Supplementary Material (ESI) for *Green Chemistry*

Supporting information

Bio-Supported Palladium Nanoparticles as a Catalyst for Suzuki-Miyaura and the Mizoroki-Heck Reactions

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General methods for the bacteria strains

The two bacterial strains used in this article were *Cupriavidus necator* ATCC 43291 and *Pseudomonas putida* ATCC 12633. They were grown in liquid media (DSMZ #1) at pH = 7.0 containing; Peptone 5g/L and Meat Extract 3g/L.

Growth of the bacterial strains

The bacterial strains were grown in 150 mL growth liquid media for 16 h at 30 °C until a total optical density of OD_{600}=1. The bacteria were hereafter transferred to 50 mL falcon tubes prior to harvesting; where they were centrifuged (10 min, 5000 rpm) and washed with MOPS-buffer (20 mM, 3x 30 mL) and finally resuspended in MOPS-buffer to an OD_{600}=1.

Bio-reduction of the palladium

The bacterial cell suspension (10 mL, OD_{600}=1) and a degassed solution of Na_2PdCl_4 (6.80 mM, 0.5 mL) in MilliQ water were added to a sealed glass tube and flushed with nitrogen. After 5 min, a degassed solution of formate (1M, 0.25 mL) in MilliQ water was added and the tube was placed on a shaking table overnight at 30 °C giving bio-Pd as black aggregates. The glass tube was hereafter centrifuged and the water was removed giving a bio-Pd pellet which was used without further purification.

Fixation method for TEM

The bacterial cell suspension after bioreduction (100 μL) was added to a sterile eppendorf tube and a 25% aqueous solution of glutaric aldehyde (20 μL) was added. The eppendorf tube was shaken and left for 10 min. The solution was hereafter centrifuged (14000 rpm, 2 min), washed with MilliQ water (3x 200 μL) and finally diluted in MilliQ water to a total volume of 200 μL.

General Methods for the reactions

Solvents were dried according to standard procedures, reactions were monitored by thin-layer chromatography (TLC) analysis and flash chromatography was carried out on silica gel 60 (230-400 mesh). The chemical shifts are reported in ppm relative to solvent residual peak.[1] MS spectra were recorded on a LC TOF (ES) apparatus. All Suzuki-Miyaura couplings and Mizoroki-Heck reactions were carried out in 7 mL sample vials with a teflon sealed screwcap in a glovebox under an argon atmosphere. All purchased chemicals were used as received without further purification.

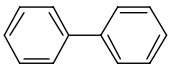
It is important to note that the precise amount of bio-palladium added to each reaction was difficult to determine since the complete removal of the water from the centrifuged bio-palladium pellet was not possible. Therefore, the palladium loading, in each reaction, was stated as a maximum amount. This maximum amount is calculated from the initial

concentration of the palladium salt added and based on the fact that no palladium remained in the buffer after centrifugation which was confirmed by Atomic Absorption Spectroscopy (AAS).

General Procedure for the Suzuki-Miyaura Cross-couplings

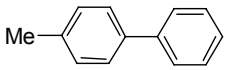
The boronic acid (1.1 equiv.), aryl-iodide (1.0 equiv.), tetrabutylammonium bromide (TBAB) (2.0 equiv.), Na_2CO_3 (3.0 equiv.) and bio-Pd (0.02 equiv. of Pd(0)) were dissolved in a mixture of EtOH/H_2O (2:1). The sample vial was then fitted with a teflon sealed screwcap and removed from the glovebox. The reaction mixture was heated for 6-24 h at the temperature stated for each product. After completed reaction, the crude reaction mixture was filtered through a filter paper and concentrated *in vacuo*. The crude product was purified by column chromatography.

Biphenyl (Table 1, entry 1)[2,3]



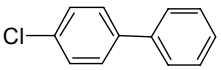
A mixture of iodobenzene (61.2 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromotagraphy on silica gel using pentane/CH_2Cl_2 (4:1) as eluent affording the title compound (39.7 mg, 86 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.65 (d, 4H, J = 7.6 Hz), 7.50 (dt, 4H, J = 8.0, 1.6 Hz), 7.42-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 141.4 (2C), 128.9 (4C), 127.4 (4C), 127.3 (2C). GCMS calcd for $C_{12}H_{10}$ [M]: 154, found: 154.

