Experimental (Supporting information)

General

Novozym 435 (immobilized *Candida antarctica* lipase B*)* and SP525 (purified *Candida antarctica* lipase B*)* were kindly donated by Novo Nordisk. All reagents were purchased from Acros.

Analysis

Samples were dissolved in eluent and measured by HPLC using a custom-packed, 8x100 mm 6µ Waters Symmetry C18 RadialPak cartridge contained in a Waters RC 8 X 10 compression unit, a Waters 510 pump (flow 1 ml/min) and detected using a Shimadzu SPD-6A detector at 215 nm, a Shodex SE-61 RI detector and a Spectra Physics SP4270 integrator.

The conversion of ethyl butanoate was measured using as eluent methanol-water (60:40, v/v), containing 0.01M acetate buffer pH 4.3; reactions of ethyl octanoate, octanoic acid and cyclohexene were monitored using as eluent methanol-water (75:25, v/v), containing 0.01M acetate buffer pH 4.3 as eluent.

Reactions

In all cases, a blank reaction was performed in the absence of enzyme. All reactions were carried out at 40°C, unless noted otherwise.

Transesterification of ethyl butanoate. Ethyl butanoate (5 µl, 0.04 mmol, 0.04M) and butan-1-ol (0.2 mmol, 0.2M) were dissolved in solvent (1 ml) and enzyme (25 mg) was added. *m*-Dimethoxybenzene (7 µl) was used as internal standard.

Transesterification of ethyl octanoate. Ethyl octanoate (4 µl, 0.02 mmol, 0.01M) and alcohol (0.12 mmol) were added to solvent (0.5 ml) and Novozym 435 (25

mg) was added. *m*-Dimethoxybenzene was used as internal standard.

Ammoniolysis of ethyl octanoate and octanoic acid. Ethyl octanoate (29 μl, 0.3 M) was added to $[C_4mim][BF_4]$ or *tert*-BuOH (0.5 ml) previously bubbled with ammonia. Lipase (0.1025 KLU) was added as different preparations: free enzyme (SP525), SP525 immobilized in EP100 and Novozym 435 (immobilized on Lewatit E). *m*-Dimethoxybenzene used as internal standard. In the case of reaction with acid, 25 mg of Novozym 435 and molecular sieves 3 Å (0.1 g) were present.

Oxidation of cyclohexene by *in situ* generation of peroctanoic acid. Octanoic acid (30 μl, 0.189 mmol) and cyclohexene (150 μl, 1.48 mmol) were dissolved in solvent (0.5 ml). Novozym 435 (10 mg) was added and *m*-dimethoxybenzene (20 μl) was used as internal standard. H_2O_2 60% was added in 6 portions of 15 μl, with an interval of one hour. The reaction was carried at room temperature.

Isolation of products

Products were isolated by extraction with diethyl ether, followed by evaporation *in vacuo*, affording pure compounds according to HPLC (except when hydrolysis product is also formed, referred in text).