

Electronic Supporting information (ESI)

Ecocatalyzed Suzuki-Miyaura cross coupling of Heteroaryl Compounds

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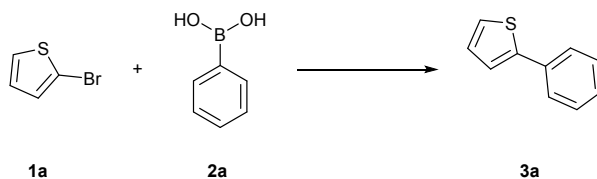
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Large scale synthesis of 3a for EcoPd₁ recycling process (S1)

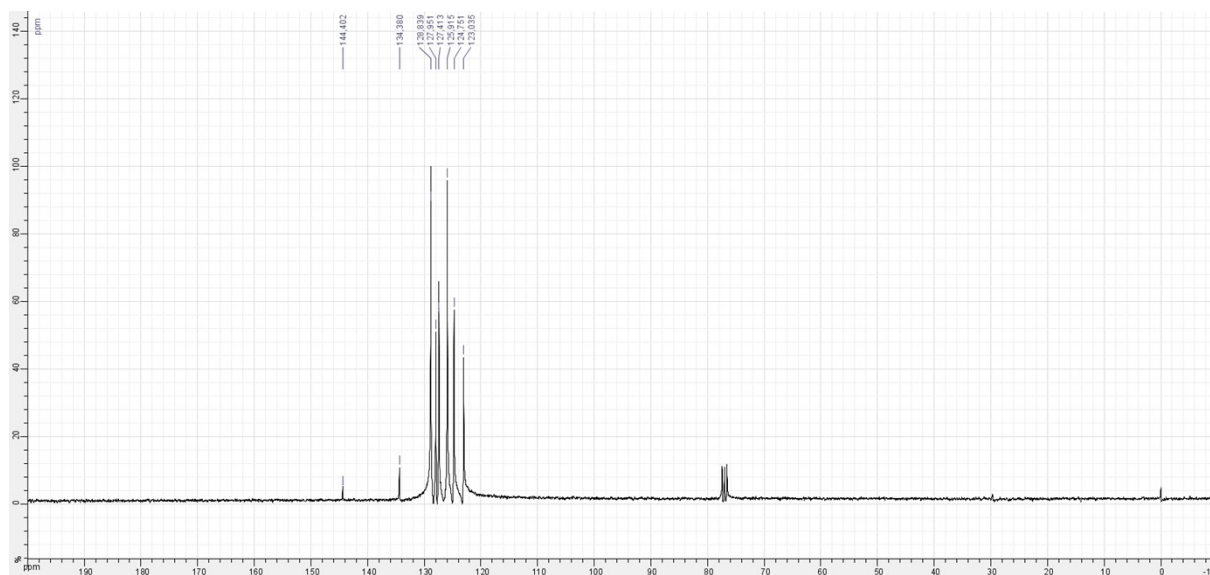


2-Bromothiophene (20 g, 125 mmol), Phenyl boronic acid (16.8 g, 138 mmol), potassium carbonate (20.7 g, 150 mmol) and EcoPd₁ (113 mg, 125 μ mol of Pd, 13.3 mg of Pd, EcoPd₁ at 11.7 wt% of Pd) were suspended into degassed glycerol (200 mL). The mixture was stirred at 120°C for 4h thanks to an oil bath under an argon atmosphere. The reaction was checked for completion by TLC (cyclohexane) and GC-MS analysis after a short extraction of the organic material: 10 μ L of the crude were added into a 1 mL microtube containing a mixture of water and AcOEt (800 μ L, 1:1, v/v) ; the microtube was vortexed before using the organic layer to perform analysis. Deionised water (500 mL) and AcOEt (500 mL) were added into the flask and the mixture filtered through fritted glass to isolate black Pd for recycling. The organic layer was further washed by deionised water (500 mL x 3) before drying over Na₂SO₄. The organic layer was filtered and concentrated under vacuum. The residue was then purified by chromatography on a silica gel column (250 g) with pure cyclohexane as the mobile phase, giving the desired coupled compound as a white powder (18 g, 112.5 mmol, yield 90%) R_f = 0.7 (cyclohexane). ¹H NMR (300 MHz, CDCl₃): δ = 7.10-7.13 (m, 2H), 7.44-7.26 (m, 5H), 7.38-7.33 (m, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 123.0, 124.8, 125.9, 127.4, 128.0, 128.8, 134.4, 144.4. MS (EI): m/z = 160 (M⁺, 100%), 128 (21%), 115 (54%), 89 (17%) calcd for C₁₀H₈S: 159.99.

Nuclear Magnetic Resonance Spectra of 3a ^1H NMR (300 MHz, CDCl_3).



Nuclear Magnetic Resonance Spectra of 3a ^{13}C NMR (75.5 MHz, CDCl_3).



