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Ullmann reaction through ecocatalysis: insights from bioresource and synthetic potential

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Abstract: We report the elaboration of novel bio-sourced ecocatalysts for Ullmann coupling reaction. Ecocatalysis is based on the recycling of metals issued from phytoremediation or rehabilitation, and an innovative chemical valorization of the subsequent biomass in the field of catalysis. Here, we describe the efficient copper accumulation by plants *via* phytoextraction and rhizofiltration. These phytotechnologies were revisited to demonstrate a novel potential of these natural resources for the Green Chemistry. Taking advantage of the remarkable ability of the selected plants to accumulate Cu(II) species into their roots or leaves, these latter can be directly used for the preparation of ecocatalysts, called Eco-Cu[®]. The formed Eco-Cu[®] catalysts are thoroughly characterized via ICP-MS, IR study of pyridine sorption/desorption, TEM, XRD, SM and model reactions, in order to elucidate the chemical composition and catalytic activity of these new materials. Significant differences of properties and activities were observed between Eco-Cu[®] and conventional Cu catalysts. Eco-Cu[®] appear as highly active catalysts in Ullmann coupling reactions with lower Cu quantity compared to known copper catalysts.

Keywords: phytoextraction; Congolese mining sites; rhizofiltration; contaminated effluents; ecological recycling; ecocatalysis; copper catalysis; Ullmann coupling

1. Introduction

Intensive mining and industrial metallurgic activities are responsible for the pollution of soils and aquatic systems with metal trace elements (TEs). This is incredibly worrying, since the soil plays an essential role largely determining food production and water quality. Moreover, TEs are some of the

most harmful pollutants. They are not biodegradable and persist in organisms and contaminated ecosystems.

For instance, the devastating effects of mining in the southern province of the Democratic Republic of the Congo characterize one of the critical patterns implicated in global environmental change. In Katanga, the negative consequences of mining operations for the local population are clear: large-scale destruction of natural ecosystems and arable soils, severe impacts on hydrological processes, increased sediment pollution in rivers and the groundwater table, reduction of biodiversity, soil erosion, and release of Cu and Co, which leads to contamination of soils, surface and ground water. Animals are contaminated upon contact, through the inhalation of metal dust, ingestion of contaminated water and food. Metal pollutants travel through the food chain, and thus they have also a significant impact on human health.

Phytoremediation is used to solve environmental problems caused by TEs. Given their phytotoxicity, metalliferous soils are under high selection pressure and generate particular habitats for plant species and their associated microorganisms. This results in a unique biological resource, metallophytes. These plants are defined as being capable of tolerating high concentrations of TEs, surviving and reproducing on such sites¹. Phytoextraction is one of the few interesting solutions for sustainable phytoremediation of soils degraded or contaminated by TEs. It is defined as the partial rehabilitation of soils through the accumulation of TEs in aerial parts of hyperaccumulator plants (*e.g.* *A. murale*², *A. vulneraria*³, *G. exul*⁴). Rhizofiltration is equivalent to phytoextraction process, but it takes place in an aqueous medium instead of the rhizosphere⁵.

However, the development of phytoextraction and rhizofiltration is still restricted because contaminated biomass is not recovered: the aerial parts of hyperaccumulator plants, or roots of plants derived from rhizofiltration are considered as contaminated waste. Moreover, the extraction of TEs by the root system increases the fraction of soluble elements. The sustainability of phytoextraction and rhizofiltration is entirely related to the recycling of the generated biomass.

Our group has recently proposed a unique use and valorization of phytoextraction and rhizofiltration: ecocatalysis⁶⁻⁸. Plant waste produced is recovered using an innovative concept of ecological recycling. Taking advantage of the remarkable adaptive capacity of some plants to hyperaccumulate metals, ecocatalysis is based on an original use of metal species of plant origin as reactants and catalysts in fine organic chemical reactions. This allows the preparation of biomolecules using an eco-responsible and bio-inspired approach. The obtained results demonstrate that these new catalytic systems present unique chemical reactivity. Ecocatalysts constitute an entire new generation of Lewis acid catalysts⁹⁻¹⁵, very efficient green oxidative¹⁶, reductive¹⁷, and sustainable coupling agents in organic synthesis¹⁸. They can be used as alternative reagents in place of those prohibited by the European legislation REACH. Finally, we could use these reagents to develop innovative bio-inspired syntheses capable of reducing the environmental impact of implemented procedures.

Ecocatalysis created a change in the paradigm: biomass from phytoextraction and rhizofiltration is no longer considered as contaminated waste, but as a natural restoration system with high added value. This biomass is a natural reservoir of transition metals, precious in organic synthesis. In other words, wastes have become useful and innovative chemical tools.

This article aims at describing new results in the field of phytoremediation of systems contaminated by copper from anthropogenic activities, and to study the recovery of the derived biomass through the

concept of ecocatalysis. Comparatively, the copper phytoextraction is studied on mining sites in Katanga, while copper rhizofiltration is carried out with contaminated copper solutions. Results clearly allow the preparation, characterization and study of the reactivity of these first Eco-Cu[®] catalysts in N- and O-arylation coupling reactions.

2. Results and Discussion

2.1.1. Phytoextraction:

TEs contaminants occurrence and impact on humans and other organisms have already been reported in Katanga (Democratic Republic of the Congo)¹⁹. Tropical soils contaminated by metal smelters and mining represent a secondary source of contamination with major environmental issue related to low pH²⁰ of Ferralsol increasing TEs mobility, intense erosion by rainfall in the rainy season, and aerial dispersal of metal particles by wind in the dry season. Reduction of environmental risks and TEs dispersion can be performed by phytoremediation, using TEs tolerant and hyperaccumulator plants from the plant biodiversity of natural habitats enriched in Cu²¹⁻²³. This study is the first investigation on the phytoextraction of soils contaminated by copper smelters and mining associated to the preparation of Cu ecocatalysts.

Copper concentrations in plant shoots of Anisopappus chinensis

Mean of Cu concentration in *A. chinensis* plant shoots (FCu) was 230 $\mu\text{g g}^{-1}$ dry weight (DW) (range: 45–504 $\mu\text{g g}^{-1}$ DW). The high variation of Cu accumulation observed in *A. chinensis* in accordance with previous studies²²⁻²⁴. As already highlighted for other Cu-accumulating species, such variations can be genetic, especially due to genetic differentiation within and between populations^{25, 26}. Better understanding of such accumulation variations requires an accurate characterization of the soil-root interface properties and mechanisms controlling Cu mobility and availability^{24, 27}. Soil parameters like pH, redox potential, organic matter quality and quantity, oxides, clays, sulphides and carbonates are known to be essential factors controlling TEs mobility in soils²⁸. In Congolese metalliferous soils, Cu is known to be mostly adsorbed by organic matter and iron oxide species^{20, 24}.

Evaluation of phytoextraction parameters for one year of plant growth

Mean of shoot biomass of individuals of *A. chinensis* ($n = 20$) was 1.18 g (range: 0.14–3.79 g). Biomass productivity (Ybio) was estimated to 17.7 $\text{g/m}^2/\text{year}$ whether 177 kg/ha/year (range: 20–568 kg/ha/year). Mean Cu content in *A. chinensis* plant shoots was 287 μg of Cu per plant from the DW (range: 29–1781 $\mu\text{g plant}^{-1}$). A comparable amount of Cu per plant can be phytoextracted using the Cu-tolerant species *Elsholtzia splendens*^{29, 30}.

Total Cu phytoextracted (YCu = FCu.Ybio) /ha/year on contaminated soil using plants of *A. chinensis* from “Mine de l’Etoile” could reach 286 g/ha/year. A much more higher yield of phytoextracted Cu can be obtained with *E. splendens* (1.7 kg Cu ha⁻¹)^{29, 30}, but compared to some crop species, such a yield of phytoextraction could be about five times higher (e.g. sunflower with 59 g Cu ha⁻¹)³¹. *A. chinensis* appears to be a good candidate for Cu phytoextraction. However, due to the great variability of its ability to extract Cu from the soil, phytoextraction using *A. Chinensis* should be improved by

plant selection and genotyping. Indeed, an individual from another natural population could accumulate Cu up to 1 335 $\mu\text{g g}^{-1}$ DW for 5.1 g:6.7g plant⁻¹, *i.e.* a yield almost quadrupled (1 kg/ha/year)²⁴. Potentially, Cu phytoextraction might be improved by performing a multispecies system introducing other Cu tolerant and accumulator species. Such an innovative system on Cu contaminated soils could lead to an increased phytoextraction yield as some species are known to accumulate Cu in their shoots more effectively than *A. chinensis* (*e.g. Haumaniastrum robertii*)³².

