Tuning lipase B from *Candida antarctica* C-C Bond Promiscuous Activity by immobilization on Poly-Styrene–Divinylbenzene beads

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**General Procedure for the Preparation of Nitroalcohols.** A typical experiment procedure is as follows: Over a suspension of the corresponding aldehyde (0.57 mmol) in water (2.80 mL) were added nitromethane (5.7 mmol) and supported enzyme (200 mg). The mixture was shaken at 40 °C and 250 rpm for the corresponding time. After that time, the reaction was quenched by adding H2O (5 mL) and the aqueous phase extracted with CH2Cl2 (3 × 5 mL). The organic phases were combined, dried over Na2SO4 and filtered, and the solvent was removed by distillation under reduced pressure. The reaction crude was analyzed by NMR to determine the conversion.

The products were isolated and purified by column flash chromatography using hexane/AcOEt as already reported by us and others1,2
2-Nitro-1-(4-nitrophenyl)ethanol: *Rf* (20% EtOAc/hexane) 0.25; 1H NMR (CDCl₃, 300.13 MHz): δ 2.25 (brs, 1H), 4.58-4.61 (m, 2H), 5.63-5.68 (m, 1H), 7.64 (d, 3JHH ) 6.5 Hz, 2H), 8.26 (d, 3JHH ) 6.5 Hz, 2H);

13C NMR (CDCl₃, 75.5 MHz): δ 70.4 (CH2), 81.0 (CH), 125.5 (2CH), 127.4 (2CH), 145.5 (C), 148.5 (C).

**Figure 1.** ¹H NMR of 2-nitro-1-(4-nitrophenyl)ethanol. The conversion had been calculated using the following equation:

\[
C = \frac{A_c}{nH_c} \times 100 \div \left( \frac{A_c}{nH_c} + \frac{A_{c'}}{nH_{c'}} \right),
\]

where A is proton integration area and nH is number of protons of the corresponding signal.
2-Nitro-1-(4-nitrophenyl)propan-1-ol: *R**(20% EtOAc/hexane) 0.29; 1H NMR (CDCl₃, 300.13 MHz): δ 1.35 (d, 3JHH 7.1 Hz, 3Hsyn), 1.52 (d, 3JHH 7.1 Hz, 3Hanti), 3.20 (brs, 1Hsyn+1Hanti), 4.59-4.72 (m, 1Hsyn+1Hanti), 5.20 (d, 3JHH 9.3 Hz, 1Hsyn), 5.55 (d, 3JHH 3.5 Hz, 1Hanti), 7.58-7.63 (m, 1Hsyn+1Hanti), 8.21-8.35 (m, 1Hsyn+1Hanti); 13C NMR (CDCl₃, 75.5 MHz): δ anti 11.7 (CH₃), 72.3 (CH), 86.6 (CH), 123.8 (2CH), 126.9 (2CH), 145.2 (C), 148.1 (C). δ syn 16.1 (CH₃), 74.9 (CH), 87.7 (CH), 124.0 (2CH), 127.8 (2CH), 145.5 (C), 148.1 (C).

Figure 2. ¹H NMR of 2-nitro-1-(4-nitrophenyl)propan-1-ol. The conversion had been calculated using the following equation:

\[
C = \left[ \frac{(A_{c(syn)}^He)/H_{c(syn)}}{\sum (A_{e(syn)}^He)/H_{c(syn)}} + \frac{(A_{c(anti)}^He)/H_{c(anti)}}{\sum (A_{e(anti)}^He)/H_{c(anti)}} \right] \times 100
\]

where A is proton integration area and nH is number of protons of the corresponding signal.
Figure 3. $^1$H NMR spectrums of kinetic reaction carried out by PS-DVB-CALB at different times; a) 4h, b) 8h, c) 12h, d) 16h y e) 24h.