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II- from ecological recycling of Pd to greener sonogashira cross-coupling reactions

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A B S T R A C T

Based on a new process derived from biosorption technology that uses roots from aquatic and wetland plants (*Mentha aquatica*, *Eichhornia crassipes*, *Pistia stratiotes*, *Ludwigia peploides*, *Fallopia japonica*), materials rich in lignin (pinecone, bark pine) and wastes rich in tannins (coffee grounds), we were able to prepare a new class of ecocatalyst, called Eco-Pd. The formed Eco-Pd are characterized via MP-AES and XRDP in the order to elucidate the chemical composition and the structure of the new formed materials. Interestingly, the presence of higher-oxidation-state palladium species, namely K_2PdCl_6 , is observed. We describe the use of this new generation of Eco-Pd for a green and sustainable Sonogashira reaction. The absence of copper, ligands, additives, a lower Pd loading (0.05 mol% - 0.1 mol%), the use of green solvents (glycerol/n-BuOH), and the use of biosourced Pd and base (Eco-Ca), are significant advantages of this approach. The combination TON/TOF ($10^3/250\text{ h}^{-1}$) can be advantageously compared with literature and demonstrates the remarkable practical utility of these new catalysts. Most importantly, the Eco-Pd can be easily recycled by biosorption and reused, that is another asset in terms of sustainable Chemistry.

Keywords:

Sonogashira cross-coupling reactions
Greener conditions
Low Pd loadings
Ecocatalysis
Recyclability of Pd

1. Introduction

The Sonogashira coupling reaction is an efficient method to build C–C bonds between activated C_{sp^2} and C_{sp} of terminal alkynes (Alacid et al., 2006; Chinchilla and Nájera, 2011; Chinchilla and Nájera, 2007; Wu et al., 2020). The catalytic process requires the use of a Pd-phosphine ligand complex in the presence of a base (e.g. an amine) and a cocatalyst (generally a copper salt) in polar solvents. However, in these classic conditions, traces of oxygen lead to a side reaction, the Hay-Glaser homocoupling. Two strategies have been studied to prevent it: the replacement of copper salts by other cocatalysts such as zinc, tin, boron, aluminum, and silver salts (Liao et al., 2003; Mori et al., 2000; Negishi and Anastasia, 2003; Tykwinski, 2003; Zhou et al., 2010), and/or the use of additives such as TBAB, TBAF and TMSA (Affani and Dugat, 2007; Palimkar et al.,

2007; Sanz et al., 2007), which can stabilize active palladium nanoparticles generated during the coupling. However, these strategies require additional steps for the preparation of the ligand, the cocatalyst or the additive. Furthermore, many of the additives used are hazardous.

Driven by the need to develop more sustainable procedures, many efforts have been made to develop ligand-free, cocatalyst-free, and additive-free conditions, and/or routes using a recyclable Pd catalyst. Although the immobilization of Pd species onto a suitable solid support has been widely studied, leaching remains a problem and recyclability must be improved (Chinchilla and Nájera, 2011; Albéniz and Carrera, 2011; Ayogu and Onoabedje, 2019; Corma et al., 2006; Crudden et al., 2005; Cui et al., 2017; Dantas Ramos et al., 2004; Dioso et al., 2006; Elhampour and Nemati, 2017; Gao et al., 2010; Garg et al., 2005; Khalafi-Nezhad and Panahi, 2011; Li, 2005; Li et al., 2017; Liang et al., 2005; Lohmann et al., 2005; Mori et al., 2008; Mpungose, 2017; Nasrollahzadeh et al., 2014a; Rajender Reddy et al., 2006; Raju et al., 2006; Sadjadi, 2018; Sadjadi et al., 2019; Yi et al., 2012). Recently,

these problems have been addressed using natural systems to synthesize new and active heterogeneous Pd catalysts. The preparation of Pd nanoparticles (NPs) supported on pectin was described to promote copper-free, ligand-free and amine-free Sonogashira–Hagihara coupling; however it required the use of a toxic solvent, the DMF, at a high 100 °C temperature (Khazaei et al., 2013). An ecofriendly and non-toxic method has been reported for the preparation of Pd NPs using fruits of *Piper longum*, without neither stabilizer nor surfactant. Although the catalytic performance of the system was interesting for the Sonogashira coupling reaction (Nasrollahzadeh et al., 2014b), *Piper longum* trees cannot be cultivated and this resource is thus non-renewable (Sathelly et al., 2016). Another preparation of Pd NPs has been described using gum of sour cherry tree (*Genus species*) as a reducing and stabilizing agent. Pd NPs thus prepared exhibited good activity in ligand-free, amine-free and copper-free Sonogashira coupling between aryl iodides and terminal alkynes, although yields of the isolated product were not reported (Nasrollahzadeh et al., 2014b, 2014c). Moreover, the availability of sour cherry tree gum may be extremely limited since gum is produced by the tree in only very small quantities. (Thomidis and Exadaktylou, 2008).