This first evaluation on phytoextraction of soils contaminated by Cu in Tropical Africa has shown a medium yield of Cu phytoextracted. Perspectives would be to test it at field scale with a multi-species system, introducing functional diversity of Cu-tolerant plants (species and populations).

2.1.2. Rhizofiltration

Choice of the plants

Three plants have been studied to test their ability to accumulate copper into their roots from aqueous medium. *Bacopa monnieri* was already known to well accumulate copper into its roots^{5, 33}. *Lolium multiflorum* was known to accumulate other metallic elements than copper, such as palladium, and its main asset relies on its well-developed root biomass^{18, 34}. Finally, *Eichhornia crassipes* was also known to accumulate copper³⁵, to multiply easily and also for its amazing root biomass, which of course are assets to perform ecocatalysis.

Plant growth

Before studying the efficiency of these plants in rhizofiltration, it was interesting to have an insight of the plant biomass growth, and of the biomass measuring (Table 1). The amount of root biomass is important for the removal of copper from aqueous media, and also affects the quantity of ecocatalyst (Eco-Cu[®]) possibly formed.

B. monnieri and *E. crassipes* were directly bought in a garden center. *L. multiflorum* was grown in our laboratory, and the germination percentage after 9 days was 82%.

Table 1. Biomass measuring (mg/plant) for *Lolium multiflorum*, *Bacopa monnieri* and *Eichhornia crassipes*.

Species	Substrate for growth	Growth period	Root biomass (mg/plant)	Shoot biomass (mg/plant)
<i>Lolium multiflorum</i>	Fleximix Root Riot Organic Starter Cubes	8 weeks	6.8	20.2
<i>Bacopa monnieri</i>	Natural substrate Manado	5 months ^a	54	840.8

<i>Eichhornia</i>	/	5743	1629
<i>crassipes</i>			

^aPeriod between the start of the cultivation on Manado substrate until the beginning of Cu accumulation

In terms of root biomass, *E. crassipes* gave better results than the other plants, which is an asset for copper accumulation, and for ecocatalysts preparation. Moreover, this plant is easy to handle because it can grow without any substrate thanks to its inflated petiole.

Plant analysis: determination of metal concentrations in roots and leaves

Copper concentrations in roots and leaves of the three plants were determined by an ICP-MS analysis. The results are shown in table 2.

Table 2. Copper concentration in roots and leaves (wt% \pm standard deviation), and BCF and TF calculation.

Plant	Cu concentration in effluent (mg/L)	Roots (wt% \pm SD)	BCF (in roots)	Leaves (wt% \pm SD)	BCF (in leaves)	TF
<i>Bacopa monnieri</i> ^a	10.5	1.34 \pm 0.011	1279	0.097 \pm 0.0011	92	0.072
<i>Lolium multiflorum</i> ^b	10.6	0.71 \pm 0.0036	666	0.0031 \pm 0.000007	2.9	0.0044
<i>Eichhornia crassipes</i> ^c	10.5	2.55 \pm 0.027	2430	0.082 \pm 0.00073 0.19 \pm 0.0014 (petiole)	78 180.4 (petiole)	0.032 0.074 (petiole)

^aDuring Cu accumulation the substrate used for growth was removed

^b*Lolium multiflorum* was still on Fleximix Root Riot Organic Starter Cubes during copper accumulation

^cNo substrate used

Concentration of copper in root biomass is much higher in *E. crassipes* than in *L. multiflorum* and *B. monnieri*. Besides, the translocation factors in the petiole and leaves of *E. crassipes* remain low, with values between those obtained with *L. multiflorum* and *B. monnieri*. These results combined with biomass measuring make *E. crassipes* a good candidate for rhizofiltration to produce ecocatalysts.

2.2.1. Preparation of the Eco-Cu[®] catalysts

Eco-Cu₁₋₂[®] (*A. chinensis*), were prepared from harvested plants' leaves and Eco-Cu₃₋₄[®] (*B. monnieri*), Eco-Cu₅₋₆[®] (*L. multiflorum*) and Eco-Cu₇₋₈[®] (*E. crassipes*), were prepared from harvested plants' roots following the described procedure (see experimental part, section 3.4.). Each ecocatalyst must be subjected to a heat treatment sufficient to destroy organic matter. Eco-Cu₂[®], Eco-Cu₄[®], Eco-Cu₆[®] and Eco-Cu₈[®] were activated by chemical treatment with hydrochloric acid from Eco-Cu₁[®], Eco-Cu₃[®], Eco-Cu₅[®] and Eco-Cu₇[®] respectively. This step enables metal chlorides formation inside of the ecocatalysts.

2.2.2. ICP-MS characterization of the Eco-Cu[®]

Table 3 shows mineral composition of the different Eco-Cu[®] catalysts. It can be divided in two parts: ecocatalysts derived from phytoextraction (Eco-Cu₁₋₂[®]) and those obtained from rhizofiltration (Eco-Cu₃₋₈[®]). Copper concentrations in Eco-Cu[®] catalysts are quite different depending on the nature of the plant, which is in agreement with phytoextraction and rhizofiltration studies reported in the previous sections 2.1.1. and 2.1.2. It is clear that ecocatalysts derived from plants used in rhizofiltration are more concentrated in Cu than ecocatalysts derived from plants used in phytoextraction. For instance, copper concentrations in Eco-Cu₃₋₄[®] are 20 times higher than in Eco-Cu₁₋₂[®], which confirms that *B. monnieri* is a much better copper accumulator than *A. chinensis*. However, as reported previously (see section 2.1.1. and 2.1.2.), the biomass of *A. chinensis* is more abundant than the biomass of *B. monnieri*, which is an asset to produce ecocatalysts in larger quantities. *E. crassipes* is the best plant tested for rhizofiltration, with a weight percentage of copper in its resulting ecocatalyst at least twice higher than in the other ecocatalysts. Moreover, some significant differences between the compositions of the catalysts are observed: *A. chinensis* catalysts are poor in sodium and rich in potassium whereas these rates are reversed in case of *B. monnieri*. In the case of plants used in rhizofiltration, the main difference, apart from the copper rate, is the calcium rate: *L. multiflorum* is richer in calcium than *E. crassipes*.

Even if the two phytotechnologies, phytoextraction and rhizofiltration, gave different results in terms of accumulation and biomass, they are complementary for the remediation of contaminated targets, soil or water. This article is an opportunity to study the recovery of these different types of biomass through the preparation and the activity of ecocatalysts.

Table 3. Mineral composition of Eco-Cu[®] catalysts (wt% ± standard deviation) established by ICP-MS.

Ecocatalyst	Plant	Na	Mg	Al	K	Ca	Fe	Zn	Cu
Eco-Cu ₁ [®]	<i>Anisopappus chinensis</i>	0.11	7.85	1.01	23.29	8.44	0.92	0.08	0.38
		±4.05	±0.59	±3.83	±4.66	±1.46	±0.59	±1.59	±0.38
Eco-Cu ₂ [®]		0.31	6.40	0.68	18.73	7.80	0.78	0.06	0.26
		±1.55	±0.64	±0.77	±0.60	±0.91	±0.80	±0.48	±0.97

Eco-Cu ₃ [®]		9.60	3.23	3.40	6.23	8.28	1.97	0.06	9.15
	<i>Bacopa monnieri</i>	±0.86	±0.36	±0.95	±0.83	±0.93	±0.72	±1.15	±0.77
Eco-Cu ₄ [®]		5.29	1.86	1.93	3.48	4.91	1.21	0.04	4.75
		±0.18	±0.53	±1.14	±0.29	±0.77	±0.34	±0.77	±0.45
Eco-Cu ₅ [®]		0.78	0.60	0.00	1.11	34.61	0.04	0.09	3.29
	<i>Lolium multiflorum</i>	±0.70	±0.13	±2.96	±0.36	±0.35	±0.71	±0.49	±0.52
Eco-Cu ₆ [®]		0.50	0.36	0.00	0.72	22.18	0.02	0.05	2.02
		±0.69	±1.48	±6.00	±0.71	±0.59	±1.86	±0.72	±1.05
Eco-Cu ₇ [®]		1.26	0.43	0.13	0.38	0.97	1.85	0.06	18.15
	<i>Eichhornia crassipes</i>	±0.06	±0.30	±1.01	±1.51	±1.02	±0.55	±3.50	±0.25
Eco-Cu ₈ [®]		0.84	0.26	0.05	0.14	0.61	0.81	0.03	10.37
		±0.57	±0.95	±1.82	±0.34	±6.97	±0.21	±5.86	±0.23

2.2.3. XPS Analysis

XPS analysis was performed on Eco-Cu₈[®] to study the oxidation state of copper after thermal treatment and activation with HCl.