4-Methylbiphenyl (Table 1, entry 2)[2,3]



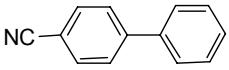
A mixture of 4-iodotoluene (85.0 mg, 0.39 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using pentane as eluent affording the title compound (53.1, 96 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.62 (d, 2H, J = 7.6 Hz), 7.53 (d, 2H, J = 6.4 Hz), 7.46 (t, 2H, J = 7.6 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.28 (d, 2H, J = 7.6 Hz), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 154.4, 141.3, 138.5, 137.1, 129.6 (2C), 128.8 (2C), 127.13 (2C), 127.11 (2C), 21.2. GCMS calcd for $C_{13}H_{12}$ [M]: 168, found: 168.

4-Chlorobiphenyl (Table 1, entry 3)[2]



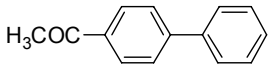
A mixture of 4-chloro-iodobenzene (71.5 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using pentane as eluent affording the title compound (33.9 mg, 60 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.58-7.52 (m, 4H), 7.48-7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 140.1, 139.8, 133.5, 129.05 (2C), 129.02 (2C), 128.5 (2C), 127.7, 127.1 (2C). GCMS calcd for $C_{12}H_9Cl$ [M]: 189, found: 189.

4-Phenylbenzonitrile (Table 1, entry 4)[4]



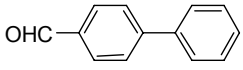
A mixture of 4-iodobenzonitrile (68.7 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) as eluent affording the title compound (45.2 mg, 84 % yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.72 (d, 2H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 6.8 Hz), 7.51-7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 145.8, 139.3, 132.7 (2C), 129.2 (2C), 128.8, 127.9 (2C), 127.4 (2C), 119.1, 111.1. GCMS calcd for $C_{13}H_9N$ [M]: 179, found: 179.

4-Acetylbiphenyl (Table 1, entry 5) [3]



A mixture of 4-iodoacetophenone (81.2 mg, 0.33 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent affording the title compound (63.1 mg , 97 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.04 (d, 2H, J = 6.8 Hz), 7.68 (d, 2H, J = 6.8 Hz), 7.63 (d, 2H, J = 7.2 Hz), 7.49-7.45 (m, 2H), 7.43-7.38 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 197.8, 145.8, 139.9, 135.9, 129.05 (2C), 129.00 (2C), 128.3, 127.34 (2C), 127.29 (2C), 26.7. GCMS calcd for $C_{14}H_{12}O$ [M]: 196, found: 196.

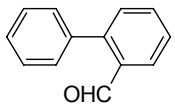
Biphenyl-4-carboxaldehyde (Table 1, entry 6) [4]



A mixture of 4-iodobenzaldehyde (69.6 mg, 0.30 mmol),

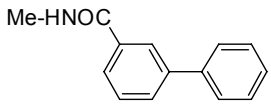
phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) as eluent affording the title compound (43.2 mg, 79 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 10.05 (s, 1H), 7.95 (d, 2H, J = 8.4 Hz), 7.75 (d, 2H, J = 8.4 Hz), 7.64 (d, 2H, J = 7.2 Hz), 7.51-7.39 (m,3H). ^{13}C NMR (100 MHz, CD_3CN) δ_C (ppm) 193.1, 147.5, 140.4, 136.5, 131.0 (2C), 130.0 (2C), 129.5, 128.5 (2C), 128.2 (2C). GCMS calcd for $C_{13}H_{10}O$ [M]: 182, found: 182.

Biphenyl-2-carboxaldehyde (Table 1, entry 7)[5]



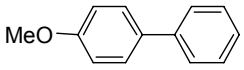
A mixture of 2-iodobenzaldehyde (61.2 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) as eluent affording the title compound (40.8 mg, 75 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 9.99 (s, 1H), 8.04 (dd, 1H, J = 8.0, 1.2 Hz), 7.64 (t, 1H, J = 7.6 Hz), 7.52-7.44 (m, 5H), 7.40-7.34 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN) δ_C (ppm) 192.9, 146.6, 138.8, 134.7, 134.6, 131.9, 131.0 (2C), 129.4, 129.0 (2C), 128.9, 128.3. GCMS calcd for $C_{13}H_{10}O$ [M]: 182, found: 182.

