Supplementary Materials

S1. General materials and methods

Optical densities of *E. coli* cultures were determined using a DU 730 Life Sciences UV/Vis spectrophotometer (Beckman Coulter) by measuring absorbance at 600 nm. *E. coli* were routinely cultured at 37 ˚C with shaking (190 rpm), unless stated otherwise.

Proton nuclear magnetic resonance spectra (^{1}H-NMR) were recorded using a Varian INOVA 500 (500 MHz) NMR spectrometer at 23 ˚C. Proton chemical shifts are expressed in parts per million (ppm, ∂ scale) and are referenced to residual protium in the NMR solvent ($CDCl_3$, ∂ 7.26 ppm; $(CD_3)_2SO$, 2.50 ppm; CD_3OD, 3.31 ppm). Coupling constants, *J*, are measured to the nearest 0.1 Hz and are presented as observed. Data is represented as: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet and/or multiple resonances), coupling constant (*J*) in Hertz. Carbon nuclear magnetic resonance spectra (^{13}C-NMR) were recorded using a Varian INOVA 500 (125 MHz) NMR spectrometer at 23 ˚C. Chemical shifts are quoted in parts per million (ppm, ∂ scale) and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, ∂ 77.2 ppm; $(CD_3)_2SO$, 39.5 ppm; CD_3OD, 49.0 ppm). Mass spectral data was acquired on an Advion Expression CMS mass spectrometer in electrospray ionization (ESI) mode. The capillary voltage was set to 3.5 kV, the drying gas temperature was set to 200 ˚C with a flow rate of 0.1 mL/min and a nebulizer pressure of 22 psi. Infrared (IR) spectroscopy was carried out using a Bruker ALPHA Platinum single reflection diamond ATR spectrometer. Gas chromatography (GC) was carried out using an Agilent 7890A GC instrument equipped with an Agilent HP-MoleSeive column (30 m x 0.53 mm, 50 μm film). The GC inlet was maintained at 250 ˚C and the samples were injected in split 10:1 mode. The carrier gas was helium (1 mL/min). Samples were equilibrated for 90 s at 40 ˚C and the heated to 180 ˚C at a rate of 25 ˚C per minute before the oven temperature was held at 180 ˚C for a final 5 minutes. The total run time was 12.1 minutes. Analytes were detected using a flame ionization detector (FID) with a heater temperature of 300 ˚C.

All non-aqueous reactions were performed in oven-dried round-bottom flasks fitted with rubber septa under a positive pressure of nitrogen. Air and moisture sensitive reagents were transferred by syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore-size, 230-400 mesh, Merck KGA) impregnated with a fluorescence indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light and then stained by submersion in aqueous ceric ammonium molybdate (CAM) or potassium permanganate solutions followed by brief heating

with a heat gun. Flash-column chromatography was performed as described by Still *et al.* employing silica gel (60 Å, 60-200 μM, standard grade, BDH silica gel).[1]

All chemicals and solvents were purchased from Sigma Aldrich. All catalysts used in the initial screen were purchased from Sigma Aldrich. 4-Vinyl anisole was purified by vacuum distillation prior to each experiment. The reagent 2-diazo-1-morpholinoethan-1-one was synthesized in two steps from bromoacetyl bromide according to a known procedure.[2] All water used experimentally was purified with a MilliQ (MQ) purification system. All NMR solvents were purchased from Cambridge Isotope Laboratories. Luria-Bertani Lennox (LB) medium was purchased from EMD Millipore. For all quantitative measurements by ^{1}H-NMR spectroscopy or GC, 1,3,5-trimethoxybenzene (TMB) was used as an internal standard. When quantifying by GC a standard curve was constructed over a range of analyte concentrations (10 μM-5.0 mM) providing linear relationships of $pA_{styrene}/pA_{TMB} = 1.167c_{styrene} + 0.01316$ (Figure S2), $pA_{\mathbf{1}}/pA_{TMB} = 1.401c_{\mathbf{1}} - 0.03179$ (Figure S3), $pA_{\mathbf{2}}/pA_{TMB} = 1.619c_{\mathbf{2}} + 0.07902$ (Figure S7), $pA_{\mathbf{3}}/pA_{TMB} = 1.601c_{\mathbf{3}} - 0.01831$ (Figure S8) and $pA_{\mathbf{4}}/pA_{TMB} = 1.543c_{\mathbf{4}} - 0.05021$ (Figure S9) (pA = peak area). Diastereomer ratios were calculated via integration of the corresponding product peaks by GC.

S2. Strains, media and culture conditions

E. coli BL21(DE3) and phenylalanine overproducing *E. coli* NST74(K-12) [aroH367, tyrR366, tna-2, lacY5, aroF394(fbr), malT384, pheA101(fbr), pheO352, aroG397(fbr)] were purchased from ATCC. Plasmid *p*Trc99A_*PAL2-FDC1* was obtained from Professor David R. Nielsen (Arizona State University). For use in reaction screening, electrocompetent *E. coli* BL21(DE3) cells were transformed with an empty commercial *p*ET-29b(+) expression plasmid (Addgene). Cells were recovered in 1 mL of LB for 1 h at 37 ˚C. Transformants were selected by plating on LB agar containing 50 mg/L kanamycin and incubating at 37 ˚C overnight. A single colony was picked and grown overnight in 5.0 mL of LB containing 50 mg/L kanamycin. The resulting overnight culture (0.8 mL) was added to 0.8 mL of 1:1 v/v LB:glycerol solution. The resulting cell-stock was frozen in liquid nitrogen, stored at –80 ˚C and used as required. Electrocompetent *E. coli* NST74(K-12) cells were transformed with a modified *p*Trc99A plasmid harbouring the *PAL2* gene (*Arabidopsis thaliana*) inserted into the *NcoI* and *XBalI* restriction sites, and the *FDC1* gene (*Saccharomyces cerevisiae*) inserted into the *SalI* and *HindIII* restriction sites. Cells were recovered in 1 mL of LB for 1 h at 37 ˚C. Transformants were selected by plating on LB agar containing 100 mg/L ampicillin and incubating at 37 ˚C overnight. A single colony was picked and grown overnight in 5.0 mL of LB containing 100 mg/L ampicillin. The resulting overnight culture (0.8 mL) was added to

0.8 mL of 1:1 v/v LB:glycerol solution. The resulting cell-stock was frozen in liquid nitrogen, stored at –80 ˚C and used as required.