The strong peak at 202 ± 0.1 eV corresponding to chlorine $2p_{3/2}$ illustrates the formation of chloride due to the aq. HCl activation of the material.

High resolution analysis of the copper element was carried out. The $2p_{3/2}$ Cu signal consists of a combination of two components: 933 and 935 ± 0.1 eV. The more intense one is characterized by a binding energy of 933 ± 0.1 eV, indicating the expected presence of Cu(II). The component at 935 ± 0.1 eV has a lower intensity (about 13% of the main peak) and may be assigned to Cu(I), in agreement with the literature³⁶. It is assumed that the observation of Cu (I) is not due to Eco-Cu₈[®], because it is well known that Cu(II) is easily reduced to Cu(I) when subjected to XPS analysis³⁷. Finally, strong $2p_{3/2}$ satellite peaks of Cu(II) are present in the region of $940-950 \pm 0.1$ eV³⁶.

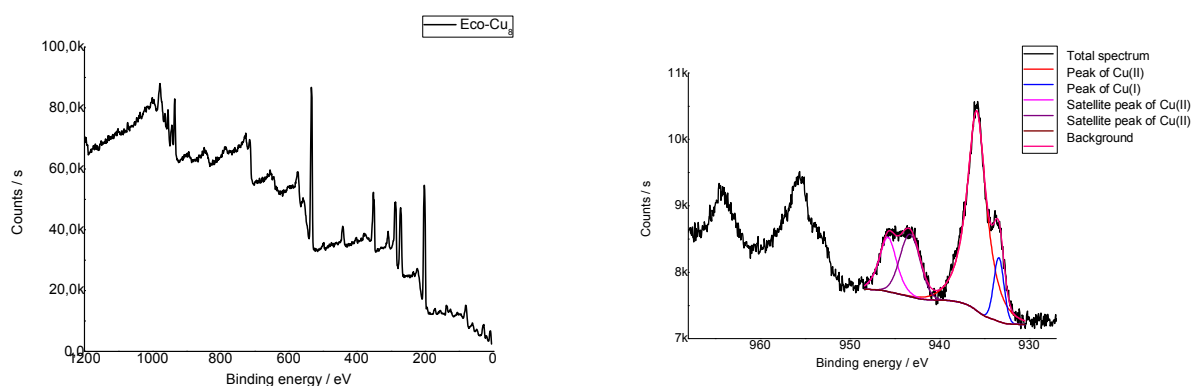


Figure 1. XPS analysis of Eco-Cu₈[®]

The formation of Cu(II) is the consequence of an oxidative thermal treatment under air flow of plants' roots. This hypothesis is reinforced by the reaction of Eco-Cu₈ with aqueous ammonia and the formation of a deep blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complexes.

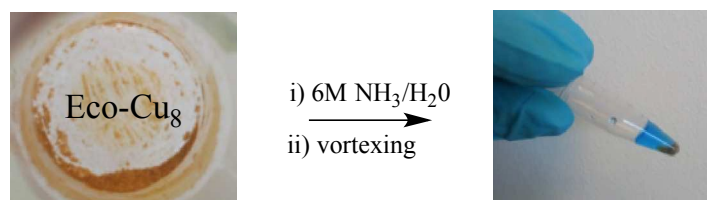


Figure 2. Analytical characterization of Eco-Cu₈[®]

In the aim to specify the nature of copper (II) chloride salts, mass spectrometry analysis were performed by direct-injection mass spectrometric method.

2.2.5. Direct-injection mass spectrometric analysis

Structural information for Eco-Cu₈[®] was collected using mass spectrometry with electrospray ionization operated in the negative ion mode. This MS method provided sufficient sensitivity and selectivity for the rapid identification of an anionic inorganic species, but it led to the electrochemical reduction of Cu(II) into Cu(I) according to Gianelli works³⁸.

With Eco-Cu₈[®], two Cu chlorides species were detected: CuCl₃²⁻ and CuCl₂⁻. Taking into account the copper oxidation state reduction of Cu by the ESI method, we can conclude that Eco-Cu₈[®] consists of a mixture of CuCl₄²⁻ and CuCl₃⁻. This hypothesis is consistent with the XPS analysis.

2.2.6. XRD studies

XRD analyses of Eco-Cu₈[®] were performed in order to determine the crystalline structure of the complexes in the catalyst (Figure 3). One polymetallic compound was detected: K₆Fe₂O₅. Manganese was present in the manganosite form MnO, in the presence of sodium chloride and calcium sulfate hydrate. Copper was present in the amorphous form.

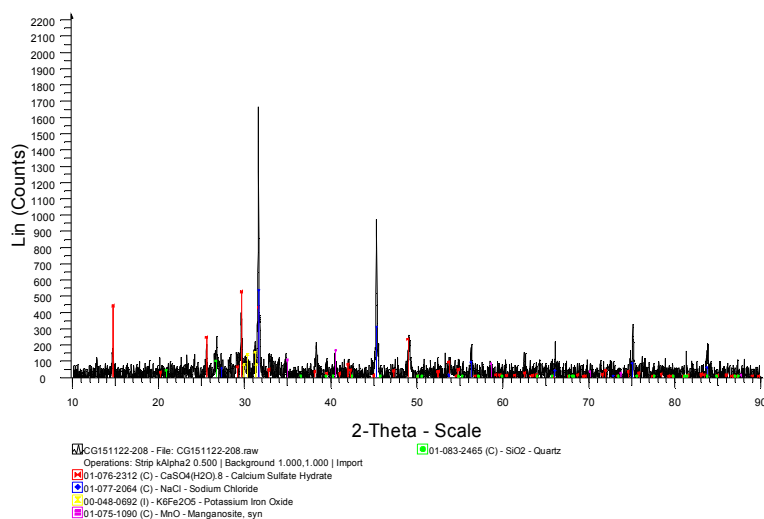
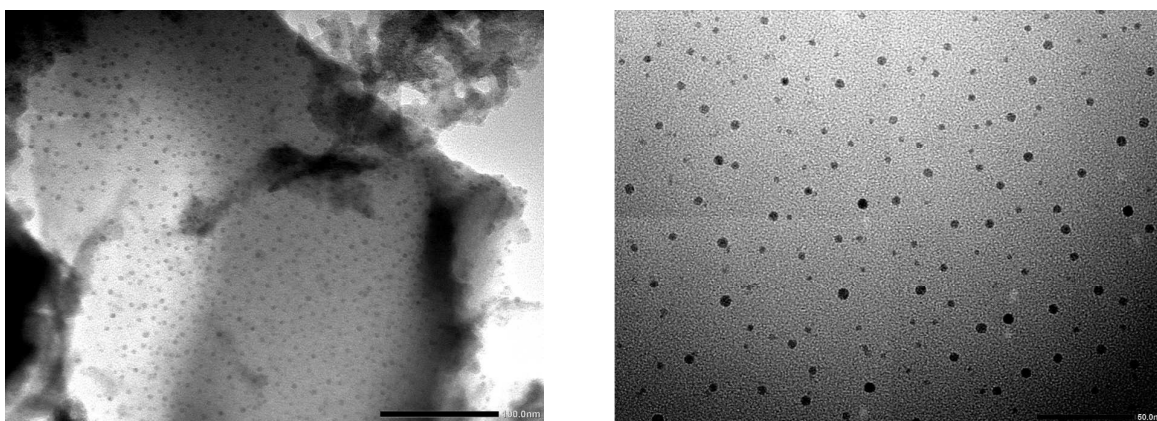


Figure 3. XRD analysis of Eco-Cu₈[®]

2.2.7 TEM studies

The morphology and structure of Eco-Cu₈[®] was further characterized using TEM. Figures 4a and 4b shows the TEM images. The microstructure of the ecocatalyst is layered with dark shades and clear areas, indicating a satisfactory uniformity in the composition of the ecocatalyst. TEM images of Eco-Cu₈[®] in figure 4b reveal Cu nanoparticles, which are embedded in the solid matrix. These nanoparticles are not aggregated and are well dispersed at the surface of the matrix. The particle size has been determined based on the average size of 40 particles. The particles show a relatively narrow size distribution centered around 4-8 nm.