***N*-Methylbiphenyl-3-carboxamide (Table 1, entry 8)[6]**



A mixture of 3-iodo-*N*-methylbenzamide (78.3 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent affording the title compound (61.3 mg, 97 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.00 (s, 1H), 7.69 (dd, 2H, J = 13.6, 7.6 Hz), 7.58 (d, 2H, J = 7.6 Hz), 7.46-7.40 (m, 3H), 7.37-7.33 (m, 1H), 6.64 (brs, 1H), 2.99 (d, 3H, J = 4.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 168.4, 141.7, 140.3, 135.3, 130.0, 129.0, 128.9 (2C), 127.8, 127.2 (2C), 125.9, 125.7, 26.9. GCMS calcd for $C_{14}H_{13}NO$ [M]: 211, found: 211.

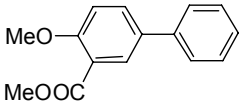
4-Methoxybiphenyl (Table 1, entry 9)[2,7]



A mixture of 4-methoxy-iodobenzene (70.2 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol),

Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 16 h at 80 °C. The crude product was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 (1:1) as eluent affording the title compound (55.0 mg, 100 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.60-7.55 (m, 4H), 7.44 (t, 2H, J = 8.0 Hz), 7.35-7.31 (m, 1H), 7.01 (d, 2H, J = 8.4 Hz), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 159.3, 141.0, 133.9, 128.8 (2C), 128.3 (2C), 126.9 (2C), 126.8, 114.3 (2C), 55.5. GCMS calcd for $C_{13}H_{12}O$ [M]: 184, found: 184.

Methyl 4-methoxybiphenyl-3-carboxylate (Table 1, entry 10)

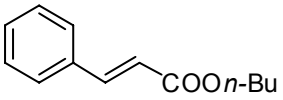


A mixture of methyl 4'-iodo-4-methoxybiphenyl-3-carboxylate (87,6 mg, 0.30 mmol), phenylboronic acid (40.2 mg, 0.33 mmol), bio-Pd (10 mg, 7 μmol), Na_2CO_3 (95.4 mg, 0.90 mmol) and TBAB (193.4 mg, 0.60 mmol) was dissolved in EtOH/H_2O (2:1, 1.5 mL) and allowed to react for 6 h at 50 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent affording the title compound (65.5 mg, 89 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.05 (d, 1H, J = 2.4 Hz), 7.70 (dd, 1H, J = 2.8, 0.8 Hz), 7.56 (d, 2H, J = 8.4 Hz), 7.43 (dt, 2H, J = 8.0, 0.4 Hz), 7.35-7.31 (m, 1H), 7.05 (d, 1H, J = 8.8 Hz), 3.94 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 166.7, 158.6, 139.8, 133.4, 132.0, 130.3, 128.9 (2C), 127.2, 126.8 (2C), 120.4, 112.5, 56.3, 52.2. GCMS calcd for $C_{15}H_{14}O_3$ [M]: 242, found: 242.

General Procedure for the Mizoroki-Heck reactions

The aryl halide (1.0 equiv.), the olefin (2.0 equiv.), tetrabutylammonium bromide TBAB (2.0 equiv.) when it is stated, Na_2CO_3 (2.5 equiv.) and bio-Pd (0.01 equiv. of Pd(0)) were dissolved in DMF (2mL). The sample vial was fitted with a teflon sealed screwcap and removed from the glovebox. The reaction mixture was heated for 12-24 h at 80°C and monitored by TLC. After completed reaction and cooling, the crude reaction mixture was poured into water and extracted with CH_2Cl_2. The collected organic phases were washed with water and brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography.