M9-glucose media was prepared according to the following procedure: Na_2HPO_4 (9.0 g), KH_2PO_4 (4.5 g), NH_4Cl (1.5 g) and NaCl (0.8 g) were dissolved in 1.0 L of MQ water and autoclaved at 121 ˚C for 20 min. Upon cooling to room temperature 150 µL of 10 mg/mL of a filter-sterilized aqueous thiamine hydrochloride solution, 3.0 mL of a filter-sterilized aqueous 1.0 M $MgSO_4$ solution, 150 µL of a filter-sterilized aqueous 1.0 M $CaCl_2$ solution and 38 mL of a filter-sterilized aqueous 20% w/v glucose solution (0.5% w/v final concentration) were added. The total volume was adjusted to 1.5 L using autoclaved water. M9-glucose media was stored at 4 ˚C.

M9CA-glucose media was prepared according to the following procedure: Na_2HPO_4 (9.0 g), KH_2PO_4 (4.5 g), NH_4Cl (1.5 g), NaCl (0.8 g) and casamino acids (7.5 g) were dissolved in 1 L of MQ water and autoclaved at 121 ˚C for 20 min. Upon cooling to room temperature 150 µL of 10 mg/mL of a filter-sterilized aqueous thiamine hydrochloride solution, 3.0 mL of a filter-sterilized aqueous 1.0 M $MgSO_4$ solution, 150 µL of a filter-sterilized aqueous 1.0 M $CaCl_2$ solution and 38 mL of a filter-sterilized aqueous 20% w/v glucose solution (0.5% w/v final concentration) were added. The total volume was adjusted to 1.5 L using autoclaved water. M9CA-glucose media was stored at 4 ˚C.

MMI media was prepared according to the following procedure: Solid KH_2PO_4 (0.3 g) and K_2HPO_4 (1.0 g) were dissolved in 500 mL of MQ water and autoclaved at 121 ˚C for 20 min. Upon cooling to room temperature 100 mL of an autoclaved aqueous solution of $(NH_4)_2SO_4$ (40 g/L) and 100 mL of a filter-sterilized aqueous solution of MOPS (250 g/L) were added and the pH of the resulting solution was adjusted to 7.4 using NH_4OH. To this mixture, 100 mL of an autoclaved solution of 20% w/v glucose solution, 50 mL of a filter-sterilized aqueous solution of $MgSO_4 \cdot 7H_2O$ (10 g/L) and 10 mL of ATCC Trace Mineral Supplement (Catalog No. MD-TMS) [consisting of EDTA (0.5 g/L), $MgSO_4 \cdot 7H_2O$ (3.0 g/L), $MnSO_4 \cdot 7H_2O$ (0.5 g/L), NaCl (1.0 g/L), $FeSO_4 \cdot 7H_2O$ (0.1 g/L), $Co(NO_3)_2 \cdot 6H_2O$ (0.1 g/L), $AlK(SO_4)_2$ (0.01 g/L), H_3BO_3 (0.01 g/L), $Na_2MoO_4 \cdot 2H_2O$ (0.01 g/L), Na_2SeO_3 (0.001 g/L), $Na_2WO_4 \cdot 2H_2O$ (0.1 g/L) and $NiCl_2 \cdot 6H_2O$ (0.02 g/L)] were added. The total volume was adjusted to 1 L using autoclaved water. The media was then filter-sterilized and stored at 4 ˚C.

LB Lennox media was prepared according to the manufacturers instructions.

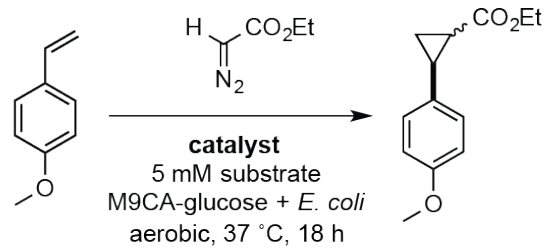
S3. Small-scale reaction screening in growth media and in *E. coli* BL21(DE3) cultures

Meso-tetraphenylporphyrin iron(III) chloride (FeTPPCl, 4.4 mg, 0.5 mM, 0.1 equiv) was weighed out into autoclaved 25 mL Hungate tubes. To these tubes, the appropriate growth media (12.5 mL) and kanamycin (50 mg/L) were added under aseptic conditions. When *E. coli* was used, a –80 ˚C LB:glycerol stock of *E. coli* BL21(DE3) harbouring the *p*ET29b(+) plasmid were inoculated on to LB agar plates containing 50 mgL^{-1} kanamycin using a sterile inoculation loop and incubated at 37 ˚C overnight. Overnight cultures were then grown by inoculation of a single colony from this plate into 5.0 mL LB containing 50 mg/L kanamycin. The resulting saturated overnight culture (1.0 mL) was then inoculated into 100 mL of either M9CA-glucose or LB media containing 50 mgL^{-1} kanamycin. Day cultures were carried out in baffled Erlenmeyer flasks. Cultures were grown aerobically at 37 ˚C (190 rpm) to an OD_{600} = 0.5–0.6, at which point 12.5 mL aliquots were transferred into autoclaved 25 mL Hungate tubes containing FeTPPCl. To these tubes, IPTG (0.6 mg, 0.2 mM), 4-vinylanisole (8.3 μL, 5.0 mM, 1.0 equiv) and ethyl diazoacetate (EDA, 13 μL, 10 mM, 2.0 equiv) were added. Tubes were quickly sealed with butyl rubber septa and aluminium crimp seals and inverted 2-3 times to ensure thorough mixing. Reactions were shaken horizontally at 190 rpm on a table-top shaker at 37 ˚C for 18 h. After this time, the reaction mixtures were extracted using ethyl acetate (4 x 5.0 mL) and concentrated under reduced pressure. The crude residue was dissolved in 1.5 mL $CDCl_3$ containing 8.0 mM TMB, dried over anhydrous sodium sulphate and analyzed by ^{1}H-NMR spectroscopy.