Figures 4a and 4b. TEM images of Eco-Cu₈[®]

2.2.8. Acidity characterization of the Eco-Cu[®] catalyst

We decided to study Lewis and Brønsted acid properties of our best ecocatalyst (Eco-Cu₈[®], see 2.3 section) *versus* commercial copper chlorides. Lewis acidity is usually defined by its strength and its hardness according to the HSAB principle, described by Pearson^{39,40}. Two conventional methods were used: the first one is based on the infrared study of pyridine adsorption/desorption on the catalysts. The second, introduced by Corma *et al.* consists in studying the rearrangement of a cyclic acetal. The first method enables a comparison of the Lewis acid strength and Brønsted acidity between different catalysts. The method implemented by Corma *et al.* enables also a comparison of the hardness of Lewis acidity.

Pyridine is often used as a probe to evaluate Lewis and Brønsted acidity of solid acids^{41, 42} by monitoring its infrared absorption bands between 1400 and 1660 cm⁻¹. Infrared spectra of pyridine adsorbed on Eco-Cu₈[®], on commercial anhydrous CuCl₂, and on CuCl₂.2H₂O were recorded at 23°C and at 150°C in order to distinguish physisorbed pyridine from pyridine coordinately bonded to Lewis acid sites. The absorption bands around 1450 cm⁻¹ observed on the spectra are characteristic of strongly bonded pyridine to Lewis acid sites^{41, 42} (Figure 5). Because the frequencies of these absorption bands were similar in the three catalysts, we can conclude that the strength of the Lewis acidity is not really different between Eco-Cu₈[®], anhydrous CuCl₂ and CuCl₂.2H₂O. Besides, two

absorption bands, characteristic of pyridinium ion, were observed at 1530 and 1537 cm^{-1} with Eco-Cu₈[®] only. Thus Eco-Cu₈[®] present a Brønsted acidity contrary to both commercial copper chlorides.

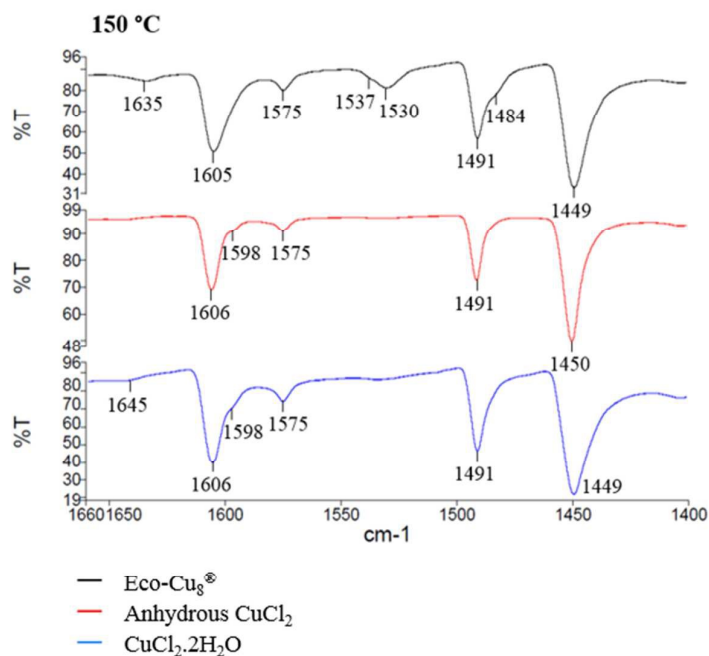
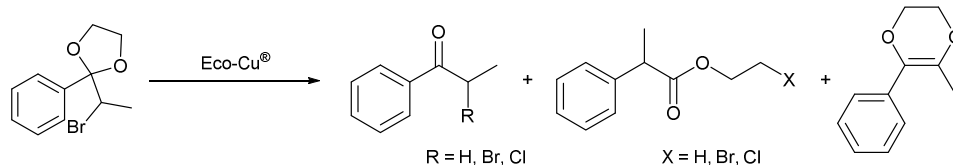
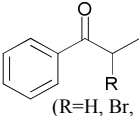
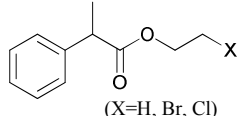
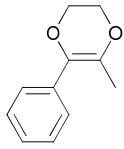


Figure 5. IR spectra of pyridine adsorbed on Eco-Cu₈[®], on commercial anhydrous CuCl₂ and CuCl₂·2H₂O.

These first conclusions were completed and supported by another method, implemented and tested by Corma *et al.*^{43, 44}. This method consists in studying the rearrangement pathway of the cyclic acetal of α -bromopropiophenone, in the presence of a catalyst. The selectivity of products formed during the reaction provides informations to assess the hardness of the Lewis acid sites of the catalysts. It can also highlight their Brønsted acid property. The selectivity results obtained are presented in Table 4. The Brønsted acid pathway is slightly stronger in Eco-Cu₈[®] than in both commercial copper chlorides, which supports the previous infrared study of adsorbed pyridine. According to conversion rates, Eco-Cu₈[®] is more active on cyclic acetal than both commercial copper chlorides, which might result from its stronger Brønsted acid character. Finally, the product from the soft Lewis acid pathway is only formed with commercial copper chlorides but not with Eco-Cu₈[®]. Therefore, the Lewis acidity of Eco-Cu₈[®] is harder than the Lewis acidity of commercial copper chlorides, which might be due to the presence of other elements known to be hard Lewis acids⁴⁵, such as iron or calcium as shown by the ICP-MS analysis (Table 3).

Table 4. Conversion rates and selectivities of products coming from the rearrangement of cyclic acetal of α -bromopropiophenone with Eco-Cu₈[®] and commercial anhydrous CuCl₂ and CuCl₂·2H₂O.



Catalysts	Conversion rate ^a [%]	Selectivity ^a [%]		
		 (R=H, Br, Cl) Brønsted acidity products	 (X=H, Br, Cl) Hard Lewis acidity products	 Soft Lewis acidity product
Eco-Cu ₈ [®]	100	64	36	0
Anhydrous CuCl ₂	49	52	41	7
CuCl ₂ ·2H ₂ O	65	39	58	3

^a Determined by GC-MS analysis

2.3. Reactivity of Eco-Cu[®] in Ullmann coupling reaction

Copper was the first metal used in cross-coupling reactions^{46, 47} decades before palladium- and nickel-catalyzed procedures had emerged. Copper has the advantage of being inexpensive, earth-abundant, non-toxic and then found in widespread applications in homogeneous chemical catalysis. Indeed for more than a century, copper is an effective catalyst for the useful and practical formation of C(aryl)-N, C(aryl)-C, and C(aryl)-O bonds⁴⁸⁻⁵⁰. Such copper-mediated coupling reactions have numerous industrial applications, including the synthesis of intermediates as well as synthetic targets for the life sciences, agrochemical and polymer industries^{51, 52}. However, Ullmann-type coupling reactions have been neglected for a long time because of their drawbacks: harsh reaction conditions often used, limited range of suitable substrates and moderate yields obtained. These condensations are usually conducted in aprotic polar solvents such as N-methylpyrrolidone or N,N-Dimethylformamide at high temperature, with copper reagent rarely used in catalytic quantities. Therefore important efforts are provided among the community of organic chemists to discover new milder, inexpensive and environmentally benign reaction conditions. Recently, several research groups obtained interesting results in producing inexpensive copper catalysts complexed with simple ligands⁵³, able to perform economical and efficient N-arylation of nitrogen-containing heterocycles with aryl halides. These ligands derived from phosphines⁵⁴, amino acids⁵⁵, β-diketones⁵⁶ or 1,2-diamines^{57, 58}. They are important to improve both the catalyst concentration and its electronic density. With these ligands, the coupling reactions are more efficient, but this implies increasing cost, bad ecological footprint and contamination of the final product. The past few years, to circumvent those inconveniences, ligand-

free Ullmann coupling have been performed using CuI and Cu₂O as catalysts with good results. Indeed Ullmann-type coupling reaction can be catalyzed by all copper species from Cu(I) to Cu(II) and even by metal copper since the original work of Ullmann and Goldberg^{46, 47, 59, 60}. In 1928, Weston *et al.* published results concerning the Ullmann reaction comparing a wide range of catalyst sources, leading them to say that: “almost any copper or copper compound may be used as a source of catalyst”, although Cu(I) salts appeared to give better results. In fact, it has been demonstrated later by analytical meanings that the active species is the cuprous salt (Cu⁺) which if not directly introduced, can be generated by *in situ* reduction of Cu(II) or oxidation of Cu(0)⁶¹⁻⁶⁴. Besides it is known that common nitrogen heterocycles such as phtalimide, pyrrole, imidazole and pyrazole derivatives are more reactive in Ullmann coupling⁶⁵⁻⁶⁸. In spite of the significant progress, more efficient, air or/and moisture-stable and easy-synthesized ligands are still in demand, in order to facilitate these coupling reactions under relatively mild conditions. The copper-mediated Ullmann reaction still suffers from required drastic reaction conditions: ligands and large amount of Cu are necessary for successful coupling reactions. From these observations, and regarding the efficiency of palladium ecocatalysts (Eco-Pd[®]) developed in our laboratory in cross-coupling reactions¹⁸, the catalytic potential of Eco-Cu[®] should be investigated.

