Supporting informations

1.1 General

^{1}H and ^{13}C NMR spectra were recorded in the indicated deuterated solvents in a Bruker Avance™ 400 spectrometer at 400.13 and 100.62 MHz, respectively. Chemical shifts (δ) are given as parts per million relative to the residual solvent peak and coupling constants (J) are in hertz. Column chromatography was performed on silica gel 60 (70-230 mesh) using the specified eluants. HPLC analyses were carried out in a DIONEX® apparatus equipped with a XTerra MS C_{18} (Phenomemex) column (3.5 µm, 3.0x100 mm) using (water+2.5% formic acid)/acetonitrile mixtures as the mobile phase (and detection by UV-vis detector at 225, 250, 266 and 275 nm). Optical densities (OD) were measured on a DAD-UV-Visible Agilent® spectrophotometer at 610 nm. ESI-MS spectra were acquired in positive or negative modes in a Waters® Micromass ZQ2000, using a 10 V cone voltage, 3 kV capillary voltage and 150°C source temperature. Melting points are uncorrected. The chemicals, solvents and materials for microbiological cultures were obtained from Sigma-Aldrich®, Fluka®, Carlo Erba®, Riedel-de Haen®, Difco® and used without further purification unless expressly specified.

1.2. Synthesis of ferrocenenitrile, (1)

To a homogeneous mixture of ferrocenecarboxaldehyde (107.0 mg, 0.5 mmol), $NH_2OH{\cdot}HCl$ (45.2 mg, 0.65 mmol), KI (83.0 mg, 0.5 mmol) and ZnO (40.7 mg, 0.5 mmol) in a round-bottom flask at room temperature under argon was added acetonitrile (5.5 ml). The resulting mixture was then refluxed for 2 h with efficient stirring and heating (oil bath temperature during the reflux should not exceed 100°C). Subsequently, aqueous $Na_2S_2O_3$ (5%, 1 mL) was added to the cooled mixture and the stirring was continued for additional 15 min. After the mixture was filtrated to remove solid particles, it was diluted with water (10 mL) and extracted with ethyl acetate (2 · 25 mL). Collected organic layers were dried on Na_2SO_4 anhydrous and concentrated in a rotary evaporator. The crude ferrocenenitrile (**1**) was purified by flash chromatography on silica gel using 19:1 hexane/ethyl acetate followed by 9:1 and 4:1 hexane/ethyl acetate, respectively, as the eluent. The orange fraction with Rf = 0.7 (2:1 hexane/ethyl acetate) was collected to give ferrocenenitrile (89.7 mg, 0.42 mmol, 85% yield; mp 106.7–107.0 °C, lit.[1] mp 107–108 °C). MS (ESI+): m/z 212 $[M+H]^+$. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 4.59 (t, 2H, J = 1.75 Hz, H(Cp)), 4.32 (t, 2H, J = 1.75 Hz, H(Cp)), 4.27 (s, 5H, H(Cp)); ^{13}C NMR ($CDCl_3$; 100 MHz): δ 120.1 (CN), 71.7 (C_5H_4), 70.6 (C_5H_4), 70.5 (C_5H_5), 51.8 (ipso-C_5H_4). Anal. calcd for $C_{11}H_9FeN$: C, 62.60; H, 4.30; N, 6.64. Found: C, 62.72; H, 4.31, N, 6.63.

