}$-C357S: Fe^{III}, 423; Fe^{II}, 427; Fe^{II}-CO, 421. Fe^{II}-CO displays α and β bands at 538 and 568 nm.
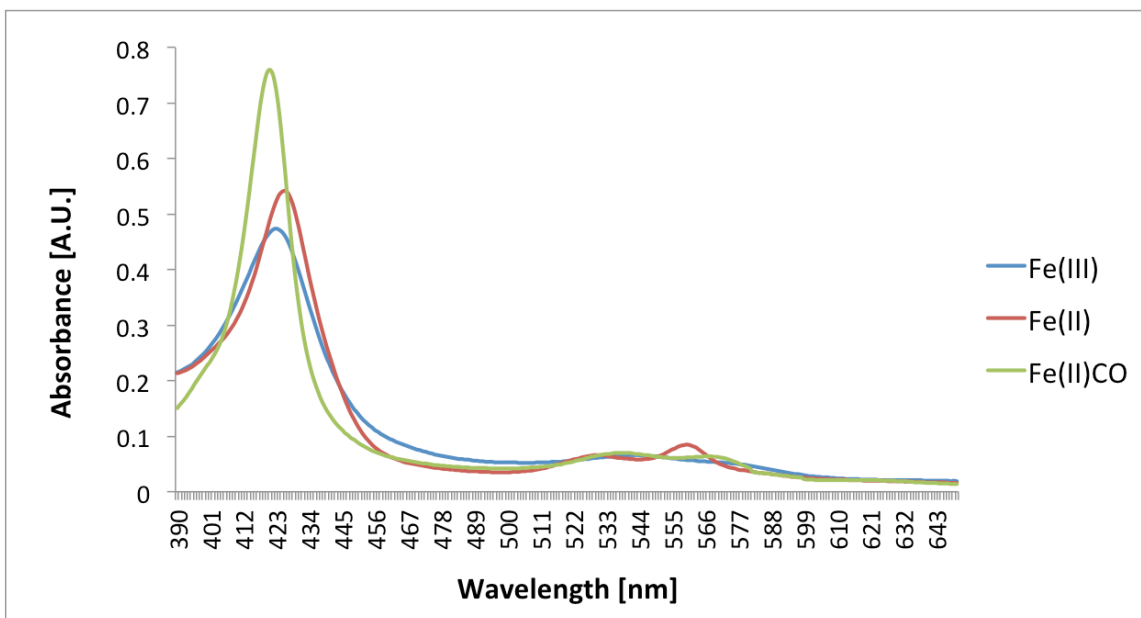
C) CYP119-C316S: Fe^{III}, 404; Fe^{II}, 422; Fe^{II}-CO, 407. Fe^{II}-CO displays α and β bands at 530 and 563 nm.
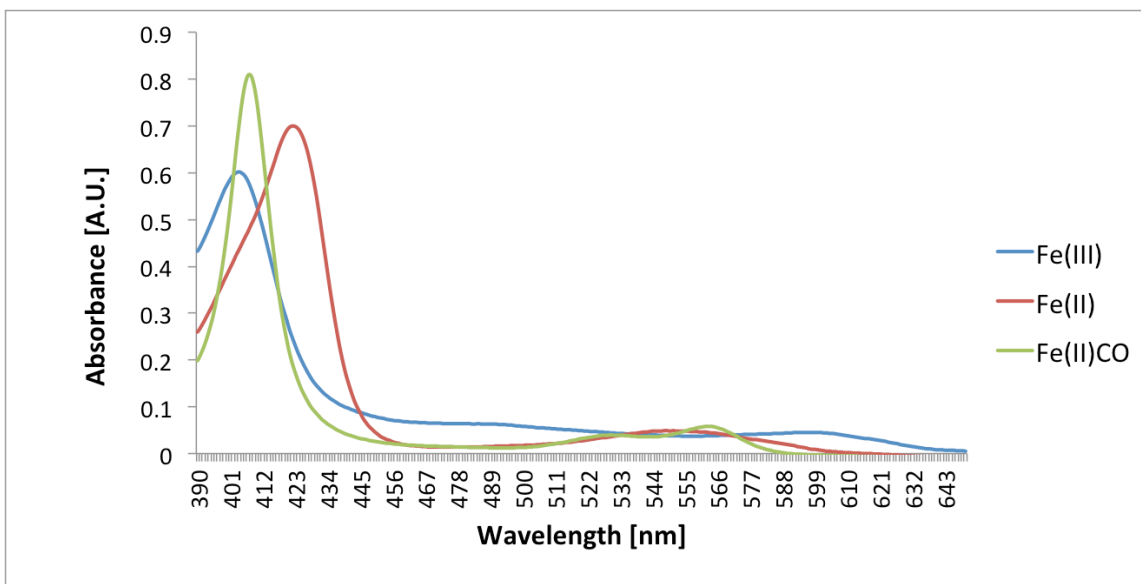
Supplementary Figure 3 A) Quantification of heme concentration of *E. coli* pET28 (empty plasmid) cell lysate used for whole cell cyclopropanation reactions. (**1**) without δ-ALA addition during cultivation, (**2**) 250 μM δ-ALA added during cultivation and (**3**) 1000 μM δ-ALA added during cultivation. **B**) Cell pellets of *E. coli* pET28 (empty) cultivation: (**1**) without δ-ALA addition, during cultivation, (**2**) with 250 μM δ-ALA addition, and (**3**) 1000 μM δ-ALA addition. Quantification represents duplicate measurements.
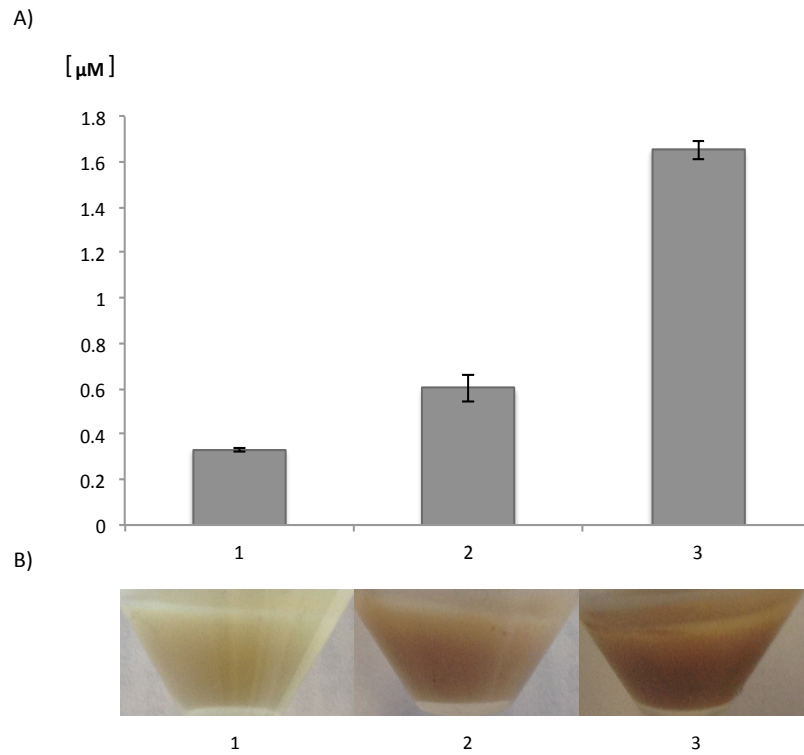
Supplementary Table 2. Whole cell catalysis of the reaction between styrene and EDA. M9-media was used as negative control. 5% EtOH co-solvent, 16 mM styrene, 8 mM EDA. The data represent triplicates with standard errors within the range of 20%. *rac* indicates enantioselectivity below 5% *ee*.