Despite significant advances in Sonogashira reaction protocols, it remains challenging to combine the necessary conditions (aerobic, amine-free, ligand-free, cocatalyst-free, additive-free, innocuous solvent, low Pd loadings, abundance of natural raw materials, recyclability of Pd) for sustainable and efficient production of Pd NPs. In this context, our group had previously reported the design of bio-sourced ecocatalysts used in cross-coupling reactions. The concept was based on the recovery of palladium from wastewater, by using specific living plants capable of bioconcentrating Pd in roots (rhizofiltration). Pd-enriched roots were transformed into bio-based metal catalysts, called Eco-Pd, that promoted Suzuki and Heck coupling reactions (Clavé et al., 2017; Garel et al., 2015). Using catalysts derived from living plants presents several drawbacks (necessity to propagate plants and growing and harvesting large amounts of biomass, phytoaccumulation of Pd in large basins, sometimes limited reproducibility of rhizofiltration parameters).

Based on a new process derived from biosorption technology that uses abundant plants and even dead plant biomasses, we were able to prepare a new class of Eco-Pd. We describe the use of this new generation of Eco-Pd for a green and sustainable Sonogashira reaction. The absence of copper, ligands, additives, the use of green solvent, and the use of biosourced Pd and base (Eco-Ca), are significant advantages of this approach. Most importantly, the Eco-Pd can be easily recycled by biosorption and reused, that is another asset in terms of Green Chemistry.

2. Results and discussion

2.1. Preparation of Eco-Pd

Based on recent work on PGMs (Platinum Group Metals) biosorption, Eco-Pd were prepared from three types of material of plant origin (Table 1): i) roots from aquatic and wetland plants rich

in carboxylate moieties such as *Mentha aquatica*, *Eichhornia crassipes*, *Pistia stratiotes*, *Ludwigia peploides*, and *Fallopia japonica* (Stanovych et al., 2019); ii) materials rich in lignin such as pinecone and bark pine; and iii) wastes rich in tannins such as coffee grounds. *Mentha aquatica* is an herbaceous perennial aromatic herb growing in marshes and damp places in Europe, tropical Africa, West Asia and North America (De Laet et al., 2019). *Eichhornia crassipes*, *Pistia stratiotes*, *Ludwigia peploides* and *Fallopia japonica* are invasive species that occur in all five continents. They were also known to be easily propagated vegetatively and to form impressive quantities of root biomass. Pinecone, bark pine and coffee grounds are abundant natural resources. Consequently, the natural raw materials were readily available and had no competing food uses.

We carried out Pd bioconcentration from dried roots and other biomaterials in powder form by biosorption, in solutions enriched with 14 mg/L palladium in synthetic effluent.

After filtration and drying, dried powder rich in Pd was transformed into Eco-Pd. The first step was a thermal treatment of powder under air flow. In a second step, thermal residues were treated with hydrochloric acid following the previously described procedure. Eco-Pd were stable and could be stored at room temperature under nitrogen for several months.

2.2. Characterization of Eco-Pd

2.2.1. MP-AES analysis of Eco-Pd

Eco-Pd were analyzed by MP-AES. The mineral compositions of the catalysts are depicted in Table 2. The weight-percent of Pd is the combination of two factors: the biosorption capacity of the biomaterial and the composition of its physiological elements (Ca, Mg, K, Na). Mineral composition of Eco-Pd₁₋₅ made from aquatic and wetland plants contained a high proportion of Ca (11.45–20.81%; entries 1–5). Despite the great capacity of Pd biosorption of the corresponding plant species, %Pd (3.7–18.10%) was attenuated by the amount of sorbed Ca. The situation was different for Eco-Pd₆₋₈. %Pd was higher (11.20–46.30%), whereas the sum of physiological elements was smaller (%Ca: 1.92–13.10%). The variety of biomaterials allowed modulating the composition of Eco-Pd and detecting possible synergistic effects and the formation of mixed metallic species. (Bihanic et al., 2020).

2.2.2. XRPD analysis

XRPD analysis was performed to identify palladium species under crystalline form. XRD diffractogram of Eco-Pd₄ (see XRD diffraction pattern of Eco-Pd₄ in SI) clearly indicates the presence of CaSO₄ and hydrated CaCl₂. Surprisingly, diffractogram also shows presence of higher-oxidation-state palladium species, namely K₂PdCl₆. Pd^{IV} have been used to develop a series of new synthetic transformations which cannot be realized within Pd^{II} catalysis such as Catellani reaction, C–H activation in domino catalysis, aryl oxidation and relevant functionalization of arenes and alkenes. (Muñiz, 2009).

Moreover, this result represents the first example of Pd^{IV} which can be generated from a phytotechnology. According to literature

Table 1
Types of feedstocks for the preparation of Eco-Pd.






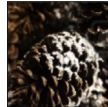


Roots from aquatic and wetland plants rich in carboxylate moieties					Materials rich in lignin		Wastes rich in tannins
<i>Mentha aquatica</i>	<i>Eichhornia crassipes</i>	<i>Pistia stratiotes</i>	<i>Ludwigia peploides</i>	<i>Fallopia japonica</i>	Pinecone	Bark pine	Coffee grounds
							

Table 2
MP AES assessments of Eco-Pd.