1.3. Synthesis of (6-nitrilehexyl)ferrocene, (3)

A mixture of (6-bromohexyl)ferrocene (67 mg, 0.19 mmol), sodium cyanide (137 mg, 15 mol-equiv.) and dry DMF (0.7 mL) was stirred for 20 h at 100 °C. Toluene (10 mL) was added to the mixture, and an insoluble material was removed by filtration. The filtrate was concentrated and the residue purified by flash chromatography on silica gel using 19:1 hexane/ethyl acetate followed by 9:1 and 4:1 hexane/ethyl acetate, respectively, as the eluent affording compound **3** as a reddish oil (39.3 mg, 0.13 mmol, 68% yield). MS (ESI+): m/z 296 $[M+H]^+$. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 4.51 (t, 2H, J = 1.75 Hz, H(Cp)), 4.29 (t, 2H, J = 1.75 Hz, H(Cp)), 4.17 (s, 5H, H(Cp)), 3.07(t, 2H, *J*=6.9 Hz, -CH2-CN), 2.31 (t, 2H, *J* = 7.5 Hz, Cp-CH2-), 1.65-1.44 (m, 12 H, -CH2-). Anal. calcd for $C_{17}H_{21}FeN$: C, 69.17; H, 7.17; N, 4.74. Found: C, 68.95; H, 7.13; N, 4.72.

1.4. Microorganisms and cultures

The bacterial strains were maintained at 4 °C on meat peptone agar (in g/L, Bacto beef extract 3, peptone 10, NaCl 5, agar 15). *Rhodococcus erythropolis* A4[28] was grown for 2 days at 28 °C in shaken 500-mL Erlenmeyer flasks containing 100 mL of basal salts broth according to Di Geronimo and Antoine,[2] supplemented with 10 g/L of glycerol and 3 g/L of yeast extract.

Preculture of *R. rhodochrous* PA-34 was prepared by inoculating 50 mL of medium M4 containing (L^{-1}) 10.0 g glycerol, 5.0 g peptone, 3.0 g malt extract and 3.0 g yeast extract (pH 7.0) with a loop full of culture from the slant and was incubated at 30 °C, 160 rpm for 24 h. To the production medium (medium M4 containing 20 mg $CoCl_2$ L^{-1}), preculture (4%, v/v) and acetonitrile, butironitrile or valeronitrile (0.2%, v/v) as inducer were added and the solution incubated at 30 °C, 160 rpm for 36 h.

1.5. Preparation of whole-cell catalysts

Whole cells of *Rhodococcus erythropolis* A4 were harvested by centrifugation and washed with Tris-HCl buffer (50 mM, pH 8). Whole cells of *Rhodococcus rhodochrous* PA-34 were harvested by centrifuging the culture at 4000 x g for 15 min, washed twice with 100 mM potassium phosphate buffer (pH 7.0). Biomasses were stored at -4°C, until their usage.

The activities of nitrile-transforming enzymes and amidase were determined with benzonitrile and benzamide, respectively, using the previously described assays.[3,4] The nitrile hydratase and amidase activities in whole cells of *R. erythropolis* A4 were approx. 1.4 and 0.3 U mg^{-1} of dry cell weight, respectively. The nitrile hydratase and amidase activities in whole cells of *Rhodococcus rhodochrous* PA-34 were approx. 1.2 and 0.5 U mg^{-1} of dry cell weight, respectively.

1.6. Preparation of cell-free extract of *Rhodococcus erythropolis* A4

Whole cells of *Rhodococcus erythropolis* A4 suspended in Tris/HCl buffer (50 mM, pH 8) were disrupted using a Retsch MM-200 oscillation mill as described previously.[3] The cell extracts were immediately used for biotransformations. The activities of nitrile hydratase and amidase were approx. 3 and 0.7 U mg^{-1} of protein, respectively.

1.7. General procedure for biotransformations with whole cells of *Rhodococcus erythropolis* A4

A 10 mM solution of substrate was prepared using a suspension of biomass in Tris-HCl buffer (50 mM, pH 8), having an optical density (OD) value of approx. 15. A percentage of MeOH up to 5% was previously used to solubilise the substrate. The suspension was shaken (200 rpm) at 35°C; aliquots were drawn at regular time intervals and analysed by TLC (80:20 hexane/ethyl acetate) and HPLC analysis.

1.8. General procedure for biotransformations with whole cells of *Rhodococcus rhodochrous* PA-34

A 10 mM solution (5 ml) of substrate was prepared using a suspension of 10 mg of wet biomass in 100 mM potassium phosphate buffer (pH 7.0). A percentage of MeOH up to 5% was previously used to solubilise the substrate. The suspension was shaken (200 rpm) at 35°C; aliquots were drawn at regular time intervals and analysed by TLC (80:20 hexane/ethyl acetate) and HPLC analysis.