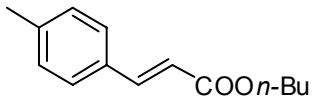
Butyl cinnamate (Table 2, entry 1)[8]



A mixtute of iodobenzene (40.8 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), TBAB (64.5 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 12 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (39.7 mg, 97 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H

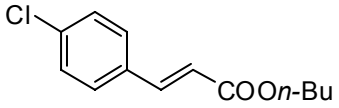
(ppm) 7.68 (d, 1H, J = 16.0 Hz), 7.54-7.52 (m, 2H), 7.39-7.37 (m, 3H), 6.44 (d, 1H, J = 16.0 Hz), 4.22 (t, 2H, J = 6.8 Hz), 1.73-1.66 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 167.2, 144.7, 134.6, 130.3, 129.0 (2C), 128.2 (2C), 118.4, 65.6, 30.9, 19.3, 13.9. GCMS calcd for $C_{13}H_{16}O_2$ [M]: 204, found: 204.

(*E*)-Butyl-3-*p*-tolylacrylate (Table 2, entry 2) [8]



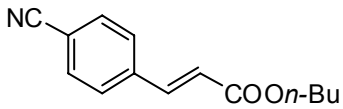
A mixture of 4-iodotoluene (43.6 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), TBAB (64.5 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (42.7 mg, 98 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.65 (d, 1H, J = 15.8 Hz), 7.42 (d, 2H, J = 8.0 Hz), 7.19 (d, 2H, J = 8.0 Hz), 6.40 (d, 1H, J = 15.8 Hz), 4.21 (t, 2H, J = 6.7 Hz), 2.37 (s, 3H), 1.73-1.65 (m, 2H), 1.47-1.41 (m, 2H), 0.97 (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 167.4, 144.7, 140.7, 131.9, 129.7 (2C), 128.2 (2C), 117.3, 64.5, 31.0, 21.6, 19.4, 13.9. GCMS calcd for $C_{14}H_{18}O_2$ [M]: 218, found: 218.

(*E*)-Butyl-3-(4-chlorophenyl)acrylate (Table 2, entry 3) [9]



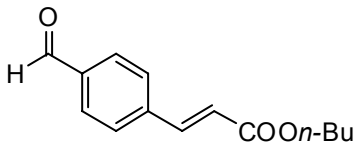
A mixture of 1-chloro-4-iodobenzene (47.7 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (47.7 mg, 100 % yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.62 (d, 1H, J = 15.9 Hz), 7.45 (d, 2H, J = 8.4 Hz), 7.35 (d, 2H, J = 8.4 Hz), 6.40 (d, 1H, J = 15.9 Hz), 4.21 (t, 2H, J = 6.7 Hz), 1.72-1.63 (m, 2H), 1.46-1.40 (m, 2H), 0.97 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 166.9, 143.2, 136.2, 133.1, 129.32 (2C), 129.28 (2C), 119.0, 64.7, 30.9, 19.3, 13.9. GCMS calcd for $C_{13}H_{15}ClO_2$ [M]: 238, found: 238.

(*E*)-Butyl-3-(4-cyanophenyl)acrylate (Table 2, entry 4) [8]



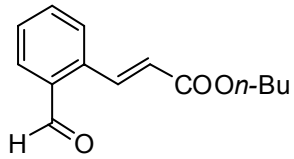
A mixture of 4-iodobenzonitrile (45.8 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (45.7 mg, 100 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.68-7.59 (m, 5H), 6.51 (d, 1H, J = 16.0 Hz), 4.22 (t, 2H, J = 6.7 Hz), 1.72-1.62 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 166.4, 142.2, 138.9, 132.7 (2C), 128.5 (2C), 122.0, 118.5, 113.5, 65.0, 30.8, 19.3, 13.8. GCMS calcd for $C_{14}H_{15}NO_2$ [M]: 229, found: 229.

(*E*)-Butyl-3-(4-formylphenyl)acrylate (Table 2, entry 5) [9]



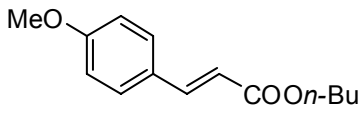
A mixture of 4-iodobenzaldehyde (46.4 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80°C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (41.1 mg, 88 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 10.0 (s, 1H), 7.89 (d, 2H, J = 8.2 Hz), 7.69 (d, 1H, J = 16.0 Hz), 7.66 (d, 2H, J = 8.2 Hz), 6.54 (d, 1H, J = 16.0 Hz), 4.22 (t, 2H, J = 6.7 Hz), 1.72-1.65 (m, 2H), 1.46-1.40 (m, 2H), 0.96 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 191.5, 166.5, 142.9, 140.3, 137.2, 130.2 (2C), 128.6 (2C), 121.6, 64.8, 30.8, 19.3, 13.8. GCMS calcd for $C_{14}H_{16}O_3$ [M]: 232, found: 232.