Entry	Nature of the biomaterial	Eco-Pd	Mineral composition (%wt)						
			Al	Ca	Fe	K	Mg	Na	Pd
1	<i>Eichhornia crassipes</i>	Eco-Pd ₁	0.12 ±0.001	20.81 ±0.156	n.d.	0.04 ±0.0001	0.13 ±0.001	0.14 ±0.002	7.35 ± 0.041
2	<i>Mentha aquatica</i>	Eco-Pd ₂	0.21 ±0.004	11.45 ±0.116	0.33 ±0.013	0.1 ±0.0006	0.33 ±0.004	0.23 ±0.004	18.1 ± 0.049
3	<i>Pistia stratiotes</i>	Eco-Pd ₃	0.47 ±0.005	18.2 ±0.067	0.75 ±0.006	0.15 ±0.002	0.1 ±0.0004	0.11 ±0.001	3.7 ± 0.014
4	<i>Ludwigia peploides</i>	Eco-Pd ₄	0.19 ±0.003	14.98 ±0.078	n.d.	0.14 ±0.002	0.3 ±0.001	0.1 ±0.002	5.62 ± 0.028
5	<i>Fallopia japonica</i>	Eco-Pd ₅	1.04 ±0.010	11.93 ±0.155	n.d.	0.39 ±0.002	0.73 ±0.003	0.13 ±0.002	12.17 ± 0.043
6	Pinecone	Eco-Pd ₆	0.34 ±0.005	1.92 ±0.012	0.27 ±0.009	0.27 ±0.003	0.27 ±0.001	0.74 ±0.012	44.25 ± 0.336
7	Bark pine	Eco-Pd ₇	0.6 ±0.003	13.1 ±0.105	0.6 ±0.009	0.18 ±0.002	0.22 ±0.001	0.17 ±0.001	11.05 ± 0.084
8	Coffee grounds	Eco-Pd ₈	0.16 ±0.002	2.65 ±0.039	0.31 ±0.009	0.17 ±0.002	0.23 ±0.001	2.21 ±0.015	40.08 ± 0.240

data (Parker et al., 2014) and our previous results (Clavé et al., 2017; Garel et al., 2015), rhizofiltration of Pd^{II} effluents led to Pd⁰ or Pd^{II} respectively. This notable aspect revealed the unusual structure of Eco-Pd₄.

2.3. Reactivity of Eco-Pd in the sonogashira coupling reaction

2.3.1. Optimization of the reaction conditions

The coupling between iodobenzene **1a** and phenylacetylene **2a** was chosen as a model for the optimization of the reaction conditions (Scheme 1).

Full optimization results are summarized in the Table 3 of the supporting information. A fine study of reaction conditions was carried out. Seven parameters were studied: nature of biomaterial, loading in Pd, nature and amount of the base, amount of phenylacetylene, nature of the solvent, temperature, time of addition of **2a** (t_1) and time of the reaction (t_2). Given the number and range of experiments, principal component analysis (PCA) was used to analyze these data.

Main factors of the catalyzed Sonogashira coupling were the following: the nature of the solvent, the loading in Pd, the choice of the base and the time of the reaction t_2 .

PCA illustrated this result with an anticorrelation between Pd loading and yields (Fig. 1). We assumed that high Pd loading promoted the C–I reduction. Consequently, a very small amount of Pd should be used. This result is encouraging in terms of sustainable catalysis. Moreover, it actually holds great practical value because the price of Pd is exploding and constitutes a serious issue in catalysis.

In accordance with preliminary results (see full optimization in the SI, Table 3), the mixture glycerol/*n*-BuOH gave more satisfactory results than the mixture glycerol/water, because the latter promoted the concurrent reduction of iodobenzene. The best ratio was 1/1: glycerol/*n*-BuOH.

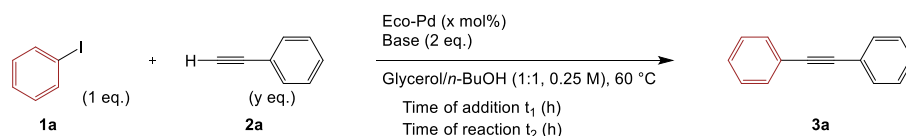
Whereas plant species had little influence on the yield, the choice of the base was important. Different bases were tried (Fig. 2),

such as K₃PO₄, Na₂CO₃, CaCO₃, CaO, Eco-CaCO₃ (Ca ecocatalyst, prepared from *Ostreidae*) and Eco-CaO (Ca ecocatalyst, prepared from *Crepidula*) (Grison, 2015). Gratifyingly, Eco-CaO and Eco-CaCO₃ turned out to be extremely efficient, even when the amount of palladium catalyst was decreased. We postulate that traces of Mg and Sr (See SI, Table 2) could explain the excellent results obtained with these two ecocatalysts. Among these two, Eco-CaCO₃ is preferable because of its better preservation under air and the more sustainable procedures used for its preparation. Moreover, Eco-CaCO₃ is cheap, abundant, environmentally friendly, derived from natural waste and non-toxic making it an obvious choice for this study. It is stimulating to conclude that the new, mild and bio-based base was the most effective.