2.3.1. Results

With regard to the unusual acid properties of the Eco-Cu[®], it was interesting to study their reactivity in arylation of amines and alcohols. The Lewis acidity of Eco-Cu[®] was an interesting parameter to modulate the reactivity of nucleophiles, and to activate the halide partners during the oxidative addition step.

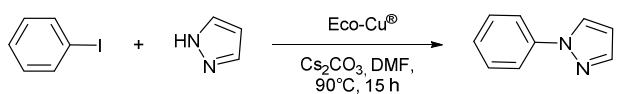
The first part of this work is a comparative study of the different Eco-Cu[®] catalysts on a model coupling reaction. It is known that common nitrogen heterocycles such as phtalimide, pyrrole, imidazole and pyrazole derivatives are particularly reactive in the Ullmann coupling reaction⁶⁵⁻⁶⁸. Thus, the model N-arylation was performed with pyrazole and iodobenzene, using the conditions described by Taillefer *et al.*⁶⁵ who developed one of the few examples of bimetallic catalysis^{69, 70}. Cesium carbonate was chosen to avoid the use of strong bases, as described by the group of Buchwald⁷¹ in diaryl ether synthesis. Many different copper salts and oxides have been used to catalyze Ullmann-type reactions. These results suggested that each Eco-Cu[®] could be efficient in the reaction. However we observed that Eco-Cu[®] activated by HCl (Eco-Cu₂[®], Eco-Cu₄[®], Eco-Cu₆[®] and Eco-Cu₈[®]) are much more efficient than Eco-Cu[®] solely thermally treated (Eco-Cu₁[®], Eco-Cu₃[®], Eco-Cu₅[®], and Eco-Cu₇[®]) (Table 5). Then, we observed a direct correlation between coupling efficiency and copper concentration inside the catalyst, which is an essential observation concerning the recovery of biomass obtained *via* phytoextraction or rhizofiltration technics. Indeed, although Eco-Cu₄[®], Eco-Cu₆[®] and Eco-Cu₈[®] give similar good conversion rates with copper concentrations from 2 to 10 percent by weight (Table 5), Eco-Cu₂[®] with only 0.26 percent by weight of copper, has shown a much lower conversion rate.

Moreover, with most of the ecocatalysts, we managed to get good yields with only 1mol% of copper, which is a very low catalytic loading compared to studies described in previous literature (10-20 mol%)⁷²⁻⁷⁴. Using small amounts of catalyst is a significant advantage for this type of C-N coupling

reaction, both for practical, environmental and economic reasons. Thus, we attempted to optimize the catalyst amount using the most active ecocatalyst, Eco-Cu₈[®], (entries 8, 9, 10). The coupling reaction was still possible with 0.25 mol% of copper (entry 10). Surprisingly, increasing the catalyst amount did not improve the conversion rate (entry 9). As the results show, the catalytic loading of 1 mol% is a very good compromise between catalyst economy and chemical efficiency. It is important to mention that similar reactions under ligand-free conditions, described in literature, require a considerably higher loading of copper sources and more drastic reaction conditions e.g. 20 mol%, 8h at 120°C in n-PrCNas described by Hu and coworkers⁷⁵, or 10 mol%, 24h at 120°C in DMF as described by Zhang et al.⁷⁴. In comparison, the same authors reported that the N-arylation of pyrazole with iodobenzene using an excess of tetraethylenepentamine (TEPA) (2 equiv.), as a base, and 10 mol% of copper source were still necessary, TBAB (0.3 equiv.) and reaction time of 12 h at 125°C⁷⁶. The loading of copper could be reduced to 5 mol%. However, if the amount of copper is reduced, then use of unusual copper sources such as CuO hollow nanospheres immobilized onto acetylene black⁷⁷, or Cu₂O coated Cu nanoparticles⁷⁸, must be used. Unfortunately, both protocols require harsh reaction conditions, 18h at 180°C and 18h at 150°C, respectively. Finally the loading of copper sources of 0.08 mol% for the N-arylation of pyrazole with iodobenzene under ligand-free-like conditions was reported by Bolmet. al.⁷⁹. However the reaction described requires the presence of DMEDA (20 mol%). It was carried out at 135°C for 24 h and authors did not test other aryl halides, thus the scope of the reaction remains unknown. It can be concluded therefore, that the use of Eco-Cu[®] catalysts represents a clear advantage over the literature protocols.

Finally, the results obtained with the use of Eco-Cu[®] catalysts can also be advantageously compared to commercial Cu catalysts, such as CuCl₂, CuCl and CuO (entries 11, 12, 13 and 14). Commercial CuO exhibited poor activity in the conditions used. Commercial CuCl₂ and CuCl promoted the reaction, but conversion rates were lower than those obtained with Eco-Cu₈[®]. These results demonstrated the performance of Eco-Cu[®].

Table 5. Screening of Eco-Cu[®] using fixed reaction conditions.



Entry ^a	Eco-Cu [®] catalyst	Cu in catalyst (wt. %)	Cu quantity (mol%)	Yields (%) ^b
1	Eco-Cu ₁ [®]	0.38	1	25 ^c
2	Eco-Cu ₂ [®]	0.26	1	37 ^c
3	Eco-Cu ₃ [®]	9.1	1	18 ^c
4	Eco-Cu ₄ [®]	4.8	1	84
5	Eco-Cu ₅ [®]	3.3	1	11 ^c
6	Eco-Cu ₆ [®]	2.0	1	77
7	Eco-Cu ₇ [®]	18	1	66

8	Eco-Cu ₈ [®]	10	1	85
9	Eco-Cu ₈ [®]	10	4	83
10	Eco-Cu ₈ [®]	10	0.25	57
11	CuCl ₂	-	1	48 ^c
12	CuCl ₂	-	3	79 ^c
13	CuCl	-	1	76 ^c
14	CuO	-	1	9 ^c

^aReaction conditions: iodobenzene (5 mmol), pyrazole (7.5 mmol), Eco-Cu[®] (50 μmol), Cs₂CO₃ (10 mmol), DMF (5 mL), 90 °C, 15 h, argon atmosphere

^bIsolated yields

^cYields were determined by GC-MS analysis

Eco-Cu₈[®] appears as a highly active catalyst in N-arylation reaction without ligands and additives, which represents a valuable alternative compared to classical catalytic systems used in literature. Moreover, the reaction requires a considerably low quantity of Cu (1 mol%). This is important in light of the need to lower the residual copper levels in the product after work-up, especially in the case of pharmaceutical synthesis.

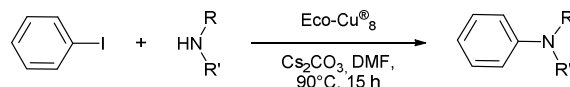
The very good performance of Eco-Cu₈[®] could be partially explained by its polymetallic composition, and more precisely by the presence of alkaline metals, as highlighted by ICP-MS analysis (see section 2.2.2). Indeed, Zhang *et al.*⁸⁰, have demonstrated the benefits of inorganic salt particles in transition metal-catalyzed coupling reactions. The partial negative charges on the salt surface create an electron-donating effect, which increases the electron density of the metal center. Besides, the anions at the surface of the solid salt particles have a similar influence on the aryl halide. The combination of these effects promotes the oxidative addition step and enhances the reaction rate.

Furthermore, Fan *et al.* have described the activity of several Lewis acids to assist the polarization of the aryl-halogen bond. Significant rate-enhancement has been reported by addition of catalytic amounts of Lewis acids during transition metal-catalyzed cross coupling reactions^{81, 82}. As metallic elements highlighted by ICP-MS analysis in Eco-Cu₈[®] are Lewis acids, they might thus promote the reaction.

