Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supporting information (ESI)

Ecocatalyzed Suzuki-Miyaura cross coupling of Heteroaryl Compounds

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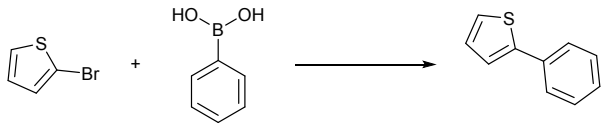
Table of contents

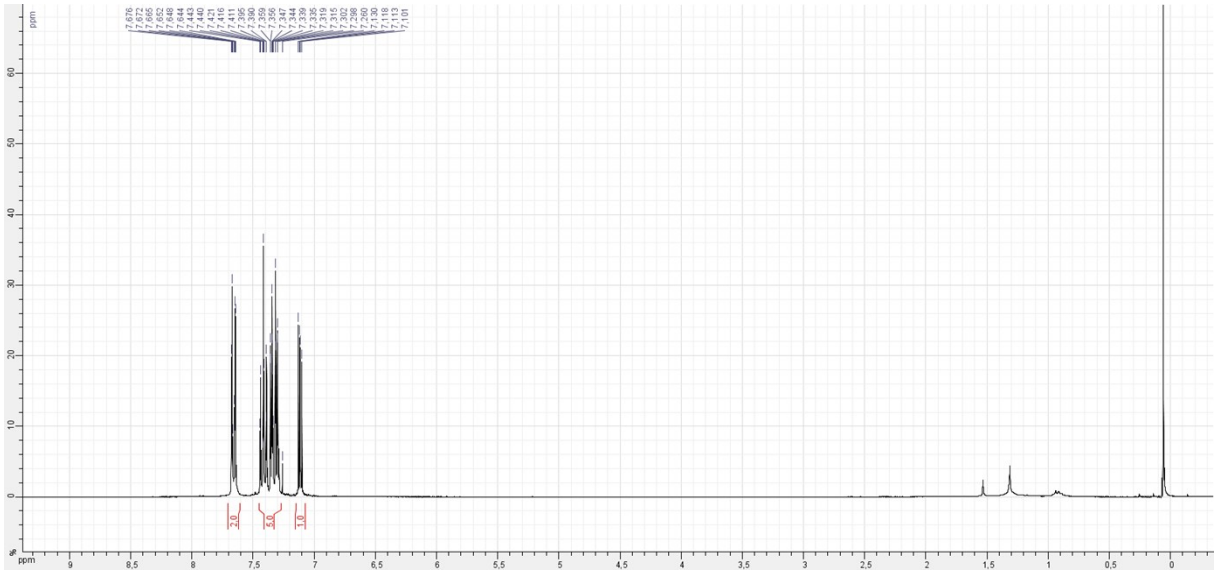
Large scale synthesis of 3a for $EcoPd_1$ recycling process (S1)



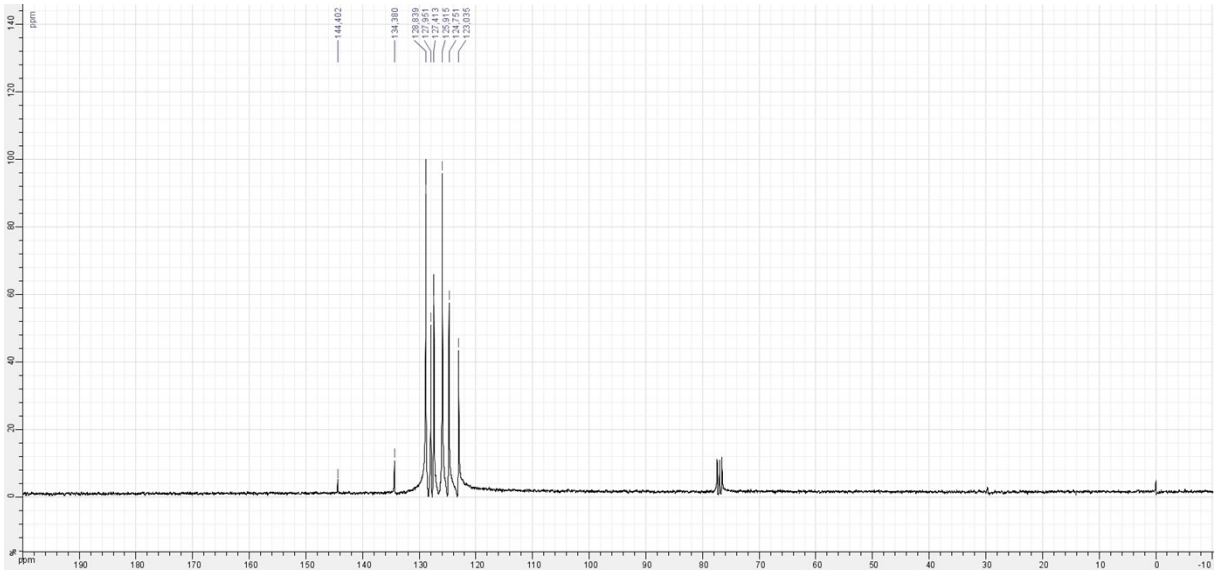
1a 2a 3a

2-Bromothiophene (20 g, 125 mmol), Phenyl boronic acid (16.8 g, 138 mmol), potassium carbonate (20.7 g, 150 mmol) and $EcoPd_1$ (113 mg, 125 µmol of Pd, 13.3 mg of Pd, $EcoPd_1$ 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 µL of the crude were added into a 1 mL microtube containing a mixture of water and AcOEt (800 µL, 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 Na_2SO_4. 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). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10-7.13 (m, 2H), 7.44-7.26 (m, 5H), 7.38-7.33 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 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 $C_{10}H_8S$: 159.99.

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



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



Recycling of the $EcoPd_1$: 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 MΩ·cm, final pH ≈ 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 $EcoPd_2$ 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).

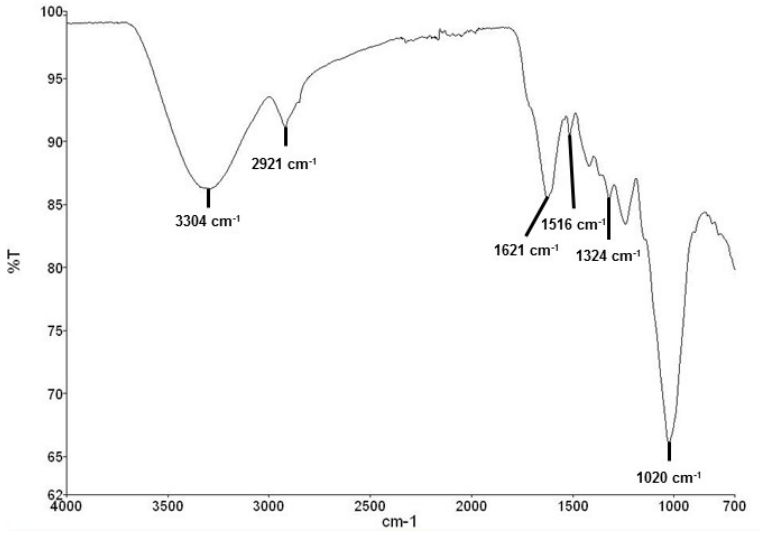


Figure S2. FT-IR spectrum of *E. crassipes* dried roots after the rhizofiltration leading to $EcoPd_2$.

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 MΩ·cm, final pH ≈ 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 $EcoPd_2$, 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 it 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 rhizolfiltration recycling of palladium determined by MP-AES analysis (wt% for solid sample, mg/L for liquid sample).