Finally, very low loading in Pd (0.05 mol% - 0.1 mol%) led to the best yields (98 - 97%) at 60 °C for 6h or 4h respectively. Overall, the reaction required small catalytic amount and was performed under mild conditions in terms of temperature, reaction time and pH. These experimental conditions produced here through the ecocatalysis surpass systems produced by conventional methods by a large margin (Albéniz and Carrera, 2011; Ayogu and Onoabedje, 2019; Corma et al., 2006; Crudden et al., 2005; Cui et al., 2017; Dantas Ramos et al., 2004; Dioos et al., 2006; Elhampour and Nemati, 2017; Gao et al., 2010; Garg et al., 2005; Khalafi-Nezhad and Panahi, 2011; Li, 2005; Li et al., 2017; Liang et al., 2005; Lohmann et al., 2005; Mori et al., 2008; Mpungose, 2017; Nasrollahzadeh et al., 2014a; Rajender Reddy et al., 2006; Raju et al., 2006; Sadjadi, 2018; Sadjadi et al., 2019; Yi et al., 2012; Khazaei et al., 2013; Nasrollahzadeh et al., 2014b; Sathelly et al., 2016; Nasrollahzadeh et al., 2014c; Thomidis and Exadaktylou, 2008).

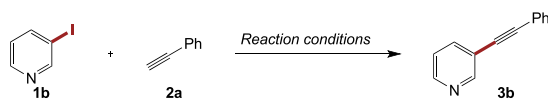
2.3.2. Scope of the reaction

Subsequently we investigated the scope of the EcoPd₄/Eco-CaCO₃/*n*-BuOH-glycerol system for the Sonogashira reaction under the optimized conditions (*i.e.* 0.1 mol% of Pd at 60 °C for 4h) that is depicted on Scheme 2. Interesting results were achieved with different substrates. An electron-donating group on the iodoaryl



Scheme 1. Model reaction for the optimization of the Sonogashira coupling.

Table 3
Comparison with the literature.



Entry	Conditions	Yield ^a	TON ^b	TOF ^c	Ref.
1	Mn(OAc) ₃ ·2H ₂ O (10 mol%) DABCO (2.5 eq.) PEG-400, 70 °C, 24 h ^d	65%	10	0.41 h ⁻¹	Qi et al. (2016)
2	Fe(III)@SiO ₂ -DABCO (1.6 eq.) Cs ₂ CO ₃ (2 eq.) H ₂ O/DMF, 110 °C, 24 h	77%	0.6	0.025 h ⁻¹	Hajipour et al. (2018)
3	10% Pd/C (0.4 mol%) 50% <i>i</i> -PrOH, Na ₃ PO ₄ ·12H ₂ O (2 eq.) Ar, 80 °C, 3 h ^e	83%	250	83 h ⁻¹	Mori et al. (2008)
4	PdCl ₂ (1 mol%) Pyrrolidine (5 eq.), H ₂ O, 24 h, 50 °C	95%	100	4.2 h ⁻¹	Liang et al. (2005)
5	Pd(OAc) ₂ (1 mol%) Gallic acid (1 mol%), Cs ₂ CO ₃ (2 eq.) EtOH, 40 °C, 12 h	90%	100	8.3 h ⁻¹	Sarmah et al. (2017)
6	Eco-Pd (0.1 mol%) Eco-CaCO ₃ (2 eq.) Glycerol/ <i>n</i> -BuOH, 80 °C, 4 h	>99%	10 ³	250 h ⁻¹	This study

^a Isolated yield.

^b TON = n (converted reactant)/n (catalyst).

^c TOF = TON/time of reaction.

^d DABCO: 1,4-diazabicyclo[2.2.2]octane; PEG: Polyethylene glycol; DMF: *N,N*-Dimethylformamide.

^e Calculations did not consider the use of argon.