Finally, these results are consistent with our previous work on Heck-Mizoroki and Suzuki-Miyaura cross coupling reactions with Eco-Pd[®] catalysts¹⁸, characterized by an excellent dispersion of active centers on the saline matrix.

After this first screening of different Eco-Cu[®] catalysts, the methodology has been extended to different amines, by using the most active catalyst, Eco-Cu₈[®], with Cs₂CO₃ at 90°C. As shown in Table 6, azole derivatives are the most reactive substrates, whereas no conversion rate was observed with aniline. Besides, low conversion rates were obtained with secondary amines such as pyrrolidine and morpholine (entries 5 and 6).

Table 6. Screening of amines using fixed reaction conditions.



Entry ^a	Nucleophile	Yield (%) ^b	GC/MS spectral data ^d
1	pyrazole	85	rt = 11.63 min, m/z = 144 (51, 77, 90, 117)
2	imidazole	54	rt = 12.76 min, m/z = 144 (51, 77, 90, 117)
3	2-pyrrolidone	31 ^c	
4	aniline	0 ^c	
7	pyrrolidine	6 ^c	
8	morpholine	5 ^c	

^aReaction conditions: iodobenzene (5 mmol), nucleophile (7.5 mmol), Eco-Cu₈[®] (50 μmol), Cs₂CO₃ (10 mmol), DMF (5 mL), 90°C, 15 h, argon atmosphere

^bIsolated yields

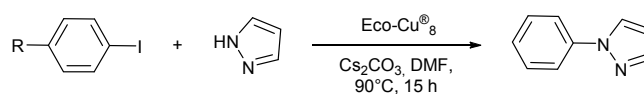
^cYields were determined by GC-MS analysis

^dAll compounds synthesized were fully characterized and found to be in agreement with the literature data. GC retention time and mass spectrometry (EI) data are given.

After those preliminary results, our efforts have been focused on pyrazole as nucleophile for Ullmann condensation. Numerous aryl halides substituted with various electron-withdrawing and -donating groups were investigated (Table 7) at different temperatures, with Cs₂CO₃ as base, 1mol% of catalytic charge and without ligands. The Ullmann reaction required DMF as solvent. Indeed water, toluene and γ -valerolactone were tested as green solvents⁸³ but the reaction did not occur, except in γ -valerolactone with limited conversion rate (results not shown). The usual influence of the nature of the halide in coupling reactions was respected (entries 1, 5 and 9). Eco-Cu₈[®] was efficient in cross-coupling reactions with aryl iodides, aryl bromides and even aryl chlorides. The use of aryl chlorides in Ullmann type reactions is especially desirable to industries, because they are often less expensive than iodides and bromides, thus their use has a real economic advantage⁸⁴.

Tertiary amines were formed in good to excellent yields if temperature was adjusted. Noteworthy, the coupling reaction of pyrazole was sensitive to electronic effects of substituents on aryl halides partners. The presence of *p*-OMe electron-donating substituent clearly diminished the efficiency of the reaction. This could be counter balanced by a moderate elevation of the reaction temperature (entries 1, 2 and 3) from 90 to 110°C. Finally, electron-withdrawing groups facilitated the coupling reaction depending on the electronegativity of the groups (entries 4-9). Thus, the reaction was quantitative in 4h at 90°C using iodoacetophenone (entry 4).

Table 7. Aryl halides and temperature conditions screening.



Entry ^a	Aryl halide	T ^o C	Time (h)	Yield(%) ^b	GC/MS spectral data ^d
1		90	15	85	rt = 11.63 min, m/z = 144 (51, 77, 90, 117)
2		90	15	63 ^c	rt = 13.97 min, m/z = 174 (77, 131, 159)
3		110	15	93	
4		90	4	>98	rt = 15.31 min, m/z = 186 (89, 116, 143, 171)
5		90	15	31 ^c	
6		90	4	>98	rt = 15.55 min, m/z = 189 (65, 89, 116, 131, 159)
7		90	4	>98	
8		90	15	73	rt = 14.61 min, m/z = 169 (75, 102, 115, 142)
9		110	15	89	

^aReaction conditions: Aryl halide (5 mmol), pyrazole (7.5 mmol), Eco-Cu₈[®] (50 μmol), Cs₂CO₃ (10 mmol), DMF (5 mL), argon atmosphere

^bIsolated yields

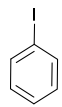
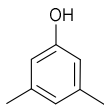
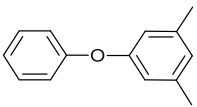
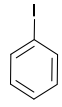
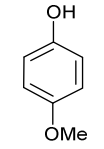
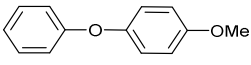
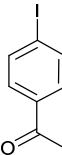
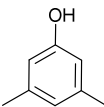
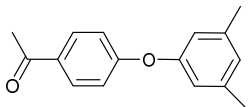

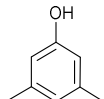
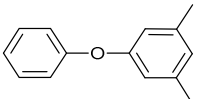
^cYields were determined by GC-MS analysis


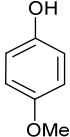
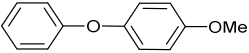
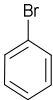
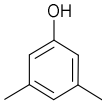
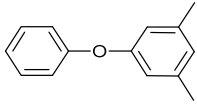

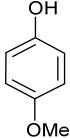
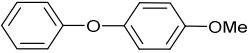

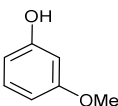
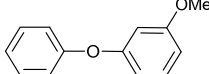


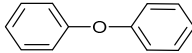
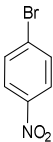
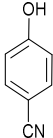
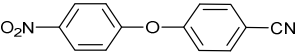
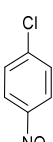
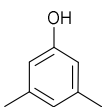
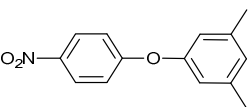
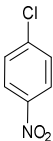
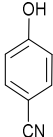
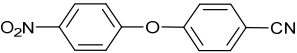
^dAll compounds synthesized were fully characterized and found to be in agreement with the literature data⁸⁵. GC retention time and mass spectrometry (EI) data are described.

Finally, regarding the encouraging results obtained in arylation of amines, the efficiency of Eco-Cu₈[®] catalyst was studied in the synthesis of alkyl aryl ethers (Table 8). The synthesis of the latter was already described by Ullmann in his original articles^{46, 47}. However, despite the recent progress in the catalytic Ullmann reaction, less articles have appeared for the C-O than for the C-N coupling reaction. The most convenient approach is based on the reaction of aryl bromides or iodides with phenols and usually involves the presence of high ligand and copper loadings (10-30%mol)⁸⁶⁻⁸⁹ and elevated temperatures (50-110°C)⁸⁷⁻⁸⁹. In the case of the use of aryl chlorides even higher temperatures are necessary (135°C)⁹⁰. Importantly, examples involving “ligand-free” coupling of aryl halides with phenols are scarcely described in the literature and they usually require extreme reaction conditions (temperatures of 150-160°C)^{91, 92}.

The Eco-Cu[®]-catalyzed C-O bond-forming reactions were very efficient, without ligands and with Cs₂O₃ as base. In the presence of 1 mol% of Cu, satisfactory to high yields were obtained for various aryl alkyl ethers. Contrary to conventional procedures, the reaction was sensitive to both electron-withdrawing and -donating groups on the substrates, and also to the nature of the halide partner. Indeed good conversion rates were obtained with aryl iodides and aryl bromides in mild conditions (entries 1-5), whereas strong activating substituents and an increase in the reaction temperature were required to perform the coupling reaction with aryl chlorides (entries 11-12). These conditions were compatible with a wide range of functionalities including nitriles, ketones, ethers, alkyl and nitro groups.