(*E*)-Butyl-3-(2-formylphenyl)acrylate (Table 2, entry 6) [9]



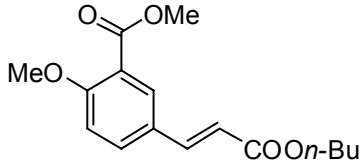
A mixture of 2-iodobenzaldehyde (46.4 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (40.0 mg, 86 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 10.3 (s, 1H), 8.52 (d, 1H, J = 15.8 Hz), 7.89 (dd, 1H, J = 7.2, 0.98 Hz), 7.64-7.60 (m, 3H), 6.40 (d, 1H, J = 15.8 Hz), 4.24 (t, 2H, J = 6.7 Hz), 1.73-1.67 (m, 2H), 1.48-1.42 (m, 2H), 0.97 (t, 3H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 191.9, 166.4, 141.0, 136.8, 134.0 (2C), 132.3, 130.0, 128.1, 123.5, 64.9, 30.9, 19.3, 13.9. GCMS calcd for $C_{14}H_{16}O_3$ [M]; calculated: 232, found: 232.

(*E*)-Butyl-3-(4-methoxyphenyl)acrylate (Table 2, entry 7) [8]



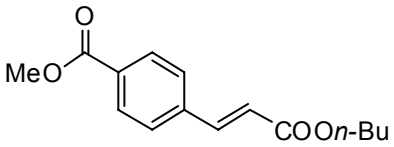
A mixture of 1-iodo-4-methoxybenzene (46.8 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (45.1 mg, 96 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.63 (d, 1H, J = 15.9 Hz), 7.47 (d, 2H, J = 8.7 Hz), 6.90 (d, 2H, J = 8.2 Hz), 6.31 (d, 1H, J = 15.9 Hz), 4.20 (t, 2H, J = 6.9 Hz), 3.83 (s, 3H), 1.72-1.64 (m, 2H), 1.46-1.41 (m, 2H), 0.96 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 167.5, 161.4, 144.3, 129.8 (2C), 127.4, 115.9, 114.4 (2C), 64.4, 55.5, 30.9, 19.3, 13.9. GCMS calcd for $C_{14}H_{18}O_3$ [M]: 234, found: 234.

(*E*)-Methyl 5-(3-butoxy-3-oxoprop-1-enyl)-2-methoxybenzoate (Table 2, entry 8)



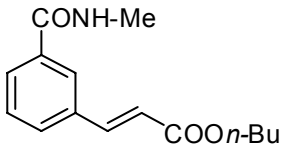
A mixture of methyl 5-iodo-2-methoxybenzoate (58.4 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (99:1) as eluent affording the title compound (47.3 mg, 81 % yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.98 (d, 1H, J = 2.2 Hz), 7.63-7.59 (m, 2H), 6.98 (d, 1H, J = 8.8 Hz), 6.35 (d, 1H, J = 16.0 Hz), 4.19 (t, 2H, J = 6.7 Hz), 3.93 (s, 3H), 3.90 (s, 3H), 1.71-1.64 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 167.2, 166.1, 160.6, 143.1, 133.2, 131.6, 126.9, 120.6, 117.3, 112.5, 64.5, 56.3, 52.3, 30.9, 19.3, 13.9. GCMS calcd for $C_{16}H_{20}O_5$ [M]: 292, found: 292.