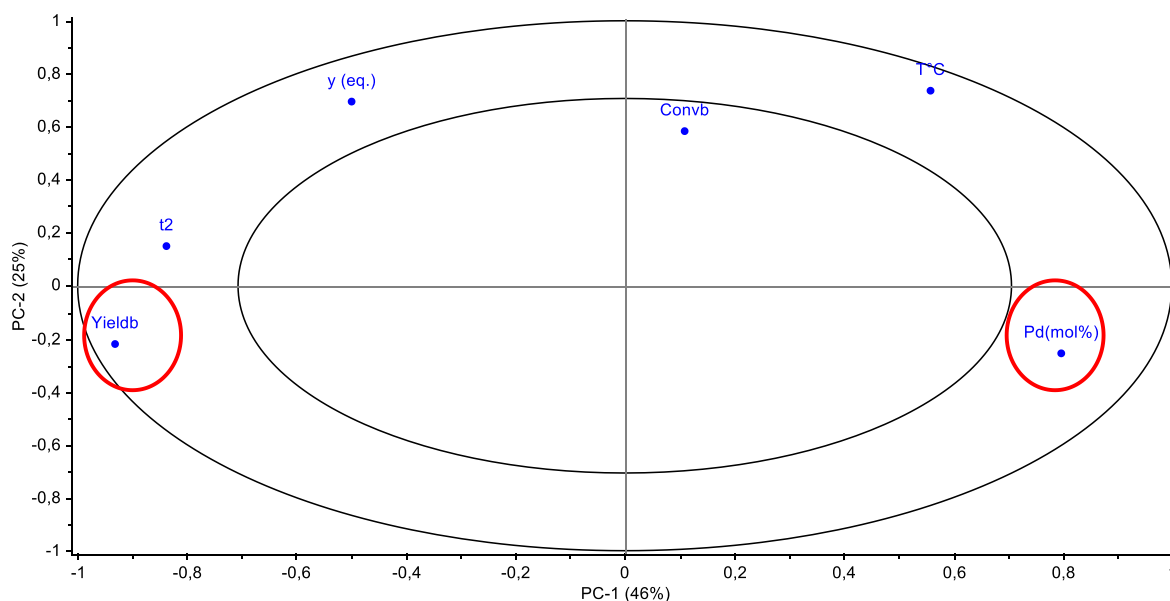


Fig. 1. PCA of Sonogashira coupling: anticorrelation between Pd loading and yields.

moiety was compatible with the mild reaction conditions. With a methoxy group, the expected product **3c** was isolated with satisfactory yield (70%). When R¹ was a halogen moiety (F, Cl), the couplings were quantitative. These results reflected a total selectivity of the reaction between an iodine atom and fluorine or chlorine atoms. However, when R¹ was Br, a partial competitive reaction was observed with the iodine atom and a mixture of the expected product and **3h** was observed. The 1,4-diiodobenzene could undergo a double copper-free Sonogashira reaction giving **3h** in a good 65% yield. This dialkyne **3h** is particularly interesting as a synthon for the preparation of microporous photoluminescent polyphenylenes. (Sedláček et al., 2018).

By changing the terminal alkyne partner to an aliphatic alkyne, the expected product **3f** was observed. This reaction was still efficient and tolerated the presence of an unprotected alcohol function.

Interestingly, the reaction could be extended to heteroaryl substrates. Electron-poor heteroaryl iodides such as iodopyridine could couple efficiently with phenylacetylene to form **3b**. Conversely, the reaction of 2-ethynylthiophene with iodobenzene gave the product **3g** in a quantitative yield. We can conclude that the N- and S- atoms of iodo aryl partner did not deactivate Eco-Pd. This demonstrates the higher stability of EcoPd compared to conventional Pd catalysts, which are associated with a ligand or an additive (Chinchilla and Nájera, 2011).