Table 8. Eco-Cu[®]-catalyzed synthesis of alkyl aryl ethers

$\text{R}-\text{C}_6\text{H}_4-\text{X} + \text{HO}-\text{C}_6\text{H}_4-\text{R}' \xrightarrow[\text{Cs}_2\text{CO}_3, \text{DMF}, 15 \text{ h}]{\text{Eco-Cu}_8^{\text{®}}} \text{R}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{R}'$						
Entry ^a	Aryl halide	Nucleophile	T°C	Product	Yield(%) ^b	GC/MS spectral data ^d
1			110		66 ^c	rt = 14.17 min, m/z = 198 (77, 91, 155, 183) ⁹³
2			110		64 ^c	rt = 14.72 min, m/z = 200 (51, 77, 129, 185) ⁹³
3			110		>98	rt = 17.13 min, m/z = 240 (77, 105, 225) ⁹⁴
4			130		>98	

5			130		>98	
6			130		84	
7			130		82	
8			130		92	rt = 14.62 min, m/z = 200 (51, 77, 92, 129, 157) ⁹⁵
9			130		51 ^c	
10			110		>98	rt = 18.18 min, m/z = 240 (80, 108, 210) ⁹⁶
11			110		>98	rt = 17.29 min, m/z = 243 (77, 108, 170, 213) ⁹⁷
12			110		>98	

^aReaction conditions: Aryl halide (5 mmol), phenol (6mmol), Eco-Cu₈[®] (50 μmol), Cs₂CO₃ (10 mmol), DMF (5 mL), 15 h, argon atmosphere

^bIsolated yield

^c Yields were determined by GC-MS analysis

^dAll compounds synthesized were fully characterized and found to be in agreement with the literature data: GC retention time / Mass spectrometry (EI) / literature references for NMR spectroscopy are given

Innovative reusability technologies of Eco-Cu₈[®] through ecological recycling based on rhizofiltration were under investigation"

3. Experimental Section

3.1. General remarks

NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature, ^1H frequency is at 300 MHz, ^{13}C frequency is at 75 MHz. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer in ATR mode. GC-MS analyses were performed on a Shimadzu QP2010SE apparatus. Two different methods were used for analysis. Method A: GC-MS (Phenomenex ZB-5MSi Guardian column, $0.25\ \mu\text{m} \times 0.25\ \text{mm} \times 30\ \text{m}$) with hydrogen as carrier gas using the following temperature program: isothermal at 80°C (4 min), then linear gradient from 80°C to 270°C at $20^\circ\text{C}/\text{min}$. Method B: GC-MS (Phenomenex ZB-5MSi Guardian column, $0.18\ \mu\text{m} \times 0.18\ \text{mm} \times 20\ \text{m}$) with hydrogen as carrier gas using the following temperature program: isothermal at 100°C (1 min), then linear gradient from 100°C to 145°C at $50^\circ\text{C}/\text{min}$, then isothermal at 145°C (0.50 min), then increasing from 145°C to 190°C at $50^\circ\text{C}/\text{min}$, then isothermal at 190°C (0.60 min), and finally increasing from 190°C to 320°C at $90^\circ\text{C}/\text{min}$. GC-MS samples were prepared in dichloromethane using 1,1'-biphenyl as internal standard. Mass spectra were recorded in electron impact (EI) mode at 70 V and identified by comparison with data of the NIST 11 software library and by comparison of the retention time of the standard compounds. X-ray photoelectron spectroscopy (XPS) analysis were performed with a Kratos Analytical Axis Ultra DLD, using an Al $K\alpha$ source monochromatized at 1486.6 eV. We used a hemispheric analyzer working at pass energy of 50 eV for the global spectrum and 20 eV when focusing on the sole core levels. Direct-injection mass spectrometry was performed with a Micromass Quattro micro APITM, which was combined with HPLC detector and triple quadrupole mass analyser for determining mass-to-charge ratio (m/z). The transmission electron microscopy (TEM) images were taken using a Jeol 1400 Plus Transmission Electron Microscope at accelerating voltage of 120 kV. Ecocatalyst was put in suspension in EtOH 70% and was dropped off on a grid CF 300-Cu (carbon film on 300 Mesh copper grids).

3.2. Elemental analyses

Chemical element analyses of plants and ecocatalysts were determined by ICP-MS analyses (inductively coupled plasma mass spectrometry). ICP-MS analyses were performed using the metal analysis of total dissolved solutes in water. The samples were first digested either in a mixture of hydrochloric acid (37%) (8 mL) and nitric acid (65%) (2 mL) (*L. multiflorum*, *E. crassipes* and ecocatalysts Eco-Cu[®]), or in pure nitric acid (*B. monnieri*, *A. chinensis*) using a microwave-assisted digestion. Microwave digestions were performed on a Mileston ETHOS Touch Control device with two different temperature programs: 1. Linear gradient from 20 to 90°C at $10^\circ\text{C}/\text{mn}$, then from 90 to 170°C at $16^\circ\text{C}/\text{mn}$, then from 170 to 210°C at $10^\circ\text{C}/\text{mn}$ and then 20 min isothermal at 210°C (*L. multiflorum*, *E. crassipes*, and ecocatalysts Eco-Cu[®]); 2. Linear gradient from 20°C to 180°C at $32^\circ\text{C}/\text{mn}$, then 10 min isothermal at 180°C (*B. monnieri*, *A. chinensis*). Samples were then diluted to $0.1\ \text{mg}\cdot\text{L}^{-1}$ in 2.5% aqueous nitric acid. Three blanks were recorded for each step of the digestion and dilution procedure. ICP-MS analyses were performed on a Thermo ScientificTM ELEMENT XRTM ICP-MS. All analysis results were performed in triplicate.

3.3. Phytoextraction

Study site

The study site is the “Mine de l’Etoile”, in the vicinity of Lubumbashi, a “*locus classicus*” of Cu and Co hyperaccumulation by plants in Katanga (Democratic Republic of the Congo)²². Soil of “Mine de l’Etoile” is contaminated by tailings which were spontaneously colonized by some Cu-Co tolerant species. Total Cu concentrations in soil vary from 10,000 to 30,000 mg.kg⁻¹²⁰.

A. chinensis L. Hook.f. & Arn. (Asteraceae) is a perennial pseudo-metallophyte presenting a large variation of Cu concentrations in shoots *in natura*^{23, 24}. Plant shoots of 20 individuals of *A. chinensis* were collected all over the “Mine de l’Etoile” (11° 38' S; 27° 35' E, 1277 m asl). This site is characterized by a subtropical humid climate including a rainy season (from November to March) and a dry season (from May to September). Maximum density of individuals (ind) of *A. chinensis* were estimated to 15 ind/m² from field observations (*i.e.* mean of 10 quadrats of m²). Biomass productivity (BP) of monospecific crop of *A. chinensis* was then estimated: BP = mean biomass of *A. chinensis* individual x 15.

Determinations of Cu concentration in plant shoots

After harvesting, plants were carefully brushed (whole shoots), washed with Alconox[®] 1% in deionized water, dried at 65°C for 48h²² and weighted. Determination of Cu concentration in *A. chinensis* was performed in two steps. A mass of leaves was digested using a mixture of 8 mL HNO₃ and 2 mL HCl⁹⁸. Vessels containing the mix were heated by microwaves for digestion^{24, 99}. Then, Cu concentration in samples was determined by ICP-MS.

Evaluation of phytoextraction parameters

Cu amount phytoextracted per hectare and per year was calculated by the following formula:

$$Y_{Cu} = F_{Cu} \cdot Y_{bio}$$

F_{Cu}: Average fraction of Cu in *A. chinensis* biomass

Y_{bio}: Biomass productivity of hyperaccumulator (kg/ha/year)

Y_{Cu}: Total Cu gain (g/ha/year)

3.4. Rhizofiltration

Germination and growth

B. monnieri was bought directly in a garden center Jardiland. It was then immersed in a hydroponic reservoir with a natural substrate called Manado (pozzolan) and 17 L of distilled water. The plants were fed once every week with a fertilizer called “S7 Vitamix”, mainly containing 0.65% K₂O, 0.14% Mg, 0.41% S, 0.06% N, 0.065% Fe, 0.026% Mn. The plants were grown under neon light (12 h per day) and under ambient temperature. The cultivation lasted 5 months in these conditions before the beginning of copper accumulation.

L. multiflorum was grown in our lab. Seeds were first transferred in Fleximix Root Riot Organic Starter Cubes[®], 82% of seeds were germinated after 9 days. The culture plate was placed in a shallow hydroponic reservoir, to be sure that only the roots of the plants were immersed in water at ambient temperature. The plants were fed with a fertilizer called “water lily dream” containing 1% K₂O, 0.14% Mo, 0.0028% Zn, 0.0027% Cu, 0.0004% Li. They were exposed during 8 weeks, 12 h per day, under mercury lamp UV (37,000 lumens), before the beginning of copper accumulation.

E. crassipes was bought in a garden center Jardiland. They were put in an outdoor pool with water during 6 months without additional fertilizer.