(*E*)-Methyl 4-(3-butoxy-3-oxoprop-1-enyl)benzoate (Table 2, entry 9)[10]



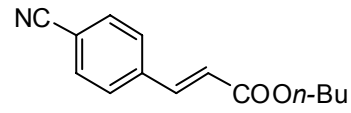
A mixture of methyl 4-iodobenzoate (43.0 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (45.0 mg, 86 % yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.05 (d, 2H, J = 8.3 Hz), 7.69 (d, 1H, J = 16.0 Hz), 7.55 (d, 2H, J = 8.3 Hz), 6.52 (d, 1H, J = 16.0 Hz), 4.22 (t, 2H, J = 6.7 Hz), 3.93 (s, 3H), 1.72-1.66 (m, 2H), 1.47-1.41 (m, 2H), 0.97 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 166.8, 166.4, 143.3, 138.9, 131.5, 130.2 (2C), 128.0 (2C), 120.9, 64.8, 52.4, 30.9, 19.3, 13.9. GCMS calcd for $C_{15}H_{18}O_4$ [M]: 262, found: 262.

(*E*)-Butyl 3-(3-(methylcarbamoyl)phenyl)acrylate (Table 2, entry 10)



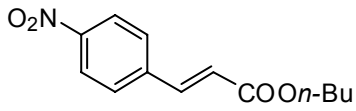
A mixture of 3-iodo-*N*-methylbenzamide (52.2 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (98:2) as eluent affording the title compound (50.1 mg, 96 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.91 (brs, 1H), 7.73 (d, 1H, J = 7.7 Hz), 7.66 (d, 1H, J = 16.0 Hz), 7.61 (d, 1H, J = 7.7 Hz), 7.42 (t, 1H, J = 7.7 Hz), 6.48 (d, 1H, J = 16.0 Hz), 6.43 (s, 1H), 4.20 (t, 2H, J = 6.7 Hz), 3.00 (d, 3H, J = 4.9 Hz), 1.71-1.64 (m, 2H), 1.47-1.38 (m, 2H), 0.95 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 167.7, 166.9, 143.5, 135.5, 135.0, 130.8, 129.2, 128.5, 126.6, 119.7, 64.5, 30.8, 27.0, 19.3, 13.8. GCMS calcd for $C_{15}H_{19}NO_3$ [M]: 261, found: 261.

(*E*)-Butyl-3-(4-cyanophenyl)acrylate (Table 2, entry 11)[8]



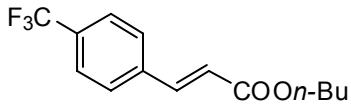
A mixture of 4-bromobenzonitrile (36.4 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), TBAB (64.5 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (44.6 mg, 97 % yield) as a colourless oil. Spectral data in accordance with the ones obtained above (see Table 2, entry 4).

(*E*)-Butyl 3-(4-nitrophenyl)acrylate (Table 2, entry 12)[8]



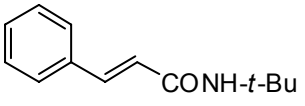
A mixture of 1-bromo-4-nitrobenzene (40.4 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), TBAB (64.5 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (24.0 mg, 88 % yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.23 (d, 2H, J = 8.8 Hz), 7.68 (d, 1H, J = 15.9 Hz), 7.66 (d, 2H, J = 8.8 Hz), 6.55 (d, 1H, J = 15.9 Hz), 4.22 (t, 2H, J = 6.7 Hz), 1.72-1.65 (m, 2H), 1.47-1.38 (m, 2H), 0.95 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 166.2, 148.2, 141.7, 140.8, 128.8 (2C), 124.3 (2C), 122.8, 65.1, 30.8, 19.3, 13.9. HRMS calcd for $C_{13}H_{15}NO_4$ $[M+Na]^+$: 272.0899, found: 272.0897.

(*E*)-Butyl 3-(4-(trifluoromethyl)phenyl)acrylate (Table 2, entry 13)[8]



A mixture of 1-bromo-4-(trifluoromethyl)benzene (45.0 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), TBAB (64.5 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title compound (28.7 mg, 53 % yield) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.68 (d, 1H, J = 16.0 Hz), 7.67-7.61 (m, 4H), 6.51 (d, 1H, J = 16.0 Hz), 4.23 (t, 2H, J = 6.7 Hz), 1.73-1.66 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, 3H, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 166.6, 142.8, 138.0, 131.9 (q, J = 33.0 Hz), 128.3 (2C), 126.0 (q, J = 3.8 Hz, 2C), 124.0 (q, J = 272.1 Hz), 121.0, 64.9, 30.9, 19.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F (ppm) -62.75. GCMS calcd for $C_{14}H_{15}F_3O_2$ [M]: 272, found: 272.