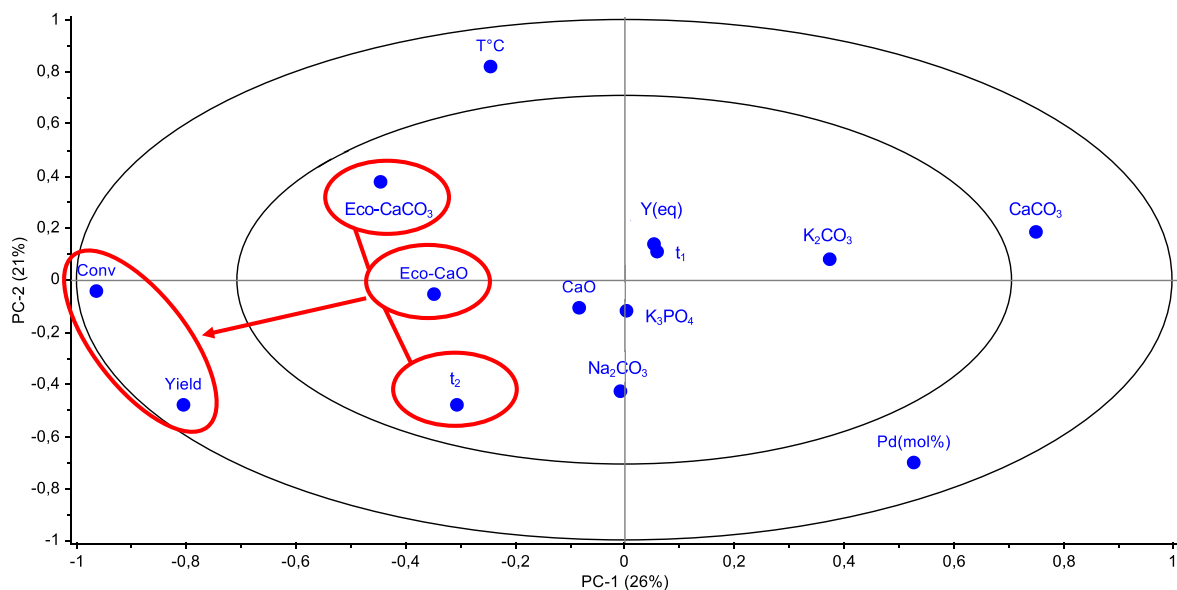
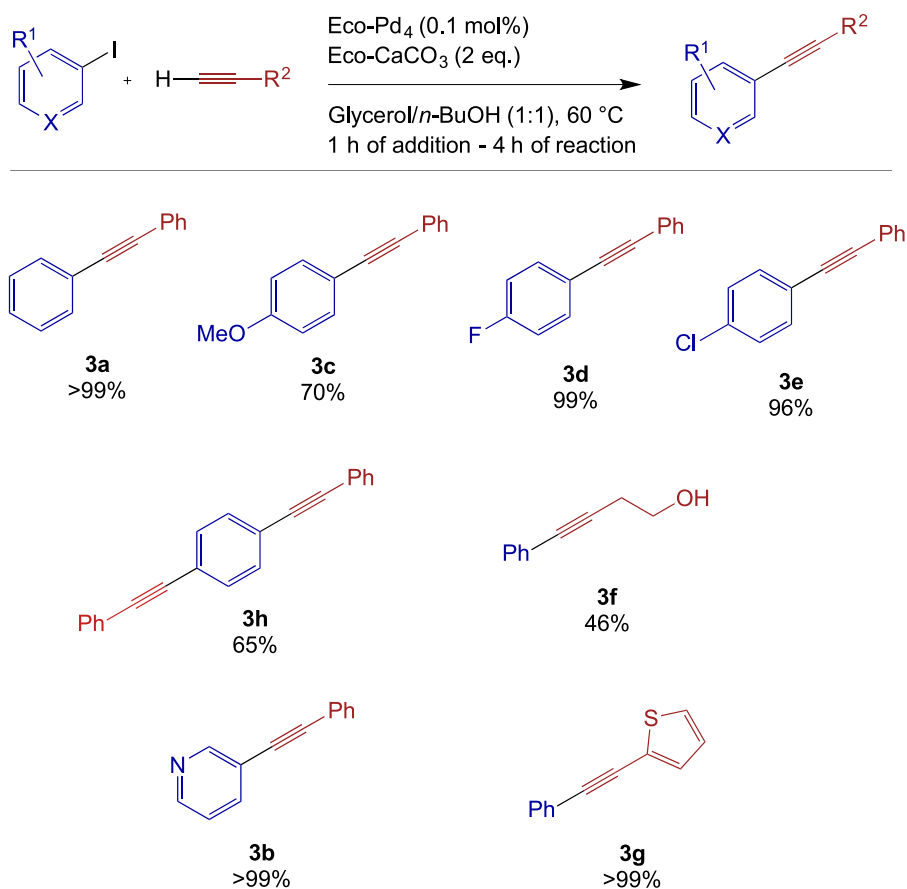


Fig. 2. PCA of Sonogashira reaction: correlation between yield, conversion, base and time of the reaction t_2 .

