Supporting Information

Photobiocatalytic decarboxylation for olefin synthesis

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Material and Methods

Enzymatic decarboxylation of fatty acids

To 70 mL of a solution of stearic acid (0.5 mM) in Tris-HCl buffer (50 mM Tris, 200 mM NaCl, pH 7.5), cell-free extract containing recombinantly expressed $OleT_{JE}$ (7 mL), FMN (0.05 mM) and EDTA (50 mM) were added and incubated in a beaker at 28 °C. The beaker was illuminated using a white light bulb. After 15 h, the solution was acidified with hydrochloric acid (1 M) and extracted twice with ethyl acetate. The organic phase was washed twice with brine. Evaporation of the ethyl acetate, dissolution in n-hexane and washing with brine yielded 9 mg of a white solid containing a mixture of 1-heptadecene (74 %), β-hydroxy-stearic acid (21 %) and stearic acid (5 %), corresponding to 95% conversion of the starting material. Formation of 1- heptadecene and β-hydroxy-stearic acid was monitored by gas chromatography using a HP-5-MS column (30 m by 0.25 mm; 0.25 µm film) on a GC2010 device (Shimadzu Corp., Kyoto, Japan) with an FID detector or a GC/MS ITS40 device (Varian Deutschland GmbH, Darmstadt, Germany) using myristic acid as internal standard. To prevent degradation of hydroxy-fatty acids in the injector, samples were derivatized with an equal volume of N,O-bis(trimethylsilyl)trifluoro-acetamide with 1% trimethylchlorosilane (Sigma-Aldrich, Steinheim, Germany) to silylate the hydroxyl group. Stearic acid, 1-heptadecene and β-hydroxystearic acid were identified by comparison to their TMS-derivatized authentic standards. Formation of 1-heptadecene was further confirmed by NMR-analysis of the reaction product.

1-Heptadecene: yield: 6.5 mg (56% purity). ^{1}H NMR: δ=0.88 (3H, t, CH_3), 1.2 (26H, m, CH_2), 2.1 (2H, dt, CH_2), 4.9 (1H, dd, CHC**H$_2$**), 5.1 (1H, dd, CHC**H$_2$**), 5.8 (1H, m, C**H**); ^{13}C NMR: δ = 14.1, 22.7, 29.0-29.7, 29.1, 29.3, 29.5, 29.6, 29.7, 31.9, 33.8, 114.1, 139.3.

72.7 (q, J=33 Hz), 77.0 (s), 79.6 (s), 123.2 (q, J = 285 Hz), 125.9 (s), 129.0 (s), 131.6 (s), 139.7 (s); MS (EI): m/z=238 (M+), 111, 97, 83, 69, 55.

Supporting Figures

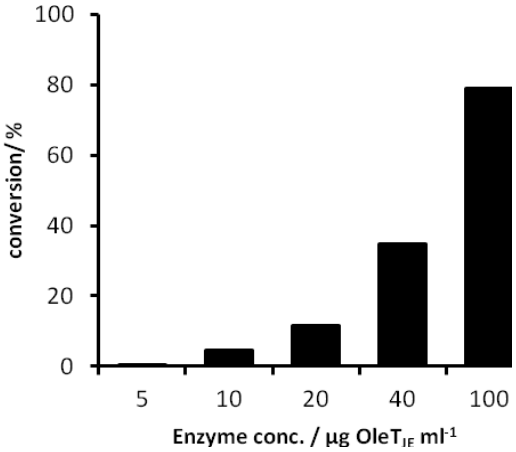

Figure S1 Photobiocatalytic conversion of stearic acid using different concentrations of His-tag purified OleTJE. General conditions: buffer: Tris-HCl (50 mM Tris, 200 mM NaCl, pH 7.5), T=25°C, OleTJE, Stearic acid (0.5 mM), FMN (0,01 mM), EDTA (50 mM), reaction volume (2 ml). Samples were taken after 2 h illumination with white light.