S4. Catalyst screen in *E. coli* BL21(DE3) cultures

Catalysts were weighed out into 25 mL Hungate tubes. Day cultures of *E. coli*_ *p*ET29b(+) were grown as described above. Cultures were grown aerobically at 37 ˚C (190 rpm) to an OD_{600} =0.5–0.6, at which point 12.5 mL aliquots were transferred into the Hungate tubes containing the catalysts. IPTG (0.2 mM), 4-vinylanisole (8.3 μL, 5.0 mM, 1.0 equiv) and EDA (13 μL, 10 mM, 2.0 equiv) were added to the cultures, the tubes were quickly sealed with butyl rubber septa and aluminium crimp seals and inverted 2-3 times to ensure thorough mixing. Reactions were shaken horizontally at 190 rpm on a table-top shaker at 37 ˚C. After the required amount of time, the cultures were extracted using ethyl acetate (4 x 5.0 mL) and concentrated under reduced pressure. The crude residue was dissolved in 1.5 mL $CDCl_3$ containing 8.0 mM TMB, dried over anhydrous sodium sulphate and analyzed by ^{1}H-NMR spectroscopy. Substrate/product concentrations were calculated relative to the TMB internal standard. Diethyl maleate (DEM) and diethyl succinate (DES) concentrations were calculated in an analogous manner.

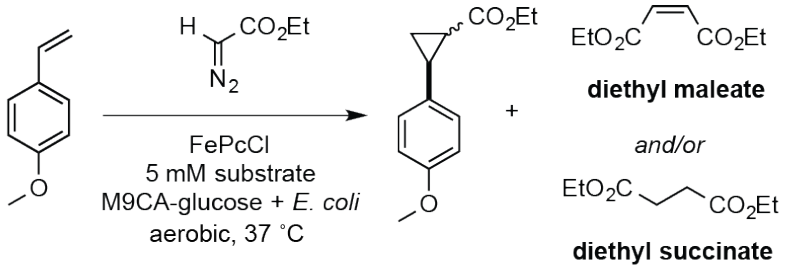
Table S1: *Catalyst screen*



Entry	Catalyst (mol %)	Yield (%)	*trans*:*cis*
1	5,10,15,20-tetraphenyl-21H,23H-porphine iron(III) chloride (10)	75	3.9:1
2	*meso*-tetrakis(pentafluorophenyl)porphine iron(III) chloride (10)	55	5.1:1
3	*meso*-tetrakis(*p*-methoxyphenyl)porphine iron(III) chloride (10)	7	2.9:1
4	iron(III) phthalocyanine chloride (10)	95	3.4:1
5	iron(II) phthalocyanine (10)	68	3.0:1
6	manganese(II) phthalocyanine (10)	0	–
7	*meso*-octaethylporphyrin iron(III) chloride (10)	0	–
8	hemin (10)	0	–
9	iron(III) chloride (10)	0	–
10	–	0	–
11	iron(III) phthalocyanine chloride (5)	93[a]	3.4:1
12	iron(III) phthalocyanine chloride (2.5)	90[b]	3.7:1
13	iron(III) phthalocyanine chloride (1)	80[b]	4.0:1

[a] 24 h reaction
[b] 48 h reaction

Table S2: *Diethyl maleate and diethyl succinate production*



Entry	Catalyst (mol%)	diethyl maleate (mM)	diethyl succinate (mM)
1	FePcCl (10)[a]	2.42	–
2	FePcCl (5)[b]	2.32	–
3	FePcCl (2.5)[c]	0.32	2.25
4	FePcCl (1)[c]	0.29	2.10
5	FePcCl (2.5)[c,d]	2.72	–

[a] 18 h reaction
[b] 24 h reaction
[c] 48 h reaction
[d] cells were boiled for 15 min prior to adding the reaction components

S5. Reaction toxicity screen

A series of reactions were set-up using the general procedure outlined in *Section S4*. To 12.5 mL cultures of *E. coli* BL21(DE3)_*p*ET29b(+) was added styrene (2.2 µL, 1.5 mM, 1.0 equiv), EDA (3.9 µL, 3.0 mM, 2.0 equiv) and FePcCl (0.3 mg, 38 µM, 2.5 mol%). Cultures containing no reagents or catalyst were also set up alongside these reactions. All experiments were performed in triplicate. Tubes were sealed with butyl rubber septa and aluminium crimp seals and inverted 2-3 times to ensure thorough mixing. Reactions were shaken horizontally at 190 rpm on a table-top shaker at 37 ˚C. After 48 h, 100 µL of each reaction mixture was removed and added to 900 µL of media (either M9CA-glucose or MM1). These aliquots were subjected to serial 10-fold dilutions (10^2–10^8). Aliquots (100 µL) of three different dilutions (10^5, 10^6, 10^7) were plated onto individual LB agar plates containing kanamycin (50 mg/L). The plates were incubated at 37 ˚C overnight. The number of colonies on the 10^6-dilution plate were used to calculate the number of colony-forming units (CFU's) in each original reaction mixture. The spent cultures were extracted using hexanes (4 x 5.0 mL) and concentrated under reduced pressure. The crude residue was dissolved in 1.5 mL $CDCl_3$ containing 8.0 mM TMB, dried over anhydrous sodium sulphate and analysed by ^{1}H-NMR spectroscopy.

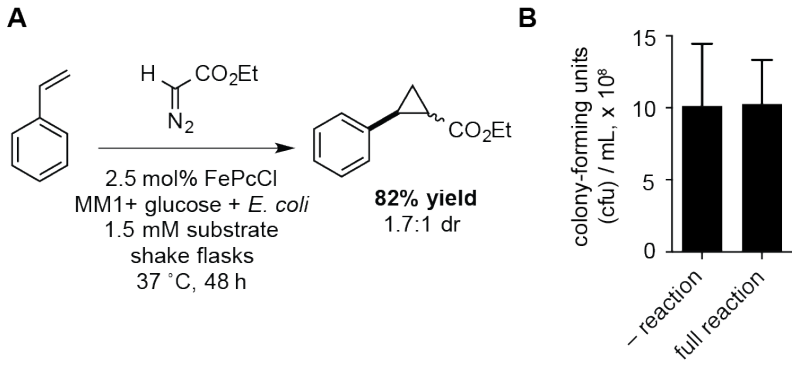


Figure S1: *(A) Assessing the reaction under conditions required for styrene production (B) Plate count assay*