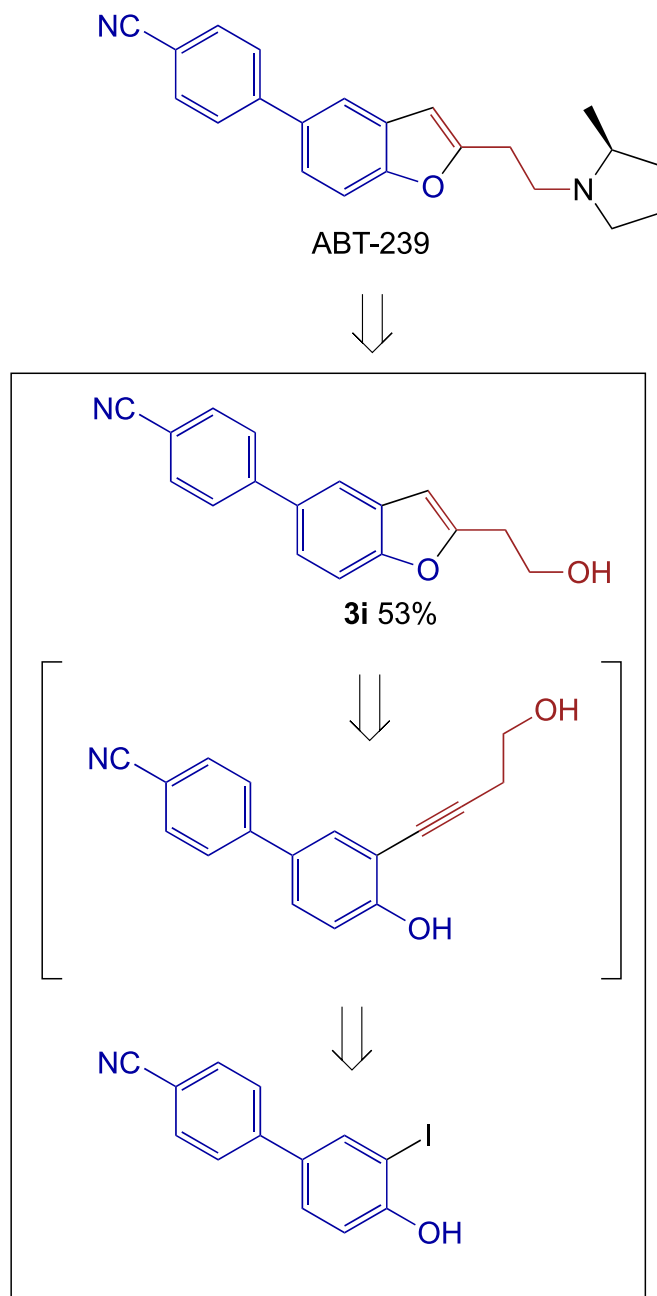


Scheme 2. Scope of the reaction*

*NMR yield was measured using allyl phenyl ether as internal reference.

Particular interest relies on the possibility of using Eco-Pd derived from plant species in multi-step synthesis. 4-(2-(2-(2-methyl-1-pyrrolidinyl)ethyl)-1-benzofuran-5-yl)benzotrile, called ABT-239, was an attractive target to complete the scope of this study. It is an H₃-receptor inverse agonist that has been investigated for ADHD, schizophrenia and Alzheimer's disease

(Coward et al., 2002, 2004, 2005; Esbenshade et al., 2005; Hancock, 2006). The synthesis was based on a key step: the Sonogashira coupling between 4-cyano-4'-hydroxy-3'-iodio-biphenyl with butyn-3-ol, followed by the cyclization of the expected product into benzofuran **3i** (Pu et al., 2005). We devoted particular attention to the direct preparation of **3i** (Scheme 3).



Scheme 3. Retrosynthesis strategy for the preparation of ABT-239.

The compound **3i** was prepared from the commercially available iodoaryl, showing the good tolerance towards the nitrile group during the coupling. The hydroxybutynyl-phenol intermediate subsequently cyclized *in situ* to give the benzofuran alcohol **3i** in a one-pot reaction. The conversion of iodoaryl was quantitative. It should be noted that the cyclization was the rate-limiting step and led to an overall yield of 53%. The Eco-Pd system can also be applied in domino reaction, showing the compatibility of the ecocatalyst with different conditions to demonstrate its value as a powerful synthetic tool.

2.3.3. Comparative analysis with other catalytic systems

In view of the low loading and the rapidity of the coupling reaction catalyzed by EcoPd₄, it was interesting to evaluate the

turnover number (TON) and the turnover frequency (TOF) of the coupling. The assessment was carried out for the synthesis of **3b** because cross-coupling substrates that include nitrogen heterocycles are the most challenging. Results are compared with data from the literature (Table 3).

The coupling reaction of entries 1–2 and 4 required the presence of problematic nitrogen bases. DABCO and pyrrolidine are irritant, corrosive and inflammable. Moreover, DABCO is hazardous to the aquatic environment with long lasting effects.

The example of entry 1 needed a surfactant, PEG-400 and entry 2 required a toxic solvent, DMF. DMF has long been known to be toxic and could cause cancer in humans.

The performance of EcoPd₄ compares favorably with these data. Without hazardous components, Eco-Pd₄ (Entry 6) exhibited unusually high TON, four times greater than that of the best-performing alternative of those listed above (Entry 3). This data showed that Eco-Pd₄ was able to promote the coupling with lower Pd quantity and without any poisoning effect of the heterocyclic atom of pyridine.

As shown in entry 6, EcoPd₁ led to excellent TOF (250 h⁻¹), demonstrating the higher stability of Eco-Pd compared to classic Pd catalysts.

The absence of toxic solvents and bases, the use of low Pd loading and the performances of ecocatalysis, make Eco-Pd more appealing for the Sonogashira coupling to any previously reported systems.

2.3.4. Recycling and reuse of Eco-Pd

A classic limitation of homogeneous catalysts is the lack of ability to recover and reuse Pd catalyst from the reaction mixture. Because of the high value of palladium, we demonstrated here that Eco-Pd can be recycled by biosorption methodology.

To test the capacity for recycling, we studied the coupling model between phenylacetylene and iodobenzene promoted by Eco-Pd₄, and determined the best experimental conditions for recycling the Pd with Eco-CaCO₃ as base. After completion of the reaction, direct biosorption of Pd was performed by roots of *L. peplodes* directly in the organic media. After centrifugation, the post-solution was diluted with AcOEt to extract the product of the coupling reaction. The filtered Pd-loaded roots of *L. peplodes* and black Pd were