Catalyst:	yield [%]	EDA	cis/trans	cis_{ee} [%]	$trans_{ee}$ [%]
M9-media	-	8 mM	-	-	-
pET28-emtpy no δ-ALA	16	8 mM	12:88	*rac*	-26
pET28-emtpy 250 µM δ-ALA	28	8 mM	14:86	*rac*	-11
pET28-emtpy 1000 µM δ-ALA	43	8 mM	12:88	*rac*	-9

Supplementary Table 3. Activities, reported in terms of yield and total turnover number, of purified wild-type and axial Cys to Ser mutants of P450 enzymes for cyclopropanation of styrene using EDA under aerobic conditions. The data represent the average of triplicates with standard errors within the range of 20%. - denotes product formation below 1% yield; *rac* indicates enantioselectivity below 5% *ee*. *n/a* : enzyme could not be purified.

Catalyst:	yield [%]	TTN	cis/trans	cis_{ee} [%]	% $trans_{ee}$ [%]
P450$_{BM3}$-h	-	-	-	-	-
P450$_{BM3}$-h-C400S	-	-	-	-	-
CYP119	-	-	-	-	-
CYP119-C316S	7	71	87:13	38	17
CYP153A6	-	-	-	-	-
CYP153A6-C363S	12	117	10:90	*rac*	*rac*
TxtE	7	70	30:70	33	11
TxtE-C356S	*n/a*	*n/a*	*n/a*	*n/a*	*n/a*
P450$_{cam}$	10	102	49:51	-39	*rac*
P450$_{cam}$-C357S	22	220	10:90	-6	*rac*
hemin	-	-	-	-	-