S6. Styrene production using engineered *E. coli* NST74

A –80 ˚C LB:glycerol stock of *E. coli* NST74 harbouring the *p*Trc99A-*PAL2*/*FDC1* plasmid were inoculated onto LB agar plates containing 100 mg/L ampicillin using a sterile inoculation loop and incubated at 32 ˚C overnight. Overnight cultures were then grown by inoculation from a single colony on this plate into 5.0 mL LB containing 100 mg/L ampicillin

(32 ˚C, 220 rpm, 12–15 h). The overnight culture was then diluted 1:50 into an appropriate volume of MM1 media containing 100 mg/L ampicillin. Day cultures were carried out in Erlenmeyer flasks sealed with glass stoppers in order to avoid the loss of styrene via evaporation. A culture:headspace volume ratio of 1:5 was used at all times to maintain an aerobic atmosphere. Cultures were grown aerobically at 32 ˚C (220 rpm) to an OD_{600} =0.5–0.6, at which point protein expression was induced by the addition of IPTG to a final concentration of 0.2 mM. The pH of the culture was monitored frequently (typically every 3–6 h), and readjusted to pH 7.4 if necessary using autoclaved aqueous 6.0 M NaOH solution. Styrene production was monitored over a period of 48 h. Monitoring was accomplished by first transferring 800 µL of culture to a 2.0 mL Eppendorf vial. To this sample, hexanes (720 µL) was added, followed by TMB (80 µL, 10 mM in hexanes). The biphasic mixture was then vortexed for 20 min and pelleted via centrifugation (10 min, 13000 rpm). The organic layer (10 µL) was analysed by GC.

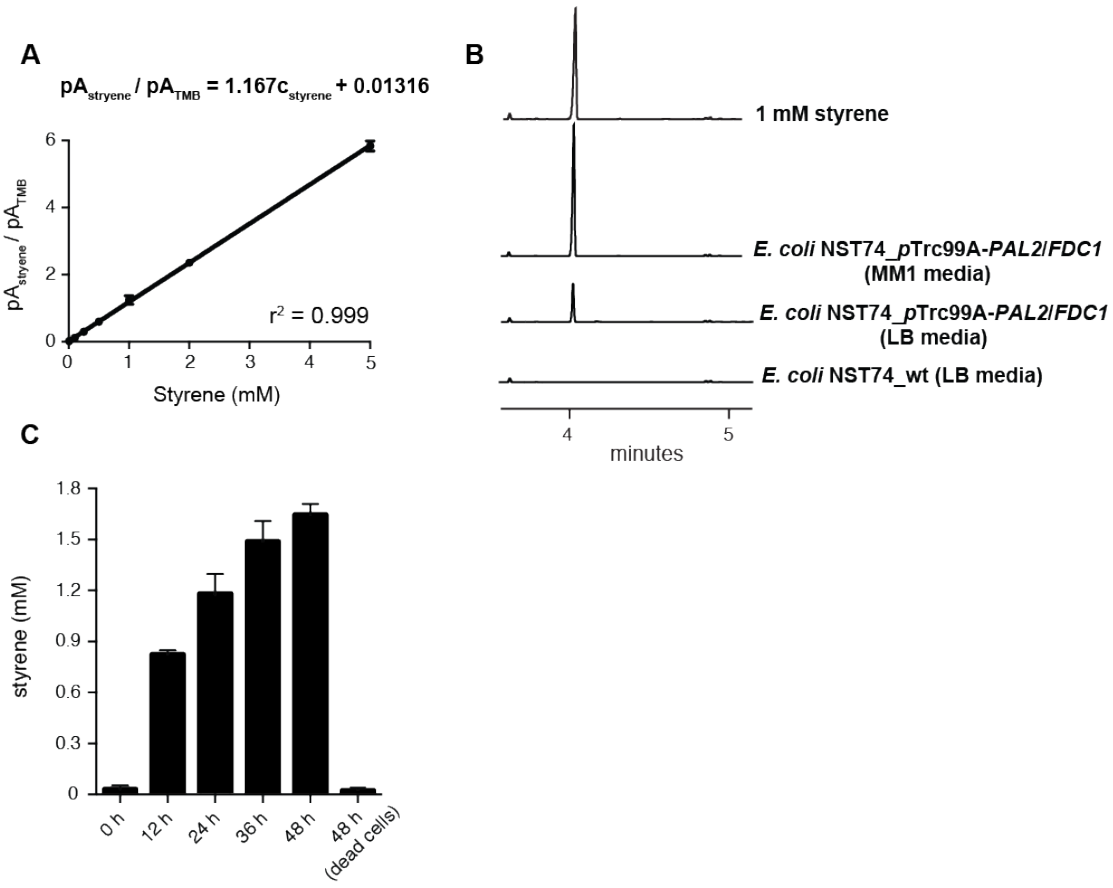
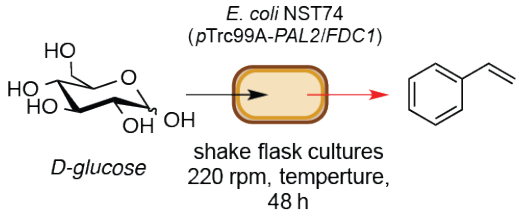


Figure S2: *(A) Standard curve for styrene quantification (B) GC trace of culture extracts and (C) Styrene production levels after IPTG induction*

Table S3. *Styrene production levels at various incubation temperatures*



Entry	Temperature (˚C)	styrene concentration (mM)
1	37	0.98
2	32	1.65
3	30	0.75

S7. Biocompatible cyclopropanation using metabolically-generated styrene

Day cultures of *E. coli* NST74_*p*Trc99A-*PAL2*/*FDC1* were grown as described in Section S6. Day cultures were grown aerobically at 32 ˚C (220 rpm) to an OD_{600} =0.5–0.6. Protein expression was induced by the addition of IPTG to a final concentration of 0.2 mM. At this point FePcCl (41 µM, 2.5 mol%) and EDA (1.0 mM, 0.6 equiv) were added to the cultures and the Erlenmeyer flasks were sealed using glass stoppers. Reactions were incubated at 32 ˚C (220 rpm) for 60 h. The pH of the culture was monitored frequently (typically every 4–6 h) and readjusted to pH 7.4 if necessary using autoclaved aqueous 6.0 M NaOH. Further portions of EDA (1.0 mM, 0.6 equiv) were added 12, 24, 36 and 48 h post-induction. After 60 h, 0.8 mL an aliquot of the culture was transferred to 2.0 mL Eppendorf vials. To this sample, hexanes (720 µL) was added, followed by TMB (80 µL, 10 mM in hexanes). The biphasic mixture was then vortexed for 20 min and pelleted via centrifugation (10 min, 13000 rpm). The organic layer (10 µL) was analysed by GC.