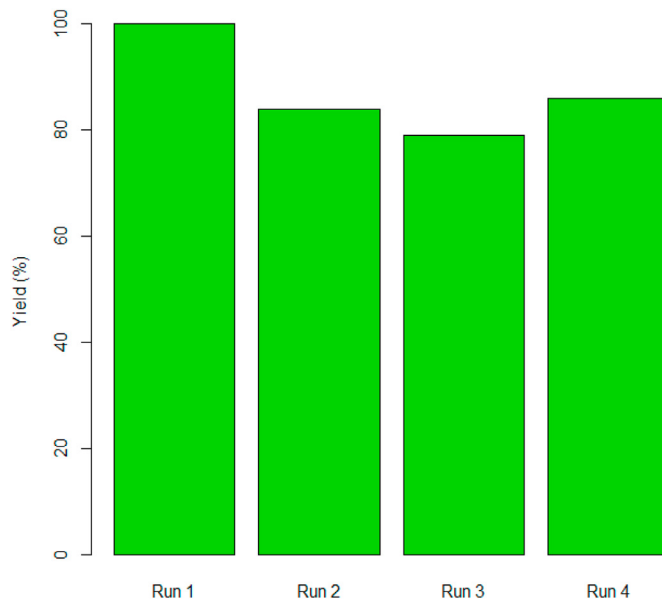


Fig. 3. Recyclability and reuse of Eco-Pd₄.

subjected to the sequence thermal treatment/activation and a new Eco-Pd₄ was reused for a new Sonogashira coupling reaction.

Fig. 3 shows that catalytic activity was maintained after recycling. Although a slight reduction of activity was observed after the first run, conversions and yields were not affected in subsequent runs. Eco-CaCO₃ as a base led logically to variation in the composition of Eco-Pd (See SI, table 4), without modification of performances.

This result constitutes one of rare available solution on the recovery of a precious metal such as Pd, from wastewater effluents. The biosorption methodology for recycling and reuse of Pd is of especial interest due to the availability of biomass and the efficiency of the method.

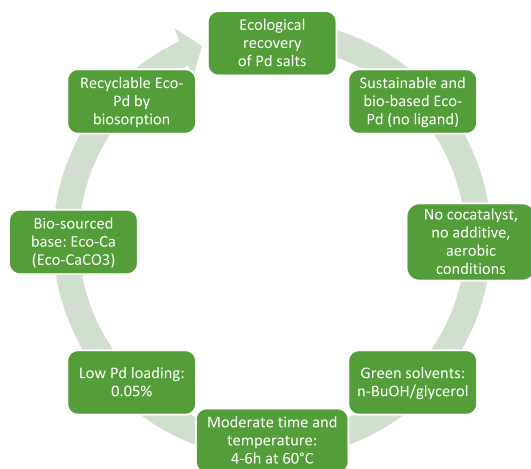
3. Conclusion

A greener and more straightforward approach to Sonogashira coupling was reported. Bio-sourced Eco-Pd in conjunction with Eco-Ca allowed promoting the reaction in a glycerol/n-BuOH mixture.

The addition of a ligand, a cocatalyst such as a copper salt, or an additive, were not necessary. The conditions for this reaction were fairly mild, as they were conducted at 60° for 4h–6h with a low Pd loading (0.1–0.05 mol%). Different iodoaryl and heteroaryl substrates were used successfully, and high yields were obtained. The reaction showed excellent tolerance of several functional groups, including fluoro, chloro, cyano, hydroxy, and methoxy groups.

Results on TON and TOF for this system compared favorably with this from known systems reported in the literature. Moreover, the sequenced synthesis of a key precursor of the ABT-239, manufactured in the pharmaceutical industry, highlighted the performances of the catalytic system as a valuable alternative to classical catalysts.

In the present study, many efforts were performed to conform to the criteria of green and sustainable chemistry. We can conclude that catalysts, bases and solvents can all be derived from readily available renewable feedstocks. The low Pd-loading, the absence of ligand, cocatalyst, and additive, the moderate time and temperature and also the capacity to recycle and reuse Eco-Pd provided a technically and economically strong process. The described strategy for Sonogashira coupling is direct, robust, ecofriendly, safer and cost-effective. We can assume that such reaction conditions would not introduce negative ecological impacts.



We believe that the ecocatalysis and results demonstrated above represent a step change in the design of cleaner processes in organic chemistry. In addition to the environmental gain brought by the advantages of green chemistry, this approach provides other major environmental benefits:

- restoring degraded aquatic ecosystems by the recycling of Pd salts with different materials derived from plant feedstocks. The technology can be advantageously compared with existing metallurgical recovery processes;
- using of invasive plants as plant filters to recycle Pd salts. It is an opportunity for the recovery of invasive plants and provides strong motivation for the control of their proliferation.

These ecological solutions generate a novel type of biomass rich in Pd, which has become a source of innovation in greener catalytic chemistry. The overall methodology suggests a promising life-cycle analysis.

CRediT authorship contribution statement

Pauline Adler: Syntheses experiments. **Timothé Dumas:** Syntheses experiments. **Pierre-Alexandre Deyris:** Syntheses experiments. **Eddy Petit:** Chemical assessments. **Sébastien Diliberto:** Formal analysis. **Clotilde Boulanger:** Formal analysis. **Claude Grison:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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