Recycling of the EcoPd₁: preparation of the effluent subjected to rhizofiltration (S2)

Black palladium recovered by filtration through sintered glass after large scale Suzuki coupling reaction (13.3 mg, 125 μmol) was treated with freshly prepared *aqua regia* (2 mL) at room temperature. Complete dissolution is achieved in less than 30 minutes. The mixture was directly diluted with 1L of Milli-Q water (18.2 M Ω -cm, final pH \approx 2.5) and then subjected to rhizofiltration with one plant (*E. crassipes*) for palladium recovery. The accumulation was carried out over 3 days (1 plant/L of effluent) with periodic mechanical homogenization of the solution. The EcoPd₂ was prepared by following the general procedure from roots. Its mineral composition was determined by MP-AES analysis. Dried plant roots were analysed by FT-IR to confirm the reproducibility of the palladium recycling process (Figure S2).

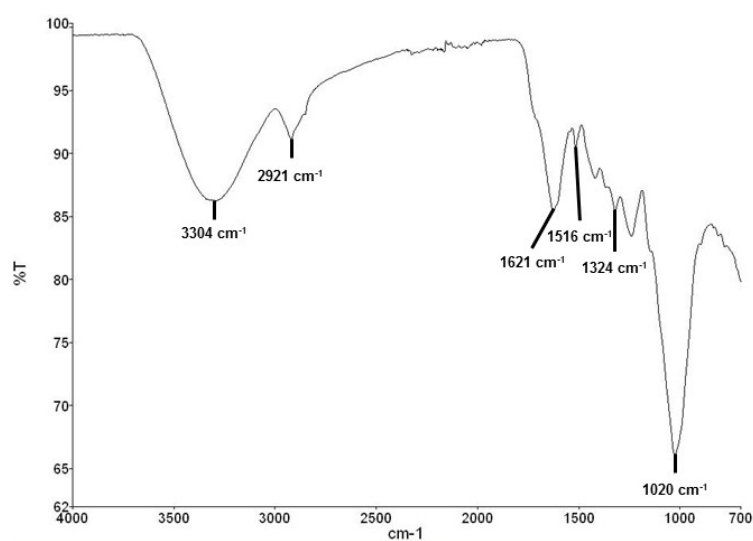


Figure S2. FT-IR spectrum of *E. crassipes* dried roots after the rhizofiltration leading to EcoPd₂.

Quantitative recovery of palladium by decreasing the Pd concentration relative to the quantity of biomass (S3)

Black palladium recovered after large scale Suzuki coupling reaction (7.5 mg, 71 μmol) was treated with freshly prepared *aqua regia* (2 mL) at room temperature. Complete dissolution is achieved in less than 30 minutes. The mixture was directly diluted with 1L of Milli-Q water (18.2 M Ω -cm, final pH \approx 2.5) and then subjected to rhizofiltration with one plant (*E. crassipes*) for palladium recovery. The accumulation was carried out over 3 days (1 plant/L of effluent) with periodic mechanical homogenization of the solution.

The EcoPd_{2b} was prepared by following the general procedure. Its mineral composition was determined by MP-AES analysis. The mineral compositions of the various liquid and solid samples involved in the procedure were determined by MP-AES analyses. All the palladium present in the effluent was absorbed by the biomass but its final concentration into the roots and consequentially EcoPd_{2b} is lower (Table S3).

Liquid sample (mg/L)	Pd	Fe	Ca	K	Mg	Al	Na
Effluent before rhizofiltration	7.35	0	32.66	8.78	2.21	0	11.58
Effluent after rhizofiltration	0	3.95	14.5	47.05	13.98	1.73	27.7
Solid sample (wt%)	Pd	Fe	Ca	K	Mg	Al	Na
Roots	0.56	0.20	0.49	0.14	0.03	0.03	0.09
EcoPd _{2b}	4.4	4.6	6.1	1.9	1.6	0.7	2.1

Table S3. Mineral composition of solid samples and solutions involved in the recycling of palladium leading to EcoPd_{2b} determined by MP-AES analysis (wt% for solid sample, mg/L for liquid sample).

Quantitative recovery of palladium by carrying out two successive rhizofiltration (S4)

After the rhizofiltration which allow the production of EcoPd₂, the effluent still contains 3.08 mg/L of Pd (1L). In order to completely decontaminate the solution, we carried out a second rhizofiltration with a new plant (*E. crassipes*). The accumulation was carried out over 3 days (1 plant/L of effluent) with periodic mechanical homogenization of the solution. The mineral compositions of the various liquid and solid samples involved in the procedure were determined by MP-AES analyses. All the palladium present in the effluent was absorbed by the biomass but its final concentration into roots is very low (Table S4). No EcoPd was generated from this biomass due to its low palladium loading.

Liquid sample (mg/L)	Pd	Fe	Ca	K	Mg	Al	Na
Effluent before rhizofiltration	3.08	2.6	47.5	60.3	17.9	1.29	30.0
Effluent after rhizofiltration	0	0.97	227.4	82.6	24.6	0.89	44.0
Solid sample (wt%)	Pd	Fe	Ca	K	Mg	Al	Na
Roots	0.20	0.21	2.53	0.23	0.08	0.07	0.11

Table S4. Mineral composition of solid samples and solutions involved in the second rhizofiltration recycling of palladium determined by MP-AES analysis (wt% for solid sample, mg/L for liquid sample).