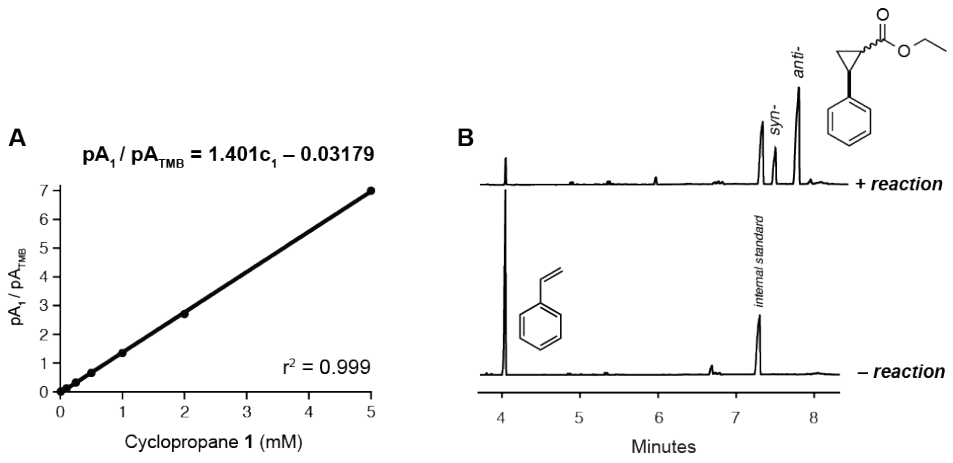


Figure S3: *(A) Standard curve used for cyclopropane* ***1*** *quantification (B) GC traces of culture extracts in the presence and absence of the reaction components after 60 h*

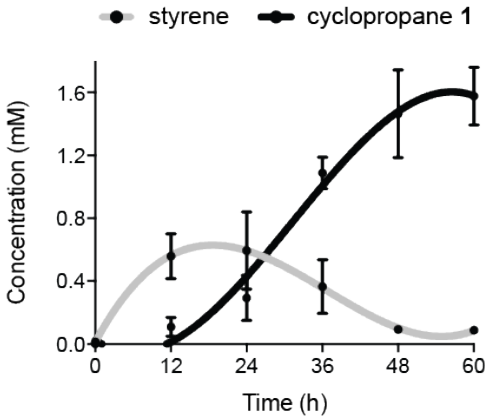


Figure S4: *Metabolite production during fermentations*

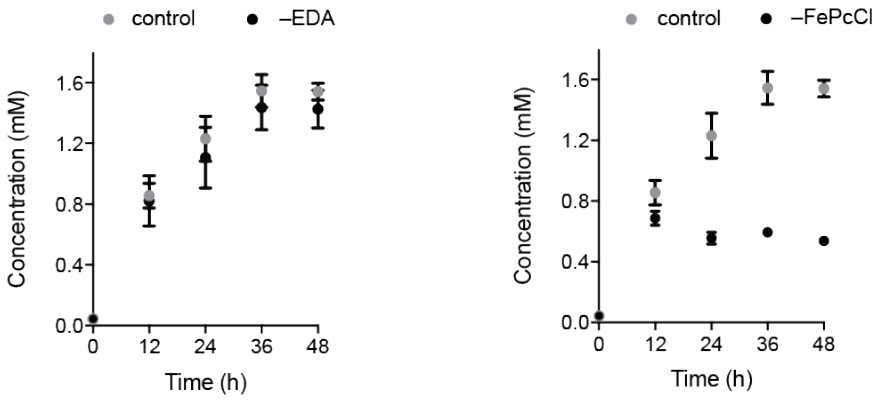
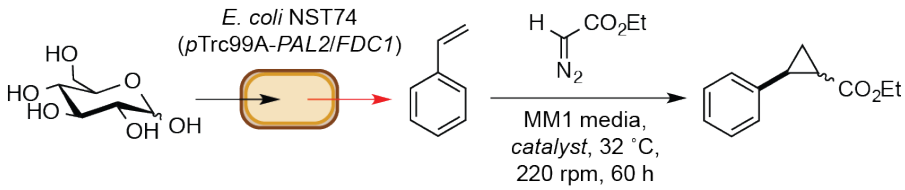


Figure S5: *The effect of EDA and FePcCl on overall styrene production*

Table S4: *Varying the catalyst and the catalyst loading*



Entry	Catalyst (mol%)	Conversion (%)	*trans*:*cis*
1	FePcCl (2.5)	95	3.5:1
2	FePcCl (1)	66	3.3:1
3	hemin (2.5)	27	2.2:1

S8. Three-phase test using a polymer-supported styrene

A solid-supported styrene substrate was synthesized using a commercially available Wang resin. To load the substrate, Wang resin (2.0 g, 1.0 mmol/g loading) was stirred in dichloromethane:*N*,*N*-dimethylformamide (9:1, 20 mL) for 15 min. To this mixture *N*,*N'*-diisopropylcarbodiimide (930 µL, 6.0 mmol), 4-vinylbenzoic acid (1.5 g, 10 mmol) and 4-(dimethylamino)pyridine (1.0 mg, 8.2 µmol) were added. The resulting mixture was stirred at room temperature for 3.0 days. After this time the solid resin was collected by filtration, washed with dichloromethane (3 x 20 mL) and dried under vacuum. Successful loading of 4-vinylbenzoic acid was confirmed by the appearance of a characteristic ester stretch in the IR spectrum of the product at 1615 cm^{-1}. Substrate loading was determined by treating 0.2 g of the product resin with trifluoroacetic acid (TFA):dichloromethane (1:1, 2.0 mL) and stirring for 2.0 h. After this time the resin was collected by filtration and washed with dichloromethane (3 x 20 mL). Remaining TFA was quenched in the organic filtrate by the addition of sodium bicarbonate solution (sat., aq.) until CO_2 evolution ceased. The organic phase was separated and discarded, the aqueous layer was acidified to pH 2.0 using HCl (1.0 M, aq.) and then washed with chloroform (3 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure to yield 4-vinyl benzoic acid (30 mg, 0.2 mmol, 100% yield).