Conditions of accumulation

After five months of growth, *B. monnieri* was placed in another hydroponic reservoir, without substrate, and with 17 L of an aqueous solution made of distilled water and 40 mg/L of Cu(NO₃)₂·3H₂O (10.5 mg/L of Cu). The accumulation occurred under ambient temperature, and under neon light (12 h per day), during 7 days.

After 8 weeks of growth, *L. multiflorum* was exposed to an aqueous media made of distilled water with 40 mg/L of Cu(NO₃)₂·3H₂O (10.5 mg/L of Cu). The accumulation occurred under ambient temperature, and under mercury lamp UV (37,000 lumens), during 7 days.

After 6 months in the pool, *E. crassipes* was exposed to an aqueous solution made of 40 mg/L of Cu(NO₃)₂·3H₂O (10.5 mg/L of Cu). The accumulation occurred outside (the plants suffered from necrosis quickly in inside pool), during 7 days.

Crops

The plants were collected and separated into roots and aerial parts. Plant tissues were washed with distilled water to remove any metallic particles attached to the plant surfaces. Then the biomass was dried in an oven at 80°C during 48 h.

Evaluation of rhizofiltration parameters

Biomass measuring:

Once harvested and dried, the root biomass and the shoot biomass were weighted for each plant.

BCF (bioconcentration factor):

The BCF was calculated as the ratio of a given element concentration in the plant tissues (P, mg/kg dry weight) at harvest to the concentration of the element in the effluent (E, mg/L) according to Eq.(1)

$$\mathbf{BCF=P/E} \quad (1)$$

TF (translocation factor):

TF was calculated by dividing the Cu concentration in shoot tissues (A_s, mg/kg dry weight) by the concentration of Cu accumulated in root tissues (A_r, mg/kg dry weight) (Eq.(2)):

$$\mathbf{TF = (A_s/A_r)} \quad (2)$$

Determination of metals concentration in roots and shoots

Metal concentrations in roots and shoots were determined by ICP-MS. The procedure is the same as described in section 3.2., Elemental analyses.

3.4. Preparation of Eco-Cu[®] catalysts

Eco-Cu[®] catalysts were prepared either from roots of plants used for rhizofiltration, or from harvested leaves of plants used for phytoextraction. Biomasses were first dried into an oven at 80°C, then thermally treated in an oven using the following temperature program: linear gradient from 20 to 550°C (1 h) and then 4 hours at 550°C before a slow cooling overnight to obtain ashes (Eco-Cu₁[®] (*A. chinensis*), Eco-Cu₃[®] (*B. monnieri*), Eco-Cu₅[®] (*L. multiflorum*) and Eco-Cu₇[®] (*E. crassipes*)). Thereafter the ashes obtained were subjected to a chemical treatment. The typical procedure used was as follow: around 50 mg of ashes were suspended in concentrated hydrochloric acid (5 mL). The solutions were stirred at 80 °C for 4h and then evaporated to dryness under vacuum to get Eco-Cu₂[®] (*A. chinensis*), Eco-Cu₄[®] (*B. monnieri*), Eco-Cu₆[®] (*L. multiflorum*) and Eco-Cu₈[®] (*E. crassipes*)) respectively, as yellow powders. Eco-Cu[®] catalysts were stored under vacuum in a desiccator.

Thermic treatment: Eco-Cu₁[®], Eco-Cu₃[®], Eco-Cu₅[®], Eco-Cu₇[®]

Thermic and chemical treatment; Eco-Cu₂[®], Eco-Cu₄[®], Eco-Cu₆[®], Eco-Cu₈[®]

3.4. Characterization of Eco-Cu[®] catalysts

3.4.1. Chemical element analysis

ICP-MS was used to determine the composition of the various ecocatalysts prepared. ICP-MS analyses were performed as described section 3.2. Elemental analyses.

3.4.2. Acidity characterization

Pyridine-FTIR (Fourier transform infrared spectroscopy):

Excess pyridine was adsorbed on catalysts, then the samples were degassed for 15 min at 23 °C (10⁻³ Pa) and a first IR spectrum was recorded. The samples were then degassed for 30 min at 150 °C (10⁻³ Pa) to eliminate the physisorbed pyridine and a second IR spectrum was recorded.

Rearrangement of α -bromopropiophenone cyclic acetal:

A solution of α -bromopropiophenone cyclic acetal (75.8 mg, 295 μ mol, 1 equiv.) in 1,2-dichlorobenzene (3.35 mL) was poured onto catalyst (mass corresponding to 12.4 μ mol of Cu, 0.04 equiv.). Thereafter water was added (5.31 μ L, 295 μ mol, 1 equiv.) and the resulting suspension was stirred at 175°C for 20 h. The crude was analyzed by GC-MS (method B).

3.4.3. Analytic test of Eco-Cu₈[®]

EcoCu₈[®] (8.1 μmol of Cu, 5 mg) was suspended into aq. 30 w% ammonia (200 μL). The suspension was vortexed and the liquid phase turned deep blue within 1 minute demonstrating the presence of Cu²⁺ into our catalyst by forming [Cu(NH₃)₄]²⁺ complexes. The mixture was centrifuged for better observation of the solution.

3.5. General procedure for catalytic Ullmann coupling reaction and analysis of reaction products

The general procedure is described here with the case of 1H-pyrazole.

To a solution of 1H-pyrazole (510 mg, 7.5 mmol) and iodobenzene (560 μL, 5.0 mmol) in dry DMF (5 mL) were sequentially added: Eco-Cu[®] catalysts (3.3 mg, 0.05 mmol of Cu) and Cs₂CO₃ (3.25 g, 10.0 mmol). The resulting mixture was stirred at 90°C under inert atmosphere for 15 h. After cooling to room temperature, the crude was diluted with ethyl acetate, filtered and concentrated under reduced pressure. The resulting residue was purified on a silica gel column (Cyclohexane/ethyl acetate 8:2) to give 1-phenyl-1H-pyrazole as a colourless oil (647 mg, 90% yield). ¹H NMR (300 MHz, CDCl₃) ppm: δ = 7.93-7.92 (dd, 1H), 7.76-7.70 (m, 3H), 7.49-7.42 (m, 2H), 7.32-7.26 (m, 1H), 6.48-6.46 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) ppm: δ = 143.6, 142.7, 131.9, 129.2, 128.9, 121.7, 110.1; MS (EI): m/z 144 (M⁺, 100%), 117, 104, 90, 77, 51.

4. Conclusion

The aim of this work was to prepare and to study novel copper catalysts based on using Cu hyperaccumulator plants which present an interest for the phytoremediation of mining sites and contaminated aqueous systems. From these studies, it may be concluded that the new catalytic systems show a very interesting activity in the arylation of nucleophiles. The chemistry described in this article demonstrated that Eco-Cu[®] catalysts are original and show valuable physicochemical properties, especially regarding their polymetallic composition. Eco-Cu[®] catalysts offer unexplored potential for coupling reactions, especially those deriving from rhizofiltration (*E. crassipes*). Eco-Cu[®]-catalyzed C-N and C-O bond forming reactions are interesting methods for the synthesis of tertiary amines and aryl ethers. The development of these new ecocatalytic systems represents exciting opportunities to valorize phytoremediation of polluted ecosystems and for future organic synthesis. The combination of these beneficial properties will undoubtedly prompt further research efforts toward the development of ecocatalysis.

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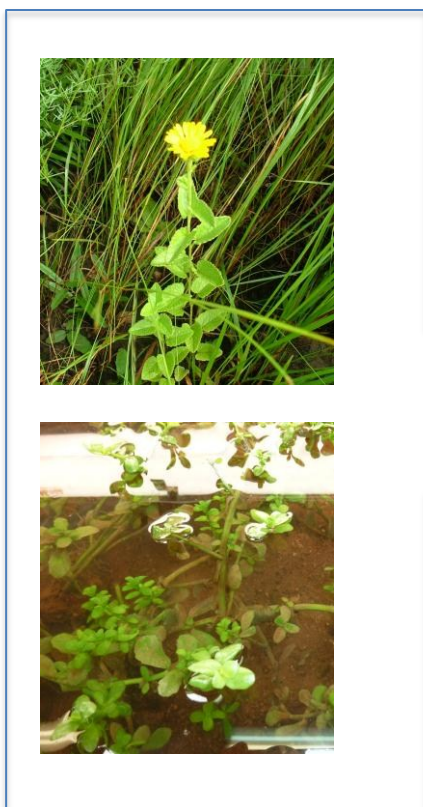
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Ullmann reaction through ecocatalysis: insights from bioresource and synthetic potential

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