1.9. Synthesis of ferrocenyl carboxamide (4): biotransformation of 1 catalysed by whole cells from *Rhodococcus rhodochrous* PA-34

Substrate **1** (10 mg, 0.05 mmol) was dissolved in 150 µl of MeOH and used to prepare a 10 mM solution with a suspension of 10 mg of wet biomass in 100 mM potassium phosphate buffer (pH 7.0). The mixture was shaken (200 rpm) at 35°C for 24 hours, then stopped by centrifugation of the solution, extracted with ethy acetate, dried over Na_2SO_4 anhydrous, and evaporated under vacuum at 40°C. The mixture was purified by flash chromatography on silica gel using 19:1 hexane/ethyl acetate followed by 9:1, 4:1 and 3:2 hexane/ethyl acetate, respectively, as the eluents, and yielded compound **4** (10.1 mg, 0.045 mmol, 90% yield). The course of the reaction was monitored by TLC and HPLC analysis. MS (ESI+): m/z 230 $[M+H]^+$. All NMR data were in accordance with data reported in literature.[5] Anal. calcd for $C_{11}H_{11}FeNO$: C, 57.68; H, 4.84; N, 6.11. Found: C, 57.72; H, 4.81; N, 6.09.

1.10. Synthesis of ferrocenyl methylcarboxamide (6) and ferrocenylmethyl carboxylic acid (7): biotransformation of 1 catalysed by whole cells from *Rhodococcus rhodochrous* PA-34

Substrate **2** (10 mg, 0.04 mmol) was dissolved in 150 µl of MeOH and used to prepare a 10 mM solution with a suspension of 10 mg of wet biomass in 100 mM potassium phosphate buffer (pH 7.0). The mixture was shaken (200 rpm) at 35°C for 24 hours, then stopped by centrifugation of the solution, extracted with ethyl acetate, dried over Na_2SO_4 anhydrous, and evaporated under vacuum at 40°C. The mixture was purified by flash chromatography on silica gel using 19:1 hexane/ethyl acetate followed by 9:1, 4:1, 3:2 and 1:1 hexane/ethyl acetate, respectively, as the eluents, and yielded compound **6** (5.9 mg, 0.024 mmol, 61% yield) and compound **7** (2.4 mg, 0.01 mmol, 25% yield). The course of the reaction was monitored by TLC and HPLC analysis.

Ferrocenyl methylcarboxamide (6): MS (ESI+): m/z 244 $[M+H]^+$. ^{1}H-NMR (DMSO): ^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.22 (bs, 1H, CONHa), 6.95 (bs, 1H, CONHb), 4.68 (d, 2H, *J* = 4.7 Hz, H(Cp)), 4.34 (d, 2H, *J* = 4.8 Hz, H(Cp)), 4.17 (s, 5H, H(Cp)), 3.84 (d, 1H, *J* = 13.2 Hz, CHa), 3.38 (d, 1H, *J* = 13.2 Hz, CHb); ^{13}C NMR (DMSO); 100 MHz): δ 172.0 ($CONH_2$), 71.5 (C_5H_4), 70.7 (C_5H_4), 70.5 (C_5H_5), 51.4 (ipso-C_5H_4), 45.1 (CH_2). Anal. calcd for $C_{12}H_{13}FeNO$: C, 59.29; H, 5.39; N, 5.76. Found: C, 59.20; H, 5.43; N, 5.69.

Ferrocenylmethyl carboxylic acid (7): MS (ESI-): m/z 243 $[M-H]^-$. ^{1}H-NMR (DMSO): ^{1}H NMR ($CDCl_3$; 400 MHz): δ 4.64 (d, 2H, *J* = 4.7 Hz, H(Cp)), 4.32 (d, 2H, *J* = 4.8 Hz, H(Cp)), 4.18 (s, 5H, H(Cp)), 3.91 (d, 1H, *J* = 13.0 Hz, CHa), 3.42 (d, 1H, *J* = 13.0 Hz, CHb); ^{13}C NMR ($CDCl_3$); 100 MHz): δ 177.0 (COOH), 71.9 (C_5H_4), 70.8 (C_5H_4), 70.6 (C_5H_5), 52.4 (ipso-C_5H_4), 41.5 (CH_2). Anal. calcd for $C_{12}H_{12}FeO_2$: C, 59.05; H, 4.96; Found: C, 59.10; H, 4.94.