To conduct the three-phase test, iron(III) phthalocyanine chloride (0.9 mg, 0.1 mM, 2.5 mol%) was weighed out into 25 mL Hungate tubes. To these tubes, M9CA-glucose growth media (12.5 mL) and kanamycin (50 mg/L) were added under aseptic conditions. IPTG (0.6 mg, 0.2 mM), polymer-supported 4-vinylbenzoic acid (63 mg, 5.0 mM, 1.0 equiv) and EDA

(13 µL, 10 mM, 2.0 equiv) were added to the cultures, the tubes were quickly sealed with butyl rubber septa and aluminium crimp seals and inverted 2-3 times to ensure thorough mixing. Reactions were shaken horizontally at 190 rpm on a table-top shaker at 37 ˚C for 48 h. After this time, the polymer was collected by vacuum filtration, washed with dichloromethane (4 x 5.0 mL), dried under vacuum, dissolved in TFA:dichloromethane (9:1, 2.0 mL) and stirred at room temperature for 2.0 h. After this time the resin was collected by vacuum filtration and washed with dichloromethane (4 x 5.0 mL). Remaining TFA was quenched in the filtrate by the addition of sodium bicarbonate solution (sat., aq.) until CO_2 evolution ceased. The organic phase was extracted and discarded, the aqueous layer was acidified to pH 2.0 using HCl (1.0 M, aq.) and then washed with chloroform (3 x 20 mL). The combined organic layers were concentrated under reduced pressure. Control reactions were carried out under identical reaction conditions, except methyl 4-vinylbenzoate (10 mg, 5.0 mM, 1.0 equiv) was used as the olefin component in place of the polymer-supported 4-vinylbenzoic acid. After 48 h these reactions were extracted using ethyl acetate (4 x 5.0 mL) and concentrated under reduced pressure. The crude residue was dissolved in 1.5 mL $CDCl_3$ containing 8.0 mM TMB, dried over anhydrous sodium sulphate and analyzed by ^{1}H-NMR spectroscopy.

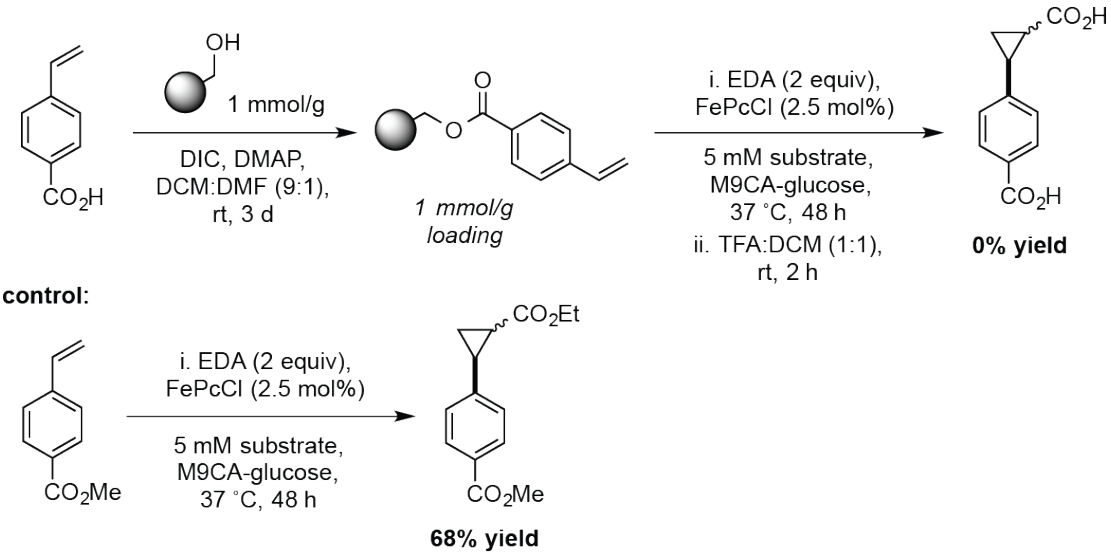


Figure S6: *Three-phase test*

S9. Cyclopropane isolation from 800 mL scale productions

Large-scale 800 mL productions were conducted as outlined in Section S7. After 60 h, a 0.8 mL aliquot from each culture was transferred to a separate 2.0 mL Eppendorf vial. To each sample, hexanes (720 µL) was added, followed by TMB (80 µL, 10 mM in hexanes). The biphasic mixtures were then vortexed for 20 min and pelleted via centrifugation (10 min, 13000 rpm). The organic layers (10 µL) were analysed by GC. The remaining spent cultures were extracted with chloroform (5 x 200 mL). The combined organic layers were washed with saturated aqueous sodium cholride solution (500 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Cyclopropanes **1**-**3** were purified by flash chromatography (0–5% ethyl acetate in hexanes for **1** and **2**, 0–5% diethyl ether in hexanes for **3**, 20–50% ethyl acetate in hexanes for **4**). Products were isolated as mixtures of *syn*- and *anti*- diastereomers. Isolated yields: **1** (233 mg, 93%), **2** (158 mg, 80%), **3** (203 mg, 75%), **4** (121 mg, 50%).