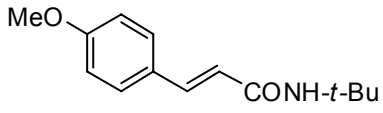
***N*-*tert*-Butylcinnamamide (Table 2, entry 14)[11]**



A mixture of iodobenzene (40.8 mg, 0.20 mmol), *t*-butylacrylamide (50.9 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 μmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on

silica gel using CH_2Cl_2/MeOH (99:1) as eluent affording the title compound (33.1 mg, 81 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.57 (d, 1H, J = 15.5 Hz), 7.48- 7.46 (m, 2H), 7.34- 7.32 (m, 3H), 6.34 (d, 1H, J = 15.5 Hz), 5.56 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 165.3, 140.3, 135.1, 129.6, 128.9 (2C), 127.8 (2C), 122.1, 51.6, 29.0 (3C). GCMS calcd for $C_{13}H_{17}NO$ [M]: 203, found: 203.

(*E*)-*N*-*tert*-Butyl-3-(4-methoxyphenyl)acrylamide (Table 2, entry 15)[12]



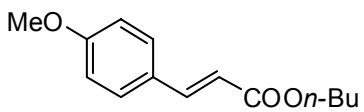
A mixture of 4-iodotoluene (46,8 mg, 0.20 mmol), *t*-butylacrylamide (50,9 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol) and bio-Pd (3 mg, 2 µmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (99:1) as eluent affording the title compound (46.0 mg, 99 % yield) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.50 (d, 1H, J = 15.5 Hz), 7.40 (d, 2H, J = 8.8 Hz), 6.85 (d, 2H, J = 8.8 Hz), 6.22 (d, 1H, J = 15.5 Hz), 5.58 (s, 1H), 3.80 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm) 167.8, 140.0, 129.3 (2C), 127.8, 119.7, 114.3 (2C), 55.4, 51.5, 29.0 (3C). GCMS calcd for $C_{14}H_{19}NO_2$ [M]: 233, found: 233.

Preparation and treatment of the waste

The in-house generated waste was prepared from a hydrogenation reaction of (*E*)-3-(4-methoxyphenyl)-*N*-methylacrylamide (431.3 mg, 2.26 mmol) with Pd/C, 10% (120.0 mg, 5 mol%) in a mixture of THF/H_2O (10 mL, 1:1) under a atmosphere of hydrogen for 36 h at rt. The solution was concentrated *in vacuo*. In order to obtain a full oxidation of the Pd, aqua regia (6 mL) was added slowly to the flask and the solution was heated with a heat gun until boiling point. The mixture was then left and stirred for 1 h at rt. To be tolerated by the bacteria, the suspension was hereafter cooled to 0°C on an ice bath and neutralised to pH 7 using conc. NaOH. This resulted in 0.11 mM Pd waste solution (20 mL).

The bacterial cell suspension (5 mL, OD_{600}=1, *C. necator*) was added to a sealed glass tube and flushed with nitrogen. Then, a 0.11 mM solution of the Pd waste (3.8 mL) was added to the resuspension. After 5 min, a 1 M solution of formate (1 mL) in MilliQ water was added and the tube was placed on a shaking table overnight at 30 °C. The glass tube was hereafter centrifuged and the water was removed giving bio-Pd which was used without further purification.

(*E*)-Butyl-3-(4-methoxyphenyl)acrylate (Scheme 2)[8]



A mixture of 1-iodo-4-methoxybenzene (46.2 mg, 0.20 mmol), *n*-butylacrylate (51.3 mg, 0.40 mmol), Na_2CO_3 (53.0 mg, 0.50 mmol), TBAB (65.4 mg, 0.4 mmol) and bio-Pd_{waste} (15 mg, 11 µmol) was dissolved in DMF (2 mL) and stirred 24 h at 80 °C. The crude product was purified by flash chromatography on silica gel using CH_2Cl_2/pentane (1:1) as eluent affording the title

compound (42.0 mg, 90 % yield) as a colourless oil. Spectral data in accordance with the ones obtained above (see Table 2, entry 7).

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