1.11. Synthesis of compounds (6-carboxamidohexyl)ferrocene (8) and 6-ferrocenylhexyl carboxylic acid (9): biotransformation of 3 catalysed by whole cells from *Rhodococcus erythropolis* A4

Compound **3** (15 mg, 0.05 mmol) was dissolved in 550 µl of MeOH, and added to a suspension containing whole cells from *Rhodococcus erythropolis* A4 (OD = 17; approx. 3.9 mg dry cell weight mL^{-1}) in Tris-HCl buffer (50 mM, pH 8). The mixture was shaken (200 rpm) at 35°C for 24 hours, then stopped by centrifugation of the solution, extracted with ethyl acetate, dried over Na_2SO_4 anhydrous, and evaporated under vacuum at 40°C. The mixture was purified by flash chromatography on silica gel using 19:1 hexane/ethyl acetate followed by 9:1, 4:1, 3:2 and 1:1 hexane/ethyl acetate, respectively, as the eluents, and yielded compound **8** (4.7 mg, 0.015 mmol,

30% yield), and compound **9** (5.5 mg, 0.017 mmol, 35% yield). The course of the reaction was monitored by TLC and HPLC analysis.

(6-Carboxamidohexyl)ferrocene (8): MS (ESI+): m/z 314 $[M+H]^+$; ^{1}H-NMR (CD_3OD): ^{1}H NMR ($CDCl_3$; 400 MHz): δ 4.49 (t, 2H, J = 1.75 Hz, H(Cp)), 4.28 (t, 2H, J = 1.75 Hz, H(Cp)), 4.17 (s, 5H, H(Cp)), 2.31 (t, 2H, *J* = 7.5 Hz, Cp-CH2-), 2.25 (t, 2H, *J*=6.9 Hz, -CH2-$CONH_2$), 1.65-1.48 (m, 12 H, -CH2-); ^{13}C NMR (CD_3OD); 100 MHz): δ 176.1 ($CONH_2$), 71.7 (C_5H_4), 70.6 (C_5H_4), 70.5 (C_5H_5), 51.8 (ipso-C_5H_4), 36.5 (CH_2), 35.6 (CH_2), 31.7 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 25.1 (CH_2). Anal. calcd for $C_{17}H_{23}FeNO$: C, 65.19; H, 7.40; N, 4.47. Found: C, 65.11; H, 7.35; N, 4,46.

6-Ferrocenylhexyl carboxylic acid (9): MS (ESI-): m/z 313 $[M-H]^-$; ^{1}H-NMR (CD_3OD): ^{1}H NMR ($CDCl_3$; 400 MHz): δ 4.48 (t, 2H, J = 1.75 Hz, H(Cp)), 4.31 (t, 2H, J = 1.75 Hz, H(Cp)), 4.16 (s, 5H, H(Cp)), 2.30 (t, 2H, *J* = 7.4 Hz, Cp-CH2-), 2.41 (t, 2H, *J*=6.9 Hz, -CH2-COOH), 1.68-1.49 (m, 12 H, -CH2-); ^{13}C NMR (CD_3OD); 100 MHz): δ 179.2 (COOH), 71.6 (C_5H_4), 70.4 (C_5H_4), 70.3 (C_5H_5), 51.8 (ipso-C_5H_4), 36.0 (CH_2), 34.3 (CH_2), 32.1 (CH_2), 28.8 (CH_2), 28.3 (CH_2), 24.2 (CH_2). Anal. calcd for $C_{17}H_{22}FeO_2$: C, 64.98; H, 7.06. Found: C, 64.85; H, 7.03.

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