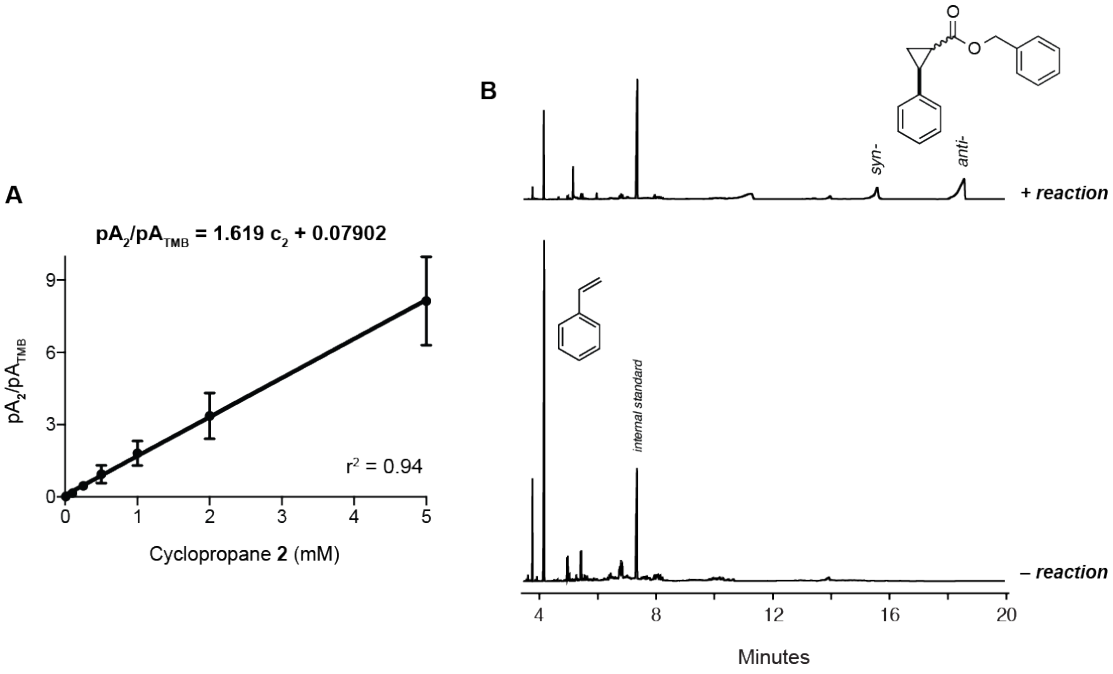


Figure S7: *(A) Standard curve used for cyclopropane* ***2*** *quantification (B) GC traces of culture extracts in the presence and absence of the reaction components after 60 h*

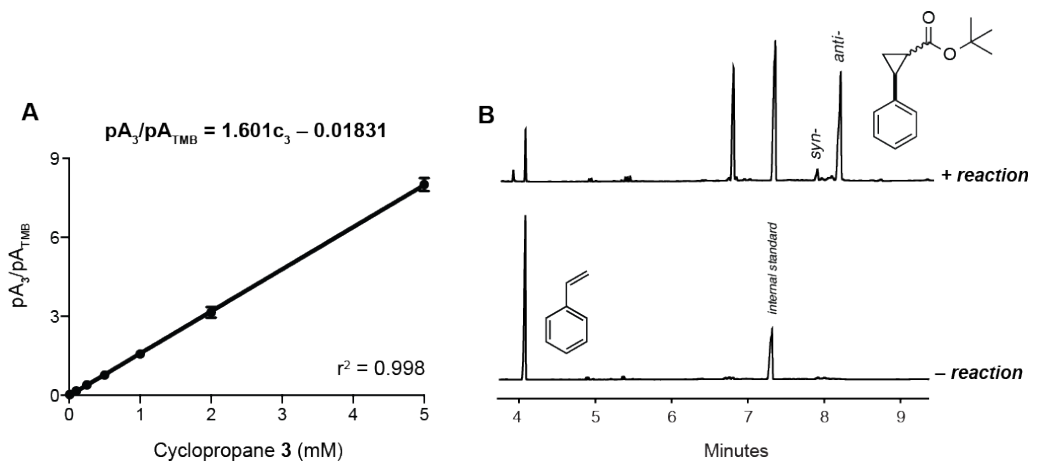


Figure S8: *(A) Standard curve used for cyclopropane* ***3*** *quantification (B) GC traces of culture extracts in the presence and absence of the reaction components after 60 h*

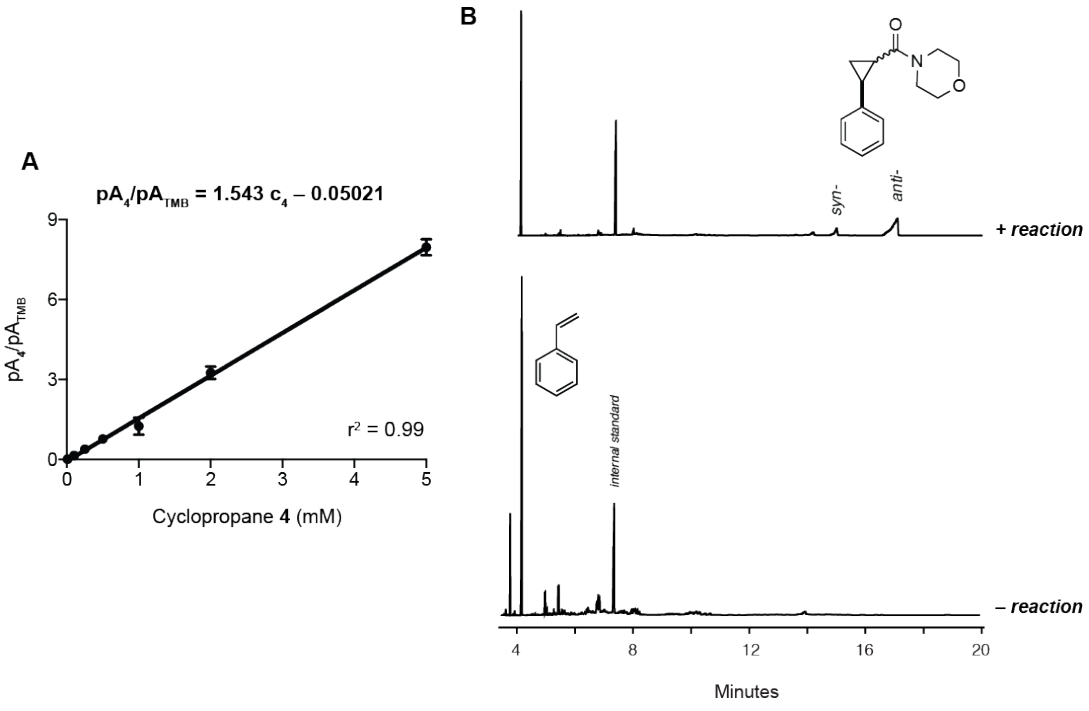
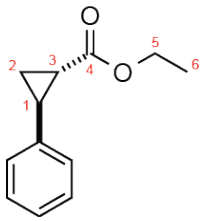


Figure S9: *(A) Standard curve used for cyclopropane* ***4*** *quantification (B) GC traces of culture extracts in the presence and absence of the reaction components after 60 h*

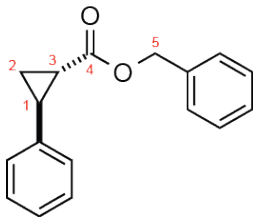
S10. Spectral characterization

*Characterization of cyclopropane **1***



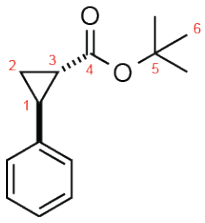
1 (*major diastereomer*): ∂_H ($CDCl_3$, 500 MHz); 7.32–7.05 (5H, m, Ar*H*), 4.18 (2H, q, *J* = 7.2 Hz, *H*5), 2.53 (1H, ddd, *J* = 9.2, 6.5, 4.2 Hz, *H*1), 1.91 (1H, ddd, *J* = 8.4, 5.3, 4.2 Hz, *H*3), 1.61 (1H, ddd, *J* = 9.2, 5.3, 4.6 Hz, $H2_a$) 1.35–1.29 (1H, m, $H2_b$), 1.29 (3H, t, *J* = 7.1 Hz, *H*6); ∂_C ($CDCl_3$, 125 MHz); 173.4 (*C*4), 140.1 (Ar), 128.4 (Ar), 126.4 (Ar), 126.1 (Ar), 60.7 (*C*5), 26.2 (*C*1), 24.2 (*C*3), 17.1 (*C*2), 14.3 (*C*6); υ_{max} (film)/cm^{-1} 1721 (C=O), 1177 (C–O); LRMS (ESI^+): m/z 212.9 (55% $[M+Na]^+$). The spectral data for both diastereomers was in accord with the literature.[3]

*Characterization of cyclopropane **2***



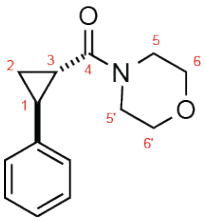
2 (*major diastereomer*): ∂_H ($CDCl_3$, 500 MHz); 7.41–7.10 (10H, m, Ar*H*), 5.19 (2H, s, *H*5), 2.60 (1H, ddd, *J* = 9.2, 6.5, 4.1 Hz, *H*1), 2.00 (1H, ddd, *J* = 8.4, 5.3, 4.2 Hz, *H*3), 1.69–1.65 (1H, m, $H2_a$), 1.39–1.34 (1H, m, $H2_b$); ∂_C ($CDCl_3$, 125 MHz); 173.2 (*C*4), 139.9 (Ar), 136.0 (Ar), 128.6 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 126.5 (Ar), 126.2 (Ar), 66.6 (*C*5), 26.4 (*C*1), 24.2 (*C*3), 17.3 (*C*2); υ_{max} (film)/cm^{-1} 1721 (C=O), 1163 (C–O); LRMS (ESI^+): m/z 275.0 (41% $[M+Na]^+$). The spectral data for both diastereomers was in accord with the literature.[3]

*Characterization of cyclopropane **3***



3 (*major diastereomer*): ∂_H ($CDCl_3$, 500 MHz); 7.32–7.04 (5H, m, Ar*H*), 2.44 (1H, ddd, *J* = 9.2, 6.4, 4.1 Hz, *H*1), 1.84 (1H, ddd, *J* = 8.4, 5.3, 4.2 Hz, *H*3), 1.53 (1H, ddd, *J* = 9.2, 5.3, 4.5 Hz, $H2_a$), 1.47 (9H, s, *H*6), 1.24 (1H, ddd, *J* = 8.4, 6.4, 4.5 Hz, $H2_b$); ∂_C ($CDCl_3$, 125 MHz); 172.5 (*C*4), 140.5 (Ar), 128.4 (Ar), 126.3 (Ar), 126.1 (Ar), 80.5 (*C*5), 28.2 (*C*6), 25.7 (*C*1), 25.3 (*C*3), 17.0 (*C*2); υ_{max} (film)/cm^{-1} 1719 (C=O), 1151 (C–O); LRMS (ESI^+): m/z 241.0 (54% $[M+Na]^+$). The spectral data for both diastereomers was in accord with the literature.[3]

*Characterization of cyclopropane **4***



4 (*major diastereomer*): ∂_H ($CDCl_3$, 500 MHz); 7.30–7.26 (2H, m, Ar*H*), 7.22–7.18 (1H, m, Ar*H*), 7.12–7.09 (2H, m, Ar*H*), 3.72–3.58 (8H, m, *H*5/*H*6), 2.50 (1H, ddd, *J* = 9.0, 6.2, 4.2 Hz, *H*1), 1.93 (1H, ddd, *J* = 8.3, 5.3, 4.3 Hz, *H*3), 1.69–1.65 (2H, m, *H*2); ∂_C ($CDCl_3$, 125 MHz); 170.6 (*C*4), 140.7 (Ar), 128.5 (Ar), 126.3 (Ar), 126.0 (Ar), 66.83 (*C*6), 66.75 (*C*6'), 46.0 (*C*5), 42.6 (*C*5'), 25.5 (*C*1), 22.9 (*C*3), 16.2 (*C*2); υ_{max} (film)/cm^{-1} 1633 (C=O), 1231 (C–N), 1114 (C–O); LRMS (ESI^+): m/z 231.3 (60% $[M+H]^+$). The spectral data for both diastereomers was in accord with the literature.[4]

S11. References

[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem*. **1978**, *43*, 2923–2925.

[2] A. Kaupang, T. Bonge-Hansen, *Beilstein J. Org. Chem*. **2013**, *9*, 1407–1413.

[3] M. P. A. Lyle, P. D. Wilson, *Org. Lett.* **2004**, *6*, 855–857.

[4] J. V. Ruppel, T. J. Gauthier, N. L. Snyder, J. A. Perman, X. P. Zhang, *Org. Lett*. **2009**, *11*, 2273–2276.